

CHAPTER II

LITERATURE SURVEY

2.1 Artificial Marble

Marble stone is a natural product welcomed in various applications due to its gorgeous and supra physical properties. However, it shows some disadvantages such as weight, lack of color variety, limit of shape, and high cost. Accordingly, the approach for synthetic material has received attention. It is known that an artificial marble can be prepared by filling inorganic materials which have the refractive index close to that of matrix resin. Various types of matrix resins have been studied in order to obtain the appearance similar to the marble. The artificial marble is required to have an appearance which gives a gorgeous impression with the internal patterns of the molded product to be seen through together with the mechanical strength, i.e.; flexural strength, and impact strength and the improved surface hardness or the heat resistant properties. One of the potentially useful matrix resins is an unsaturated polyester (Oda et al., 1989); however, it has the problem on the transparency. Accordingly, an attention has been drawn to a methylmethacrylate resin which has a high degree of polymerization, good transparency, mechanical strength, flame retardancy and rigidity (Hayashi, 1990; Sasaki et al., 1987).

In order to achieve significant physical properties; fillers for artificial marble have been studied extensively. Inorganic fillers used for the artificial marble are as aluminium hydroxide, magnesium hydroxide, silica, calcium carbonate, calcium silicate, kaolin, clay or talc, etc. However, for these types of artificial marble, the required internal affinities such as miscibility,

adhesion, etc. are important parameters due to the substantial differences in properties between the inorganic filler and organic resin. Furthermore, the increased viscosity by incorporation makes the difficulty for uniform dispersion of the filler. Thus, the improvement for the artificial marble properties and cost reduction by adding the filler is limited. In order to overcome these shortcomings, treatment of filler surface by a silane coupling agent is an attractive approach.

2.2 Silica and Silane Coupling Agent

2.2.1 Synthetic Silica (Wason, 1987)

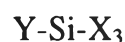
Silicas are grouped into two major categories: natural mined silicas and synthetic silicas. Commercially available synthetic silicas are of five types: fumed, electric arc, fused, gel, and precipitated. The surface of synthetic silica contains hydroxyl groups called silanol groups. Because of surface moisture and the presence of silanol groups, the synthetic silicas are hydrophilic in nature. All synthetic silicas are amorphous in nature, colorless, odorless, tasteless, fine-particle and white powders. Silicas are chemically inert and insoluble powders except in strong alkali (NaOH) and hydrofluoric acid (HF). The refractive index of synthetic silica is 1.45, making it useful for producing translucent and transparent filled polymer stock. Although among the synthetic silicas, fumed silica is the most expensive and the precipitated silica for the lowest-priced. However, precipitated silica creates not only external surface area but also the internal surface area, while fumed silica contributes mainly external surface area. It is well known that the degree of reinforcement obtained with silica is related to the external surface area. Therefore, fumed silica is preferred as a reinforcing filler than precipitated silica. Furthermore, fumed silica is used as a thixotrope in polyester and

epoxy resins. To a lesser degree, fumed silica is also used in thermoplastics as a rheology control agent and a plate-out agent. Like fumed silica, precipitated silica also exhibits thixotropic characters in resins and liquid systems, but it is not as effective as the fumed silica.

The compatibility of synthetic silicas and the improvement for their use in polymers via hydrophobizing the silica surface can be achieved by some suitable coupling agents and chemical treatments.

2.2.2 Silane Coupling Agent (Plueddemann, 1982; Ishida, 1993)

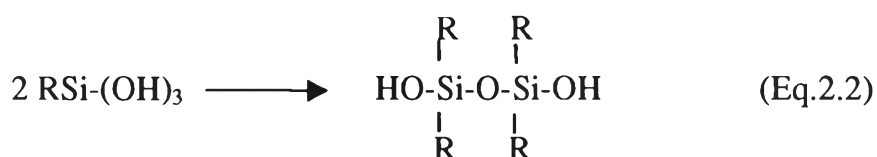
2.2.2.1 *Structure of Silane.* Silane coupling agents usually possess a dual functionality of the form,



where Y is the organofunctional group and X for the hydrolyzable group.

