CHAPTER II
LITERATURE REVIEW

2.1 The Approach to Improve Thermal Conductivity of Polymer Composite

Thermally conducting but electrically insulating materials are needed for die attachments and encapsulations for use in electronic packaging. Metals are both thermally and electrically conducting, so they cannot be used for this purpose. Diamond is outstanding in its high thermal conductivity while it is electrically insulating, but it is expensive, even in powder form. Almost all polymers are electrically insulating, but they are also thermally insulating. Thus, polymers alone cannot be used for this purpose. On the other hand, polymers have low processing temperatures, which allow them to be easily made into polymer-matrix composites in bulk or coating forms. By using a filler which is thermallly conducting but electrically insulating, a polymer-matrix composite can become thermally conducting while electrically insulating. In order to obtain material of desired thermal, mechanical and electrical properties, matrix materials, such as polymers, are processed with different kinds of fillers. Fillers may be in the form of fibers or in the form of particles uniformly distributed in the polymer matrix material. Many materials have been investigated to make thermally conductive polymer-based composites including metallic fillers, ceramic fillers, and carbon based materials. Some ceramic fillers have high thermal conductivity, but are prohibitively expensive. Metal fillers are more affordable, but suffer the disadvantage of high density. The use of lighter weight material-based compounds as conductive fillers are now being investigated including carbon black, boron nitride, aluminum nitride, carbon fiber, graphite, and carbon nanotubes. In the present work the use of boron nitride in an epoxy polymer matrix was investigated.

2.1.1 Minimizing Phonon Scattering
In 1973, Berman explained that the transport of heat in non-metals is by the flow of phonons or lattice vibrational energy. The thermal resistance is caused by various types of phonon scattering, boundary scattering, and defect or impurity

scattering. Therefore, in order to maximize the thermal conductivity in materials, these phonon scattering processes must be suppressed. Phonons travel in matter with the speed of sound. In theory, the scattering of phonons in composite materials is mainly due to the existence of an interfacial thermal barrier from acoustic mismatch, or the damage of the surface layer between the filler and the matrix. These interfacial phonon scattering phenomena are similar to the scattering of light due to differences in refractive indices of the media. The thermal resistance can be reduced by a combination of various techniques. The selection of particles having perfect lattice or crystal structures as much as possible to suppress the scattering of phonons by lattice defects is essential. This kind of filler is normally found in highly thermally conductive ceramics, such as boron nitride or aluminum nitride. Moreover, the layer of the matrix resin between the particles must be as thin as possible, to such a degree that its mechanical properties are still high enough for the application, to reduce the thermal resistance due to the resin itself. This can be achieved by using a resin which has low melt viscosity. The low viscosity resin generally aids in filler mixing during the molding compound preparation. These hypotheses are based on one important assumption that the adhesion between the filler and the matrix resin is good; otherwise, the third phase, an air gap, may occur and will also have a high contribution to the overall conductivity of the composites. In addition, it is known that the interfaical thermal contact resistance between different constituent phases in a composite can arise from the combination of poor mechanical or chemical adherence at the interface and a thermal expansion mismatch. In order to enhance the filler matrix interface thermal conductance, the chemical surface modification of the filler can be helpful to improve the wettability, uniform dispersion, and interfacial adhesion between filler and matrix.

Dong *et al.* (2005) studied the effect of silane surface treatment on the enhancement in thermal conductivity of alumina-filled PS composite. Their results show that the functionalization of alumina particle using GPS silane coupling agent can increase the thermal conductivity by 16.5%. They also found that the effect of interfacial functionalization can well go beyond the thermal conductivity, for example, the mechanical properties and humidity resistance of the composite materials may also be enhanced..

In 2006, Lee *et al.* investigated the improvement in thermal conductivity of AlN-filled epoxy composite using titanate coupling agent. They revealed that the sample containing surface-treated fillers exhibited a slightly improved thermal conductivity than the sample containing untreated fillers. They suggested that improvements in both the dispersion and interfacial adhesion by filler surface treatment would lead to increased thermal conductivity by minimizing the phonon scattering at the interface.

