



CHAPTER II

LITERATURE REVIEW

2.1 Natural Rubber

Although natural rubber can be isolated from more than a thousand different species of plants, the Para rubber tree, *Hevea brasiliensis*, is practically the sole source of commercial rubber today. The tree is indigenous to the Amazon valley. Natural rubber has been known to the inhabitants of South America for centuries. Christopher Columbus is considered to be the first European to discover it during his second voyage in 1493-1496. Rubber was introduced to the western world by Charles de la Condamine, who sent samples to France from Peru in 1736 and published the result of his observations in 1745. By the end of the eighteenth century, Europe and America were using a few tons of rubber per year. However, users found it difficult to work with solid rubber. Moreover, articles made from natural rubber turned sticky in hot weather and stiffened in the cold.

Two important developments in the nineteenth century enabled these problems to be solved and laid the foundation for the multibillion-dollar modern rubber industry. In 1820, Thomas Hancock invented a machine called the "masticator" that allowed solid rubber to be softened, mixed, and shaped. In 1839, Charles Goodyear discovered the process of vulcanization. He found that heating a mixture of rubber and sulfur yielded products that had much better properties than raw rubber.

The British considered the possibility of cultivating rubber in Asia, and the rubber tree arrived in Sri Lanka in 1876 and Malaysia the following year. In 1880, *Hevea seedlings* were widely distributed in Asia. The land used for rubber cultivation and the production of natural rubber has grown steadily, as expected, since World War II. In 1983, more than 7.5 million hectares of land were under rubber cultivation and about 4 million metric tons of rubber were produced. The Southeast Asia region accounted for 80% of the total production, with Thailand the biggest producer,

followed by Indonesia and Malaysia. The world production of natural rubber is shown in Table 2.1.

Table 2.1 World production of natural rubber (2004)

Country	Percentage
Thailand	36.33
Indonesia	21.49
Malaysia	11.99
India	8.32
Philippines	1.06
Others	20.81
Total	100 % (8.34 Mil tons)

Source: XIRSG, Rubber Statistical Bulletin, 2004

2.1.1 Natural Rubber in Thailand

The data from the Industrial Economics and Planning Division, Ministry of Industry, showed that in 1992 Thailand produced 1,520,000 tons of natural rubber and exported 1,400,000 tons or 92.1% of total production. The remaining 7.9% was used in the country. Since 1994, Thailand has been the biggest in the world production of natural rubber. An area of about 12 million hectares is employed in Thailand for rubber cultivation. In 2004 Thailand produced 302.99 million tons of natural rubber. It is uneconomical to transport preserved field latex over long distances to consumer countries; the normal procedure is to change the latex form before shipment. Therefore, after the natural rubber latex has been collected from the field, it is changed into many forms, which are shown in Table 2.2

Table 2.2 Different types of rubber in Thailand, 2004

Type of rubber	% wt
Smoked sheet	66
Block rubber	18.3
Crepe rubber	0.73
Concentrated latex	9.48
Other rubber	5.46

Source: Southern Industrial Economics Center in Thailand

Natural rubber latex is 60% dry rubber content by the concentration method. In 2004, Thailand exported 131,888 tons to the USA, Taiwan, Germany and Singapore and the remaining 32,736 tons was used in the country.

2.1.2 Properties of Raw Natural Rubber

Natural rubber latex produced by the *tree Hevea brasiliensis*, consists of particles of rubber hydrocarbon and non-rubber constituents suspended in an aqueous serum phase. The average dry rubber content of latex may range between 30% and 45%. The typical composition of fresh latex is shown in Table 2.3.

Table 2.3 Composition of fresh latex and dry rubbers

Composition	Latex (%)	Dry rubber (%)
Rubber hydrocarbons	36.0	93.7
Protein	1.40	2.20
Carbohydrates	1.60	0.40
Neatral lipid	1.00	2.40
Glycolipids and Phospholipids	0.60	1.0
Inorganic constituents	0.5	0.2
Others	0.4	0.1
Water	58.5	-

2.1.3 Production of Natural Rubber Latex Concentrate

In general, natural rubber is known as natural rubber (NR) latex. The latex appears in the bark outside the cambium layer in ducts spiraling from the left to right as the latex ascends the tree. These ducts are found in concentric rings around the cambium and are really more concentrated near the cambium.

The procedure to obtain the latex, called tapping, is to make a spiral cut that is made downwards from left to right through the bark of the tree. This cut is manipulated to promote the latex to flow into a receptacle such as a plastic, glass, or earthenware cup. Fresh latex coagulates rapidly after tapping, especially in the ambient temperature. Fresh latex has a pH of 7.0. Bacteria decomposes the sugar substances of latex, and therefore the stability of the latex decreases continually as the pH decreases. Bacteria comes from various places such as the atmosphere, the bark, and from the tapping. The preservation of NR latex was first introduced by Johnson and Norris (1853). They suggested using ammonia as an anticoagulant to the latex. The ammonia acts as an alkali to increase the pH of the fresh latex; thus the bacteria remains inactive and the stability of the latex improves. In addition, the electrophoretic mobility of rubber tends to be negatively charged in a base environment. Fresh NR latex exuded from the tree has a dry rubber content of 33% wt. In industry, the latex is concentrated to about 60 %wt, which is economical and uniform in quality. There are several processes to concentrate latex: (1) evaporation, (2) creaming, (3) centrifuging and electrodecantation.

The freshly-tapped NR latex is a whitish fluid with a density of between 0.975 and 0.980 g.m⁻¹, and a pH from 6.5 to 7.0. Its viscosity is variable.

The composition of latex is given below:

total solids content	36%
dry rubber content	33%
proteinous substances	1-1.5%
resinous substances	1-2.5%
ash	up to 1%
sugars	1%
water	ad. 100%

Hauser (1962) found that rubber particles were quite pear-shape rather than spherical, and consisted of a tough, hard, elastic shell which enclosed a viscous liquid. However, many studies have reported that the rubber particles are spherical in shape, especially the latex from young trees. It is also suggested that the shape of the latex depends on the age and type of tree.

The structure of the *Hevea brasiliensis* latex is:

rubber hydrocarbons	86%
water (dispersed in the rubber hydrocarbons)	10%
proteinous substances	1%
lipid substances	3%

Trace metals such as magnesium, potassium, and copper are included with the rubber particles at about 0.05%.

Figure 2.1 shows the structure of the NR latex particles. The NR consists of the protein structure at the outer layer of the surface. The adsorbed layer of protein determines the charge on the particle, electrophoretic mobility, and coacervation characteristics. The lipids associated with rubber particles are sterols and sterol esters, and fats and waxes such as eicosyl alcohol and phospholipids. They are found in the bulk of latex particles. They may be dissolved in rubber hydrocarbons. The phospholipids are adsorbed on the particle and are associated with the protein which are anchored to the rubber.