The organofunctional groups (Y) are chosen for reactivity or compatibility with the polymer while the hydrolyzable groups (X) are merely intermediates in formation of silanol groups for bonding to mineral surfaces. The structure of an organofunctional group is chosen so as to copolymerize with a thermosetting resin or to be compatible with a thermoplastic resin.

2.2.2.2 *Reaction of Hydrolyzable Groups on Silicon.* Upon contact with water, the following reactions take place.

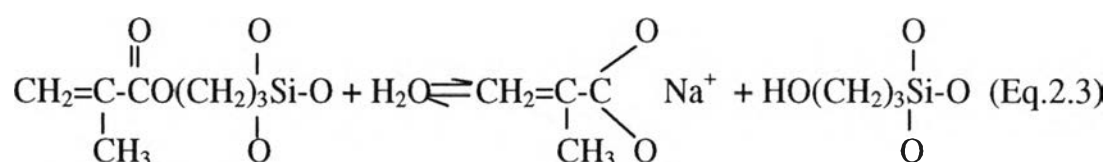


The hydrolysis of trialkoxy groups takes place in a stepwise fashion to give the corresponding silanols, which ultimately condense

to siloxanes. Nishiyama and Horie investigated the mechanisms of hydrolysis and condensation of γ -MPS in 70% EtOH/H₂O solution by the use of ¹³C and ²⁹Si NMR (Nishiyama and Horie, 1987). Nishiyama et al. found that there are several kinds of hydrolysis and condensation species. The order in the amount of hydrolysis species is $-\text{CH}_2\text{-Si}(\text{OCH}_3)_2\text{-OH} > -\text{CH}_2\text{-Si}(\text{OH})_3 > -\text{CH}_2\text{-Si}(\text{OCH}_3)\text{-(OH)}_2$. Meanwhile the condensation process produces the $-\text{CH}_2\text{-Si}(\text{OH})_2\text{-O-Si-}$ mainly. It is found that the longer the time for condensation the higher the molecular weight. It is also found that water accelerates the hydrolysis.

Another parameter influenced the adsorption behavior of silane coupling agent is the solution pH. It is found that hydrolyzates obtained from solution studied by SEC and FTIR appear to be polysiloxane with molecular weight distribution depending on the solution pH (Miller et al., 1984).

In acidic environments (below pH 4), γ -MPS forms polycyclic blocks. At near neutral pH extremely high-molecular-weight and polydisperse polysiloxanes are generated at near neutral pH due to the formation of the double chain ladder configuration and the high silanol instability. In strongly basic environments, the methacrylate function of γ -MPS is partially hydrolyzed to form sodium carboxylate, and carbon dioxide is absorbed from the air and reacts to form sodium carbonate (Eq. 2.3) (Miller et al., 1984; Ishida, 1993).



2.2.2.3 Silane Treating Solutions (Binaghi et al.).

1) Aqueous silane treatment

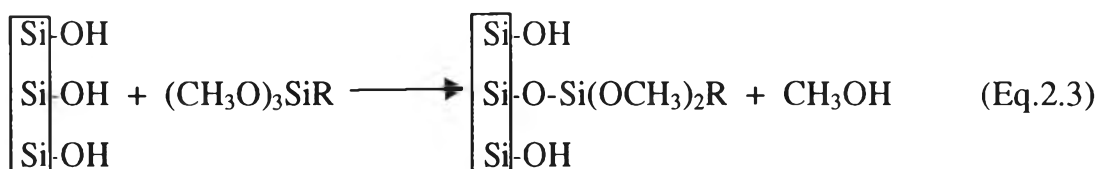
In this method, the treatment of aqueous silane start with complete hydrolysis of the alkoxy groups in the silane molecule. The low concentration of silane allows the highly reactive silanetriol to be the dominant species. Thus, the solution must be freshly prepared to prevent oligomer formation among silane hydrolyzate species.

