CHAPTER II
LITERATURE REVIEW

2.1 Rice Husk

Rice is harvested from the field in the form of paddy. Paddy is a complete seed of rice, one grain of paddy contains one rice kernel. Each paddy consists of many layers. The outermost layer is rice shell called "husk" as shown in Figure 2.1. Husk consists of two interlocked half shells, each protects one half side of paddy. Husk consists mostly of silica and cellulose. Silicon enters the rice plant through its root in a soluble form, probably as a silicate or monosilicic acid, and then moves to the outer surface of the plant, where it becomes concentrated by evaporation and polymerization to form a cellulose silica membrane. There is a general agreement that the silica is predominantly in inorganic linkage, but some of the silica is also bonded covalently to the organic compounds. This portion of the silica cannot be dissolved in alkali and can withstand very high temperatures. Characterizations by SEM, energy-dispersive X-ray analysis, AES, etc., suggest that the silica is mainly localized in the tough interlayer (epidermis) of the rice husk and that it also fills in the spaces between the epidermal cells.
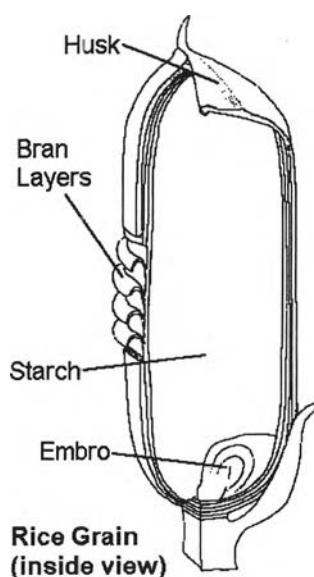
Husk

Bran Layers

Starch

Embro

Rice Grain (inside view)

Figure 2.1 The inside view of a rice grain.

2.1.1 Composition of Rice Husk

The major constituents of rice husk are cellulose, lignin, and ash (>90% silica) (James and Rao, 1986 and Khunthon et al., 1997). Though the actual composition is variable depending on the variety, climate, yearly fluctuations and geographic location. The following values may be considered typical, as shown in Table 2.1.

Table 2.1 Main components in rice husk

Component	Percentage average
Ash	20%
Lignin	22%
Cellulose	38%
Pentosans	18%
Other organics	2%

Rice husk also contains a little protein, moisture, and small amounts of metallic impurities. This can be removed further by a simple acid-leaching treatment. Table 2.2 shows the results obtained from the chemical analysis using X-ray fluorescence (XRF) of a white ash sample obtained by burning the rice husks at 600°C for 3 h under a helium flow of 100 cm^3/min, followed by the combustion of the residual carbon under a pure oxygen flow of 100 cm^3/min (sample A). The percentages of the different metals have been calculated with respect to the weight of the sample annealed at 800°C to outgas the adsorbed water vapor. This sample contains 8.22% metal oxides as impurities (Real et al., 1996).

Table 2.2 X-ray fluorescence analysis of calcined rice husk samples

Impurities	Sample[*]		
	A	B	C
SiO_2	91.77	98.92	99.44
Al_2O_3	0.58	0.39	0.40
Fe_2O_3	0.03	0.00	0.00
CaO	0.94	0.00	0.00
MgO	0.71	0.00	0.00
Na_2O	0.00	0.00	0.00
K_2O	5.46	0.52	0.01
TiO_2	0.05	0.00	0.00
P_2O_5	0.29	0.04	0.04
SrO	0.00	0.00	0.00
ZnO	0.02	0.02	0.01
MnO	0.08	0.06	0.05
Others	0.05	0.04	0.04

[*] A is untreated sample, B is sample treated with HCl after combustion of the residual carbon, and C is sample treated with HCl before burning the husks.

2.1.2 Acid-Leaching Treatment of Rice Husk

The most outstanding property of rice husk ash is its high amount of silica (>90% by weight). Utilization of rice husk ash as a resource of amorphous silica is based on removal of impurities with low effort and the high specific surface area. Yalçin and Sevinç (2001) have shown that reasonably pure silica (99.66%) and high specific surface area (321 m^2/g) can be obtained from rice husk ash by a simple acid-leaching procedure. Many kinds of acids (HCl, H_2SO_4, HNO_3, HF) have been reported for use in pretreatment, but HCl is the most often used (Sun and Gong, 2001).

