# CHEMTECH

TAILORING SURFACES WITH SILANES

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Tailoring surfaces with silanes

It isn't surprising that a great number of encounters between dissimilar materials involves at least one member that's siliceous or has surface chemistry with siliceous properties; silicates, aluminates, borates, etc., *are* the principal components of the earth's crust. Interfaces involving such materials have thus become a dynamic area of chemistry in which surfaces have been modified in order to generate desired heterogeneous environments or to incorporate the bulk properties of different phases into a uniform composite structure. Our purpose here then is to use this work to exemplify how surfaces can be tailored. Our chemical and physical basis will be organosilanes.

The general formula of an organosilane (I) shows the two classes of functionality one encounters.

$$R_n Si X_{(4-n)}$$
$$(I)$$
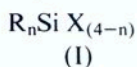
X is a hydrolyzable group typically halogen, alkoxy, acyloxy, or amine. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups, for example, those on the surface of siliceous fillers, to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. Less stable bonds are formed with oxides of boron, iron, and carbon. Alkali metal oxides and carbonates do not form stable bonds with $Si-O-$.
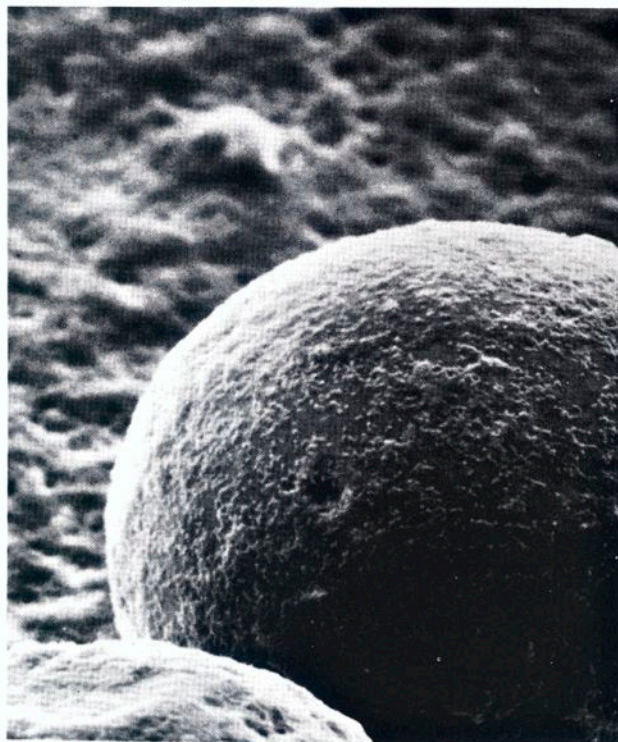
The R group of (I) is a nonhydrolyzable organic radical that may posses a functionality that imparts desired characteristics.

The final result of reacting an organosilane with a substrate ranges from altering the wetting or adhesion characteristics of the substrate, utilizing the substrate to catalyze chemical transformations at the heterogeneous interface, ordering the interfacial region, and to modifying its partition characteristics. Let's look at some examples. Rather than annotating references, a general reading list arranged by broad categories is appended. To see just how ubiquitous the subject is, the reader may want to use that

Scanning electron micrographs of glutaraldehyde-treated mitochondria bound to an octadecylsilylated silica bead surface. 500×. (author's work)

After recognizing the need for the production of silane and silicone specialty products, **Barry Arkles** became cofounder of Petrarch Systems, Inc. The company takes its name from the Fourteenth Century inventor of the sonnet who created a new medium of expression. Organosilanes, likewise, represent a new medium for chemical technology. Dr. Arkles previously held the position of Manager of Technical Development at Liquid Nitrogen Processing, Engineering Plastics. His responsibilities included product and process development from bench to plant start-up in all four of the company's product lines: thermoplastic and fluorocarbon composites, fluorocarbon lubricants, and coating powders. A member of ACS, SME, ASLE, SPE, AIChE, and Mensa, he completed graduate work in chemistry at Temple University. At 28, Dr. Arkles has contributed over fifty articles and patents in the areas of thermoplastic composites, wear and lubrication, protective coatings, silanes, and immobilized organelles.

list now to view the categories to be covered. There's something for everyone.

