

CHAPTER I

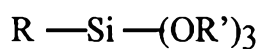
INTRODUCTION

1.1 Silane coupling agents

Silane coupling agents are effective adhesion promoters. Improved adhesion can be achieved by coating very thin layers of coupling agent onto surfaces. Silanes are usually applied to inorganic substrates from dilute aqueous or organic solution and then dried, or are sometimes added to the polymer directly during the processing, typically in the concentration range of 0.01-1.00 % by weight.

In the production of fiber glass reinforced plastics silane coupling agent is often used to improve the adhesion between glass fiber surface and matrix polymer. The performance of the final composites depends on the molecular structure of interphase which is easily affected by many factors such as the type the coupling agent, the composition of sizing agents and conditions of application. The molecular structure of silane deposited on the glass surface has been studied by many researchers including the molecular structure of silane in solution without the substrate.

The general structural formula of silane is $R-Si-(OR')_3$ as shown below, OR' being hydrolyzable groups such as methoxy or ethoxy groups, and R an organofunctional groups which is designed to copolymerize with the thermosetting resin or to be compatible with the thermoplastic resin.



R= an organofunctional group such as amino, mercapto, methacrylate or vinyl group.

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

The “coupling” mechanism of organofunctional silanes depends on a stable link between the organofunctional group and the adhering surface.

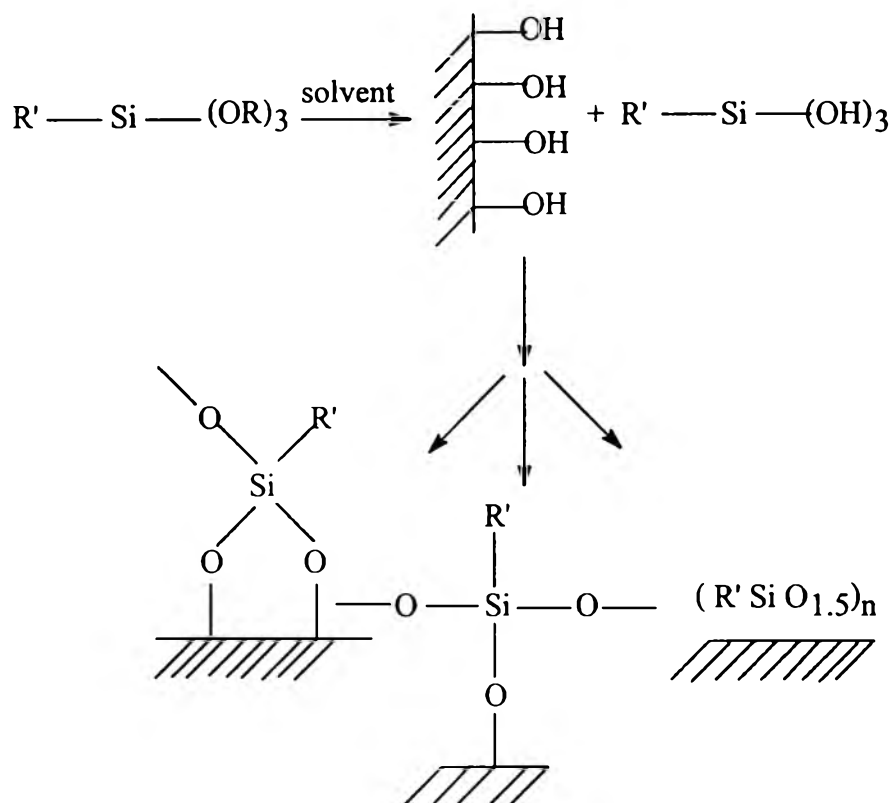


Figure 1.1 Structural formula of silanol hydrolyzate and polysilsesquioxane.

Figure 1.1 shows a simplified picture of the bonding mechanism of silane coupling agent at the interface between inorganic (such as glasses, metals and minerals) and organic materials (such as polymer, coatings and adhesives).

Silanol (SiOH) groups may first form hydrogen bonds with the substrate surface, and during drying, they condense to siloxane structures and chemically bond to the surface. The extent of adhesion between siloxane film and polymer matrix influences the mechanical properties of the composites. Greater adhesion gives stronger composite materials.