Metal oxides strongly affect the production of silica. It has been found that some kinds of metal oxides, especially potassium oxide, contained in rice

husk ash cause the surface melting of SiO_2 particles and accelerate the crystallization of amorphous SiO_2 into cristobalite and tridymite (Sun and Gong, 2001; Real *et al.*, 1996; and Leela-Adisorn, 1992). Real *et al.* (1996) found that if the leaching with HCl is performed on the white ash obtained by combustion of rice husk at 600°C, an amorphous silica with the same purity also is obtained. But its specific surface area decreases to 1 m^2/g as shown in Table 2.3. This behavior is due to a strong interaction between the silica and the potassium contained in the rice husk, which leads to a dramatic decrease of the specific surface area if K^+ cations are not removed prior to the heat treatment at 600°C.

Table 2.3 BET specific surface area (S_{BET}) and specific pore volume of calcined rice husk samples

Sample[*]	S_{BET} (m^2/g)	Pore specific volume (cm^3/g)
A	< 1	-
B	< 1	-
C (600°C)	260	0.43
C (800°C)	211	0.36
D	209	-

[*] A is untreated sample, B is sample treated with HCl after combustion of the residual carbon, C is sample treated with HCl before burning the rice husk, and D is sample treated with H_2O before burning the rice husk.

2.1.3 Calcination of Rice Husk

Rice husk can be directly calcined to produce silica without any pretreatment. However, the properties of silica in rice husk ash are strongly influenced by the temperature of formation and the duration of heating. Besides these parameters, the calcination instruments also strongly affect the quality of the silica produced (Sun and Gong, 2001).

In addition, at too high temperature and too low soaking time, crystallization occurs after a collapse of pore size smaller than 10 nm. To preserve

amorphous nanostructure, 600-650°C at less than 10 h was recommended (Leela-Adisorn, 1992).

In 1989, Nakata *et al.* studied the properties of the ash obtained by combustion between 400 and 1500°C. The SiO_2 in rice husk ash formed by combustion below 800°C was found to be amorphous. Particles of the ash having an average diameter of 20 μm were aggregates of small particles with a diameter of 2-5 μm. At combustion temperatures above 900°C, the SiO_2 in rice husk ash consisted of cristobalite and a small amount of tridymite. The surfaces of the ash particles melted, and the particles bonded to each other. The particle size was 40-60 μm.

James and Rao (1986) studied about silica in the rice husk and concluded that the physical characteristics and the chemical reactivity of silica in rice husk ash depend on both the temperature and the soaking time. Figure 2.2 shows the variation trends in the surface areas of ash samples soaked for 1, 3, 6, 12, and 18 h. The surface areas peaked around 400-500°C.
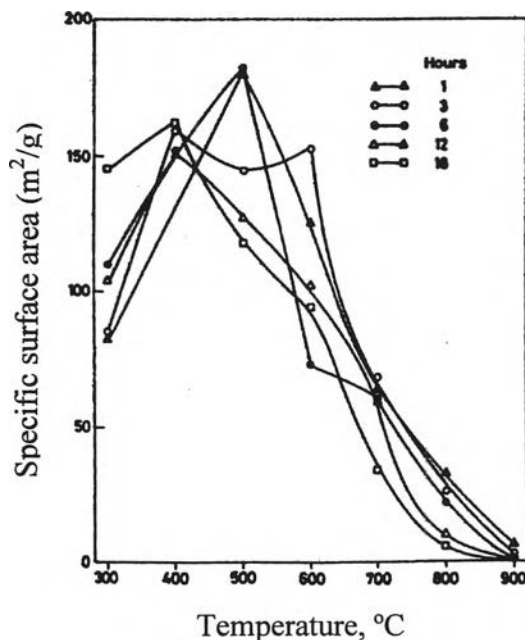

Figure 2.2 Variation of surface area of rice husk ash with heating temperature and different times of heating.

