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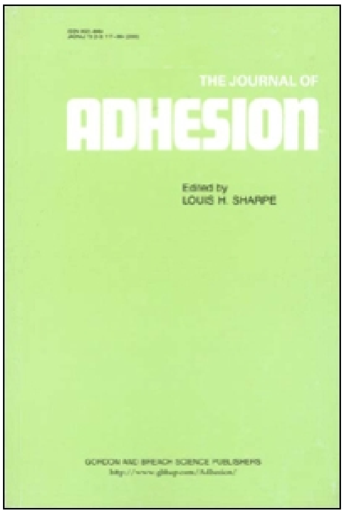

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Adhesion Through Silane Coupling Agents

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ABSTRACT

From a study of silane coupling agents in reinforced plastics, a general mechanism of adhesion to hydrophilic mineral surfaces has been devised. According to this theory, adhesion of polymers to dissimilar surfaces is described as a dynamic equilibrium of making and breaking of adhesion bonds between polymer segments and the surface through the agency of a low molecular weight material—usually water. A dynamic equilibrium at the interface allows relaxation of thermal stresses. Water resistance results from a favorable equilibrium toward bonding through polar groups in the polymer. Silanol groups generally give optimum bonding to hydrophilic mineral surfaces.

Such a dynamic mechanism of adhesion not only explains many complex adhesion problems of plastics to mineral surfaces, but also is compatible with the adhesion of ice, barnacles and tooth plaque to surfaces in an aqueous environment and with the requirements for rubber reinforcement by finely divided particulate fillers.

INTRODUCTION

ALTHOUGH A large body of literature exists on studies of the interface between plastics and mineral surfaces, there has been no generally accepted theory of adhesion of plastics to minerals or the function of adhesion-promoting coupling agents at the interface. Any meaningful theory of adhesion of plastics to minerals must be consistent with a broad range of observations on adhesion. It should be consistent with known effects of:

1. Fundamental surface chemistry and physics of minerals and plastics.
2. The action of water and other potential weak boundary layers at the interface.
3. Morphology of the plastic at the interface.
4. Mechanical requirements of a plastic-mineral interface to allow distribution of shrinkage stresses especially at edges of voids or other areas of stress concentration.
5. Benefits and limitations of adhesion through silane coupling agents.
6. Adhesion of ice and bio-adhesives to surfaces.

A sound working theory of adhesion of plastics to minerals should be beneficial in developing improvements in present plastic-mineral composites. On the other hand, the large mass of data accumulated on the effect of variables on the mechanical and electrical properties of reinforced plastics should be helpful in arriving at an understanding of interfacial phenomena for all bonding applications.

Attempts to correlate performance of reinforced plastics with basic concepts have been notoriously unsuccessful. Adhesion of paints, rubbers and

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sealants to mineral surfaces and strengths of glass-reinforced plastics (especially after exposure to water) show very little correlation with contact angles, wettability, surface tensions, potential weak boundary layers, surface morphology, chemistry of mineral surfaces, or any of the other fundamental concepts. It is quite likely that adhesive performance as measured by mechanical properties of a composite involves some parameters that have not been considered essential for adhesion of polymer segments on a molecular scale.

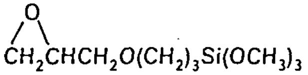
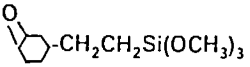
The marked improvement in properties imparted to many mineral-plastic composites by traces of appropriate reactive silanes at the interface suggests that an understanding of the nature of adhesion through silane coupling agents might be the key to understanding the general mechanism of adhesion.

NATURE OF SILANE COUPLING AGENTS

1. Chemical Structure

All commercial silane coupling agents are of the general structure $X_3Si(CH_2)_n$ Y where n = 0 – 3, X is a hydrolyzable group on silicon, and Y is an organofunctional group selected for compatibility with a given resin (Table 1). The total amount of silane coupling agent applied is generally 0.1 – 0.5% of the weight of glass.

Table 1. Commercial Silane Coupling Agents

No.	Name	Formula	Application
1	Vinyltriethoxysilane	$CH_2 = CHSi(OC_2H_5)_3$	Unsaturated polymers
2	Vinyl-tris (β-methoxyethoxy)-silane	$CH_2 = CHSi(OCH_2CH_2OCH_3)_3$	Unsaturated polymers
3	Vinyltriacetoxysilane	$CH_2 = CHSi(OOCCH_3)_3$	Unsaturated polymers
4	γ-Methacryloxypropyltri-methoxysilane	$CH_2 = C(CH_3)COO(CH_2)_3Si(OCH_3)_3$	Unsaturated polymers
5	γ-Aminopropyltriethoxy-silane	$H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$	Epoxies, phenolics, nylon
6	γ-(β-aminoethyl) aminopropyltrimethoxy-silane	$H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3$	Epoxies, phenolics, nylon
7	γ-Glycidoxypropyltrimeth-oxysilane	 $CH_2CHCH_2O(CH_2)_3Si(OCH_3)_3$	Almost all resins
8	γ-Mercaptopropyltrimeth-oxysilane	$HSCH_2CH_2CH_2Si(OCH_3)_3$	Almost all resins
9	β-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane	 $-CH_2CH_2Si(OCH_3)_3$	Epoxies,
10	γ-Chloropropyltrimethoxy-silane	$ClCH_2CH_2CH_2Si(OMe)_3$	Epoxies

Since silane coupling agents are generally applied to glass from water solutions, the hydrolyzable groups are only essential for generating intermediate silanols.