2.1.2 Using High Intrinsic Thermal Conductive Filler

Composite materials with high thermal conductivities can be obtained by using fillers with high intrinsic conductivities. However, as discussed by Bigg (1986), when the intrinsic thermal conductivity of the filler is greater than 100 times that of the polymer matrix, there is no further significant improvement in the thermal conductivity of the composite. This phenomenon is illustrated in Figure 2.1.
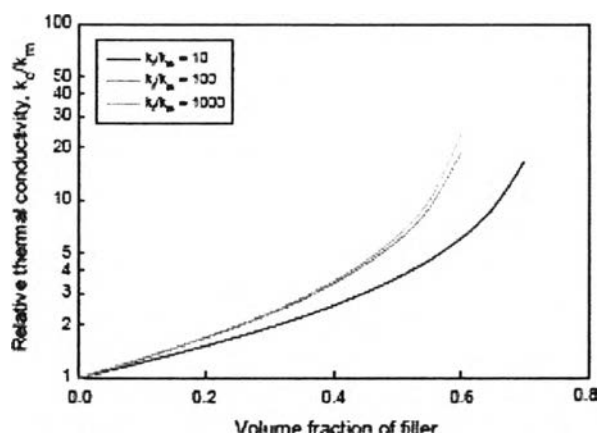
Figure 2.1 Relative thermal conductivity as a function of filler volume fraction (K_f, thermal conductivity of filler, K_m, thermal conductivity of matrix or polymer) (Bigg, 1986).

2.1.3 Forming Conductive Network

The aspect ratio of the filler is another factor that can contribute significantly to the conductivity of a composite, because the fillers with large aspect ratios can more easily form bridges between them, known as conductive network.

The formation of random bridges or networks from conductive particles facilitates electron and phonon transfer leading to high conductivity. The maximum packing ratio of the filler in the matrix is another factor that can assure formation of the near-perfect conductive networks. There is however a practical limit in loading the maximum amount of filler since it often causes problems in processibility as well as mechanical performance of the composite. To achieve high packing density composites, the use of large size particles with multimodal particle size distribution and low aspect ratio with smooth surface texture as a second phase was suggested.

Kirillov *et al.* (1972) studied the effect of filler content on thermal conductivity of composite using various mineral fillers. Their results reveal that at higher filler content, the thermal conductivity of composite is greater than that at lower filler content. They concluded that, at high filler content, the distance between filler particles is decreased resulting in the conductive network formation.

Gojny *et al.* (2006) studied the influence of filler content and the aspect ratio using CNT-filled epoxy composite. Their results reveal that CNT with a high aspect ratio at a given volume fraction is the most favourable type of CNT for enhancing the thermal conductivity of a polymer composite due to their small surface area and lowest interfacial boundary scattering.

In 2009, Sanada *et al.* demonstrated another approach to improve thermal conductivity of composite. They investigated the thermal conductivity of polymer composites with nanofillers and microfillers. The nano fillers used were multi-walled carbon nanotubes (MWCNTs) and alumina nanoparticles, and the spherical alumina particles were selected as the microfillers. They found that the addition of nanofillers to the polymer-matrix which filled in the spaces between the microfillers significantly increased thermal conductivity of the composite. They also suggested that the composite containing MWNTs showed a higher thermal conductivity compared to the composites containing alumina nanoparticles due to the high thermal conductivity and aspect ratio of MWNTs leading to an ease in the forming of conductive pathway.

2.1.4 Exfoliation of Graphite

Fukushima *et al.* (2006) present the improvement in thermal conductivity of polymer composite using exfoliated graphite flakes (xGnP) as a thermal conductive filler in HDPE. They found that exfoliated graphite nanoplatelet composites with up to 20 vol% xGnP exhibited thermal conductivities of more than 4 W/mK.

Debelak and Lafdi (2007) used three sets of exfoliated graphite having three different particle sizes as conductive fillers. They investigate that thermal conductivity for the polymers containing 20 wt% exfoliated graphite has been drastically improved, increasing from 0.2 to 4.3 W/mK. The exfoliated graphite proved to be superior as a conductive filler than carbon nanofiber. Their result also suggest that the addition of exfoliated graphite assists the enhancement for the mechanical property of the composite.

