



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Natural Rubber

The milky aqueous dispersion of rubber called latex is produced by the tree *Hevea brasiliensis* (Blow and Hepburn, 1982). Solid natural rubber (NR) is obtained by the latex coagulation using some acids. Raw NR contains 93-95% cis-1,4-polyisoprene, 2-3% proteins, 2% acetone-soluble resins (including fatty acids), water, small amounts of sugars and a little mineral matter. The hydrocarbon component of NR which consists of over 99.99% of linear cis-1,4-polyisoprene (Lim-ochakun, 2000) is shown in Figure 2.1.

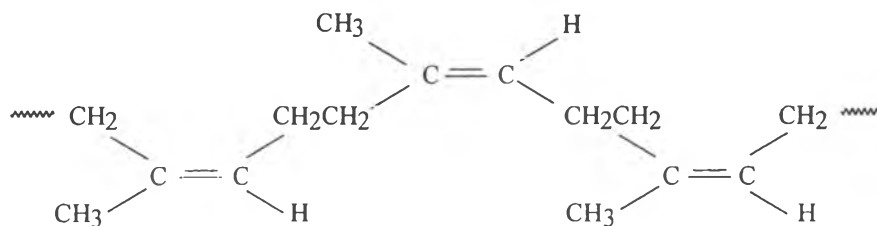


Figure 2.1 Chemical structure of NR (cis-1,4-polyisoprene)

The average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution, leading to 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 reactive groups for vulcanization with sulfur. The transition temperature (T_g) of uncured NR is approximately $-72.6 \pm 0.5^\circ\text{C}$, far below room temperature. As a result, rubber is soft and can be melted by heat. On the other hand, it will be rigid and brittle at low temperatures. Therefore, NR can be utilized in a narrow temperature range (Lim-ochakun, 2000).

The thermal properties of NR can be improved by vulcanization with sulfur. Although the vulcanized rubber has advantages such as high impact strength, low T_g and flexibility, it also has many undesirable properties such as, low hardness, stiffness, abrasion, and tear resistance. Fillers are thus utilized to improve performance in these properties (Lim-ochakun, 2000).

Kohjiya and Ikeda (2000) produced silica *in situ* in natural rubber by the sol-gel reaction of tetraethoxysilane before crosslinking. This resulted in a homogenous dispersion of silica particles in the NR matrix. It was estimated that the concentration of silanol groups on the silica surface was lower than those on the conventional silica surface. Therefore, the silica-silica interaction of the *in situ* silicas seems to be weaker than that of silica-rubber, resulting in better dispersion than the conventional silicas. The results suggested that NR, which is a renewable resource, and the *in situ* silica composite have considerable potential as a “green” material, useful for studying the reinforcement mechanism of inorganic fillers in NR.

2.2 Silica Fillers

Silica fillers can be classified as either natural or synthetic, which comprise the crystalline and amorphous forms, respectively. Among the synthetic silicas, precipitated silicas are 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 silicas 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 the silica has also been shown to be a good indicator of silica performance as filler (Waddell, 1995). In addition to reinforcement, dispersibility and freedom from dusting are important practical characteristics, which are related to silica manufacturing operations. Suppression of gel during precipitation prevents formation of large particles, visible in mixed compounds, which contain un-milled silica.

One of important silica properties relevant to rubber reinforcement is particle size. The smallest size of silica provides the highest tensile, tear strength, and abrasion resistance. The actual size of the reinforcing unit, however, is not that

of the individual particle, but that of agglomerate. Small particles produce small agglomerates; while large particles produce large agglomerates. Although particle size is the essential silica property, which governs its performance in rubber, a more usual, and convenient, means of classification is surface area, expressed in square meters per gram.

Second on the list of characteristic silica properties is water, either in the form of tightly bound silanol groups or as loosely held free moisture. Free water content usually 5 to 7%, as shipped, tends to remain in equilibrium with relative humidity. Bound water in the term of silanol groups is the source of much singular behavior or silica in rubber.

