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Silicones Simplified

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A Guide to Silane Solutions

Plastics, Polymerization and Rubber

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The unique properties of silanes are used to enhance performance and improve processes in the plastics and rubber industries. Silanes function as coupling and dispersing agents for fillers in rubber and plastics formulations, as polymerization modifiers in the synthesis of polypropylene, and as crosslinking agents for polyethylene homopolymers and copolymers.

Plastics Compounding

Vinyl silanes have been used commercially since the 1970s to crosslink polyethylene homopolymer and its copolymers. Vinyltrimethoxysilane and vinyltriethoxysilane are the most common silanes used in the process. In an extruder in the presence of peroxide and heat, the vinyl group will *graft* to the polyethylene backbone, yielding a silane-modified polyethylene that contains pendant trialkoxysilyl functionality. The grafted polyethylene can then be immediately crosslinked in the presence of a tin catalyst, moisture and heat to create a silane-crosslinked product. Diagrams of the grafting of vinyltrimethoxysilane (VTMOS) to polyethylene and the moisture crosslinking process are shown in Figures 1 and 2. The ease of processing and the simple equipment required make this the preferred method of producing crosslinked ethylene polymers and copolymers. The process also allows crosslinking to be delayed until after the grafted product is

Figure 1. Grafting of VTMOS to polyethylene – *Sioplas*[®] process.

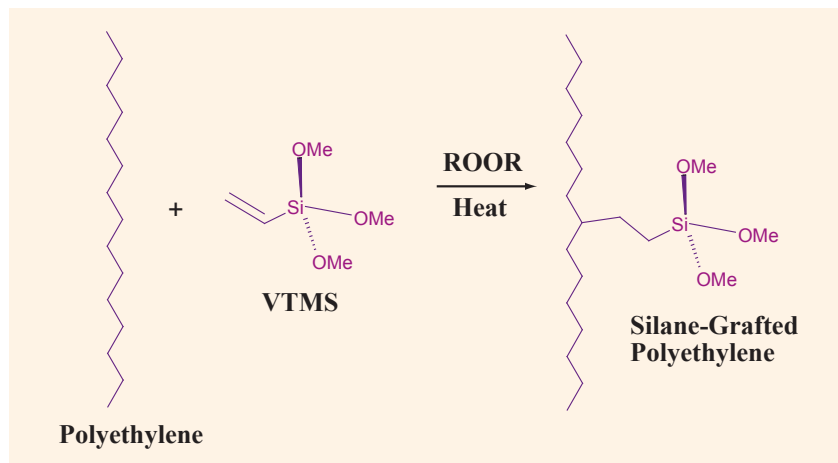
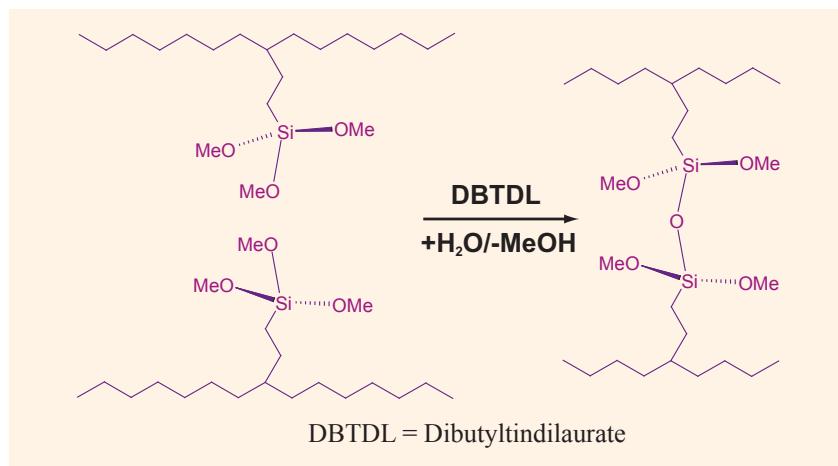


Figure 2. Crosslinking of polyethylene in the presence of moisture – *Sioplas*[®] process.



transformed into its final product configuration. Using the same silanes, it is also possible to copolymerize the vinyl silane with ethylene monomer to make trialkoxysilyl-functionalized polyethylene. This then can be crosslinked in the same manner as the graft version.

Silane-crosslinked polyethylene is used for electrical wire and cable insulation and jacketing where ease of processing, increased temperature resistance, abrasion resistance, stress-crack resistance, improved low-temperature properties and retention of electrical properties are

needed. Other applications for this technology include:

- Cold- and hot-water pipe where resistance to long-term pressure at elevated temperatures is essential
- Natural gas pipe with good resistance to stress cracking
- Foam for insulation and packaging with greater resiliency and heat resistance
- Other product and process types, such as film, blow-molded articles, sheeting and thermoforming

Polymer Manufacturing

Selected silanes, known as “external donors,” or electron donors, are used in conjunction with Ziegler-Natta catalysts in the manufacture of polypropylene. Ziegler-Natta catalysts are organometallic compounds. Organoalkoxysilanes can chemically coordinate with the organometallic catalyst to modify the course of the polymerization. Specific variations in the tacticity of the propylene polymer are possible by optimizing the use of a silane donor in the process. Different silane donors with differing organoalkoxy structures are used depending on the exact nature of the catalyst and the type of polypropylene being manufactured. Organic substituents, such as cyclohexyl, cyclopentyl, methyl, isobutyl, and phenyl, are some of the organic groups attached to silicon. The

alkoxy groups are either methoxy or ethoxy with one, two, or three alkoxy groups on the silane molecule. Two of the more common silane donors are Donor C, cyclohexylmethyldimethoxysilane (XIAMETER® OFS-6187 Silane); and Donor D, dicyclopentylmethoxydimethoxysilane (XIAMETER® OFS-6228 Silane).

