SILYLATING AGENTS

1. Introduction

1.1. Silylation of Organic Compounds. Silylation is the replacement of one or more active hydrogens from an organic molecule by a trisubstituted silyl, R_3Si-, group. The active hydrogen is usually an alcohol, carboxylic acid, or phenol, ie, $-OH$; an amine, amide, or urea, $-NH$; or a thiol, $-SH$, and the silylating agent is usually a trimethylsilyl halide, dimethylsilyl dihalide, or a trimethylsilyl nitrogen-functional compound. Newer, more reactive, silylating agents cleave esters and ethers. A mixture of silylating agents may be used. A mixture of trimethylchlorosilane and hexamethyldisilazane is more reactive than either reagent alone, and the by-products combine to form ammonium chloride.

$$(CH_3)_3\,SiNHSi\,(CH_3)_3 + (CH_3)_3\,SiCl + 3\,ROH \rightarrow 3\,(CH_3)_3\,SiOR + NH_4Cl$$

Derivatizing an organic compound for analysis may require only a few drops of reagent selected from silylating kits supplied by laboratory supply houses. Commercial synthesis of penicillins requires silylating agents purchased in tank cars from the manufacturer.

Typical commercial silylating agents are listed in Table 1. The first three silylating agents in the table are available in bulk quantities and are most suitable for large-scale commercial silylation. The chlorosilanes are generally used in combination with an acid acceptor, eg, triethylamine. The nitrogen-functional silanes each have certain advantages for particular applications. Fluorinated silylating agents give enhanced rates of reaction and more volatile by-products.

The chlorosilanes are clear liquids that should be treated as strong acids. They react readily with water to form corrosive HCl gas and liquid. Liquid chlorosilanes and their vapors are corrosive to the skin and extremely irritating to the mucous membranes of the eyes, nose, and throat. The nitrogen-functional silanes react with water to form ammonia, amines, or amides. Because ammonia and amines are moderately corrosive to the skin and very irritating to the eyes, nose, and throat, silylamines should be handled like organic amines. Trimethylsilyltrifluoromethanesulfonate and trimethylsilyliodide form very corrosive acidic products.

The techniques of silylation and their application in analysis have been reviewed (1,2), as have the intermediate steps in organic synthesis (3). Summaries of silylation applications are available (4,5).

1.2. Derivatization for Analysis. Silylation of organic materials has been an invaluable tool in analytical chemistry to allow ready analysis by gas–liquid chromatography (glc), mass spectrometry (qv), and thin-layer chromatography (tlc). There are four main reasons to derivatize a compound for analysis: to increase volatility, to increase thermal stability, to enhance detectability, and to improve separation. Silylating kits offered by laboratory supply houses may contain mixtures of chlorine- and nitrogen-functional silylating agents and activating solvents or catalysts. Methodology for derivatization and recommended specific reagents for the various applications may be found in the catalogs of suppliers.

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N-Trimethylsilyldiethylamine is a strongly basic silylating reagent and is particularly useful for derivatizing low molecular weight acids. The reaction by-product, diethylamine, is volatile enough to be easily removed from the reaction medium.

N-Trimethylsilylimidazole is the strongest hydroxy silylator available and is the reagent of choice for carbohydrates and steroids. This reagent is unique in that it reacts quickly and smoothly with hydroxyls and carboxyl groups, but not with amines. This characteristic makes TSIM particularly useful in multiderivatization schemes for compounds containing both hydroxyl and amine groups.

N,O-Bis(trimethylsilyl)acetamide reacts quantitatively under relatively mild conditions with a wide variety of compounds to form volatile, stable trimethylsilyl (TMS) derivatives for glc analysis. It has been used extensively for derivatizing alcohols, amines, carboxylic acids, phenols, steroids, biogenic amines, alkaloids (qv), etc. It is not recommended for use with carbohydrates (qv) or very low molecular weight compounds. Reactions are generally fast and the reagent is usually used in conjunction with a solvent, eg, pyridine or dimethylformamide (DMF). When used with DMF, it is the reagent of choice for derivatizing phenols.