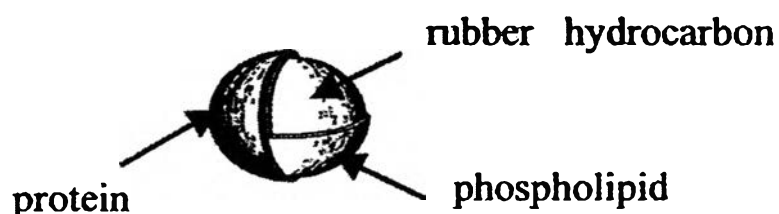


Figure 2.1 Structure of the NR latex particles.

2.1.4 Chemical formula of Natural Rubber

The empirical formula for the natural rubber molecule appears to have been first determined by Faraday, who reported his finding in 1826 (Ronald B,

1999). He concluded that carbon and hydrogen were the only elements present and his results correspond to the formula C_5H_8 . While this result was obtained using a product which contained associated non-rubbery materials, subsequent studies with highly purified materials have confirmed Faraday's conclusion.

The first, isoprene, was found to have the formula C_5H_8 for which Tilden and Dunbrook (1996), proposed the structure shown in Figure 2.2.

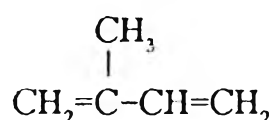


Figure 2.2 Schematic representation of the structure of a NR latex particle.

The linear structure proposed by Pickles¹³² provided for the possibility of structure isomerism with both *cis*- and *trans*- repeating units as shown in Figure 2.3.

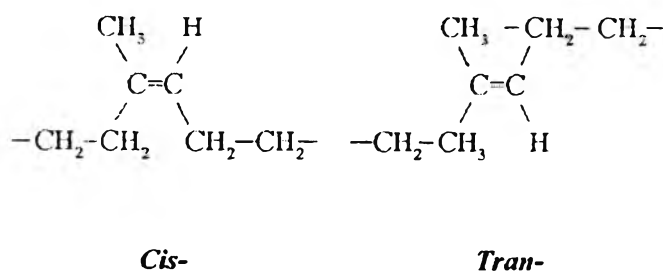


Figure 2.3 Schematic representing the structure isomerism with both *cis*- and *trans*-isoprene, repeating units.

It is known that the major hydrocarbon component of both gutta percha and balata (at the time important in belting submarine cable, in golf balls and in container applications) was a polyisoprene which, when reacted with bromine and

ozone, gave similar results to those obtained with natural rubber. It was therefore tempting to suggest that one isomer was that of gutta percha and balata and the other of natural rubber. The earlier work of Staudinger suggested that the *trans*-isomer was natural rubber and gutta percha the *cis*-. However, later studies of X-ray fiber diagrams of stretch rubber but Lea Meyer and Mark viewed that natural rubber was the *cis*-polymer, like that observed by Bunn (1942), who elucidated the structure and unit cell (Figure 2.4) of the crystalline stretched rubber molecule, as shown in Figure 2.5.

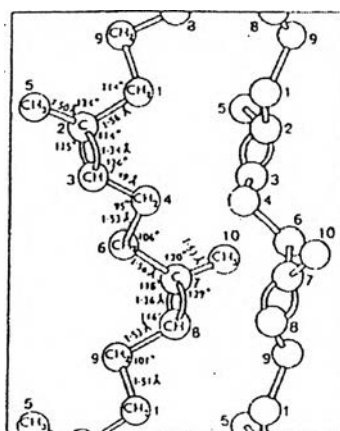


Figure 2.4 Unit cell structure of the natural rubber molecule.

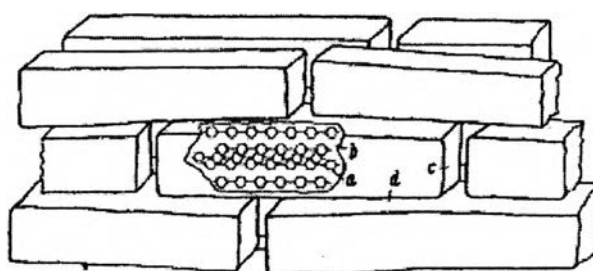


Figure 2.5 Effects of the stretched rubber molecule .

when $a = \text{Hauptvalenzketten}$; $b = \text{intramicellar regions}$
 $c = \text{intermicellar holes}$; $d = \text{intermicellar long spaces}$

The possibility that the natural rubber molecule might contain a mixture of *cis*- and *trans*- groups was considered to be unlikely because such a

mixed polymer would have an irregular structure and be unable to crystallize in the manner of natural rubber. Figure 2.6 illustrates the structure of this rubber, which is *cis*-1,4-polyisoprene.

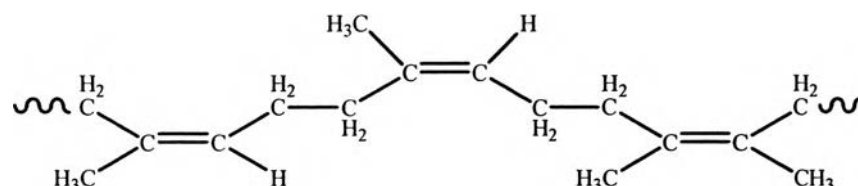


Figure 2.6 Typical structure of NR latex from *Hevea brasiliensis*.

Infrared studies have subsequently confirmed that natural rubber was the *cis*-polymer. It has indeed been shown for a long while that natural rubber is at least 97% *cis* 1,4-polyisoprene. The absence of measurable amounts of 1,2- structure but an infrared band at 890 cm⁻¹, was at one time thought to be due possibly to the products of a 3,4- structure, as shown in Figure 2.7. (Chantarak, 2006).

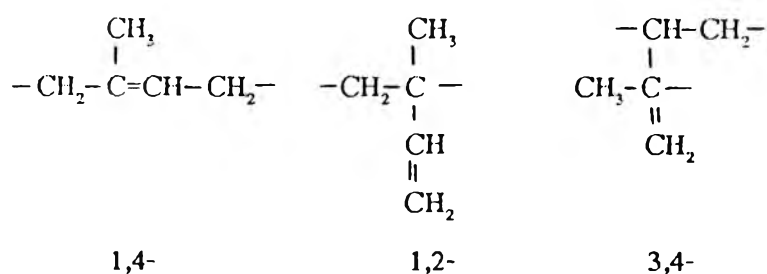


Figure 2.7 Schematic representation of the structure of *cis*-polymer : *cis*-1,4-polyisoprene (~97%), *cis*-1,2- polyisoprene(~2.7) and *cis*-3,4- polyisoprene(<0.3%).