Reactive tetra-substituted silanes

Silicon compounds that are fully substituted by hydrolyzable groups (i.e., n = 0) not only provide a model for substrate reactivity of organosilanes, but can themselves be utilized in modifying surfaces. If hydrolyzed carefully under neutral conditions, they yield silicic acid $Si(OH)_4$, which behaves as though it is dibasic with pKs at 9.8 and 11.8. Silicic acid readily forms polymers such as silica gel, quartz, or silicates by condensation of the silanol groups or reaction of silicate ions.

$$2 -Si-OH \longrightarrow -Si-O-Si- + H_2O$$
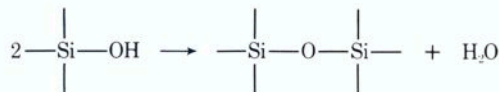
The relative rate of hydrolysis for halogen substituted silanes is I > Br > Cl > F. The byproduct of hydrolysis is the hydrohalic acid.

Tetrachlorosilane is of commercial importance since it can be hydrolyzed in the vapor phase to form amorphous *fumed* silica.

Chlorosilanes react with alcohols to form alkoxysilanes, which undergo most of the reactions of chlorosilanes.

Since they generate no acid on hydrolysis and are generally less reactive, they are generally more convenient reagents than tetrahalosilanes. Increasing the size of the alkoxy group and decreasing the number of alkoxy substitutions decreases rate of hydrolysis. They undergo exchange reactions with hydroxyl containing materials under conditions similar to those of carboxylic esters:

$$MeSi(OEt)_3 + 3\,Bu^nOH \rightarrow MeSi(OBu^n)_3 + 3\,EtOH$$

Tetramethoxysilane is used for deposition coating of "glass" in television tubes, fluorescent lights, and similar applications. The hydrolyzed silane binds in the form of silica to the inner surface. Tetraethoxysilane is used, with hydrolysis, as a refractory mold binder in precision casting. The silicate is mixed with water 5% in excess of that

necessary for hydrolysis, then slurried with ground fireclay or fused silica, which has been preblended with a small amount of magnesium oxide. The slurry sets in the mold in about an hour. In this case the hydrolysis product binds the siliceous substrates together. Ethoxysilane solutions have been used to bond zirconium in cathode tubes, as binders for paints and films on ceramic bases, and as bore stabilizers in oil wells. In silicone bathtub sealant formulations ethylsilicates often play a dual role as crosslinking agent and binder to the vitreous surface. As the size of the alkoxy substituent increases, the silanes become increasingly resistant to hydrolysis. Finally, tetrakis(2-ethylbutoxy)silane and tetrakis(2-ethylhexoxy)silane are utilized as heat transfer media, and low temperature lubricants.

Acyloxy- and amino-substituted silanes are far more susceptible to hydrolysis than the alkoxysilanes. They hydrolyze in minutes in water, whereas alkoxysilanes are stable for several hours in water (pH ~7). The increased rate of hydrolysis of the former is due to the acidic or basic character of the byproducts. Thus catalytic amounts of amine or acid are often added to accelerate the rate of hydrolysis of alkoxysilanes.

Table 1 summarizes properties of some tetra-substituted silanes.

Mono organosilanes

In contrast with the bond to electronegative elements, the bond of silicon to carbon is usually stable to hydrolysis. Several preparative routes are used to form such bonds. Halo- or alkoxysilanes can be reacted with either Grignard reagents or alkali metal organics:

$$RMgCl + HSiCl_3 \rightarrow RHSiCl_2 + MgCl_2$$

$$RLi + SiCl_4 \rightarrow RSiCl_3 + LiCl$$

A more efficient route is through hydrosilylation of an olefin, which is catalyzed by materials such as chloroplatinic acid, t-butylperoxide and amine complexes. The silicon generally ends up on the least substituted carbon atom.

$$RCH = CH_2 + HSiCl_3 \rightarrow RCH_2CH_2SiCl_3$$

The greatest quantities of organosilanes are methyl and phenyl substituted. They are produced by direct synthesis.