Ganguli *et al.* (2008) prepared the chemically functionalized exfoliated graphite-filled epoxy. They recognized that the silane treated exfoliated graphite composite at 20 % loading level had a thermal conductivity of 5.8 W/mK, a 35% increase, from 4.3 W/mK of untreated graphite composite.
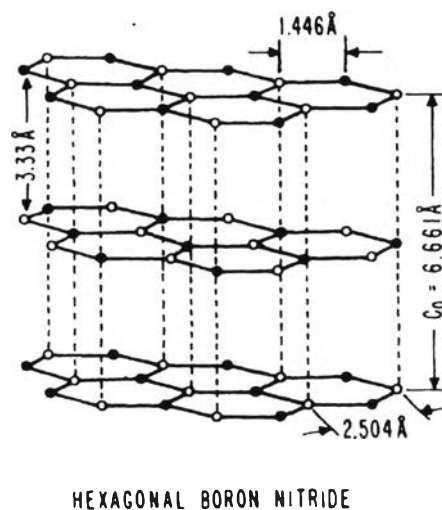
2.2 Boron Nitride

Boron nitride (BN) is a unique material. It offers outstanding thermal conductivity, excellent dielectric strength, very good thermal shock resistance and is easily machinable. This material is an advanced synthetic ceramic available in powder, solid, liquid and aerosol spray forms. In an oxidizing atmosphere it can be used up to 900°C. However, in an inert atmosphere, some grades can be used as high as 3000°C (Baeraky, 2005).

2.2.1 The Structure of Boron Nitride

Up to now, there are four BN polymorphic modifications: hexagonal BN (h-BN), rhombohedral BN (r-BN), cubic BN (c-BN) and wurtzite-like BN (w-BN), which can be reliably synthesized and identified. The c-BN and w-BN are hard phases bonded with strong diamond-like sp^3 hybridization, whereas h-BN and r-BN

are softer phases bonded through localized graphite-like sp^2 hybridization in hexagonal plane and delocalized weak π orbital (Xia and Li, 2007).

The hexagonal layer structures h-BN and graphite are isomorphic. The lattice constants are similar, i.e., for h-BN, a_0=2.504 A°, c_0=6.661 A°, as shown in Figure 2.2, and for graphite a_0=2.456 A° and c_0=6.696 A°. The differences between h-BN and graphite are also notable. Hexagonal BN is a white insulating material and looks much like mica. Graphite is black and an electrical conductor. Both materials are strongly bonded within an atomic layer, but bonding between layers is weak, of the Van der Waals type (Sichel *et al.*, 1976).

HEXAGONAL BORON NITRIDE

Figure 2.2 The structure of Hexagonal Boron Nitride

Hexagonal BN platelets appear as very small discs. There are two different sets of reactive sites on BN. One set is at the edge plane and the other is on the basal plane. On the edge plane, the crystal structure of BN must terminate, usually with either hydroxyl species or amino groups (Wank *et al.*, 2004)

2.2.2 The Thermal Conductive BN-Filled Polymer Composite

In 1988, Bujard studied the temperature dependence and influence of sample preparation in the thermal conductivity of boron nitride-filled epoxy resin as

a function of filler content. He used flake-like boron nitride crystals with small particle size and was able to make a composite with a maximum filler content of 31 vol% and a corresponding thermal conductivity value of 2.3 W/mK. The author mentioned the use of percolation theory to explain the formation of filler networks in his composite system. However, his system did not show a sharp discontinuity associated with a percolation threshold at 15 vol% which was normally observed in electrically conductive composites. He suggested that there were two important parameters that regulated the conductivity in the composite, i.e. the number of conducting paths and the real particle density along the heat-flow paths. The effect of the mode of sample preparation can lead to different particle distributions in the matrix which produces the variations in the thermal conductivity.

Ishida and Rimdusit (1998) prepared a highly thermally conductive BN-filled benzoxazine at its maximum loading of 78.5 vol%. A thermal conductivity of 32.5 W/mK is achieved. They suggested that the extraordinarily high conductivity value results from outstanding properties of the polybenzoxaxine matrix, the boron nitride filler, and bimodal particle size distribution. Bimodal distribution assists in increasing the particle packing density. This filler-matrix system provides a highly thermally conductive composite due to the capability of forming conductive networks with low thermal resistance along the conductive paths.