Time-averaging techniques using high resolution NMR which are capable of detecting 3,4-groups at a concentration of less than 0.3%, have, however, failed to establish the existence of any such moiety and have also failed to show any

trace of *trans*-material. The conclusion must therefore be that the molecule is more than 99% *cis*-1,4-polyisoprene. Since all the evidence points to the conclusion that the natural rubber molecule is not obtained in nature by the polymerization of isoprene, the absence of detectable pendent groups as would be produced by 1,2- and 3,4- addition is hardly surprising.

2.2 Styrene

Styrene, also known as vinyl benzene as well as many other names (see table), is an organo compound with the chemical formula $C_6H_5CH=CH_2$. Under normal conditions, this aromatic hydrocarbon is an oily liquid. It evaporates easily and has a sweet smell, although common impurities confer a less pleasant odor. Styrene is the precursor to polystyrene, an important synthetic material.

2.2.1 Occurrence, History, and Use

Styrene is named after the styrax trees from whose sap (benzoin resin) it can be extracted. Low levels of styrene occur naturally in plants as well as a variety of foods such as fruits, vegetables, nuts, beverages, and meats. The production of styrene in the United States increased dramatically during the 1940's to supply the war needs for synthetic rubber.

Because the styrene molecule has a vinyl group with a double bond, it can polymerize to give plastics such as polystyrene, acrylonitrile butadiene styrene (ABS), styrene-butadiene (SBR) rubber, styrene-butadiene latex, styrene-isoprene-styrene (SIS), styrene-ethylene/butylene-styrene (S-EB-S), styrene-divinylbenzene (S-DVB), and unsaturated polyesters. These materials are used in rubber, plastic, insulation, fiberglass, pipes, automobile, boat parts, food containers, and carpet backing.

2.2.2 Production and Dehydrogenation of Ethylbenzene

Styrene is produced in industrial quantities from ethylbenzene, which is in turn prepared from benzene and ethylene.

Styrene is most commonly produced by the catalytic dehydrogenation of ethylbenzene. Ethylbenzene is mixed in the gas phase with 10–15 times its volume

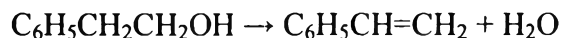
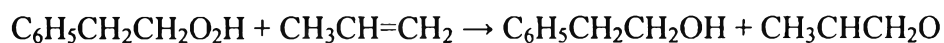
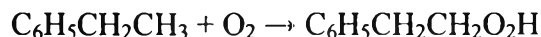
in high-temperature steam, and passed over a solid catalyst bed. Most ethylbenzene dehydrogenation catalysts are based on iron(III) oxide, promoted by several percent potassium oxide or potassium carbonate. On this catalyst, an endothermic, reversible chemical reaction takes place.

Steam serves several roles in this reaction. It is the source of heat for powering the endothermic reaction, and it removes coke that tends to form on the iron oxide catalyst through the water gas shift reaction. The potassium promoter enhances this decoking reaction. The steam also dilutes the reactant and products, shifting the position of chemical equilibrium towards products. A typical styrene plant consists of two or three reactors in series, which operate under vacuum to enhance the conversion and selectivity. Typical per-pass conversions are ca. 65% for two reactors and 70-75% for three reactors. Selectivity to styrene is 93-97%. The main byproducts are benzene and toluene. Because styrene and ethylbenzene have similar boiling points (145 and 136 °C, respectively), their separation requires tall distillation towers and high return/reflux ratios. At its distillation temperatures, styrene tends to polymerize. To minimize this problem, early styrene plants added elemental sulfur to inhibit the polymerization. During the 1970s, new free radical inhibitor consisting of phenol-based retarders were developed. These reagents are added prior to the distillation.

Improving conversion and so reducing the amount of ethylbenzene that must be separated is the chief impetus for researching alternative routes to styrene. Other than the propylene oxide-styrene monomer process (POSM), none of these routes like obtaining styrene from butadiene have been commercially demonstrated.

2.2.3 Via Ethylbenzenehydroperoxide

Commercially styrene is also co-produced with propylene oxide in a process known as POSM (Lyondell Chemical Company) or SM/PO (Shell) for Styrene Monomer / Propylene Oxide. In this process ethylbenzene is reacted with oxygen to form the hydroperoxide of ethylbenzene. This hydroperoxide is then used to oxidize propylene to propylene oxide. The resulting phenylethanol is dehydrated to give styrene:



2.2.4 Health Effects

Styrene is only weakly toxic, with an LD50 of 500-5000 mg/kg (rats). The US Agency for Toxic Substances and Disease Registry (ATSDR) states that human exposure to high levels of styrene (more than 1000 times higher than levels normally found in the natural environment) may induce adverse nervous system effects. These health effects include changes in color vision, tiredness, feeling drunk, slowed reaction time, concentration problems, or balance problems.

Styrene is classified as a possible human carcinogen by the International Agency for Research on Cancer (IARC). The U.S. Environmental Protection Agency (EPA) does not have a cancer classification for styrene, but is evaluating its potential carcinogenicity. The EPA has described styrene as "a suspected carcinogen" and "a suspected toxin to the gastrointestinal, kidney, and respiratory systems, among others."

2.3 **Methyl Methacrylate**

Methyl methacrylate is an organic compound with the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$. This colourless liquid, the methyl ester of methacrylic acid (MMA) is the monomer for the production of the transparent plastic polymethyl methacrylate (PMMA).

2.3.1 Production

Major producers worldwide include Cyro, Arkema, BASF, Dow Chemical, Lucite, Celanese and Rohm and Haas, Mitsubishi Rayon, and Sumitomo. The United States production in 1993 amounted to 600 thousand metric tonnes per annum (mt/a), and the worldwide production in 2005 was estimated at 3.2 million mt/a.

Most producers apply an acetone cyanohydrin (ACH) route, with acetone and hydrogen cyanide as raw materials. The intermediate cyanohydrin is

converted with sulfuric acid to a sulfate ester of the methacrylamide, hydrolysis of which gives ammonium bisulfate and MAA. Some Asian producers start with an isobutylene or, equivalently, tert-butanol, which is oxidized to methacrolein, and again oxidized to methacrylic acid. MAA is then esterified with methanol to MMA. Propene can be carbonylated in the presence of acids to isobutyric acid, which undergoes subsequent dehydrogenation.

A newer palladium-catalysed MMA production technology, announced 18th September 2007, uses a homogeneous palladium-phosphine catalyst. Lucite's Alpha process uses ethylene, carbon monoxide, and methanol as raw materials to produce methyl propionate, which is then combined with formaldehyde to produce MMA and water.

2.3.2 Uses

The principal application of methyl methacrylate is the production of polymethyl methacrylate acrylic plastics. Also methyl methacrylate is used for the production of the co-polymer methyl methacrylate-butadiene-styrene (MBS), used as a modifier for PVC. Methyl methacrylate polymers and co-polymers are used for waterborne coatings, such as latex house paints. It is also used in adhesive formulations. A modern application is the use in plates that keep light spread evenly across LCD computer and TV screens. Methyl methacrylate is also used to prepare corrosion casts of anatomical organs, such as coronary arteries of the heart.