Precipitated silicas are often used in the production of translucent and colored products. Using admicellar polymerization-modified silica in rubber compounding significantly reduces cure times, increases tensile strength, and lowers the compression set and heat buildup compared to compounds made with unmodified silicas (Waddell, 1995). Precipitated silicas are used in both tires and shoe soles applications. In combination with reinforcing blacks they improve tear resistance and adhesion to fabrics. Hydrated silicas retard the cure time and require the use of an accelerator or the addition of materials such as glycols or amines to promote curing (Katz, 1987).

Silicas are considered as polymers of silicic acid, in which the bulk structure is produced by interlinking SiO₄ tetrahedrals. At the surface, the structure consists of siloxane groups (-Si-O-Si-) and one of the several forms of silanol groups (-Si-OH) is shown in Figure 2.2. The silanol groups make precipitated silicas hydrophilic. Unmodified silicas do not interact well with most polymers, requiring high amounts of shear and energy to incorporate them evenly (Wagner, 1976).

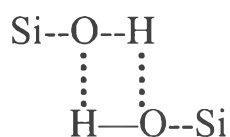


Figure 2.2 The silanol to silanol reaction by hydrogen bonding.

To increase silica-polymer bonding, silane coupling agents provide a unique and extremely effective method. The coupling agent is capable of forming new chemical bonds at each end, one to the silica surface and the other to the polymer. The process typically takes place during the initial mixing, but the extent of the polymer bonding varies according to polymer types and modification methods. For example, uncured mercaptan modified neoprene reacts to coupling during mixing, but sulfur modified types show no evidence of coupling until curing occurs. It was reported that there are several competing compound ingredients interfering with silanol coupling such as fatty acids and zinc compounds that are usually present in the polymer formulations. Moreover, 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 agents is the admicellar polymerization process (Waddell *et al.*, 1995; Thammathadanukul *et al.*, 1996; and Chinpan, 1996). It was reported that modified-silicas may offer greater overall improvements in natural rubber compound performances than the silane-modified silica (Thammathadanukul *et al.*, 1996). For instance, the admicellar polymerization modified silicas increase compound cure rates dramatically when compared to the rates of the silane-modified mixtures. Hence, the use of the modified-silicas can reduce the energy consumed in the compounding process as well as the compounding time.

2.3 Surfactant Structure

Surfactant is an abbreviation of “surface active agent”. Surfactants are a very versatile class of chemical compounds due to their chemical structures. A surfactant molecule consists of a hydrophilic head group composing of a water soluble species and a hydrophobic tail composing of organic derivative groups, usually with the carbon numbers greater than eight. This dual-natured structure is referred to as *amphiphilic*, and thus surfactants are also called *amphiphiles*. Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, nonionic or zwitterionic (Rosen, 1989).

2.4 Cationic Surfactant Salt

The term “cationic surfactant salt” is used to denote an ionic compound in which the cation is amphipathic and strongly surface-active. Considering the effect of pH on molecular structure and physical chemistry, the cationic hydrophilic groups (water-loving) can be divided into two sub-groups: neutral and acidic. Cetyltrimethylammoniumbromide (CTAB) is a familiar cationic surfactant salt in the neutral sub-group (see Figure 2.3).

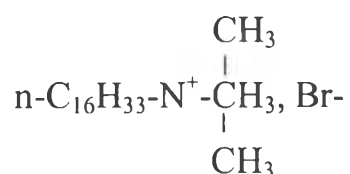


Figure 2.3 The structure of CTAB

Quaternary ammonium ions have four carbons bond to a positive nitrogen atom. Quaternary ammonium surfactants will have one or more of these substituent groups be lypophilic (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 nonbonding 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 is true of bromide, the molecular structure of this salt is independent of pH (Rubingn 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. Using of the MFA and the silane coupling agent not only contributes to a better silica-elastomer adherence but also improves dispersion, which results in a lower hysteresis.

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 the 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 adsorbed surfactant and the equilibrium concentration of the surfactant in the liquid phase. The adsorption isotherm for an ionic surfactant onto an oppositely charged substrate is typically S-shaped and can be divided into four distinct regions (Rosen, 1989) as shown in Figure 2.4.

