



CHAPTER I INTRODUCTION

Admicellar polymerization is the process in which monomers are polymerized inside a surfactant aggregates adsorbed on a substrate surface. This method is the surface analogous to emulsion polymerization. Many types of monomers and substrates can be used by this process, forming ultra-thin films which vary in extent on the substrate surface.

Reinforced polymeric compounds that require high physical property performance depend on adhesion between the polymer matrix and the reinforcing filler. Good adhesion provides high composite strength and other improvements in physical and cure properties. In previous studies, admicellar polymerization has been used to improve the adhesion between a filler substrate (usually amorphous precipitated silica) and polymer matrix (natural, butyl and SBR rubber compounds) by modifying the substrate surface with an ultra-thin polymer film. The differences in the properties between unmodified silica and rubber can cause poor dispersion of the silica, resulting in poor physical properties. Additionally, rubber compounds are incapable of strongly adhering to an unmodified silica surface. To improve the compatibility of silica in rubber as well as the adhesion of rubber to the silica, ultra thin films of organic polymer can be formed on the silica surface. In many previous studies, homo-polymer and co-polymer were chosen, and then the results were reported on the rubber testing properties such as tear strength, abrasion resistance, and tensile properties. (Waddell *et al.*, 1995, O'Haver *et al.*, 1996 and Thammathadanukul *et al.*, 1996)

Though previous studies showed the process capable of producing high performance filler, there is a lack of fundamental knowledge about the process, specifically, how changes in the process variables (amounts of adsorbed surfactant and adsolubilized monomer) affect the polymer formed. A better understanding of the process will allow researchers to more accurately predict the best conditions for different applications of admicellar polymerization.

This research focused on the effects of surfactant loading, monomer loading, and reaction time on the characteristics of polymer formed by admicellar

polymerization. The polymerization reaction was carried out on a nonporous silica (Aerosil[®]OX50) using styrene as monomer. The silica was modified by admicellar polymerization using various conditions and then the polystyrene formed on silica particles were extracted by tetrahydrofuran (THF) solvent. The adsorption isotherm of surfactant and adsolubilization isotherm of styrene in various adsorbed surfactant concentration on nonporous silica were also studied in order to set the conditions for admicellar polymerization. In the characterization part, the modified silica was examined by TGA, SEM, and AFM, the extracted silica was investigated by TGA and AFM, and the extracted polystyrene was characterized by FTIR, TGA, and GPC.

1.1 Surfactant 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, i.e. the surface concentration of the surfactant (“adsorbate”) at the given temperature, since this is a measure of how much of the surface adsorbent has been covered, and hence changed, by the adsorption; (2) the equilibrium concentration of surfactant in the 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. (Rosen, 1989) Results from surfactant adsorption experiments are usually expressed in the form of adsorption isotherm, which display 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 1.1.

Region I corresponds to both very low concentration and low adsorption of surfactant. This region is commonly referred to as 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 of 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. Typically, the equilibrium surfactant concentration at the transition point from region III to region IV is approximately at the critical micelle concentration (cmc).

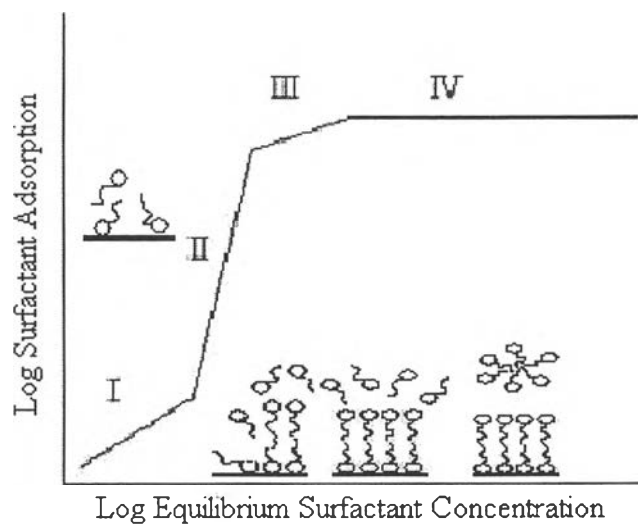


Figure 1.1 S-shaped adsorption isotherms for an ionic surfactant on an oppositely charged substrate.

