

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Natural Rubber

Hevea brasiliensis, a tropical tree, is a major source of the world's rubber. Thailand has approximately 5 million acres of rubber plantations located mostly in the southern and eastern parts of the country and is the world's largest rubber producer. Natural rubber (NR) is known chemically as polyisoprene and consists of tens of thousands of linked molecules, each one a simple 13-atom combination of carbon and hydrogen. Similar to other olefin molecules, the double bond on the repeating unit of NR can be modified by various chemical reactions. Natural rubber is a renewable polymer material exhibiting excellent physical and chemical properties. It 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 is less resistant to environmental damage (for example, 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, a little mineral matter and water. The hydrocarbon component of NR, which consists of over 99.99% of linear *cis*-1,4-polyisoprene is shown in Figure 2.1 (Werner, 1989)

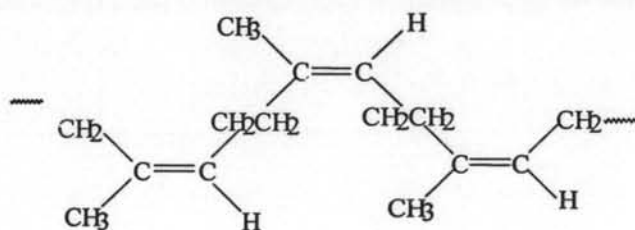


Figure 2.1 Chemical structure of NR (*cis*-1,4-polyisoprene).

The cause of its excellent processing behavior is due to the average molecular weight of the polyisoprene in NR ranging from 200,000 to 400,000 with a

relatively broad molecular weight distribution. There is one double bond for each isoprene unit, which along with the α -methylene groups contained in an NR molecular chain, are reactive groups for vulcanization with sulfur. The glass transition temperature (T_g), the temperature or range of temperature which the polymer exhibits a remarkable change in several physical properties, of uncured NR is approximately $-76.2 \pm 0.5^\circ\text{C}$, far below room temperature. Therefore, rubber is soft and can be melted by heat. Conversely, it is rigid and brittle at low temperatures. Hence, NR can be utilized in a narrow temperature range (Werner, 1989).

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

2.2 Silica Filler

Fillers have played an important role in the plastics industry. Because of the expanding industrial activities, there is a continual demand for improved materials to satisfy the increasingly stringent requirements. Silica has been widely used in the paint and plastics industry. In thermoplastics, silica provides many functions such as reduction in shrinkage and crack formation, reinforcement, improvement in electrical properties and hardness, faster molding cycles as a result of increased thermal conductivity (Gachter and Muller, 1984).

Silica fillers can be classified into two major classes, natural and synthetic silica. 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 yearly silica usage in rubber (Hewitt, 2000). Two fundamental properties of silica that influence their use in rubber compound reinforcement are particle size and extent of hydration (Mark *et al.*, 1994). Precipitated silica is often used in the production of highly reinforced white or light colored polymer compounds.

Silanol (SiOH) groups on the silica surface can react with oxygen or nitrogen containing material such as glycol, alcohol, water, amine, and divalent metal salts. The silanol to silanol reaction by hydrogen bonding (Figure 2.2) is responsible for the formation of an extensive network that produces a stiff and highly viscous mixture. This type of structure makes processing more difficult while the presence of silanol groups makes precipitated silica hydrophilic. Unmodified silica does not interact well with most polymers, requiring high amounts of shear and energy to incorporate them evenly.

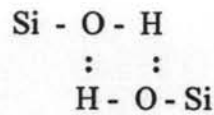


Figure 2.2 Silanol to silanol reaction by hydrogen bonding.

Moreover, it was found that the development of surface functional groups leads to a significant physical change in silica surfaces, such as microstructures and surface free energy parameters (Park *et al.*, 2001).

2.3 Surfactants

A surfactant is a molecule composed of both lyophilic (solvent loving) and lyophobic (solvent hating) sections. When the solvent is water, these sections are said to be hydrophilic and hydrophobic. The hydrophilic section is called the head while the hydrophobic section, usually a long hydrocarbon chain, is called the tail. The tail may be depicted either as a straight line or a wavy tail, Figure 2.3. Surfactants can form various types of aggregates, micelles in solution and admicelles and hemimicelles on surfaces.