2) Dry blending

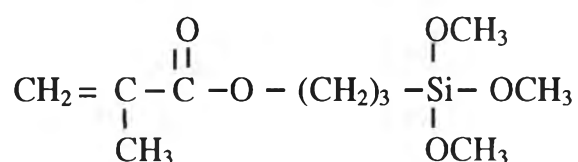
In this method, the alkoxy group of silane molecule was partially hydrolyzed in alcohol solution or the addition of trace amount of water in alcohol solution. The concentration of silane is usually around 10-20wt%. Particulate fillers are often treated with this partially hydrolyzed silane by spraying onto fillers for homogeneous covering. The amount of adsorbed silane on filler surface is not controlled by the adsorption mechanism but by the relative weight of the silane and the filler.

3) Integral blends

Integral blend has the advantage about the elimination of pretreatment, drying and repulverization step. Here, the unhydrolyzed silane is directly incorporated onto an uncured resin. However, the silane has lower efficiency than direct treatment, thus, the large amount of silane is required. The integral technique relies on the preferential adsorption of the silane onto the substrate. Hydrolysis may proceed with time if sufficient water is available from either the resin or the substrate surface. Direct chemical reaction with the substrate can also proceed via the following exchange reaction.



However, to process the integral blend, catalyst is required. Catalyst such as amines or heat treatment helps accelerate the reaction since the reactivity of the above reaction is lower than the condensation reaction of silanol groups. Because there are few silanols available, the silane in this treatment method tends to be near a monomolecular equivalent. Furthermore, the matrix material acts as a solvent for the unhydrolyzed silane, and only the hydrolyzed silane can remain at the filler/matrix interface. In the present work, the γ -MPS is applied as silane coupling agent for fumed silica in MMA by integral blend method. Dodecylammonium oleate is used as a catalyst for hydrolysis reaction of γ -MPS. The structure of γ -MPS is shown below.



The methacrylate group of the coupling agent can react and is compatible with the methylmethacrylate while the methoxy group (hydrolyzable group) is merely intermediate in formation of silanol group for bonding at fumed silica surface.

2.3 Physisorbed and Chemisorbed Silane

Silanes can form many structures due to their tri-functional condensation mechanism. Monomeric and oligomeric silanes can react with the surface of a filler. The motion of physisorbed and chemisorbed silanes are used based on the reaction with the substrate surface. Chemisorbed silane is the one that possesses at least one covalent bond with the substrate. This type of silane does not desorb even washing with an anhydrous organic solvent.

Physisorbed silane does not possess any covalent bonds with the substrate. The physisorbed silane may be small oligomers or large polymer. Quite often, oligomers take the form of cyclic silanes where concentration of unreacted silanol group in the molecule is low despite the small molecular size. These physisorbed oligomers can be eliminated by washing with an organic solvent. However, high molecular weight physisorbed silanes are not as easily eliminated as the small oligomers. Many silanol groups can form hydrogen bonds with the substrate surface or chemisorbed silanes.

If a small amount of water exists in the solvent, water can hydrolyze the siloxane bonds of the loosely chemisorbed silane to desorb. The time scale for desorption and hydrolysis of the siloxane bonds might be comparable for a large, loosely chemisorbed molecules. For small oligomers, it is not important since the time necessary to hydrolyze the siloxane bonds is much longer than the extraction time.

The structure of the physisorbed silanes tends to be cyclic oligomers, and their molecular weight are strongly dependent on the pH of the filler. Ishida and Miller (Ishida and Miller, 1984) studied the substrate effects on the chemisorbed and physisorbed layers of γ -MPS modified particulate minerals by DRIFT and SEC. γ -MPS layers on the substrate surface are influenced by the acid/base nature of the surface, the chemical functionality on the surface and the adsorbate loading. The near-neutral pH substrates showed the greatest

