# CHAPTER II
LITERATURE SURVEY

2.1 Silica Fillers

It has long been known that silica (silicon dioxide) fillers added to polymer composites cause a considerable change in both the polymer dynamic and cure properties. Silica fillers can be classified into two major classes, natural and synthetic, which comprise the crystalline and amorphous forms, respectively. Among the synthetic silicas, precipitated silica is manufactured with a wide range of particle sizes and specific surface areas for different applications. Reinforcing fillers account for 90% of the total yearly silica usage in rubber (Hewitt, 2000). Two fundamental properties of silica that influence their use in rubber compounds reinforcement are particle size and the extent of hydration (Mark *et al.*, 1994). However, the actual size of the reinforcing unit is not determined by that of the primary particles, but rather by that of the agglomerate. However, smaller primary particles produce smaller agglomerates, which provide greater improvement in rubber reinforcement due to the formation of more complex aggregate structures (Hewitt, 2000). In case of hydration, the first water driven off during drying (at 25 to 105°C) is what is condensed in the pores. After heating to over 200°C, adsorbed water (water hydrogen bonded to silanol groups, Si-OH) is removed. Finally constitutional water (chemisorbed water) is evolved between 700 to 900°C (Barlow, 1993).

Precipitated silica is often used in the production of highly reinforced white or light colored compounds. Using admicellar polymerization-modified silica in rubber compounding significantly reduces cure times, increases tensile strength, lowers the compression set and heat buildup compared to compounds made with unmodified silicas. (Barlow, 1993). Precipitated silica

is used in a variety of tire applications. Using precipitated silica at very high levels in tire treadsimparts outstanding wet traction and rolling resistance to passenger tires, while improving vehicle handling and fuel economy. In off-the-road (OTR) tire formulations, silica is used to improve tear and cut-growth resistance and decrease chunking of treads. It is also used in shoe soles to provide resistance to wear and tearing, for non-scuffing characteristics and in order to obtain light-colored or transparent compounds (Jacqueline *et al.,* 1997).

Silanol (SiOH) groups on the silica surface can react with oxygen or nitrogen containing materials such as glycol, alcohol, water, amine, divalent metal salts and to each other. The silanol to silanol reaction by hydrogen bonding (see Figure 2.1) is responsible for the formation of an extensive network that produces a "stiff" and highly viscous mixture. This type of structure, which makes processing more difficult, is not permanent and can be significantly reduced by addition of any materials noted above. Moreover, the presence of silanol groups makes precipitated silicas hydrophilic. Unmodified silicas do not interact well with most polymers, requiring high amounts of shear and energy to incorporate them evenly. Although several methods have been applied to overcome the incompatibility of silica and rubber, only a few will be mentioned here.

$$Si-O-H$$
$$H-O-Si$$
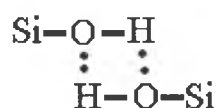
**Figure 2.1** The silanol to silanol reaction by hydrogen bonding.

To increase silica-polymer bonding, mercapto 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 rubber compound performances than do the silane-modified silica (Thammathadanukul *et al.*, 1996). For instant, the admicellar polymerization modified silica increases compound cure rates dramatically when compared to the rates of the silane-modified mixtures. This decreases the energy consumed in the compounding process as well as the compounding time.

2.2 Cationic Surfactant Salt

The term "cationic surfactant salt" is used to denote an ionic compound in which the cation is amphipathic and is 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. Cetyltrimethylammonium bromide (CTAB) is a familiar cationic surfactant salt in the neutral sub-group. CTAB structure is shown in Figure 2.2.

$$CH_3$$
$$|_+$$
$$H-C_{16}H_{33}-N-CH_3, Br^-$$
$$|$$
$$CH_3$$
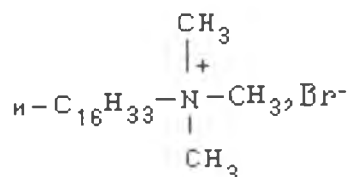
Figure 2.2 The structure of cetyltrimethylammonium bromide (CTAB).

In quaternary ammonium ions, four carbons (or carbon chains) are bonded to a positively charged nitrogen atom. For the quaternary ammonium ion to be surface active, one or more of this substituent groups must be lipophilic (oil loving). This cationic molecule only 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, from an acid-base perspective, it is "neutral" (nonacidic and nonbasic) in water. If the anionic partner in such a salt is also neither acidic nor basic, as is true of bromide, the molecular structure of this salt is independent of pH (Rubingh and Holland, 1990).