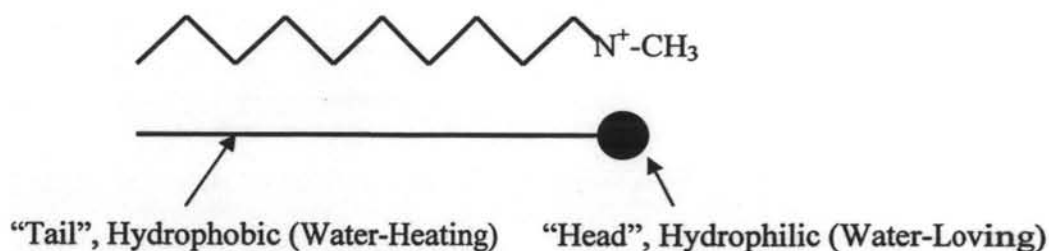


Figure 2.3 Surfactant structure.

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)

- Anionic. The surface-active portion of the molecule bears a negative charge, for example, RCOO^-Na^+ (soap), $\text{RCH}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate).
- Cationic. The surface-active portion bears a positive charge, for example, $\text{RNH}_3^+\text{Cl}^-$ (salt for a long-chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quarternary ammonium chloride).
- Zwitterionic. Both positive and negative charges may be present in the surface-active portion, 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 charge depends on pH of solution. At low pH (acidic solutions), they form cations, and at high pH (alkaline solutions), they form anions. For example, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid), $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ (sulfobetaine).
- Nonionic. The surface-active portion bears no apparent ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol).

2.3.1 Cationic Surfactants

The term “cationic surfactant salt” is used to denote an ionic compound in which the cation is amphiphilic (contains nonpolar structural elements as well as the cationic site) and strongly surface active. In true quarternary ammonium ions, four carbons are bound to a positive nitrogen atom, and in surfactant

ammonium ions one or more of these substituent groups is lipophilic. Generally, the cationic hydrophilic groups can be divided into two sub-groups; neutral and acidic.

Cetyltrimethylammoniumbromide (CTAB) is a familiar cationic surfactant in the neutral sub-group as shown in Figure 2.4.

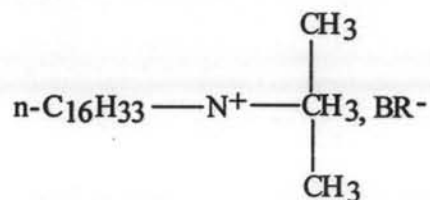
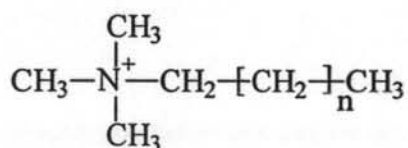


Figure 2.4 Structure of CTAB.

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" (nonacidic and nonbasic) in water from an acid-base perspective. If the anionic partner in such a salt is also neither acidic nor basic, as with bromide, the molecular structure of this salt is independent of pH (Rubingh and Holland, 1990).

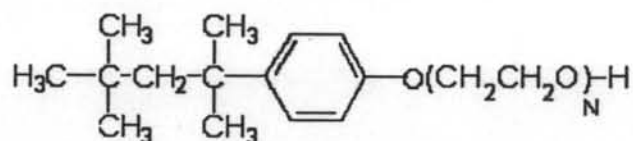


n=16

Figure 2.5 Structure of Arquad[®]T-50.

However, in this study we used Arquad[®]T-50 (Octadecyl trimethyl ammonium chloride) as a commercial grade cationic surfactant instead of the chemical grade surfactant. Arquad[®]T-50 has a similar structure to CTAB although it has a longer chain than CTAB as shown in Figure 2.5.

2.3.2 Nonionic Surfactants



N = 9-10

Figure 2.6 Octyl phenol ethoxylates (Teric[®]X-10).