Figure 2.3 illustrates the weight loss of rice husk versus temperature (Yalçin and Sevinç, 2001). The sample weight is stabilized, after a 78% weight loss, at 500°C. The total weight loss of 78% is observed, which means that the sample obtained by burning the rice husk consisted of 22 wt.% silica and metallic impurities and 78 wt.% H_2O and CO_2 that can be removed by heating at 600°C under air atmosphere. Cellulose material can be broken down thermally by two mechanisms: 1) dehydration followed by charring and 2) depolymerization and volatilization of hydrocarbons (Leela-Adisorn, 1992). From ash color, (Chakraverty et al., 1988) it was found that the lowest incineration temperature to get white ash is 500°C for 5 h or at 700°C for 1.5 h.
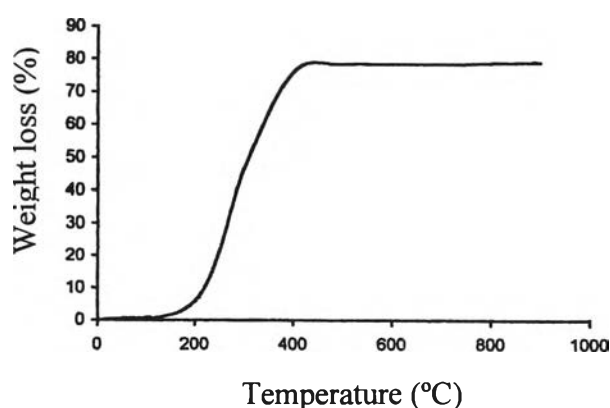
Figure 2.3 Weight loss-temperature curve of rice husk.

Fuad et al. (1994) studied the effects of applying titanate (LICA 38), zirconate (NZ 44) and silane coupling agents (PROSIL 2020 and PROSIL 9234) to rice husk ash in polypropylene composites. The results showed that for most of the composites, the flexural modulus increased with filler content while tensile strength, elongation at break and Izod impact strength showed a decrease. In contrast to the composite filled with commercial fumed silica, most of the rice husk ash composites have better impact properties but lower tensile and flexural strengths. So, suitable applications for the rice husk ash composites would be in components demanding high stiffness, excellent dimension stability with reasonable tensile and impact properties.

In 2001, Chuayjuljit *et al.* used silica from rice husk as a reinforcing filler in natural rubber. Silica was prepared from rice husk which cleaned with tap water, then treated with 0.4 M hydrochloric acid at 105°C for 3 hours. The treated rice husk was burnt at 600°C for 6 hours. The resulting white ash contained as high as 99.6% silica. The ash was ground with a jet mill and tested for its properties. It was found that silica from rice husk had higher specific surface area (182 m^2/g), most of the silica particles were finer and had lower moisture content than commercial silica commonly used in rubber industries (0.60 and 7.50 % relative humidity at 105°C for 2 h, respectively).

2.2 Admicellar Polymerization

Admicellar polymerization is the phenomena of surfactant adsorption, admicelle formation, adsolubilization of molecules in surfactant admicelles, and subsequent reactions in these surfactant admicelles.

2.2.1 Surfactant Adsorption

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface —whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of the atoms of which these sites or groupings are constituted; (2) the molecular structure of the surfactant being adsorbed (the adsorbate) —whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic; and (3) the environment of the aqueous phase-its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes (alcohol, urea, etc.), and its temperature. Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption (Rosen, 1989).

At the solid-liquid interface, it is interesting to determine (1) the amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent, that is, the surface concentration of the surfactant ("adsorbate") at a given temperature,

since this is a measure of how much of the surface of the adsorbent has been covered, and hence changed, by the adsorption; (2) the equilibrium concentration of surfactant in the liquid phase required to produce a given surface concentration of surfactant at a given temperature, since this measures the efficiency with which the surfactant is adsorbed; (3) the concentration of surfactant on the adsorbent at surface saturation at a given temperature, since this determines the effectiveness with which the surfactant is adsorbed; (4) the orientation of the adsorbed surfactant and any other parameters that may shed light on the mechanism by which the surfactant is adsorbed, since a knowledge of the mechanism allows us to predict how a surfactant with a given molecular structure will adsorb at the interface; and (5) the effect of adsorption on other properties of the adsorbent (Rosen, 1989). Results from surfactant adsorption experiments are usually expressed in the form of adsorption isotherm, which displays the amount adsorbed as a function of equilibrium surfactant concentration. The adsorption isotherm for an ionic surfactant onto an oppositely charged substrate is typically S-shaped on logarithmic scale which can be separated into four regions (Rosen, 1989) as shown in Figure 2.4.

