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CONTROLLED INTERPHASES IN GLASS FIBER AND PARTICULATE REINFORCED POLYMERS: STRUCTURE OF SILANE COUPLING AGENTS IN SOLUTIONS AND ON SUBSTRATES

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ABSTRACT

The structure of silane coupling agents in solution and on solid substrate is reviewed with special emphasis on the fundamentals of structural development. Factors affecting the molecular weight, adsorption behavior, and chemical bond formation are discussed. Molecular aspects of the reinforcement mechanisms are discussed in relation to the interfacial bond formation. Effects of surface treatment on the rheological and hydrothermal properties of filled systems and composites are described.

G. Akovali (ed.), The Interfacial Interactions in Polymeric Composites, 169–199.

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1. Introduction to Composite Interfaces and Interphases

It is now well-recognized that the interface and interphase play an important role in the mechanical and physical properties of composite materials (1-9). The number of studies dealing with the characterization of interfaces and interphases and their influence on mechanical properties has increased dramatically over the past decade. Among many areas of composite interface studies, the fundamental understanding of the application of silane coupling agents has advanced substantially. This paper intends to describe the structure and role of silane coupling agents on glass fibers and particulate fillers. A special emphasis will be placed on the systematic description of the understanding and controlling of the structure of silanes.

The terms interface and interphase have been sometimes used interchangeably. However, an *interface* is a hypothetical molecular or atomic plane separating two dissimilar phases and is seldom associated with an actual material unless there is a bond passing through the separating plane and the structure differs from either of the phases. On the other hand, *interphase* is defined as an "interfacial region" whose properties are similar to, but distinguishably different from, the bulk properties. Thus, the interphase is associated with a finite thickness which depends upon the cause of the structural difference from the bulk. The thickness of the measured interphase also depends strongly on the characterization methods used despite studying the same interphase. Accordingly, one must be careful to mention the characterization methods whenever interphase thickness measurements are discussed. The definitions of the interface and interphase are schematically illustrated in Figure 1.

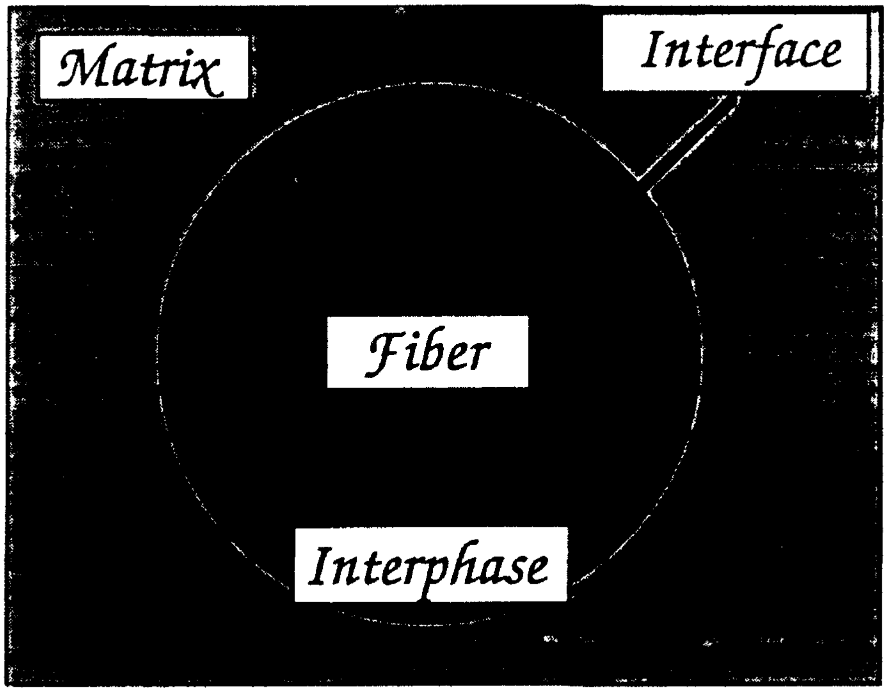


Figure 1. Conceptual drawing of interface and interphase in fiber reinforced composites.

The nature and thickness of the interphase are influenced by the substrate surface and its specific interaction with the matrix resin. Representative effects of the substrate surface are illustrated in Table 1.

Table 1. Effect of Substrate Surface on the Structure of Matrix Interphase

- Chemical Effects
    - ◊ Reaction with matrix
    - ◊ Catalytic activity
        - - Acceleration of polymerization
        - - Degradation of matrix
    - ◊ Catalyst poisoning
    - ◊ Selective reaction with a certain component
- Physicochemical Effects
    - ◊ Preferential adsorption of a catalyst
        - - Inhibition of cure
    - ◊ Diffusion of a surface treating agent
        - - Interpenetrating networks
    - ◊ Topochemical reaction
        - - Restriction of reactivity
- Physical Effects
    - ◊ Nucleation of crystallites
        - -transcrystallization
    - ◊ Chain packing
        - -epitaxial crystallization
    - ◊ Restriction of mobility
        - -molecular orientation
    - ◊ Preferential adsorption of non-reactive component

An interphase may possess a sharp or graded boundary, examples of which are listed in Table 2. For a sharp boundary, recognizing the filler/matrix interface or matrix interphase/matrix bulk is relatively straightforward. For a graded boundary, determining the thickness of the interphase is not possible unless either an average quantity or relative concentration reduction is defined to be the boundary of the interphase. Determination of the concentration profile thus becomes an important task to understand the structure of a graded interphase. A graded interphase is often useful for diffusing a stress concentration by avoiding a sudden change of material properties.

The concept of an interphase is well-established. Yet, it can only be defined through a collective description of many complex phenomena, and thus at the present time, no single explanation or approach exists which enables the complete understanding of the nature of any particular interphase. Therefore, it is essential to characterize the interphase using many characterization methods prior to attempting its structural control. If the interphase structure can be controlled, tailoring the mechanical and physical properties of a composite through the knowledge of the structure/property relationship becomes feasible. This systematic approach may be termed *interphase engineering*. It is the purpose of this article to discuss the principles of silane structure formation in solutions and on substrates rather than to present a summary of all published work in this field. Therefore, papers published from our laboratory will be reviewed whenever applicable, although there may be many other papers on the subject.

Table 2. Structure of Matrix Interphase

- Sharp Boundary
    - ◊ Epitaxial crystal
    - ◊ Transcrystal
    - ◊ Interfacial reaction with matrix
    - ◊ Totally incompatible filler/matrix combination
        - No surface treatment
- Graded Interphase Structure
    - ◊ Diffusion of coupling agent
        - Interpenetrating networks (IPN)
    - ◊ Preferential adsorption
    - ◊ Restricted mobility

2. Introduction to Silane Coupling Agents

2.1. Structure of Silanes

Silane coupling agents usually possess a dual functionality of the form, $YSiX_3$, where Y is the organofunctional group and X the hydrolyzable group. X is typically an alkoxy group and sometimes Cl. Some representative silanes are listed in Table 3. The structure of an organofunctional group is chosen so as to copolymerize with a thermosetting resin or to be compatible with a thermoplastic resin.

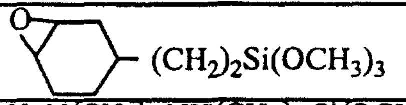
2.2. Hydrolysis Reactions of Silanes

Upon contact with water, the following reactions take place.

$$RSi(OR')_3 \xrightarrow{H_2O} RSi(OH)_3 + 3R'OH$$

The hydrolysis of the trialkoxy groups takes place in a stepwise fashion. As the first alkoxy group is hydrolyzed, the steric hindrance to the other two alkoxy groups decreases. It is expected that the final alkoxy group is easier to hydrolyze than the first alkoxy group. The hydrolysis of silanes must be carefully controlled to be effective. Ordinary neutral silanes form oily droplets upon mixing with water. Thus, the dissolution of the silane molecules into water is the kinetic limiting step. The formation of the first silanol group increases the solubility of the silane into water. However, it is not known whether the unhydrolyzed trialkoxysilane first dissolves into water with the alkoxy groups hydrolyzed in a stepwise fashion or if the formation of the first silanol group is the driving force for the silane to dissolve into water.

Table 3. Typical industrially used silane coupling agents

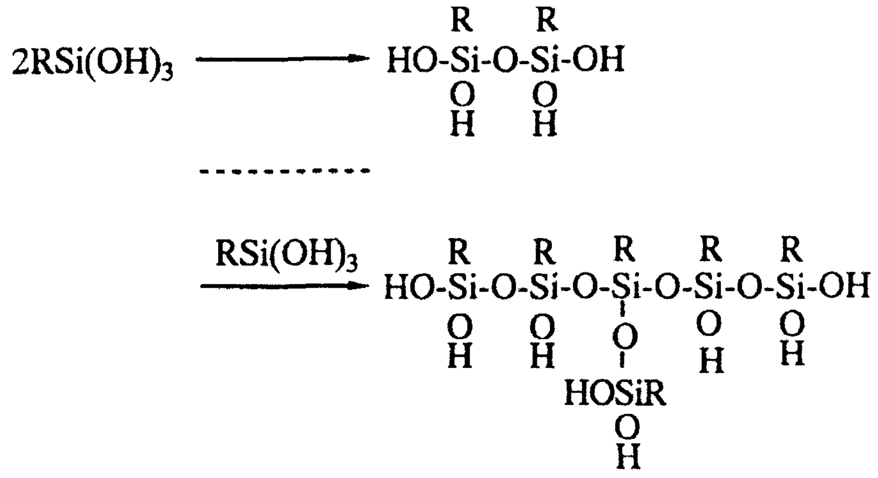
Organofunctional Group	Chemical Formula
Cationic styryl	$CH_2{=}CHC_6H_4CH_2NH(CH_2)_2NH(CH_2)_3Si(OCH_3)_3.HCl$
Chloropropyl	$Cl(CH_2)_3Si(OCH_3)_3$
Cycloapliphatic epoxide	 $(CH_2)_2Si(OCH_3)_3$
Diamine	$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$
Epoxy	 $CH_2CHCH_2O(CH_2)_3Si(OCH_3)_3$
Mercapto	$HS(CH_2)_3Si(OCH_3)_3$
Methacrylate	 $CH_2{=}C(CH_3){-}COO(CH_2)_3Si(OCH_3)_3$
Primary amine	$H_2N(CH_2)_3Si(OCH_3)_3$
Vinyl	$CH_2{=}CHSi(OCH_3)_3$

Usually, acidic water with a pH ranging from 3.0 to 4.0 is used to catalyze the hydrolysis reaction. However, a glycidoxy-functional (epoxy-functional) silane readily opens its oxane ring in this pH range. For this silane, pH 5-6 may be needed to prevent the ring opening reactions. These neutral silanes may need to be hydrolyzed for tens of minutes at room temperature for complete hydrolysis, provided that the concentration of the silane is relatively low.