Nonionic surfactants are surface-active compounds where the hydrophilic portion is polar, but not charged. They have good performance in a variety of applications, are compatible with all other types of surfactants and are 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, electrolyte at high concentration (Rosen, 1989). Commercial surfactants are a mixture of products with a wide distribution of polyoxyethylene chain lengths. Triton[®]X-100, a common nonionic surfactant that has a commercial grade name of Teric[®]X-10, is a familiar nonionic surfactant. Teric[®]X-10 is often used in biochemical applications to solubilize proteins, which has no antimicrobial properties. It is considered a comparatively mild detergent and is non-denaturing. It is a clear to slightly hazy, colorless to light yellow liquid. Teric[®]X-10 structure is shown in Figure 2.6.

2.4 Mixed-Surfactants System

Nonionic surfactant can enhance micelle formation with either anionic or cationic surfactants. It seems reasonable that nonionic surfactant could also enhance the formation of micelles in mixed cationic-anionic systems.

Penfold *et al.* (2002) investigated the structure and composition of the mixed anionic and nonionic surfactants adsorbed at the hydrophilic silica solid-solution interface by using secular neutron reflectivity. Measurements showed that

the anionic surfactant sodium dodecyl sulfate (SDS) was adsorbed at the hydrophilic silica surface in the presence of the nonionic surfactant hexaethylene monododecyl ether but had an affinity for the surface in the absence of the nonionic surfactant. The variations of adsorbed amount, composition, and structure of the adsorbed layer were shown to reflect the different affinities of the two surfactants for the hydrophilic surface. At a solution concentration greater than the critical micellar concentration, the adsorbed amount decreased for solutions increasingly rich in SDS, and the surface composition was not consistent with the pseudo phase approximation.

2.5 Surfactant Adsorption

Adsorption is the tendency for a surfactant molecule to collect at an interface. Common examples are the taking up of a gas or liquid at the surface of another substance, usually a solid (for example, activated charcoal adsorbs gases). The adsorption properties of surfactants mean that surfactant molecules are usually found at the interface between an oil phase and a water phase or a water phase and an air phase. This molecular property leads to the macroscopic properties of wetting, foaming, detergency and emulsion formation.

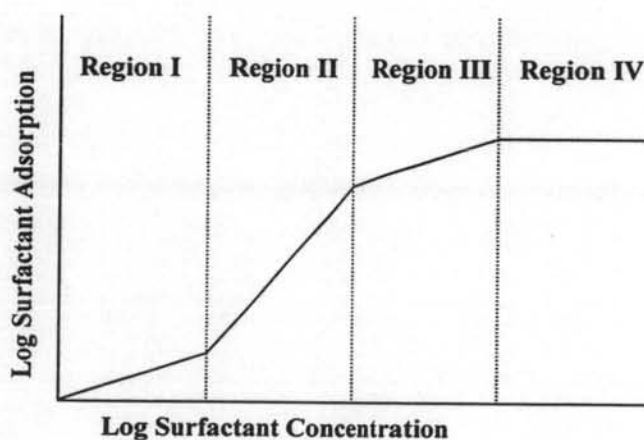
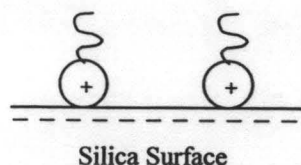


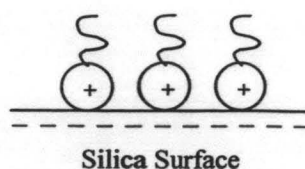
Figure 2.7 Typical adsorption isotherm of surfactants on a solid surface.

(Scamehorn *et al.*, 1982)