Figure 1. Deposition of silanes
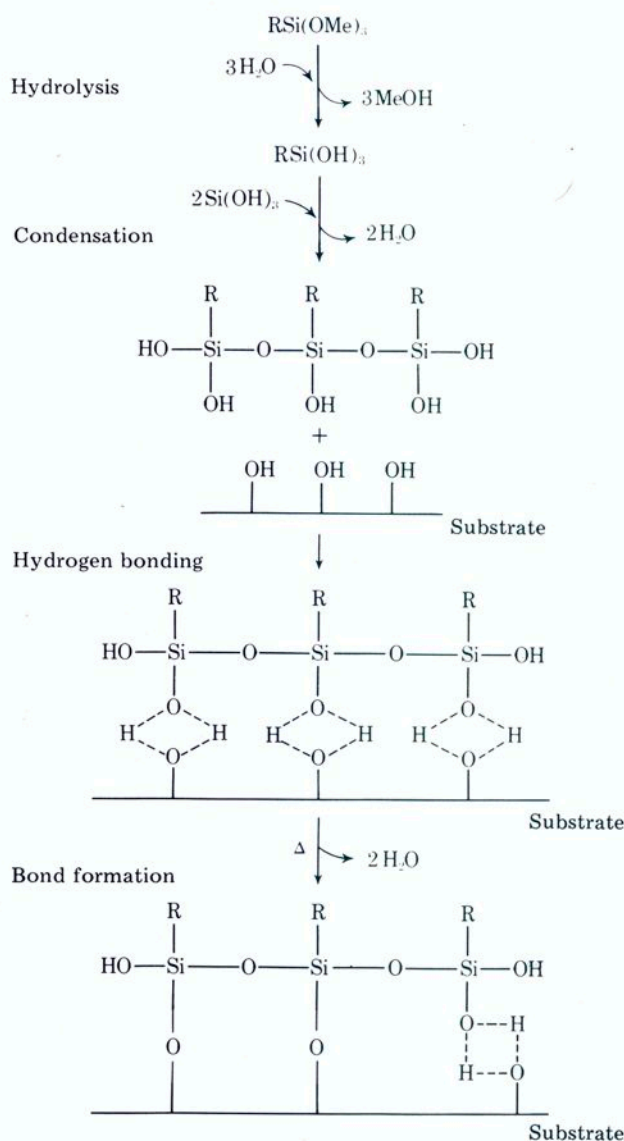
Table 1. Properties of tetra-substituted silanes

	bp (mp)	Density
SiF$_4$	−86° (90°)	1.66 (−95)
SiCl$_4$	52° (−70°)	1.48
Si(OMe)$_4$	121°	1.03
Si(OEt)$_4$	169° (−85°)	0.93
Si(OnPr)$_4$	94°/5 mm	0.92
Si(OnBu)$_4$	115°/3 mm	0.90
Si(OEtBu)$_4$	168°/2 mm	0.89
Si(OEtHe)$_4$	194°/1 mm	0.88
Si(OAc)$_4$	148°/6 mm	—
Si(Oϕ)$_4$	236°/1 mm (49°)	1.14 (60°)
Si(NMe$_2$)$_4$	157°/14 mm (3°)	0.90

Table 2. Silane wetting surfaces

Silane	Specific wetting surface, m²/g
Vinyltrichlorosilane	480
Vinyltriethoxysilane	410
Vinyltris(methoxyethoxy)silane	280
Methacryloxypropyltrimethoxysilane	315
Glycidoxypropyltrimethoxysilane	330
Aminopropyltriethoxysilane	355
Trichlorosilane	240

The specific wetting surface of a silane is determined from the minimum amount of silane rquired to provide a uniform surface.

Figure 2. Contact angle

$$MeCl + Si \xrightarrow[\Delta]{Cu} \begin{cases} MeSiCl_3 \\ Me_2SiCl_2 \\ Me_3SiCl \\ + \text{ small amounts} \\ \text{of other products} \end{cases}$$
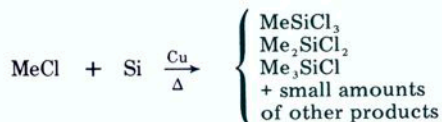
Most of the widely used organosilanes have one organic substituent. Reaction of these silanes involves four steps. Initially, hydrolysis of the three labile groups occurs. Condensation to oligomers follows. The oligomers then hydrogen bond with OH groups of the substrate. Finally during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. The two remaining silanol groups are present either in condensed or free form (Figure 1).

Water for hydrolysis may come from several sources. It may be added, it may be present on the substrate surface, or it may come from the atmosphere. Water for hydrolysis may also be generated *in situ* by dissolving chlorosilanes in excess alcohol. Reaction with alcohol yields alkoxysilanes and HCl, which can react with additional alcohol to form alkylhalide and water.

The degree of polymerization of the silanes is determined by the amount of water available and the organic substituent. If the silane is added to water and has low solubility, a high degree of polymerization is favored. Multiple organic substitution, particularly if phenyl or tertiary butyl groups are involved, favors formation of stable monomeric silanols.

The thickness of a polysiloxane layer is determined by the concentration of the siloxane solution. Although a monolayer is generally desired, multilayer adsorption results from solutions customarily used. It has been calculated that deposition from a 0.25% silane solution onto glass could result in eight molecular layers (Table 2). These multilayers could be either interconnected through a loose network structure, or intermixed, or both, and are in fact formed by most deposition techniques. The orientation of functional groups is generally horizontal, but not necessarily planar, on the surface of the substrate.