When the silane treated glass fiber is made into composites, the interphase is formed between glass fiber surface and matrix polymer as shown in Figure 1.2. “Interphase” is defined as the interfacial region whose properties are similar but distinguishably different from the bulk properties

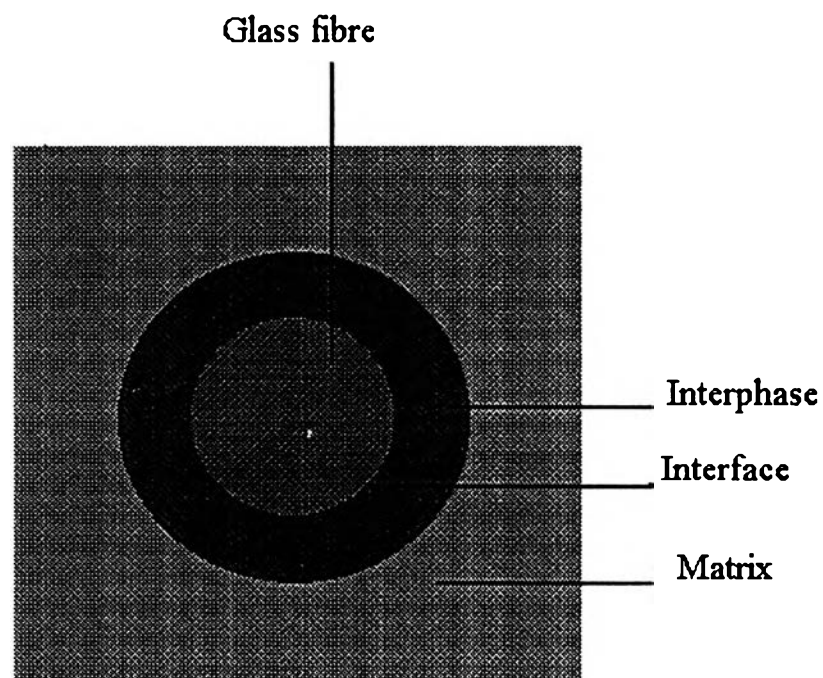


Figure 1.2 Conceptual drawing of interphase and interface in fiber reinforced composites.

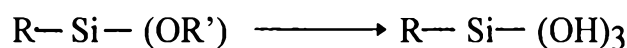
The molecular structure of silane at interphase is an important parameter which influences mechanical properties of the final composites. Graf, et.al. used Fourier transform diffuse reflectance spectroscopy (DRIFT) to investigate the amount and structure of γ -methacryloxypropyltrimethoxysilane (γ -MPS) on the glass fiber surface. They concluded that the mechanical responses of the final composites made from γ -MPS treated glass fiber reinforced polyester depend on the structure of γ -MPS on the glass fiber surface as well as the chemistry of silane in the treating solution .

Naviroj, Ishida and Koenig(1983) studied the structure of γ -MPS as well as glass/silane interface by using Fourier transform infrared spectroscopy (FTIR). Ishida studied the structure of silane in solution and on solid substrate[Miller et. al. (1984)]. In his study, factors influencing the molecular weight of silane condensate, the adsorption behavior and chemical bond formation were discussed. Molecular aspect of the reinforcement mechanism was also discussed in relation to the interfacial bond formation.

