

CHAPTER I

INTRODUCTION

Thin-film coatings on solid substrate have been a popular research topic because they have many applications in composite materials, health care products, microelectronic, and electronic devices. Moreover, they can provide many beneficial physical and chemical properties, such as improvement in adhesion between polymer matrix and reinforcing filler in composite materials, increase in composite strength, reduction of cure time, increase in tear strength, improvement of elongation at break, and improvement of processibility property.

The new method used to produce thin-film coating on solid substrate is called admicellar polymerization or the thin film via surfactant template (TFST). This technique was invented more than two decades ago. The film thickness is in range of nanometers to tens of nanometers. There are many types of polymer-substrate systems produced successfully by admicellar polymerization. Examples are polystyrene on alumina, silica and glass fiber, polypyrrole on alumina and natural rubber, poly(tetrafluoroethylene) on alumina, and so on.

In this study, polystyrene was coated on natural rubber by admicellar polymerization technique and the effect of styrene and salt concentration on adsorption isotherm were investigated followed by characterization of the coated rubber. The objective of this research was to improve the mechanical properties of polystyrene, which is brittle, by natural rubber, which is flexible. Natural rubber is an inexpensive material and an important agricultural product of Thailand. The mechanical properties of the product from this research may be comparable to the mechanical properties of high impact polystyrene (HIPS) for use in several applications. It may be able to replace HIPS by having lower investment cost.

1.1 Theoretical Background

1.1.1 Surfactant

A surfactant or a surface-active agent is a chemical substance that is the most versatile product in the chemical industry. It is used in automobiles, detergents pharmaceuticals, and also applied to many high-technology areas. In a system with low surfactant concentration, the surfactant tends to adsorb at a surface or interface.

The molecular structure of a surfactant is called an amphipathic structure (Figure 1.1) because it consists of a lyophobic and a lyophilic group (a hydrophobic and a hydrophilic group, respectively in the case of aqueous solution.). In general, the molecules at the surface or interface have higher potential energy than that in the interior because the interaction between the same substance is stronger than that between different substances. When the surfactant is dissolved in a solvent, the lyophobic group of the surfactant in the interior of the solvent causes an increase in free energy of the system. Therefore, displacement of the surfactant molecules to the surface or interface is easier than that of the solvent molecule. From these reasons, the amphipathic structure of the surfactant is the cause of (1) high concentration of surfactant at the surface; (2) reduction of the surface tension of water; and (3) orientation of the surfactant molecules at the surface or interface. The chemical structure of surfactant molecule must have an amphipathic structure in the solvent under the condition used for good surface activity in a particular system. The lyophobic group of surfactant is usually a long-chain hydrocarbon while the hydrophilic group is an ionic or highly polar group.

The surfactant can be divided into 4 types depending on the nature of the hydrophilic group.

1. Anionic surfactant. The hydrophilic group consists of negative charge for example, $\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ (alkylbenzene sulfonate).

2. Cationic surfactant. The hydrophilic group consists of positive charge, for example, $\text{RNH}_3^+ \text{Cl}^-$ (salt of long chain alkyl amine).

3. Zwitterionic surfactant. The hydrophilic group may give both negative and positive charge, for example, $\text{RNH}_2^+\text{CH}_2\text{COO}^-$ (long-chain amino acid)

4. Nonionic surfactant. The hydrophilic group does not contain any ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid)

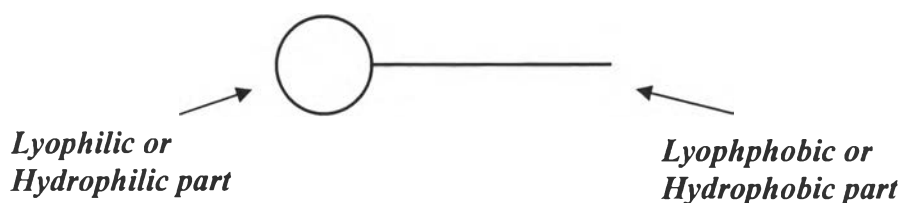


Figure 1.1 Molecular structure of a surfactant.

1.1.2 Surfactant Adsorption

The adsorption of surfactant is influenced by a number of factors:

1. The nature of the structural groups on solid surface (e.g., polar group, or nonpolar group).

2. The molecular structure of the surfactant (e.g., anionic, cationic, or nonionic surfactant).

3. The environment of the aqueous phase (e.g., pH, electrolyte content, and temperature).

The point of zero charge (PZC) is the most critical parameter to manipulate the surfactant adsorption. The point of zero charge is specific for a substrate. When the solution pH is equal to PZC, the substrate surface has zero charge. If the pH solution is above this point, the substrate surface will be negatively charged. If the pH solution is below this point, the substrate surface will be positively charged. The negative and positive charges on substrate surface are suitable for cationic and anionic surfactants, respectively. Therefore, a cationic surfactant is used when the solution pH is above PZC, and an anionic surfactant is used when the solution pH is below PZC.