2.4 Admicellar Polymerization Technique

An admicellar polymerization technique is based on the physically adsorbed surfactants onto the substrate, so called admicelle. The feasibility of the phenomena of admicelle formation and adsolubilization to form polymerized and organized ultrathin film of molecular dimension on substrates has been investigated for several years (Dunn,1997). Wu et al. (1993) were the first to propose the formation of styrene-sodium dodecyl sulfate (SDS) on alumina by this polymerization. The bilayer structure of this polymerization is shown in Figure 2.8.

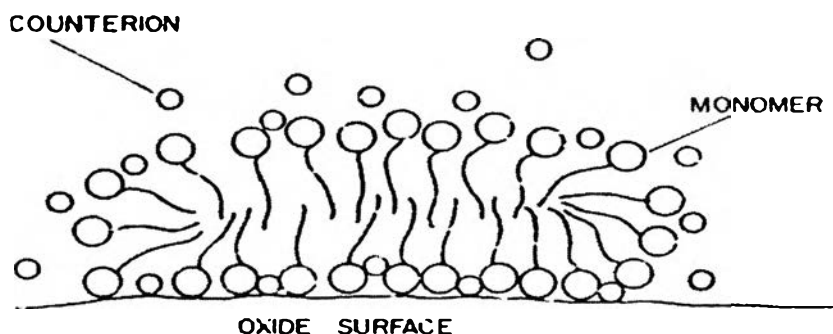


Figure 2.8 Formation of a sodium dodecyl sulfate admicelle on an alumina surface.

Thin film coating by admicellar polymerization can be divided into four steps as shown in Figure 2.9 (a-d).

2.4.1 Step 1: Admicelle Formation

The formation of an admicelle (Harwell *et al.*, 1985) occurs by the adsorption of a surfactant bilayer at the solid/ aqueous solution interface (Figure 2.9 a). The surfactant aggregate formation at the surfactant concentration below the critical micelle concentration (CMC) is manipulated by the solution pH, counterion concentration, and surfactant structure (Scamehorn *et al.*, 1982). The common parameter used to manipulate the admicelle formation is the solution pH at which the substrate surface exhibits a net zero charge (the point of zero charge, PZC).

Admicelle Formation

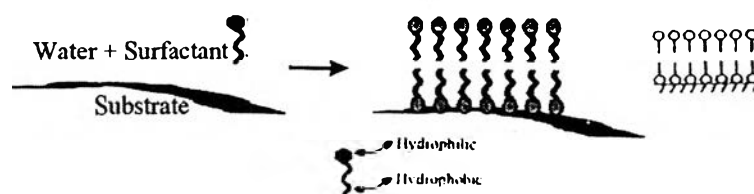


Figure 2.9a Admicelle formation of polymerization process.

2.4.2 Step 2: Monomer Adsolubilization

The partitioning of organic solutes from aqueous solution into the interior of adsorbed surfactant aggregates is termed adsolubilization. The suggested definition of adsolubilization is “the incorporation of a compound into surfactant surface aggregates, which compound would not be in excess at the interface without surfactant”. This phenomenon is an analogue of solubilization, with the adsorbed surfactant bilayer playing the role of micelles, as shown in Figure 2.9b-1, and Figure 2.9b-2.

Monomer Adsolubilization

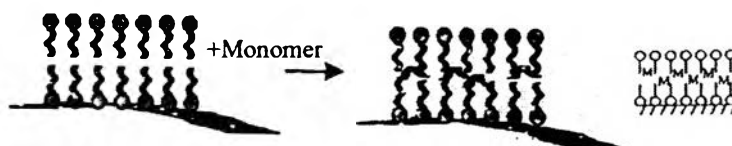


Figure 2.9b-1 Admicelle Adsolubilization of polymerization process.

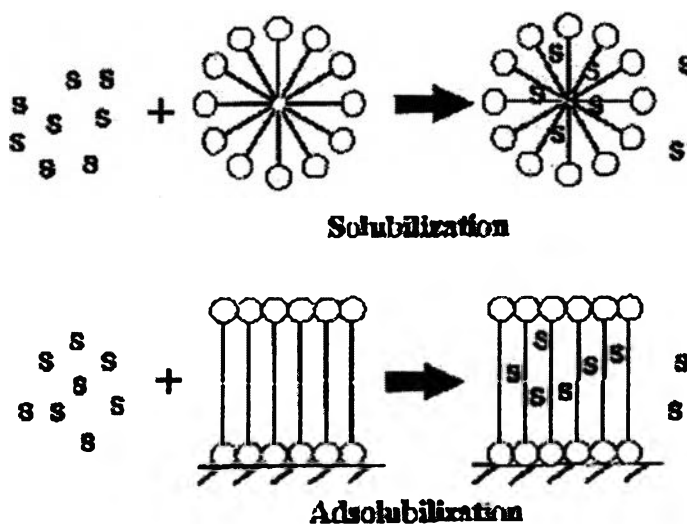


Figure 2.9b-2 Solubilization and adsolubilization phenomena.

2.4.3 Step 3: Polymerization of Adsorbed Monomer

The monomer concentrated at the surfactant bilayers (step2) is reacted with a water-soluble initiator. The polymerization is occurred and the monomers are converted to polymer (Figure 2.9 c).

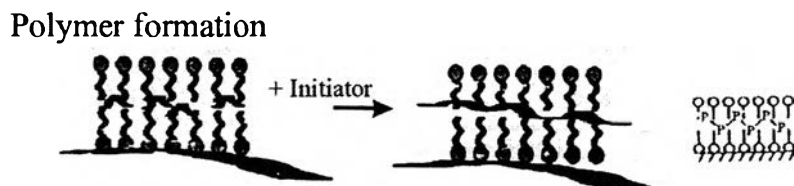


Figure 2.9 c Polymer formation of polymerization process.

2.4.4 Step 4: Surfactant Removal

After the polymerization is completed, the upper layer of the surfactant (excess surfactant) is removed by washing. In order to obtain an ultrathin polymer film, the excess surfactant is removed by washing with water (Figure 2.9 d).

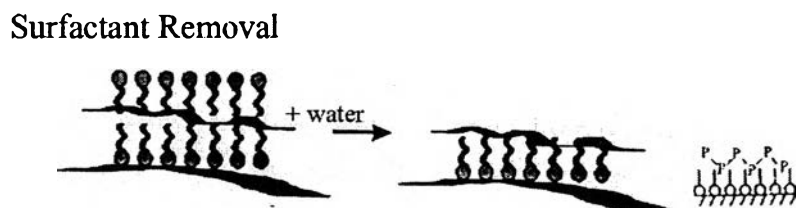


Figure 2.9 d Surfactant removal of polymerization process.

This technique is simple with low energy consumption and is more economical than other coating techniques.