Xu and Chung (2000) used surface treatment of the filler to improve the affinity between filler and matrix, thereby significantly increasing the thermal conductivity of the composite. The thermal conductivity of epoxy-matrix composites was increased by up to 97% by surface treatment of the particles prior to composite fabrication. Effective treatments for BN involved acetone, acids (nitric and sulfuric) and silane. The most effective treatment involved silane such that the coating resulted from the treatment amounted to 2.4% of the weight of the treated BN.

In 2006, Lee *et al.* investigated the effectiveness of hybrid filler consisting of different conductive fillers in type and shape on the fabrication of thermally conductive composites. They attempted to maximize the abundance of thermally conducting paths by using hybrid filler at its maximum packing loading, and also tried to minimize the interfacial phonon scattering by chemical surface treatment of the filler, which led to an improvement in the wettability and uniform

dispersion. Various inorganic fillers including aluminum nitride (AlN), wollastonite, silicon carbide whisker (SiC) and boron nitride (BN) with different shape and size were used alone or in combination to prepare thermally conductive polymer composites. Their results reveal that the maximum packing fraction of BN fillers is below 30 vol%. This means BN filler forms the thermally conductive networks at lower filler content than other fillers. The larger difference between the maximum packing fraction and the filler content of the sample is responsible for the highest thermal conductivity value of the sample containing 50 vol% of BN which has lower intrinsic thermal conductivity than AlN.
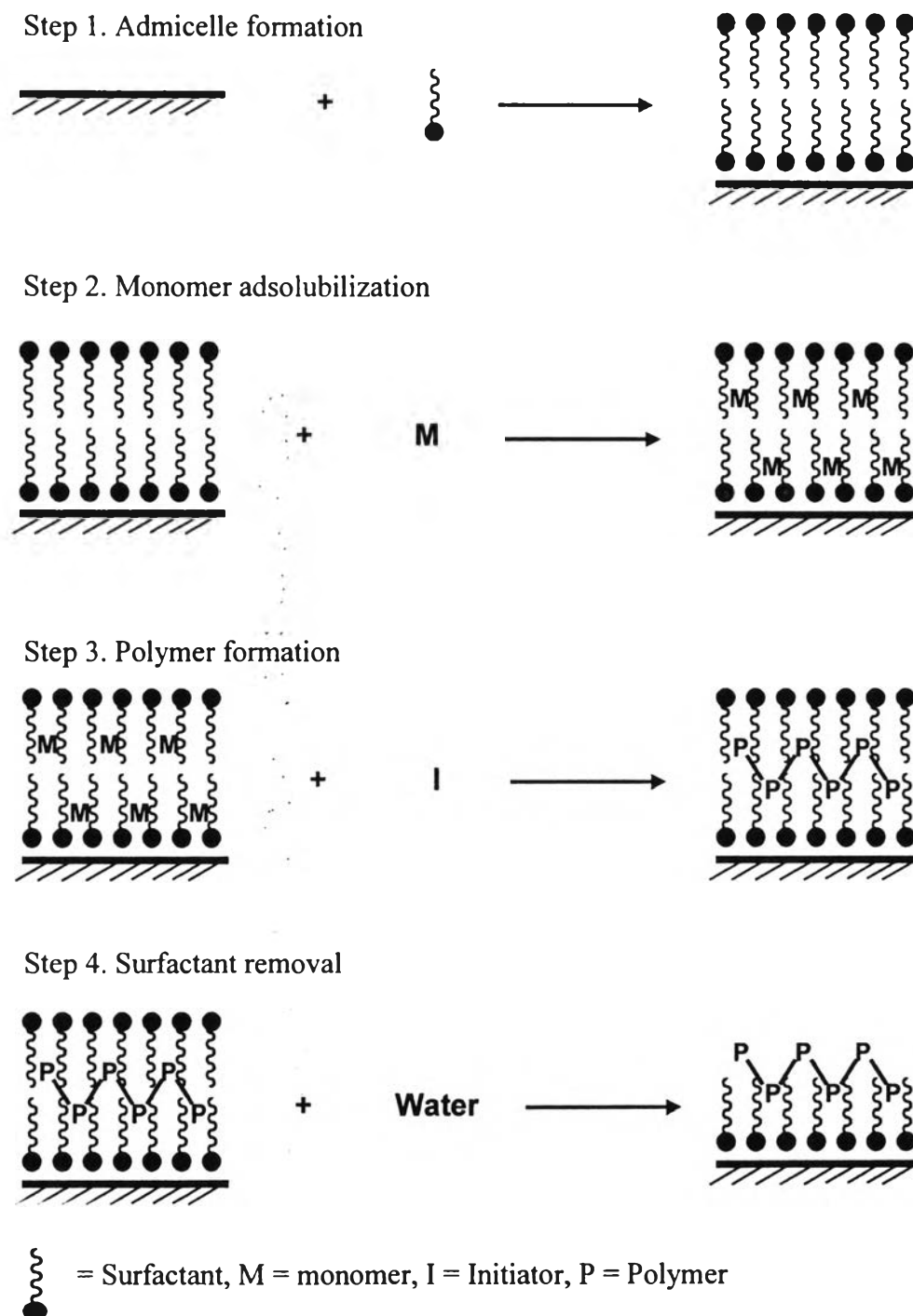
2.3 Admicellar Polymerization Process