Region I corresponds to both very low concentration and low adsorption of surfactant. This region is commonly referred to as the Henry's law region because the adsorbed surfactant is considered to be in infinite dilution in the surface phase and, thus, the interaction between molecules of surfactants is negligible. Adsorbed surfactants in this region are viewed as being adsorbed alone and not forming any aggregates.

In Region II there is an increase in adsorption, resulting from interaction of the hydrophobic chains of oncoming surfactant ions with those of previously adsorbed surfactant and with themselves. These adsorbed surfactant aggregates are called admicelles or hemimicelles, depending upon whether the aggregates are viewed as bilayers or monolayers. The admicelle is considered as a local bilayer structure with a lower layer of head groups adsorbed on the surface and an upper layer of head groups in contact with solution. The hemimicelle is a monolayer structure having the head group adsorbed on the surface while the tail group is in contact with the aqueous phase. The transition of adsorption from Region I to Region II, representing the first formation of adsorbed surfactant aggregates, is

called the critical admicelle concentration (cac) or the hemimicelle concentration (hmc).

In Region III the slope of the isotherm is reduced, because adsorption now must overcome electrostatic repulsion between the oncoming ions and the similarly charged solid.

Region IV is the plateau region, having almost constant surfactant adsorption with increasing surfactant concentration. The plateau at high surfactant adsorption levels can indicate the onset of the CMC (critical micelle concentration), however this plateau can also indicate that the maximum bilayer coverage has been reached. Typically, the equilibrium surfactant concentration at the transition point from Region III to Region IV is approximately at the CMC.
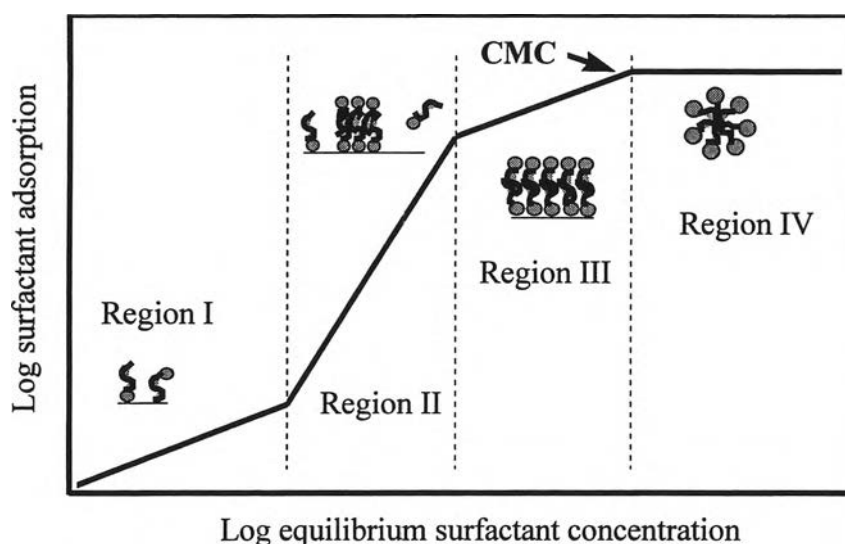

Figure 2.4 S-shaped adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

Kitiyanan *et al.* (1996) and Chaisirimahamorakot (2001) investigated the adsorption of CTAB onto Hi-Sil®255 silica, precipitated silica which had the reported specific surface area of 170 m^2/g. The isotherm illustrated the characteristics of Regions II, III, and IV. From the results, the plateau adsorption region indicates the maximum adsorption was approximately 550 and 600 µmol/g of silica, respectively.