1.2 Adsolubilization

The partitioning of organic solutes from aqueous solution into interior of adsorbed surfactant aggregates is termed adsolubilization. The suggested definition of adsolubilization is “the incorporation of compound into surfactant surface aggregates, which compound would not be in excess at the interface without surfactant” (Scaemhorn, 1988). This phenomenon is analogue of solubilization, with adsorbed surfactant bilayers playing the role of micelles as shown in Figure 1.2.

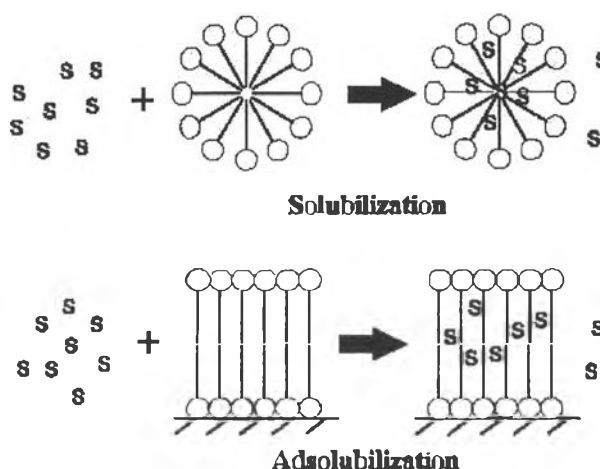


Figure 1.2 Phenomena of solubilization and adsolubilization.

1.3 Admicellar Polymerization

The method utilized for modification of inorganic powder by admicellar polymerization can be considered to occur in four steps. (Figure 1.3)

Step one Surfactant adsorption

First step consists of admicelle (adsorbed micelle) formation by the adsorption of a suitable surfactant bilayer onto the surface of the substrate. The choice of surfactant is influenced by the chemical and electrostatic nature of the substrate as well as by the chosen initiator system selected. A study of the point of zero charge for the substrate provides information as to pH ranges in which either cationic or anionic surfactants might be utilized (O'Haver, 1993) By adjusting the pH of the aqueous 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 point of zero charge (PZC) of the substrate, the surface will be positively charged; if the pH is above the PZC the surface will be negatively charged. Silica has a PZC of 3 (Iier R.K., 1979). Therefore, in this study, a surfactant solution pH 8 was chosen. After equilibration, the surfactant concentration in the aqueous phase was below the surfactant's critical micelle concentration (CMC) in order to avoid emulsion polymerization during step 3.

Step two Monomer adsolubilization

Step two, monomer adsolubilization, involves the solubilization of monomer into the admicelle, called adsolubilization. In the admicelle, the bilayer acts as a two-dimensional solvent to concentrate the monomer near the surface of the substrate.

Step three Polymerization

Third step is the *in situ* polymerization of the monomer. For free-radical polymerization, this is accomplished through the generation of radicals capable of initiating polymerization

Step four Surfactant Removal

Forth is the washing of the treated powder to remove excess surfactant in order to expose the polymer-modified surface.

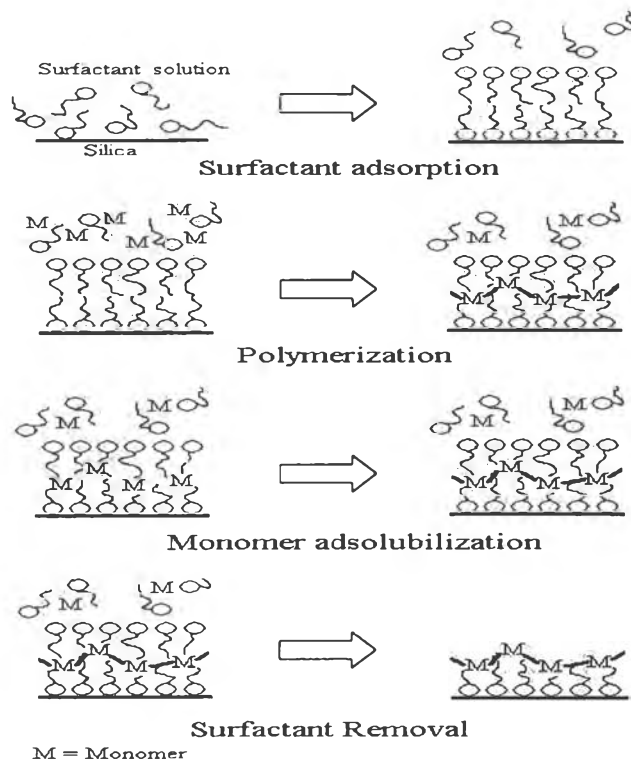


Figure 1.3 Ultra-thin film forming process.