



CHAPTER II

LITERATURE SURVEY

Nano-ordered composite materials consisting of organic polymers and inorganic compounds have been investigated for a wide range of scientific and practical interests. The term “polymer hybrid” described blends of organic and inorganic components with molecular-level dispersion (Chujo and Saegusa, 1992). Recently, the preparation of inorganic-organic mesostructured materials using supramolecular assemblies of surfactants to template the reactions of inorganic species has attracted increasing interest for the fabrication of hybrid materials.

2.1 Adsorption of Surfactant on the Solid Oxide Surface

The adsorption of ionic surfactant onto an oppositely charged solid surface has been extensively studied. When a mineral oxide surface is brought into contact with an aqueous solution, the adsorption of H_3O^+ or OH^- ions from the solution onto the surface can cause variations in the surface charge. As the pH of the solution is lowered, the mineral oxide surface will usually become more positively charged (or less negatively charged) because of the adsorption of the H_3O^+ ions onto the surface, with the consequence of an increase in the adsorption of anionic surfactants and a decrease in the adsorption of cationic surfactants. The reverse is true when the pH of solution is raised.

Adsorption data have usually been presented as a log-log plot of the surfactant adsorption (amount of surfactant adsorbed per gram of adsorbent) versus the equilibrium concentration of the surfactant in bulk solution. Adsorption isotherms usually take on very characteristic shapes, depending upon the surfactant and substrate. Rosen (1988) described the adsorption isotherm of ionic surfactants onto an oppositely charged substrate and also sometimes – but not always – nonionic surfactants are typically S-shaped. In case of nonionic surfactants, an ethoxylated nonylphenol, for example, will exhibit a similar isotherm on silica, but will not adsorb sufficiently strongly to show all the details of such an isotherm on alumina. Commonly, S-shaped isotherm can be divided into four regions as shown in Figure

2.1 and in each these regions corresponds to a different mechanism of surfactant adsorption.

In region I the surfactant adsorbs mainly by ion exchange and also the charge density, or potential at the Stern layer of the solid, remains almost constant. This region corresponds to very low adsorption densities and is sometimes referred to as the Henry's law region. The most important point is that there are no aggregates of adsorbed surfactants in this region and may not even be detectable because it occurs at such low surfactant concentrations.

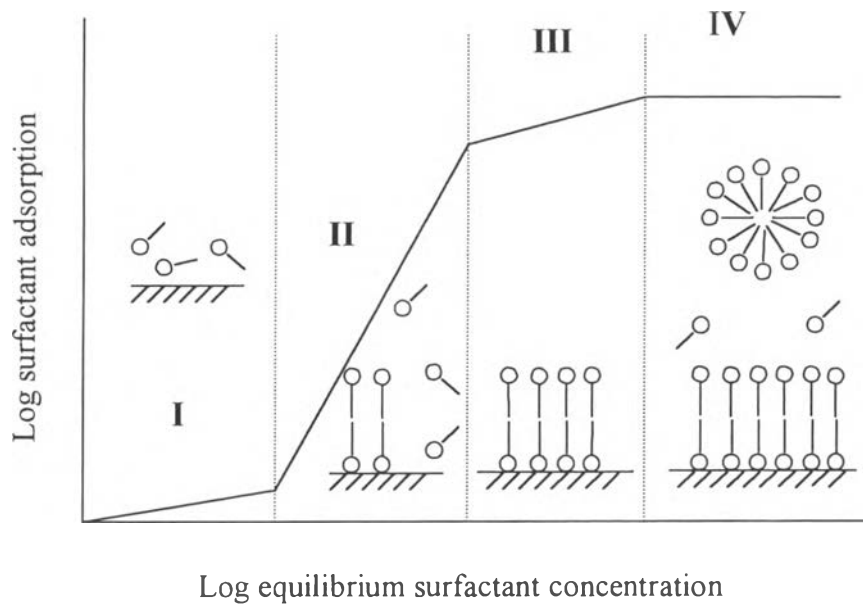


Figure 2.1 Adsorption isotherm for an ionic surfactant on an oppositely charged substrate (Rosen, 1988).

