

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Natural Rubber

Natural rubber (NR) is a renewable polymer material exhibiting excellent physical and chemical properties. Natural rubber latex occurs in many plants, including the white sap of the common milkweed and dandelion. The most important source of natural rubber latex is the *Hevea brasiliensis* tree, which contains hundreds of proteins, including enzymes that are involved in the biosynthesis of the rubber molecules. NR is the strongest of all rubbers and also has excellent dynamic properties, such as resistance to fatigue, but it is less resistant to environmental damage (example, by ozone in the atmosphere and by oils) than some synthetic rubbers. Raw NR contains 93-95% *cis*-1,4-polyisoprene of about 5×10^5 g/mol, 2-3% proteins, 2% acetone-soluble resins (including fatty acids), small amounts of sugars, traces of minerals and water (Blow and Hepburn, 1982). The hydrocarbon component of NR, which consists of over 99.99% of linear *cis*-1,4-polyisoprene is shown in Figure 2.1.

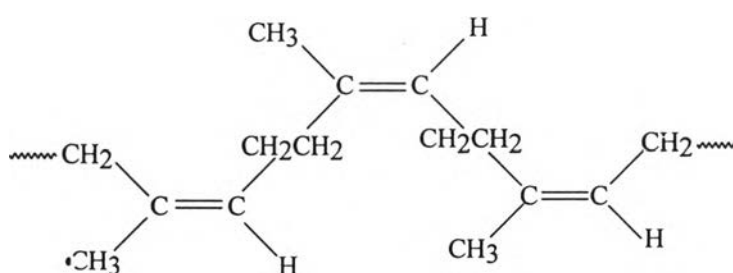


Figure 2.1 Chemical structure of NR (*cis*-1,4-polyisoprene).

Average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution, the cause of 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

the reactive groups for vulcanization with sulfur. The glass transition temperature (T_g) of uncured NR, the temperature or temperature range over which the polymer exhibits a remarkable change in several physical properties, is approximately $76.2 \pm 0.5^\circ\text{C}$, far below room temperature. Therefore, rubber is soft and can be melted by heat. Conversely, it is rigid and brittle at temperatures below the T_g . Hence, NR can be utilized in a narrow temperature range (Blow and Hepburn, 1982).

The thermal properties of NR can be enhanced by vulcanization with sulfur. Although vulcanized rubber has many advantages such as low T_g and high impact strength, it also has many undesirable properties such as low hardness, abrasion, stiffness and tear resistances. Consequently, fillers are utilized to improve the performance of these properties.

O'Haver *et al.* (1996) studied the modified silica surface by using copolymer prepared with a nonpolar and polar monomer to improve the performance of rubber compounds. The admicellar polymerization process serves to improve the rubber cure properties and the cured compound physical properties.

Kudisri (1997) produced polystyrene-isoprene copolymer on clay via admicellar polymerization. This study examined the effect of the amount of surfactant and monomer on the process. It was found that the increase in the compound cure rate decreases t_{90} cure time and improves tensile property, tear strength, hardness, flex cracking resistance and compression set.

2.2 Surfactant Structure

The word surfactant is a contraction of the term "Surface active agent". Surfactants are among the most unique and versatile materials due to their chemical structure. Generally, water-soluble surface-active agents are comprised of a hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8-18 carbon atoms, attached to hydrophilic or water soluble functional groups. This dual-natured structure is referred to as *amphiphilic* and thus the molecules are called *amphiphiles*. Surfactants are said to have a "tail" and a "head" as shown in Figure 2.2. In aqueous systems, the tail is hydrophobic, which

means water-hating, therefore oil-loving. It is typically depicted either as a straight line or a wavy line. The head is hydrophilic, which means water loving and is generally depicted as a circle.

Surfactants are classified according to the charge present in the hydrophilic portion of the molecule (after dissociation in aqueous solution). They can be categorized into 4 types (Rosen, 1989).