N,O-Bis(trimethylsilyl)trifluoroacetamide is a powerful trimethylsilyl donor having approximately the same donor strength as the unfluorinated analogue BSA. Reactions of BSTFA are similar to those of BSA. The main advantage of BSTFA over BSA is the greater volatility of the former's reaction by-products, ie, monotrimethylsilyltrifluoroacetamide and trifluoroacetamide. This physical characteristic is particularly useful in the gas chromatography (gc) of some of the lower boiling TMS-amino acids and TMS Krebs cycle acids where the by-products of BSA may have similar retention characteristics and thus obscure these derivatives on the chromatogram. The by-products of BSTFA usually elute with the solvent front.

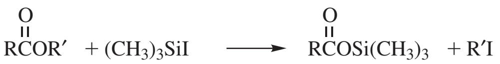
For the derivatization of fatty acid amides, slightly hindered hydroxyls, and other difficultly silylatable compounds, BSTFA containing 1 wt% trimethylchlorosilane is used. This catalyzed formulation is stronger than BSTFA alone. When silylation reagents are consumed in the hydrogen flame, silicon dioxide, SiO_2, is formed. *N,O*-Bis(trimethylsilyl)trifluoroacetamide contains three fluorine atoms that form HF in the detector flame and react with the SiO_2 to form volatile products. This removal of SiO_2 provides a decrease in detector fouling and background noise.

N-Methyl-*N*-trimethylsilyltrifluoroacetamide is the most volatile TMS-amide available; it is more volatile than BSTFA or BSA. Its by-product *N*-methyltrifluoroacetamide has an even lower retention time in glc than MSTFA. This is of considerable value in glc determinations where the reagent or by-products obscure the derivative on the chromatogram. Silylation of steroids (qv) shows MSTFA to be significantly stronger in donor strength than BSTFA or BSA. *N*-Methyl-*N*-trimethylsilyltrifluoroacetamide silylates hydrochloride salts of amines directly.

The *tert*-butyldimethylsilyl group introduced by TBDMIM has a number of advantages in protecting alcohols (6). The silylated alcohol hydrolyzes more slowly than an alcohol silylated with TMS by a factor of 10^4. The silyl ether is also stable to powerful oxidizing and reducing agents, but it can easily be removed by aqueous acetic acid or tetrabutylammonium fluoride in tetrahydrofuran (thf).

The TMS triflate is an extremely powerful silylating agent for most active hydrogens. It surpasses the silylating potential of TMCS by a factor of nearly 10^9. It readily converts 1,2- and 1,3-diketones into disilylated dienes (7).

Trimethylsilyliodide is an effective reagent for cleaving esters and ethers. The reaction of hexamethyldisilane [1450-14-2] with iodine gives quantitative conversion to TMSI. A simple mixture of trimethylchlorosilane and sodium iodide can be used in a similar way to cleave esters and ethers (8), giving silylated acids or alcohols that can be liberated by reaction with water.

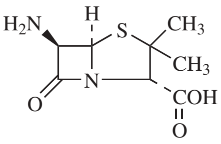


$$\mathrm{R\overset{\overset{O}{\|}}{C}OR'} + (\mathrm{CH_3})_3\mathrm{SiI} \longrightarrow \mathrm{R\overset{\overset{O}{\|}}{C}OSi(CH_3)_3} + \mathrm{R'I}$$

$$\mathrm{ROR'} + (\mathrm{CH_3})_3\,\mathrm{SiCl} + \mathrm{NaI} \rightarrow \mathrm{ROSi}\,(\mathrm{CH_3})_3 + \mathrm{R'I} + \mathrm{NaCl}$$

It is possible to use halogen-sensitive detectors in glc analysis of active hydrogen compounds by silylating them with a halogenated silylating agent, eg, CMDMS (9).

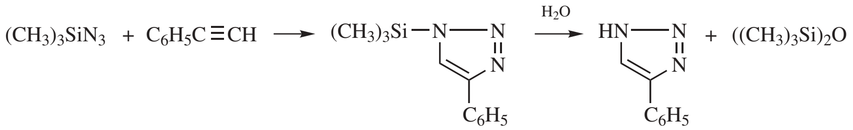
1.3. Silylation in Organic Synthesis. Silyl blocking agents are used in organic synthesis to protect sensitive functional groups, to alter reactivity and solubility, and to increase stability of intermediates. Silylation applications in pharmaceutical synthesis have been used to protect a wide range of OH groups, eg, alcohols in prostaglandins (qv) and steroid synthesis, enols in the synthesis of nucleosides and steroids (qv), and carboxylic acids and sulfenic acids in the synthesis of penicillins and cephalosporins (6). Silylation has its broadest use in the commercial synthesis of penicillins. The blocking effect of trimethylsilyl and dimethylsilyl groups on 6-aminopenicillanic acid (6-APA) (**1**) has played an important role in the total synthetic production of semisynthetic penicillins.



