

CHAPTER I INTRODUCTION

Admicellar polymerization, polymerization of monomers solubilized in adsorbed surfactant aggregates, has been extensively investigated for more than a decade. Existing studies have examined various kinds of surfactants, monomers, and initiators under varying reaction conditions. Modified substrates include silica, alumina, glass fibers, glass cloth, titanium oxide, cotton, and nickel (Methachan, 2002) The development of research in this area has been growing due to the potential applications of admicellar polymerization.

Most reinforced polymeric compounds require high physical performance which depends upon good adhesion between the polymer matrix and reinforcing material to provide high composite strength. Admicellar polymerization can be applied to improve the adhesion between the reinforcing substrate and polymer matrix by modifying the substrate surface with an ultra-thin polymer film. Good adhesion and dispersion can be achieved by modifying the substrate with a polymeric film that is relatively similar to the polymer matrix.

There are many types of fillers used in the rubber industry. Carbon blacks are the most widely used but produce a product that is black, a drawback in some applications. Silica is usually used as the reinforcing filler in cases where a natural color or white product is desired (Wager, 1976). Unfortunately, unmodified silica cannot form chemical bonds with rubber. Also, since the rubber and silica are different in nature, organic vs. mineral, the silica may be poorly dispersed in the rubber unless high shear and long mixing times (compared to those for carbon blacks) are used. Improvements in the compatibility of silica in rubber may be achieved by admicellar polymerization where *in-situ* polymerization of organic monomers in surfactant layers adsorbed from aqueous solution onto the surface of precipitated silica forms an ultra thin polymer film on the silica surface. This film will help lower the energy of mixing while helping to form bridges connecting the silica to the polymer matrix. The modification changes the nature of the silica surface from hydrophilic to hydrophobic (Waddell et al., 1995). Studies have shown the impact of the surface modification by examining the physical and cure

properties of the rubber composite, such as tear strength, abrasion resistance, T_{90} , and tensile properties (Thammathadanukul *et al.*, 1995).

Although previous studies showed that the admicellar polymerization process is capable of producing high performance fillers, there is a lack of fundamental knowledge about the process. Few studies have examined the effect of changes in the process variables on filler performance. Understanding the distribution and properties of the formed polymer is important when considering the various current and potential applications of the process.

This research will focus on characterization of ultra thin polystyrene films formed via admicellar polymerization under various polymerization conditions. It will examine the effect of the amount of monomer, surfactant, and initiator on the formed polymer as well as on the distribution and structure of the formed film. The polymerization reaction will be carried out on a nonporous silica substrate so that all of the polymer can be extracted (O'Haver *et al.*, 1993, Arayawongkul *et al.*, 2001). Modified silica and extracted polymer will be examined by thermo gravimetric analysis (TGA), gel permeable chromatography (GPC), Fourier transform infrared (FTIR) and atomic force microscopy (AFM).

Theoretical Background

1.1 Silica filler

Use of silica in rubber compounds provides beneficial properties such as increases in tensile strength, modulus and resilience. Silica filler can be classified into two major classes, natural and synthetic, which comprise the crystalline and amorphous forms, respectively. Among the 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 compounds 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. Using admicellar

polymerization modified silica in rubber compounding significantly reduces cure times, increases tensile strength, lower the compression set and heat build up compared to compounds made with unmodified silicas (Waddell, 1995).

Silanol (SiOH) groups on the silica surface can react with oxygen or nitrogen containing materials such as glycol, alcohol, water, amine, and divalent metal salts. The silanol to silanol reaction by hydrogen bonding (Fig 1.1) 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 make precipitated silicas hydrophilic. Unmodified silicas do not interact well with most polymers, requiring high amounts of shear and energy to incorporate them evenly.

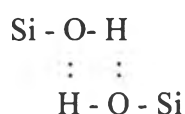


Figure 1.1 The silanol to silanol reaction by hydrogen bonding.

1.2 Surfactant

A surfactant (contraction of the term surface active agent) is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces. (Scamehorn *et al.*,1985). Surfactants are used in such fields as detergency, enhance oil recovery, and pharmaceuticals. Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent (lyophobic, or in the case of water, hydrophobic) together with a group that has strong attraction for the solvent, (lyophilic, or in the case of water, hydrophilic). Depending on the nature of the hydrophilic group, surfactants are classified into four categories- anionic, cationic, nonionic and zwitterionic (Rosen,1989).