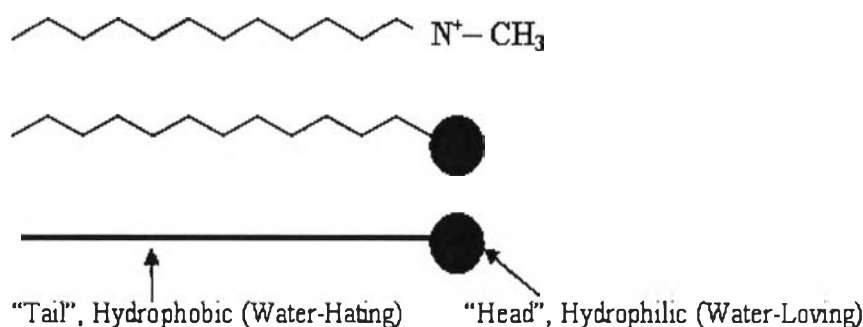


Figure 2.2 Surfactant structure.

Anionic surfactant: a surfactant molecule whose polar group is negatively charged. For example, alkylbenzene sulfonate, sodium dodecylsulfate.

Nonionic surfactant: no ion charge appears on the hydrophilic portion; for example, polyoxyethylenated alkylphenol.

Cationic surfactant: the hydrophilic portion bears a positive charge, examples include quaternary ammonium chlorides and laurylamine hydrochloride.

Ampholytic or zwitterionic surfactant: a surfactant molecule which has both positive and negative charged portions. The presence of both charged hydrophilic groups in the same molecule leads to the head group hydrophilicity being an intermediate between the ionic and conventional nonionic classes (Laughlin, 1991). The charges present depend on solution pH. Examples include polyoxyethylenated alkylphenol and lauramidopropylbetaine.

2.3 Cationic Surfactant

The term “cationic surfactant” is used to denote an ionic compound in which the cation is amphiphatic and strongly surface active. Considering the effect of pH on molecular structure and physical chemistry, the cationic hydrophilic groups can be divided into two sub-groups; neutral and acidic.

Cetyltrimethylammoniumbromide (CTAB) is a familiar cationic surfactant in the neutral sub-group as shown in Figure 2.3.

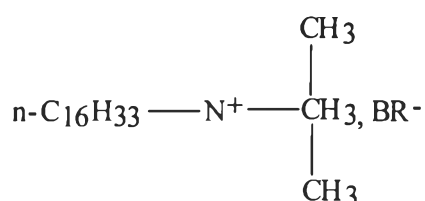


Figure 2.3 Structure of CTAB.

Quaternary ammonium ions have four carbons bonded to a positive nitrogen atom. Quaternary ammonium surfactants have one or more of these substituent groups that are lyophilic (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 non-bonding electron pairs; therefore, it is neutral 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 (Rubingh 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. The results showed that the MFA (EN444) not only contributes to a better silica-elastomer adherence but also improves dispersion, resulting in a lower hysteresis and enhanced mechanical properties of the natural rubber compound.

2.4 Nonionic Surfactant

Nonionic surfactants are surface-active compounds which have no net charge in the hydrophilic section. They are compatible with all other types of surfactants and generally available as 100% active material free of electrolyte. They are soluble in water and organic solvents, including hydrocarbons. Solubility in water decreases with increasing temperature. They can be made resistant to hard water, polyvalent metallic cations, and electrolytes at high concentration (Rosen, 1989). Commercial products are a mixture of structures with a wide distribution of polyoxyethylene chain lengths. Triton X-100 is a familiar nonionic surfactant, which is often used in biochemical applications to solubilize proteins. Triton X-100 has no antimicrobial properties. It is considered as a comparatively mild detergent, non-denaturing. It is a clear to slightly hazy, colorless to light yellow liquid. Triton X-100 structure is shown in Figure 2.5.

