

19. Organo-Functional Silanes

F. de Buyl, Dow Corning Europe SA, Seneffe (Belgium)

The synergy between organic and silicon chemistries has been investigated for more than 50 years, and has led to the development of many organo-functional silanes that are essential today in many applications [1-2-3].

Monomeric silicon chemicals are known as silanes. A silane that contains at least one silicon-carbon bond (e.g., Si-CH₃) is an organosilane. The carbon-silicon bond is very stable and nonpolar, and in the presence of an alkyl group it gives rise to low surface energy and hydrophobic effects.

Organo-functional silanes are molecules carrying two different reactive groups on their silicon atom so that they can react and couple with very different materials (e.g., inorganic surfaces and organic resins via covalent bonds and often via a polymeric “transition” layer between these different materials).

The value of organo-functional silanes as coupling agents was discovered in the 1940s, during the development of fiberglass-reinforced composites [1].

When initially fabricated, these new composites were very strong, but their strength declined rapidly during aging underwater. This weakening was caused by a loss of bond strength between the glass fibers and the resin. Researchers found that certain organo-functional silanes prevented ingress of water and bond displacements at the fiber/resin interface but also significantly increased the composite initial strength (see Figure 1).

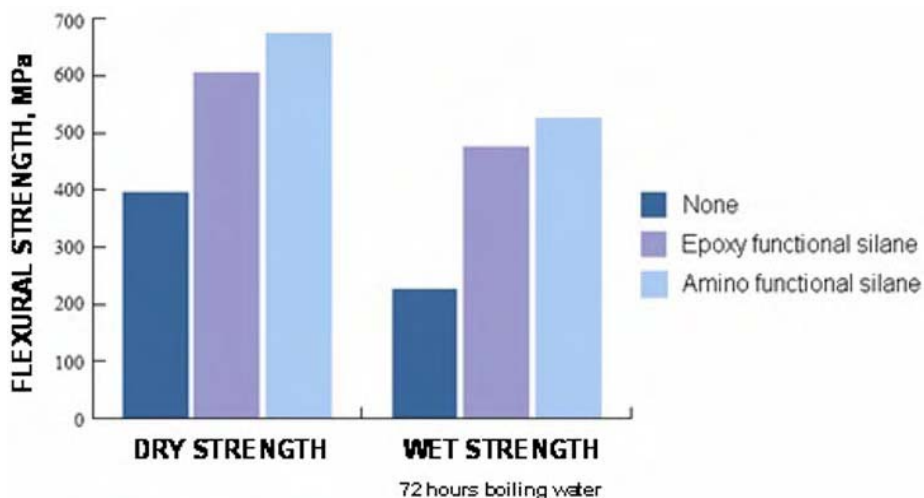


Figure 1. Effect of silane coupling agents on the strength of glass-reinforced epoxy.

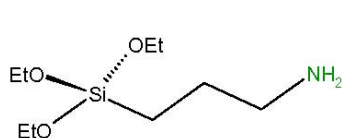
Other applications were later discovered for such silanes, like the treatment of fillers to increase reinforcement, as additives in inks, coatings and sealants to improve adhesion or in plastics and rubbers to allow for cross-linking.

Chemistry of Coupling with Organo-Functional Silanes

Organo-functional silanes have the following typical molecular structure:

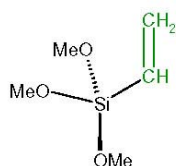


Many combinations are possible, but these are characterized by the fact that they contain two different types of reactive groups. The OR groups are hydrolyzable groups such as methoxy, ethoxy or acetoxy groups. The group X is an organo-functional group, such as epoxy, amino, methacryloxy, or sulfido. The presence of some Si-alkyl groups ensures low surface tension and good wetting properties (see Figure 2).