Pradubmook (2001) studied the effect of pH (5 and 8) on adsorption of CTAB on Hi-Sil®255 silica. The results showed that for every equilibrium concentration, CTAB adsorption at pH 8 was higher than at pH 5. This was because higher pH resulted in more negative charge on the silica surface leading to higher amount of surfactant head adsorbed on the precipitated silica.

2.2.2 Admicellar Polymerization

The admicellar polymerization method developed from a fundamental understanding of the interactions between surfactants and surfaces. The conditions of the aqueous solution containing surfactant and suspended inorganic particles can be tailored to favor the formation of a surfactant bilayer on the surfaces of the particles. The formation of ultra-thin films in adsorbed surfactant bilayer has been first investigated by Wu *et al.* (1987).

The method utilized for modification of inorganic powder by admicellar polymerization can be considered to occur in four steps (Figure 2.5).
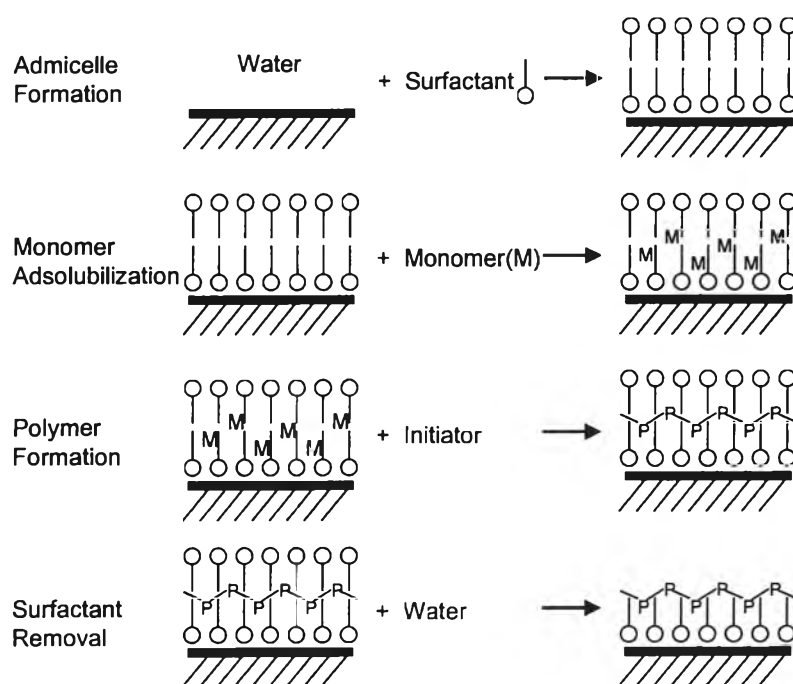

Figure 2.5 Admicellar polymerization process for the formation of an ultra-thin polymer film.

Step one: Surfactant Adsorption

First step consists of admicelle formation by the adsorption of a surfactant bilayer onto the surface of the substrate. Adsorption is accomplished through the use of a suitable surfactant under appropriate system conditions. The choice of a surfactant is influenced by the point of zero charge of the substrate (the pH value at which the surface charge is completely neutralized is called the point of zero charge, or PZC), the chemical nature of the polymer to be formed, and the chosen polymerization initiator system. A study of the PZC for the substrate provides information of the pH ranges in which cationic or anionic surfactants might be utilized. At a pH solution above the PZC, the surface of the substrate will be negatively charged; while below the PZC, the surface will be positively charged. Silicon dioxide has a PZC of approximately 2.9. (Brady, 1996). Thus at a pH of 8, the SiO_2 surface would have a negative charge. Adsorption by ionic surfactants is achieved by adjusting the surface charge on the substrate to be opposite that of the surfactant head group. Moreover, the equilibrium concentration of surfactant must be below its critical micelle concentration in order to prevent the formation of micelles in the bulk solution. In the absence of micelles, the organic interior of the surfactant bilayer became the only locus for the adsolubilization of organic monomers.