For an aqueous alcohol solution and other organic solution, the situation changes due to homogeneous reactions. Because of this, a high concentration of silane in water changes its behavior after certain degree of hydrolysis due to the increased alcohol content produced as a byproduct of the reaction. Amino-functional silanes readily dissolve into water and their alkalinity catalyzes the hydrolysis. For this reason, aminosilanes utilize neutral water for hydrolysis. Hence, upon contact with water, the hydrolysis will immediately take place in a matter of seconds. Since silanols are unstable in an alkaline media, immediate condensation also follows. For a few percent by weight of neutral silane solution, nearly all of silane molecules are silanetriol. In contrast, the same concentration of an aminosilane yields a solution with nearly one hundred percent oligomeric silanes. The content of the monomeric aminosilanetriol dramatically increases if the silane concentration in water is a fraction of a percent (10).

2.3. Condensation Reactions of Silanes

Upon drying, or with time in solution, the silanol groups condense to form siloxane groups, SiOSi:



$$2RSi(OH)_3 \longrightarrow HO\text{-}\overset{R}{\underset{OH}{Si}}\text{-}O\text{-}\overset{R}{\underset{OH}{Si}}\text{-}OH$$

$$\xrightarrow{RSi(OH)_3} HO\text{-}\overset{R}{\underset{OH}{Si}}\text{-}O\text{-}\overset{R}{\underset{OH}{Si}}\text{-}O\text{-}\overset{R}{\underset{\underset{\underset{\underset{OH}{HOSiR}}{|}}{O}}{Si}}\text{-}O\text{-}\overset{R}{\underset{OH}{Si}}\text{-}O\text{-}\overset{R}{\underset{OH}{Si}}\text{-}OH$$

The simplified structures shown above are only to demonstrate that the molecular size increases by condensing with silanetriols and oligomeric silanes. The actual structures may be far more complex since the trifunctionality of the silane can lead to many possible structures. A similar condensation reaction takes place with the surface silanol and other hydroxyl groups of a filler and fiber, thus allowing the silane to bind chemically to the surface. This is a typical reaction path for a treatment using a prehydrolyzed silane solution. The rate of silanol condensation to siloxane depends strongly on the pH, concentration and temperature of the solution, but weakly on the structure of the organofunctional group.

The molecular weight of the condensed silane is also influenced by the same factors. Another factor that is important for the silane coupling effect is the molecular architecture of the siloxane networks. Caged structures and ladder structures are the extreme cases of the different siloxane structures (11,12). The solution pH, topochemical effects of the solid surface, the structure of the organofunctional group, and the concentration of the silane are all believed to influence siloxane structure, although no detailed study has yet been reported.

An indirect observation is shown in Figure 2 where γ-methacryloxypropyltrimethoxysilane (γ-MPS) is hydrolyzed and condensed in an aqueous alcohol solution in the absence of a filler (13). The solvents were evaporated at room temperature to simulate the typical treatment of a filler. The molecular weight was then measured by size exclusion chromatography as a function of time. When the solution was adjusted below pH 4.0, Figure 2 resulted showing a discrete increase of the molecular size until the column no longer separated individual species. On the other hand, the solution near neutral pH, as well as alkaline pH's, exhibited a quite different behavior. A monomeric species existed until the solvents were mostly evaporated and suddenly a large molecular weight species appeared as shown in Figure 3, unlike stepwise increase of the molecular weight in an acidic media. This may be an indication of a ladder-like structure or more open structure than the cage-like structure.

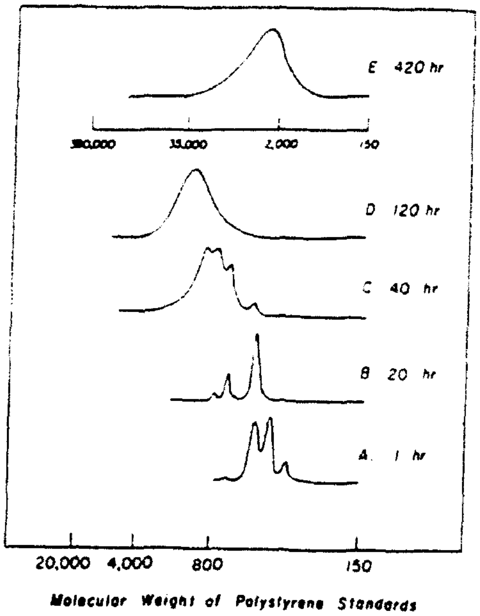


Figure 2 SEC chromatograms of the hydrolyzate of γ-MPS after the solution pH was adjusted to 3.6. Time from pH adjustment: (A) 1 h in solution, (B) 20 h during drying, (C) 40 h, dry, (D) 120 h, dry, (E) 420 h, dry.

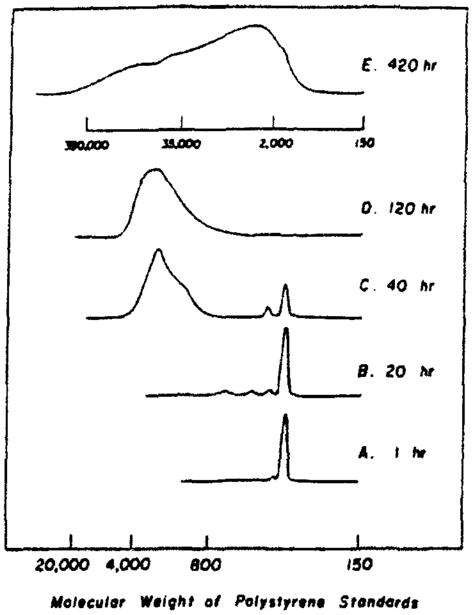
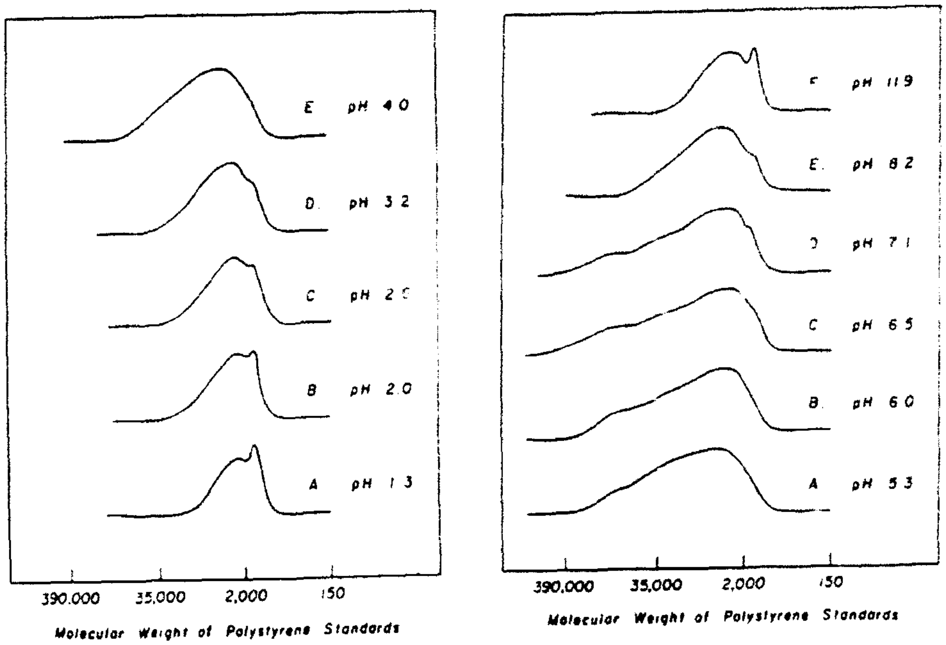


Figure 3 SEC chromatograms of the hydrolyzate of γ-MPS after the solution pH was adjusted to 6.9. Time from pH adjustment: (A) 1 h in solution, (B) 20 h during drying, (C) 40 h, dry, (D) 120 h, dry, (E) 420 h, dry.



A B

Figure 4 SEC chromatograms of the pH-adjusted hydrolyzate of γ-MPS. Figure 4A: (A) pH 1.3, (B) pH 2.0, (C) pH 2.6, (C) pH 3.2, (D) pH 4.0. Figure 4B: (A) pH 5.3, (B) pH 6.0, (C) pH 6.5, (D) pH 7.1, (E) pH 8.2, (F) pH 11.9.