In region II there is a marked increase in adsorption as the equilibrium concentration of surfactant increases. It is believed that this increase is caused by the interactions of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves, which caused the adsorbed surfactants to form aggregates on the surface. This aggregation of the hydrophobic groups has been termed hemimicelle or admicelle depending upon whether the aggregates are viewed as monolayers or bilayers. The formation of these aggregates locally or patchwise at the interface is due to the heterogeneity of the surface. The

locally or patchwise at the interface is due to the heterogeneity of the surface. The original charged surface of the solid is neutralized by the adsorption of oppositely charged surfactant ions and eventually reverse, indicate the end of region II.

However, region III is characterized by a reduced slope in the adsorption isotherm not only because adsorption must overcome electrostatic repulsion between the oncoming ions and the identically charged head groups on the surfaces, but also because adsorption is now taking place on the more and more similarly charged surfaces. As the equilibrium concentration of surfactant further increases and eventually approaches the critical micelle concentration (CMC), adsorption is usually completed. The beginning of constant adsorption marks the onset of region IV.

Region IV is referred to as the plateau adsorption region and in this region the surface concentration of surfactant has reached saturation. The adsorption does not increase while the equilibrium concentration of surfactant is raised above the CMC. Further addition of surfactants only contributes to the formation of additional micelles in the bulk solution. In most systems the transition of region III/region IV occurs near the CMC of the surfactants.

2.2 Surfactant Layers at the Solid/Liquid Interfaces

According to Grosse and Estel (2000), the formations of thin surfactant layers on solid surfaces play an important role in many technological processes. Such layers influence the properties of the solid such as hydrophobicity, hydrophilicity, wetting, and electrostatic characteristics. Thus, the formation of surfactant layers is a significant operation in the surface modification of solids. Surfactants often do not form continuous monolayers or bilayers at the solid/liquid interface but they form discrete aggregates of different shape and size depending on different factors including surface charges, hydrophobic or hydrophilic surfaces, ionic nature of the surfactant, and length of the carbon and/or ethylene oxide chains. Different types of surfactant layers on solids form depending on the conditions of formation.

At concentrations below the CMC the surfactant molecules mostly form monolayers or spherical aggregates. The structure on the surface corresponds to that

in the bulk phase at much higher concentration. Surfactant concentrations well above the CMC lead to “wormlike” aggregates; i.e., parallel full or half cylinders. There is a good correlation between the hydrophilic /hydrophobic behavior of the solid and the form of the surfactant aggregate. Hemicylinders dominate on hydrophobic materials because a large contact area between the hydrophobic chains of the surfactant and the solid surface is thermodynamically favorable, whereas structures similar to that in solution (rods, full cylinders) are found on hydrophilic surfaces. The contact between the solid and the hydrophilic headgroups of the surfactant molecules is preferred in this case.

In a similar approach, Manne and Gaub (1995) also described surfactant orientation on oppositely charged hydrophilic surfaces which interact primarily with surfactant headgroups, giving rise to aggregate structures that depend on the density of the electrostatically bound headgroups. In addition, Grosse and Estel (2000) evaluated the diameter of these aggregates, which was approximately equal to the diameter of the micelles. These aggregates are aligned parallel in the same direction, owing to micelle-micelle interactions, and are influenced by the symmetry axes of the underlying solid.

It has been previously reported by Tiberg *et al.* (2000) that ionic surfactants, at concentrations around and above the CMC, adsorb on oppositely charged surfaces with the head groups oriented towards the surface, while the hydrophobic tails are located in the center of the aggregates. In a subsequent investigation, the adsorption of nonionic surfactants on oxides and other hydroxyl terminated surfaces leads to preferential orientation of the polar headgroups towards the surface (i.e. formation of micellar or bilayer structures) even on quite hydrophobic surfaces, as long as there is a sufficient density of hydroxyl groups present at the surface. The adsorption of poly(ethylene oxide) surfactants at ‘hydrophilic’ oxide surfaces seems, despite this, to be driven mainly by hydrophobic attraction between the surfactant and the solid surface.