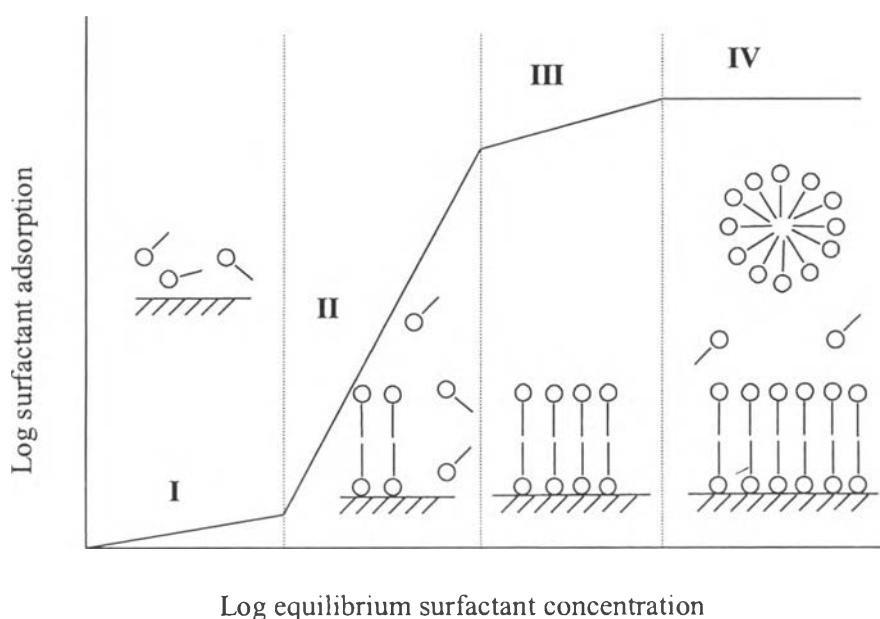


Figure 2.4 Adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

Region I, corresponding to both very low bulk surfactant concentration and low adsorption of the surfactant, is commonly referred to as the Henry's law region. Because the interaction between molecules of the surfactants is negligible, the

adsorbed surfactants in this region are viewed as being adsorbed alone and not forming any aggregates.

Region II is distinguished by a sharply increased isotherm slope relative to the slope on the region I. This indicates the beginning of lateral interactions between the surfactant molecules, which results in the formation of surfactant aggregates on the most energetic surface patches. These adsorbed surfactant aggregates are called admicelles or hemimicelles depending upon whether the aggregates are viewed as bilayers or monolayer. The admicelle is a local bilayer structure with a lower layer of head groups 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 the tail groups expose to the solution. The transition point from the 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) or the hemimicelle concentration (HMC). During aggregate formation, the original charged 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.

The rapid 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-charges head groups on the surface of the beginning of adsorption on lower energy surface patches, so additional adsorption becomes more difficult.

Region IV is the plateau adsorption region, having almost constant surfactant adsorption with increasing surfactant concentration. The transition point from region III to region IV, representing the equilibrium concentration at which micelles first form, is the critical micelle concentration (CMC).

Nunn *et al.* (1982) demonstrated the surface solubilization of the dye pinacyanol hydrochloride by surfactant aggregates adsorbed at the alumina-aqueous solution interface. The dye, which is purple in aqueous media, becomes light blue as it partitions into the organic environment of the adsorbed surfactant aggregates, producing light blue particles.

Yeskie *et al.* (1988) found that while there are conditions under which a second layer of surfactant will always form simultaneously with the first layer of

surfactant (admicelle formation), there is also a wide range of conditions under which hemimicelle will form, i.e., under certain conditions, surfactants will aggregate to form a first layer without the simultaneous formation of second layer. This was shown to be because the electrostatic contributions to the free energy of transferring a monomer from a hemimicelle to an admicelle are potentially much larger in magnitude than the largest possible hydrophobic contributions to the free energy of transfer. In addition, when admicelles do form, there is little if any interpenetrating of the hydrocarbon tails of the second layer of surfactant monomers 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.

Lee *et al.* (1990) showed that the behavior of adsorbed surfactant aggregates, admicelles, was found to be very similar to that of micelles in the presence of alkanes. However, peculiar phenomena were observed in the incorporation of alcohols into micelles: (i) very high ratios of alcohol to surfactant adsorption at lower coverage, (ii) remarkable increases of surfactant adsorption below the CMC, and (iii) a slight decrease of plateau adsorption. The hypothesis is that while the alkanes are adsolubilized only in the hydrocarbon core of the admicelle, there are two sites at which alcohols are adsolubilized, at the core and at the hydrophobic perimeter of the admicelle.