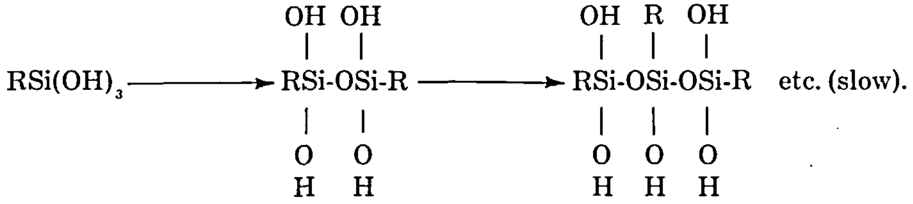
$$\mathrm{X_3Si\,(CH_2)_nY + 3H_2O \longrightarrow (HO)_3Si\,(CH_2)_nY + 3HX}$$

For example, essentially equivalent performance was obtained from aqueous vinylsilane coupling agents derived from all common hydrolyzable vinylsilanes.[1]

2. Aqueous Solutions

The composition of silane coupling agents in dilute aqueous solution depends on the nature of the organofunctional group on silicon and the pH of the solution. Neutral organofunctional silane coupling agents (where Y = methacryloxy, glycidoxy, vinyl, chloro, etc.) as generally prepared in dilute acetic acid solution (pH about 4) hydrolyze rapidly to silane triols, and then condense slowly to oligomeric siloxanols. The monomer and lower oligomeric siloxanols are soluble in water, but higher oligomers precipitate from solution. Aqueous silane coupling agent solutions, therefore, have only limited stability and must be used within a few hours. A fresh aqueous solution of vinyltrimethoxysilane contained 82% monomer, 15% dimer and 3% trimer, but after aging until precipitation started, it contained 34% monomer, 23% dimer, 30% trimer and 13% tetramer.

$$\mathrm{RSi(OCH_3)_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3CH_3OH}\ \text{(fast)}$$



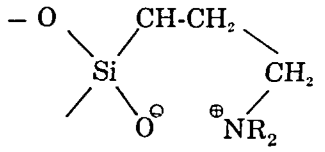
$$\mathrm{RSi(OH)_3 \longrightarrow R\overset{OH}{\underset{OH}{Si}}\text{-}O\overset{OH}{\underset{OH}{Si}}\text{-}R \longrightarrow R\overset{OH}{\underset{OH}{Si}}\text{-}O\overset{R}{\underset{OH}{Si}}\text{-}O\overset{OH}{\underset{OH}{Si}}\text{-}R}\quad \text{etc. (slow).}$$

As commonly applied from solution the coupling agents are largely monomers or dimers with smaller proportions of higher oligomers.[2] Films of coupling agents deposited from solution (X = methacryloxy or glycicloxy) are oils that are soluble in common organic solvents, but insoluble in water. When hydrolyzed coupling agents are completely condensed to siloxane structure by warming in toluene in the presence of a trace of alkali catalyst, the products are no longer effective as coupling agents.[3]

Amino-organofunctional silane coupling agents show unique solution properties when nitrogen is on the 3-carbon atom. These alkoxy silanes hydrolyze almost immediately in water, but form dilute aqueous solutions of unlimited stability. Stable solutions are obtained only in polar hydrogen-bonding solvents like water or alcohols. Dilute solutions of 3-amino-alkyl silane coupling agents in toluene or other nonpolar solvents give precipitates upon contact with moist atmosphere.

The stability of aqueous solutions of amino-functional silane coupling agents is surprising since amines cause immediate precipitation of alkylsilanols as insoluble siloxanes.

Since it is well known that cyclic 6-membered chelate rings have extraordinary stability, it is proposed that an internal cyclic chelate structure is formed in solutions of 3-amino substituted organic silanols.



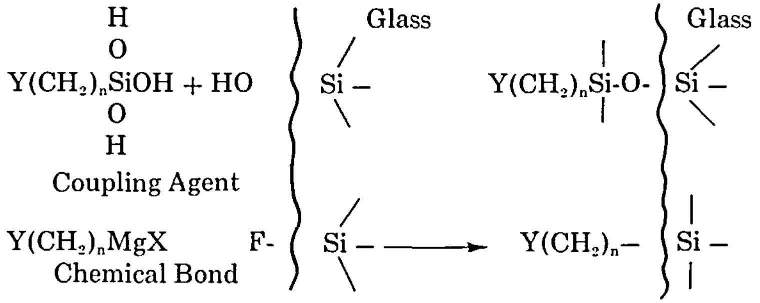
Evaporation of an aqueous solution of a 3-amino functional silane coupling agent leaves a brittle powdery deposit that is readily redissolved in water. The chelate structure is apparently lost when the polar ionizing solvent evaporates, but reforms in water. Aqueous solutions do not contain free Si-OH groups but apparently are relatively low molecular weight siloxanes with stabilized silanolate ions.

Amino-organofunctional silanes with nitrogen on other than the 2- or 3-carbon atom do not form stable solutions in water, but precipitate as insoluble gels as would be expected of silane-triols in the presence of amines.