proportion of chemisorbed silane. SEC indicated that the physisorbed layers consist of hydrolyzed or partially hydrolyzed monomer and polysiloxane with a molecular weight up to several thousand. The molecular weight of oligomeric species depends strongly on acid/base nature of substrate surface and descends in the following order; neutral > basic \geq acid. This effect can be modified by adjusting the pH of the treating solution. The adsorption behavior of γ -MPS deposited onto silica is examined as a function of drying time and silane concentration. At low silane concentration, chemisorbed silane molecules are lying parallel to the silica surface (C=O band at 1706 cm^{-1}). With increasing amounts of chemisorption, additional chemisorbed molecules are forced to move away from the silica surface (new C=O band at 1726 cm^{-1}). Addition of acid accelerates the intermolecular condensation of the silane molecules. The amount of physisorbed silane decreases with increasing drying time, thereby indicating an increase in the chemisorbed fraction of silane (Ishida et al., 1991).

2.4 Rheological Properties of Silica/Polymer Composites

The viscosity of a filled system is usually much higher than a non-filled system mainly due to the formation of filler aggregates. The viscosity is a nonlinear function of the filler fraction and increases much more rapidly at higher filler fraction. In most silica suspensions, since the amount of polymer adsorbed on the silica surfaces is at the plateau of the adsorption isotherms for the corresponding polymer, the resulting silica suspensions are stable. Kawaguchi et al. reported that the silica contents could not be greater than 15wt% without silane coupling agent (Kawaguchi et al., 1997).

A dramatic viscosity reduction of a highly filled system can be achieved by breaking up the aggregates of the filler. This can be achieved by applying a shear or tensional force which mechanically separate the aggregates or changing the surface energy of the filler so that the force of filler/matrix interaction overcomes that of the aggregation. The aggregation force, due to hydrogen bonding between the surface hydroxyl group of silica compound and hydroxyl group of water molecules, can be reduced by treating the filler surface with silane coupling agents. Silane can compete for and react with the surface hydroxyl groups and cover the filler with organo-functional groups. Since the van der Waal's force between the organo-functional groups is similar to that between the silane and resin, a small shearing force can easily break up the agglomerated filler particles. Furthermore, a physisorbed silane can further reduce the viscosity. In general, the higher the concentration of the silane in the treating solution, the more the physisorbed silane.

When the integral blending method was used to treat a filler surface, the quantity of the deposited silane increased as the amount of the silane solution. However, the increase in the deposited silane halted suddenly for a certain amount of silane where the filler was completely wetted by the silane solution. Accordingly, there is an upper limit of silane that can be deposited by the integral blending method (Ishida, 1993).

A highly filled system is of great technological significance in the ceramic, artificial marble, and other industries. Due to the very high filler contents, the viscosity of the filled system is usually extremely high to the extent that the mixture of initial ingredients is dough-like in consistency, even if a silica filler is mixed with such a low viscosity material as methylmethacrylate. The viscosity reduction process is a function of the surface coverage of the filler by the silane. The complete coverage of the filler surface is necessary to achieve low viscosity. Since this type of treatment is done in an organic solvent without any water added, the rate of

hydrolysis is very slow. Thus, the addition of an alkaline catalyst greatly accelerates the chemical reaction of the silane with the filler.

2.5 Dynamic Mechanical Properties of Silica Polymer Composites

It is known that the mechanical properties of polymeric composite materials are controlled by the interphase. The properties of an interphase comprised of silane coupling agents are strongly influenced by the adsorption amount and behavior of the silane. Therefore, the determination of these parameters is essential for a fundamental understanding of the reinforcement mechanism in polymer composites. Nishiyama and Ishida (Nishiyama and Ishida, 1990) studied the influence of the silane adsorption behavior on the mechanical properties of the silica filled methacrylate composites. It was shown that there was little change with increasing silane coverage until the amount of chemisorbed silane became saturated and the silane began to physisorb. The presence of physisorbed silane caused dramatic differences, due to reinforcement. Eckstein (Eckstein, 1988) studied the dynamic mechanical properties of glass fibers impregnated with γ -MPS and methyltrimethoxy silane as a function of concentration of silane. An increase of the concentration of the silanes increases the molecular weight of polymeric coatings, as well as the extent of their crosslinking, glass transition, modulus and damping.