

The Use of Mixed Silane Coupling Agents

The information in this Silane Lab Note is based on the work of Edwin P. Plueddemann and Peter G. Pape.

Overview

Organofunctional silanes used as coupling agents or primers for the adhesion of organic polymers to mineral substrates are almost invariably used at more than mono-layer coverage of the mineral surface. Regardless of the method of application, they are believed to condense on the mineral surface to build an oligomeric siloxane network capable of forming covalent “oxane” bonds to the mineral surface. The oligomeric siloxane (condensed silane) layer is modified by its reactions with the resin during fabrication of composites. The resin phase diffuses into the siloxane layer and reacts to form an interpenetrating polymer network (IPN) during fabrication. The resulting interphase region must have certain characteristics for optimum performance.

- Oxane bond formation with the mineral surface should be completed. This may require controlled drying at an elevated temperature or use of a catalyst.
- The interphase region should have low water absorption, best accomplished by incorporating hydrophobic substituents in the coupling agents.
- A well-developed network in the interphase region is necessary, through cross-linking of the siloxane and reaction with the resin.

It is not always possible to optimize all of these factors in a composite with a single silane, but many composites can be improved greatly by using a mixture of silanes.

Mixed silanes have been used for years in primers and coupling agents for composites. Commercial compositions are generally proprietary and are formulated for specific handling properties of the glass or of the finished composite.

General Guidelines

Some typical silanes to consider in mixed silane applications are shown in Table 1. Methylsilane G, phenylsilane I and chloropropylsilane B are not generally considered to be coupling agents with most resins, but they may contribute hydrophobic siloxane structures to mixed silane coupling agents. Vinyl silane A is a coupling agent for polymers curing by a free radical mechanism, but it may also

Table 1. Representative Commercial Coupling Agents

Organofunctional Group	Chemical Structure	Dow Corning® Product
A Vinyl	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$	Z-6300 Silane
B Chloropropyl	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Z-6076 Silane
C Epoxy	$\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Z-6040 Silane
D Methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Z-6030 Silane
E Primary Amine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Z-6011 Silane
F Diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Z-6020 Silane
G Methyl	$\text{CH}_3\text{Si}(\text{OCH}_3)_3$	Z-6070 Silane
H Vinyl-Benzyl Amine	$\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 \cdot \text{HCl}$	Z-6032 Silane
I Phenyl	$\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$	Z-6124 Silane

contribute hydrophobic siloxane structures to mixed silanes. Silanes with small organic groups on silicon (A and G) will crosslink to tighter siloxane structures than can be obtained with silanes with large organofunctional groups. Amine-functional silanes E, F and H can act as catalysts for siloxane formation in mixtures with neutral silanes.

The total siloxane structure at an interface determines the effectiveness of silane coupling agents in promoting adhesion between different phases. Individual silanes in a mixture may contribute certain properties not attainable with single silanes.

Free-Radical Curing Matrix Polymers

Free-radical curing matrix polymers benefit least from mixed silanes on the reinforcement. Single reactive silanes with methacrylate, vinyl or vinyl-benzyl functionality react completely in free-radical initiated polymerization. Dilution with other silanes may increase the degree of siloxane crosslinking, but decrease the degree of polymerization through free radicals. A catalytic amount of an amino-functional silane (about 1% of total silane) may be beneficial in condensing the siloxane with an inorganic substrate. However, larger proportions of aminosilanes introduce more hydrophilicity into the interphase region that reduces hydrolytic stability.

Condensation Polymers

Condensation polymers such as urethanes or epoxies may benefit greatly by mixing neutral, hydrophobic silanes with reactive silanes. A condensed siloxane layer derived from a reactive silane presents more reactive sites than the functional groups of the condensation polymer can consume. Unreacted functional groups remain, then, as hydrophilic points for attack by water. About 90% of neutral, hydrophobic silane seems about optimum in these mixes, and phenyl or chloropropylsilanes seem to provide the best compatibility with most polymers.

High-Temperature Composites

High-temperature composites benefit the most if stable aromatic silanes are mixed with organofunctional silanes in the coupling agent. Phenyltrimethoxy silane is the preferred aromatic silane. A major proportion of the mix should be aromatic. Only enough organofunctional silane should be included to give initial compatibility and reactivity with the matrix resin. During cure, the siloxane layer further condenses to improve the integrity of the siloxane/resin IPN. Even after the aliphatic organofunctional groups are burned off from the siloxane, an interpenetrating aromatic silicone remains that has heat and oxidation resistance comparable to the most stable organic resins.

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