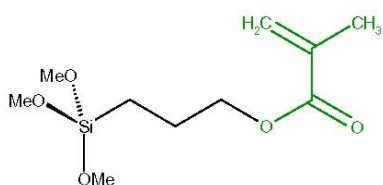
Amino-silane

γ -Aminopropyltriethoxysilane



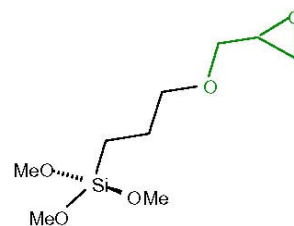
Vinyl-silane

Vinyltrimethoxysilane



Methacryloxy-silane

γ -Methacryloxypropyltrimethoxysilane



Epoxy-silane

γ -Glycidyloxypropyltrimethoxysilane

Figure 2. Examples of organo-functional silanes showing the two different functionalities available for reaction on the Si atom: hydrolyzable alkoxy groups and organic-functional group.

The Si-OR bonds hydrolyze readily with water, even if only with moisture adsorbed on the surface, to form silanol Si-OH groups. These silanol groups can then condense with each other to form polymeric structures with very stable siloxane Si-O-Si bonds. They can also condense with metal hydroxyl groups on the surface of glass, minerals or metals to form stable Si-O-M bonds (M = Si, Al, Fe, etc...). This allows surface treatment, coupling and assembling of very dissimilar surfaces chemically, as between inorganic and organic materials (see Figure 3).

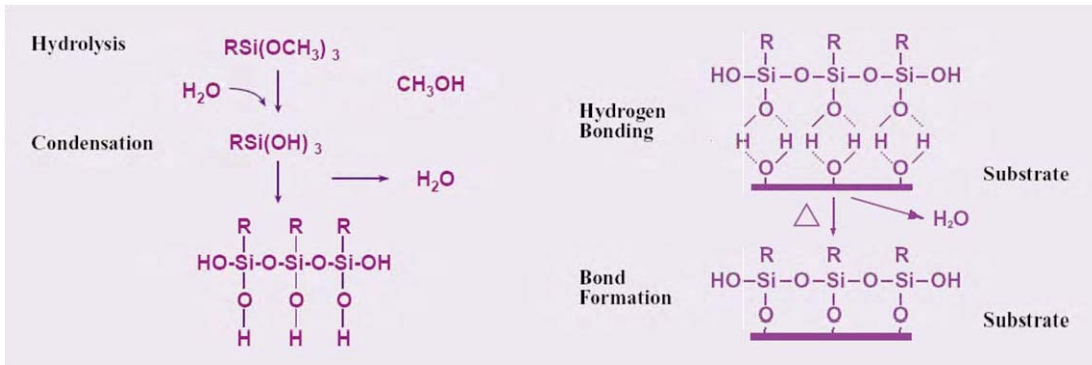


Figure 3. Organo-functional silane hydrolysis, condensation and covalent bonding to an inorganic substrate.

The organo-functional silane concentrations used here are such that more than a monolayer is being built at the interface. A tight polymeric siloxane network is created on the inorganic filler or metal surface, which becomes more diffuse into the adjacent organic resin.

The properties of the organo-functional silane should match the reactivity of the resin with appropriate groups on the silane to react with the resin (e.g., epoxy or amino groups to react with epoxy resins, amino groups to react with phenolic resins or a methacrylate group to react with styrene in unsaturated polyester resins). But also the organo-functional silane should match the solubility parameter of the adjacent resin to ensure a smooth transition at the interphase. The formation of an interpenetrating network (IPN) at the boundary interphase appears essential and probably also explains the improved adhesion observed with thermoplastic polymers (see Figure 4) [4-5].

Organo-functional silanes have shown greatest benefits in three areas: mineral filler treatment, cross-linking and as adhesion promoters.