At the liquid-solid interface, the adsorption isotherm is used to help explain the mechanism of surfactant adsorption. The adsorption isotherm curve is the plot between the log of adsorbed surfactant and the log of equilibrium concentration of surfactant in the bulk solution.

The shape of an adsorption isotherm curve can be classified into 2 types depending on the adsorbent.

1. Adsorption isotherm of surfactant from aqueous solution onto strongly charged site adsorbents.

The adsorption isotherm curve is typically an S-shape curve and can be separated into four regions as shown in Figure 1.2

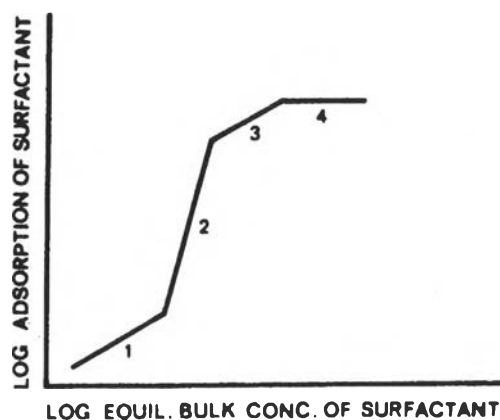


Figure 1.2 Typical adsorption isotherm of ionic surfactant onto strongly charged surface. (Rosen, 1989)

In region 1, the surfactant adsorbs mainly by ion exchange. In region 2, there is a marked increase in adsorption, resulting from interaction of the hydrophobic chain of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. In region 3, the slope of isotherm is reduced, because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid surface. Adsorption in this fashion is usually complete in region 4 when the surface is covered with a monolayer or bilayer of the surfactant and micelles are starting to form.

2. Adsorption isotherm of surfactant from aqueous solution onto nonpolar, hydrophobic adsorbents.

The adsorption isotherm curve is in the form of Langmuir type or L-shape curve as in Figure 1.3

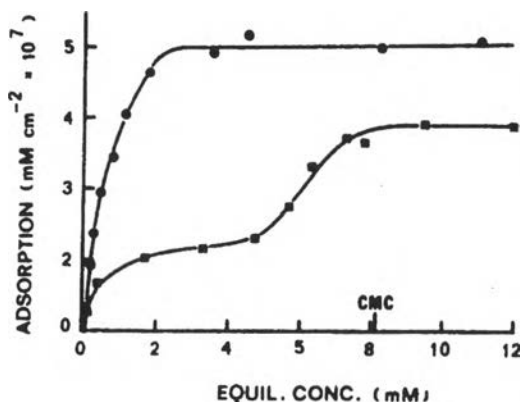


Figure 1.3 Typical adsorption isotherm of ionic surfactant onto nonpolar charged surface. (Rosen, 1989)

The hydrophobic tail of surfactant is adsorbed on the solid surface, so the orientation of the molecule of surfactant is mostly parallel to the surface.

When the molecules of surfactant continue to adsorb on the surface, the orientation is more and more perpendicular to the surface. The inflection point may be from the change of orientation from parallel to perpendicular.

1.1.3 Admicellar Polymerization

Admicellar polymerization is generally divided to three steps. (Figure 1.4)

1. *Admicelle Formation.* The molecule of surfactant is adsorbed onto the solid substrate in the form of a surfactant bilayer called admicelle.

2. *Monomer Adsolubilization.* In this step, the monomers, which have hydrophobic property, will partition to the hydrophobic region of the admicelle. This process is the similar to the solubilization of monomer into the micelle of surfactant, so it is named adsolubilization.

3. *Polymer Formation.* The monomers were polymerized in the bilayers after an initiator is added to the system.

The mechanism of this process will start in aqueous phase and move to the admicelle as in conventional emulsion polymerization, and monomer will continue to partition into the admicelle during polymerization process. After the polymerization reaction is complete, the excess surfactant is washed by water to expose the thin film coating on the solid substrate.

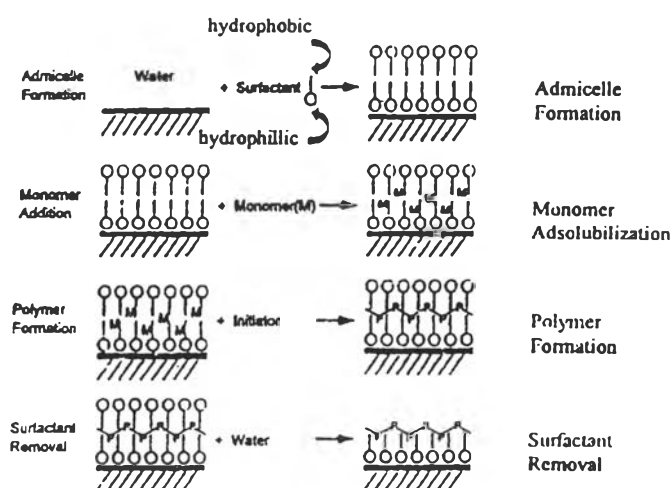


Figure 1.4 Admicellar polymerization process. (Wei *et al.*, 2003)