Admicellar polymerization, a termed derived from "adsorption" and "micelle", defines a class of *in-situ* polymerization taking place inside an adsorbed surfactant bilayer on a substrate surface.

In a solution of an ionic surfactant under suitable conditions, the surfactant molecules will tend to form aggregates at the hydrophilic surfaces in aqueous solution. To minimize the free energy, the surfactant molecules will tend to form bilayer with the hydrophilic head groups of the upper layer facing the aqueous water and hydrophobic tails facing inside to form a hydrophobic core in the center of the bilayer admicelle.

Admicellar polymerization is a three-step chemical process with an additional fourth step to remove the outer-layer surfactant. The process is shown schematically in Figure 2.3.

Step 1: *Admicellar formation*. Surfactants are adsorbed on the substrate surface to form a bilayer structure or admicelle. The adsorption isotherm of ionic surfactants onto a substrate surface can be divided into four regions as shown in Figure 2.4.

Step 1. Admicelle formation

Step 2. Monomer adsolubilization

Step 3. Polymer formation

Step 4. Surfactant removal

= Surfactant, M = monomer, I = Initiator, P = Polymer

Figure 2.3 Schematic of the steps in the admicellar polymerization.

This curve is a plot between the log of adsorbed surfactant versus the log of equilibrium surfactant concentration which can be used to obtain the appropriate concentration of surfactant for admicellar polymerization process. This concentration is slightly below the critical micelle concentration or CMC to avoid emulsion

polymerization. The adsorption of the surfactant on the substrate surface is controlled by several factors: the electrochemical nature of the substrate, the type of surfactant molecule, the pH of solution, and added counterion. At pH values below the PZC (point of zero charge), the surface is positively charged; above the PZC, the surface is negatively charged. Consequently, anionic surfactants adsorb well below the PZC and cationic surfactants above the PZC. An electrolyte can be added to reduce the repulsion between the head groups of the surfactant to enhance surfactant adsorption. Hence, the important parameters that need to be manipulated are pH value and counterion concentration.
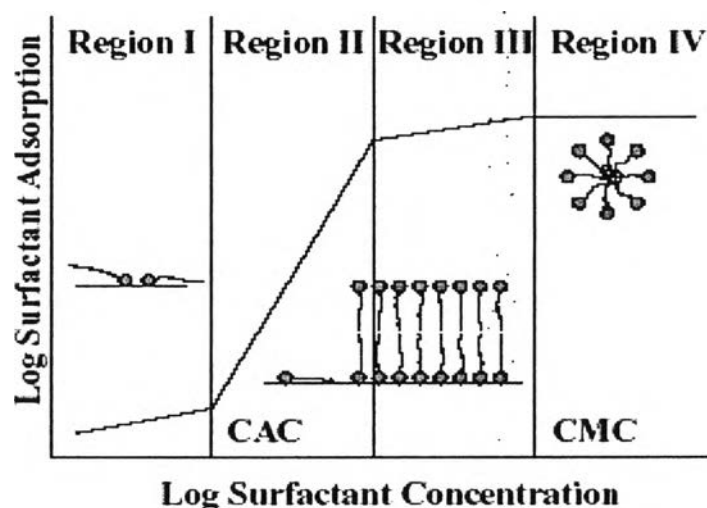
Figure 2.4 Adsorption isotherms of an ionic surfactant on a solid surface.

