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A Guide to Silane Solutions

Silane Coupling Agents

The Concept of Coupling with Organofunctional Silanes

Silane Coupling Agents

Silane coupling agents are silicon-based chemicals that contain two types of reactivity – inorganic and organic – in the same molecule. A typical general structure is

$$(RO)_3SiCH_2CH_2CH_2\text{-}X,$$

where RO is a hydrolyzable group, such as methoxy, ethoxy, or acetoxy, and X is an organofunctional group, such as amino, methacryloxy, epoxy, etc.

A silane coupling agent will act at an interface between an inorganic substrate (such as glass, metal or mineral) and an organic material (such as an organic polymer, coating or adhesive) to bond, or couple, the two dissimilar materials. A simplified picture of the coupling mechanism is shown in Figure 1.

Figure 1. The silane coupling mechanism.

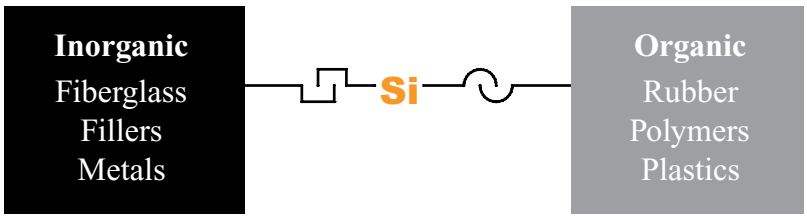
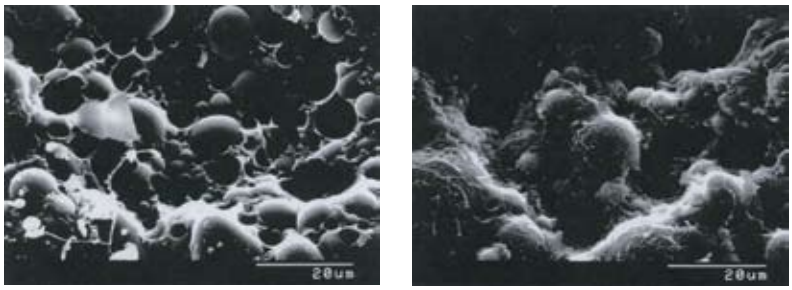


Figure 2. SEM of silica-filled epoxy resin.



Without Silane **With Silane**

Why Silane Coupling Agents Are Used

When organic polymers are reinforced with glass fibers or minerals, the interface, or interphase region, between the polymer and the inorganic substrate is involved in a complex interplay of physical and chemical factors. These factors are related to adhesion, physical strength, coefficient of expansion, concentration gradients and retention of product properties. A very destructive force affecting adhesion is migration of water to the hydrophilic surface of the inorganic reinforcement. Water attacks the interface, destroying the bond between the polymer and reinforcement, but a “true” coupling agent creates a water-resistant bond at the interface between the inorganic and organic materials. Silane coupling agents have the unique chemical and physical properties not only to enhance bond strength but also, more importantly, to prevent de-bonding at the interface during composite aging and use. The coupling agent provides a *stable* bond between two otherwise poorly bonding surfaces. Figure 2 shows (via an SEM of the fracture surface) the difference in adhesion between a silica-filled epoxy resin *with* silane vs. *without* silane. With silane, the epoxy coating on the silica particles is apparent; without silane, clean silica particles can be seen in the epoxy matrix.

In composites, a substantial increase in flexural strength is possible through the use of the right silane coupling agent. Silane coupling agents also increase the bond strength of coatings and adhesives as well as their resistance to humidity and other adverse environmental conditions.

Other benefits silane coupling agents can provide include:

- Better wetting of inorganic substrates
- Lower viscosities during compounding
- Smoother surfaces of composites
- Less catalyst inhibition of thermoset composites
- Clearer reinforced plastics

The Silane Bond to the Inorganic Substrate

Silane coupling agents that contain three inorganic reactive groups on silicon (usually methoxy, ethoxy or acetoxy) will bond well to the metal hydroxyl groups on most inorganic substrates, especially if the sub-strate contains silicon, aluminum or a heavy metal in its structure. The alkoxy groups on silicon hydrolyze to silanols, either through the addition of water or from residual water on the inorganic surface. Then the silanols coordinate with metal hydroxyl groups on the inorganic surface to form an oxane bond and eliminate water. See Figures 3 and 4.

Figure 3. Hydrolysis of alkoxysilanes.