Based on Grosse and Estel (2000), the effect of the length of the ethylene oxide chain, i.e., of the hydrophilicity of the surfactant is evident: in contrast to the hemicylindrical, parallel-arranged micelles of the poly(ethylene oxide) surfactants

with short ethylene oxide chains, long ethylene oxide chains lead to featureless layers on the hydrophobic graphite, indicating flat bilayers.

Until now only atomic force microscope (AFM) measurements have been suitable to characterize the structure of surfactant layers at the solid/liquid interface; the technique includes AFM topographic methods and direct-force of measurements, determination of the amount adsorbed and assessment of the layer thickness, change in the surface charges (zeta potential) and heterocoalescence (Grosse and Estel, 2000). Using a similar approach, the atomic force microscope measurements have confirmed the existence of both surface micelles and bilayer type aggregates on silica as well as other surfaces containing surface hydroxyl groups (Tiberg *et al.*, 2000). The morphology of CTAB molecules adsorbed onto a graphite substrate was determined using AFM by Manne *et al.* (1994). They found parallel, epitaxially oriented stripes with a spacing of about twice the surfactant molecule length near the CMC. They concluded that the stripe pattern was indicative of cylindrical hemimicelles at the graphite surface. In addition, atomic force microscope has revealed that many of the aggregate geometries seen in a bulk solution also occur near an interface (Patrick *et al.*, 1997).

2.3 Adsorption and Aggregation of Nonionic Surfactants at the Interfaces

The behavior of nonionic surfactants at the interface of aqueous solution and mineral oxide surfaces is important in many applications, such as detergency, enhanced oil recovery, froth flotation, and surfactant-based chromatographic techniques. Consequently, many investigations of nonionic surfactant adsorption have been performed towards acquiring a better understanding of the adsorption nature of different surfactant molecules at solid surfaces.

Nonionic surfactant adsorption on a number of solid surfaces has been studied by a variety of techniques. The force between mica surfaces in solutions of pentakis (oxyethylene) dodecyl ether with added electrolyte were studied by Rutland and Christenson (1990) using the surface force apparatus. They found that the adsorption of nonionic surfactant to mica was weak. Force measurement on silica surfaces in an aqueous solution as a function of the concentration of the same

nonionic surfactant (pentakis (oxyethylene) dodecyl ether) have been studied by Rutland and Senden (1993). They found that in the absence of surfactant the interaction between silica surfaces was purely repulsive, being composed of electrostatic and hydration forces, whereas at low surfactant concentration ($\approx 2 \cdot 10^{-5}$ M, about one-third the CMC) the repulsion was replaced at short separations by an attractive force which pulled the surfaces into adhesive contact. At higher concentration ($\approx 4 \cdot 10^{-5}$ M) the surfaces still experienced an attractive force at small separations, but the adhesion decreased markedly. At concentrations above the CMC repulsive steric forces are observed.

With the exception of mica, adsorption isotherms usually show strong, cooperative adsorption below CMC from which the existence of aggregates has been inferred. Patrick *et al.* (1997) studied the adsorption of nonionic surfactants in an aqueous solution onto graphite, observed that nonionic surfactants adsorb strongly to graphite and the adsorption increases with increasing concentration up to the critical micelle concentration after which it remains fairly constant.