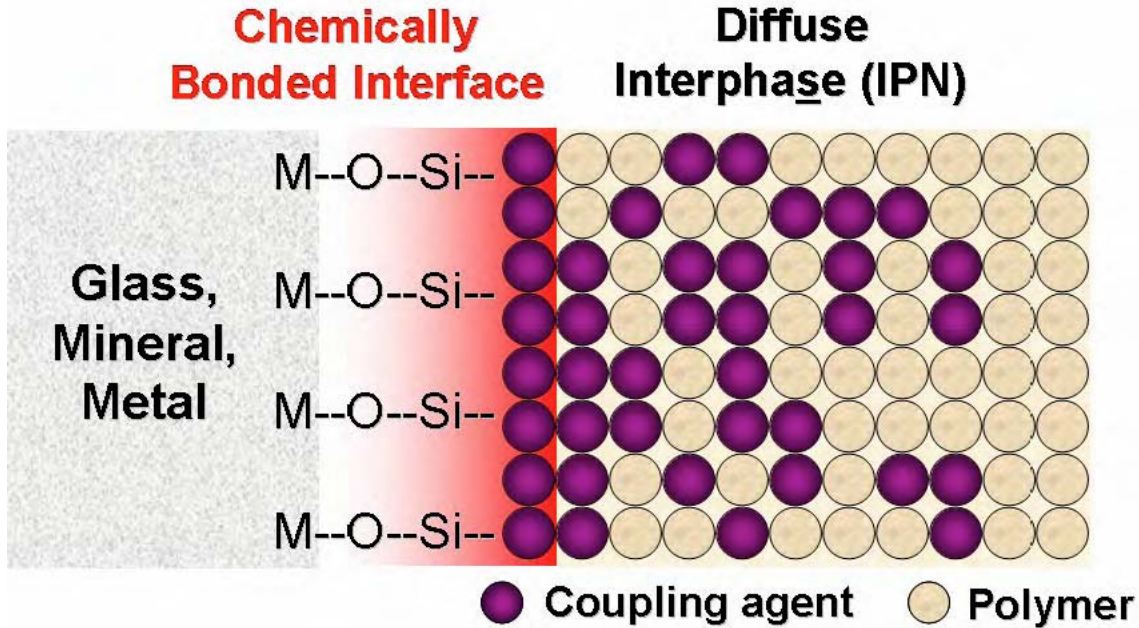
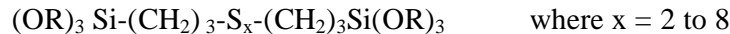


Figure 4. IPN structure created by an organo-functional silane at the interphase between an inorganic glass, mineral, metal substrate ($M = Si, Al, Fe, \dots$) and an organic polymer.

Mineral Filler Treatment. Mineral fillers have become increasingly important modifiers for reinforcing organic polymers, thermoplastics or thermosets. Yet, the metal hydroxyl groups on the mineral filler surface are hydrophilic, and this translates to incompatibility with organic polymers. Organosilanes are ideal for treating the filler surface, making the filler more compatible and easier to disperse in the polymer. Any minerals with silicon or aluminum hydroxyl groups on their surfaces (e.g., silica, glass bead, quartz, sand, talc, mica, clay or wollastonite) can be treated with organo-functional silanes. These will ease dispersion of the fillers and improve wetting by, and adhesion to, the polymer. This results in lower filler/polymer mix viscosities and improved mechanical properties [6].

A typical example is the sulfido-silanes:



Selecting the adequate sulfido-silane enables surface treatment of the silica used in green tires and bonding to organic rubber, which was proven extremely effective for optimizing the viscoelastic and mechanical properties of the silica-rubber composite for “more miles per gallon.”

Cross-Linking. Polymers and polymeric composites are becoming increasingly attractive as engineering materials. They are highly competitive compared to metal or metal alloys due to their low cost and low density, ease of compounding using extrusion or injection molding processes, and inherent lack of corrosion-related problems.