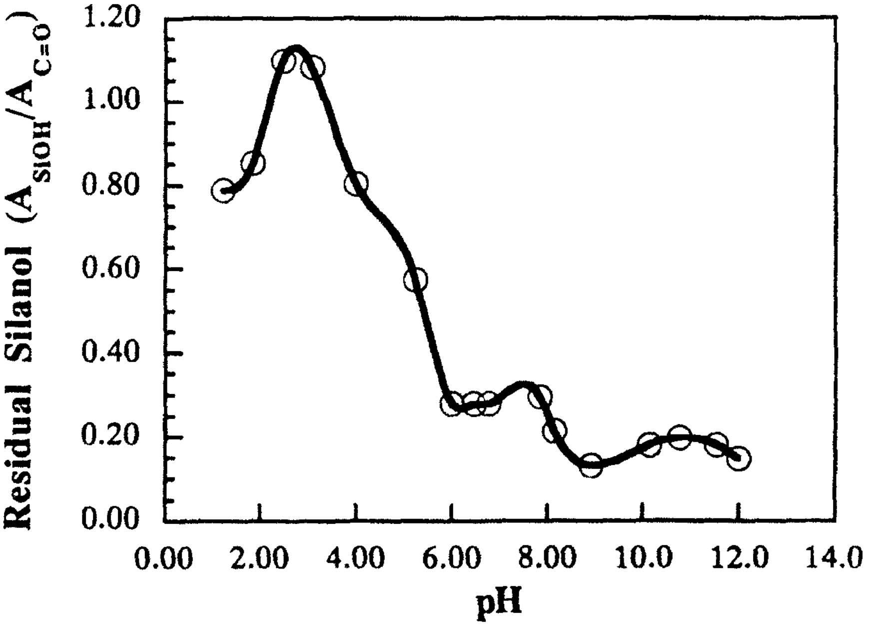


Figure 5. Stability of silanol as a function of the pH of the original solution from which the precipitates were prepared

A similar solution was prepared with varying pH's and the solvents evaporated. The molecular weight of the precipitated silane is illustrated in Figure 4 as a function of the solution pH. The average molecular weight of the silane strongly depended on the initial pH of the solution. In both acidic and alkaline pH's, the molecular weight was equivalent to a few thousand of the polystyrene standard. On the contrary, the neutral pH's yielded quite large molecules.

In summarizing the above two experiments, it is possible to suggest a change in the condensation mechanism around pH 4 to 5. The mechanisms in the neutral and alkaline pH's are similar, except that the silanol group in an alkaline media forms a silanolate, SiO^-, which is resistant to condensation. Thus as shown in Figure 4, small oligomers resulted at higher pH's. Similar structures can be observed on a solid surface due to the pH effect.

The stability of silanol depends highly on the pH of the environment. Figure 5 shows the amount of the residual silanol of the precipitated silane molecules from aqueous solutions which are adjusted to respective pH's. It shows that the silanol is most stable around pH 3 and the stability quickly decreases around pH 4-5 (13).

2.4. Silane Treating Solutions

2.4.1. Aqueous Treatment

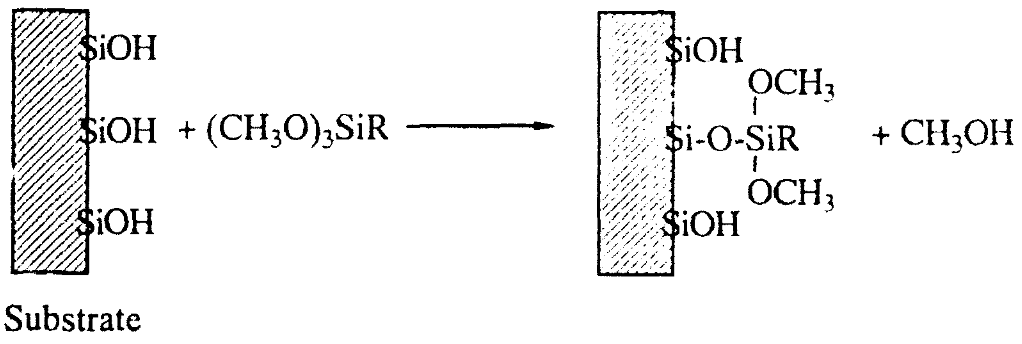
Ordinarily, silanes are applied to a substrate as monomeric, hydrolyzed species. The effectiveness of a silane is better when applied as monomeric silane rather than condensed oligomers. These silane films are very thin with a thickness on the order of several nanometers and, thus the strength of the film is rather insignificant in terms of the overall mechanical properties of a composite material. However, a silane primer is applied as a rather concentrated, condensed species, forming a film of a few hundred nanometers. Thus, the mechanical properties of the film itself can contribute to the composite properties. For this type of silane primer as well as the structure of silane on a solid surface, consideration of a kinetic effect and a thermodynamic effect is very important.

For example, an aminofunctional silane can condense almost instantaneously after hydrolysis due to the high pH of the amine group, leading to a kinetically controlled structure which is thermodynamically unequilibrated. Provided that a sufficiently high concentration was used, the solution turns into a gel. With time, in the presence of water, the catalytic action of the amine reorganizes the siloxane structure by rehydration and condensation reactions, and redissolves the silane. Thus, the time factor is also important when silane structures are to be studied.

When an aqueous solution of a silane is to be applied, the concentration used is on the order of a fraction of a percent. In this range, a concentration exists at which isolated silane monomers can form associated molecules through hydrogen bonding of the silanol groups. This concentration may be termed *onset concentration of association* (14). The associated silanes adsorb differently from the monomeric silanes as described in the following section. Furthermore, the amount of physically adsorbed silanes, also discussed in the following section, vary depending on the concentration of the silane treating solution. The solution with a concentration lower than the onset concentration of association yields less physisorbed silanes by decreasing the defect of the adsorbed layers.

2.4.2. Integral Blends

In addition to being used as a substrate pretreatment prior to mixing with a matrix resin, silanes can also be used as *integral blends*. This method eliminates the steps of pretreatment, drying, and repulverization by incorporating the unhydrolyzed silane directly into an uncured resin. However, the integral blending method usually requires a greater amount of silane than direct treatment due to its lower efficiency of silane utilization. The integral technique relies on the preferential adsorption of the silane onto the substrate. Immediately following blending, many of the reactive groups may remain completely or partially unhydrolyzed. Hydrolysis may proceed with time if sufficient water is available from either the resin or the substrate surface. An additional source of water is the adsorbed water on the substrate surface. Direct chemical reaction with the substrate can also proceed via the following exchange reaction.



Catalysts 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. A similar situation is also observed when a filler is heated in a silane solution of a hydrophobic solvent such as toluene.

3. Structure of Silane on Solid Surfaces

3.1. Adsorption and Deposition of Silanes

The adsorption process of a silane molecule onto a substrate surface is influenced by the number of functional groups which are capable of strongly interacting with the surface via hydrogen or ionic bonding. Although it is difficult to distinguish it from the adsorption phenomenon, deposition of silane molecule will occur when the solvent is a poor solvent for the silane monomer or oligomers. It is important to note that the solubility changes as a function of the silane molecular weight. For example, water dissolves the silanetriol of the methacryl-functional silane (γ-MPS). However, the oligomers greater than the trimer precipitate from the solution. *Adsorption* is related to the active participation of the adsorbent toward the substrate usually with a special mechanism to anchor the molecule to the surface. Studies dealing with the adsorption phenomenon of a silane coupling agent have been reported by Nishiyama et al. (15,16).

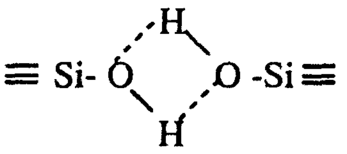
On the other hand, *deposition* is the process in which the adsorbent molecule is forced out of the solution and onto the substrate surface. Deposition and orientation of methacryl-functional silanes have also been studied as a function of the length of the aliphatic spacer group (17). When the solubility of the silane is poor or has become poor by the structural or concentration changes due to evaporation of the solvent, deposition may take place. Although both of these processes lead to the accumulation of silane layers on the substrate surface, it is important to recognize that the molecular architecture of the condensed silane is different for each situation.

The orientation of a silane molecule influences the molecular architecture of the condensed silane and the chemical reactivity of the silane with the substrate surface as well as the matrix. Silanes usually possess multiple sites with quite different electronegativity or hydrophilicity on one molecule. The pH of the solution influences the state of charge density on the functional group as well as the substrate surface. Hence, the pH of the solution strongly influences the orientation of the silane either attracting or repelling a certain portion of the silane molecule. Under ordinary treatment conditions, silanols are believed to adsorb onto the hydroxyl-covered surface. However, if the silane molecule possesses another ionic portion that can compete with this process, it is possible for the molecule to adsorb upside-down (3).

3.2. Mode of Adsorption

Silanes adsorb onto solid surfaces differently depending upon the roughness of the surface with respect to the dimension of the silane molecules. For example, a high surface area silica typically adsorbs a few monomolecular layer equivalents whereas a smooth surface such as glass fibers adsorb many layers. The thickness of the silane on the glass fiber increases monotonously until the onset concentration of association at which the hydrolyzed silane molecules start forming hydrogen bonded species (14). Thus, the orientation of the associated silanes is disturbed and the thickness buildup slows. The disturbance of the packing is schematically shown in Figure 6.

The silane molecules tend to adsorb head-to-head in an extreme case where relatively rigid organofunctional groups such as cyclohexyl and phenyl groups are on the silane molecule. The crystal structure of cyclohexylsilanetriol exemplifies this extreme case (18). It is these silanes that form relatively stable silanetriol crystals due to good packing. In these crystals, silanols are hydrogen bonded in a bifurcated manner as shown below, meaning that the crystal possesses a rather disorganized hydrogen bonding structure.



The packing of the silane molecules in the coupling agent layers strongly depends on the structure of the organofunctionality. This trend of organized packing relaxes as the flexibility of the organofunctional group increases, resulting in an increased free volume. An important ramification of this statement is that the degree of penetration of the matrix molecules into the coupling agent layers is highly influenced by the molecular packing. It is interesting to note that many useful coupling agents belong to this flexible organofunctional type.