(1)

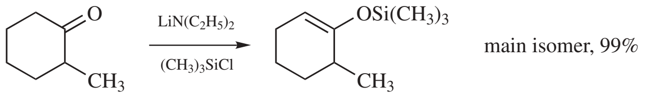
Protection of carboxylic acids and sulfenic acids requires efficient silyl donors, eg, BSA, MTSA, and bis(trimethylsilyl)urea. The BSU is often prepared *in situ* from hexamethyldisilazane and urea to yield $> 90\%$ of the silylated derivative in synthesis of cephalosporins (5).

It is possible to synthesize 1,2,3-triazoles from acetylenes and hydrazoic acid, but the instability of hydrazoic acid has limited this application. Sodium azide is silylated readily with trimethylchlorosilane to produce trimethylsilyl azide [4648-54-8], $(CH_3)_3SiN_3$, which reacts with acetylenes to produce high yields of 1,2,3-triazoles (10).



In this case, the substitution of the TMS group for hydrogen in HN_3 imparts a degree of thermal stability to the otherwise unstable azide and also acts as a blocking agent in allowing the direct synthesis of the triazole. Trimethylsilyl azide can be distilled at atmospheric pressure without decomposition (bp 95°C). Similarly, diazomethane, potentially very explosive, is thermally stable when trimethylsilated, $(CH_3)_3SiCHN_2$ [18107-18-1].

Two techniques have been described for producing trimethylsilyl enol ethers from aldehydes or ketones (10): reaction of $(CH_3)_3SiCl$ and $(C_2H_5)_3N$ in DMF; and reaction of $LiN(C_2H_5)_2$, which generates enolate ions in the presence of $(CH_3)_3SiCl$. The resulting enol ethers can undergo a wide variety of reactions at the double bond, making this type of reaction important in hormone synthesis (11).



Group-transfer polymerization (GTP) is a method of methacrylate polymer formation that uses the intermolecular transfer of a trimethylsilyl group, $-Si(OCH_3)_3$, to an incoming monomer during the polymerization process to regenerate a new silyl ketene acetal for reaction with more monomer (12). A silane modified organic monomer, a silyl ketene acetal, $(CH_3)_2C{=}C[OSi(CH_3)_3]OR$ ($R = CH_3$[31469-15-5], or R = an organofunctional group), with either anionic or Lewis acid catalysis, gives a polymerization process with excellent control of: molecular weight, type of end-groups, pendant functionality and chain configuration. Organic functionalities, eg, hydroxyl, carboxyl, and epoxy can be placed in the polymer structure by using a silyl ketene acetal that contains an hydroxyl, carboxyl, or epoxy functional organic group.

2. Silylation of Inorganic Compounds

2.1. Silicate Modifications. A method has been described in which silicate minerals are simultaneously acid leached and trimethylsilyl end-blocked to yield specific trimethylsilyl silicates having the same silicate structure as the mineral from which these were derived (13). Olivine, hemimorphite, sodalite, natrolite, laumontite, and sodium silicates are converted to TMS derivatives of orthosilicates, pyrosilicates, cyclic polysilicates, etc, making it possible to classify the minerals according to their silicate structure. The same technique is used to analyze the siloxanol structure of aqueous solutions of vinyltrimethoxysilane (14). Certain anionic siliconates stabilize solutions of alkali silicates to give stable solutions in water or alcohols at any pH (15). Such silicate–siliconate mixtures are used as corrosion inhibitors in glycol antifreeze.

2.2. Ziegler-Natta Polymerization. The polymerization of propylene with Ziegler-Natta catalysts, ie, complexes of $TiCl_3-(C_2H_5)_3Al$ on $MgCl_2$ supports, is significantly affected by external addition to the reactor of organo(alkoxy)silanes with the propylene feed. The nature of the organic group(s) and alkoxy group(s) affects the catalyst activity and the microstructure of the polymer (16). Silane donors, eg, phenyltriethoxysilane [780-69-8], cyclohexylmethyldimethoxysilane [17865-32-6], and dicyclopentyl dimethoxysilane [126990-35-0] are used commercially. The silane coordinates with the Ziegler-Natta catalyst to increase the isotacticity of polypropylene to 98% or higher and increase the polymer yield per amount of catalyst.