2.5 Surfactant

A surfactant, or surface active agent, is a chemical substance that is the most versatile product in the chemical industry. Surfactants are used in automobiles, detergents, pharmaceuticals, and are also applied to many high technology areas.

2.5.1 Fundamentals of Surfactants

A Surfactant, surface active agent, consists of two different structural groups, as shown in Figure 2.10. One is the hydrophilic head group and the other is hydrophobic tail group.

In general, the molecules at the surface or interface have higher potential energy than these in the interior because the interaction between same substances is stronger than that between different substances. When the surfactant is dissolved in a solvent, the lypophobic group of the surfactant in the interior of the solvent causes an increase in free energy of the system. Therefore, displacement of the surfactant molecules to the surface or interface is easier than that of the solvent molecule. From these reasons, the amphipathic structure of the surfactant is the cause of

- (1) High concentration of surfactant at the surface,
- (2) Reduction of the surface tension of water, and
- (3) Orientation of the surfactant molecules at the surface or interface in the aqueous phase.

Surfactants are one of the most unique chemical compounds, having the property of adsorbing onto surfaces or interface of the system and of altering to a marked degree the surface free energies of these surfaces.

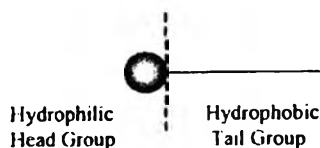


Figure 2.10 A surfactant molecule.

The surfactant can be classified into four categories, which depends on the nature of the hydrophilic group.

1. **Anionic surfactant:** The hydrophilic group consists of a negative charge; for example, $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate).

2. **Cationic surfactant:** The hydrophilic group consists of a positive charge; for example, $\text{RNH}_3^+\text{Cl}^-$ (salt of long chain alkyl amine).

3. **Zwitterionic surfactant:** The hydrophilic group may give both negative and positive charge; for example, $\text{R}^+\text{NH}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid).

4. **Nonionic surfactant:** The hydrophilic group does not contain any ionic charge; for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid).

Figure 2.11 illustrates an adsorption isotherm for an ionic surfactant adsorbed on an oppositely charged hydrophilic surface.

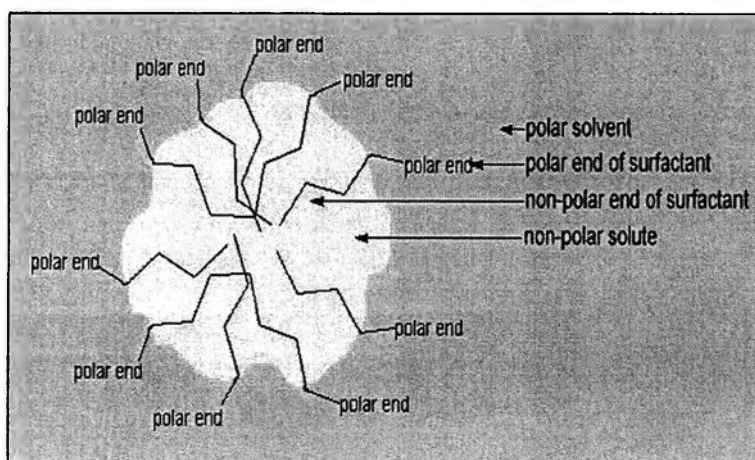
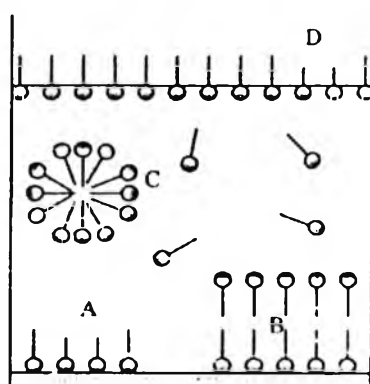


Figure 2.11 Molecular structure of a surfactant.

In aqueous solution, surfactant molecules nucleate to form micelles at concentrations higher than the critical micelle concentration (CMC). The CMC is a specific characteristic of each surfactant. Surfactants can form at least three different types of aggregates: Monolayer, called a hemimicelle, or bilayer, called an admicelle at the liquid-solid interface, a micelle in solution, and a monolayer aggregate at the air-liquid interfaces, as shown Figure 2.12.



A : Hemimicelle

B : Admicelle

C : Micelle

D : Monolayer aggregate at air-liquid interface.

Figure 2.12 Surfactant aggregates.

Surfactant adsorbs onto the solid surface at the interface to form hemimicelle and admicelle aggregate that can be quantified by adsorption isotherm. Surfactant adsorption is one of its singularly important features in an oriented fashion. This property has been studied and applied in many areas, such as detergent to remove soil or dust from clothes and the adsorption polymerization process that has been increasingly utilized in nanocoated film of polymer onto substrates for various purposes.

2.5.2 Adsorption of Surfactant at Solid-Liquid Interface

The adsorption of a surfactant at the solid-liquid interface is strongly influenced by three main factors:

1) The grouping of the natural structure, of solid surface whether the surface contains a highly charged site or essentially nonpolar groupings, and the

nature of atoms of which these sites or grouping are constituted (e.g. polar group, or nonpolar group);

2) The molecular structure of the surfactant as the adsorbate, whether it is ionic or nonionic and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic. (e.g. anionic, cationic, or nonionic surfactant); and,

3) The surrounding aqueous phase – its pH, its electrolyte content, the presence of any additive, such as short-chain polar solutes, and its temperature (e.g. pH, electrolyte content, and temperature).

These factors can influence the mechanism of adsorption. Generally, there are many types of mechanisms of surfactant adsorption onto substrates involving single ions. These mechanisms consist of ion exchange, ion pairing, acid-base interaction, adsorption by polarization of π electrons, and adsorption by dispersion forces. (Bitting, D. 1985)

In a solid aqueous system, the adsorption isotherm has been studied to understand the behavior of the surfactant on a solid surface and in solution. The amount of surfactant adsorption per unit mass or unit area of solid adsorbent is a convenient way to indicate the amount of adsorbent cover in a constant-temperature system. The amount of adsorbed surfactant can be calculated from the simple basic equation:

$$n_i^s = \frac{\Delta n}{m} = \frac{(\Delta C)V}{m} \quad (2.1)$$

where

n_i^s = the number of moles of adsorbed surfactant per gram of solid adsorbant at equilibrium,

Δn = the change in the number of surfactant molecules in solution,

m = the mass of the adsorbant in grams,

ΔC = the change of the molar concentration of surfactant in solutions.

V = the volume of liquid phase in liters.