O'Haver *et al.* (1996) showed that the performance of rubber compounding was improved by using precipitated silicas as a reinforcing filler. The silica surface was directly modified by (i) adsorption of a surfactant onto the surface, (ii) adsolubilization of an organic monomer, (iii) *in situ* polymerization of the monomer in the surfactant bilayer, and (iv) partial surfactant removal. Silicas were thus surface modified with polar copolymers. With using the modified silicas in rubber compounds, the cure times were decreased, and break strength, tear energy, elongation to break, and cut growth resistance were increased.

A four-region model based on electrostatic and hydrophobic interactions adequately explains adsorption of anionic surfactants on positively charged solids such as alumina. Fan *et al.* (1997) studied the cationic surfactants adsorption on negatively charged alumina at pH 10 and at a constant ionic strength of 0.03 M NaCl.

In this case, only three distinct regions were observed in the adsorption isotherms and there seemed to be lack of adsorption region III. Although the adsorption region III may still exist, the difficulty in detecting it from the adsorption isotherm is probably the result of similar slopes for regions II and III. And this may be attributed to the loose and interpenetrating colloid structure in the case of the cationic amine/negatively charged alumina system.

2.6 Solubilization

Solubilization is an important property of surfactants that is directly related to the presence of micelles. Surfactant solutions above their CMCs can dissolve considerably larger quantities of organic materials than pure water or surfactant solutions with concentrations below the CMCs. A large capacity in solubilization is attributed by solubilizing the solute in the micelles. Rosen (1989) defines solubilization as “the spontaneous dissolving of substance (solid, liquid, or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material”. 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 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 solubilize), the exact location in the micelle at which solubilization occurs can vary.

2.7 Adsolubilization

Similar to the solubilization of organics into micelles, organic molecules will be incorporated into surfactant aggregates adsorbed at the solid-liquid interface. This phenomenon is termed *adsolubilization*. Adsolubilization is defined as “the

incorporation of compounds into surfactant aggregates adsorbed on surfaces, of which compounds would not be in excess at the solid-solution interface in the absence of the surfactant” (Scamehorn and Harwell, 1988) as shown in Figure 2.5. This definition conveys the idea that the particular solute of interest does not adsorb onto the adsorbent surface by itself, or that it adsorbs to a much lower degree. The removal of the solute from bulk solution occurs because of the presence of adsorbed surfactant aggregates and the incorporation of the solute into the aggregates.

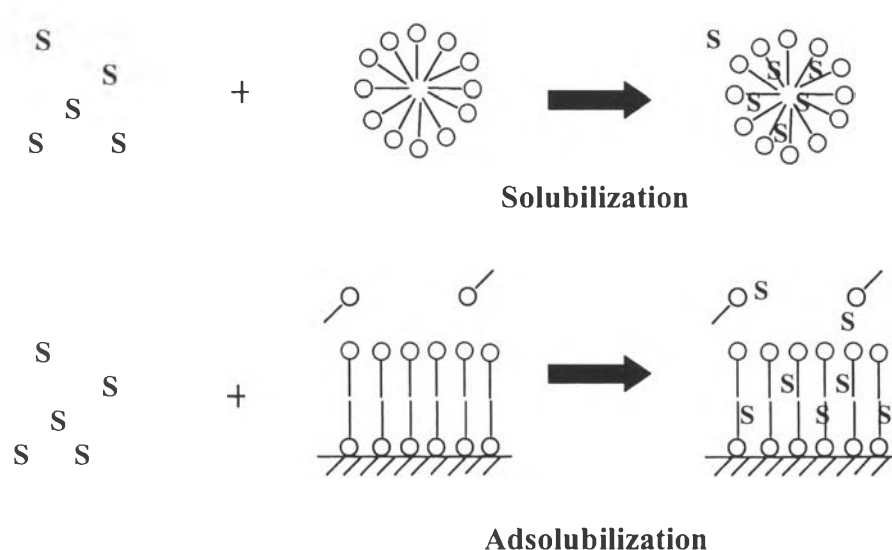


Figure 2.5 The phenomena of solubilization and adsolubilization.

The adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into CTAB bilayers (admicelles) on precipitated silicas was investigated by Kitiyanan *et al.* (1996). The styrene adsolubilization constant is nearly unchanged with increasing styrene equilibrium concentration in the aqueous phase while the isoprene adsolubilization constant increases with increasing isoprene partial pressure. The adsolubilization constants suggest that styrene adsolubilizes into both the palisade layer and the core of the admicelle while isoprene adsolubilizes into the palisade layer.

2.8 Ultra-Thin Film Formation

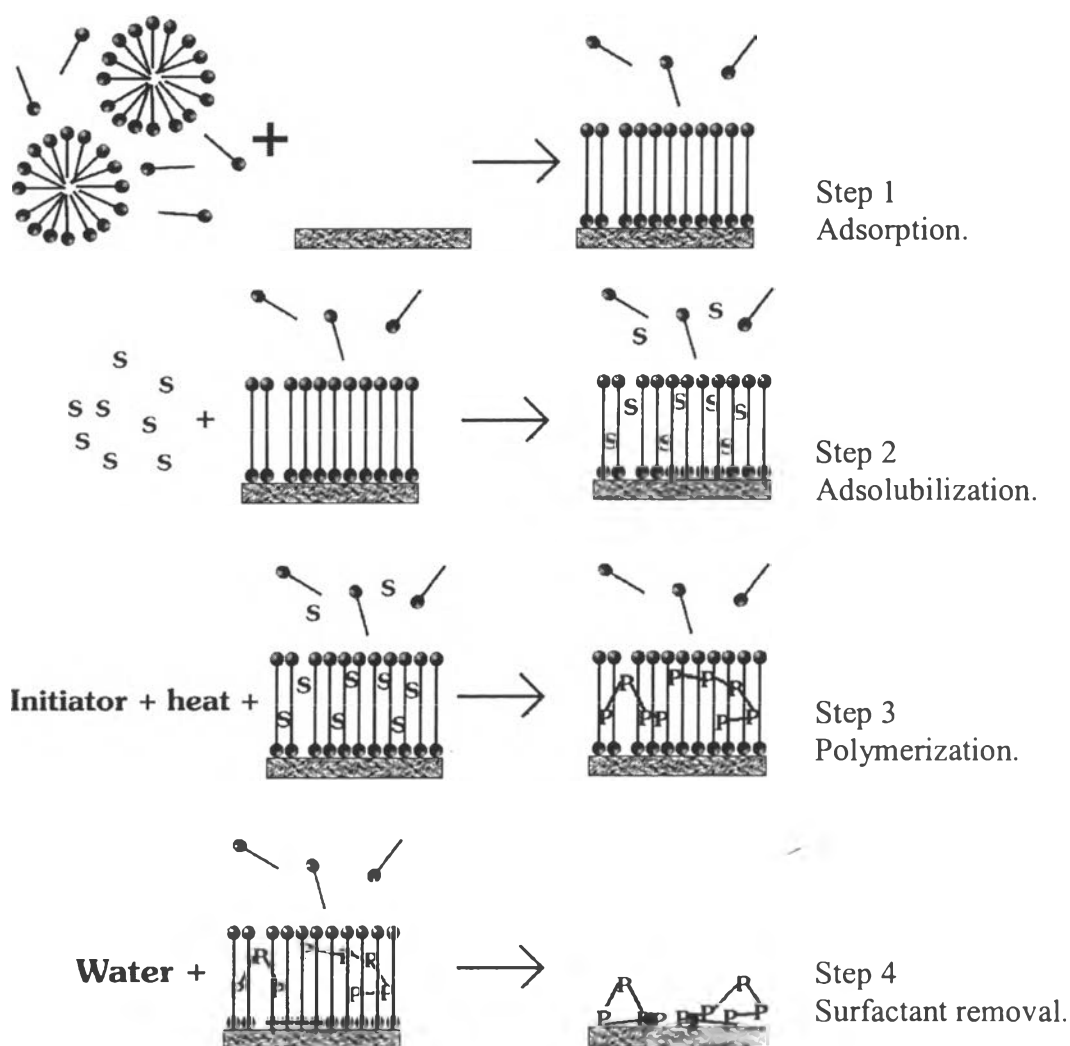
Wu *et al.* (1987) proposed that there are four steps involved in the formation of ultra-thin polymer films as shown in Figure 2.6. Step 1 consists of admicelle formation by the adsorption of a surfactant bilayer onto the surface of the substrate. Adsorption is accomplished through the use of a suitable surfactant under appropriate system conditions. The choice of a surfactant is influenced by the point of zero charge of the substrate, the chemical nature of the polymer to be formed, and the chosen polymerization initiator system. A study of the point of zero charge (PZC) for the substrate provides information on the pH ranges in which cationic or anionic surfactants may readily be utilized. At pH values below the PZC, the surface becomes protonated and more positively charged; above the PZC the surface is negatively charged. As a result, anionic surfactants adsorb well below the PZC, while cationic surfactants adsorb well above the PZC. For example, silica having $3 \geq \text{PZC} \geq 2$ (Iler, 1979) is negatively charged when the pH of the aqueous solution exceeds 3. Therefore, cationics such as CTAB adsorb readily on the surface of silica when the pH of the contacting aqueous phase is greater than 3. Care must be taken to keep the equilibrium concentration of surfactant below its critical micelle concentration in order to prevent the formation of micelles in the bulk solution. In the absence of micelles, the organic interior of the surfactant bilayer became the only locus for the adsolubilization of organic monomers.