3. Adsorbed Organosilane Coupling Films

The nature of adsorbed coupling agent films deposited on glass, silica, and other mineral surfaces has been studied by numerous investigators[4] and discussed critically by Zisman.[5] It is agreed from these reports that silane coupling agents are not generally deposited on mineral surfaces as simple oriented monomolecular films, but as multi-layers with variable orientation depending upon conditions of deposition. A major portion of the deposited film is removed readily by water or organic solvents, but a small residue (often less than a monomolecular film) is retained tenaciously by the surface. Only the last trace of coupling agent on the surface is necessary for improved bonding. The major portion of silanes, as generally applied, is of no value in bonding, and may even be detrimental. In practice, much of the coupling agent film dissolves in the plastic mass and is dispersed harmlessly.

A significantly different approach was used by Chamberlain to bond a coupling agent chemically to a glass surface.[6] A fluorinated glass surface was allowed to react with a difunctional Grignard reagent to give a firmly bonded organofunctional group. Coupling agents, in contrast, cannot bond to glass surface through more than one silanol group per molecule.



Coupling agents can be removed from glass by hydrolysis of a single siloxane bond while chemically bonded groups remain bonded to glass until three siloxane bonds are hydrolyzed simultaneously. Chamberlain observed that chemical modification of about 5% of the glass surface gave performance in epoxy laminates comparable to a silane coupling agent applied from water, but that a higher degree of chemical modification gave inferior results.

Many studies have been made of wettability, contact angles, and critical surface tensions (γ_c) of mineral surfaces treated with silane coupling agents. Observed values of γ_c were, in general, in ranges predicted from known polarities of the organofunctional groups on silicon.

A parallel relationship was observed by Gardon[7] between solubility parameters of amorphous polymers and their critical surface tensions. There is a similar parallel relationship between solubility parameters of silane coupling agents and the critical surface tension of treated surfaces as shown in Table 2.

Table 2. Silane Coupling Agent Films on Mineral Surfaces

R- of Silane Coupling Agent	*Solubility Parameter of R-H (δ)*	*Critical Surface Tension of Silane-Treated Surface (γ_c) (ref. 5)*
CH_3-	6.3*	22.5
CH_3-CH_2-	7.3*	26-33
$CH_2 = CH$	7.4*	25-30
$CH_2 = C(CH_3)COO(CH_2)_3$-	8.1	28
$Cl(CH_2)_3$-	8.3	40.5-43
$HS(CH_2)_3$-	8.7	41
$H_2N(CH_2)_3$-	8.7	35
CH_3-C_6H_4-	8.9	34
C_6H_5-	9.2	40
$\overset{O}{CH_2\text{-}CH}CH_2O(CH_2)_3$-	9.2	38.5-42.5
$ClC_6H_4(CH_2)_2$-	9.3	40-45
BrC_6H_4-	9.9	43.5

*Solubility Parameter of R_4Si; others of R-H

Variability in critical surface tension of silane-treated surfaces could arise from different degrees of condensation of deposited siloxanols, and to orientation of organic- or silanol-portions of the molecules toward the air interface. Lee observed that γ_c of a vinylsilanol-treated surface increased from 25 to 40 after warming to 80° for 15 hours in air.[4a] Bascom also observed that γ_c of ethylsilanol-treated surfaces varied from 24 to 38 depending upon presence or absence of acidic or basic catalysts during treatment.[4c]

The use of silane coupling agents as integral blend additives often gives performance comparable to that obtained by separate treatment of the reinforcement.[8] As additive, the necessary reactive silane is dissolved directly into the resin system prior to putting it in contact with the inorganic filler, reinforcement or substrate to be bonded. Under these conditions the silane migrates to the hydrophilic surface where it reacts with absorbed moisture to produce silanol groups which bond to the surface. The amount of silane needed may be as low as that calculated to give a monomolecular film on the mineral. However, because the process involves migration of the silane to the surface, it is necessary to permit sufficient time for reaction to occur at the surface. Integral blends are especially convenient in preparing composites of resins with particulate fillers.

PERFORMANCE OF SILANE COUPLING AGENTS

1. Effective Silane Coupling Agents Become Part of the Resin

All coupling agents for thermosetting resins are reactive with the resins, and no non-reactive silane is effective as a coupling agent for these resins. There is no correlation between polarity of the silane, or wettability of silane-treated glass and the effectiveness of the silane coupling agent. The specificity of organofunctional silane coupling agents is well illustrated by chloropropyl trimethoxysilane. Glass treated with chloropropylsilane coupling agent has a relatively high surface energy and is readily wet by resin solution. Such treatment, however, is completely ineffective in laminates with polyester, melamine, or phenolic resins. It is very effective with amine cured epoxies, but not with anhydride cured epoxies. Chemical reaction between the coupling agent and resin is possible only with amine cured epoxies.

Polyester laminates were prepared from glass treated with silane coupling agents of varying polarities as estimated from the solubility parameters (δ) of compounds R-H corresponding to the organic group R-Si of the silane.[9] Properties of the laminates as summarized in Figure 1 show no trends in laminate properties with variations in δ of the coupling agent. Among non-reactive groups like ethyl, chloropropyl, dichlorophenyl, cyanopropyl and hydroxypropyl it was found that none of the treatments was an improvement over bare glass. Most of them were substantially poorer than the control. Properties of similar polyester laminates with reactive silanes show a good correlation between performance and reactivity of the silane in free-radical polymerization.

