

CHAPTER II

LITERATURE SURVEY

The formation of thin films on solid surfaces has been the object of intense study in recent years because of a wide variety of possible applications for these films. In particular, the surface modification of substrates using admicellar polymerization—polymerization of monomer solubilized in adsorbed surfactant bilayers—has been investigated for approximately a decade.

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 were selected as the substrate-surfactant system for experimentation. The surfactant template, which on solid substrates occurs by adsorption, was obtained as a bilayer of surfactant molecules on the substrate surface. Styrene monomer was used in this system. The monomer was dissolved in the surfactant template under suitable conditions resulting in a 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 may be used to coat film onto the surface of objects with non-planar surfaces, porous objects, or particulate matter. Subsequent studies in this field (Esumi *et al.*, 1991) still focused on the styrene monomer/alumina substrate system but the type of surfactant was varied. They studied the adsolubilization of styrene within a bilayer of sodium 10-undecenoate on an alumina substrate. The results showed that the ζ potential of alumina decreases, reaches zero, and finally becomes negative with an increase in concentration of surfactant, while the adsorbed amount of sodium 10-undecenoate within the bilayer increases gradually and reaches a plateau. The change in the ζ potential of alumina corresponds to the change

found for the mean particle size of the alumina. Thus, alumina is flocculated and then re-dispersed depending on the equilibrium concentration of sodium 10-undecenoate. Further, the dispersion stability of alumina having a polystyrene layer is increased with UV irradiation time and somewhat enhanced compared with that of alumina without the polystyrene layer, probably due to an increase in electric repulsion force between the alumina particles.

O'Haver *et al.* (1993) utilized the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) and the virtually water-insoluble initiator 2,2'-azobis-2-methylproprionitrile (AIBN) as a thermal initiator to form thin polymer films of styrene on precipitated silicas. The results showed that the polymer/surfactant layer which formed obstructs a portion of the total pore surface area and may slightly increase the average particle size of silica. Extraction and PA-FTIR evidence supported the presence of polystyrene on the silica and the entwinement of the polymer chains in the pore structure of the silica. Shortly after this study, O'Haver *et al.* (1994) studied the effect of various surfactant types including the water-insoluble cationic surfactant ADOGEN[®] 464 (methyltri ammonium chloride) and a nonionic surfactant, MACOL[®] OP10SP (octylphenoxy poly(ethoxy) ethanol with an average of 10 mol of ethylene oxide), to form thin polymer films of styrene on amorphous precipitated silica substrates. Results from the polymerization of styrene in the surfactant showed effective conversion of adsolubilized styrene monomer to polystyrene. In addition, a polymer of reasonable molecular weight ($\overline{M}_w \sim 30,000$) was obtained with this process, although at higher conversions the higher molecular weight material may be unextractable. This study also showed that, for precipitated silica substrates at least, the organic polymer produced is quite firmly attached to the substrate even though it is not chemically bonded to it.

Waddell *et al.* (1995) improved the performance of rubber compounds using precipitated silica as a reinforcing filler. The silica surface was directly modified by polymerizing various comonomer combinations of styrene with isoprene or butadiene onto the substrate via the admicellar polymerization technique. They concluded that the nature of the monomer, surfactant, polymerization initiator, and reaction time are important variables for producing modified silicas useful in reinforcing elastomeric compounds in terms of reduced compound cure times and improved rubber product performance. Atomic force micrographs of precipitated silica and polystyrene-modified silica, in addition, showed nanometer scale areas resulting from polymerization that stretch from one pore to another in a silica aggregate, but did not significantly fill the pore. Copolymer modifications are considered most promising since compound cure time and hysteresis (G'') decrease, while tear energy, the ratio of 300% to 100% modulus, and cut growth resistance values all increase compared to the control silica. Two further studies have looked at the improvement of rubber compound performance using modified reinforcing filler. O'Haver *et al.* (1996) used the admicellar polymerization technique to modify the surface of precipitated silica by using copolymers of isoprene or 1,3-butadiene with vinyl acetate, acrylonitrile, 4-methoxystyrene, 4-chlorostyrene, and methyl methacrylate in order to produce a new class of reinforcing fillers capable of improving the rubber cure and the cured compound's physical properties. It was shown that the process of admicellar polymerization is successful even with monomers having a relatively high solubility in water. However, one surprising observation that emerged from the experiments was that the addition of the methyl group to butadiene causes a significant change in the rubber compound properties using the modified silicas. Three possible explanations were proposed to explain this observation. One possible explanation is that because butadiene is a relatively small molecule it is able to penetrate more deeply into