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Surfactants are typically referred to as having a “head” and a “tail”. The head is lyophilic/hydrophilic and is graphically depicted as a circle. The tail is generally a long hydrocarbon chain and is hydrophobic, which is graphically depicted either as a straight line or a wavy line (see Figure 1.2).

Several types of surfactant aggregates can be formed under varying bulk concentrations as shown in Figure 1.3. At low concentration, surfactants are in molecular form in the solution. An admicelle or hemimicelle structure can be formed on surfaces or other interfaces of the system as the concentration increases. Micelle formation occurs when the concentration of surfactant reaches the critical micelle concentration (CMC).



Figure 1.2 Structure of a surfactant molecule.

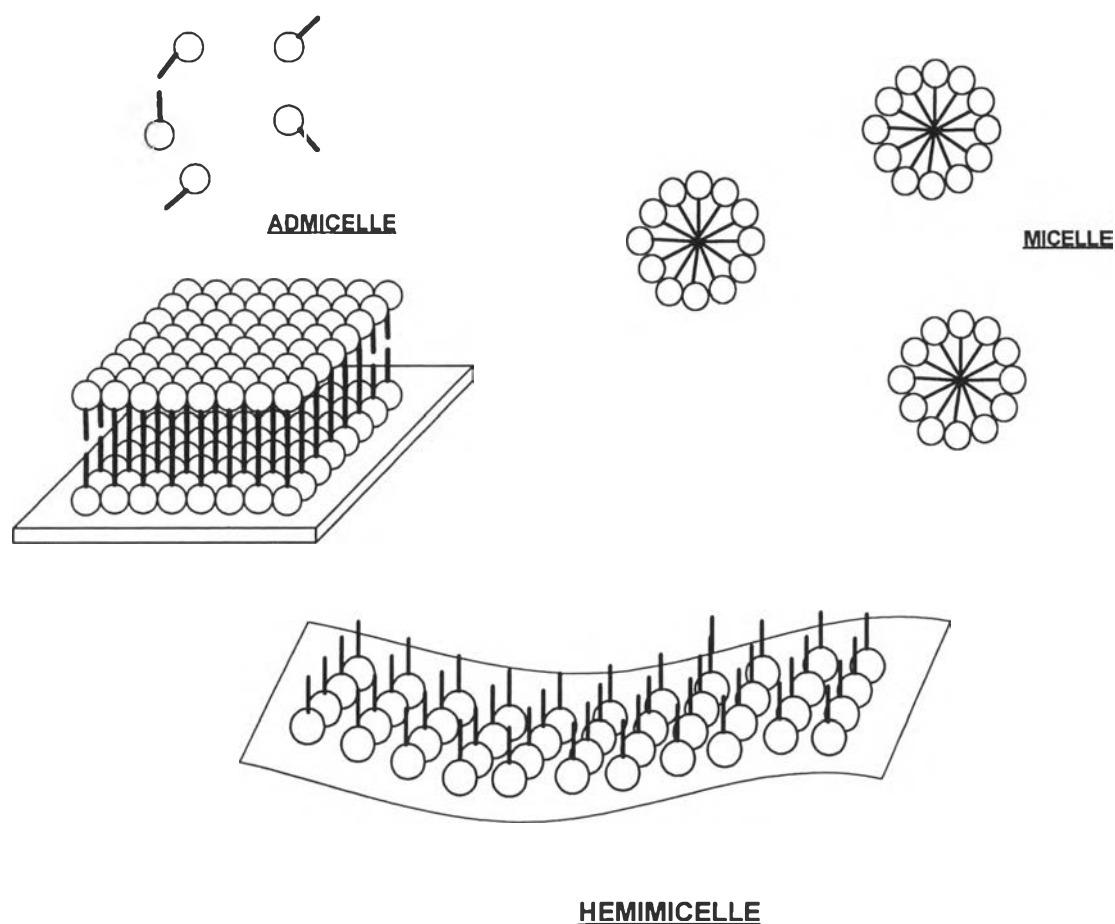


Figure 1.3 The types of surfactant formation.