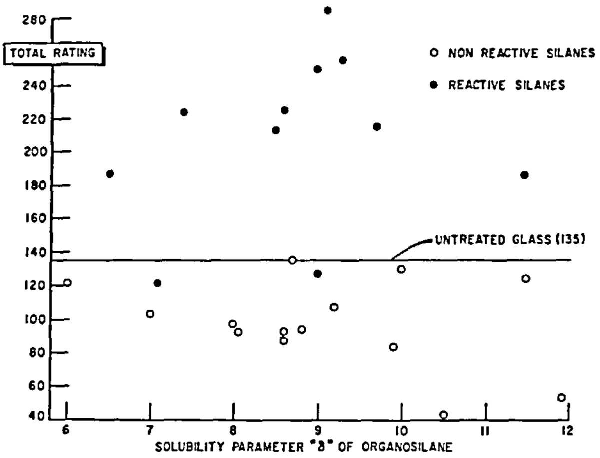


Figure 1. Polyester laminates 70% glass.

Wetting studies on silane-treated glass are futile in arriving at a coupling agent adhesion mechanism since the interface between coupling agent and resin disappears during preparation of the composite. The only interface of significance is that between the silanol-modified polymer surface and the mineral.

After fundamental requirements of coupling activity are met through reactivity of coupling agent with resin, further practical improvements in performance and ease of fabrication may be accomplished by increasing the critical surface tension and wettability of silane-treated mineral reinforcement. Better wetting of silane-treated glass will allow more complete displacement of air from the glass surface and reduce the number of voids in the composite.[10] Good coupling activity with poor wetting, however, gives much better composites than poor coupling and good wetting.

2. Silane Coupling Agents Do Not Function by Depositing a Tough, Rubbery, Water-Resistant Boundary Layer

The amount of silane coupling agent required on a glass surface is too small to measure by ordinary analytical means. By use of radio-active tracers it has been determined that less than a monomolecular layer of the proper silane on a glass surface will function as coupling agent[1d,e]. Silane coupling agents are equally as effective when added as integral blends in resins at concentrations calculated to be equivalent to a monomolecular layer of silane on the mineral surface.[8] Thicker films deposited by hydrolysis and condensation of silane coupling agents are oils, cheesy gels, or friable powders, but not tough, water-resistant polymers. They are not effective unless they are deposited in a silanol form. When applied as alkoxysilanes, it is essential that water be present at the interface,[11] and if condensed completely to siloxanes and deposited from organic solvents they are not effective as coupling agents.

In a study of the adhesion of polyester resin to glass, Trivisono[12] compared numerous materials as primers for polyester resins in adhesion of glass blocks and as coupling agents on glass fibers. He observed that vinyltriethoxysilane primers were improved by addition of film-forming resins, but that resinous additives did not improve vinyltriethoxysilane as a coupling agent on glass fibers. Whereas primers on massive mineral sections commonly function as tough water-resistant boundary layers, coupling agents on minerals with high surface area must function on a molecular basis.

3. Silanols are Unique Among Polar Groups in Coupling Activity

Although it might be expected that any polar functional group in a resin structure would improve its adhesion to mineral surfaces, it has been shown that silanes and, to a lesser extent, chrome complexes are uniquely effective with glass and are the only known true coupling agents. Properties of glass-reinforced polyesters are improved only slightly by modification with functional methacrylates containing carboxyl, hydroxyl, amide, epoxy, nitrile, amine, acid phosphate, titanate, zirconate, germanate or stannate groups.[13] The difference may be more in degree than in mechanism of bonding, since very high levels of hydroxyl content in a resin give results comparable with that obtained in the presence of a trace of silane coupling agent.

Other functional groups like phosphates, chromates, phenols, etc., may be the preferred polar functional group on minerals like boron, magnesium, calcium carbonate, and calcium phosphate where silanols are known to be ineffective.

4. Silane Coupling Activity Does Not Require Stable Covalent Bonding to a Mineral Surface

Physical properties of filled polymer castings are improved by addition of appropriate silane coupling agents with a wide range of mineral fillers.[8, 24] Greatest improvement was observed with silica, alumina, glass, silicon carbide, and aluminum needles (Table 3). Good but somewhat lesser response, was observed with talc, wollastonite, iron powder, clay and hydrated aluminum oxide. Only slight improvement was imparted to asbestine, hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$), titanium dioxide and zinc oxide. Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite, and boron.

Although coupling activity of silanes is not universal to all mineral surfaces, response is broad enough to indicate that silanols need not condense with surface hydroxyl groups to form water-resistant "oxane" bonds with the surface. The oxane bond between silicon and iron or aluminum, for example, is not resistant to hydrolysis. Even covalent siloxane bonds are hydrolyzed to silanols by water with an activation energy of 23.6 kcal./mole. Hydrolysis catalyzed by benzoic acid has an activation energy of 6 kcal./mole[5] which is comparable to the strength of a hydrogen bond. Compression set of silicone

Table 3. Silanes in Filled Castings

Resin	Filler	Silane (Table 1)	Flexural Strength Improvement (%) Dry	Wet
Buton[a]	Silica	2	200	250
Buton	Alumina	2	180	200
Buton	Hydrated Alumina	2	100	100
Buton	Glass Flakes	2	150	500
Buton	ASP-400 Clay	2	55	65
Buton	Talc	2	80	80
Buton	Calcium Carbonate	2	None	None
Epoxy	Silica	5	20	150
Epoxy	Al-Needles	5	100	200
Epoxy	Al-Powder	9	50	—
Epoxy	Fe-Powder	9	40	—
Epoxy	Wollastonite	7	20	50
Epoxy	ASP-400 Clay	7	5	10
Polyester	Silica	2	50	50
Polyester	Wollastonite	4	18	50

(a) A butadiene-styrene copolymer from the Enjay Chemical Company

rubber has been attributed to a stress relaxation involving hydrolytic breaking and remaking of siloxane bonds of the silicone. Activation energy for stress relaxation of silicone rubber was reported by Osthoff[16] as 22.8 kcal./mole or 5 kcal./mole, in the presence of KOH or benzoic acid.