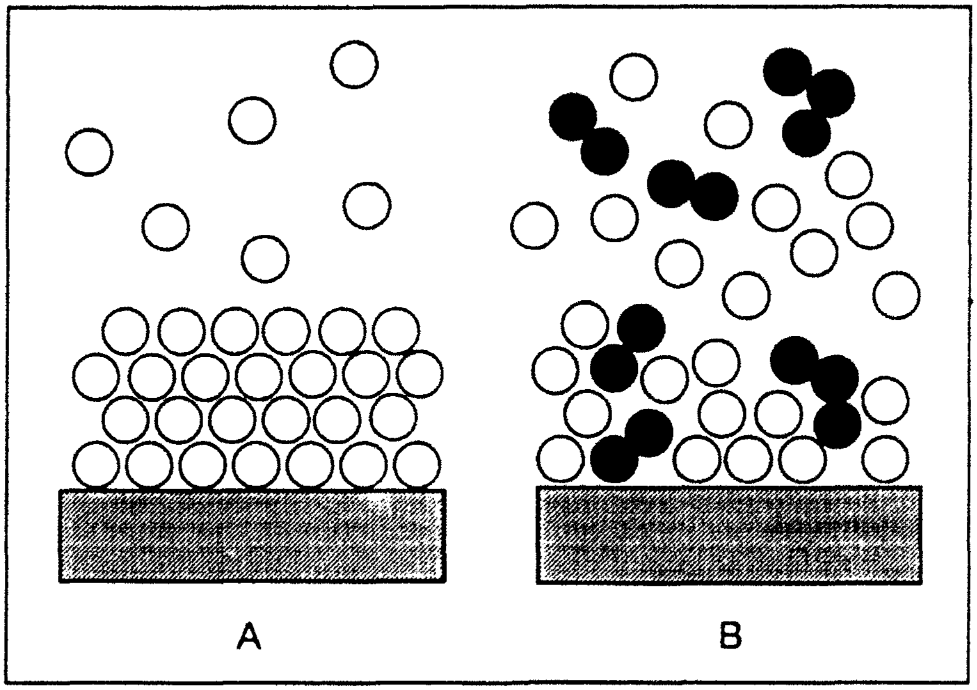


Figure 6. Schematic representation of the adsorption of silane coupling agent molecules onto glass fiber surface. A) The silane solution is a low concentration below the onset of association, and B) the silane solution is a high concentration above the onset of association. Open circle indicates isolated silanes whereas the closed circle denotes hydrogen bonded or oligomeric silanes. Note the disturbance in packing is created at a high concentration.

3.3. Physisorbed and Chemisorbed Silanes

3.3.1. Chemisorbed Silanes

Silanes can form many structures due to their tri-functional condensation mechanism. Monomeric silanetriol can directly react with the surface of a filler and fiber. Silane oligomers can also react with the surface as some unreacted silanol groups remain in the oligomers. The notion of physisorbed and chemisorbed silanes is used based on the reaction with the substrate surface. *Chemisorbed silanes* are the ones that possess at least one covalent bond with the substrate. Within the chemisorbed silanes, further distinction may be made between *tightly chemisorbed silanes* and *loosely chemisorbed silanes*. Tightly chemisorbed silanes use many silanol groups for covalent bonding with the substrate surface whereas the loosely chemisorbed silanes use only a few silanols to bond to the surface. An extreme case of this loosely chemisorbed silane is the oligomers or polymers with one covalent bond to anchor the entire molecule to the surface. Both silanes do not desorb when washed with an anhydrous organic solvent.

3.3.2. Interfacial Bond Formation

Although chemical bonding of a silane with the substrate surface is expected from the knowledge of the traditional chemistry, few direct observations of the interfacial bonds have been reported. This is because the interfacial bond, $Si_{substrate}$-O-Si_{silane} bond, is very similar in nature to the $Si_{substrate}$-O-$Si_{substrate}$ and Si_{silane}-O-Si_{silane}. Using a lead oxide as a model filler, this difficulty can be circumvented since the interfacial bond is now a unique Pb-O-Si against the Pb-O-Pb bond of the substrate and the Si-O-Si bond of the silane. Figure 7 shows the infrared spectrum of the interfacial bond as a function of the surface coverage of the silane from one fifth of a monolayer to several monolayer equivalents (19). Notice that the intensity reached the maximum at the third spectrum where the coverage is approximately a monomolecular equivalent. A theoretical calculation of the Pb-O-Si frequency using a harmonic oscillator also indicates a good agreement with the observed frequency. Furthermore, this band was not observed either in the silane condensate or in the substrate as the absorbance contribution of the organic functionality and the substrate have been subtracted.

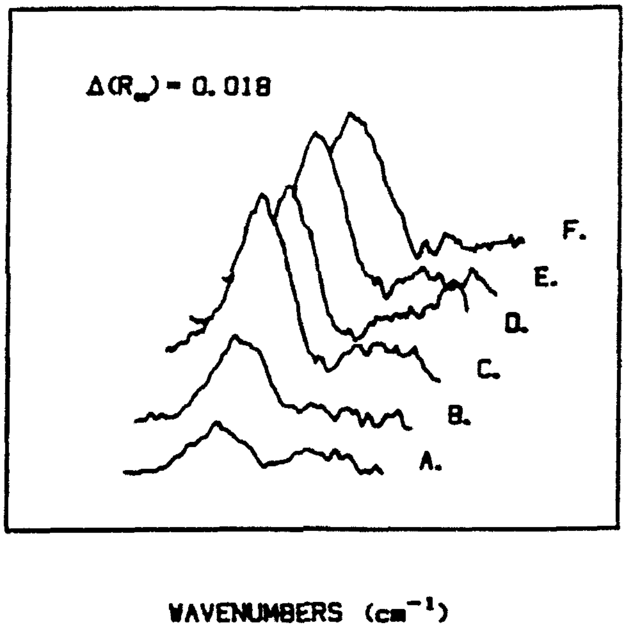


Figure 7. Diffuse reflectance infrared difference spectra from 100 to 910 cm^{-1} of only the plumbosiloxane contribution near 965 cm^{-1}. Spectra were obtained using the digital subtraction method and are not scale expanded. The adsorbate concentrations and measured peak to baseline intensity differences in Kubelka-Munk units are respectively, (A) 0.40 mg/m^2 and 0.005, (B) 0.80 mg/m^2 and 0.009, (C) 1.50 mg/m^2 and 0.018, (D) 2.00 mg/m^2 and 0.015, (E) 4.00 mg/m^2 and 0.016, (F) 6.00 mg/m^2 and 0.014.

In addition to the interfacial bonds, a quantitative observation of the inter-silane bonds can be made. Figure 8 exhibits the intensity of the inter-silane bonds as a function of the surface coverage (20). Two observations are especially noteworthy. First, the intensity of the inter-silane bonds was near-zero until certain surface coverage was reached despite the presence of the silane could be observed. This is an indication that the silane did not adsorb as an island but rather adsorbed separately in a random fashion so that the inter-silane distance is too far to form a siloxane bond. As the surface coverage increases, the distance becomes sufficiently short to form the siloxane bond. The second observation is the presence of a plateau near the surface coverage of the 0.5 mg silane/g substrate. If the silane molecules are forming the second and higher layers randomly, instead of first completing the bottom layer and then the second layer, the intensity increase is expected to be monotonous. It seems that during the plateau, the same process as the first layer is repeated. The adsorption is random in position thus inter-silane bond formation is retarded. As the coverage of the second layer becomes high, the inter-silane bonds again started forming. This process may be repeated for the third layer and beyond. As the number of layers increases, the registration of the orientation becomes more disarrayed, and it becomes more difficult to observe the plateau discussed above. However, a much smoother surface like mica showed the same phenomenon to the third and possibly the fourth layers (21). Understanding the mode of surface coverage is important because the interaction of the treated filler with the matrix is strongly influenced by the way the silane covers the surface.

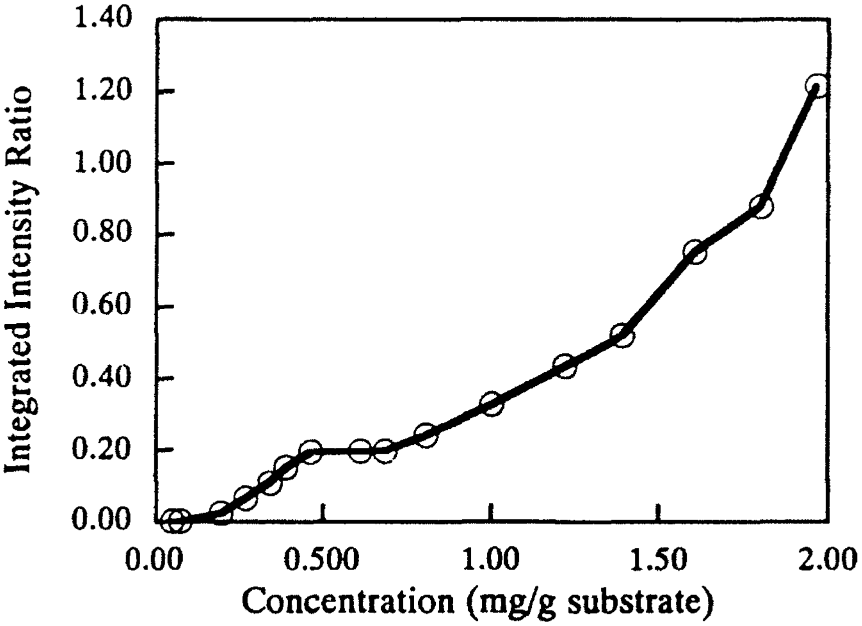


Figure 8. Intensities of the infrared band due to the intersilane bonds as a function of the amount of silane on a substrate

3.3.3. Physisorbed Silanes

Those silanes which do not possess any covalent bonds with the substrate surface are termed *physisorbed silanes*. The physisorbed silanes may be small oligomers or large polymers. The unreacted silanol groups on the molecules must be sterically hindered such that they are not readily available for condensation with the substrate surface or with the chemisorbed silane. Quite often, oligomers take the form of cyclic silanes where concentration of the unreacted silanol group in the molecule is low despite the small molecular size. A perfect cubical octamer for example does not have any silanol groups although the molecular weight is less than a few thousand.

