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A Technical Review of Organosilanes and Adhesion

Anthony A. Parker, Ph.D.

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Polymer Synergies LLC
P.O. Box 456
Mullica Hill, New Jersey 08062
USA

Organosilanes, otherwise known as coupling agents or adhesion promoters, can be extremely valuable molecules to the adhesion chemist, but only when put to proper use. Unfortunately, the definition of "proper use" has been somewhat elusive. For example, industrial chemists have generally recognized that silane hydrolysis is required for interactions to occur between silanes and various materials (both organic and inorganic), but they have seldom appreciated that silane hydrolysis must be controlled in ways that are commensurate with both end-use applications and processes.

Many potential organosilane applications have either been prematurely deemed as "failures" or have been completely overlooked, at least in part due to a misunderstanding of the importance of controlling hydrolysis either before, during, or after product manufacture processes. With little to no information on the subject, many chemists have simply added silanes to their formulations in attempts to see if the "magic" takes effect in their particular applications. With the immediate absence of an "effect," the experiment is often deemed a failure, and the formulator moves on to the next "magic bullet."

For the more serious practitioner, there is a growing body of evidence which supports the idea that not only is hydrolysis required to produce controllable and predictable effects in many industrial processes, but hydrolysis must be made to occur at the "right time" within any sequence of steps that define an industrial process. Before considering this concept further, let's first review some of the general literature in this extremely versatile field of surface chemistry.

Trialkoxyorganosilanes have been long known to enhance adhesion of organic polymers to inorganic substrates such as glass and metals [1,2]. Silanes are also used to treat the surfaces of inorganic additives such as aluminum trihydrate [3], alumina [4,5], and silica [6] for use in reinforced polymer systems. In addition, they can also be blended directly into the matrix of a polymer for subsequent bonding to an inorganic substrate as has been accomplished with ceramic green tapes [7], with polymeric interlayers for use in photovoltaic modules [8,9], and with polymeric interlayers for use in automotive and architectural safety glazings [10,11,12].

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Several articles have been written which describe the commercial application of silanes, as well as the general chemical reactivity of these molecules [13-25]. Trialkoxysilanes are hypothesized to promote adhesion through a combination of two general mechanisms. In the first mechanism, a "coupling" reaction may occur between the organic functional group of the silane molecule and the polymer matrix, resulting in a chemically covalent bond between the two species. This reaction is accompanied by the hydrolysis of alkoxy groups to form silanols, which can either directly condense to form covalent bonds with the inorganic surface, or can physically adsorb and bond through forces such as hydrogen bonding or electrostatic interactions. In a second mechanism, the alkoxy groups can hydrolyze to form silanols, which then condense to form silsesquioxane networks that can compatibly blend and interpenetrate with the polymer matrix at the interface, while simultaneously adsorbing onto the surface of the inorganic substrate either through direct condensation, or through physical adsorption via secondary chemical bonding interactions.

The exact mechanism of bonding will depend on several factors including: the relative acidity or basicity at the interface (pH); the thermodynamic compatibility of the polymer with the organosilane and its condensation products; the temperature dependence of hydrolysis and condensation; the temperature dependence of polymer creep compliance and chain disentanglement (to facilitate interpenetration); and the activation energy for achieving a covalent bond (coupling) between the polymer matrix, and the organic functionality of the silane molecule. For example, when the organic functional group is a primary amine, no external acid or base catalysts are needed for hydrolysis since the amine will catalyze auto-condensation in the presence of water [1].

> The exact mechanism of silane reactivity with inorganic surfaces is still controversial.

This reaction has been studied both in solutions and on surfaces by several authors. Chiang, Ishida, and Koenig [26] have found that aminosilanes will hydrolyze to form stable solutions of cyclic oligomeric structures that condense further upon solvent removal during the "drying" stage on a glass surface. Plueddemann has shown that better polymer adhesion to glass fibers is achieved when glass fibers are treated with this pre-hydrolyzed form of aminosilanes [1], most likely because the oligomeric structures contain free silanol groups which can facilitate further condensation with other surface bound oligomers, or with inorganic hydroxy groups on the surface itself.

Silanes can also react with other molecules through the organofunctional group. In cases involving aminosilanes, certain condensation reactions can be employed, such as ester hydrolysis and amide formation, or epoxy ring opening. Other common "reactive" functionalities include vinyl, styrenic, epoxy, acryloxy, and mercapto [1,27]. When silanes are used as coupling agents for treating inorganic fillers for use in polymers, the choice of the organic functional group can affect polymer/filler interactions, and hence will affect final macroscopic mechanical properties [28]. Vinyl and acrylic functional silanes can be formulated together with peroxides to achieve grafting onto polymers such as polypropylene and poly(ethylene-co-vinylacetate). Such formulations result in higher adhesion to inorganic substrates like glass and aluminum [8].