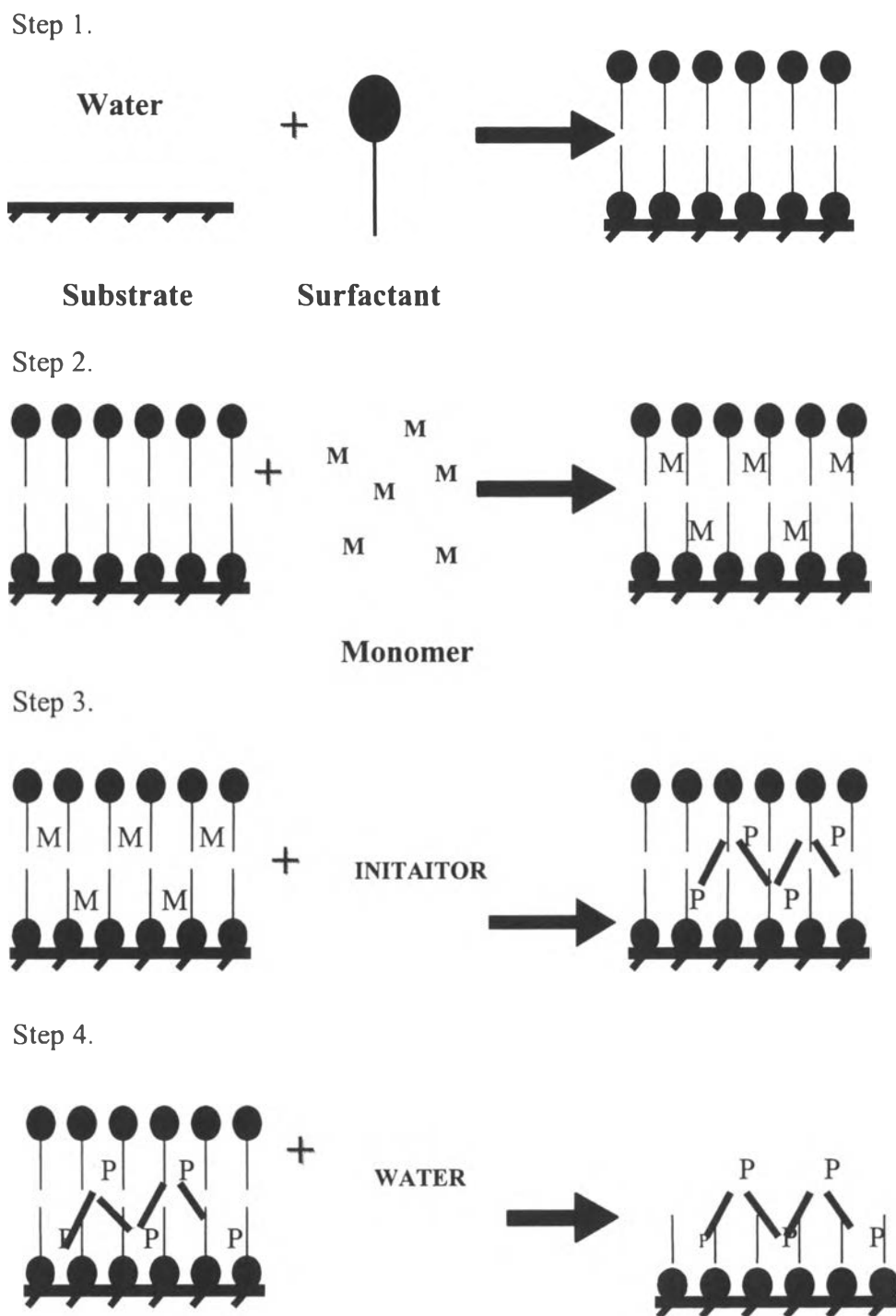
The adsorption isotherms of nonionic surfactants from aqueous solutions on hydrophilic silica surfaces are sigmoidal in shape, indicative of a cooperative adsorption mechanism. Well below the CMC, isolated surfactant molecules are adsorbed weakly on polar sites (by hydrogen bonding to surface silanol groups, etc.) represented by a low-affinity regime on the isotherm. The physically anchored amphiphiles induce an incipient surface aggregation process as the critical surface aggregation concentration (csac) is reached, after which the extent of adsorption dramatically increases. The aggregates are formed from single surfactant molecules coming from the bulk solution. Király, Börner, and Findenegg (1997) clearly verified that the major driving force of the aggregative adsorption is similar in nature to that of the formation of micelles in the bulk solution (entropically driving hydrophobic interactions). Slightly above the CMC, the adsorption levels off and a plateau is reached, attributable to the stabilization of the monomer surfactant chemical potential as the CMC is exceeded. In general, the shape of ascending section of the isotherm becomes sharper, its position is shifted to lower concentrations and the plateau value increases with decreasing pH, with increasing temperature and salinity, and with increasing hydrophobicity in a surfactant homologue series.