Step two: Monomer Adsolubilization

This step may be done subsequently to the first step, or simultaneously with it. It involves the solubilization of monomer into the admicelle called adsolubilization. Many organic monomers are nearly insoluble in water. Thus, when they are introduced into the system, they preferentially partition into the organic interior of the admicelle. In the admicelle, the bilayer acts as a two-dimensional solvent to concentrate the monomer near the surface of the substrate.

Step three: Polymerization of Adsolubilized Monomer

Third step is the *in situ* polymerization of the monomer. For free radical polymerization, the reaction is started by the generation of radicals from the initiator. Once the reaction has begun, additional monomer from the bulk solution diffuses into the admicelle (O'Rear *et al.*, 1987). If the reaction is continued for a

sufficient length of time, essentially all of the monomer dissolved in the solvent can be converted to polymer.

Step four: Surfactant Removal

Last step is the washing of the treated substrate with water to remove as much as possible the outer surfactant layer to expose the polymer film. Removing all of the surfactant is usually difficult, especially on porous substrates. Mass balances on porous systems suggest that even after vigorous washing, half of the surfactant remains on the modified particle.

The result of an admicellar polymerization is a surface covered with a very thin polymer layer. Because surfactant adsorption is almost universal, admicellar technology is an aqueous phase method to coat arbitrary surfaces with a polymer (Grady *et al.*, 1998). Many researchers recognized almost immediately that admicellar polymerization might have significant commercial application. For example, to improve interfacial adhesion in polymer-matrix composites, to modify wetting behavior and friction coefficient on surface, to enhance the conductivity of conductive composites, and so on. These positive findings were the motivation for an evaluation of admicellar polymerization as a surface treatment in thermoplastic and thermosetting structural composites.

In 1993, O'Haver *et al.* formed ultra-thin polystyrene film on silica. Polystyrene was successfully polymerized in cationic surfactant cetyl trimethyl ammonium bromide (CTAB), using a water-insoluble initiator, 2,2'-azobis-2-methylpropionitrile (AIBN). The polymer formed was extracted and characterized by FTIR and GPC. The molecular weight of formed polymer was investigated with respect to polymerization time. Polymeric film on porous silica causes increase in particle size and decrease in surface area of silica. FTIR was used to determine the presence of polystyrene on the silica and GPC was used to study molecular weight distribution of extracted polymer.

In 1998, Grady *et al.* studied modified glass cloth by admicellar polymerization for use as a composite manufacture. The forming of thin polymeric film of polystyerne-isoprene on glass cloth was successfully carried out using SDS as the surfactant. The treated glass cloth was combined with epoxy and polyester resins

to make a composite. The composite showed improvement in flexural strength and physical properties when compared to the untreated glass cloth composite.

Chaisirimahamorakot (2001) studied the effect of retention time and monomer loading on the properties of silicas modified by the *in situ* polymerization using a continuous system. It was concluded that the continuous stirred tank reactor was used successfully. The results showed that the optimum conditions for the modification were 5 g of co-monomers per kg of the silica at 60 min polymerization time. At these conditions, the largest amount of polymer on silica surface was achieved.

Nontasorn (2002) studied the effects of co-monomer loading and retention time on the modified silicas by *in situ* polymerization of organic monomers in t he s urfactant l ayer a dsorbed o nto t he s urface o f p recipitated s ilicas i n o rder to enhance silica/elastomer interactions leading to improvement in the performance of rubber products. The results showed that 5 g co-monomer loading with 30 min retention time gave the highest overall improvement of surface characterization and rubber compound properties.

Arayawongkul (2002) investigated the characterization of polystyrene produced by admicellar polymerization. The polymerization reactions were carried out on nonporous silica (Aerosil®OX50) in CTAB aggregates to form an ultra-thin polystyrene film using sytrene monomer. The results showed that a maximum CTAB adsorption value is approximately 130 $\mu mol/g$ on the nonporous silica. And the adsolubilization of styrene into the adsorbed CTAB bilayer increases with increasing styrene concentration in the aqueous phase. The reaction time for conducting admicellar polymerization should not be shorter than two hours to obtain relatively high molecular weight polystyrene. The extent of the polystyrene film and amount of polystyrene formed on silica increased with increasing CTAB adsorption and adsolubilized styrene.