2.3 Surfactant Adsorption

The adsorption of ionic surfactants onto oppositely charged surfaces involves many mechanisms, but only a few parameters affect this adsorption. These parameters include: (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 and ionic strength) (Rosen, 1989). Data from adsorption experiments are normally presented in an adsorption isotherm, which shows the relationship between the amount of adsorbed surfactant and the equilibrium concentration of the

surfactant in the bulk 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 2.3.
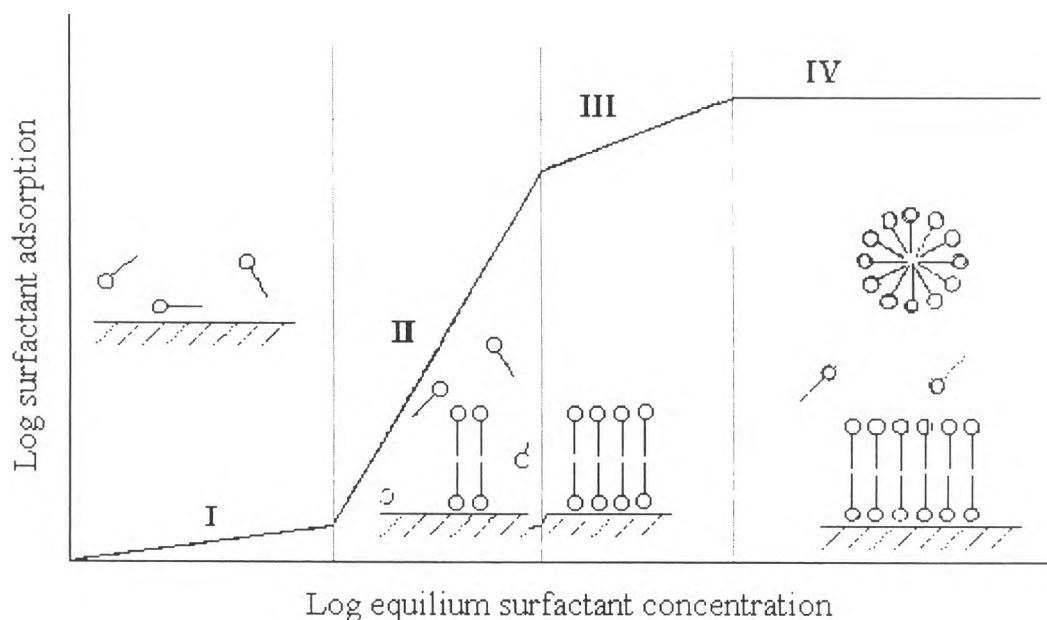
Figure 2.3 Adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

Region I, corresponding to both very low 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.

Region II, distinguished by a sharp increase in isotherm slope, indicates the beginning of lateral interaction between the surfactant molecules. These interactions result 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 monolayers. The admicelle is a local bilayer structure with a lower layer of head groups adsorbs on the substrate surface and an upper layer of head groups exposes to the solution. (a diagram might be good comparing the two) The hemimicelle is a monolayer structure having the head groups adsorb 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 charge on the solid surface is neutralized and may eventually be reversed with sufficient adsorption. In many cases, by the end of region II, the solid surface has the same sign on its overall charge, as does the surfactant ion.

A marked decrease in the slope of the isotherm indicates the beginning of region III. This is thought to be caused by the repulsion between the like-charged head groups on the surface or the beginning of adsorption onto lower energy surface patches, thus making additional adsorption less favorable.

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). (Rosen, 1989).

2.4 Solubilization and Adsolubilization

Solubilization is an important property of surfactants that is directly related to micelle formation. Surfactant solutions above the CMC can dissolve considerably larger quantities of organic materials than pure water or surfactant solutions with concentrations below the CMC. The additional