Moreover, the dominant interaction between nonionic surfactants and the hydrophilic surface of silica due to hydrogen bonding of the ether oxygens of the ethylene oxide group and the surface OH groups. It is well established that the formation of silanol groups (Si-OH), when a surface is exposed to water, makes the surface hydrophilic (Penfold *et al.*, 2002). However, a polyoxyethlenated nonionic, by itself, showed very weak adsorption onto positively charged alumina (Rosen, 1988).

In 1998, Grant *et al.* have studied the adsorption of a series of alkylpoly (ethylene oxide) C_nE_m surfactants on three different substrates which are graphite, hydrophobic silica, and hydrophilic silica by using atomic force microscope. The researchers indicated the adsorption to hydrophilic silica results in the formation of globular structures, which are similar to bulk micelles. On silica that has been made hydrophobic by reaction with the organosilane, adsorption results in a surface layer that is laterally homogeneous and is probably a monolayer with ethylene oxide groups in contact with the solution. This large perturbation from the solution aggregate structure on the hydrophobic surface is driven by a minimization of the area of contact between water and the hydrophobic silica. On the graphite, the surface layer is either long, thin aggregates (consistent with a hemicylindrical structure) or a laterally homogeneous layer (consistent with a monolayer with the headgroups facing solution).

2.4 Ultrathin Polymer Film Formation by Polymerization inside a Two-Dimensional Solvent

The polymerization of thin films is carried out in four-step process, which is based on the formation of micelle-like aggregates of physically adsorbed surfactants at a solid-solution interface (Wu *et al.*, 1987). The thin-film polymerization process can be envisioned as occurring in four major steps (Figure 2.2) that are described briefly below:



“M”s represent solute molecules, monomers.

“P”s connected by lines represent polymer chains formed during the reaction.

Figure 2.2 The admicellar polymerization process for the formation of a thin polymer film.

Step 1 Admicelle Formation

The formation of aggregate structures at solid/liquid interfaces to form bilayers (admicelles) through adsorption from an aqueous solution below critical micelle concentration is a well-known phenomena. Adsorption is accomplished through the use of suitable surfactant under appropriate system conditions. Two layers should form simultaneously on local patches of the surface, rather than by monolayer coverage preceding formation of the second layer (Wu *et al.*, 1987). To achieve admicelle formation, the adsorption of surfactants on solid substrates is controlled by a several parameters including the electrochemical nature of the substrate, the pH of the solution, and the type of surfactant molecule. The most critical parameter to be manipulated is the solution pH (Sakhalkar and Hirt, 1995).

The solid oxide surface can be manipulated to possess either net positive or negative charge by adjusting the pH of the contacting aqueous solution, and hydrogen and hydroxyl ions are potential determining ions for metal oxides. The pH at which the net charge on the surface is zero is called the point of zero charge (PZC). At pH values below the PZC, the surface becomes protonated and more positively charged; above the PZC, the surface is negatively charged. Consequently, anionic surfactants adsorb below the PZC and cationic surfactants above the PZC. As an example, silica having $2 \leq \text{PZC} \leq 3$, will be negatively charged when the pH of the aqueous solution exceeds 3 (Iler, 1979).

Penfold *et al.* (2002) have previously shown that the adsorption of nonionic surfactants on silica is highly pH dependent. At high pH (~9.0) desorption of nonionic surfactant occurs. The adsorption at pH 2.4 is significantly greater than that at pH 7.0. Decrease pH will decrease

the surface charge density, which can be used to control the density of hydroxyl groups on the surface. Consequently, decrease the solution pH from 7.0 to 2.4 enhanced the adsorption. Exposure of the surface to solutions at low pH has produced a greater affinity of the nonionic surfactant for the surface than at higher pH. This is a clear evidence of the delicate nature of cooperative adsorption of nonionic surfactants at the hydrophilic silica.