5. Silane Coupling Agents are Effective with all Organic Resins, but the Degree of Improvement Varies with the Nature of the Resin

Although silane coupling agents were first introduced to improve the water resistance of reinforced plastics, it was soon observed that they also imparted significant improvement to initial properties of laminates. The degree of improvement obtained even under optimum conditions varied with the resin, the glass content, and the severity of the test. The improvements in laminate properties imparted by silane coupling agents in typical glass cloth laminates are summarized in Table 4. All results are based on compression molded test samples containing 60-70% glass in the laminate. Heat-cleaned glass cloth treated with 0.5% silane coupling agent in each case was compared with untreated heat-cleaned cloth.[4]

Certain trends are clear in comparing the response of different resins to the presence of coupling agents (Table 4 and Figure 2). Epoxy-anhydride resins are unique in initial bonding and in resistance to water. An epoxide-anhydride reaction in the presence of water at the glass surface provides a resin with a high hydroxyl content at the interface. Amine-cured epoxies also have a high hydroxyl content, but there is a lesser tendency for hydroxyls to be formed at the surface.

Table 4. Silanes in Glass Cloth Laminates

Resin System	*Silane (Table 1)*	*Flexural Strength Improvement (%)*	
		Dry	*Wet*
Epoxy (anhydride)	7, 9	10	10
Epoxy (amine)	5, 6, 7, 10	30	80
Polyester	1-4	50	150
Styrene-butadiene[a]	1-4	50	300
Phenolic	5, 6, 7	40	150
Melamine	5, 6	100	250
Styrene-D.V.B. (cast)	4	90	300
Poly (styrene-coacrylonitrile)	7	50	150
Nylon	5, 6, 7	110	100
Polypropylene	4	150	250

[a] Buton—from the Enjay Chemical Company

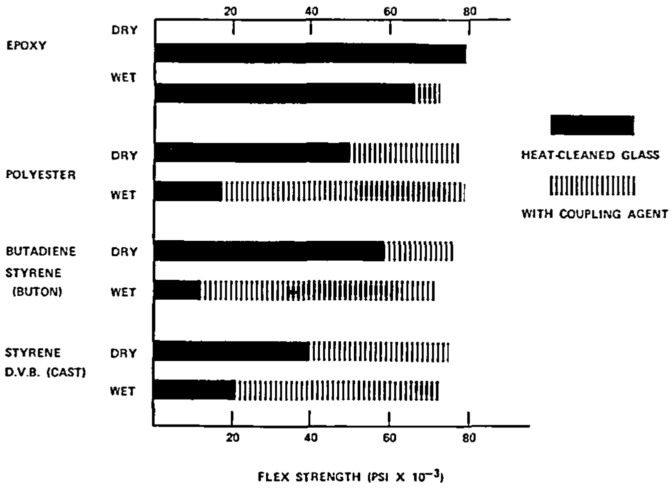


Figure 2. Glass cloth laminates.

Condensation polymers (phenolics, melamine) that eliminate volatile byproducts during cure benefit greatly from silane coupling agents. Although the resin intermediates are highly polar, they become less polar during cure, and polar volatiles are generated at the interface.

Non-polar resins benefit most from coupling agents in both dry and wet-strength. Although the resins themselves are very resistant to water, they have only weak van derWaals bonding to the glass and, therefore, are least capable of competing with water for the surface.

The equalizing effect of silane coupling agents is well illustrated in Figure 2, based on data of Vanderbilt,[17] who laminated and tested four types of resins under similar conditions.

Absolute values of dry and wet strength of laminates of various resins with silane-treated glass are surprisingly uniform at about 80,000 psi. This suggests that silanols, or a massive concentration of organic hydroxyls perform a necessary function at the interface during preparation of the laminate and in resisting the action of water. Optimum utilization of resin properties in the composite are best obtained if silanol groups are present at the interface.

6. Flexible Polymers Cannot Form Water-Resistant Bonds to Hydrophilic Mineral Surfaces

Surface morphology of a polymer at a composite interface is extremely important in determining whether the polymer can compete favorably with potential weak boundary layers for the surface. A rigid interface is necessary for a polymer to compete with oils or low molecular weight polymers at any interface. Rigidity, alone, will not impart water resistance to the bond of a polymer to a hydrophilic mineral surface. Rigidity, combined with silanol functionability will give water resistance of any polymer bond to most hydrophilic mineral surfaces. A flexible polymer, however, will not retain wet adhesion to a hydrophilic mineral surface even in the presence of the best silane coupling agent. Many examples can be given.