3. Silylation of Inorganic Surfaces

3.1. Alkyl Silylating Agents. Alkyl silylating agents convert mineral surfaces to water-repellent, low energy surfaces useful in water-resistant treatments for masonry, electrical insulators, packings for chromatography, and noncaking fire extinguishers. Methylchlorosilanes react with water or hydroxyl groups at the surface to liberate HCl and deposit a thin film of methylpolysiloxane, which has a low critical surface tension and is therefore not wetted by water (17). Ceramic insulators can be treated with methylchlorosilane vapors or solutions in inert solvents to maintain high electrical resistivity under humid conditions (18). The corrosive action of the evolved HCl can be avoided by prehydrolyzing the chlorosilanes in organic solvent and applying them as organic solutions of organopolysiloxanols. Hydrolyzed methylchlorosilanes also dissolve in aqueous alkali and are then applied as aqueous solutions of sodium methylsiliconates. The siliconates are neutralized by carbon dioxide in the air to form an insoluble, water-resistant methylpolysiloxane film within 24 h. Treatment of brick, mortar, sandstone, concrete, and other masonry protects the surface from spalling, cracking, efflorescence, and other types of damage caused by water.

Silylation of inorganic surfaces with *hydrophobic* alkoxy silanes imparts water repellent properties to concrete, bridge decks, and other mineral based surfaces in construction and infra-structure applications. Octyltrimethoxysilane [3069-40-7], octyltriethoxysilane [2943-75-1], *iso*-butyltrimethoxysilane [18395-30-7], and *iso*-butyltriethoxysilane [17980-47-1] are the most commonly used silanes. The silane is usually diluted in an alcoholic solvent and applied to the masonry surface where it bonds to the surface and gives long-lasting hydrophobicity. Octyltriethoxysilane has special properties in water and can be made into a stable aqueous emulsion to give a water-based product for application as a masonry water repellent (19).

Silanes can alter the critical surface tension of a substrate in a well-defined manner. Critical surface tension is associated with the wettability or release qualities of a substrate. Liquids having a surface tension below the critical surface tension, γ_c, of a substrate wet the surface. Critical surface tensions of a number of typical surfaces are compared to γ_c of silane-treated surfaces in Table 2 (20).

Celite or firebrick packing for glc columns is often treated with TMCS, DMCS, or other volatile silylating agents (see Table 1) to reduce tailing by polar organic compounds. A chemically bonded methyl silicone support is stable for temperature programming to 390°C and allows elution of hydrocarbons up to C_{50} (21).

High performance liquid chromatography (hplc) combines the bonded solid phase of gc with the methodology of column liquid chromatography. The most popular type of hplc involves low polarity silicone-bonded surfaces having more highly polar liquids in a process termed reversed-phase chromatography (22). A favorite stationary phase is fine particle silica treated with octadecyltrichlorosilane [112-04-9]. In some instances, octyl-, phenyl-, cyclohexyl-, or ethylsilanes can be used to obtain improved selectivity. Metal ions on the bonded phase can be used to enhance separation of polar molecules through liqand-exchange chromatography (lec) (23). Metal ions, eg, copper, are retained on silica gel that has been treated with chelating functional silanes (see CHELATING AGENTS).

4. Organofunctional Silylating Agents

Whereas alkylsilylating agents provide low energy surfaces designed for release, a series of organofunctional silylating agents is offered commercially as adhesion promoters. Principal applications have been as coupling agents in glass- or mineral-reinforced organic resin composites and as adhesion promoters for paints, inks, coatings, and adhesives. Organofunctional silanes are also used to control orientation of liquid crystals, bind heavy-metal ions, immobilize enzymes and cell organelles, modify metal oxide electrodes, and to bind antimicrobial agents to surfaces. These and other applications have been described (24). Representative commercial silane coupling agents are listed in Table 3. These compounds can also be used as chemical intermediates for preparing other more specialized organofunctional silanes (25).

