

Silane Coupling Agents

SECOND EDITION

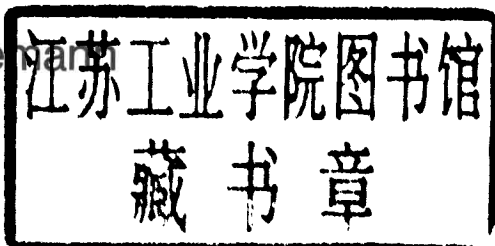
Edwin P. Plueddemann

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Preface to the Second Edition

Much progress has been made in the last 8 years in understanding the theory and practice of silane coupling agents. A major advance in this direction was the measurement of true equilibrium constants for the hydrolysis and formation of siloxane bonds. Equilibrium constants for bond retention are so favorable that a silane coupling agent on silica has a thousandfold advantage for bond retention in the presence of water over an alkoxysilane bond formed from hydroxy-functional polymers and silica. In practice, the bonds of certain epoxies to silane-primed glass resist debonding by water about a thousand times as long as the epoxy bond to unprimed glass.

Oxane bonds of silane coupling agents to metal oxides seem to follow the same mechanism of equilibrium hydrolysis and rebonding, although equilibrium constants have not been measured for individual metal-oxygen-silicon bonds. This suggests, however, that methods of improving bond retention to glass will also improve the water resistance of bonds to metals. Modification of standard coupling agents with a hydrophobic silane or one with extra siloxane cross-linking have improved the water resistance of bonds to glass and metals another hundredfold over that obtained with single coupling agents.

Bonds of polymers to silane-treated surfaces may involve simple reaction of the polymer with functional groups of the silane, but most often involve an interdiffusion of siloxane oligomers into the polymer with subsequent cross-linking to form interpenetrating polymer networks in the interphase region. This mechanism correlates with the observation that a silane primer that bonds two different polymers to glass can also be used to bond the two polymers to each other.

A simple screening test has been used for evaluating silane primers in bonding many thermosetting and thermoplastic polymers to glass and

metals. Ratings from these tests provide a guide for formulators in developing optimum bonding primers.

Bonding through silane coupling has been disappointing in processes, such as extrusion or injection molding, that involve high shear in the melt. Bonds between coupling agent and polymer are made and broken during the time of high-temperature shear, so that the full value of coupling agents are not retained. A new method has been proposed that bonds silane-treated particulate fillers to polymers through ionomer linkages. Under conditions of high-temperature shear, the ionomers are fluid, but they set to bonded structures when cooled to room temperature.

Edwin P. Plueddemann



Preface to the First Edition

It has been rumored that a bumblebee has such aerodynamic deficiencies that it should be incapable of flight. Fiberglass-reinforced polymer composites, similarly, have two (apparently) insurmountable obstacles to performance: (1) Water can hydrolyze any conceivable bond between organic and inorganic phases, and (2) stresses across the interface during temperature cycling (resulting from a mismatch in thermal expansion coefficients) may exceed the strength of one of the phases.

Organofunctional silanes are hybrid organic-inorganic compounds that are used as coupling agents across the organic-inorganic interface to help overcome these two obstacles to composite performance. One of their functions is to use the hydrolytic action of water under equilibrium conditions to relieve thermally induced stresses across the interface. If equilibrium conditions can be maintained, the two problems act to cancel each other out.

Coupling agents are defined primarily as materials that improve the practical adhesive bond of polymer to mineral. This may involve an increase in true adhesion, but it may also involve improved wetting, rheology, and other handling properties. The coupling agent may also modify the interphase region to strengthen the organic and inorganic boundary layers.

Primary suppliers of coupling agents have been cooperative in describing the composition and chemistry of their products in order to help formulators to use them intelligently. Commercial formulated sizes, primers, and adhesives, however, are generally considered proprietary and are described only in terms of performance. This book discusses applications of silane coupling agents in areas where full disclosure of chemistry and composition are possible, with essentially no mention of proprietary formulations.

Fiberglass-reinforced plastic composites have been developed to high-performance materials since their introduction in 1940. For the first 20 years,

the development was based on practical performance tests, and concepts of mechanisms involved were based largely on indirect evidence. In recent years, the interface has been studied extensively by advanced analytical techniques of surface science. This book covers both areas of study into the early 1980s. It combines practical technology with fundamental science to arrive at a useful understanding of the interface in composites. It should help scientists design experiments to further their studies of the interface, and should help technologists develop better composites from available materials.