Hansen and Schonhorn[18] observed good adhesion to polyethylene in spite of the presence of low molecular weight oils when the polyethylene surface was made rigid by controlled crystallization or by crosslinking.

Vanderbilt and Clayton[19] observed that elastomers could be bonded to glass using a reactive silane and a difunctional monomer at the interface. The reactive silane alone, or the silane with a monofunctional monomer was much less effective. Crosslinking at the interface seemed to be a requirement for good adhesion.

Simple silane coupling agents and polyhydroxy-functional organic molecules are effective in converting silica and certain silicate minerals into reinforcing fillers for organic rubbers.[20] The same silanes are completely ineffective as primers on glass or metal panels for wet adhesion of the same rubbers. It has been proposed[21] that reinforcement of rubber requires a two-dimensional mobility of polymer segments on the filler surface. Slippage of polymer segments under tension on the filler brings about a homogeneous distribution of stresses among the many polymer segments on the filler surface.

Copolymers of methacryloxypropyltrimethoxysilane with other acrylic monomers are effective primers for retaining wet-adhesion of polystyrene or acrylic polymers to metal or glass at temperatures below the glass transition temperature of the primer. Flexible copolymers (e.g. with ethyl acrylate) are ineffective as primers in the presence of water at room temperature.

Certain flexible reactive siloxane polymers deposit films on glass or metals that suffer complete loss of adhesion in water, and yet will promote water-resistant adhesion to reactive polymers like urethanes and epoxies. It is evident that these reactive flexible siloxanes become rigid through chemical reaction when used as primers with reactive polymers.

Adhesion of polyethylene to glass or steel is lost upon exposure to water, but is regained when the coating is dried.[22] This suggests an equilibrium of bonding and debonding in the presence of water.

The difficulties in modifying isotactic polypropylene to obtain water-resistant adhesion to glass are obvious, since any modification of polypropylene at the interface destroys the crystallinity that is necessary for adhesion.

PROBLEMS IN BONDING TO HYDROPHILIC MINERAL SURFACES

In preparing a composite of a hydrophilic mineral surface and an organic polymer it is obvious that the organic phase must make intimate contact with the mineral surface as proposed by older theories of adhesion. This system also requires that the cured interface withstand differential shrinkage of mineral and plastic, and survive in spite of the intrusion of water into the hydrophilic interface.

1. Shrinkage Stresses

Most polymers undergo some shrinkage during cure. Internal hydrostatic pressures of 2000 to 3000 psi were measured[23] on strain gage transducers embedded in a polyester resin cured at 120°C.

Since the coefficient of thermal expansion of glass is about 6×10^{-6} in./°C while that of a typical rigid plastic is about 60×10^{-6} in./°C, large additional stresses are set up at the interface between glass and plastic when a composite cools.

Stresses in a polymer are not dispersed uniformly throughout the mass, and the interface between resin and mineral reinforcement is not smooth on a micro scale. The result is that stresses much higher than the average are concentrated at certain points at the interface. Such stresses can initiate cracks in the resin or the reinforcement causing a major loss in physical strength. Shrinkage stresses on single glass fibers embedded in a cured plastic were measured by Haslett and McGarry[24] by a photoelastic technique. They oberved about 2000 psi radial pressure and 1000 psi axial compression at the interface for every 50°C of cooling below maximum cure temperature. Radial compression offers no problem, but axial or tangential forces tend to cause failure at the interface.

Similar stresses were calculated from deformations measured in constantan wires acting as a tensiometer embedded in polyester and epoxy resins.[25]

Differential expansion was observed by Bolotina[26] in unidirectional glass fiber reinforced phenolic laminates which showed coefficients of thermal expansion along the fiber axis of 5 to 7.5×10^{-6} /°C, and across the fiber axis of 26 to 39×10^{-6} /°C.

Coefficients of thermal expansion of a few common plastics and minerals are shown in Table 5. It is obviously impossible to avoid shrinkage stresses between most polymers and common mineral substrates even if they are heated to only moderately elevated temperatures. Rigid thermoplastics may suffer most from such shrinkage stresses since they have high coefficients of expansion and they are often fabricated at relatively high temperatures.

Table 5. Linear Thermal Expansion of Common Materials

Material	*Coefficient of Thermal Expansion ($c \times 10^{-6}/°C$)*
Silica Glass	0.6
Corning 774 Glass	3.2
Alkali (soft) Glass	9.0
Alumina (alundum)	8.7
Aluminum	23
Steel	10-14
Graphite	7.8
Brass	19
Polyimide	38-54
Epoxy	45-65
Polyester	55-100
Phenolic	60-80
Polystyrene	60-80
Polypropylene	100-200
Cellulose Acetate Butyrate	110-170
Polyurethane Resins	100-200
Silicone Resin	160-180

2. Water at the Interface

Bernett and Zisman[27] observed that a clean glass surface exposed to ordinary atmospheric conditions immediately picks up a molecular layer of water. Water can penetrate to the glass resin interface through even the most water resistant resins by diffusion through the resin, by filtering through cracks or by capillary migration along the fibers. It has also been demonstrated by Gutfreund[28] that glass treated with a hydrophobic silylating agent and dried, will reabsorb a molecular layer of water upon exposure to the atmosphere. In a study of the water resistance of glass reinforced thermoset plastics Vanderbilt[17] found no correlation between water absorption and wet strength retention of epoxy laminates with various silane coupling agents. The sorption and diffusion of water in silicone rubber was interpreted by Barrie and Machin[29] to involve very little interaction between polymer and water, but at high relative humidities to involve clustering of water molecules within the polymer. The effect of NaCl filler on water absorption was almost negligible up to 0.6 relative humidity, but silica filled samples sorbed appreciably more than unfilled rubber even at lower relative pressures.