One way to improve performance of such plastics is to cross-link them to some degree. One well-known example using organo-functional silanes is the cross-linking of polyethylene to give partially cross-linked polyethylene or PEX [7-8]. This is achieved by grafting vinyl-functional alkoxy silanes on the PE chains using peroxide as an initiator. The vinyl groups

allow for grafting on the PE backbone, and the alkoxy groups allow for subsequent cross-linking between the PE chains upon exposure to heat and moisture. The main applications are for piping of various kinds (e.g., under floor heating, drinking water) and wire and cable insulation.

Similarly, cross-linking is used to enhance mechanical properties in thermoplastic vulcanisates (TPVs), through dynamic vulcanization process and where the silanes play many roles: cross-linker, adhesion promoter and even intermediate to generate in situ filler.

Adhesion Promoter. Organo-functional silanes are known for surface modification. So as additives, they can enhance adhesion between dissimilar materials because of their low surface tension (which ensures good surface wetting), their reactivity to different surfaces and their ability to create interactions and make an adequate transition interphase between the adhesive layer and the substrate to bond [3-9-10].

Trends and Perspectives

Today, there are two major trends:

- The optimization of organo-functional silane molecules and conditions for processing them, aiming to reduce emissions of volatile organic compounds (VOCs)
- The design of new and sustainable composite materials with improved end-user benefits, taking advantage of the wide variety that commercially available silanes or those under development offer in terms of functionalities, reactivities and processing flexibility at relatively mild conditions

Low VOC Silanes and Processes. Conventional organo-functional silanes rely on the hydrolysis of their Si-OR groups and subsequent condensation for their coupling with inorganic surfaces or cross-linking within plastic matrices. Human health and environmental concerns are leading to the development of new products with less hydrolysis/condensation byproducts such as hydrolyzed, lower alkoxy-containing intermediates or solventless products. Prehydrolyzed silanes under well controlled conditions [11-12], water-based silane solutions, or solid carrier supported silanes that could be added during plastic extrusion, and plasma surface treatment in presence of silanes are among the approaches currently investigated to address VOC issues.

Design of New Materials. Sustainable composites that exploit the reinforcement properties of natural fillers like cellulose are being developed, in which silanes are considered to “manage” the highly hydrophilic nature of the surfaces of such fillers to improve compounding and load transfer to the surrounding plastic matrix [13-14].

Sol-gel processes refer to the polymerization in aqueous or organic medium of metal alkoxides into a monolithic gel via the formation and growth and/or network extension of discreet nanoparticles [15]. As such, traditional materials generated via sol-gel process include stable silica sol and colloids [16], thin films and coatings, composites such as ceramics generated by specific drying conditions of aerogels or xerogels [17], fibers, porous gels and membranes [18]. The potential added properties sol-gel materials bring to plastics in general therefore encompasses a wide variety of properties, including antigraffiti, antimicrobial, antifouling, anticorrosion [19], optical, protective, adhesive or anti-adhesive, mechanical, dielectric [20], and reinforcing.