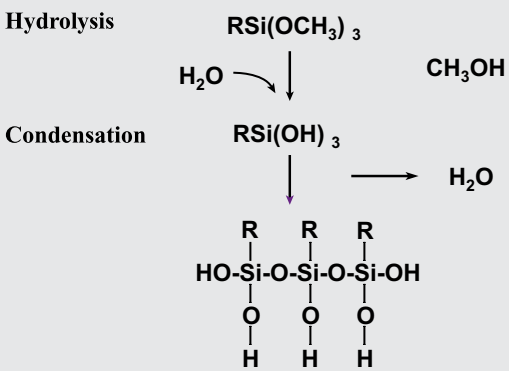
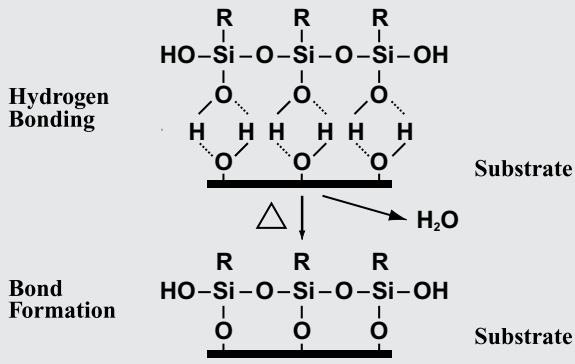


Figure 4. Bonding to an inorganic surface.



Silane molecules also react with each other to give a multimolecular structure of bound silane coupling agent on the surface. More than one layer, or monolayer equivalents, of silane is usually applied to the surface. This results in a tight siloxane network close to the inorganic surface that becomes more diffuse away from the surface.

The Silane Bond to the Polymer

The bond to the organic polymer is complex. The reactivity of a thermoset polymer should be matched to the reactivity of the silane. For example, an epoxysilane or amino-silane will bond to an epoxy resin; an aminosilane will bond to a phenolic resin; and a methacrylate silane will bond through styrene crosslinking to an unsaturated polyester resin. With thermoplastic polymers, bonding through a silane coupling agent can be explained by inter-diffusion and inter-penetrating network (IPN) formation in the interphase region. See Figure 5.

To optimize IPN formation, it is important that the silane and the resin be compatible. One method is to match the chemical characteristics of the two materials. This will help improve the chances of forming a good composite with optimum properties. Even with thermoset polymers, where reactivity plays an important role, chemical structure matching will enhance the physical properties of the composite.

How to Choose a Silane Coupling Agent

All silane coupling agents with three OR groups on silicon should bond equally well with an inorganic substrate. The XIAMETER® brand product line includes a variety of organofunctional alkoxysilanes. See Figure 6.

Matching the organofunctional group on silicon with the resin polymer type to be bonded will dictate which silane coupling agent should be used in a particular application. The organic group on the silane can be either a reactive organic group (i.e., an organofunctional group), or it can be a non-reactive organic group. The groups can be hydrophobic or hydrophilic, with varying thermal stability characteristics.

Figure 5. The inter-penetrating network (IPN) bonding mechanism.

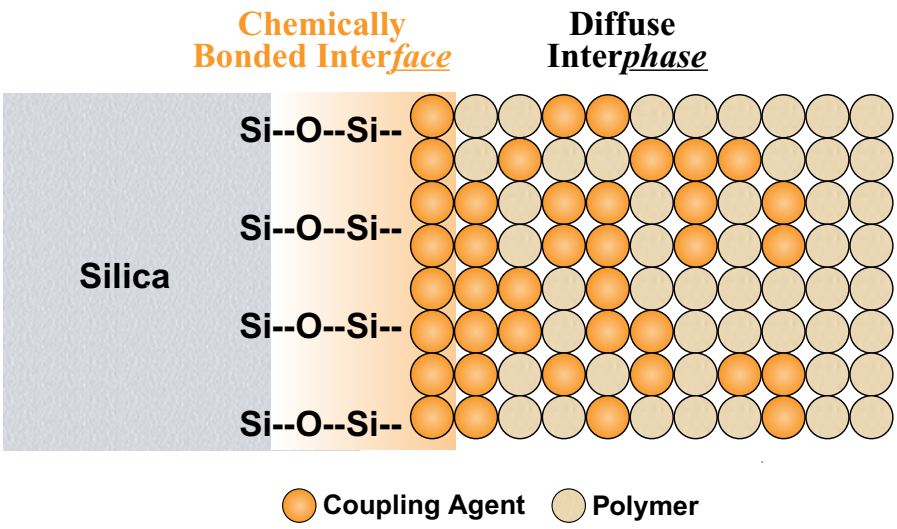
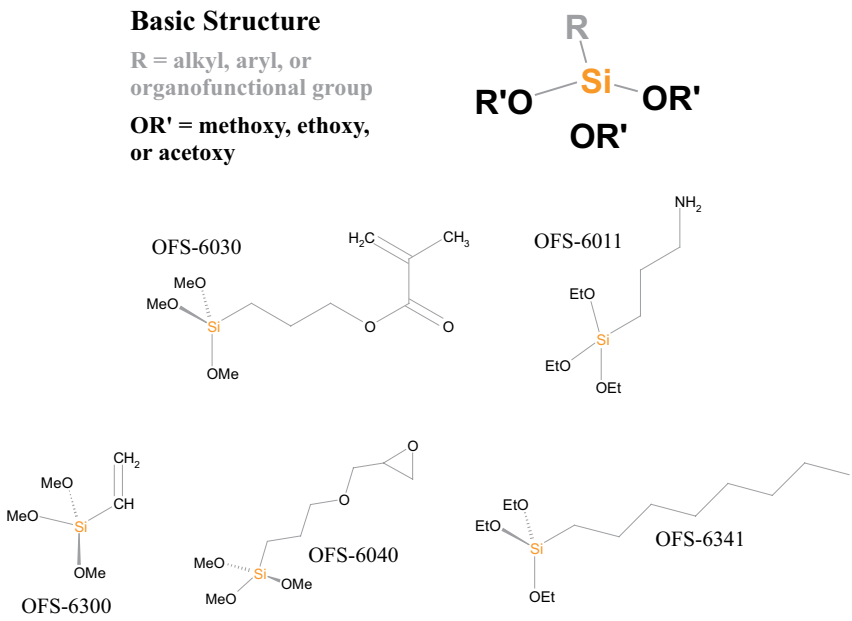