4.1. Liquid Crystals. In liquid-crystal displays, clarity and permanence of image is enhanced if the display can be oriented parallel or perpendicular to the substrate. Oxide surfaces treated with dimethyloctadecyl-3-trimethoxysilylpropylammonium chloride [27668-52-6], $C_{18}H_{37}N^+(CH_3)_2CH_2CH_2CH_2Si(OCH_3)_3Cl^-$, tend to orient liquid crystals perpendicular to the surface; parallel orientation is obtained on surfaces treated with *N*-methylaminopropyltrimethoxysilane [3069-25-8], $CH_3NHCH_2CH_2CH_2Si(OCH_3)_3$ (26).

4.2. Ion Removal and Metal Oxide Electrodes. The ethylenediamine (*en*)-functional silane, shown in Table 3 (No. 5), has been studied extensively as a silylating agent on silica gel to preconcentrate polyvalent anions and cations from dilute aqueous solutions (27,28). Numerous other chelate-functional silanes have been immobilized on silica gel, controlled-pore glass, and fiber glass for removal of metal ions from solution (29,30).

Metal oxide electrodes have been coated with a monolayer of this same diaminosilane (Table 3, No. 5) by contacting the electrodes with a benzene solution of the silane at room temperature (31). Electroactive moieties attached to such silane-treated electrodes undergo electron-transfer reactions with the underlying metal oxide (32). Dye molecules attached to silylated electrodes absorb light coincident with the absorption spectrum of the dye, which is a first step toward simple production of photoelectrochemical devices (33).

4.3. Antimicrobials.

Surface-bonded organosilicon quaternary ammonium chlorides have enhanced antimicrobial and algicidal activity (34). Thus, the hydroysis product of dimethyloctadecyl-3-trimethoxysilylpropylammonium chloride [27668-52-6] exhibits antimicrobial activity against a broad range of microorganisms while chemically bonded to a variety of surfaces. The chemical is not removed from surfaces by repeated washing with water, and its antimicrobial activity is not attributed to a slow release of the chemical, but rather to the surface-bonded chemical.

4.4. Polypeptide Synthesis and Analysis.

Silica or controlled-pore glass supports treated with (chloromethyl)phenylethyltrimethoxysilane [68128-25-6] or its derivatives are replacing chloromethylated styrene–divinylbenzene (Merrifield resin) as supports in polypeptide synthesis. The silylated support reacts with the triethylammonium salt of a protected amino acid. Once the initial amino acid residue has been coupled to the support, a variety of peptide synthesis methods can be used (35). At the completion of synthesis, the anchored peptide is separated from the support with hydrogen bromide in acetic acid.

Edman degradations can be accomplished by treating aminopropylsilylated supports (a silica of 1.0–7.5-nm pore size yields aminopropylsilane in concentrations of $\sim 2 \times 10^{-7}$ mol/g of glass) with the peptide to be analyzed in the presence of dicyclohexylcarbodiimide (36). The carboxyl end of the peptide bonds to the amino group of the silane through an amide group. The bound peptide is then treated with phenylthiocyanate in the presence of base to yield an *N*-terminal phenylthiocarbamyl derivative which, on treatment with acid, cyclizes to a phenylthiohydantoin and cleaves. The hydantoin is analyzed and the process is repeated with the bound peptide residue.

4.5. Immobilized Enzymes and Metal-Complex Catalysts.

Use of enzymes to catalyze reactions in cell-free systems has been limited by the difficulty of enzyme isolation, lability of the enzymes, and difficulty in effecting clean separations of enzymes from reaction mixtures. An approach that has circumvented some of these problems is to attach enzymes to solid support materials (37,38). The most frequently used technique for immobilizing enzymes on a solid support involves reducing *N*-(3-triethoxysilylpropyl)-*p*-nitrobenzamide [60871-86-5] groups after attachment to silica or controlled-pore glass to give aniline derivatives, then converting them to diazonium salt, and effecting coupling through azo linkage to the tyrosine of the proteins.

Two general methods are available for immobilizing metal-complex catalysts on metal oxide surfaces by the use of ligand–silane coupling reagents of the type X_3SiL, where X is a hydrolyzable group and L is a ligand (39). In Method A, the ligand silane reacts with surface hydroxyl groups to form a ligand metal oxide, usually a ligand silica, and then a metal-complex precursor, M, reacts with the functionalized surface. In Method B, a metal–liquid silane complex is first formed in solution and then reacts with surface hydroxyls of the support. Both methods give the same metal–silane complex on the metal surface: metal–O–SiX_2LM, eg, $\{\equiv SiOSi(CH_2)_2P(C_6H_5)_2\}_2RhCl(CO)$. Supported metal-complex catalysts have been used in hydrogenation, hydroformylation, hydrosilylation, isomerization, and other chemical reactions.