It is now possible to obtain silane coupling agents to modify common mineral surfaces for reinforcement of almost any organic polymer.

Even the best coupling agent for a given composite may perform poorly if it is not applied properly. Orientation of the molecules and physical properties of the film (solubility, fusibility, and mechanical properties) can be controlled by the method of application, and may be as important as the chemistry of the selected silane.

An understanding of materials and mechanisms of adhesion should allow consistent preparation of composites that utilize the full capabilities of fillers, reinforcements, and matrix resins.

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1 | General Concepts

1.1. History of Coupling Agents

Although bonding of organic polymers to inorganic surfaces has long been a familiar operation (e.g., protective coatings on metals), a major need for new bonding techniques arose in 1940 when glass fibers were first used as reinforcement in organic resins. The specific strength-to-weight ratios of early glass-resin composites were higher than those of aluminum or steel, but they lost much of their strength during prolonged exposure to moisture. This loss in strength was attributed to the debonding of resin from hydrophilic glass by the intrusion of water.

Careful preparation of glass-resin bonds under dry conditions did not produce more water-resistant composites. Even bonds of resin to fresh glass surfaces, fractured in liquid resin before polymerization, did not withstand the action of water. Clearly, the interface between such dissimilar materials as an organic polymer and a mineral did not allow the formation of a water-resistant bond.

The concept that two dissimilar materials may be held together by a third intermediate material as coupling agent was used by Plato¹ to explain how a universe made up of four elements—earth, air, fire, and water—could exist as a homogeneous whole:

It is not possible for two things to be fairly united without a third, for they need a bond between them which shall join them both, that as the first is to the middle, so is the middle to the last, then since the middle becomes the first and the last, and the last and the first both become middle, of necessity, all will come to be the same, and being the same with one another, all will be a unity.

Because organofunctional silicones are hybrids of silica and of organic materials related to resins, it is not surprising that they were tested as coupling agents to improve bonding of organic resins to mineral surfaces.

Modification of the interface between an organic polymer and an inorganic substrate may have many beneficial results in composite manufacture, but “coupling agents” should be defined as materials that improve the chemical resistance (especially to water) of the bond across the interface. Although any polar functional group in a polymer may contribute to improved adhesion to mineral surfaces, a methacrylate–chrome complex (Volan A[®])² and the various organofunctional silanes have shown the most promise as true coupling agents.

In 1947, Ralph K. Witt et al. of Johns Hopkins University, in a “confidential” report to the Navy Bureau of Ordnance, observed that allyltriethoxysilane on glass fibers gave polyester composites with twice the strength of those where the glass was treated with ethyltrichlorosilane.

The Bjorksten organization was given a contract by the U.S. Air Force in about 1949 (AFTR 6220) to explore the effect of glass fabric treatments on polyester laminate wet strength properties. A total of 2000 compounds was screened. The best of these, and still good by today’s standards, was a nonaqueous solvent treatment (BJY) based on an equimolar adduct of vinyl trichlorosilane and β -chloroallyl alcohol.³

Polyester laminate strength data obtained by the Bjorksten group using their BJY treatment are shown in Figure 1.1. Laminates with treatments 114 (chrome) and 112 (no finish) are also shown for comparison. After 5 hr

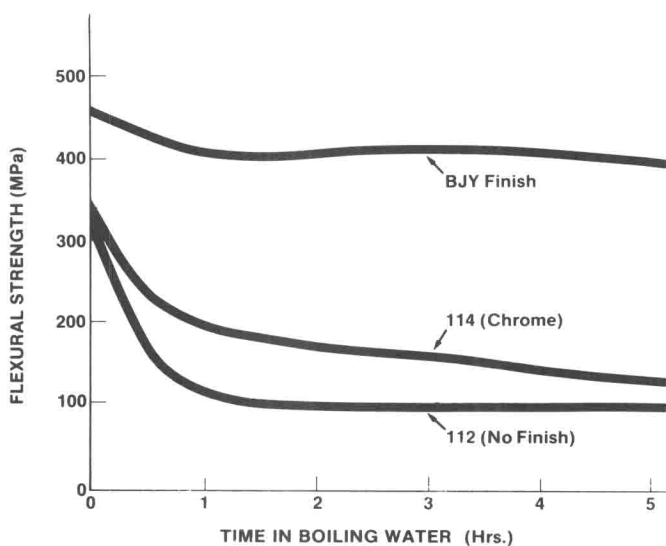


Figure 1.1. Polyester laminate strengths in 1950 from data of Bjorksten.³

in boiling water, the flexural strength of the BJY laminate was still above 400 MPa and was, in fact, substantially greater than the original dry strength of the other laminates.