Step 2: *Monomer adsolubilization.* A known amount of monomer was added to the solution. Since the bulk concentration of the surfactant is below the critical micelle concentration, the relatively hydrophobic monomers preferentially partition into the hydrophobic interior of the admicelle in the process called "adsolubilization".

Step 3: *Polymer formation.* The admicellar polymerization is started by the addition of an initiator. Polymerization occurs in the admicelle bilayer with reaction similar to the emulsion polymerization.

Step 4: *Surfactant removal.* The upper-layer surfactant is removed by washing with water, exposing the polymer film on the substrate surface.

2.3.1 Applications of Admicellar Polymerization to Inorganic Substrates

In 2000, Cho *et al.* prepared highly conducting PPY-coated alumina composite particles by using admicellar polymerization process. In the atomic force microscopy studies, the morphology of the resulting PPY on alumina particles showed multigranular images similar to those of pure polypyrrole films and all alumina particles were completely coated by polypyrrole films. The contact conductivity of these PPY-alumina composites is more than 3 times that of a pure polypyrrole powder, even with a very low amount (12 wt%) of polypyrrole incorporated onto alumina.

Admicellar polymerization was used to deposit polystyrene and poly (methyl methacrylate) onto aluminum surface in order to migitate corrosion caused by water (Materredona *et al.*, 2003). The films on aluminum surfaces were characterized by FTIR, SEM, and AFM. Dynamic contact angles indicated that the modified aluminum substrates exhibited hydrophobic nature. Water uptake measurements showed that PS delayed water penetration for almost 4 h. Accelerlated corrosion tests also revealed the protective characteristics of poly(methyl methacrylate).

Wei *et al.* (2003) modified the surface of two porous solids: titanium dioxide and alumina by admicellar polymerization process. The results showed that polymer formed on both the outside and the inside surfaces of a rough, porous solid using admicellar polymerization. X-ray photoelectron spectroscopy (XPS) measurements clearly indicated that, after admicellar polymerization, organic material and surfactant were present on the surface of the solids. Water washes, performed immediately after admicellar polymerization, were successful in removing approximately 30% of the organic material, presumably mostly surfactant. In terms of removal of either polymer or surfactant, definite differences were found between the two types of surfaces: as expected, more material could be removed from the outer surfaces versus the inner surfaces using solvent washes. However, even for the outside surface, only about half of the material could be removed after both water and soxhlet extractions. On the outside surface, the ratio of surfactant to polymer after admicellar polymerization and the solvent washes (a water wash followed by

soxhlet extraction with toluene) is approximately 1:1, whereas the ratio on the interior surface is approximately 3:1.

Poly(2,2,2-trifluoroethyl acrylate) (PTFEA) was applied to aluminum alloys by admicellar polymerization for corrosion control in the aerospace (Duc *et al.*, 2004). XPS depth profiling helped determine the film thickness to be around 10 nm, which is ultrathin. The modified surface was highly hydrophobic and able to delay salt solution uptake (3.5 wt% NaCl) for a period of up to 6 h in crevice corrosion tests. PTFEA film reduced the corroded area to 20% compared to 65% for a bare aluminum control and to 33% for poly(methyl methacrylate) (PMMA) film in a 24 h crevice test. PTFEA film exhibited better corrosion protection than PMMA film because it has higher hydrophobicity than a PMMA-modified surface.