4.6. Metal Protectants. Alkoxysilanes by virtue of their ability to silylate and bond tenaciously to metals are used in formulating protective coatings for metal surfaces. Alkoxysilanes are exceptionally effective in bonding to silicon, aluminum, and titanium, but good adhesion has been observed to steel, copper, and brass (40). One method of metal protection is to use a suitable silane adhesion promoter from the list in Table 3 and use it to adhere a compatible organic coating to the surface and thereby provide the protective function. Formulations to replace hazardous chromate protective coatings have utilized mixtures of aminosilane and epoxysilane (Table 3, Nos. 5 and 6) (41). Cold-rolled steel can be treated with a formulated solution of vinylbenzyl or mercapto silanes (Table 3, Nos. 3 and 7) to provide a corrosion-resistant conversion coating or bonded coating (42).

4.7. Reinforced Composites. Silane coupling agents modify the interface between inorganic surfaces and organic resins to improve the adhesion between resin and surface, thus improving physical properties and water resistance of reinforced plastics. Suitable coupling agents are available for any of the common plastics and metal, glass, or many other inorganic reinforcements. Principal applications for these coupling agents are in reinforced plastics for boats, storage tanks, pipes, automobiles, and architectural structures. Other applications are in the treatment of mineral fillers and pigments for paint and rubber, in primers to improve the adhesion of paints, inks, coatings, and adhesives to metals and other inorganic surfaces.

Commercial silane coupling agents are soluble in acidified water or become soluble as the alkoxy groups hydrolyze from silicon. The resulting aqueous solutions are stable in water for at least several hours, but they may become insoluble as the silanols condense to siloxanes. Freshly prepared aqueous solutions of the silane coupling agents are therefore applied to glass filaments by the fiber manufacturer with a polymeric substance, a lubricant, and an antistatic agent as a complete size for glass mat or woven roving. Glass cloth woven from glass fiber with a starch–oil size can be heat cleaned to burn off the organic size and treated with a dilute solution of the desired silane coupling agents. This operation is accomplished by the glass weaver for electronic applications (43). The total amount of silane coupling agent applied is generally 0.1–0.5% of the weight of the glass. The improvement in laminate properties imparted by silane coupling agents in typical glass-cloth laminates is summarized in Table 4 (44). All results are based on compression-molded test samples containing 60–70 wt% glass in the laminate.

The nature of adhesion through silane coupling agents has been studied extensively by advanced analytical techniques (43,44). It is fairly well established that silane coupling agents form M–O–Si bonds on mineral surfaces where M=Si, Ti, Al, Fe, etc. Condensation and hydrolysis of coupling agent silanols on a silica surface are in true equilibrium in water (45). Equilibrium constants suggest that bonding of a typical silane coupling agent, $RSi(OH)_3$, to silica has a 1000-fold advantage in water resistance over a simple alkoxy bond between a hydroxyl-functional polymer and silica. Mechanical properties of filled polymer castings are improved by treatment of a wide range of mineral fillers with appropriate silane coupling agents (46).

Oxane bonds, M–O–Si, are hydrolyzed during prolonged exposure to water, but reform when dried. Adhesion in composites is maintained by controlling conditions favorable for equilibrium oxane formation, ie, maximum initial oxane bonding, minimum penetration of water to the interface, and optimum morphology for retention of silanols at the interface. The inclusion of a hydrophobic silane, eg, phenyltrimethoxysilane [2996-92-1], with the organofunctional silane increases thermal stability of the silane and make the bond more water resistant (47).

Although simplified representations of coupling through organofunctional silanes often show a well-aligned monolayer of silane forming a covalent bridge between polymer and filler, the actual situation is much more complex. Coverage by hydrolyzed silane is more likely to be equivalent to several monolayers. The hydrolyzed silane condenses to oligomeric siloxanols that initially are soluble and fusible, but ultimately can condense to rigid cross-linked structures. Contact of a treated surface with polymer matrix is made while the siloxanols still have some degree of solubility. Bonding with the matrix resin then can take several forms. The oligomeric siloxanol layer may be compatible in the liquid-matrix resin and then form a true copolymer during resin cure. Partial solution compatibility is also possible and an interpenetrating polymer network can form as the siloxanols and matrix resin cure separately with a limited amount of copolymerization. Probably all thermosetting resins are coupled to silane-treated fillers by some modification of these two extremes.