Over a hundred different organofunctional silanes were evaluated as coupling agents in glass-reinforced polyester and epoxy composites by Plueddemann et al.⁴ in 1962. In general, the effectiveness of the silane as a coupling agent paralleled the reactivity of its organofunctional group with the resin. Styrene-diluted polyester resins are complex mixtures of oligomeric maleates and fumarates in a reactive monomer, but the performance of silanes showed good correlation with their expected relative reactivity in copolymerizing with styrene (Table 1.1).

Two events in 1963 had an impact on subsequent interface investigations. The first event was the formation of the Ad Hoc Committee on the Interface Problem in Fibrous Composites by the Materials Advisory Board. This committee was charged with investigating the problem in depth in order to define problem areas and to come up with recommendations on what sort of research should be sponsored. Universities, government, and industry were represented by persons from many disciplines. The committee report (MAB-214-M) was published in 1965. A most important finding was that the principles of surface chemistry related to the problem had been virtually ignored for about 15 years. A major recommendation was that research efforts be scaled up to a level of 50 senior investigators for a period of 5 years.

The second event to have an impact on the type of research done was a 2-day meeting by invitation only on the interface problem at the Naval

Table 1.1. Relation of Reactivity with Styrene to Effectiveness of Silane Finishes in Polyester Composites

Silane finish reactive group	Relative reactivity with styrene	Order of wet strength of polyester laminates
Fumarates	3.3	2
Methacrylates	1.9	1
Acrylates	1.34	3
Isoprene	1.3	9
Styrene	1.0	5
Vinyl sulfides	0.2	6
Maleates	0.15	4
Crotonates	0.05	11
Vinyl Si	0.05	7
Allyl Si	0.03	8
Allyl esters	0.011	10
Vinyl ethers	0.01	12

Research Laboratory in Washington in June 1963. This was attended by about 75 persons from government, universities, and industry. The proceedings were not published, but this meeting had an impact on the type of interface research that the government sponsored in succeeding years. Surface chemistry investigations began in earnest exploring basic phenomena at the interface. The Air Force followed by sponsoring interface research using radioisotope methods.

Instrumental techniques have been developed in recent years to study the chemistry of the interface in reinforced composites through laser Raman spectroscopy and Fourier transform infrared spectroscopy. It is now possible to observe chemical reactions at the interface that had previously been inferred from indirect evidence⁵ (Chapter 4).

A consistent forum for discussion of interface phenomena have been the “interface” sessions held for over 40 years at the Annual Technical Conferences of the Reinforced Plastics Division of the Society of Plastics Industry (SPI). In recent years, many technical societies have organized symposia on “the interface.” The International Conference on Composite Interface was first held at Case-Western Reserve University in 1986 and now is established as a biannual meeting devoted entirely to composite interface studies.

1.2. Definitions

Organofunctional silanes may be used as adhesion promoters between organic polymers and mineral substrates under a variety of circumstances. The silane adhesion promoter, or “coupling agent,” may function as (1) a finish or surface modifier, (2) a primer or size, or (3) an adhesive, depending on the thickness of the bonding material at the interface.

A surface modifier or “finish” may theoretically be only a monomolecular layer, but in practice it may be several monolayers thick. The material functions to chemically modify a surface without contributing any mechanical film properties of its own.

A primer or size is generally 0.1 to 10 μm thick, and must have adequate mechanical film properties, such as rigidity, tensile strength, and toughness to carry the mechanical load when the composite is stressed. The primer may be a layer of hydrolyzed silane or a silane-modified polymer. It is generally applied from a solvent to ensure uniform coverage of the surface.