From the number of moles of surfactant adsorbate per gram, n_i^s , the surface concentration, C_i^s , in mol/cm² of surfactant adsorbate can be calculated when the surface area per unit mass of solid adsorbent (a_s) in cm²/g, or specific surface area, is known. The calculation equation is:

$$C_i^s = \frac{(\Delta C)V}{a_s x m} \quad (2.2)$$

Either n_i^s or C_i^s can be chosen to plot the adsorption isotherm curve. The surface area per adsorbate molecule on substrate, a_i^s , in square angstroms, may be calculated from the adsorption isotherm curve by the following equation:

$$a_i^s = 2x \frac{10^{16}}{N C_i^s} \quad (2.3)$$

The a_i^s of the completely formed admicelle can be obtained by using C_i^s from the curve at CMC, and N is avogadro's number.

Many studies have been reported on the adsorption of surfactant on high surface area solids such as metal or glass. Somasundaram and Furerstenau (1996) were the first introducing the adsorption isotherm shape obtained for surfactant on alumina. (Chantarak S. *et. al.*, 2006)

The shape of an adsorption isotherm curve can be classified into 2 types depend on the adsorbent.

2.5.2.1 S-Shaped Curve

The curve has shown an S-shape that can be divided into four regions by following the change in the slope that is related to the phenomena of surfactant adsorption at the solid interface. (Bitting, D. 1985)

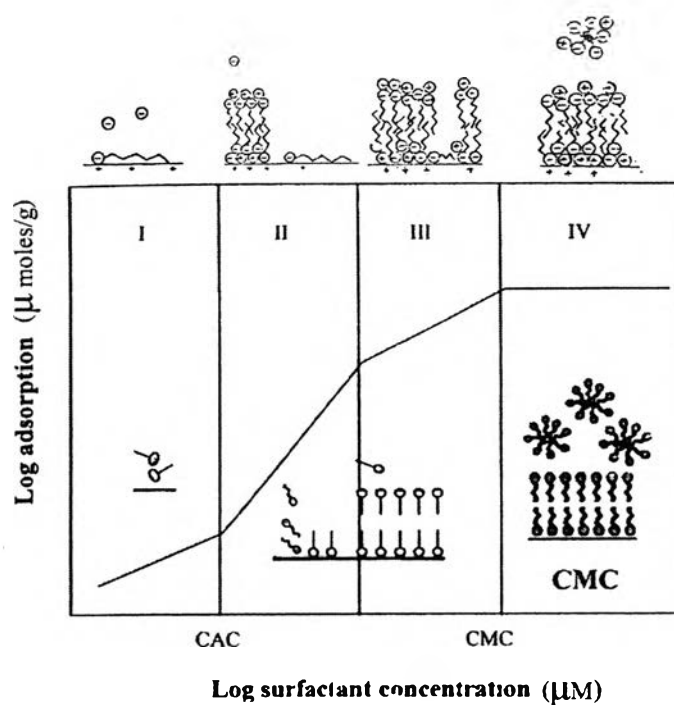


Figure 2.13 Typical adsorption isotherm of a surfactant in solution (S-shaped curve).

Region 1 is commonly referred to as the Henry's law region because there is a unique slope describing the adsorption under low concentration of surfactant. The equilibrium adsorption is proportional to the surfactant concentration in the solution. The drive for the adsorption is largely due to the electrostatic attraction between the charge surfactant species and the oppositely charged mineral oxide surface. As a result of sparsely adsorbed surfactant ion in Region 1, there is little or no interaction between individually adsorbed surfactant ions. It could be generally accepted that the surfactant/ surfactant interactions are negligible in this region. However, there can be significant interaction between the hydrophobic tail and the surface as evidenced by calculations of the chemical potential change per methylene group for monomers adsorbing out of solution.

Region 2 is characterized by a sharp increase of the slope. This slope of the isotherm indicates a cooperative effect of adsorption with the increase of surface coverage and an enhancement of the affinity of surfactant to the surface.

At this concentration, the surfactants start to aggregate on the substrate and the changing point from Region 1 and 2 is called “Critical admicellar concentration” or “CAC”. (Bitting D, 1985)

Region 3 is characterized by a decrease in slope with the increase of surfactant adsorption. According to Harwell (1985), a common explanation for adsorption behavior in this region is that with increasing adsorption of like-charged head groups on the surface, they begin to repel each other under the action of columbic repulsion force. Another fine distinction may be expressed as the more energetic site offering more favorable adsorption density in Region 2 than the less energetic site in Region 3. Besides the electrostatic effect, there is always the hydrophobic interaction effect present in the tail-tail interactions of the surfactant in both regions.

In the final region, **Region 4**, the adsorption level is nearly constant while total surfactant concentration increase. In this region, the surface concentration of adsorbed surfactant has reached a saturation point, so a further addition of surfactant is only distributed to the bulk liquid. This plateau adsorption is due to the formation of micelles to account for the excess amount of surfactant added to the system. The concentration at which micelle formation begins, or the changing point from Region 3 to 4, is called the “Critical Micelle Concentration” or “CMC”. Surfactant surface coverage can be limited either by the attainment of CMC below bilayer coverage at low surface charge densities or by the attainment of bilayer coverage below CMC at high surface charge denser (Scamehorn *et al.*, 1982). In either case, the adsorbed surfactant adsorption remains constant with further increase in surfactant concentration.

Parameters for surfactant adsorption

The important parameters for surfactant adsorption are the structure of the substrate surface, the molecular structure of the surfactant, and the environment of the aqueous phase.

The most critical parameter is pH of the solution, relative to the pH at which the surface exhibits a net surface charge of zero (or point of zero charge, PZC) as shown in Figure 2.14.

At pH values below the PZC, the surface becomes protonated and more positively charged. At pH values above the PZC, the surface is negatively charged. Therefore, anionic surfactants adsorb well below PZC and cationic surfactants adsorb above PZC.

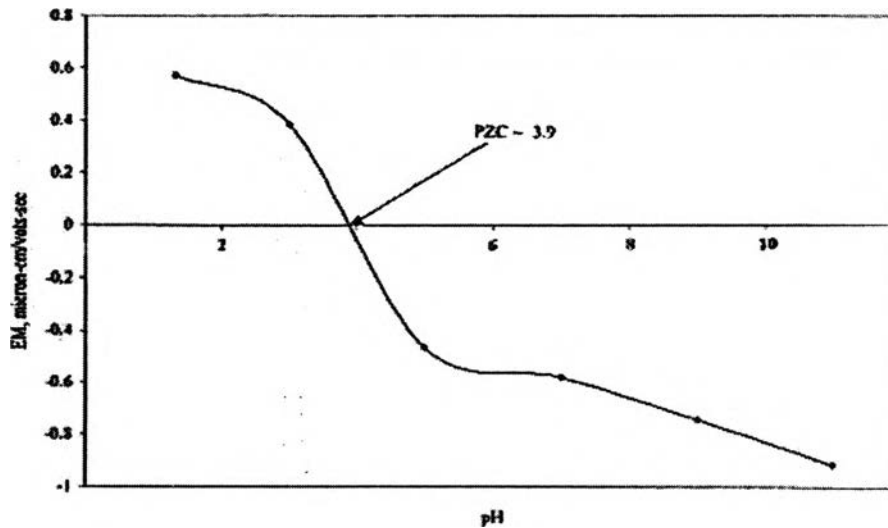


Figure 2.14 Point of zero charge on a natural rubber surface.