Step 2 is the solubilization of monomer into the admicelle, a phenomenon called adsolubilization. Many organic monomers are nearly insoluble in water. Thus, when they are introduced into the system, they preferentially partition into the organic interior of the admicelle. Addition of monomer and surfactant solution may be simultaneous or sequential.

Step 3 is the *in situ* polymerization of the monomer. This is done through the generation of free radicals capable of initiating the polymerization reaction. In some cases, the compatibility of the initiator system with anionic or cationic surfactants may also affect the choice of an appropriate surfactant and suitable reaction conditions. Once the reaction has started, additional monomer from the bulk

solution diffuses into the admicelle O'Rear *et al.* (1987). If the reaction is continued for a sufficient length of time, virtually all monomers can be converted to polymer.

Step 4 is the washing of the treated powder with water to remove as much as possible the outer surfactant layer in order to expose the polymer film. 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.



“S”s represent solute molecules, monomers.

“P”s connected by lines represent polymer chains formed during the reaction.

Figure 2.6 The admicellar polymerization process for the formation of a thin polymer film.

Wu *et al.* (1987) showed that the rate of polymerization of styrene monomers in an adsorbed two-dimensional surfactant bilayer solvent (admicelle) that used a water/ethanol-sodium dodecyl sulfate-styrene-alumina system was found to be proportional to the first order of monomer concentration and half-order of initiator concentration and the average number of radicals per alumina particle is less than unity. The results from polymerization of styrene in sodium dodecyl sulfate bilayers adsorbed on alumina showed 75% and higher conversions of adsolubilized monomer to polymer after 25 min. Uniform films of 3.4-3.6 nm thickness were formed on aluminum oxide layers on glass slides for reaction times of 30-45 min. Under varying conditions, film thicknesses of 13.0 nm were also obtainable (O'Rear *et al.* 1987).

Waddell *et al.* (1995) showed that the performance of a rubber compound was improved by using modified precipitated silicas as reinforcing filler. Compound physical testing showed that cure times were decreased, and break strength, tear energy, elongation to break, and cut growth resistance was increased.

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

Chinpan (1996) studied the admicellar polymerization-modified silicas with used butadiene and isoprene as co-monomers with styrene. The polymer was capable of forming bonds with the rubber compound during the curing process. Significant improvements in the compound properties were achieved, and it was also found that those lower loading of monomer and surfactant achieved the greatest improvement in the largest number of rubber properties.

The study of the effect of retention time and monomer loading on the properties of silicas modified by the *in situ* polymerization using a continuous system was carried out by Chaisirimahamorakot (2001). It was concluded that the continuous stirred tank reactor system was used successfully. The results showed

that the optimum conditions for the modification were 5 g of the monomers per kg of the silica at 60 min resident time.