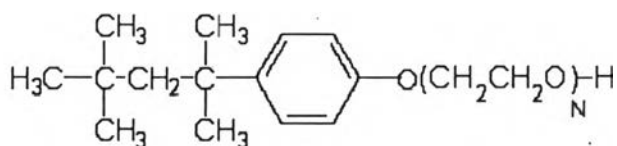


Figure 2.4 Octyl phenol ethoxylates (Triton X-100).

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 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 the adsorbed surfactant and the equilibrium concentration of the surfactant in liquid phase. The

adsorption isotherm for an ionic surfactant onto an oppositely charged substrate is typically “S-shaped” when plotting the log of the adsorbed surfactant density versus the log of the equilibrium concentration of surfactant. It can be divided into four regions (Rosen, 1989) as shown in Figure 2.5.

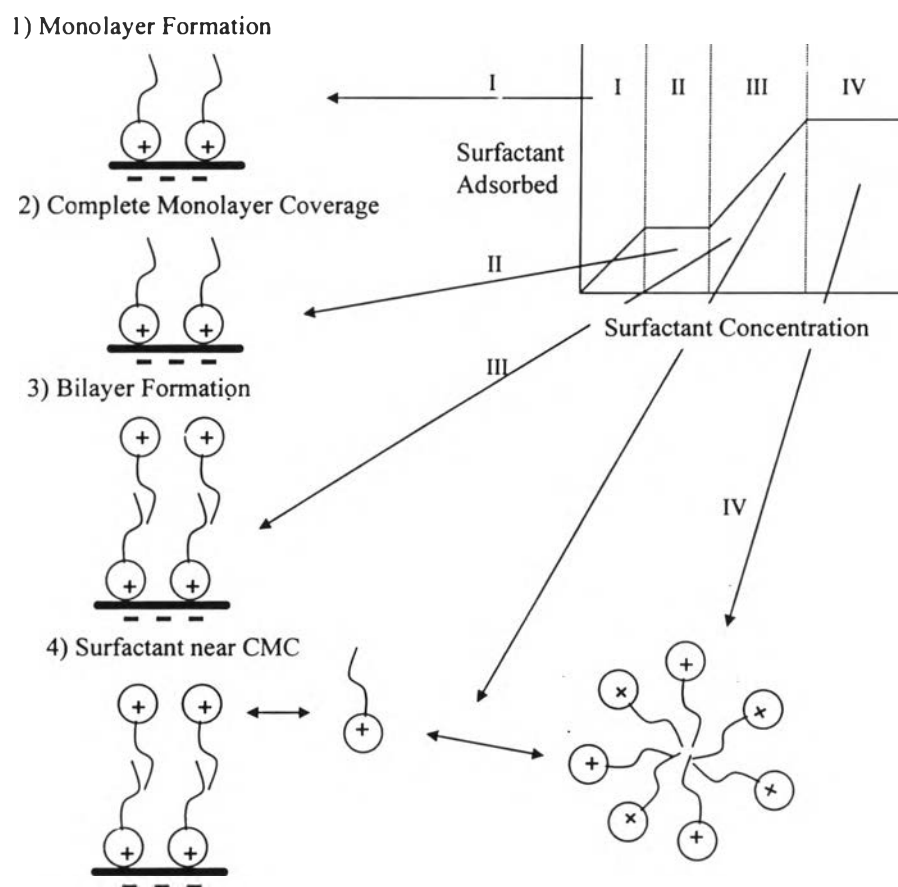


Figure 2.5 Adsorption isotherm of an ionic surfactant on an oppositely charged substrate.

Region I of the adsorption isotherm, corresponding to both very low bulk concentration of surfactant and low adsorption of the surfactant, is commonly referred to as the Henry's law region. The adsorption driving force is largely due to electrostatic attraction between the surfactant head groups and the oppositely charged surface. Because the interaction between molecules of the surfactants is negligible,

the adsorbed surfactants in this region are viewed as being adsorbed alone and aggregates are not thought to be present.