Wu *et al.*, (1988) studied the adsorption of an anionic surfactant, sodium dodecyl sulfate, SDS, on the solid surface of alumina. The PZC of the alumina was pH 9.5 at 30°C, thus the solution was adjusted to pH 4.0 to be suitable for the anionic surfactant.

2.5.2.2 L-Shape Curve

The adsorption isotherm of a surfactant from aqueous solution onto nonpolar, hydrophobic adsorbents gives an adsorption isotherm curve in the form of Langmuir type or L-shape curve as shown in Figure 2.15.

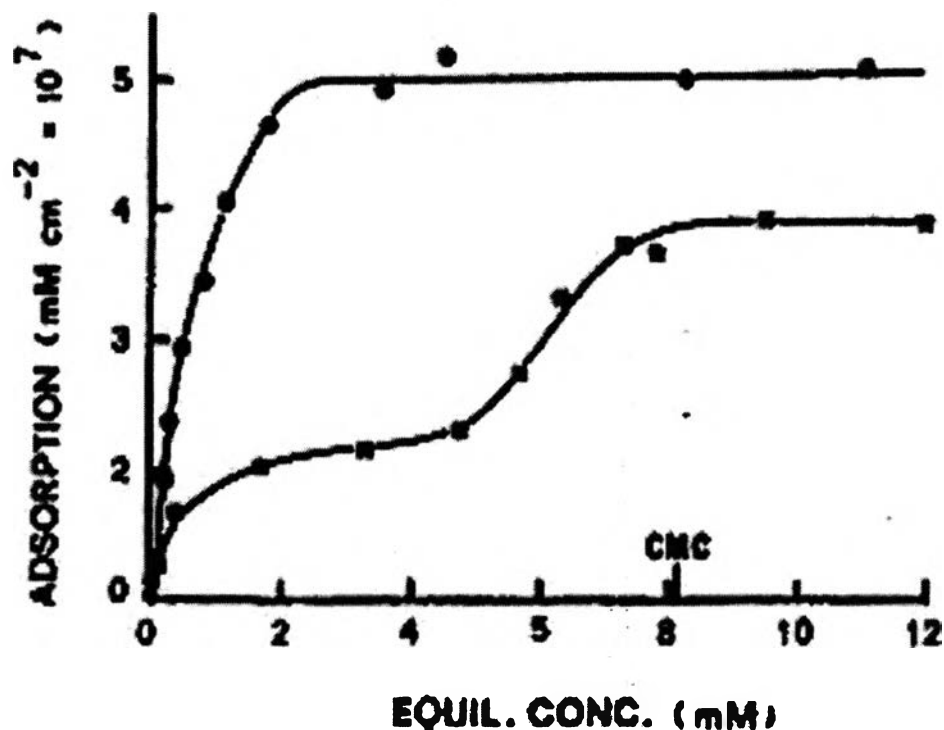


Figure 2.15 Adsorption isotherm of a surfactant from aqueous solution onto nonpolar, hydrophobic adsorbents.(L-shaped curve)

The hydrophobic tails of the surfactant are adsorbed on the solid surface, so the orientation of the molecules of surfactant is mostly parallel to the surface. When the molecules of surfactant continue to adsorb on the surface, the orientation is more and more perpendicular to the surface. The inflection point may be from the change of orientation from parallel to perpendicular (Rosen, M.J. 1989).

There are some studied researches and reviews involed the behavior of surfactant adsorption of the solid substrate and the admicellar polymerization technique from various different substrate, surfactant, monomer and coditon, which are briefly showed as follows:

In 1987, Wu *et al.* used the admicellar polymerization to form ultrathin polymer film on a solid surface. They use styrene monomer, sodium dodecyl sulfate (SDS) for surfactant and alumina for solid substrate. Their experiments illustrated that admicellar polymerization consist of three step including

admicelle formation, monomer adsolubilization and polymer formation. From adsorption isotherm of SDS, the presence of styrene was found to increase SDS adsorption. Ultrathin film of polystyrene of several nanometer thick was formed on alumina surface.

Polymerization of styrene adsolubilized in surfactant bilayer on alumina was investigated by Esumi *et al.*, (1991). They used styrene monomer, sodium 10-undecenoate surfactant and alumina for solid substrate. They found the adsolubilized amount of styrene increased with equilibrium concentration of styrene and reached a plateau. The polymerization of such a system with UV irradiation in the presence of an initiator enhanced dispersion stability of the alumina compared with the polymerization of bilayer of sodium 10-undecenoate alone on the alumina.

In 1995, Funkhouser *et al.* coated the polypyrrole on alumina surface by using SDS surfactant. The polypyrrole is a one type of conductive polymer that used in electrical conductivity application e.g. sensor, electrode, etc. They found the reverse result of SDS adsorption when adding the pyrrole and salt. The presence of pyrrole results in decreasing the SDS adsorption.

The problem of non-bonding interaction between reinforcing silica and polymer affects their compatibility, especially rubber compound. Waddell *et al.* (1995) improved those problems using admicellar polymerization to modify the silica surface by coating it with polymers. There are many types of polymers and copolymers were used for coating, the result showed that the modified silica can improve mechanical properties of rubber compounds and improve cure time. The different chemical substance and the reaction condition result in different properties of modified silica.

In 1995, Sakhalkar *et al.* found coating glass fiber with polystyrene via admicellar polymerization technique. Glass fiber can form unhomogeneous surface. The result showed that styrene in supernatant reduced with time after equilibrium of bilayer surfactant was formed on the substrate because styrene moved to the interior of micelle and polymerized. In addition, polymerization also occurred in aqueous phase but it was lower than that in the micelle. The reasons of nonuniformity of glass fiber surface were unhomogeneous of fiber surface.

In 1996, O'Haver *et al.* studied the mechanical properties of modified silica surface. They used polar comonomer and cetyltrimethylammonium bromide (CTAB) that produced new classes of reinforcing fillers. It improved the physical properties of rubber compound.

In 1996, Kitiyanan *et al.* tried to study adsolubilization mechanism of styrene and isoprene in CTAB surfactant admicell on precipitated silica. The adsolubilization equilibrium constant is important because it indicated amount of styrene adsolubilized into the palisade layer, The ore of the micelled and isoprene adsolubilized into the palisade layer, In comonomer systems, slope of adsolubilization isotherm dramatically increased. It can be concluded that comonomer adsolubilization is better than monomer system.

In 2002, thin film polystyrene coating on cotton using linear alkylbenzene (LAS) as the surfactant by admicellar polymerization was investigated by Pongprayoon *et al.* The result showed that the high pH results in low adsorption of LAS, and the increase of salt concentration causes an increase of LAS adsorption.