These physisorbed oligomers can be easily distinguished by washing with an organic solvent. However, high molecular weight physisorbed silanes are not as easily distinguished as the small oligomers since the rate of desorption is much slower than for the small oligomers. Many silanol groups, though they may be sterically hindered for covalent bond formation, can form hydrogen bonds with the substrate surface or chemisorbed silanes. These hydrogen bonded silanols are in a dynamic equilibrium in terms of their interaction with the substrate. Thus, when a driving force to desorb exists, the hydrogen bonds are gradually broken and, with time, even a large physisorbed molecule desorbs. If a small amount of water exists in the solvent used, water can hydrolyze the siloxane bonds that were used to chemisorb the silane molecule to the substrate. 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 silane molecules tends to be cyclic oligomers, and their molecular weight strongly depends on the pH of the filler (22). The pH of the filler is conveniently measured by the slurry pH method where a certain amount of filler is boiled in water for a specified time and the pH of the liquid measured. This method provides composite information about both the solubility of the selective surface components as well as the concentration of the surface acid/alkaline centers. This slurry pH directly relates to the molecular weight of the condensed silane rather than the concentration of the surface acid centers alone, since the solubility of the surface species and the concentration of acid centers both contribute to the pH of the silane solution that is on the filler surface.

As in the case of the aforementioned simulation shown in Figure 4, the molecular weights of the physisorbed silanes are small at both acidic and alkaline pH's whereas they are large near neutral pH's (23). In an acidic media, the silane oligomers are small because of the tendency to form cage-like molecules while in an alkaline media the silane oligomers are small due to the termination of the molecular weight growth by the silanolate group. Thus, the molecular architecture of the siloxane chains in these oligomers with similar molecular weight is different. Since the diffusion of the physisorbed silane molecules into the matrix resin depends on the molecular weight when a silane treated filler or fiber is mixed with the resin, it is essential to understand the nature of the physisorbed silane. The physisorbed silanes often contain residual silanol groups and these groups bridge physisorbed molecules via hydrogen bonding. Thus a desorption process is dependent not only on the molecular weight but also on the molecular architecture of the physisorbed silane.

Once the basic molecular architectural trend is predestined by the effect of the substrate surface, a heat treatment only accelerates the completion of the trend rather than creating a new class of structure (22). Figure 9 and 10 shows SEC chromatograms of γ-MPS hydrolyzates collected from the surface of a filler and from the precipitate of a silane solution without a filler. Both chromatograms of the initial samples are similar in the molecular weight and its distribution. However, after a mild heat treatment at 80 °C for 10 hr, the silane from the filler surface stays almost the same size whereas the silane from the precipitate polymerized to a size such that it can no longer dissolve in the tetrahydrofuran (THF) carrier liquid. The peak near the molecular weight of 300 may be an additive present in the initial silane.

Consequently, if the molecular architecture of the siloxane networks needs to be changed, it is necessary to change the solution pH of the silane, treat the filler by an acid or alkaline material to control the slurry pH, or add another silane which has different tendency toward forming siloxane networks. For example, a silane with a flexible organofunctional group such as γ-MPS tends to form a cyclic structure wherein a rigid functional group leads to a more open structure. Hence, if a larger molecular weight γ-MPS condensate is desired, it can be mixed with a rigid silane like phenyltrimethoxysilane or vinyltrimethoxysilane. The molecular weight changes for mixed silane systems are plotted in Figure 11 where 10 mol % of the second silane has been added (22). It seems that dilution of the organofunctional group by the second silane does not grossly affect the effectiveness of the first silane so long as the composition of the second silane does not dominate. Localization of silane near the substrate surface can be achieved either by improving chemical bonding of the silane to the substrate or by reducing the solubility to the matrix by increased molecular weight.

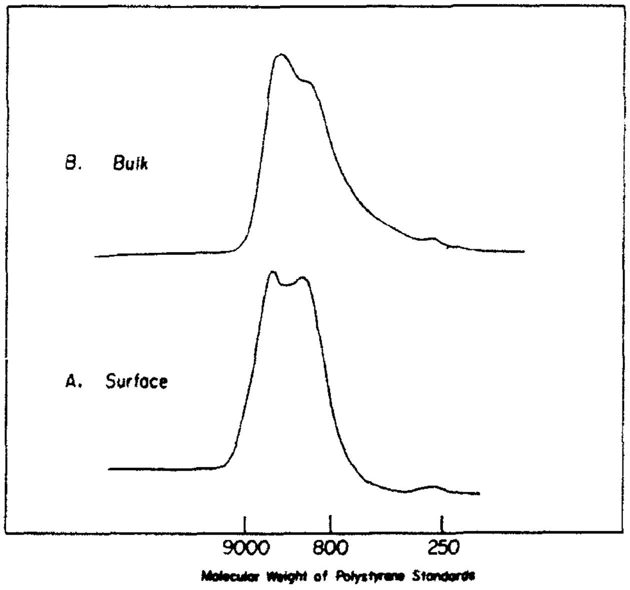


Figure 9. SEC chromatograms of the condensates of γ-MPS: (A) extracted from the surface of particulate clay, (B) dried in bulk.

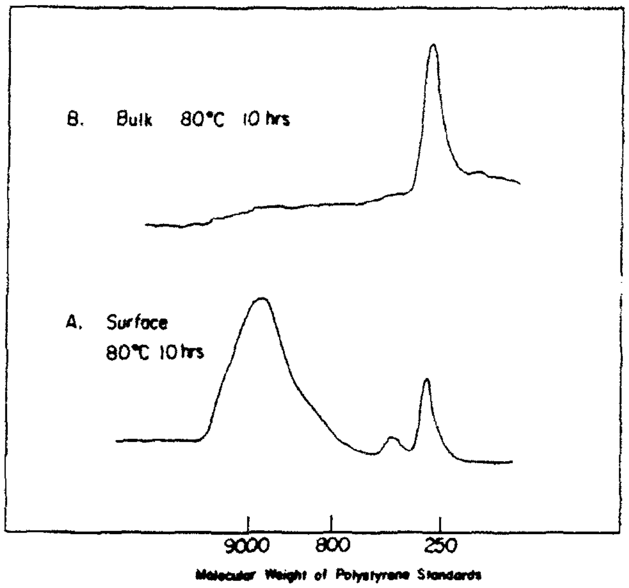


Figure 10. SEC chromatograms of the silane shown in Figure 9 except that the condensates were heat treated at 80^{o} C for 10 h.

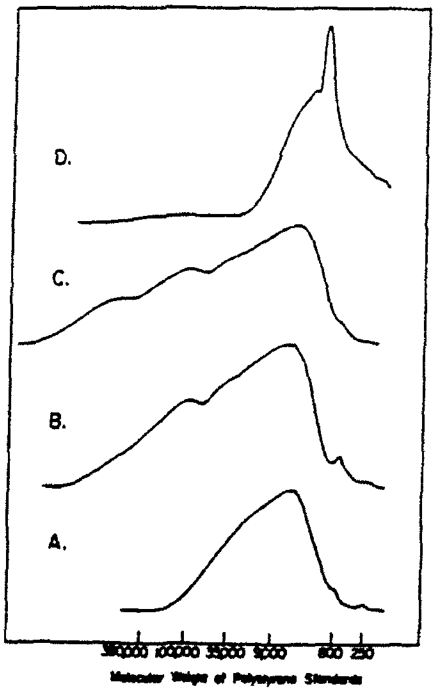


Figure 11. SEC chromatograms of of the bulk hydrolyzate of γ-MPS containing 10 mol % of a second species and heated at 80o C for 85 h: (A) 100 mol % γ-MPS, (B) with 10 mol % tetramethoxysilane, (C) with 10 mol % vinyltrimethoxysilane, (D) with 10 mol % isopropyltridioctylpyrophosphato-titanate.

3.3.4. Mechanical Properties of the Silane Interphase

At the present time, no *in-situ* measurement of the mechanical properties across an interphase containing physisorbed silane has been made. However, a simulation of the mechanical properties can be made by preparing copolymers of precipitated silane oligomers with a matrix resin. Figures 12 and 13 show the flexural modulus and the flexural strength of the copolymers of γ-MPS and unsaturated isophthalic type polyester resin as a function of the silane concentration (24). Beyond 50 % silane content, phase separation was observed and thus excluded from the study since a valid comparison could not be made. However, in reality, regions with such compositions do exist and indeed the phase separated area might be observed. Phase separation is also observed with the copolymers of γ-aminopropyltriethoxysilane (γ-APS) and an epoxy resin (diglycidylether of bisphenol-A) (25). The flexural modulus of the γ-MPS precipitate/polyester copolymers slightly increased until 20 % by weight silane and decreased beyond this composition. On the other hand, the flexural strength monotonously decreases at all silane compositions. This is a typical behavior of anti-plasticization. It is interesting to note that for the γ-MPS/unsaturated polyester, any region with physisorbed silane is mechanically weaker than the bulk matrix.

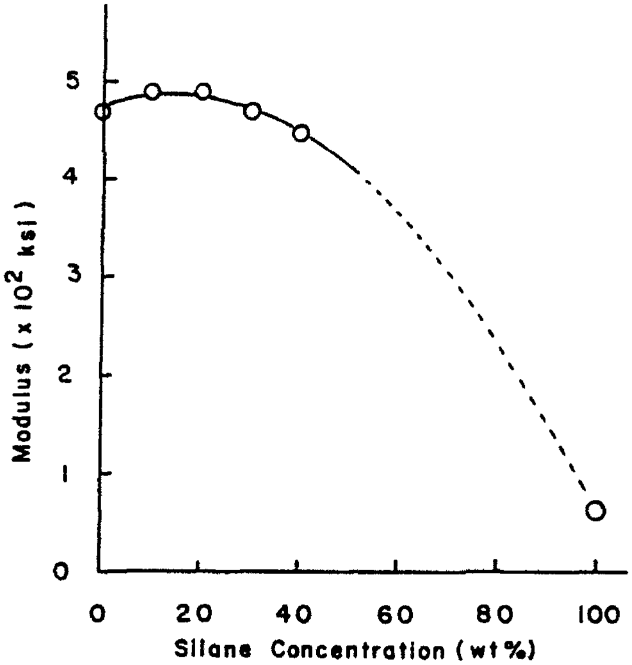


Figure 12. Flexural modulus of the copolymers of the precipitates of γ-MPS hydrolyzates and unsaturated polyester resin.