Region II, distinguishing by a sharply increased isotherm slope relative to the slope in the Henry's Law region, indicates the beginning of lateral interaction between the surfactant molecules, which results from the formation of surfactant aggregates on the most energetic surface patches. The aggregation of adsorbed surfactants are called admicelles (Harwell *et al.*, 1985) or hemimicelles (Somasundaran and Fuerstenau, 1966), depending upon whether the aggregates are viewed as monolayers or bilayers. The admicelle is a local bilayer structure with a lower layer of head group 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 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) (Harwell *et al.*, 1985) or hemimicelle concentration (HMC) (Somasundaran and Fuerstenau, 1966). During aggregate formation, the original charge 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.

A sharp 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-charged head groups on the surface, the beginning of adsorption on lower energy surface patches, or the charge neutralization of the surface. Thus, additional adsorption becomes more difficult.

Region IV is referred as the plateau adsorption region. The position of this plateau usually corresponds to a maximum adsorption, having almost constant surfactant adsorption with further increases in surfactant concentration. Normally, the equilibrium surfactant concentration at the transition point from region III to IV is roughly at the critical micelle concentration (CMC), the concentration at which micelles first form (Rosen, 1989).

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

Accordingly, there are wide ranges of condition under which only a single layer forms. This was shown to be the result of the electrostatic contributions of the free energy of transfer for a surfactant monomer from a hemimicelle to an admicelle which are potentially much larger in magnitude than the largest possible hydrophobic contributions. In addition, admicelles do form little if there is any interpenetrating of the hydrocarbon tails of second layer 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.

2.6 Solubilization

Solubilization is an important property of surfactants that is directly related to the presence of aggregates in solution called micelles. Surfactant solutions above their CMCs can dissolve considerably larger quantities of organic materials than pure water or surfactant solutions with concentrations below their CMCs. The additional capacity is obtained by solubilizing the solute in the micelles. Solubilization can be defined as “the spontaneous dissolving of substance (solid, liquid or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material” (Rosen, 1989). 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 the 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 (Rosen, 1989).

2.7 Adsolubilization

Similar to the solubilization of organics into micelles, organic molecules are integrated into surfactant aggregates at the solid-liquid interface (Figure 2.6). Adsolubilization is defined as “*the excess concentration of a species at an interface in the presence of an admicelle that would not exist in the absence of the admicelle*” (Wu *et al.*, 1987). This definition conveys the idea that the particular solute of interest does not adsorb onto the adsorbent surface by itself. The removal of solute from bulk solution occurs because of the presence of adsorbed surfactant aggregates and the incorporation of the solute into that aggregates.