Interdiffusion of silane primer segments with matrix molecules having no cross-linking may become a factor in bonding of thermoplastic polymers (48). This is the suggested mechanism when a silane–thermoplastic copolymer is used as a primer or coupling agent for the corresponding unmodified thermoplastic. A siloxanol layer may also diffuse into a nonreactive thermoplastic layer and then cross-link at the fabrication temperature. Structures, in which only one of the interpenetrating phases cross-links, have been designated pseudointerpenetrating networks. Amine-functional silanes (Table 3, Nos. 3–5) probably function in this manner in coupling to polyolefins and possibly to other thermoplastics. Layers of amine-functional siloxanols in the absence of matrix resins cure at 150°C to very hard, tough films.

Peroxides or other additives, eg, chlorinated paraffin, may also cause the thermoplastic resin to cross-link with the siloxanols. In this case, a true interpenetrating polymer network forms, in which both phases are cross-linked.

Performance of coupling agents in reinforced composites may depend as much on physical properties resulting from the method of application as on the chemistry of the organofunctional silane. Physical solubility or compatibility of a siloxanol layer is determined by the nature and degree of siloxane condensation on a mineral surface.

4.8. Mineral Reinforced Rubber. Silylation of siliceous fillers with a silane coupling agent will change those fillers into reinforcing fillers for organic rubber. Silylated siliceous fillers, eg, silica and Kaolin clay, can replace carbon black, which is a natural reinforcement for organic rubber. For sulfur-cured rubber, a polysulfido-bis-silane (Table 3, No. 7) is a very effective coupling agent (49). For peroxide cured rubber and other cure systems, vinyl, amino, and mercaptosilanes (Table 3, Nos. 1, 5, and 8) are effective. The largest application for any silane coupling agent commercially is the use of sulfido silanes in silica reinforced rubber for automotive tires. Silica reinforced rubber tires give lower rolling resistance, better gas mileage, better wet traction, and other significant benefits compared to carbon black reinforced tires. Silica reinforced rubber is also used for shoe soles, belts, hoses, and mechanical goods.

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Table 1. **Methyl Silylating Agents**

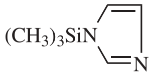
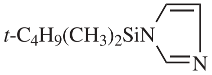
Chemical name	CAS Registry Number	Common abbreviation	Formula
trimethylchlorosilane	[75-77-4]	TMCS	$(CH_3)_3SiCl$
dimethyldichlorosilane	[75-78-5]	DMCS	$(CH_3)_2SiCl_2$
hexamethyldisilazane	[999-97-3]	HMDZ	$(CH_3)_3SiNHSi(CH_3)_3$
chloromethyldimethylchlorosilane	[1719-57-9]	CMDMS	$ClCH_2(CH_3)_2SiCl$
N,N′-bis(trimethylsilyl)-urea	[18297-63-7]	BSU	$[(CH_3)_3SiNH]_2CO$
N-trimethylsilyldiethylamine	[996-50-9]	TMSDEA	$(CH_3)_3SiNH(C_2H_5)_2$
N-trimethylsilylimidazole	[18156-74-6]	TSIM	
N,O-bis(trimethylsilyl)acetamide	[10416-59-8]	BSA	$(CH_3)_3SiN{=}C(CH_3)OSi(CH_3)_3$
N,O-bis(trimethylsilyl)trifluoroacetamide	[21149-38-2]	BSTFA	$(CH_3)_3SiN{=}C(CF_3)OSi(CH_3)_3$
N-methyl-*N*-trimethylsilyltrifluoroacetamide	[24589-78-4]	MSTFA	$(CH_3)_3SiN(CH_3)COCF_3$
tert-butyldimethylsilylimidazole	[54925-64-3]	TBDMIM	
N-trimethylsilylacetamide	[13435-12-6]	MTSA	$(CH_3)_3SiNHCOCH_3$
trimethylsilyltrifluoromethanesulfonate	[27607-77-8]	TMS triflate	$(CH_3)_3SiOSO_2CF_3$
trimethylsilyliodide	[16029-98-4]	TMSI	$(CH_3)_3SiI$