Reactive silicone polymers have also been used to produce thermoplastic vulcanizates (TPVs). TPVs are prepared by chemically crosslinking a rubbery phase in a thermoplastic matrix. TPVs are produced by dynamic vulcanization, and silane chemistry allows new and unique crosslinking chemistries to be used in the manufacturing process.

Rubber Compounding

A major use for silanes has developed in the organic rubber industry as a result of the benefits that can be obtained from the use of inorganic filler in place of carbon black in the reinforcement of rubber. Silica and other inorganic filler reinforcements for rubber provide unique physical properties and performance properties versus carbon black reinforcement; however, silane coupling agents are necessary for the non-black reinforcing fillers to be effective.

Silanes are the key to providing a method of effectively bonding inorganic fillers to organic elastomers. Silane-coupled, mineral-filled

rubber products are used for automotive and off-road tires, shoe soles, belts, hoses, and mechanical goods.

Methoxy- or ethoxy-silanes will bond tenaciously to the silica or clay surface; then the organic portion of an organo-functional silane will bond to the rubber polymer. See Figure 3.

The silane is usually added during the compounding process to treat the filler *in situ*. It must have the proper rate of reactivity to spread and react over the filler surface and still be able to react with the elastomer at a rate that allows processing of the rubber to be completed.

This can be done with silane coupling agents that have triethoxysilyl groups at both ends of a polysulfido (tetrasulfide, disulfide or mixture thereof) organic group. See Figure 4.

These coupling agents are supplied as neat liquids or as blends with a carrier such as carbon black. Even though silica can be used as the only filler, rubber tires incorporate small levels of carbon black to give consumers the uniform black color they expect. Without carbon black in the rubber compound, it is possible to make tires in a variety of colors.

A specific example of this application is the silica/silane technology used in “green” tires to impart:

- Increased abrasion resistance
- Reduced rolling resistance and improved fuel economy of tires
- Better grip on wet and snow/ice surfaces

Silica-reinforced tires are known as “green” tires because they provide improved fuel economy while maintaining or improving other tire properties

Figure 3. Bonding organic rubber to silica with sulfur silanes.

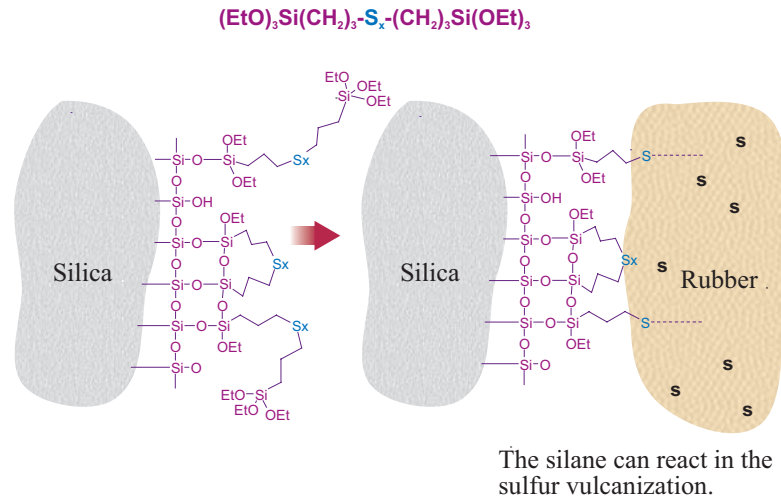
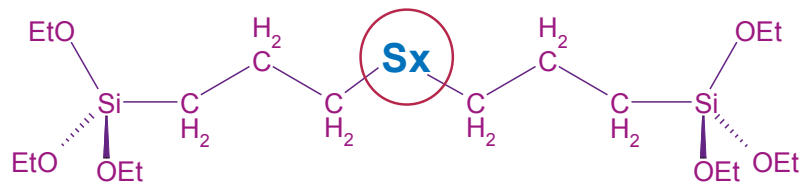


Figure 4. Structure of sulfidosilanes used in rubber compounds.



x ranges from 2 to 10

These are termed S₂, S₃, etc., monomers

Bis-TriEthoxy Silyl Propyl Polysulfide - TESPX

(as listed above). They also use a mineral-derived filler rather than one derived from a fossil fuel (natural gas or oil). This is currently the largest market for silane coupling agents.

The use of vinyl silanes as a coupling agent in kaolin clay reinforced EPDM wire and cable coatings is another important rubber application. The vinyl silane improves the electrical properties of the reinforced rubber so a stringent power-factor electrical test can be passed, but only when optimum silane coupling agent technology is used.

In addition to silanes, the XIAMETER® brand product line includes silicone rubber compounds and bases. Silicone rubber is made from silicone polymers compounded with non-black fillers, usually fumed or precipitated silica. These compounds require silanes and functional silicone fluids. Silanol-functional silicone fluids and vinyl-functional silanes are available for silicone rubber compounding.

Product Information

A complete list of XIAMETER® brand silanes for plastics compounding, polymer manufacturing, and rubber compounding is available at xiameter.com.

Dow Corning Corporation also offers a wide variety of *Dow Corning*® brand specialty silicone material and service options as well as other silicon-based materials to help you keep your innovative edge in the marketplace. Visit dowcorning.com to learn more about the many additional silicone and silicon-based options available to you from Dow Corning.



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