Step 2. Monomer Adsolubilization

Adsolubilization is the surface analogue of solubilization, where aggregates of adsorbed surfactant play the role of micelles. Under conditions favorable for the formation of admicelles on solid surface in an aqueous supernatant, adsolubilization can be accomplished. Many organic monomers that are nearly insoluble in water will preferentially partition into the bilayer core because the admicelle interior is highly hydrophobic. The organic monomers that adsolubilize into the admicelle interior share the hydrophobic interaction with the amphiphile tails (Wu *et al.*, 1987). This process can occur after the formation of the admicelles, or concurrently with surfactant adsorption. It is convenient experimentally to dissolve the monomer, and often the initiator, in the surfactant feed solution prior to surfactant adsorption

Step 3. In-Situ Polymerization of Adsolubilized Monomers

This is accomplished through the generation of free radicals capable of initiating the polymerization reaction. Once the polymerization reaction has been initiated and the monomer is being consumed in the admicelle, the monomer in the bulk solution can begin to re-equilibrate by diffusing into the admicelle. If the reaction continues for a sufficient length of time, virtually all monomers can be converted to polymer (O'Haver *et al.*, 1995). The conversion of monomer to polymer is a function of the reaction time (Wu *et al.*, 1987).

Step 4. Surfactant Removal

The modified substrate is washed with water to remove excess surfactant layer in order to expose the polymer film. The powder is then dried in an oven at high temperature to vaporize unreacted monomer and excess solvent. However, the temperature does not affect the properties of the polymer.

2.5 Synthesis of Organic/Silica Composite Materials

Hybridization of polymeric organic and inorganic precursors such as metal alkoxides has been accomplished with the objective of obtaining materials with high performance, such as more thermally resistant silicon-based hybrid materials. To achieve organic/silica composite materials, the sol-gel method has to be combined with self-assembly through the surfactant template technique. Sol-gel polymerization of inorganic precursors within surface aggregates allows the creation of highly ordered organic-inorganic composites and the encapsulation of organic aggregates, preserving the morphologies of the flexible organic supramolecular structures (Kimura *et al.*, 2001). The sol-gel process is essentially a physical chemistry route that allows one to obtain high-purity inorganic materials, with a wide variety forms, such as powders, fibers and films.

Furthermore, sol-gel technique of metal alkoxides is the most efficient method for preparation of the composite materials. An advantage of sol-gel process technique is the fact that the reaction can be carried out at ambient temperature, while conventional melt fusion techniques need high temperature. Thus, it enables introduction of organic elements into inorganic material without deteriorating their functionality.

The process involves the hydrolysis of metal alkoxides, followed by condensation reaction.



Where X can be H or R (an alkyl group). Due to the immiscibility of orthosilicate with water, the reactions are generally carried out in a homogenizing solvent like alcohol.

Silicon alkoxide, e.g., tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and tetramethoxysilane ($\text{Si}(\text{OCH}_3)_4$), which are abbreviated in the literature as TEOS and TMOS, are the most widely used metal alkoxides as far. The traditional method of preparing tetraalkoxysilanes is by reacting tetrachlorosilane with alcohol. When

anhydrous ethanol is used, the product is TEOS with hydrogen chloride as a by-product:



It has been investigated by Pedroso *et al.* (2000) that sol-gel type reactions with tetraethoxysilane (TEOS) result in linear polymers when the reaction is catalyzed by acids or in microspherical polymers in the presence of basic catalysts.

In a similar approach, Ertl *et al.* (1997) described the rate of hydrolysis and condensation of tetraethoxysilane (TEOS), which is the most widely studied precursor, varying as a function of pH. Under acidic conditions hydrolysis occurs at a faster rate than condensation and resulting gel is weakly branched. Under basic conditions the reverse is true and the resulting gel is highly branched and contains colloidal aggregates.

The properties of such hybrid networks strongly depend on various parameters such as the degree of phase dispersion, the relative amount of organic and inorganic components, type of catalyst, the molar ratio of water to silane, the reaction time, temperature and ionic strength as well as the molecular weight of polymer.

