

CHAPTER II

LITERATURE SURVEY

2.1 Admicelle Formation and Admicellar Polymerization

The formation of thin films on solid surfaces has been the subject of intense studies in recent years because of a wide variety of possible applications for these films. In particular, the surface modification of substrates using admicellar polymerization has been investigated continuously over several years.

O'Rear *et al.* (1988) invented a method for producing polymeric films in which a substrate surface is first treated with a surfactant solution. Alumina powder, aluminum plates and sodium dodecyl sulfate (SDS) were selected as the substrate-surfactant systems in their premier investigation. The surfactant template, which, on solid substrates, occurred by adsorption, was obtained as a bilayer of surfactant molecules on the substrate surface. Styrene monomers were dissolved in the surfactant template under suitable conditions, resulting in high concentration of monomer molecules within the surfactant template. Finally, the monomer molecules were polymerized to form a polymeric film, dimensionally determined by the surfactant template. The method can be used to coat films on the surface of objects having non-planar surfaces, porous objects, or even particulate matters.

The four-step process of adsorption, adsolubilization, polymerization, and washing has been demonstrated to produce silicas which had different properties than the starting materials (O'Haver *et al.*, 1994). Surfactant bilayers adsorbed on silica were used as the reaction site for the formation of ultrathin polymer films from coadsorbed or adsolubilized monomers. Results from the polymerization of styrene in cetyltrimethylammonium bromide (CTAB), in octylphenoxypoly(ethoxy) ethanol, and in methyltri(C₈-C₁₀)ammonium chloride bilayers showed effective conversion of adsolubilized styrene monomers to polystyrene, although at higher conversions, the higher molecular weight material might be unextractable. Only approximately 25% of the polymer was extractable after refluxing for 4 hours in tetrahydrofuran. The extracted polystyrene had spectroscopic and thermal characteristics consistent with its low molecular weight nature. The process has also shown that, on precipitated

silica substrates, the organic polymer treatment was quite firmly attached even though not chemically bonded. This demonstrated the uniqueness of this technique over existing technologies. It also suggested further investigation into the use of this process with other monomers and substrates.

Sakhalkar and Hirt (1995) investigated a technique, using surfactants, for producing organized thin polystyrene films on glass fibers. It appeared that, in the *in-situ* polymerization of adsorbed monomers, polymer formation was not restricted to the surface aggregates as originally thought, but a fraction of the polymerization occurred in the aqueous supernatant as well. SEM micrographs of the treated fibers showed a non-uniform coating on the fiber surface. Fibers were also subjected to a tetrahydrofuran extraction process that confirmed the formation of polystyrene. It was also clear that polymer formation definitely occurred, although the formation of a uniform polymeric coating was not achieved in this work.

Lai *et al.* (1995) succeeded in partitioning tetrafluoroethylene gas into admicelles of sodium perfluoroheptanoate on alumina in a high-pressure reactor. Polymerization of tetrafluoroethylene within the adsorbed surfactant bilayer took place after thermal initiation with the formation of fluorocarbon thin films on aluminum oxide powder. In the formation of poly(tetrafluoroethylene) (PTFE), the effects of surfactant and initiator concentrations were studied. The initiator concentration showed a marked effect on polymerization which increased remarkably with increasing initiator concentrations from 0.25 to 2.5 wt.%. The conversion reached 35% for an initiator concentration of 2.5 wt.%, while it reached 7% for an initiator concentration of 0.25 wt.%. Although the conversion was higher for an initiator concentration at or above 2.5 wt.%, it should be pointed out that at this concentration there is considerable polymerization in the bulk solution even though the concentration of surfactant is below CMC (*viz.* a murky solution was observed in the supernatant); however, this never seemed to happen for an initiator concentration at or below 0.25 wt.% (*viz.* a clear solution in the supernatant). Measurements of friction coefficients and contact angles verified that a thin PTFE film was formed on alumina plates. It was concluded that the use of perfluorosurfactants with *in-situ* formation of fluoropolymer has been successfully

demonstrated on the alumina surface and that this technique had significant potential for surface modification.