the pores of silica resulting in more entanglements of the polymer strands with the silica. Another possible explanation is that because butadiene is a gas there may be more condensation of butadiene in the smallest pores. When this liquid butadiene was polymerized, it could form firm anchors for polymer strands coming out from these silica pores. A third possible reason is that the presence of the methyl group sterically inhibits the crosslinking of polyisoprene copolymers during the vulcanization process when compared to butadiene. Consequently, they concluded that with the same amount of polymer present on the surface of modified silicas, the butadiene-modified silica would have more “anchors” attaching it to the bulk rubber compound. A further study compared rubber reinforcement using various surface-modified precipitated silicas (Thammathadanukul *et al.*, 1996). They found that both silica modified by an admicellar polymerization technique (based on the in-situ polymerization of organic monomer(s) in surfactant layers adsorbed from aqueous solution onto the surface of precipitated silica) and those modified by a silane coupling agent showed an increase in the cure rate and some specific property improvements of the natural rubber compound. They concluded that in-situ polymer-modified silicas afford greater overall improvement of natural rubber compound performance, except for flex-cracking resistance of which this result required additional studies. Moreover, their results also suggest that the type and amount of polymer modification can significantly affect the rubber compound properties.

Most research in this area has concentrated on using liquid monomers, e.g. styrene. However, Lai *et al.* (1995) were successful in forming poly (tetrafluoroethylene) thin films on both aluminum oxide powder and chips by admicellar polymerization. They found that pressure was a main factor for the success of TPE adsolubilization into the surfactant bilayers. In addition, the concentration of the initiator had a marked effect on polymerization in the range from 0.25 to 2.5 wt% indicating that this factor must be taken into

consideration during the analysis of kinetic data. The results of FTIR showed that there was a PTFE film coating on the surface of the aluminium oxide powder substrate. Also, the results from electron probe microanalysis showed fluorine to be present in the coated aluminium oxide powder. This is evidence that PTFE film can be coated on the surface of aluminium oxide powder. Furthermore, the measurements of friction coefficients and contact angles also verified that thin PTFE films were formed on the alumina plates. Frictional behavior seems to be related to film thickness and continuity. Possible reasons for this assertion are (a) it may be that the PTFE layer is not uniformly distributed over the surface of the alumina, and (b) the PTFE film is thin and therefore only loosely bonds to the surface of the alumina.

Sakhalkar *et al.* (1995) reported that the formation of thin polystyrene films on glass fiber surfaces occurs in three steps, namely the formation of surfactant admicelles, the partitioning of the styrene monomer into the admicelles, and the in-situ polymerization of the absorbed monomer. Two different cationic surfactants were used in the experiments to form the admicelles, i.e. dodecyltrimethylammonium bromide (DTAB) and cetylpyridium chloride (CPC), in systems with and without an electrolyte having the same counterion as the surfactant. The results showed that the addition of an electrolyte results in a small increase in the adsorption of the surfactant. Surface study by field emission SEM showed a non-uniform coating of polystyrene on the fiber surface. This may be caused by a non-uniform charge distribution along the glass fiber surface, surface roughness or surface cleanliness. Furthermore, THF extraction and UV spectrophotometric studies were used for confirming the formation of polystyrene on the glass fiber surface. It appears that the third step of the polymerization process (polymer formation) however, was not restricted to surface aggregates as was originally thought, but a fraction of polymerization occurred in the aqueous supernatant liquid as well.

Since the admicellar polymerization technique is reported to be quite versatile and is applicable to a variety of surfaces, Cho (1997) applied the technique to deposit polypyrrole film onto mica. He used adsorbed surfactant aggregates to concentrate monomeric species at the solution-solid interface and to localize the polymer-forming reaction over the mica surface. In his work, polypyrrole films prepared by polymerization in the self-assembled arrays (PSAA) were characterized and compared with samples made by polymerization in the absence of self assembled arrays (surface nucleation, PSN). Results from images and measurements obtained by atomic force microscopy (AFM) indicate that PSAA films on the mica surface tends to be much smoother than PSN layers under the same conditions. The ultra-thin PSAA (130 nm) could be controlled by changing the ratio between water, surfactant, and pyrrole concentration under ambient conditions. Moreover, thinner PSAA films were more stable and had higher electrical conductivity than the PSN films.

Various potential applications have been proposed for thin films formed by admicellar polymerization, e.g. in thermosetting polymer composites to improve polymer/filler adhesion. Grady *et al.* (1998) succeeded in forming thin polymer films of styrene-isoprene on glass cloth by admicellar polymerization using sodium dodecyl sulfate (SDS) as surfactant. The treated glass cloth was used to make composites with epoxy and polyester resins. The results from the epoxy composites showed that the composites made from admicellar-treated glass cloth had improved flexural strength, but not as high as that of silane-treated glass cloth. Also, single filament pull-out tests showed that the polymer/glass interfaces of these two composites are the same. The morphology of the glass fiber surface after pull-out tests from these two composites showed smooth surfaces in contrast to the coarse morphology of untreated glass fiber after pull-out tests. For the polyester/glass cloth composites, admicellar treated glass cloth composites did not show any

improvement in flexural strength when compared to untreated glass cloth composites.