Tamaki *et al.* (1997) showed that homogeneous polystyrene and silica gel polymer hybrids can be achieved by *in-situ* radical polymerization method. Styrene monomer was introduced into a sol-gel reaction mixture of tetramethoxysilane (TMOS) and the polymerization reaction was initiated by azobisisobutyronitrile (AIBN), while sol-gel reaction of TMOS proceeded to form a silica gel. The homogeneity of the hybrids was found to be dependent on the amount of acid catalyst. The homogeneity was confirmed quantitatively by measuring the porosity of charred hybrids with nitrogen porosimetry. It was found that polystyrene was dispersed at a nano-meter level in the silica gel matrix.

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In a following study of Tamaki and Chujo (1999), they investigated the synthesis of polystyrene and silica gel polymer hybrids utilizing ionic interactions between the sulfonic groups of the organic polymer and the amino groups of (3-aminopropyl) trimethoxysilane (APTMO). They found that as a consequence of APTMO incorporation to the hybrid system, the interactions between the organic polymers and silica gel were profoundly improved, resulting in the homogeneous dispersion of each phase on nanometer level. At the same time, the incorporated siloxane linkage works as cross-linker between the organic polymer chains that increase the storage modulus in elastic state.

In a same year, Gao *et al.* (2001) synthesized transparent organic-inorganic hybrid materials via sol-gel method using polyethylene-*co*-Zn-acrylic acid (Zn-PEAA) ionomer and a metal alkoxide, tetraethyl orthosilicate (TEOS). The resulting material is transparent which indicates that no phase separation exists between ionomer and silica. Moreover, the thermal stability and storage modulus of ionomer increase after hybridization.

Furthermore, Jang and Park (2002) have successfully prepared polystyrene-silica hybrid materials from styrene and tetraethyl orthosilicate (TEOS) in the presence of silane-coupling agent, which is 3-(trimethoxysilyl)-propyl-methacrylate (MPS), by an *in-situ* sol-gel process. Triethoxysilyl group can be incorporated into polystyrene as side chains by the free-radical copolymerization of polystyrene with silane-coupling agents, and simultaneously polystyrene-silica hybrid materials with covalent bond between two phases were formed via the sol-gel reaction. The presence of the silane-coupling agent produced better homogeneity in the resulting material and caused increases in glass transition temperature, T_g due to the molecular motions of the organic polymer being restricted by the inorganic phases.

Reclusa *et al.* (2002) synthesized “raspberry-like” hybrid silica/polystyrene materials consisting of spherical silica beads supporting smaller polystyrene particles by using nonionic surfactant as an emulsifying agent and sodium persulfate as an initiator. They determined that the silica is initially hydrophilic and that its surface needs to be modified to allow anchoring and polymerization of hydrophobic monomers. This is usually achieved by the adsorption of a macromolecule. They concluded that the final morphology of the nanohybrids is strongly dependent on the

presence of the adsorbed macromonomer. Moreover, the macromonomer derivative not only enables the production of raspberry-like silica-polystyrene materials, but also ensures strong attachment of the polystyrene particles on the silica surface.

2.6 Muscovite Mica

The requirement of the flat surfaces for efficient AFM operation has concentrated most of the research on systems such as glass, quartz, silica, graphite, or mica substrate. Because of its well-defined structure and atomic smoothness of the surface, mica seemed to be a convenient model adsorbent to investigate via atomic force microscope.

Muscovite mica is a 2:1 layered silicate and its crystal structure consists of two tetrahedral silica sheets sandwiching an octahedral alumina sheet. On average one silicon atom out of four is replaced by aluminum, giving rise to localized negative surface charges that are more homogeneously distributed than those of montmorillonite. Therefore, muscovite is better suited to serve as substrate for such studies (Osman *et al.*, 2000).