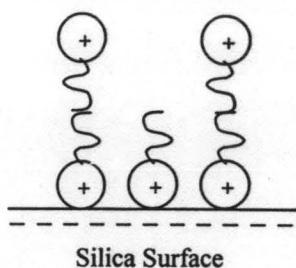
Region I Monolayer Formation
Coverage



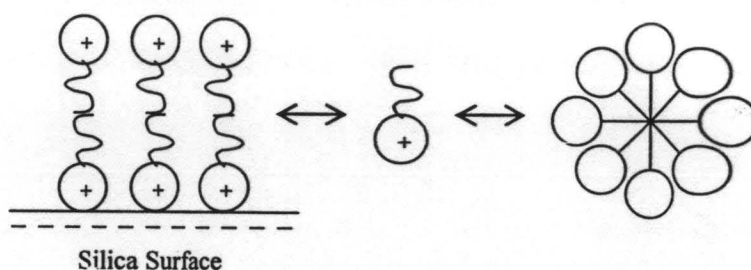
Region II Complete Monolayer



Region III Bilayer Formation



Region IV Surfactant near CMC



Results from surfactant adsorption experiments are usually expressed in the form of adsorption isotherm, which displays the amount adsorbed as a function of equilibrium surfactant concentration. The adsorption isotherm for an ionic surfactant onto an oppositely charge substrate is typically S-shaped which can be separated into four regions (Rosen, 1989) as shown in Figure 2.7.

Region I corresponds to both very low concentration and low adsorption of surfactant. This region is commonly referred to the Henry's law region because the adsorbed surfactant is considered to be in infinite dilution in the surface phase and, thus, the interaction between molecules of surfactants is negligible. Adsorbed surfactants in this region are viewed as being adsorbed alone and not forming any aggregates.

Region II. There is an increase in adsorption, resulting from interaction of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. These adsorbed surfactant aggregates are called admicelles or hemimicelles, depending upon whether the aggregates are viewed as bilayers or monolayers. The admicelle is considered as a local bilayer structure with a lower layer of head group adsorbed on the surface and an upper layer of head groups in contact with solution. The hemimicelle is a monolayer structure

having the head group adsorbed on the surface while the tail group is in contact with the aqueous phase. The transition of adsorbed from region I to region II, representing the first formation adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) or the hemimicelle concentration (HMC).

Region III. The slope of the isotherm is reduced because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid.

Region IV is the plateau region, having almost constant surfactant adsorption with increasing surfactant concentration at the transition point from region III to region IV is approximately at the critical micelle concentration (CMC).

2.6 Solubilization and Adsolubilization

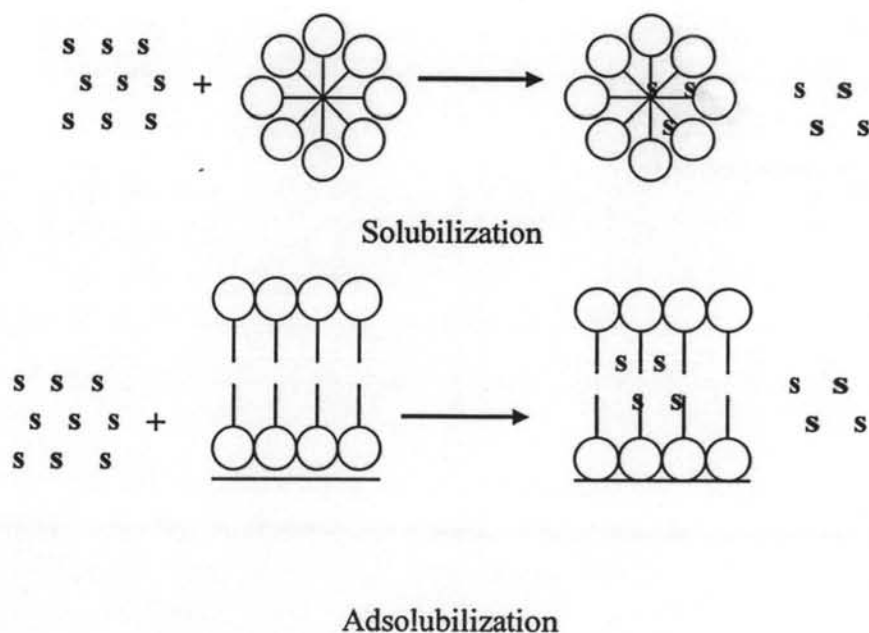


Figure 2.8 Phenomena of solubilization and adsolubilization.