From the above observations it must be concluded that water cannot be excluded from the interface between resin and a hydrophilic mineral reinforcement and that the effect of water will vary with the nature of the mineral surface. Silane coupling agents do not exclude water from the interface but somehow function to retain adhesion in the presence of water.

A THEORY OF ADHESION TO HYDROPHILIC SURFACES

A new working theory of adhesion at the polymer-mineral interface is now proposed[30] in which silane coupling agents provide a bond at the interface that is capable of using the hydrolytic intrusion of water, with self-healing, as a means of stress relaxation without disrupting the overall bond between plastic and mineral surface (Figure 3). Such a reversible hydrolytic bond mechanism controlled by equilibrium conditions accounts for all the observed phenomena of adhesion to hydrophilic surfaces through silane coupling agents.

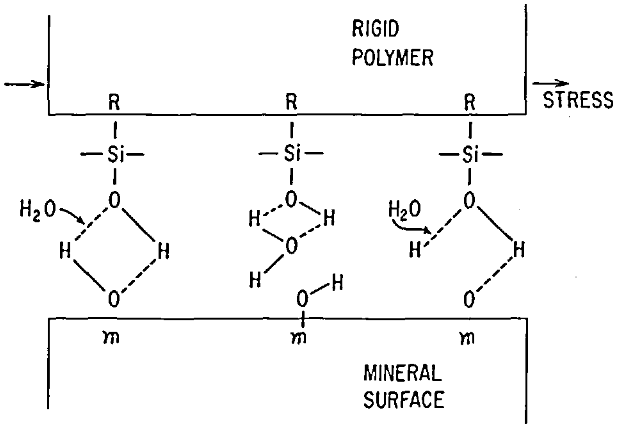
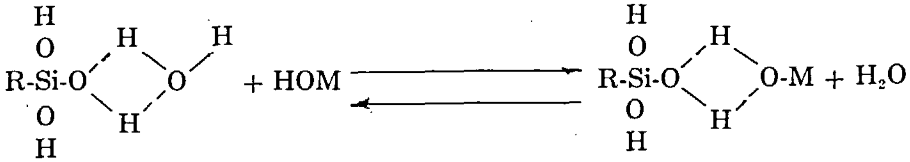
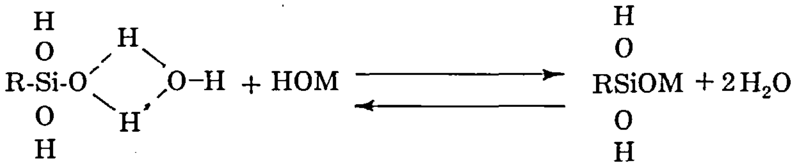


Figure 3. Bonding to hydrophilic surfaces.

As a silanol or hydrolyzable silane approaches a water-covered hydrophilic surface it is uniquely capable of competing with water because of its capacity for strong hydrogen bonding. Organofunctional siloxanes are not coupling agents since only silanols or silanes that hydrolyze to silanols are capable of competing with water. As the hydrated silanol approaches the surface it bonds to oxides of the surface—MOH (M = Si, Al, Fe, etc.) with the elimination of water. It is not known whether reaction with the surface is through hydrogen bond or -oxane bond. Either of the reactions is reversible.





During fabrication of a laminate the silane becomes part of the plastic so that the above bonds represent the final interface between the resin and glass. In a rigid system, reactive positions are held in such proximity that free silanols resulting from hydrolysis of a bond have no place to go and eventually reform the original bond or make a new bond with an adjacent group. As long as the interface is rigid, bond making and breaking in the presence of water is reversible.

Even exposure to boiling water will not break sufficient bonds to cause complete loss of adhesion as long as the resin retains its integrity. Under axial or tangential stress, there is a driving force for bonds to break and reform at adjacent positions. This results in a two-dimensional mobility along the surface of the glass to relieve stresses without loss of adhesion. A dynamic equilibrium mechanism of bonding not only resists the disruptive action of water but actually requires water at a hydrophilic interface to allow relaxation of thermal stresses induced during cooling of the laminate.

1. All Resins Bond to Solid Hydrophilic Surfaces Through a Reversible Hydrolyzable Bond Mechanism

Since the only requirements for bonding to a hydrophilic mineral surface are that a material approach the surface with functional groups capable of competing with potential weak boundary layers (usually water) and solidify to a rigid structure, this mechanism is not limited to silanols but applies generally for adhesion.

The adhesion of plastics and ice to most surfaces, barnacles to underwater structures, plaque to living teeth, etc., all are examples of the same mechanism. Bonding of epoxy resins through hydroxyl groups (hydrogen bonding or alkoxide formation) to a hydrophilic surface is hydrolytically reversible, and although the equilibrium is less favorable for bond retention than that of a silanol, water resistant bonds are obtained if the hydroxyl concentration at the interface is high enough. Bonding through reactive silanols or organic hydroxyl groups differs only in degree, and not in kind.