1.3 Surfactant adsorption

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface—whether the surface contains highly charged sites or 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, urea etc.), and its temperature. Together these factors determine the

mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

At the solid-liquid interface, it is interesting to determine (1) the amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent, that is, the surface concentration of the surfactant (adsorbate) at a given temperature since this is a measure of how much of the surface of the adsorbent has been covered, by the adsorption; (2) the equilibrium concentration of surfactant in liquid phase required to produce a given surface concentration of surfactant at a given temperature, since this measures the efficiency with which the surfactant is adsorbed; (3) the concentration of surfactant on the adsorbent at surface saturation at a given temperature, since this determines the effectiveness with which the surfactant is adsorbed; (4) the orientation of the adsorbed surfactant and any other parameters that may shed light on the mechanism by which the surfactant is adsorbed, since a knowledge of the mechanism allows us to predict how a surfactant with a given molecular structure will adsorb at the interface; and (5) the effect of adsorption on other properties of the adsorbent. An adsorption isotherm is a mathematical expression that relates the concentration of adsorbate at the interface to its equilibrium concentration in the liquid phase. Since most of the information that we desire can be obtained from the adsorption isotherm, the isotherm is the usual method of describing adsorption at the liquid-solid interface (Rosen, 1989)

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 1.4

Region I, corresponding to both very low bulk concentration and low surfactant adsorption, is commonly referred to as the Henry's law region. Because the interaction between molecules of the surfactant 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 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 adsorb 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 adsorb on the surface while the tail groups expose to the solution. The transition point from region I to region II, representing the equilibrium concentration at which the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) 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).

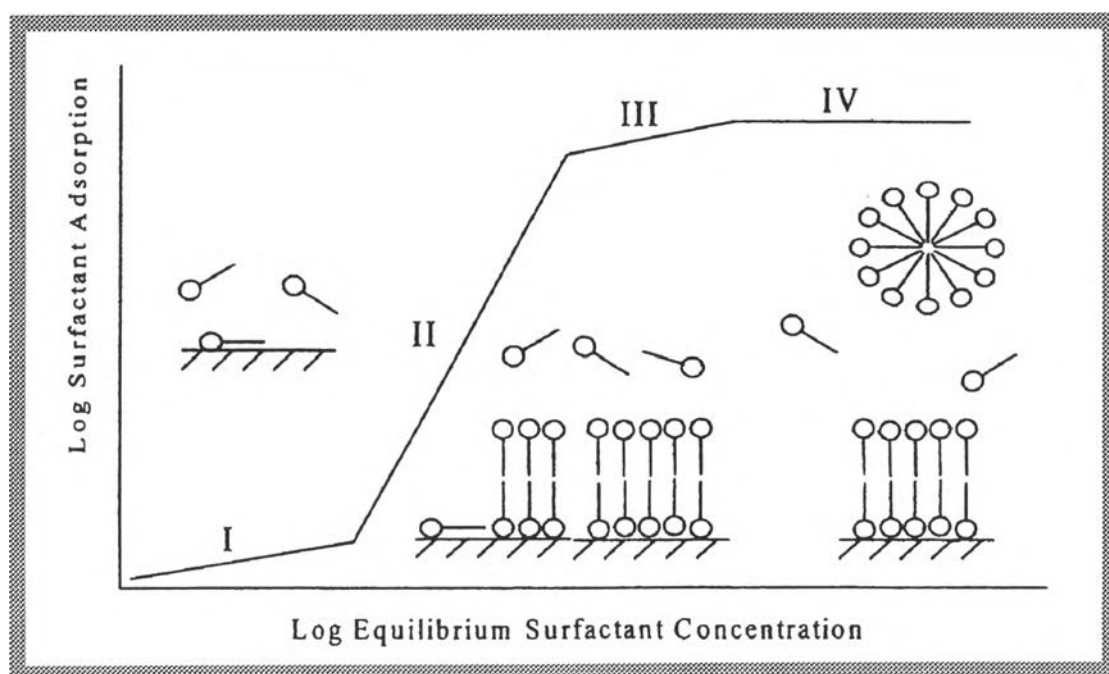


Figure 1.4 Typical adsorption isotherm of surfactant on solid surface.

1.4 Adsolubilization

Solubilization is an important property of surfactants that is directly related to micelle formation. Surfactant solution 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 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 solubilized material*”(Rosen, 1989).

