

CHAPTER I

INTRODUCTION

In composite manufacturing, there is a continuing development for high performance materials. The progress in development has been made possible by the use of coupling agents. Coupling agents are extensively used to improve the adhesion of the bond across the interface between mineral substrate and polymer matrix. Modifications of the interface between an organic polymer and mineral substrate provide many beneficial results in composite production.

1.1 Definition of “ Coupling Agents ”

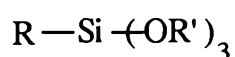
Coupling agents can be defined as materials that improve chemical resistance of the bond across the interface in composites consisting of an organic polymer and mineral substrate.

1.2 Silane Coupling Agent

In fiber glass reinforced plastic, an organosilicon compound which is called silane coupling agent plays an important role in improving the adhesion between glass fiber surface and organic polymer.

1.2.1 General structure of silane coupling agent

Silane coupling agent usually possesses a dual functionality of the following form.



R: an organofunctional group which is designed to copolymerize with the thermosetting resin or to be compatible with the thermoplastic resin.

OR': a hydrolyzable group such as ethoxy or methoxy group.

1.2.2 Nature of silane in solution

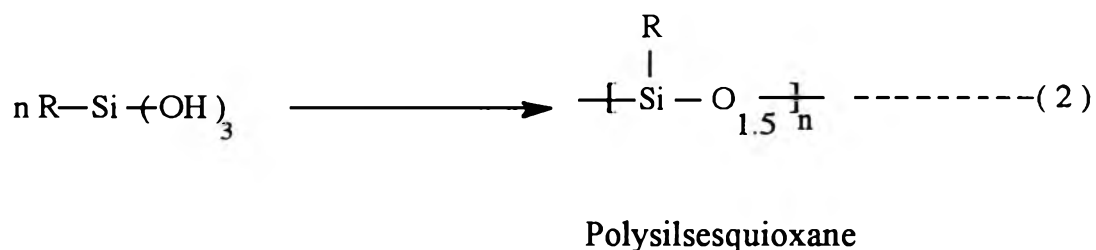
Before applying onto the glass fiber surface, silane coupling agent is first hydrolyzed in aqueous solution or alcoholic solution. The alkoxy group (OR') is hydrolyzed to hydroxy group (OH) as shown in the following reaction.

Hydrolysis



The silanol group of silane hydrolyzates resulting from the hydrolysis reaction will then condense with each other to form the siloxane structure as shown in reaction (2).

Condensation

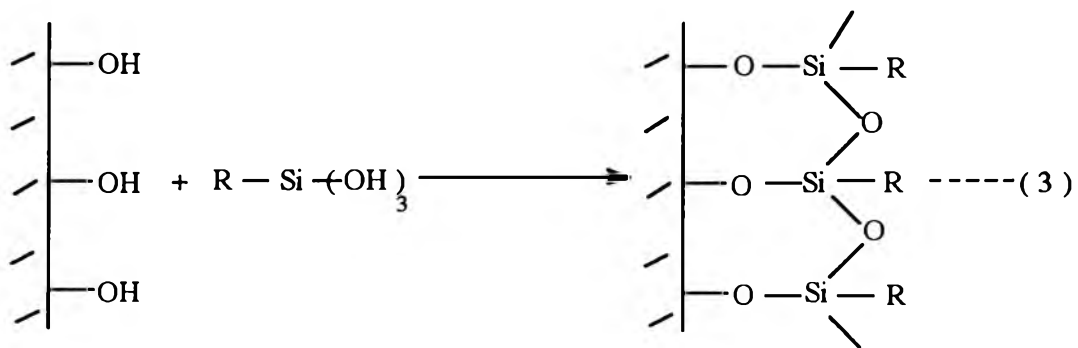


Under optimum conditions, hydrolysis proceeds slower than condensation reactions. However, the silanol groups is very reactive thus condensation becomes the dominant factor in considering the molecular weight development of polysilsesquioxane even in dilute aqueous.

Understanding the kinetics of hydrolysis and condensation reactions for a specific silane in solution is very important because its effectiveness as an adhesion promoter is influenced by the extent of condensation which, in turn, affects the structure of the interphase in composites. The rate of silanol condensation to siloxane depends strongly on pH, concentration and temperature of the solution as well as the presence of other agents in the solution, but it depends weakly on the structure of organofunctional group [Guliana, Tesoro and Yulong Wu (1991)].