capacity is obtained by solubilizing the solute in the micelle. Solubilization can be defined as "the spontaneous dissolving of a substance (solid, liquid or gas) by reversible 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 aggregates is termed adsolubilization (see Figure 2.4). This phenomenon is the surface analogy of solubilization with adsorbed surfactant bilayers playing the role of micelles (Kitiyanan *et al.*, 1996).
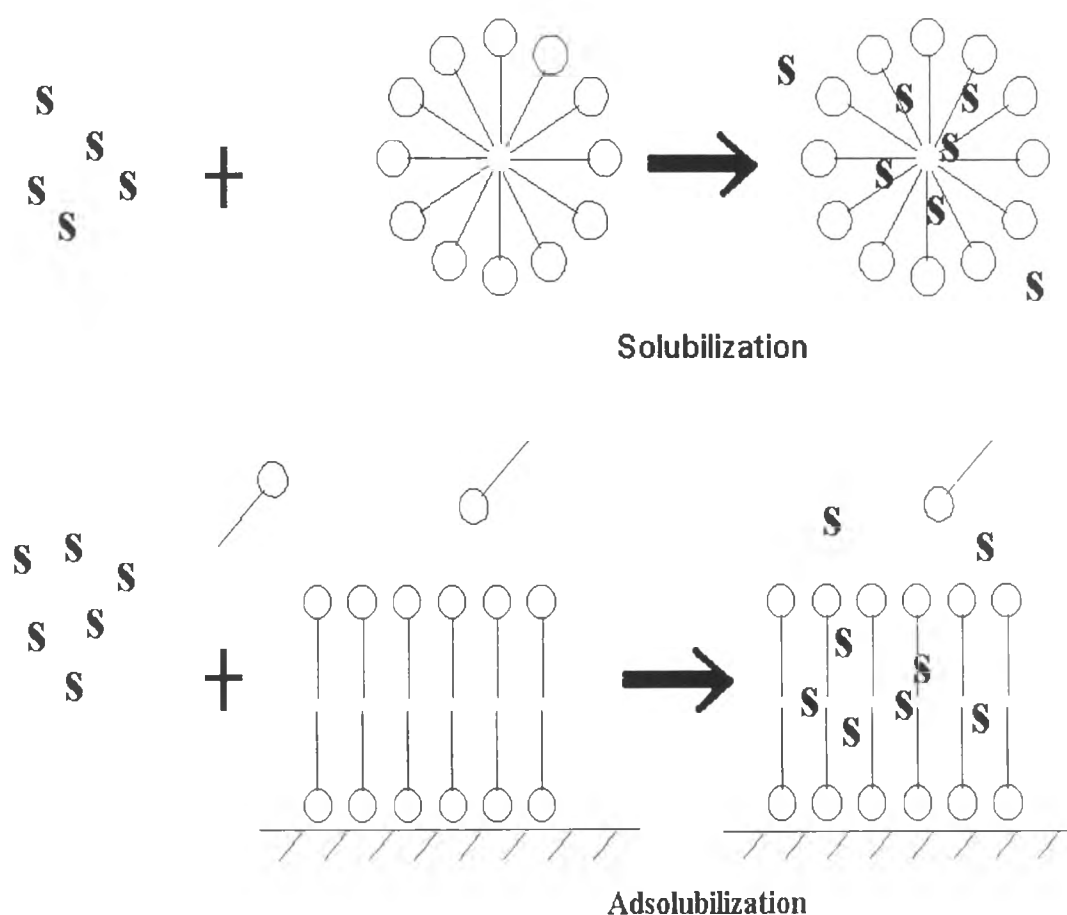
Figure 2.4 A comparison of solubilization and adsolubilization.