The organized thin polyethylene films was produced on glass fiber surfaces via admicellar polymerization using SDS as the surfactant template and sodium persulfate as the initiator (Sithitham *et al.*, 2001). Not only the polymerization was not restricted to the surface of glass fibers, as originally envisaged, but a significant amount of solution polymerization also took place in the aqueous supernatant. It appeared that composites made from admicelle-treated glass fibers had mechanical properties almost the same as composites made from solution-treated glass fibers, and were better than untreated and as-received glass fiber. This study therefore demonstrated that both the admicellar and solution polymerization techniques for coating glass fibers with polymer improved the fiber-matrix adhesion in thermoplastic composites.

Yuan *et al.* (2001) carried out chemical deposition of electrically conducting polypyrrole (PPy) thin films on mica and alumina in aqueous solutions with and without surfactant. Examination of film morphology and thickness by atomic force microscopy (AFM) indicated a strong dependence of structure on the method of preparation. Films grown in the absence of surfactant were thicker than 150 nm with wrinkles being present, indicating the overcoming of film-substrate adhesion by internal film cohesion. Oxidative polymerization with surfactant allowed reproducible synthesis of smooth, well connected, and very thin films (30-60 nm thickness) with improved adhesion and suppressed formation of wrinkles. Experimental results were discussed within the context of a Stranski-Krastanov model which used to describe PPy film growth, with the surface morphology changing from smooth to wrinkly. Surfactant, rough and hydrophobic substrates, and low monomer and oxidant concentrations were found to help suppress wrinkle formation. Thickening-induced film contraction was proposed to promote wrinkling. Film thickness and surface fractal dimensions were derived from AFM. Fractal analysis of PPy films on alumina helped discern their presence on the microscopically rough substrate and quantitatively expressed the changes in sample color by surface roughness. Fractal structures were found on mica when the reaction rate was very slow, and were suppressed in the presence of admicelles.

Bunsomsit *et al.* (2001) adapted admicellar polymerization for a latex with surfactant molecules forming bilayers on the surface of the latex particles in aqueous solution. The method was employed to form thin PPy films on the charged surface of natural rubber (NR). The NR latex exhibits a PZC of 3.9 so anionic surfactant, SDS, was chosen with the solution pH adjusted to 3.0. Adsorption of SDS and pyrrole adsolubilization were determined as a function of pyrrole and sodium chloride concentrations. Pyrrole caused a decrease in SDS adsorption at equilibrium. Suitable contents of SDS and pyrrole for admicellar polymerization were 16 and 10 mM, respectively. The presence of a small amount of salt, sodium chloride, substantially improved the surfactant adsorption and pyrrole adsolubilization. A PPy coated NR latex prepared in the absence of surfactant exhibited slightly higher conductivity than a PPy coated latex prepared with surfactant with or without salt. They concluded that the oxidative polymerization technique resulted in a relatively higher conductivity than oxidative admicellar polymerization.

Admicellar polymerizations were conducted in aqueous solutions to create ultra thin films of PPy on the surface of hydrophobic graphite and freshly cleaved mica (Yuan *et al.*, 2002). Separate adsorbing and reacting solutions were used to eliminate diffusion of monomers from the bulk solution to the reacting surface, as well as to reduce or prevent solution polymerization. The results showed that film thicknesses via this method were approximately an order of magnitude smaller than those where the two solutions were identical. PPy films formed on graphite from water or surfactant solutions were mainly composed of interlinked islands and disks (small and thin islands) at high density. On the other hand, PPy deposited on mica in water alone formed randomly scattered islands without any continuous film formation, while PPy from surfactant solutions formed the same type of films with islands and disks. This determined that, for the hydrophobic substrates, the differences between films formed with and without surfactant were minor, which indicated that the growth rate in the plane of the substrate versus that vertical to the substrate was larger. The number density of the islands and disks depended on the surfactant type and monomer concentration. Differences were much more pronounced in the case of the hydrophilic substrates; without surfactant only very discrete islands of PPy were seen.