1.2.3 Structure of silane on the glass fiber surface

Similar condensation between silanol groups can take place with the surface of glass fiber, allowing the silane to bind chemically to the surface as in the following reaction.



glass fiber surface

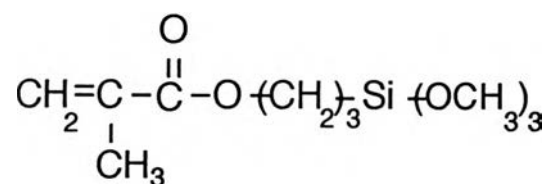
When the silane treated fiber glass is made into a composite, an “interphase” is formed between glass fiber surface and polymer matrix. The “interphase” can be defined as the interfacial region the properties of which are distinguishably different from the bulk properties.

The structure of silane at interphase region is the important factor that affects the mechanical performance of the final composite, where as the extent of silanol condensation is the important factor that affects the structure of silane at interphase. Ishida, Naviroj and Koenig (1983) had studied the structure of γ -methacryloxypropyltrimethoxysilane as well as

glass/silane interface by using Fourier transform infrared spectroscopy (FTIR). Multilayer formation of silane on the glass fiber surface was confirmed. Since the structure of silane on glass fiber surface depends on the amount of silane adsorbed on the glass surface, it is important to realize that the amount of adsorbed silane depends not only on the concentration of treating solution but also on the treating method and the nature of silane in solution. In 1993, Ishida had studied the structure of silane in solution and on solid substrate. The factors that influenced the molecular weight of silane condensate, adsorption behavior and chemical bond formation were discussed. Molecular aspect of the reinforcement mechanism was discussed in relation to the interfacial bond formation.

1.2.4 γ -Methacryloxypropyltrimethoxysilane (γ -MPS)

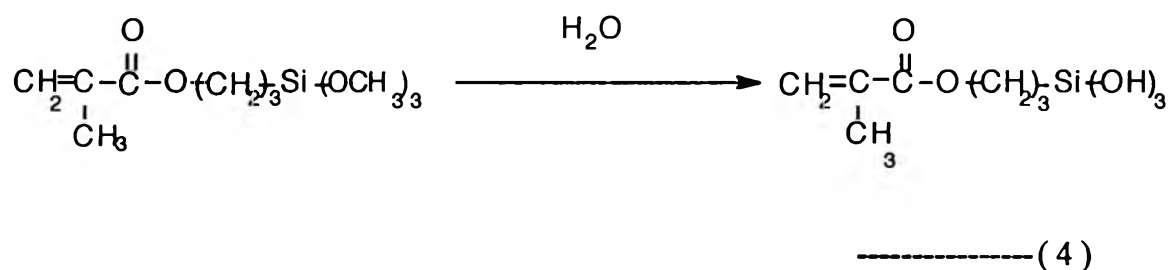
The most suitable type of silane which is used for unsaturated polyester resin is γ -Methacryloxypropyltrimethoxysilane (γ -MPS). Its structure is shown below.



γ -MPS

γ -MPS is hydrolyzed and condensed to polymethacryloxypropyl silsesquioxane (poly MPS), as shown in the following reactions.

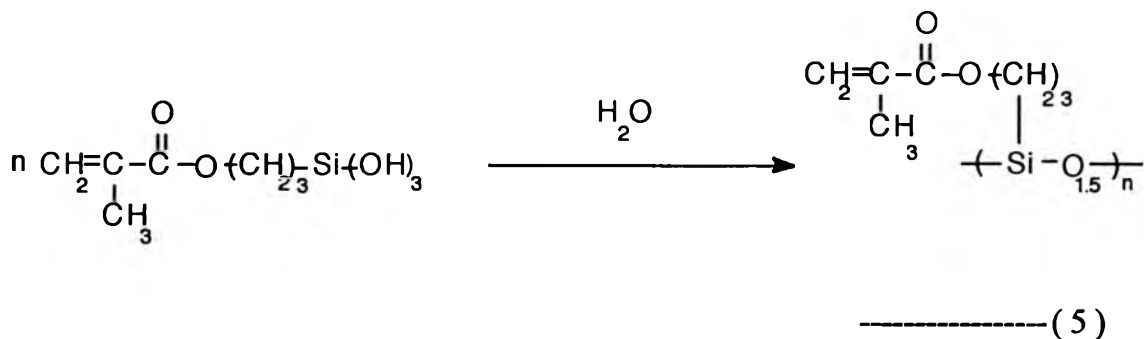
Hydrolysis



γ -MPS

γ -MPS hydrolyzate

Condensation



γ -MPS hydrolyzate

poly MPS

1.3 Sizing Agents

In actual production of fiber glass, silane is not the only ingredient which is applied onto the glass fiber surface. There are other agents used to

provide additional properties such as film forming agent, lubricant, antistatic agent and so on.