Although several authors have found evidence to indicate the existence of Al-O-Si bonds on silane treated aluminum substrates, the exact characteristics of such covalent bonds remain obscure. Furukawa et al. [29,30] have used inelastic electron tunneling spectroscopy to study the interaction of an aminosilane with an Al_2O_3 surface. Their results indicate that Al-O-Si bond formation is unlikely since the intensity of the surface -OH group band was not diminished. Instead, the hydroxyl shift from 3580cm^{-1} to 3650cm^{-1}, and complementary amine deformation shifts were attributed to amine hydrogen bonding with surface hydroxyl groups. On the other hand, Boerio et al. maintain that aluminosiloxane bonds will indeed form [31]. Naviroj et al. [32] have used FTIR to study the interaction of a model monoethoxyaminosilane on alumina to reduce the complicated overlap which may occur between Si-O-Si and Al-O-Si bands near 1000cm-1. Difference spectra of treated minus untreated alumina reveal a weak band at 963cm^{-1}, which has been attributed to the Al-O-Si bond.

The pursuit of an Al-O-Si bond as a discrete entity may be a moot point since dynamic equilibria may yield a "time averaged" species that could be more ionic than covalent as suggested by Pashchenko, et al. [33]. An ionic bond would be more susceptible to ion pair separation by surface moisture or other surface species. Along these lines, our own recent results suggest that aminosilane interacts with an aluminum oxide surface via a counterion bridge, where one of the potential counterions is a carbonate anion, which under some conditions, may "bridge" protonated amines with the aluminum oxide surface [34].

Although these studies of specific chemical interaction mechanisms are interesting, the mechanistic focus of such studies is often limited to the monomeric, or small molecule characteristics of silanes. Perhaps of more importance is the overall bonding force that results from the summation of all the individual bonding interactions (be they dynamic or static) over the spatial domain that would be occupied by a high molecular weight polysiloxane condensation polymer. The sum of these interactions, coupled with the insolubility of any resulting 3-dimensional condensate, would result in a stable, non-labile surface layer. As an example, pre-hydrolyzed n-octyltriethoxysilane remains adsorbed on the surface of Al_2O_3 powder particles even after ethanol or toluene extraction steps [36].

With these and many other works in mind, industrial chemists have generally recognized that hydrolysis is required for interactions to occur between silanes and various materials, but they have seldom appreciated that silane hydrolysis must be controlled in ways which are commensurate with end-use applications and processes. As stated earlier, many potential applications have either been prematurely deemed as "failures" or have been completely overlooked, at least in part due to a misunderstanding of the importance of controlling hydrolysis either before, during, or after product manufacture processes.

In the case of a poly(vinyl chloride) safety glass interlayer, it was found that silane hydrolysis was the key to reproducible success (as defined by predictable and controllable adhesion to glass) [11,12,35]. Even more importantly, it was found that hydrolysis had to occur at the correct time within the sequence of the process steps that led from starting materials to the final fabricated product. For example, adding a prehydrolyzed silane to a polymer blend prior to the sheeting fabrication process was not acceptable since this caused the polymer to stick to the extrusion and calendering equipment. However, hydrolysis during subsequent steps (prior to glass lamination) enabled the achievement of predictable and controllable interfacial adhesion [12].

Using a ^{13}C labeled trimethoxysilane, solid state NMR was used to show the direct link between silane hydrolysis, process history, and end-use adhesion between glass and the polymer interlayer [35]. Hence, not only was hydrolysis required, but also hydrolysis had to occur at the right time within the sequence of process steps to achieve the desired result.

Similarly, silane hydrolysis was also found to be necessary to produce the best dispersion stability of aluminum oxide powder in liquid slurries (a typical fabrication step in the processing of ceramics) [36]. More importantly, in contrast to the safety glass interlayer example, the best result for ceramic slurries was achieved when a silane was hydrolyzed before it was added to the initial mix of ingredients. Thus, like the safety glass application, not only is hydrolysis required, but hydrolysis has to occur at the right time within the sequence of process steps to achieve the desired results.

The data from this study add further support to the idea that . In the case of ceramic slurries, the "right time" is the period just prior to the mixing of the ceramic slip ingredients. In this way, controlled and reproducible dispersion stability and processability can be achieved. Interestingly, when hydrolyzed silanes are used to disperse alumina in organic solvent/polymer vehicles, the resultant green bodies are characterized as having higher density, and improved homogeneity [36]. Although in certain cases it may be possible to superficially achieve improvements through the addition of monomeric (non-hydrolyzed) silanes, this is still a risky approach since the results may be difficult to reproduce and control.

Hopefully, this review and its references will help guide you as you explore the many uses of organosilanes. Even more importantly, it should give you reason to try again when your first attempt at using a silane fails. Remember, silane hydrolysis must be controlled in ways that are commensurate with both end-use applications and processes.

> ...silane hydrolysis must be made to occur at the "right time" within any sequence of steps that define an industrial process.

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