Solubilization is defined as the spontaneous dissolving of a substance (solid, liquid or gas) by reversible interaction with the micelle of the surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (Rosen, 1989). The partitioning of organic solutes

from aqueous solution into the interior of adsorbed surfactant aggregate is termed adsolubilization (Dickson and O'Haver, 2002). This phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayer playing the role of micelle, as shown in Figure 2.8.

There are basically three locations within an admicelle where contaminants may be adsolubilized: the polar head region, the hydrophobic core region which this region consists of the hydrocarbon chains and is nonpolar in nature, and the so-called "palisade region" which is intermediate in polarity (Dickson and O'Haver, 2002), as shown in Figure 2.9.

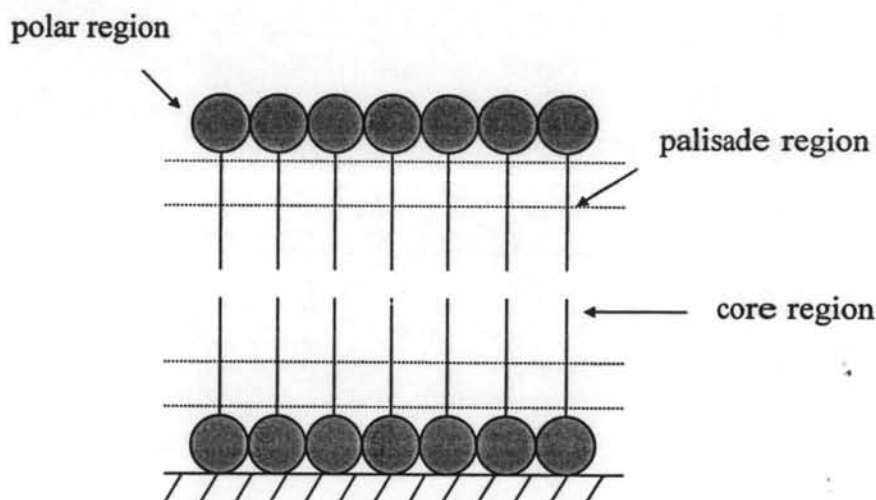


Figure 2.9 The admicelle structure.

Surfactant aggregates on solid/liquid interface, admicelles, are capable of removing hydrophobic organic compounds from solution (benzene, toluene, etc.) and enjoy a higher selectivity over other conventional technologies such as filtration and activated carbon adsorption (Lee, 2002). The location or combination of locations within the admicelle at which a particular contaminant will be adsolubilized depends primarily on the water solubility of the contaminant molecules and the structure of the compound. When the contaminant is non-polar and has low solubility in water, such as the alkanes or other hydrophobic organic compounds are preferentially adsorbed in the core region of surfactant aggregates, whereas the polar organic

compounds stay in the palisade layer or at the interface between surfactant aggregate and aqueous solution.

2.7 Admicellar Polymerization

Thin-film coating by admicellar polymerization generally consists of three steps: admicelle formation, monomer adsolubilization, and polymer formation as illustrated in Figure 2.10.

Step 1: Admicellar Formation. Adsorption of surfactants on substrates is a well-known phenomenon. For the adsorption of ionic surfactants on a solid surface, the adsorption isotherm curve is typically an S-shaped graph when one plots the log of adsorbed surfactant versus the log of equilibrium concentration of surfactant (Rosen, 1989). In admicellar polymerization, the surfactant concentration is chosen to be in region III to obtain maximum admicelle formation with no micelles in the solution to avoid emulsion polymerization.

Step 2: Monomer Adsolubilization. Many organic monomers are nearly insoluble in water. Thus, at equilibrium, they preferentially partition into the hydrophobic interior of the admicelle in the process called "adsolubilization". This process can occur either after the formation of the admicelle or concurrently with surfactant adsorption.

Step 3: Polymer Formation. In this step, initiator is added to start the polymerization in the admicelle. Water-soluble initiators are generally used and the initiation reaction is started in the aqueous phase as in the case of emulsion polymerization. After the polymerization reaction is complete, the upper layer of surfactant can be removed by washing to expose the layer of polymer on the substrate surface. Admicellar polymerization has been successfully carried out in many polymer-substrate systems. Examples are polystyrene on alumina (Wu *et al.*, 1987) and silica (O'Haver *et al.*, 1994), poly(tetrafluoroethylene) on alumina (Lai *et al.*, 1995), and styrene-isoprene copolymer on glass fiber (Grady *et al.*, 1998, Sakhalkar and Hirt, 1995). Most studies have concentrated on highly porous inorganic materials like silica and alumina. It will therefore be interesting to see if

the process also works well with a low surface area and low surface-charged organic substrate.