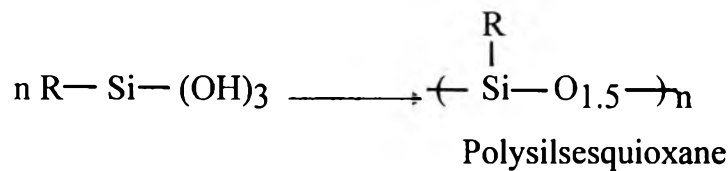
1.2 Nature of silane in solution

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

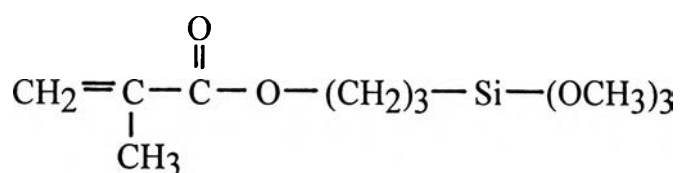


Condensation



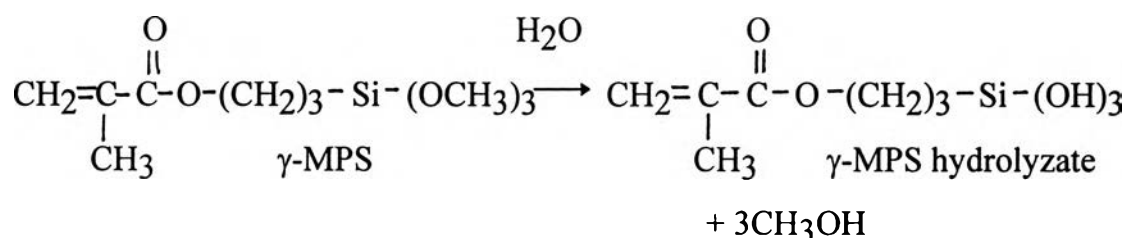
Under optimum conditions, hydrolysis proceeds slower than condensation reactions. However, the silanol groups is very reactive thus condensation becomes the dominant factor in considering the molecular weight development of polysilsesquioxane even in dilute aqueous.

One of the widely used silane coupling agent is γ -methacryloxypropyltri-methoxysilane (γ -MPS), its structure is shown below.

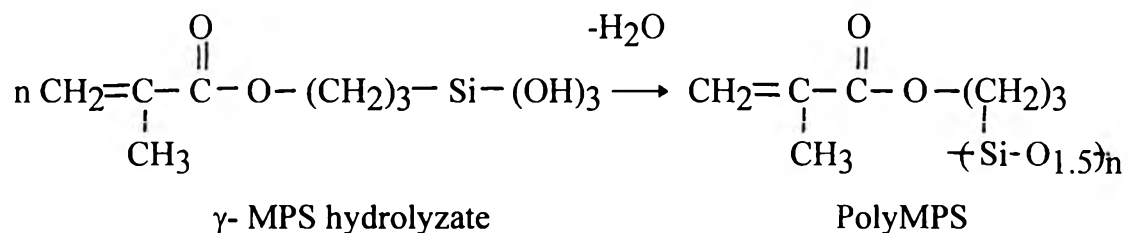


γ -MPS is hydrolyzed and condensed to polyMPS, as shown in the following reactions.

Hydrolysis



Condensation



The state of the coupling agent in aqueous solution is an essential factor in determining the mode of adsorption and consequently, the structure of the coupling agent on the surface. Some efforts have been made in the past to elucidate the structure of silane coupling agent in aqueous solution.

Koenig and Shih(1975) studied the hydrolysis and condensation of vinyltriethoxysilane and γ -methacryloxypropyltrimethoxysilane at 2% by weight using Laser Raman spectroscopy. They found that the silane quickly hydrolyzed to silanetriols and then slowly condensed to polysiloxanols.

Ishida and Koeing(1978) studied organosilanetriols by FTIR and Laser Raman spectroscopy. Ishida et. al.(1982) further studied the structure of amino-functional silanes in aqueous solution and in partially cured solid. They found that aminopropyltriethoxysilane exists as organosilanetriols in water at concentration below 0.15 % by weight.

Sprung and Guenther(1958) studied the hydrolysis of n-amytriethoxysilane and phenyltriethoxysilane in homogeneous solutions with acid and base catalysts. The mechanism of hydrolysis of alkoxy groups has been reported by Pohl and Osterholtz.(1985)

The present work is the study of the effect of sizing agents on the silanol condensation of γ -MPS in solution.