Pongprayoon *et al.* (2002) investigated thin film coating on cotton by the admicellar polymerization process. They used styrene as the monomer to coat styrene on cotton. Admicellar polymerization of styrene was carried out using a linear alkylbenzene sulfonate (LAS) as the surfactant template at concentration of 1,000 μM , which was just below the CMC of 1,050 μM at a pH of 4 and sodium chloride concentration of 0.15 M. Sodium persulfate was used as the initiator and the polymerization time was 2 hours at 70°C. The hydrophobicity results showed that the treated fabric had a much higher water repellency than the untreated cotton. Hydrophobicity of the treated cotton was found to depend on the LAS:monomer and monomer:initiator ratios. These confirmed that polystyrene thin film was successfully formed on cotton, resulting in cotton fabrics that can resist wetting by a water droplet for longer than 30 min.

Admicellar polymerization with styrene monomer was used to coat the surface of two porous solids: titanium dioxide and alumina (Wie *et al.*, 2003). X-ray photoelectron spectroscopy (XPS) measurements clearly indicated that after admicellar polymerization, organic material and surfactant were present on both the outside surface and the inside surface of a rough, porous solid. 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 vs. the inner surfaces by solvent washing. However, even for the outside surface, only about half of the material could be removed after both water and soxhlet extraction. 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) was approximately 1:1, whereas the ratio on the interior surface was approximately 3:1.

Somnuk *et al.* (2003) investigated that admicellar polymerization could be used to form a thin film of polyethylene onto the surface of milled glass fiber. They succeeded in partitioning ethylene gas into admicelles of SDS on glass fibers. Polymerization of ethylene within an adsorbed surfactant bilayer took place after thermal initiation. Sodium persulfate was used as the initiator. In the formation of polyethylene film, the effect of initiator concentration was studied when using admicelle-treated glass fibers. The results were compared with silane-treated and

untreated glass fibers. An increase in the initiator:surfactant ratio led to improved tensile strength. This indicated that the admicelle-treated glass fibers improved the adhesion between the glass fiber and polyethylene matrix, resulting in composites with greater tensile strength.

Pongprayoon *et al.* (2003) successfully synthesized ultrathin polystyrene film on cotton fabric using linear LAS adsorbed on fabric as a template. The film was formed in three mechanistic steps: (1) LAS adsorption, (2) styrene monomer solubilization into the bilayer of LAS adsorption, and (3) polymerization of styrene monomer *in-situ* LAS adsorbed. Two types of initiator, sodium persulfate and azobisisobutyronitrile (AIBN), were used to produce hydrophobic cotton. The results showed that AIBN, an organic initiator, was more efficient than sodium persulfate, an ionic initiator, as evidenced by the lower amount of initiator and styrene monomer required for making hydrophobic cotton. The treated samples had high hydrophobicity as shown by the drop test and the Wilhelmy microelectronic balance technique. SEM micrographs confirmed the formation of thin polymeric film on treated cotton surface.

2.2 CaCO₃-filled Polypropylene Composites

A polypropylene homopolymer was modified by a rigid filler consisting of three different sizes of CaCO₃ particles in various volume fractions (Goldman *et al.*, 2000). The materials were characterized by differential scanning calorimetry. Mechanical properties of extrusion-blended/injection-molded samples, including tensile, flexural, Dynatup impact energy and notched Izod impact energy, were examined as a function of temperature down to -40°C, filler particle size, and filler volume fraction. Dynatup impact tests were performed on compression-molded plastic parts. The toughening mechanism of PP homopolymer through the incorporation of CaCO₃ depended on the filler particle size and volume fraction. The toughness of the CaCO₃-filled materials increased significantly at ambient temperature for both material samples and molded plastic parts. According to the DSC results, the presence of CaCO₃ filler markedly influenced the crystallization behavior of PP. The primary role of the filler particles is to introduce into the semi-