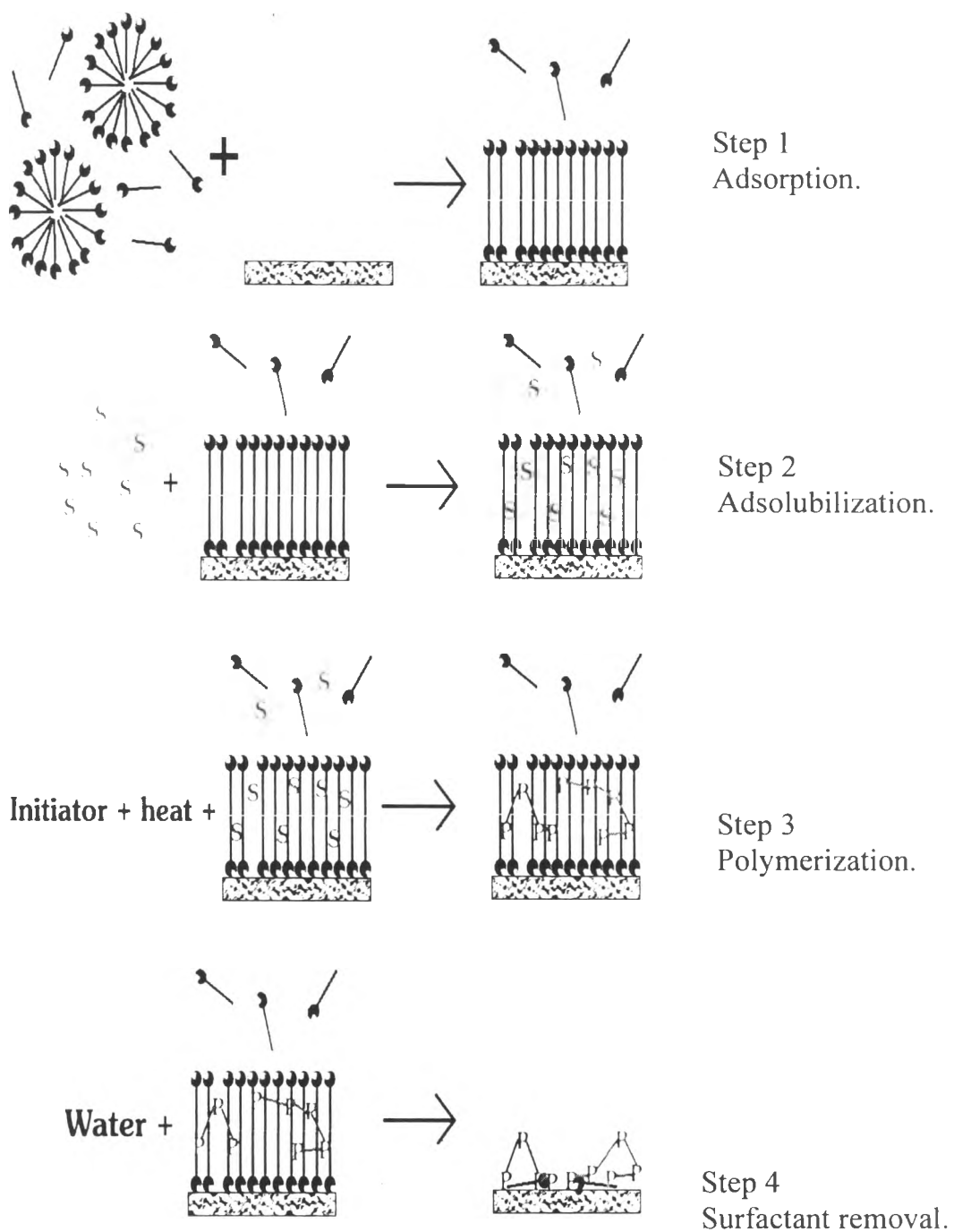## 2.5 Admicellar Polymerized Thin Film Formation

The admicellar polymerization process is usually presented as occurring in four steps (see Figure 2.5). Step 1 is admicelle formation by the adsorption of surfactant aggregates onto the surface of the substrate. The admicellar interior exhibits an organic-like environment where organic species will preferentially partition. The equilibrium surfactant concentration must be kept below the CMC to avoid solubilization in micelles and to reduce the possibility of emulsion polymerization. The most critical parameter in admicelle formation for ionic surfactants is the pH of the solution relative to the pH at which the charge on the surface equals zero (the point of zero charge, PZC). 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 $3 \geq PZC \geq 2$ (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.

Step 2 is adsolubilization, the solubilization of monomer into the admicelle. Many organic monomers are nearly insoluble in water. Thus, they preferentially partition into the admicelle when introduced into the solution. This step can occur after the formation of admicelle or concurrently with surfactant adsorption.

Step 3 is the *in situ* polymerization of the adsolubilized monomer by adding an initiator to the system and appropriately beginning initiation.

Step 4 is the removal of excess surfactant by washing in order to expose the polymer films. Waddell *et al.* (1995) suggested that the continuous, counter-current washing would be preferred since it could increased the rate of surfactant removal.

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

Figure 2.5 The admicellar polymerization process for the formation of a thin polymer film.

The admicellar polymerization method can custom-modify the surface characteristics of a substrate, adapting it for the desired end use. This method has the advantages of lower cost and increased flexibility over most coupling agents.

Waddell *et al.* (1995) investigated the modification of silica surface by admicellar polymerization of various polymers and surfactant systems. They found that both nonionic and cationic surfactants adsorb well onto silica surfaces and provide comparable levels of organic polymer. Copolymer modified silicas tended to perform better in rubber compound testing.

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

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