Narkiewicz-Michalek (1992) illustrated muscovite mica (ideal formula, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) as a layered aluminosilicate mineral consisting of 1 nm thick sheets that build up an anisotropic structure. The ionic bonds holding the sheets together in the crystal are weak compared with the covalent bonds within each sheet which facilitate cleavage between sheet planes. These molecularly smooth basal planes carry a large negative charge (1 charge/0.48 nm²) because on the average one silicon atom out of four is replaced by aluminum atom. Because of its well-defined structure and molecularly smooth surface, mica seemed to be a convenient model adsorbent to investigate the combined effect of surface heterogeneity and multisite occupancy adsorption.

In fact, Sakhalkar and Hirt (1995) have indicated the presence of inhomogeneity at the quartz surface that affects the uniformity of the adsorbed layer.

In a recent study, Cantrell and Ewing (2001) have been shown that muscovite mica is a popular choice for the study of interfacial phenomena because its almost perfect cleavage along the (001) plane removes the complexities introduced

by roughness. Furthermore, water has an affinity for the surface of mica. They also investigated thin film water on muscovite mica which shown that water adsorbed to the (001) plane of muscovite mica has an infrared spectrum consistent with a bonding network that is more structured than that found in bulk water.

2.7 Atomic Force Microscopy

The atomic force microscope (AFM), or scanning probe microscope (SPM) is becoming increasingly important in polymer characterization with regard to both surface topography and mechanical properties. Like all other scanning probe microscopes, the AFM generally operates by scanning a relative sharp tip, attached to a cantilever beam, across the surface of a sample in a raster scan. The sample to be imaged was placed on a piezoelectric tube scanner that enables an accurate scan in the horizontal (x - y) plan while moving in the vertical (z) direction (Figure 2.3). A constant load is applied while the tip is scanned. The way in which images contrast is obtained can be achieved in many ways. The three main classes of interaction are contact mode, tapping mode and non-contact mode.

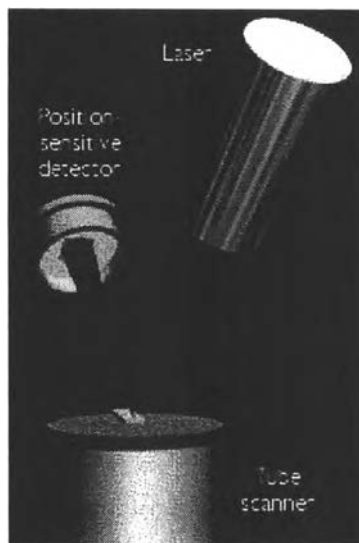


Figure 2.3 A schematic illustration of the AFM set up.

2.7.1 Contact Mode

Contact mode is the most common method of operation of the AFM. As the name suggests, contact mode is operated by scanning a tip attached to the end of cantilever across the sample while monitoring the change in cantilever deflection with a split photodiode detector. The tip contacts the surface through the adsorbed fluid layer on the sample surface. The “topographic” information about the surface is then deduced by measuring the cantilever deflection during scanning. However, the tip can exert considerable forces to the sample surface, thereby causing sample deformation, so that the height images may not represent the true topographic information of the sample surface. To overcome such difficulties, tapping mode AFM was introduced.

2.7.2 TappingModeTM

TappingModeTM AFM operates by scanning a tip attached to end of an oscillating cantilever across the sample surface. By this method, the cantilever oscillates vertically near its resonance frequency, so that the tip makes contact with the sample surface only briefly in each cycle of oscillation. When the AFM tip is

brought close to the sample surface, the vibration characteristic (i.e., the force constant, resonance frequency, phase angle, and amplitude) of the cantilever change due to tip-sample interaction and the contamination layer on the sample surface (Bar *et al.*, 1997). Additionally, the operation of tapping mode can take place in ambient and liquid environment with the high resolution of surface topography.

2.7.3 Non-contact Mode

Non-contact mode operation is another method that may be employed when imaging by AFM. The cantilever is oscillated at a frequency, which is slightly above the cantilever's resonance frequency. The tip does not contact the sample surface, but oscillates above the adsorbed fluid layer on the surface during imaging. This is very difficult mode to operate in ambient conditions with the AFM. The thin layer of water contamination which exists on the surface on the sample will invariably form a small capillary bridge between the tip and the sample and cause the tip to "jump-to-contact"