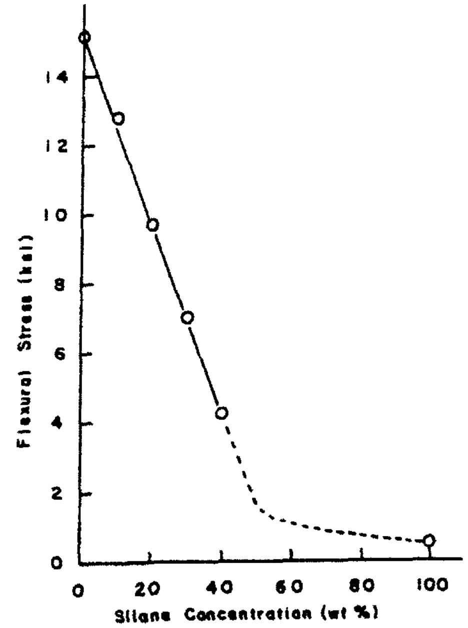


Figure 13. Flexural strength of the copolymers of the precipitates of γ-MPS hydrolyzates and unsaturated polyester resin.

Provided that it is overly simplistic, a conceptual mechanical property profile across the interphase is schematically illustrated in Figure 14 using the expected diffusion of the silane and the observed mechanical properties of the materials with various compositions. A mechanically weak portion in the diffusion region of the physisorbed silane is illustrated and the gradual increase of the strength over distance to the bulk matrix is also incorporated. Thus, if the physisorbed silanes are removed from the treated reinforcements, stronger composite materials can be manufactured. Indeed, such observations have been reported (26,27).

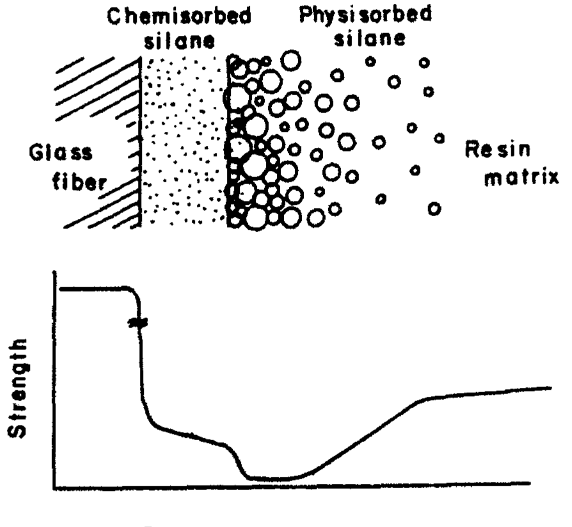


Figure 14. Conceptual mechanical property profile across the glass fiber/matrix interface.

4. Structure of the Silane/Matrix Interphase

4.1. Copolymer Formation with the Matrix Resin

The chemical reaction of the organofunctional group and the matrix is, in principle, the same as any other organic chemistry. However, the availability of the organofunctional group may be hindered if the silanes are tightly packed. Restricted molecular mobility, including the preferential interaction with the substrate surface, reduces the reactivity of the organofunctional groups. Due to the wide distribution of possible structures of the silane molecules in the silane layers, a systematic study of the silane/matrix reactivity is very difficult, although some attempts as follows have been made. Figures 15 and 16 show NMR $T_{1\rho}$ relaxation measurements of the aminosilane/epoxy copolymers at different silane contents (25). The different slopes of each carbon relaxation process, and thus different $T_{1\rho}$ values, indicate that the system is phase separated. However, the composition shown in figure 16 shows the same $T_{1\rho}$ values for all carbon atoms, suggesting that the system is homogeneous. The heterogeneity detected by the NMR method is said to be smaller than 1 nm in size.

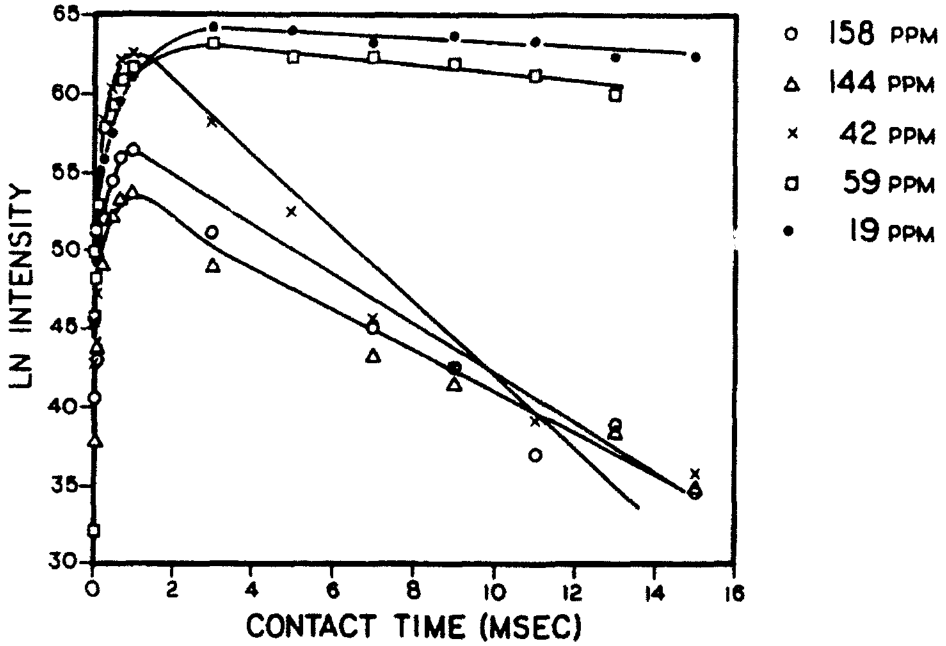


Figure 14. $T_{1\rho}$ measurements of the copolymer of 60 mol % γ-aminopropyltriethoxysilane and 40 mol % epoxy.

In spite of the altered reactivities of surface species, the general trend of copolymerization still holds. Thus, it would be helpful to know the copolymerization parameters, r and Q factors, of the organofunctional group and the matrix functional group. Depending on the r and Q values, the silane and the matrix interphase may form an alternating copolymer or terminal reaction, leading to a quite different interphase.

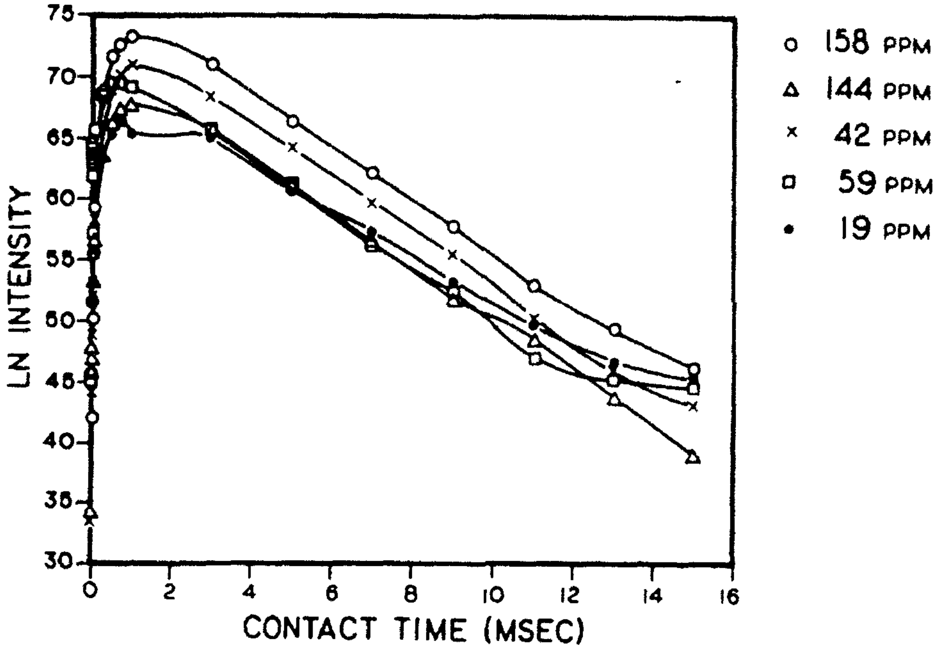


Figure 15. $T_{1\rho}$ measurements of the copolymer of 30 mol % γ-aminopropyltriethoxysilane and 70 mol % epoxy.

5. Reinforcement Mechanisms

5.1. Various Reinforcement Theories

Historically, many reinforcement theories have been proposed. Those include the chemical bonding theory (28), restrained layer theory (29), deformable layer theory (30), and coefficient friction theory (31). However, only the chemical bonding theory could sufficiently explain the observed results. However, the chemical bonding theory alone is not adequate to explain the necessity of more than a monomolecular equivalent of silane for optimum composite strength. Thus, this concept is coupled with interpenetrating network theory (31,32). These theories have been developed primarily for thermosetting resin composites. Thermoplastic-matrix composites rely on different mechanisms.