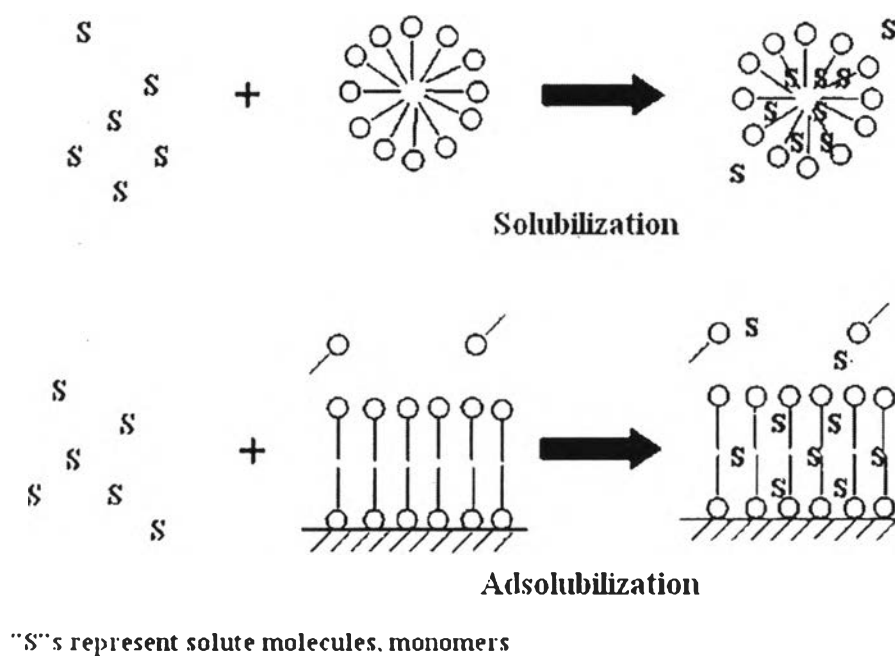


Figure 2.6 Phenomenon of solubilization and adsolubilization.

The adsolubilization of styrene, isoprene, and mixtures of these into CTAB bilayers on precipitated silica was investigated by Kitiyanan *et al.* (1996). The adsolubilization equilibrium constant is defined as $K_i = X_i / C_{ib}$, where K_i is the adsolubilization equilibrium constant of the assolubilize (i), X_i is mole fraction of adsolubilize (i) in the admicelle, and C_{ib} is the concentration of solute (i) in the

bulk aqueous phase (M). The styrene adsolubilization constant is nearly unchanged with increasing styrene equilibrium concentration in aqueous phase while the isoprene adsolubilization constant increases with increasing isoprene partial pressure. This suggests that styrene adsolubilizes into both the palisade layer and the core of the admicelle while isoprene adsolubilizes into only the palisade layer.

2.8 Ultra-Thin Film Formation

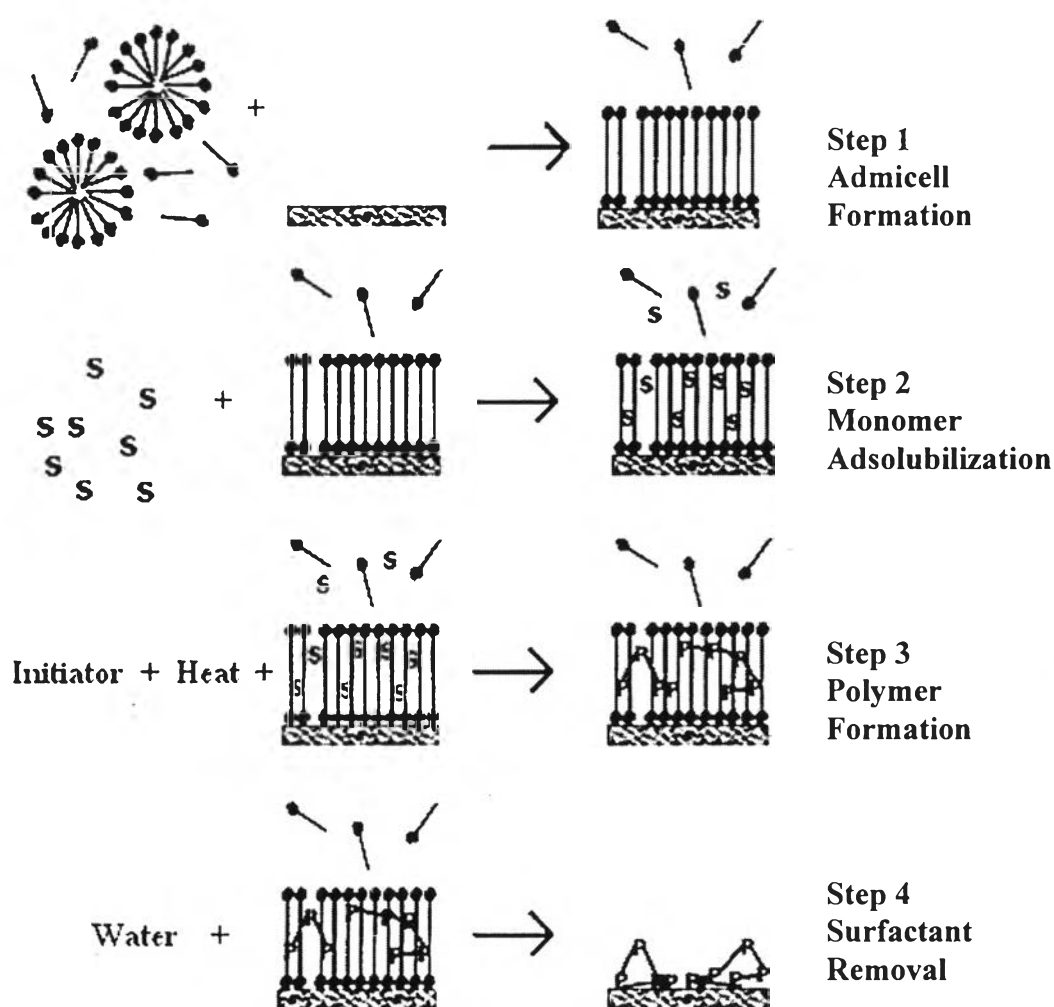
Formation of ultra-thin films on solid surfaces has been the object of powerful study in recent years because of a wide variety of possible applications of these films. The method used for the modification of inorganic powders by the formation of ultra-thin polymer films in adsorbed surfactant bilayers, called admicellar polymerization, was first developed by Wu *et al.* (1987). Admicellar polymerization can be considered to occur in four basic steps as show in Figure 2.7.