Nontasorn *et al.* (2005) developed a continuous stirred tank reactor (CSTR) for admicellar polymerization of styrene and isoprene on silica surface for improvement of compatibility between the silica and rubber. The feed comprised precipitated silica, cetyltrimethyl ammonium bromide (CTAB) cationic surfactant, styrene and isoprene comonomers, and 2,2'-azobisisobutyronitrile initiator. The results showed that the modified silica reduced T_{90} cure time and improved modulus, abrasion resistance, and compression. In comparison with the modified silica using a batch process, the modified silica obtained from the CSTR process was found to be superior in the performance of rubber compound.

Admicellar polymerization has been used to form a thin film of polyethylene onto the surface of milled glass fibers using sodium dodecyl sulfate as the surfactant (Somnuk *et al.*, 2003). The decrease in ethylene pressure was used to follow the solubilization and adsolubilization processes as well as the reaction processes. An increase in initiator $Na_2S_2O_8$ to surfactant ratio gave thicker and more uniform coatings of polymer onto the glass fiber surface according to SEM micrographs. Although a substantial amount of ethylene polymerized in solution according to the pressure drop, the decrease in pressure attributed to admicelle polymerization corresponded to the amount of polymer formed on the glass fiber, indicating that, only a small amount, if any, solution polymer deposited on the fibers. The admicellar-treated glass fiber was used to make composites with high-density polyethylene. The composites showed an increase in tensile and flexural strength

over composites made from as-received glass fiber, indicating an improvement in the fiber-matrix adhesion of the admicellar-treated glass fiber.

2.4 Surface Treatment by the Adsorption of Surfactant

Being able to characterize and even control the surface structure of the microparticles is important to their applications. Modification of the particle surface is often one of the approaches taken to improve the dispersibility and rheological properties of particulate-filled composites. Great efforts have been employed in the design and synthesis of a variety of dispersant (or surfactant) molecules with both hydrophilic and hydrophobic functional groups for modifying particle surface properties through the adsorption of these molecules onto the particle surface. Many attempts have also been made to directly modify the chemical composition and functionality of particle surfaces in order to achieve preferred interactions with the solvent molecules or affect adsorption of surfactants. Adsorption of surfactants onto solid particles controls many interfacial processes, such as stabilization of solid dispersions, selective flotation of minerals, detergency, protection of metal surfaces and lubrication. Surfactant adsorption at the solid-liquid interface is an important phenomenon in which the surfactant molecules can interact with the solid surface.

2.4.1 Effect of Surfactant Adsorption on Deagglomeration and Particle Dispersion

Meguro *et al.* (1987) examined the effects of the addition of surfactants on the aqueous dispersion of silicon carbide. They found that the addition of nonionic surfactants having relatively longer length of hydrocarbon and oxyethylene chain to the silicon carbide enhanced its dispersion stability.

Fekete and Pukanszky (1997) found that the sedimentation of the stearic acid-treated calcium carbonate was very slow.

In 2001, Esumi reported that the dispersion stability of alumina suspensions in the absence of sodium dodecyl sulfate (SDS) was very high because SDS adsorbed onto positively charged alumina particles, orienting its hydrocarbon to aqueous solution, resulting in flocculation between the hydrophobic surface particles.

2.4.2 Effect of Surfactant Adsorption on Interfacial Adhesion

The coating of an organic layer by the adsorption of a surfactant on the filler surface enhances the wetting of the filler by the polymer melt during compounding and reduces the particles tendency to agglomerate. Nano- and sub-micron particles have strong tendency to aggregate, building strong clusters with different shapes. Filling a semi-crystalline polymer with micron-sized isotropic filler particles influences its tensile properties in different ways. In addition to the component properties, the composite mechanical characteristics are influenced by the adhesion forces at the filler-matrix interface and by the thickness and properties of the interphase. During macroscopic deformation, numurous processes such as elastic deformation, yielding, crazing, orientation, debonding (dewetting), failure initiation, and propagation take place. These local processes, which occur at small or large deformations, are differently influenced by the above mentioned parameters that vary not only with the type of filler but also with the particles surface treatment.

Osman and Atallah (2007) investigated the micron-sized $CaCO_3$ particles coated with a monolayer of aliphatic carboxylic acids. They found that the dispersion of the filler could be improved even at a high filler loading. Surface treatment of $CaCO_3$ with an acid containing a long hydrocarbon chain led to composites with increases in both the tensile modulus and strength.