1.3 Sizing agents

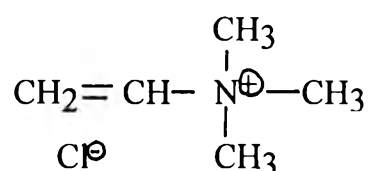
Industrially, silane coupling agent is not the only ingredient which is applied onto the glass fiber surface. There are other agents used for improving the properties of the glass surface such as film forming agent, lubricant, and antistatic agent. These agents are called 'sizing agents'. These agents, including silane coupling agent, are applied onto the fiber surface shortly after it is formed but before the composite fabrication. Typical composition of the mixture system is shown in Table 1. The role of silane coupling agents in the mixture system containing sizing agent is more complicated than the system with the silane coupling agent alone. However, the influence of sizing agents on the role of silane coupling agent is poorly understood. This work studied the effect of three sizing agents, an antistatic agent, a film forming agent, and a lubricant on the silanol condensation

Table 1 Typical composition of glass fiber sizing agents

Components	Concentrations(%)
Silane coupling agent	0.1-0.5
Antistatic agent	0.1-0.2
Film forming agent	1-5
Lubricant	0.1-0.2

1.3.1 Antistatic sizing agent

An antistatic agent is a chemical capable of reducing static charges generated on surfaces. Static charge buildup on plastic surface can cause various problems such as production obstruction, spark formation leading to possible explosions, and damage to integrated circuits in electronic equipment. Dissipation of static charge is normally achieved by decreasing the surface resistivity of the polymer by addition of antistatic agent at the level of 0.1- 2.0 % by weight [Sharma(1994)]. Antistatic agent is also used to solve this problem in the glass fiber production. It helps to improve the contact between the glass fiber surface and the polymer matrix. In the production of glass fiber for composite materials, quaternary ammonium compounds are widely used as the antistatic agent. In this work, vinyl trimethyl quaternary ammonium chloride(VTAC) was used as the antistatic agent in the model treating system. Its structure is shown below.

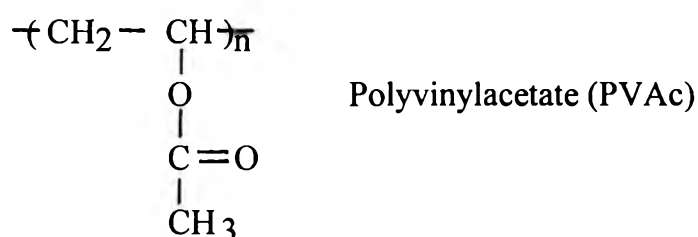


Vinyl trimethyl quaternary ammonium chloride

1.3.2 Film forming sizing agent

A film forming agent is added to the sizing agents to help form a protective film on the glass fiber. Polyvinylacetate(PVAc) is one of the widely used agents which is applied on the glass surface as a film former. The particles of polyvinylacetate coagulate to form a tough and clear continuous coating. This agent can protect the glass fiber surface and provide the

necessary flexibility. Polyvinylacetate molecules have 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 structure of polyvinylacetate(PVAc) is shown below.

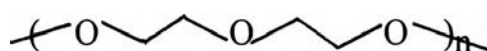


The effect of polyvinylacetate sizing agent on the γ -aminopropyltriethoxysilane (γ -APS) was discussed by Lacramp et. al. (1995). They studied the system containing 6% by weight of various polymers(sizing) with and without γ -APS. Polyvinylacetate is one of the system studied. The chemical reaction occurring in the mixture system was investigated. In the case of PVAc-based sizing, the glass transition temperature and the Young's modulus of this system increased with increasing drying time and with silane included in the system. These effects can be attributed to the remaining water in the PVAc film without silane, therefore, transesterification reaction between silanol groups of silane hydrolyzate and ester functional groups of PVAc was involved in the case of film based on γ -APS.

PVAc was used as a film forming agent in the present study.

1.3.3 Lubricating sizing agent

A lubricating agent is added to the sizing agents to reduce friction between the glass fiber surfaces. Polyethyleneglycol(PEG) is normally used as the lubricant in actual production of glass fiber. The structure of polyethyleneglycol 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.[Kulanuch(1996)]. PEG was used as a lubricating agent in this study.

Sizing agents are expected to influence silanol condensation in solution which in turn will effect the efficiency of silane coupling agent in promoting the adhesion between glass fiber surface and matrix polymer. It is therefore interesting to study the effect of sizing agents on the condensation of silane in solution.

1.4 Objective

The objective of the present work is to study the effects of sizing agents on the condensation of silane coupling agent in solution using FTIR and SEC.

The work is divided into 2 parts :

Part 1 : Antistatic sizing agent

Part 2 : Film former and lubricating sizing agent