Step 1 is admicelle formation by the aggregation of surfactants at solid/liquid interfaces to form admicelles/aggregates through adsorption from an aqueous solution. For this step to be successful, the most critical parameter to be manipulated is the solution pH, relative to which the surface exhibits a net surface charge of zero (referred to the point of zero charge or PZC). The surface becomes protonated and positively charged at pH values below the PZC and surface is negatively charged above the PZC.

Step 2 consists of hydrophobic monomer molecules concentrating in the admicelle, adsolubilization, under conditions favorable for the formation of admicelles on a solid surface and unfavorable for the presence of micelles in an aqueous supernatant (Wu *et al.*, 1987). The hydrophobic monomers (e.g., styrene and isoprene in this study) adsolubilize or partition into the adsorbed surfactant aggregates of step 1. This step can occur after the formation of admicelle or concurrently with surfactant adsorption.

Step 3 is the *in-situ* polymerization of adsolubilized monomer. Further than the purpose of concentrating monomer at the surface of the substrate, the admicelles function as reaction loci or a two-dimensional reaction solvent for polymerization. Initiators begin the formation of polymer, possibly by mechanisms similar to those

occurring in conventional emulsion techniques (Sakhalkar and Hirt, 1995). Once the reaction has started, additional monomer from the bulk solution diffuses into the admicelle (O'Rear *et al.*, 1987). If the reaction is continuous for a sufficient length of time, virtually all monomers can be converted to polymer.



“S”s represent solute molecules, monomers

“P”s connected by lines represent polymer chain formed during reaction

Figure 2.7 Admicellar polymerization process for the formation of a thin polymer film.

Step 4 is the removal of accessible surfactant by washing in order to expose the polymer-modified surface. To increase the rate of surfactant removal, Waddell *et*

al. (1995) suggested that the continuous, counter-current washing would be preferred. 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.

2.9 Silica

Silica fillers can be classified as either natural or 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 annual silica usage in rubber (Hewitt, 2000). Two fundamental properties of silica 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 silica has shown to be a good indicator of silica performance as filler (Waddell, 1995). In addition, dispersibility and freedom from dusting are important practical characteristics, which are related to silica manufacturing process. Suppression of gel during precipitation prevents formation of large particles, visible in mixed compounds, which contain un-milled silica.

The small size of silica particles provides the desired high tensile strength, tear strength, and abrasion resistance in rubber compounds. The actual size of the reinforcing unit, however, is not that of the individual particle, but that of an agglomerate (Mark *et al.*, 1994). Small particles produce small agglomerates while large particles produce large agglomerates. Although particle size is the influential property, which governs its performance in rubber, a more usual and convenient means of classification is surface area, expressed in square meters per gram (Mark *et al.*, 1994).