crystalline matrix an appropriate volume concentration of interfaces distributed randomly in the matrix. The crystallization of semi-crystalline polymers near the interfaces of particles led to the formation of layers of oriented crystalline material which reduce shear resistance around the particles. In this case, the role of the particles is passive. A similar improvement was demonstrated in Dynatup and Izod impact tests at low temperatures down to -40°C . The level of toughness increase achieved by the addition of CaCO_3 was close to the toughness produced using rubber at 23°C , and even better at lower temperatures. The additional requirement on the particles is to cavitate at the start of deformation to offer no constraint to the deforming matrix ligaments. The rubber particles could be replaced with particles having other mechanical properties such as stiff mineral filler – provided the percolation condition of oriented crystalline matter is met, and the particles are debonded from the matrix. The extensive debonding of the particles from the matrix near the yield point was observed in this work. This method of toughening using inorganic fillers would overcome the main drawback of compromising the elastic properties of the blend, and would result in improved stiffness of the blend. Polypropylene modified with stiff filler particles should demonstrate both high toughness and improved stiffness at the same time.

Thio *et al.* (2002) studied the mechanisms of deformation and fracture of iPP filled with CaCO_3 . Three types of particles with average diameters of 0.07, 0.7, and 3.5 μm were used at the filler volume fraction ranging from 0.05 to 0.30. They found that under slow tensions, addition of fillers increased the modulus and decreased the yield stress independently of the filler type. The strain at break increased with initial incorporation of fillers but decreased at higher loadings. The 0.7 μm diameter particles improved Izod impact energy up to four times that of the unfilled matrix. The other particles had either adverse or no effect on the impact toughness. The toughening mechanisms at work were plastic deformation of interparticle ligaments following particle-matrix debonding with additional contribution coming from crack deflection toughening. The failure of the 0.07 and 3.5 μm diameter particles to toughen the matrix was attributed to poor dispersion. From the point of view of choosing rigid particles as fillers, their results indicated that there existed an optimum window of particle size that was conducive to

enhancement of toughness. Particles that were too large acted as initiation sites for brittle crack behavior. On the other hand, very fine particles were difficult to disperse, creating agglomerates that behaved as large single particle. The optimum size depended on the processing of the compounds and on the tolerance of the polymer matrix to large inclusion.

Polypropylene and CaCO_3 nanocomposites were prepared by melt-mixing in a Haake mixer (Chan *et al.*, 2002). The average primary particle size of CaCO_3 nanoparticles was measured to be about 44 nm. The dispersion of the CaCO_3 nanoparticles in polypropylene was good for filler content below 9.2 vol.%. The notched fracture toughness of the nanocomposites under either quasi-static or impact loading condition was found substantially higher than that of the pure polypropylene. Tensile tests showed that the modulus of the nanocomposites increased by approximately 85%, while the ultimate stress and strain, as well as yield stress and strain were not much affected by the presence of CaCO_3 nanoparticles. Izod impact tests suggested that the incorporation of CaCO_3 nanoparticles in iPP had significantly increased its impact strength by approximately 300%. Thermal analysis and SEM studies on the iPP and nanocomposites revealed that CaCO_3 nanoparticles were an effective nucleating agent that caused the absence of detectable spherulites. Fractography of the broken specimens from the J -integral tests suggested that the nanoparticles introduced a massive number of stress concentration sites in matrix and promoted cavitation at the particle-matrix boundary when loaded. The cavities, in turn, released the plastic constraint and trigger large-scale plastic deformation of the matrix, which consumed tremendous fracture energy.

2.3 Interface Modification in Composites

Numerous researchers have studied composites made from various polymers and fillers whose surfaces were treated with certain types of chemical compounds.

Tabtiang *et al.* (2000) studied the performance of unsaturated coating for CaCO_3 filler in iPP. The surface of ground CaCO_3 was modified with several unsaturated acids and acid anhydrides of varying molecular weight. The modified

CaCO₃ were compounded with iPP, both in the presence and absence of dicumyl peroxide as an initiator, through twin screw extrusion to give compounds containing 75 phr of filler. The results showed that the level of constraint of the iPP matrix decreased with increasing alkenyl chain length of the surface modifier through a decoupling mechanism, leading to enhanced flow and deformability with consequent improvements in toughness and ductility. On the other hand, high levels of coupling led to a large increase in yield stress, but reductions in ductility: impact strengths were close to those for the compound with uncoated filler. Finally, peroxide caused matrix degradation leading to deteriorated ductility for surface coatings with alkenyl chains comprising less than 17 carbon atoms. For CaCO₃ coated with 17 or more carbon atoms, the effect of peroxide was counterbalanced by changing in the interphase properties, and hence the peroxide had no net effect.