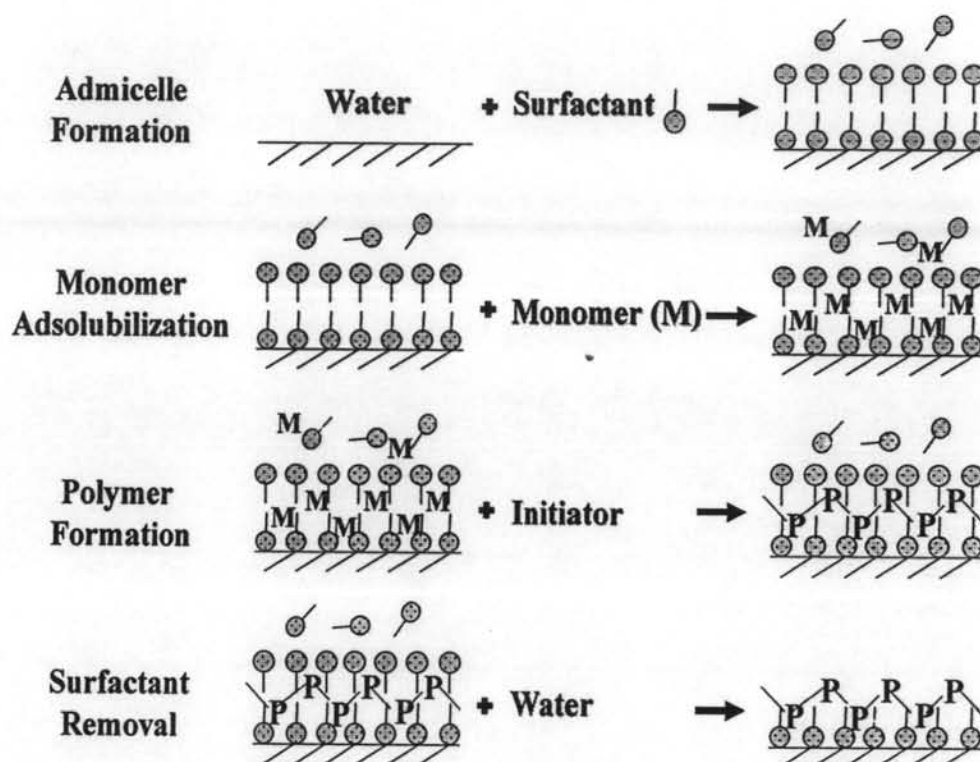


Figure 2.10 Admicellar polymerization process. (Wu *et al.*, 1987)

The adsorption of surfactant on the substrate surface is controlled by several parameters including the electrochemical nature of the substrate, the type of surfactant molecule, the pH of solution, and added counterion. Charge on the substrate surface can be manipulated to be either positive or negative by adjusting the pH of the contacting aqueous solution because both hydronium and hydroxide ions are potential determining ions for substrates. The solution pH at which the surface exhibits a net surface charge of zero is called the point of zero charge or PZC. At pH values below the PZC, the surface becomes protonated and more positively charged; above the PZC, the surface is negatively charged. Consequently, anionic surfactants adsorb well below the PZC and cationic surfactants above the PZC. The PZC of silica between 2 and 3, thus we would expect anionic surfactant to adsorb well at low pH and a cationic surfactant at high pH. With a relatively low concentration of

ionizable groups, however, this effect should not be as pronounced as substrates used previously for admicellar polymerization. Addition of an electrolyte will also help to reduce the charge on the surface, which may affect the adsorption of ionic surfactants.