If no chemical bonds exist, as is often the case in thermoplastic-matrix composites, it is helpful to have a hydrophobic matrix or semicrystalline matrix to reduce the number of water molecules diffusing to the fiber/matrix interface. It is believed that isolated water molecules are not as harmful in causing permanent damage to the composite properties as the condensed water. Even isolated water molecules can act as a plasticizer and reduce the strength of the matrix, although such property changes are often recoverable upon drying. This is in contrast to the interfacial damage caused by the condensed water where an enormous osmotic pressure causes debonding at the fiber/matrix interface.

5.2. Concentration of Interfacial Bonds

It is interesting to consider the minimum number of interfacial bonds which is necessary to provide sufficient composite strength. Very few papers are available on this subject. Figure 17 shows the strength of a composite with coupling agents specially designed to evaluate the number of interfacial bonds (33). A methacryl-functional silane is copolymerized with styrene in different concentrations in order to vary the average molecular weight, Mn, of the inter-pendant groups. The flexural strengths of the dry and wet composites are plotted as a function of the Mn. Provided that this is not exact evaluation of the interfacial bond density, qualitative information can still be obtained. Both the dry and wet flexural strengths of the composite do not markedly change until the Mn reaches approximately 1000. The dry strength gradually reduces as the Mn increases implying that compatibility alone can provide substantial dry strength. On the other hand, the wet strength decreases suddenly beyond Mn = 1000. Thus, chemical bonds are essential to provide permanence of the bond in a humid environment.

Chemical bonds can maintain bonding even in the presence of small hydrophilic molecules such as water and alcohol which compete for the hydrophilic reinforcement surface with the silane. Physical bonds including van der Waals' force, ionic bonds, and acid-base interactions are quite adequate to provide good dry strength but these effects can yield misleading results if the wet strength is also of interest.

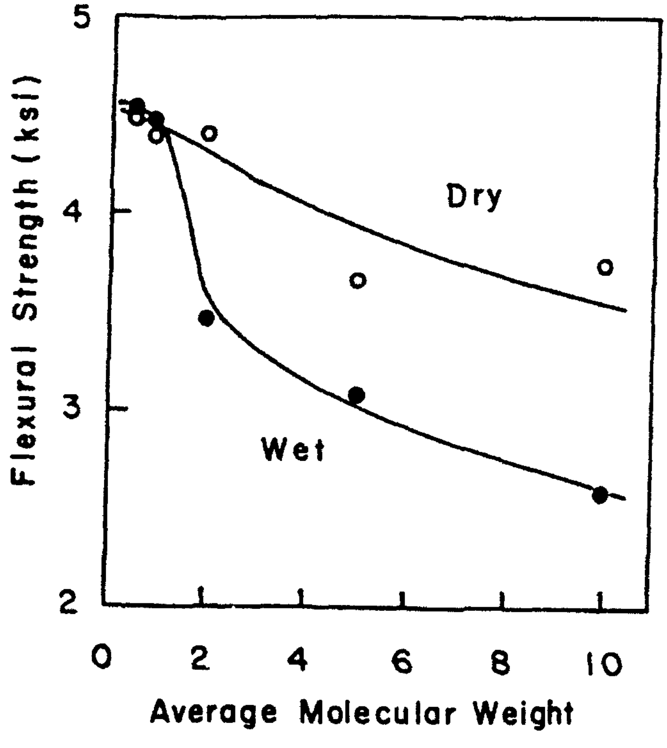


Figure 17. Flexural strength of glass cloth reinforced polystyrene with polymeric silane-treated glass: the silane to styrene ratio was varied so that the molecular weight of the polystyrene between two silane molecules become from 500 to 10,000 as shown as average molecular weight.

5.3. Adhesion of Thermoplastics to Substrates

Another adhesion mechanism for thermoplastic-matrix composites is the formation of transcrystalline layers around the reinforcement fibers. A transcrystal is a collection of columnar crystals growing transverse to the fiber axis. When a massive nucleation at the fiber surface occurs, the initial spherulitic crystals soon touch one another leaving only the direction transverse to the fiber axis to grow. This form of morphology is considered useful for the adhesion of a thermoplastic resin to the reinforcement fibers. However, the improved adhesion might be offset by the residual interfacial stress caused by the crystallization shrinkage. At the present time, the overall benefit of the transcrystalline morphology to composite properties is therefore poorly understood, although there are some papers showing the benefits of this type of morphology to the mechanical properties of composite materials.

Transcrystals can be formed by many methods as long as massive nucleation at the fiber surface is promoted. Some of those methods include an applied stress, epitaxial crystallization, coating of the fiber by a nucleating agent or liquid crystalline material. All these variations complicate the study. It is thus important to consider the thermodynamics of the interphase. Until recently, few quantitative studies of transcrystallization have been reported due to the difficulty in applying the heterogeneous nucleation theory. Heterogeneous nucleation theory allows one to study the interfacial energy difference function, $\Delta\sigma$, of the fiber/matrix interface by measuring the growth rate of the transcrystal layer and the nucleation rate. It is straightforward to measure the growth rate of the transcrystal with many composite systems. However, determination of nucleation rate is very difficult, especially for reinforcements such as carbon fibers. Even for transparent fibers, a massive appearance of nuclei makes such measurements tedious. Furthermore, the nucleation rate is thermal history dependent. For these reasons, few of the papers dealing with transcrystals reported $\Delta\sigma$ values. Recently, the induction time approach has been proposed as a new method to study transcrystallization (34,35). When an isothermal heterogeneous crystal growth takes place, a threshold period exists when the formation and remelting of the precursors of nuclei takes place. This threshold period is called the induction time, t_i. The rate of nucleation, I, is inversely proportional to the induction time, and thus the following relationship exists.

$$I \cdot t_i = C \text{ (constant)}$$

By using t_i, which is determined from the crystal growth kinetics, one can eliminate the use of I, an aforementioned difficult quantity to measure. At the present time, no quantitative study of the effect of silane structures on the transcrystal formation has been reported.

6. Effect of Silanes on the Rheological Properties of Composites

Although the rheology of silane-treated filled systems has been reported (36-38), few reports deal with the silane structure/rheology correlation.

The viscosity of a filled system is usually much higher than a non-filled system mainly due to the formation of filler aggregates. The aggregated filler shows a higher apparent filler fraction, ϕ_a, than the true filler fraction, ϕ, because the interstices of the fillers are not easily accessible space for the resin to flow. The viscosity is a nonlinear function of the filler fraction, and the viscosity increases much more rapidly at higher filler fractions, especially near the closest packing fraction, ϕ_m. A drastic 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 extensional force which mechanically separate the aggregates. The efficiency of the separation depends on the deformation rate. An alternative method is to change the surface energetics of the filler so that the filler/matrix interaction force overcomes the aggregation force.

The aggregation force might be due to the bridging effect of water molecules, direct hydrogen bonding of the surface hydroxyl groups, or ionic interactions. All of these effects can be reduced by treating the filler surface with silane coupling agents. Silanes can compete for, and react with, the surface hydroxyl groups and cover the filler with organo-functional groups. If the organo-functional group has a hydrophilic group, it tends to bend toward the hydrophilic filler surface and hence to expose the hydrophobic portion of the group. Since the van der Waals' 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.

In addition to the effects caused by the chemically bound silanes, a physisorbed silane can further reduce the viscosity. A silicon fluid is a good lubricant or a release agent. It has been previously discussed that a filler surface tends to produce cyclic oligomers of varying molecular sizes. An acidic or alkaline filler especially produces silane oligomers with a molecular weight of a few thousand. The amount of physisorbed silane varies depending on the concentration of the silane treating solution. In general, the higher the concentration of the silane in the treating solution, the more the physisorbed silane. This is especially true in the treatment method used for particulate fillers. Fillers tend to form a cake if a slurry of the filler/silane solution was dried. In order to avoid this additional processing, a treatment method termed an integral blend is adopted where a rather concentrated alcohol aqueous solution of a silane is sprayed onto a tumbling filer. Thus, the filler does not completely wet and immerse itself in the silane solution.

A mixture of a silane-pretreated filler and a polymer exhibits complex viscosity behavior. In addition to the breakup of agglomerates, silanes can interact physically and chemically with the polymer matrix. A reactive silane, such as an azide -functional silane, can form chemical bonds with aliphatic polymers and crosslink the polymer chain forming a matrix interphase around the filler. Polymer melts are usually kept at elevated temperatures and thus ordinarily unreactive silanes can form bonds with the polymer. Polymers also cleave, forming reactive polymeric free radical chain ends. These chain ends can graft onto silanes. Thus, the viscosity increases, counteracting the viscosity reduction by the break-up of the agglomerates. Another influencial factor is the acid-base interaction of the organo-functional group with the functional group of the polymer chains. Strong acid-base interactions can act as physical crosslinks modifying the rheological properties of the interphase as the silanes are multifunctional by the oligomeric or polymeric structures. Physisorbed silanes can diffuse out of the filler/matrix interface and the thickness of the physically crosslinked matrix interphase increases. As a result, the viscosity would also increases.

When the integral blending method was used to treat a filler surface and the amount of added solution was varied to change the amount of the silane coverage, peculiar results were observed. As the amount of the added solution was increased, the quantity of the deposited silane monotonously increased as expected. However, this increase in the deposited silane halted suddenly for the quantity of silane solution where the filler was completely wetted by the solution as shown in Figure 18. It is likely that the silane molecules may have coevaporated with the alcohol molecules. Accordingly, there is an upper limit of silane that can be deposited by the integral blending method. It is not clear wether this phenomenon applies to a compound such as an amino-functional silane which tends to form oligomers quickly by the catalytic action of the amine group

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 a such a low viscosity material as methyl methacrylate. The initial viscosity of the mixture can be as high as above 100 Pa.s (100,000 cp). If a silane is added and the mixture is ball-milled, the viscosity drops in time almost three orders of magnitude to below 0.1 Pa.s (100 cp), and the mixture can be readily poured (39). 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 observe low viscosity. Since this type of treatment is done in an organic solvent without any water added, the rate of hydrolysis is very slow. The consumption of the silane alkoxy group relies mostly on the water adsorbed on the filler surface and the aforementioned surface silanol/alkoxy group exchange mechanism. Thus, the addition of an alkaline catalyst greatly accelerates the chemical reaction of the silane with the filler.