An adhesive is a gap-filling polymer used to bond solid adherents such as metals, ceramics, or wood, whose solid surfaces cannot conform to one another on contact. Pure silanes are rarely used as adhesives; rather, they are used to modify gap-filling polymers or polymer precursors to improve

surface adhesion. Silane monomers may be used in integral blends of fillers and liquid resins in the preparation of composites. The modified polymer "adhesive" in this case is termed a matrix resin.

The fiberglass industry uses terminology derived from the textile industry. Much of the glass fiber made for a filament winding or as chopped roving is given a single and final treatment at the time of forming. Such a treatment is correctly called a size. The treating solution is a mixture of many things, the more important being lubricant, antistat, binder, and coupling agent. The first of these provides surface lubricity, which prevents abrasive damage during handling. A binder is necessary for strand integrity, because the single filaments do not normally pack well due to static electricity. There may also be other factors. (An antistat is added to prevent buildup of static electricity during mechanical handling.) The glass may pick up 1% or 2% of the size, of which about 10% will be silane adhesion promoter. Size formulations on commercial glass are proprietary for each manufacturer and are formulated to combine good handling properties of the roving with good adhesion (primer action) for particular resins. Different sizes are formulated for polyesters, epoxies, etc.

The other type of treatment is called a finish. Glass fibers that are to be given a finish are also given a size at the time of forming. This size contains ingredients that provide surface lubricity and binding action, but usually no coupling agent is present. These fibers in the sized condition can be plied and woven into fabric without any significant damage to the fibers. Before the finish is applied it is necessary to remove this size. This is accomplished by heating the fabric (or roving) in air-circulating ovens to burn the size away. The finish is then applied from solution to the heat-cleaned fabric to complete the treatment. The major chemical in the finish treatment is a coupling agent, but other materials may be included to improve lubricity, resin wet-out, etc. The total pickup of finish on glass fibers is generally about 0.1%. Each weaver supplies glass with proprietary finishes for reinforcement of specific resins. Although modification of silanes with organic polymers may provide some improvement in primer performance where film properties are important, a silane solution with only minor modification appears to be the best finish on glass cloth.

Silane coupling agents for reinforced composites are required to fulfill rather complex responses, which may vary with different methods of application. For treatment of fiberglass it is required that the silane be soluble in water, and that dilute aqueous solutions remain predominantly monomeric for at least one day in the treating bath. When dried on the glass surface, the coupling agent must condense to polysiloxane structures that retain a degree of solubility in order to be compatible with the matrix resin. During the curing of the composite it is advantageous if the interphase region

controlled by the coupling agent is hydrophobic and highly cross-linked. Since fiberglass may be stored for months or years, it is important that the siloxane structure does not cross-link too highly during storage.

When formulated as primers, silanes must be stable in more concentrated solutions of suitable solvents such as aqueous alcohols. A minimum shelf stability of 6 months is desired. After filming on a surface, the condensed siloxanes need to be soluble and fusible for only several minutes or hours. The dried primer film must be compatible with the matrix resin and contribute a high degree of cross-linking at the interface.

1.3. Evaluation

Although coupling agents may perform several useful functions at the interface in mineral-reinforced composites, the coupling agent is expected first of all to improve the adhesion between resin and mineral, and then to improve retention of properties in the presence of moisture. Several simple laboratory tests are recommended to evaluate any new potential coupling agent. More extensive and sophisticated evaluation then may be used to refine the application for optimum performance.

1.3.1. Thin Film Tests

A simple accelerated test for adhesion that is useful for rapid screening of adhesion promoters is to form a thin film of polymer on primed glass microscope slides or metal coupons and soak in water until the film can be loosened with a razor blade. There is usually a clear transition between cohesive failure and interfacial failure. Since diffusion of water to the interface is very rapid in this test, the time to failure depends on the interfacial properties and may differ several-1000-fold between unmodified polymers and silane-modified polymers. Different silane primers may differ several-100-fold in performance with a given polymer.⁶

Commercial microscope slides provide convenient clean surfaces for observing adhesion of resins to glass. The slides may be dipped in dilute (e.g., 0.5%) aqueous solutions of silane or wiped with a 10–25% solution of prehydrolyzed silane in an alcohol (primer). Thermoplastic resins are then fused under light pressure against the treated slides. Thermosetting resins are applied as liquids and cured against the treated slides. The finished films on glass are observed for initial adhesion and then soaked in water at room temperature or at elevated temperature to determine resistance of the bond to intrusion by water.