Table 1 Typical components of glass fiber sizing agents

Components	Percent
Film forming agent	1-5
Lubricant	0.1-0.2
Antistatic agent	0.1-0.2
Silane coupling agent	0.1-0.5

These agents including silane coupling agent are applied onto the glass fiber surface shortly after fibers are manufactured but before composite fabrication. The mixture solution between silane and cross linking agent, 1,2-bis(trimethoxysilyl) ethane (BTE) was studied as a function of composition, concentration, and pH by Jyongsic Jang et al. (1989). They found that the degree of silanol condensation of silane decreased with increasing crosslinker proportion. Drown et. al. (1991) had determined the degree of an epoxy-compatible glass fiber sizing that altered the adhesion between the fiber and matrix, and the degree that changed the mechanical properties of the obtained composites. The blend of epoxy-compatible sizing and bulk matrix was used for modeling the properties of fiber-matrix interphase in the presence of sizing agent. They found that the sizing interaction with the matrix produced a material which has a higher modulus, a greater tensile strength, but a lower toughness. It means that sizing agents have an effect

strength, but a lower toughness. It means that sizing agents have an effect on silane coupling agent. From this point of view, it is very interesting to study the effect of sizing agents on the structure of silane at the composite interphase and the properties induced in the final composite by focusing on the interaction between sizing agents and silane coupling agent in the solution before treating it onto the glass fiber surface.

1.3.1 Film forming sizing agent

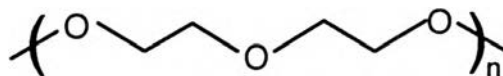
Polyvinylacetate is one of the interesting agents which is applied on the glass surface as a film former. The particles of polyvinylacetate (PVAc) coagulate to form a tough and clear continuous coating. This agent can protect the glass fiber surface and provide the necessary flexibility. Polyvinylacetate has carbonyl functional groups which are expected to interact with silane molecules through hydrogen bonding. This interaction is expected to influence the nature of silane in solution.

The effect of polyvinylacetate sizing agent on the γ -amino propyltriethoxysilane (γ -APS) was discussed by V. Lacramp (1995). The system containing 6% weight of various polymers (sizing), including polyvinylacetate, with and without γ -APS was studied. The chemical reaction occurring in the mixture system was investigated. It was concluded that in the case of PVAc based sizing, the glass transition temperature and the Young's modulus of this system increased relative to the drying time and the amount of silane in the system. These effects

could be attributed to the water remained in the PVAc film without silane, whereas transesterification between silanol groups of silane hydrolyzate and ester groups of PVAc was involved in the case of film based on γ -APS.

1.3.2 Lubricating sizing agent

Polyethyleneglycol is which normally used as the lubricant is used in actual production of glass fiber. The structure of PEG is shown below.



Polyethyleneglycol (PEG)

Since PEG has oxygen atoms in the chain, hydrogen bonding between oxygen atoms of PEG and silanol groups in γ -MPS hydrolyzate can be formed easily. This type of hydrogen bonding is expected to influence the silanol condensation. γ -MPS hydrolyzate which has hydrogen bonding with the two adjacent oxygen atoms in PEG chain is expected to condense with each other to form siloxane network.

The mechanical properties of the final composites have been shown to depend on the amount and the structure of chemisorbed and physisorbed silane present on the glass surface. Molecular packing of

silane showed an effect on the structure of silane beyond the surface and depended on the structure of silane molecules in treating solution [Schmidt (1984) and Ishida (1993)].

1.4 Objective

The present work is focused on the role of sizing agents in the silanol condensation of silane coupling agent in solution. The effects of sizing agent on silanol condensation will be elucidated in the viewpoint of the interaction between silane and sizing agent by using FTIR and GPC techniques.