Table 2. **Critical Surface Tensions, γ_c, mN/m (= dyn/cm)**[a,b]

Surface	γ_c
polytetrafluoroethylene	18.5
methyltrimethoxysilane	22.5
vinyltriethoxysilane	25.0
paraffin wax	25.5
ethyltrimethoxysilane	27.0
propyltrimethoxysilane	28.5
glass, soda–lime (wet)	30.0
polychlorotrifluoroethylene	31.0
polypropylene	31.0
polyethylene	33.0
(3,3,3-trifluoropropyl)trimethoxysilane	33.5
(3-(2-aminoethyl)aminopropyl)trimethoxysilane	33.5
polystyrene	34.0
cyanoethyltrimethoxysilane	34.0
aminopropyltriethoxysilane	35.0
poly(vinyl chloride)	39.0
phenyltrimethoxysilane	40.0
(3-chloropropyl)trimethoxysilane	40.5
(3-mercaptopropyl)trimethoxysilane	41.0
(3-glycidoxypropyl)trimethoxysilane	42.5
poly(ethylene terephthalate)	43.0
copper (dry)	44.0
aluminum (dry)	45.0
iron (dry)	46.0
nylon-6,6	46.0
glass, soda–lime (dry)	47.0
silica, fused	78.0

[a] Ref. 20.

[b] Critical surface tensions for silanes refer to treated surfaces.

Table 3. **Commercial Silane Coupling Agents**

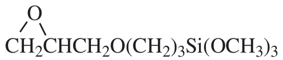
No.	Silane coupling agent	CAS Registry Number	Formula	Application in plastics
1	vinyltrimethoxysilane	[2768-02-7]	$CH_2{=}CHSi(OCH_3)_3$	polyethylene, unsaturated polymers
2	3-methacryloxypropyltrimethoxysilane	[2530-85-0]	 $CH_2{=}C(CH_3)\overset{\overset{O}{\|}}{C}O(CH_2)_3Si(OCH_3)_3$	unsaturated polymers
3	vinylbenzyl cationic silane	[34937-00-3]	$CH_2{=}CHC_6H_4CH_2NHCH_2{-}CH_2NH(CH_2)_3Si(OCH_3)_3{\cdot}HCl$	all polymers
4	3-aminopropyltriethoxysilane	[919-30-2]	$H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$	epoxies, phenolics, nylon
5	*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane	[1760-24-3]	$H_2NCH_2CH_2NH(CH_2)_3{-}Si(OCH_3)_3$	epoxies, phenolics, nylon
6	3-glycidoxypropyltrimethoxysilane	[25704-87-4]	 $\overset{O}{\overbrace{CH_2CH}}CH_2O(CH_2)_3Si(OCH_3)_3$	most thermo-setting resins
7	bis(3-triethoxysilylpropyl)tetrasulfide	[40372-72-3]	$((CH_3CH_2O)_3SiCH_2CH_2{-}CH_2SS)_2$	rubber, polysulfides
8	3-mercaptopropyltrimethoxysilane	[4420-74-0]	$HSCH_2CH_2CH_2Si(OCH_3)_3$	rubber, epoxies, polysulfides
9	3-chloropropyltrimethoxysilane	[25512-39-4]	$ClCH_2CH_2CH_2Si(OCH_3)_3$	epoxies

Table 4. **Silane Performance in Glass-Cloth-Reinforced Laminates**[a]

Resin	Silane coupling agent, No.[b]	Flexural strength improvement, %	
		Dry	
epoxy			
anhydride	9	20	300
aromatic amine	3,9	50	140
dicyandiamide	3,6	30	70
polyester	2,3	60	140
vinyl ester	2,3	40	65
phenolic	3–6	40	120
melamine	3,6	100	250
nylon	3–6	65	130
polycarbonate	3–6	65	230
polyterephthalate	3	50	50
polystyrene	3	40	110
acrylonitrile–butadiene–styrene terpolymer	3,6	30	50
styrene–acrylonitrile copolymer	3	40	70
poly(vinyl chloride)	3–5	60	80
polyethylene	3	130	130
polypropylene	3	90	90

[a] Ref. 43.

[b] See Table 3.

[c] Wet = boiling for 72 h in water for epoxies, 2 h for other resins.