Chinpan (1996) focused on the modified of silica by a process based on the in-situ polymerization by a batch reactor. It offered a potentially inexpensive method for modifying chemical and physical surface properties and has proven successful in improving cured rubber compound physical properties. The experiment showed that the amount of copolymer (styrene and isoprene) loading on the silica can significantly affect rubber compound reinforcing properties. The effect of silica loading was also investigated and the results showed that the performance increased up to a loading of 40 PHR, beyond which the properties began to deteriorate as the rubber became diluted.

Kitiyanan *et al.* (1996) studied adsolubilization of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) admicelle on precipitated silica. The results from single adsolubilization systems showed that styrene adsolubilization increased styrene equilibrium concentration in aqueous phase, while isoprene adsolubilization increased with increasing isoprene partial pressure. The adsolubilization equilibrium constants of both adsolubilizates were calculated, and suggested that styrene was adsolubilized into both the palisade layer and the core of admicelle, while isoprene was adsolubilized only into the palisade layer.

Until 2001, this process has been successfully performed only in a batch system, which is not feasible for industrial applications. So in the Chaisirimahamorakot (2001) work's, a continuous reactor for the admicellar polymerization was developed. CTAB, styrene and isoprene were used as a surfactant and co-monomers, respectively. Effects of co-monomers loading and retention time on the admicellar polymerization were also investigated. The result showed that the 5 g co-monomer per kilogram silica and 60 minutes polymerization time provided the largest amount of polymer on silica surface. Hence, it was believed that the CTAB aggregates on the silica surface was most likely in the form of a bilayer.

The next work was also studied on the continuous reactor with the focus on co-monomer loading. Nontasorn *et al.* (2005) concluded that at 5 g co-monomer

loading with low retention time (30 min) provided the highest overall improvement of surface characterization and rubber compound properties.

Kaitdamneon-ngam (2003) work's on surfactant and initiator loadings were optimized to reduce the amounts of both materials needed. Modification of the silica surface increased the mean agglomerate particle size and lowered BET surface areas as compared to the unmodified silica. This study showed that the rubber properties can be maintained by reducing the amounts of surfactant and initiator used. Imsawatkul (2004) investigated this technique using the mixtures of CTAB and Triton[®]X-100 for silica surface modification. The results showed improvement in mechanical properties of the rubber filled with the modified silica.

In order to reduce the modification cost, the commercial grade surfactants, Arquad[®]T-50 and Teric[®]X-10, were used by Supanam (2005). The Polymerization time and the molar ratio of mixed surfactant, Arquad[®]T-50 to Teric[®]X-10, are important variables that can be used to optimize the admicellar polymerization process for industrial applications. The results indicated that the increase in the best rubber compound physical properties was achieved with 3:1 Arquad[®]T-50 to Teric[®]X-10 molar ratio and 30 min polymerization time.

2.8 Factors Affecting Adsorption and Adsolubilization

The adsorption of surfactant at the solid-liquid interface is strongly influenced by a number of factor: (1) the nature of the structure groups on the solid surface-whether the surface contains highly charged sites of essentially nonpolar groupings, and the nature of the atoms of which these sites or groupings are constituted; (2) the molecular structure of the surfactant being adsorbed (the adsorbate)-whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic; and (3) the environment of the aqueous phase-its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes (alcohol, ureas, etc.), and its temperature. Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption (Rosen, 1989).

Kanjanakhunthakul (2002) researched the effects of ionic strength on the adsolubilization of toluene and acetophenone into CTAB admicelles on precipitated silica. The results showed that the adsorption of CTAB on the silica surface increased with increasing ionic strength. In the single-solute system, increasing ionic strength had little effect on the adsolubilization of toluene. However, the adsolubilization of acetophenone significantly increased with increasing ionic strength. In the mixed-solute system, the synergetic effect was observed in the adsolubilization of acetophenone in the presence of toluene and the effect was more pronounced with increasing ionic strength.

Pongprayoon *et al.* (2002) studied the effects of surfactant, styrene, initiator and electrolyte concentrations on the polymerization process. Results showed that polystyrene thin film was successfully formed on cotton, resulting in cotton that can resist wetting by a water droplet for longer than 30 min. Hydrophobicity of the treated cotton was found to depend on the LAS (Linear Alkylbenzene sulfonate):monomer and monomer:initiator ratios. An excess amount of styrene led to high MW polystyrene and in the system using more initiator, more polystyrene was formed, leading to higher hydrophobicity.