Figure 6. Silane coupling agent variations – basic structure.



The solubility parameters of the groups will vary, depending on the organic structure; this will influence, to some extent, the interpenetration the polymer network will have into the siloxane network of the surface treatment. Table 1 lists some of the characteristics for common organic substituents attached to silicon. The choice of silane should involve matching chemical reactivity, solubility characteristics, structural characteristics and, possibly, the thermal stability of the organosilane with the same parameters in the polymer structure.

Table 1. Characteristics of Various Organic Substituents on Silanes

Organosilanes R-Si(OMe)$_3$	
R	**Characteristics of "R"**
Me	Hydrophobic, Organophilic
Ph	Hydrophobic, Organophilic, Thermal Stability
i-Bu	Hydrophobic, Organophilic
Octyl	Hydrophobic, Organophilic
-NH(CH$_2$) $_3$NH$_2$	Hydrophilic, Organoreactive
Epoxy	Hydrophilic, Organoreactive
Methacryl	Hydrophobic, Organoreactive

Table 2. Non-Organoreactive Alkoxysilanes

XIAMETER® brand Silane	Organic Group	Alkoxy Group	Chemical Name
OFS-6697	-	Ethoxy	TetraEthoxysilane
OFS-6070	Methyl	Methoxy	Methyltrimethoxysilane
OFS-6366	Methyl	Methoxy	Methyltrimethoxysilane (HP)
OFS-6370	Methyl	Ethoxy	Methyltriethoxysilane
OFS-6383	Methyl	Ethoxy	Methyltriethoxysilane (HP)
OFS-2306	i-Butyl	Methoxy	Isobutyltrimethoxysilane
OFS-6124	Phenyl	Methoxy	Phenyltrimethoxysilane
OFS-6341	n-Octyl	Ethoxy	n-Octyltriethoxysilane

More Hydrophobic

Table 3. Silane Coupling Agent Recommendations for Various Polymers – Matching Organoreactivity to Polymer Type

Organic Reactivity	Application (suitable polymers)
Amino	Acrylic, Nylon, Epoxy, Phenolics, PVC, Urethanes, Melamines, Nitrile Rubber
Benzylamino	Epoxies for PCBs, Polyolefins, All Polymer Types
Chloropropyl	Urethanes, Epoxy, Nylon, Phenolics, Polyolefins
Disulfido	Organic Rubber
Epoxy	Epoxy, PBT, Urethanes, Acrylics, Polysulfides
Epoxy/Melamine	Epoxy, Urethane, Phenolic, PEEK, Polyester
Mercapto	Organic Rubber
Methacrylate	Unsaturated Polyesters, Acrylics, EVA, Polyolefin
Tetrasulfido	Organic Rubber
Ureido	Asphaltic Binders, Nylon, Phenolics; Urethane
Vinyl	Graft to Polyethylene for Moisture Crosslinking, EPDM Rubber, SBR, Polyolefin
Vinyl-benzyl-amino	Epoxies for PCBs, Polyolefins, All Polymer Types

A list of alkyl and aryl, non-organoreactive alkoxysilanes is provided in Table 2. Those silanes give modified characteristics to inorganic surfaces, including hydrophobicity, organic compatibility and lower surface energy.

Based on experience and historical applications of silanes, a list of silane coupling agents and recommendations for evaluation with various polymer types is provided in Table 3. A correlation can be seen between the chemistry and structural characteristics of the silane coupling agent and the chemistry and structural characteristics of the polymer.

Product Information

A complete list of XIAMETER® brand silanes for use as coupling agents is available at xiameter.com.

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