Similar to the solubilization of organics into micelles, organic molecules will be incorporated into surfactant aggregates adsorbed at the solid-liquid interface. The 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*” (Scaemhorn and Harwell, 1988) as shown in Figure 1.5.

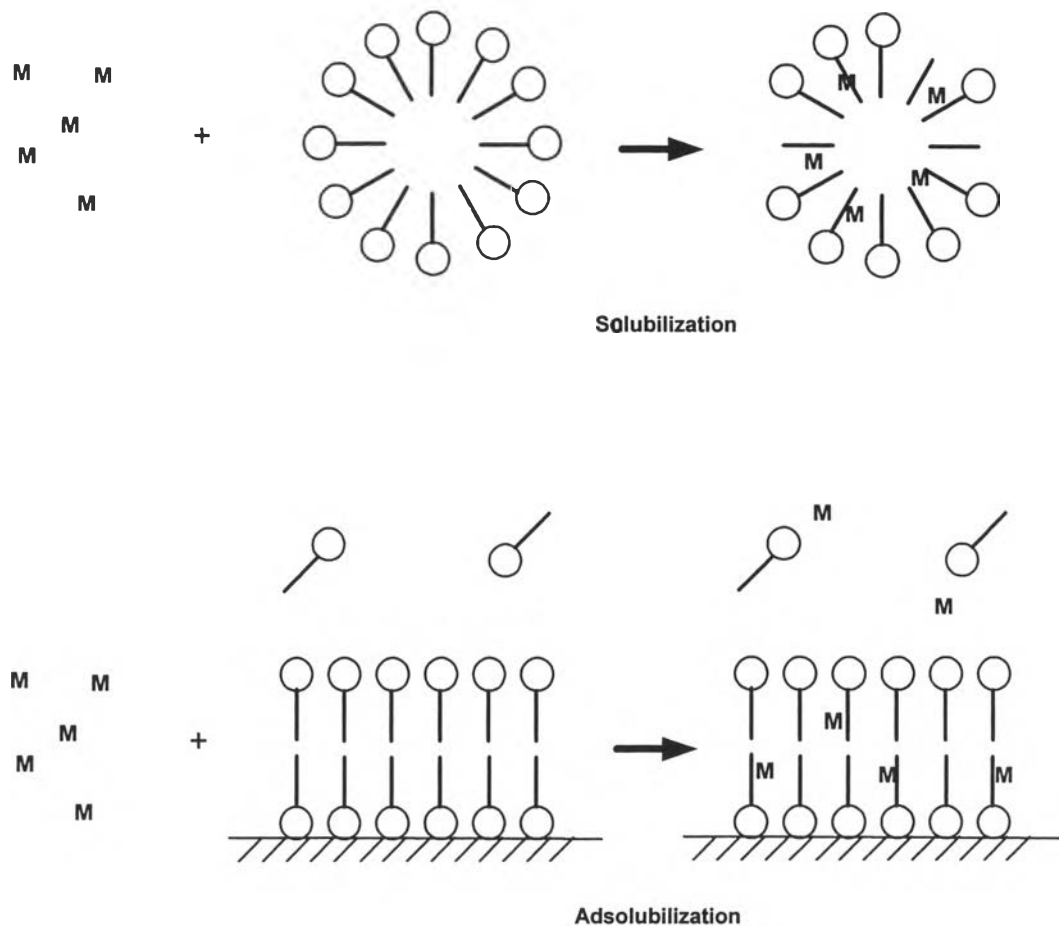


Figure 1.5 A comparison and phenomena of solubilization and adsolubilization.

1.5 Admicellar Polymerization

Admicellar polymerization is a four step process for surface modification shown in Figure 1.6 (Pongprayoon, 2002).