Pradubmook *et al.* (2003) studied the effect of pH on adsolubilization of a cationic surfactant (CTAB), on the precipitated silica and adsolubilization of toluene and acetophenone in CTAB at two pH values. Both single-solute and mixed-solute systems were investigated using batch liquid adsorption at pH 5 and pH 8. The results from the adsorption of CTAB revealed that increasing pH led to high amounts of surfactant adsorbed on the precipitated silica. In the single solute system, the adsolubilization of both solutes increased with increasing equilibrium concentration of the solute in the aqueous phase. For toluene, pH appeared to have little effect on the adsolubilization. In contrast, the pH effect was more pronounced in the case of acetophenone as indicated by significantly increase in the acetophenone adsolubilization when pH was increased from 5 to 8.

Aumsuwan (2003) focused on the characterization of ultra-thin polystyrene films formed via admicellar polymerization on a non-porous silica substrate. The results from experiment indicated that the molecular weight of the formed polystyrene increased with increasing styrene feed. Moreover, for two hours reaction

time, the ratio of initiator to styrene should not be less than 1:15 in order to obtain high molecular weight polymer.

Ou-udomying (2003) prepared high purity silica from rice husk. The results showed that specific surface area of rice husk silica was higher than commercial silica (Hi-Sil[®]255) by 47%. The average pore diameter of rice husk silica was smaller than Hi-Sil[®]255 silica by 19%. From the adsorption isotherm, it should be noted that the amount of CTAB adsorption on silica depended not only on specific surface area but also on pore size of silica.

Okamoto *et al.* (2004) investigated the effect of solution pH on the adsolubilization of 2-naphthol, biphenyl, and their binary solutes in the HTAB adsorbed layer formed on silica. It was found that the adsolubilization was significantly affected with the feed concentration of HTAB. At the low feed concentration of HTAB, competitive adsolubilization between 2-naphthol and biphenyl was observed at pH above 4.5. The adsolubilization of biphenyl was clearly enhanced over the whole pH region by incorporation of 2-naphthol at a high feed concentration. On the other hand, at the high feed concentration of HTAB, 2-naphthol adsolubilized in the palisade region, while biphenyl incorporated into the core of the layer. In addition, the admicellar partitioning coefficients demonstrated the change in the adsolubilization of the binary solutes with solution pH.

Kessadayurat (2004) investigated the influence of surfactant structure on adsolubilization of toluene and acetophenone, in a binary system of cationic surfactant (CTAB) and nonionic surfactants with different hydrocarbon chain lengths, Triton[®]X-165 and Triton[®]X-305, on precipitated silica. The results indicated that there was preferential adsorption via electrostatic interaction between CTAB and silica surface more than the hydrogen bonding between Triton[®]X and silica surface for the single-surfactant system. From the adsolubilization studies, it can be seen that the adsolubilization of toluene in both single- and mixed-surfactant systems depended on the amount of surfactant adsorbed on silica and indicated that toluene adsolubilized into both the palisade layer and the core of the admicelles. On the other hand, acetophenone adsolubilization in both single- and mixed-systems was not proportional to the amount of surfactant adsorbed on silica as observed in the case of toluene.

Hom (2004) studied the characteristics of the polystyrene film formed on precipitated nonporous silica Aerosil®OX50 surface using CTAB surfactant, and both water soluble (VA-044) and insoluble (AIBN) initiators via admicellar polymerization. The maximum adsorption of CTAB on precipitated nonporous silica Aerosil®OX50 was found to be ~130 $\mu\text{mol/g}$ of silica while the adsolubilization of styrene into CTAB bilayer increased with increasing styrene loading. The ratio of styrene to AIBN that yielded the highest molecular weight polymer was 1:15, while the ratio of styrene to VA-044 produced the highest molecular weight polymer was 1:7 and the thickness of the polymer film obtained between 2-15 nm.