Ordinarily, in the aqueous treatment of fillers and fibers, silane molecules are almost completely hydrolyzed in the solution prior to mixing with the filler and fiber. Thus, the silanol groups of the silane can be a driving force for adsorption onto the substrate surface. In the case of an anhydrous organic system, this type of adsorption mechanism may be modified. Due to the limited amount of water molecules, only one of three hydrolyzable alkoxy groups may be hydrolyzed and the incompletely hydrolyzed silane may be adsorbed. These incompletely hydrolyzed groups may be hydrolyzed with time on the filler surface. In the other mechanism, when an unhydrolyzed silane molecule encounter the surface silanol groups, the aforementioned exchange mechanism shown below takes place, releasing an alcohol molecule and the silane becomes part of the solid (40).

$$\equiv \mathrm{SiOH} + (\mathrm{CH_3O})_3\mathrm{SiR} \longrightarrow \equiv \mathrm{Si\text{-}O\text{-}Si(CH_3)_2R} + \mathrm{CH_3OH}$$

In either process, the rate of adsorption is expected to be extremely slow. Hence, the addition of an alkaline catalyst greatly aids in accelerating these adsorption processes. Heat and/or time can achieve the same viscosity reduction effect, because both increased temperature and prolonged time lead to more adsorbed silanes. Very few silane oligomers are produced in this method since the hydrolyzed silane molecules do not exist in quantity at any time of treatment. Unlike the mixing of a silane pretreated filler, it is essential to consider the kinetics of silane adsorption in this type of treatment method.

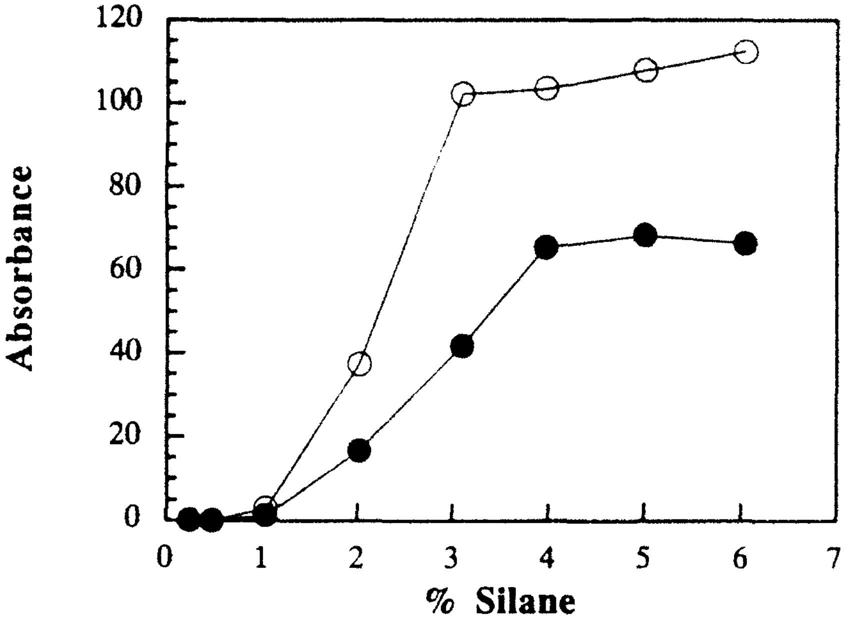


Figure 18. Amount of total and chemisorbed silane on a filler as a function of the initial silane concentration with respect to the filler

7. Hydrothermal Stability of Silane Coupling Agent

Siloxane and silanol groups establish an equilibrium depending upon the humidity level as shown below.

$$\equiv \text{SiOSi} \equiv \; \overset{H_2O}{\rightleftharpoons} \; \equiv \text{SiOH} + \equiv \text{SiOH}$$

Silanol groups are very unstable and the equilibrium is toward forming the siloxane group. Acidic and alkaline pH's catalyze the hydrolysis and condensation reactions. The bond energy of the siloxane is very high and thus the thermal stability of siloxane bonds is excellent, as exemplified by the excellent properties of polydimethylsiloxane at elevated temperatures. However, in the presence of benzoic acid catalyst, the activation energy of the hydrolysis becomes as low as 5 kcal/mol as compared to the bond energy of the siloxane, 89.3 kcal/mol. In spite of this low activation energy of hydrolysis in the presence of a catalyst, a silane coupling agent is effective even in a humid environment. This is probably because of the highly skewed equilibrium toward forming siloxane bonds.

The hydrothermal stability of the siloxane networks is not strongly dependent upon the structure of the organofunctional group. The hydrothermal stability of a silane is studied by desorption of the silane from the substrate surface. In spite of the similar time required to cleave siloxane bonds from different silane coupling agent, the desorption kinetics differs markedly due to the difference in solubility of the newly formed oligomers. If an additional mechanism exists, such as surface induced polymerization of the organofunctional groups, further difficulty for desorption is encountered.

The hydrothermal stability of the SiOR bonds where R represents C, Si, Al and other elements depends strongly on the element in the R group. It is believed that electronegativity difference between the silicon atom and the element in the R group is one of the important factors determining the hydrothermal stability of the bond. Some evaluations of the various oxane bonds have been reported (41). Pure silica, alumina, and titania were treated by a silane coupling agent and hydrothermal stability was studied by monitoring the rate of silane desorption as shown in Figure 19. It is clear from the figure that the stability of the bonds is in the following order: SiOSi > SiOTi > SiOAl. It is intriguing to speculate that a similar stability difference also exists on the surface of the glass fiber, as it consists of various surface hydroxyl groups as well as alkaline and alkaline earth elements.

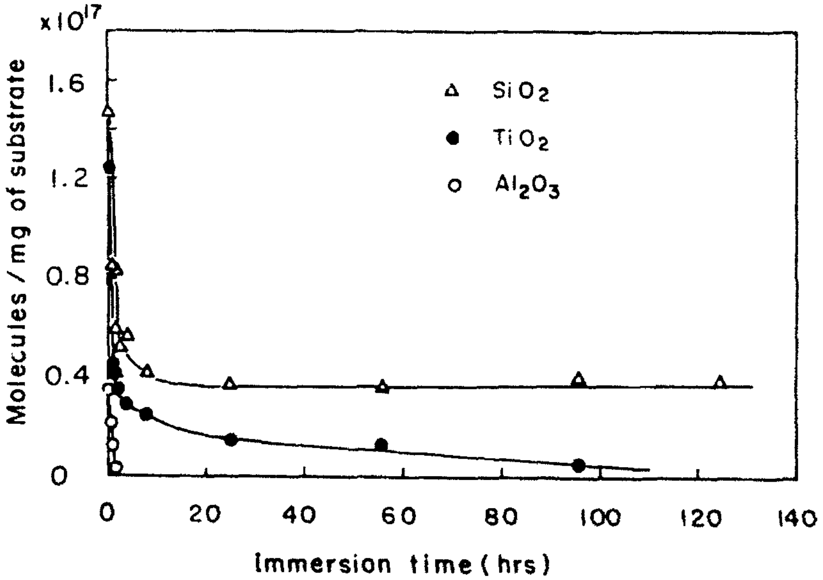


Figure 19. The desorption kinetics of γ-aminopropyldimethylethoxysilane from various substrate surfaces: (△) silica, (●) titania, (○) alumina.

When water reaches the glass/silane interface, water molecules might exist in a separate gas-like state or condensed liquid-like state. It is believed that this liquid-like water damages the interface more than the gas-like molecules. A recent dielectric study by Steeman and Maurer shows a rare insight on this subject. They measured the dielectric constant of glass bead filled polyethylene as a function of the silane coverage on the glass beads surface and the relative humidity. When the water molecules are less than a monomolecular equivalent, the effect of the water on the dielectric constant was small. As the coverage reaches several layers equivalent, the hydrolytic damage dramatically increased.

A simple concentration consideration alone is difficult to explain the above phenomenon. It is possible that the associated, liquid-like water can build a strong osmotic pressure at the interface that will stress the oxane bonds. The oxane bonds at the interface will be subjected to stress. When a tensile stress is applied to the bond, the mechanochemical effect lowers the apparent activation energy of the hydrolysis of the oxane bonds, making it easier to be hydrolytically cleaved. The aforementioned differences in the hydrothermal stability of various oxane bonds may become especially important under such circumstances. Easily cleaved, non-siloxane bonds may become the source of water collection and exert pressure on the surrounding siloxane bonds, which will be cleaved easier than the siloxane bonds with pure silica surface.

It is also necessary to consider the dissolution of the alkaline and alkaline earth elements into the water. If the water is acidic, the dissolution of the surface elements readily takes place. When large atoms near the glass fiber surface are leached out, the siloxane and other networks will be placed under tension, making the glass/silane bonds more vulnerable to hydrolytic attack. All of these phenomena described above do not exist in pure silica's such as quartz powder or fumed silica. It is known that pure silica filled polymers exhibit good hydrothermal stability. It is possible that the lack of these mechanisms to weaken the interfacial bonds may significantly contribute to the stability of the composite. While there are no rigorous studies to prove the aforementioned phenomena nor are effort correlating these subjects with the hydrothermal stability of a composite, these phenomena are well-accepted in the literature for other materials.

8. Summary

The molecular structure of silanes in solution and on substrates has been reviewed. Major advancements over the past decade have helped to elucidate the structure of silane coupling agents. With an improved understanding of the silane structures, it is now possible to control some structures of silane on a substrate. Once structure/property correlation is understood, a specific property of a composite material can be tailored by controlling the interfacial structure. Our current knowledge of silane coupling agents allows us to attempt this systematic approach that has been defined in this paper as interphase engineering.

9. Acknowledgment

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