Precipitated silica is often used in the production of translucent and colored products. Admicellar polymerization modified silica in rubber compounding significantly reduces cure time, increases tensile strength, and lowers the compression set and heat buildup as compared to compounds made from unmodified silica (Waddell, 1995). Precipitated silica is used in both tires and shoe soles applications. In combination with reinforcing carbon black, they improve tear

resistance and adhesion to fabrics. Hydrated silica retards the cure time and requires the use of accelerator or addition of materials such as glycols or amines to promote curing (Katz, 1987).

Silica is considered a polymer of silicic acid, in which the bulk structure is produced by interlinking SiO_4 tetrahedral. At the surface, the structure consists of siloxane groups (-Si-O-Si-) and one of the several forms of silanol groups (-Si-OH). The silanol groups make precipitated silica hydrophilic. Unmodified silica does not interact well with most polymers, requiring high amount of shear and energy to incorporate them evenly (Wagner, 1976).

Silane coupling agents are considered a unique and greatly effective method to increase silica-polymer interactions. The coupling agent is able to form new chemical bonds between the silica surface and the polymer. 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 agent is the admicellar polymerization process (Waddell *et al.*, 1995; Thammathadanukul *et al.*, 1995; and Chinpan, 1996).

O'Haver *et al.* (1993) studied the ultra-thin polystyrene film on silica. Polystyrene was successfully polymerized into cetyltrimethylammoniumbromide (CTAB) as a cationic surfactant and using 2,2'-azobis-2-methylpropionitrile (AIBN) as water-insoluble initiator. Extraction and characterization of polymer formed were measured by using techniques including PA-FTIR and GPC. The molecular weight of polymer formed was investigated with respect to polymerization time. Polymeric films on porous silica tend to slightly increase particle size and decrease surface area of silica. The presence of polystyrene on the silica was shown by PA-FTIR spectra and the distribution of molecular weight of extracted polymer was studied by GPC.

Thammathadanukul *et al.* (1995) studied the comparison of rubber reinforcement using various surface modifications. All copolymer-treated silicas offered greater improvements in rubber performance than silica modified by a silane coupling agent. Moreover, the improvement of filler-elastomer interaction by in situ polymerization process depends on amount and type of polymer developed on the silica surface.

Chinpan (1996) studied the admicellar polymerization modified silica with butadiene and isoprene as co-polymer with styrene. The polymer can form bonds with the rubber compound during the curing process. Significant improvements in the rubber properties were achieved, and it was also found that using the lower loadings of monomer and surfactant provided the greater improvement.

Chaisirimahamorakot (2001) studied the modification of silica surface by admicellar polymerization process using cetyltrimethylammoniumbromide (CTAB) adsorbed on the surface, comonomers styrene and isoprene dissolving into the admicelle aggregates and 2,2'-azobis-2-methylpropionitrile (AIBN) as the water-insoluble initiator. The polymeric films can be produced successfully on the surface by polymerization in a continuous stirred tank reactor. The highest amount of polymer occurred with a loading of 5 g comonomers at 60 min residence time. The effect of comonomer loading and polymerization time on the mechanical property improvements of modified-silica filled natural rubber was further studied by Nontasorn (2002). It was found that 5 g of co-monomer loading at 30 min residence time provided the highest overall improvements. Kaitdamneon-ngam (2003) studied the effect of initiator and surfactant loading of the similar system. The result showed that 1.65 grams of AIBN initiator and 146 g of CTAB provided the highest of overall improvement as indicated by surface characterization results and rubber physical properties. Imsawatkul (2004) investigated this technique using the mixtures of CTAB and TritonX-100 for silica surface modification. The results show improvement in mechanical properties of the rubber filled with the modified silica.