References

- ¹ Plueddemann, E. P. *Silane Coupling Agents*, 2nd Ed., Plenum Press: New York and London, 1991.
- ² Witucki, G. L. *J. Coat. Technol.* 1993, *65* (822), 57-60.
- ³ Plueddemann, E. P. Reminiscing on Silane Coupling Agents. In *Silanes and Other Coupling Agents*, K. L. Mittal, Ed., VSP: Utrecht, Netherlands, 1992; pp 3-19.
- ⁴ Gellman, A. J.; Naasz, B. M.; Schmidt, R. G.; Chaudhury, M. K.; Gentle, T. M. *J. Adhes. Sci. Technol.* 1990, *4* (7), 597-601.
- ⁵ Stelandre-Ladouce, L.; Flandin, L.; Labarre, D.; Bomal, Y. *Rubber Chemical and Technology* 2003, (April), Vol. 76(1), 145-159.
- ⁶ Scott, H.; Humphries, J. *Modern Plastic*, 1973, *50* (3), 82.
- ⁷ Thomas, B; Bowery, M. *Wire J.*, 1977, Vol. 10(5), 88.
- ⁸ Gutowski, W. S.; Li, S.; Filippou, C.; Hoobin, P.; Petinakis, S. *Interface/Interphase Engineering of Polymers for Adhesion Enhancement: Part II. Theoretical and Technological Aspects of Surface - Engineered Interphase-Interface Systems for Adhesion Enhancement*, The Journal of Adhesion, 2003 Vol.79, 483-519.
- ⁹ Gentle, T. E.; Schmidt, R. G.; Naasz, B. M.; Gelleman, A. J.; Gentle, T. M. Organofunctional Silanes as Adhesion Promoters: Direct Characterization of the Polymer/Silane Interphase. In *Silanes and Other Coupling Agents*, Mittal, K. L., Ed.; VSP: Utrecht, Netherlands, 1992; 295-304.
- ¹⁰ de Buyl, F.; Comyn, J.; Shephard, N. E.; Subramanian, N. P. *Int. J. Adhesives and Adhesion* 2002, *22*, 385-393.
- ¹¹ Arkles, B.; Steinmetz, J. R.; Zazyczny, J.; Mehta, P. Factors Contributing to the Stability of Alkoxysilanes in Aqueous Solution. In *Silanes and Other Coupling Agents*. Mittal, K. L., Ed.; VSP: Utrecht, Netherlands, 1992; 91-104.
- ¹² Pohl, E. R.; Chaves, A.; Danahey, C. T.; Sussman, A.; Bennett, V. Sterically Hindered Silanes for Waterborne Systems: a Model Study of Silane Hydrolysis. In *Silanes and Other Coupling Agents*; Mittal, K. L., Ed., VSP: Utrecht, Netherlands, 2000; Vol 2, 15-25.
- ¹³ Abdelmouleh, M.; Boufi, S.; Ben Salah, A.; Belgacem, M. N.; Gandini, A. *Langmuir* 2002, *18*, 3203-3208.
- ¹⁴ Abdelmouleha, M.; Boufi, S.; Belgacem, M. N.; Duarte, A. P.; Ben Salah, A.; Gandini, A., *International Journal of Adhesion & Adhesives* 2004, *24* (1), 43-54.
- ¹⁵ Brinker C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press: San Diego, CA, 1990.
- ¹⁶ Chevalier, P. M.; Ou, D. L. *J. Sol-Gel Sci. Technol.* 2003, *26* (1-3), 597-603.
- ¹⁷ Boury, B.; Chevalier, P.; Corriu, R. J. P.; Delord, P.; Moreau, J. J. E.; Wong Chi Man, M. *Chem. Mater.* 1999, *11* (2), 281-91.
- ¹⁸ Noble, K.; Seddon, A. B.; Turner, M.; Chevalier, P. M.; MacKinnon, I. A. *J. Sol-Gel Sci. Technol.* 2000, *19* (1/2/3), 807-810.
- ¹⁹ Montemor, M. F; Simoes, A. M.; Ferreira, M. G. S.; Williams, B.; Edwards, H. *Progress in Organic Coatings* 2000, *38* (1), 17-26.
- ²⁰ Su, K.; Bujalski, D. R.; Eguchi, K.; Gordon, G. V.; Ou, D. L.; Chevalier, P.; Hu, S.; Boisvert, R. P. *Chem. Mater.* 2005, *17*, 2520-29.

This article has been published in the chapter "Silicones in Industrial Applications" in *Inorganic Polymers*, an advanced research book by Nova Science Publishers (www.novapublishers.com); edited by Roger De Jaeger (Lab. de Spechtrochimie Infrarouge et Raman, Univ. des Sciences and Tecn. de Lille, France) and Mario Gleria (Inst. di Scienze e Tecn. Molecolari, Univ. di Padoa, Italy). Reproduced here with the permission of the publisher.