Polypyrrole coated on natural rubber latexes with sodium dodecyl sulfate (SDS) as a surfactant was carried out by Bunsomsit *et al.* (2002). They studied admicellar polymerization process under each step and found the influence of chemical substance to reaction. In this work, they found the PZC of natural rubber latex and adsorption isotherm. They studied the effect of salt concentration of SDS adsorption isotherm and pyrrole adsolubilization. They found salt concentration caused an increase in SDS adsorption and pyrrole adsolubilization. Moreover, they studied the effect of pyrrole concentration to SDS adsorption isotherm. They found, increasing pyrrole concentration caused a decrease in SDS adsorption at equilibrium. From this studied conductivity of polypyrrole coat natural rubber without salt was the lowest, it could be improved significantly with addition of salt.

Arayawongkul *et al.* (2002) tried to characterize polystyrene produced by admicellar polymerization. They used cetyltrimethylammonium bromide (CTAB) surfactant and extracted polystyrene from the surface of modified silica with tetrahydrofuran (THF). This research focused on the effect of surfactant loading, monomer loading and reaction time on the characteristics of polymer. The

result showed the reaction time for conducting admicellar polymerization should not shorter than two hours to obtain relatively high molecular weight polystyrene. The extent of the polystyrene film and amount of polystyrene forming on silica particles increased with increasing CTAB adsorption and adsolubilized styrene.

In 2003, See *et al.* using atomic force microscopy to investigate ultrathin polystyrene films formed by admicellar polymerization on silica disks. Their goal was to examine changes in the properties and morphology of the formed polymeric films due to changes in the surfactant and monomer feed levels. They found a smooth thin film that occurred at high concentrations of styrene but at lower styrene loading, the polystyrene film became unstable and formed droplike aggregates. When samples were examined again after 1 year, the polystyrene films had agglomerated, forming larger agglomerates in straight-line or ringlike structure at higher feed concentrations.

Xin *et al.* (2003) used X-ray photoelectron spectroscopy to study hydrophilic surfaces of a rough solid and porous solid modified via admicellar polymerization. They studied the removal of polymer after admicellar polymerization with water and water followed by Soxhlet extraction with toluene. They found organic material can be removed only 30% after water wash and 50% if followed by Soxhlet extraction with toluene. Moreover, on the outside surface, the ratio of surfactant to polymer after admicellar polymerization and the solvent washes is approximately 1:1 whereas the ratio on the interior surface is approximately 3:1.

Preparation and characterization of natural rubber dispersed in nano-matrix was studied by Kawahara *et al.* (2003). They were investigated in terms of graft-copolymerization of deprotenized natural rubber latex with styrene, using tert-butylhydroperoxide/tetraethylenepentamine as an initiator. They use ¹H-NMR spectroscopy, size-exclusion-chromatography and transmission electron microscopy after staining the films with OsO₄ for characterization. They found natural rubber particles of about 0.5 μm in diameter were dispersed in polystyrene-matrix of about 15 nm in thickness and the stress at break was found to be the highest due to not only nano-matrix of polystyrene but also the highest grafting efficiency.

In 2004, Srinarang *et al.* investigated the admicellar polymerization of polystyrene on natural rubber particles using

hexadecyltrimethylammonium bromide (CTAB) as the surfactant and 2,2'-azobis(2-methylpropionamide) (V50) as the soluble initiator. The suitable pH, time of surfactant adsorption, CTAB concentration and styrene concentration were studied. They found that the suitable pH was chosen at higher than 3.3 to achieve the adsorption of the cationic surfactant CTAB. The presence of salt resulted in increasing CTAB adsorption and styrene adsolubilization, moreover it also improved the amount, orientation and packing of CTAB. Time of 15 h was sufficient for surfactant adsorption. They also found that the higher initial styrene concentration resulted in the higher equilibrium styrene concentration and the higher the styrene adsolubilization.

In 2005, Natasorn *et al.* modified the silica surface by using admicellar polymerization in continuous stirred-tank reactor system (CSTR) to improve the compatibility between the silica and rubber. The ingredient was comprised of precipitated silica, cetyltrimethylammonium bromide (CTAB) cationic surfactant, styrene and isoprene comonomers, and 2,2'-azobisisobutyronitrile initiator. The result showed that the modified silica reduced T_{90} cure times and improved modulus, abrasion resistance, and compression set. The optimum conditions for surface modification of silica by the admicellar polymerization process were 5 g comonomer loading per kg silica and a 30 min reaction time. In comparison with the modified silica using a batch process, the modified silica obtained from the CSTR process was found to be superior in the performance of rubber compound.

The surface modified calcium carbonate (CaCO_3) particles by admicellar polymerization to be used as filler for isotactic polypropylene was investigated by Rungruang *et al.* (2006). The sodium dodecyl sulfate (SDS) and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) were used as the surfactant template and the thermal initiator, respectively. Non-isothermal crystallization was studied and indicated that surface treatment of CaCO_3 particles reduced the ability for CaCO_3 particles to nucleate the isotactic PP matrix. The behavior of these coated particles in an isotactic PP matrix was compared to that of uncoated and steric acid-coated ones. The composites made with stearic acid-coated and admicellar-treated CaCO_3 particles had lower tensile strength, Young's modulus and flexural strength, but higher impact strength.

In 2006, Preechasup *et al.* studied the admicellar polymerization of styrene coated on natural rubber using two different types of surfactants (SDS and CTAB) and optimum conditions with ratio of styrene to initiator 1:0.04. Under aging condition, the modulus, tensile strength and thermal mechanical property can be improved caused by increment of the compatibility between two components.

In 2007, Isahoh *et al.* investigated the admicellar polymerization of styrene coated on natural rubber by varying styrene concentrations from 50 to 300 mM. The cure rate and the minimum torque of admicelled PS-NR with any styrene concentration were lower than that of NR, but the maximum torque was vice versa. In the physical properties study, the cured admicelled PS-NR with 300 mM-styrene has the highest tensile strength, modulus and hardness but lowest elongation at break. The rheological behavior of admicelled PS-NR, using a Capillary Rheometer, indicated better processability after blending and mixing with 50 %wt. NR and 30 phr silica, respectively.

In 2008, Chirasakulkarun *et al.* used electrochemical and admicellar polymerization with Sodium Dodecyl Sulfate (SDS). The admicellar polymerization of PPy and PTh by electrochemical method over natural rubber particles is investigated by varying monomer content and applied voltages. A mechanical property of admicelled rubber was also developed, making it stiffer than natural rubber. The conductivity of the modified rubber is about 10^{-9} to 10^{-4} S/cm for PPy and about 10^{-12} to 10^{-6} S/cm, both of which are much higher than that of natural rubber by several orders (the conductivity of pure natural rubber is about 10^{-15} S/cm).