New reactive surfactants, containing carboxylic or carboxylic anhydride groups in the polar region and reactive double bonds in a non-polar hydrocarbon chain and synergistic reactive surfactants, containing a low molecular boron–silicon segment with reactive groups had been synthesized and applied in filled and flame-retarded polymer systems, respectively (Bertalan *et al.*, 2001). The chemical structure of these additives combines the function of dispersing and coupling agents, so they are capable of bonding the filler and iPP matrix by chemical bonds. Talc, CaCO₃, and glass fibers were used as fillers in their studies. The interface modification in filled/reinforced iPP and iPP-polyamide blends resulted in improved mechanical properties, while in pigmented PE it contributed to higher photostability. Furthermore, the efficiency of intumescent flame retardant additives in polyolefins could be enhanced. Not only the mechanical properties were improved this way, but the photostability and the flame retardancy could be improved simultaneously.

Thermogravimetric analysis was used to investigate organic contamination of calcite surface and to determine the optimal amount of fatty acid necessary to coat it with an alkyl monolayer (Osman *et al.*, 2002). It showed that optimal coating of calcite with stearic acid gave a monolayer of calcium stearate bicarbonate in which one acid molecule reacted with every Ca²⁺ on the surface irrespective of the anion presented and the chains showed a high trans population and were closely packed, building an ordered solid-like phase. Fatty acids with 10-18 carbon atoms showed

similar behavior, while shorter homologues formed dynamically disordered phases. The immobilization of oleic acid molecules on the calcite surface led to their polymerization at relatively low temperatures without an initiator. In other words, calcite particles were coated with a monolayer of oleic acid self-assembled on solid surfaces, which could be polymerized under moderate conditions to give a polymeric ultrathin coating.

Zuiderduin *et al.* (2003) prepared iPP/CaCO₃ composites on a twin screw extruder with a particle content of 0–32 vol.%. The influence of particle size (0.07–1.9 μm) and surface treatment of the particles (with and without stearic acid) on the toughening properties were studied. The iPP molecular weight was also varied (MFI 0.3–24 dg/min). The modulus of the composites increased, while the yield stress was lowered with filler content. This lowering of yield stress was connected to the debonding of the particles from the iPP matrix. The DSC experiments showed that the particle content had no influence on the melting temperature or crystallinity of the iPP phase. In addition, particle size showed no effect on the thermal properties. The impact resistance showed large improvement with particle content. The brittle-to-ductile transition was lowered from 90 to 40°C with the addition of CaCO₃ particles. Notched Izod fracture energy increased from 2 up to 40–50 kJ/m². The stearic acid coating on the particle surface showed a large positive effect on the impact strength. This was mainly due to the improved dispersion of the CaCO₃ particles. Aggregates of particles clearly had a detrimental effect on the impact behavior of the composites. The smaller particle sizes (<0.7 μm) showed coarse morphologies and this lowered the toughening efficiency. The molecular weight of the iPP matrix had a profound effect on the toughening properties. A higher molecular mass shifted the brittle-to-ductile transition towards lower temperatures. At higher filler loadings (>20 vol.%), dispersion became a problem, resulting in the lowering of the toughening efficiency. Of all particle types used, the stearic acid-treated particles of 0.7 μm were found to give the best combination of properties. From the study of the micro-toughening mechanism, it was shown that, at low strains, the particles remain attached to the matrix polymer. At higher strains, the particles debonded and this led to a change in stress state at the particle size level.

This prevented crazing of the matrix polymer and allowed extensive plastic deformation, resulting in large quantities of fracture energy.