Ester or amide groups of polyesters, alkyds, polyacrylates, polyamides, urethanes, etc., may hydrogen-bond with hydroxyl groups of a hydrophilic surface but equilibrium conditions in the presence of water are less favorable for bond formation. They show a greater benefit from addition of a trace of silane coupling agent. Hydrocarbons, and other non-polar resins have only weak dispersion forces for bonding to a hydrophilic surface and cannot compete with water unless a silane coupling agent is added. Many natural polymers (e.g. cellulose and proteins) form aggregates through a similar mechanism of reversible hydrogen bonding in the presence of water to form stable fibers or cell structures. The process of aging has been attributed to irreversible cross-linkages between giant molecules resulting in loss of elasticity and ability for renewal.[31]

The adhesion of barnacles to underwater structures was studied recently by Saroyan *et al.*[32] They observed that barnacle larva first attach themselves mechanically by means of suction cups in their antenna. The initial adhesion is soon reinforced by an adhesive cement that piles up and envelopes the antenna. The cement appears to be a liquid protein that hardens as it is secreted. Adhesion must of necessity result when a polar material like a mucosaccharide or a protein is hardened at the interface by crosslinking or some other chemical reaction. Reproduction of a similar mechanism of hardening of synthetic polymers at a moist interface would be valuable in problems such as wound closure and healing and in adhesive bonding of materials to tooth structure.

2. Bonding Must be Through a Rigid Interface

Flexible polymers cannot form water-resistant bonds to a hydrophilic surface by this mechanism even with added silane coupling agents since silanols will retract from the surface as individual bonds are hydrolyzed and be no longer available for new bond formation (Figure 4). Water will gradually interpose itself throughout the interface until adhesion is completely lost. Flexible polymers can form water resistant bonds only if a rigid intermediate layer is formed on the hydrophilic surface. Rigid intermediate bonds may be formed *in-situ* from certain silanes, by hydrolysis and condensation, or by reaction with a crosslinking monomer.

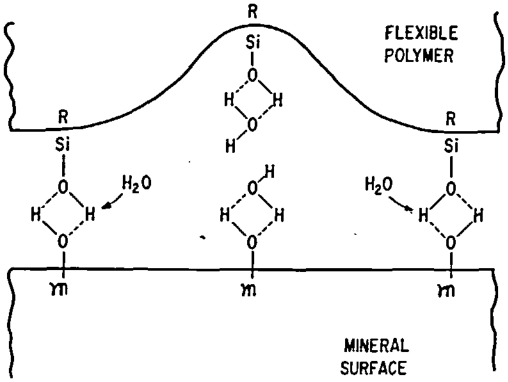


Figure 4. Bonding to hydrophilic surfaces.

Since flexibility is required in many adhesives and coatings on mineral surfaces and since flexible polymers cannot form water-resistant bonds to hydrophilic surfaces, a reactive rigid primer is often first applied to the surface. Requirements of a primer for a flexible polymer on a hydrophilic mineral surface are often mutually antagonistic, and careful balancing of properties are necessary to obtain satisfactory adhesion:

1. The primer must form a strong, hard film either by itself or by reaction with the top coating.
2. It must have polar groups (preferably silanol) for bonding to the mineral.
3. It must be compatible with the flexible resin (preferably by chemical reaction).
4. It must resist complete solution in the top coat, i.e. it must retain a rigid film structure.
5. It must survive any environment (e.g. oxidation and high-temperature degradation) that the top-coat is expected to withstand.

3. Water is Necessary for Bonding to Mineral Surfaces

A coupling mechanism will not operate between a rigid resin and a non-hydrophilic surface like graphite. Water does not attack the interface and there is therefore no mechanism for relaxation of stresses set up during resin cure and cooling. It has been observed that composites of graphite fibers in epoxy resin, before applying external stress, are full of translaminar cracks resulting from thermal stresses induced during cooling of the laminate.[33] Graphite fibers may be oxidized to obtain a hydrophilic surface[34] that can bond to epoxy resins by the dynamic equilibrium mechanism in the presence of water.

Carbon black, having a polar oxidized surface, is a reinforcing filler for rubber, while graphite of a similar particle size, but with a non-hydrophilic surface is not a reinforcing filler. Boonstra[21] proposed that rubber molecules adsorbed on carbon black and vulcanized, still possess a two dimension mobility on this surface. Slippage of polymer segments under tension on the filler brings about a more homogeneous distribution of stresses.

CONCLUSIONS

In practical adhesive systems organic polymers are in competition with low molecular weight materials (potential weak boundary layers) for adhesion to a substrate. Competition at a surface is not a static sandwich of polymer-weak boundary-substrate, but a dynamic equilibrium of making and breaking of bonds. Gross adhesion results when the polymer presents a rigid surface at the interface and contains functional groups capable of competing favorably with the low molecular weight material for the surface. Silanol groups, and to a lesser extent, organic hydroxyl groups are the best polar groups for adhesion to most hydrophilic mineral surfaces in the presence of water. Other polar functional groups may give optimum bonding to specific mineral surfaces.

Adhesion of organic polymers to mineral surfaces generally is complicated by shrinkage stresses and by thermal stresses resulting from differences in coefficients of thermal expansion across the interface. A dynamic equilibrium of bonding and debonding in the presence of water allows stress relaxation at the interface. Water is, therefore, a necessary ingredient for bonding rigid plastics to a mineral surface.

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