Step 1. Adsorption of surfactant on solid surface

In step 1, admicelle formation occurs by the adsorption of a suitable surfactant onto the surface of the substrate (Harwell et al., 1985). The adsorption of surfactants on solid substrates is controlled by several parameters, including the electro-chemical nature of the substrate, the pH of the solution, and the type of surfactant molecule. The pH that makes the charge on the surface equal to zero is

called the point of zero charge (PZC). An analysis of the point of zero charge for the substrate provides guidelines as to pH ranges in which either cationic or anionic surfactants might be utilized. By adjusting the pH of the feed solution, the surface charge of the silica particles can be adjusted to facilitate the adsorption of cationic surfactant molecules. If the pH of the solution is below the PZC of the substrate, the surface will be protonated and positively charged. Under these conditions, anionic surfactants can be adsorbed on the surface, while at pH above the PZC, the surface will be negatively charged and cationic surfactants adsorb readily on the surface. For example, Wu et al., 1988 studied the adsorption of anionic surfactant, sodium dodecyl sulfate, on the solid surface of alumina. The PZC of alumina is pH 9.5 at 30°C, thus the solution was adjusted to pH 4.0 to be suitable for anionic surfactant. For instance, silica ($2 \leq \text{PZC} \leq 3$) will be negatively charged when the pH of the aqueous solution exceeds 3 (Iler, 1979). Therefore, cationic surfactants such as cetyltrimethyl ammonium bromide (CTAB) adsorb readily on the surface of silica when the pH of the contacting aqueous phase is greater than 3. Silica has a minimum solubility in water at a pH between 7 and 8 (Iler, 1979). In this study, therefore, a feed pH of 8 was chosen. The feed concentration of the surfactant was adjusted so that the equilibrium concentration was below the surfactant's critical micelle concentration (CMC) in order to avoid emulsion polymerization during step 3.

Step 2. Monomer adsolubilization

Step 2 is the solubilization of monomer into the admicelle, known as 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. In the admicelle, the bilayer acts as a two dimensional solvent to concentrate the monomer near the substrate surface (Wu, 1987). Addition of monomer and surfactant solution may be simultaneous or sequential.

Step 3. Polymerization of adsolubilized monomer

Step 3 is the *in-situ* polymerization of the monomer. For free-radical polymerization, this is accomplished through the generation of radicals capable of initiating polymerization. Once the polymerization reaction has been initiated and the monomer is being consumed in the admicelle, the monomer in the bulk solution

will diffuse into the admicelle. If the reaction is continued for a sufficient time period, all of the monomer can be converted into polymer.

Step 4. The washing of the substrate to remove the excess surfactant

Step 4 is the washing of the treated powder to remove excess surfactant in order to expose the polymer-modified surface. The need for this step is optional, depending upon the application.

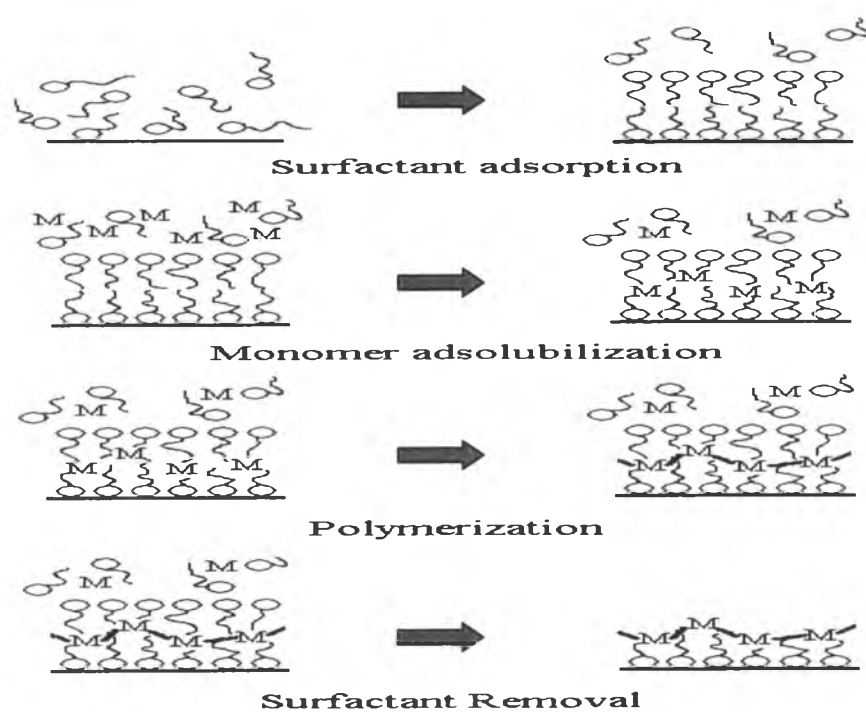


Figure 1.6 Formation of a thin film by admicellar polymerization.