The formation of covalent bonds to the surface proceeds with a certain amount of reversibility. As water is removed generally by heating to 120° for 30 to 90 minutes or evacuation for 2 to 6 hours, bonds may form, break, and reform to relieve internal stress. The same mechanism can permit a positional displacement of interface components.
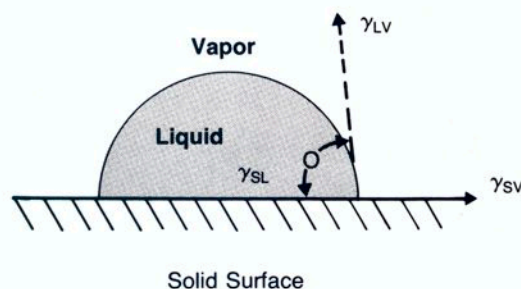
The space between homogeneous phases is sometimes called the interphase. In this region there is a steep gradient in local properties of the system. By treating a substrate with silanes the interphase can acquire specific surface energy, partition characteristics, mechanical and chemical properties.
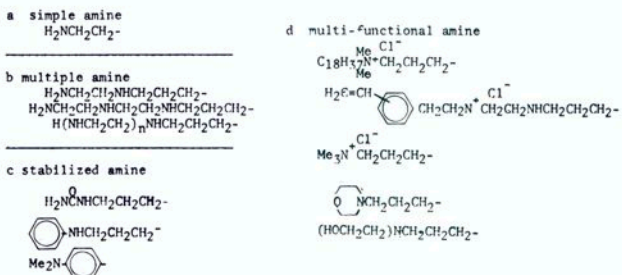
Uses

Wetting. The most widely used organosilanes, which do not possess reactive organic substitutions, are used to alter surface energy or *wetting characteristics* of the substrate. In the simplest cases, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, their alkoxy derivatives, and hexamethyldisilazane are used to render sub-

Table 3. Critical surface tensions

	γ_c
Polytetrafluoroethylene	18.5
Methyltrimethoxysilane	22.5
Vinyltriethoxysilane	25
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
Trifluoropropyltrimethoxysilane	33.5
3-(2 aminoethyl)-aminopropyltrimethoxysilane	33.5
Polystyrene	34
Cyanoethyltrimethoxysilane	34
Aminopropyltriethoxysilane	35
Polyvinylchloride	39
Phenyltrimethoxysilane	40.0
Chloropropyltrimethoxysilane	40.5
Mercaptopropyltrimethoxysilane	41
Glycidoxypropyltrimethoxysilane	42.5
Polyethyleneterphthalate	43
Copper (dry)	44
Aluminum (dry)	45
Iron (dry)	46
Nylon 6/6	46
Glass, soda-lime (dry)	47
Silica, fused	78
Titanium dioxide (Anatase)	91
Ferric oxide	107
Tin oxide	111

Note: Critical surface tensions for silanes refer to treated surfaces.

SILANE SUBSTITUTION CONTAINING REACTIVE AMINES

a simple amine
   $H_2NCH_2CH_2-$
_____

b multiple amine
   $H_2NCH_2CH_2NHCH_2CH_2CH_2-$
   $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2-$
   $H(NHCH_2CH_2)_nNHCH_2CH_2CH_2-$
_____

c stabilized amine
   $H_2NCNHCH_2CH_2CH_2-$

   ⬡–$NHCH_2CH_2CH_2-$

   Me_2N-⬡

d multi-functional amine

   $C_{18}H_{17}N^+CH_2CH_2CH_2-$ (Me, Cl⁻, Me)

   $H_2C=CH$–⬡–$CH_2CH_2N^+CH_2CH_2NHCH_2CH_2CH_2-$ (Cl⁻)

   $Me_3N^+CH_2CH_2CH_2-$ (Cl⁻)

   O⬡$NCH_2CH_2CH_2-$

   $(HOCH_2CH_2)NCH_2CH_2CH_2-$

strates water repellent. For example, glassware can be dipped into a 5% to 10% solution of dimethyldiethoxysilane and heated for ten minutes at 120 °C to render the surface hydrophobic. Laboratory pipettes and graduated cylinders so treated exhibit a flat meniscuses and completely transfer aqueous solutions.

GC packing of celites or firebrick are often treated with dimethyldichlorosilane or trimethylchlorosilane to reduce tailing.

Masonry can be treated with the sodium salt of methyltrichlorosilane hydrolysate to render it water repellent while glass surfaces of metal-glass capacitors treated with alkylsilanes exhibit reduced electrical leakage in humid conditions.

Surface energy control

The degree of control over solid-liquid interaction is much more sophisticated than indicated by the foregoing examples. 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 with a surface tension below the critical surface tension (γ_c) of a substrate will wet the surface, i.e., show a contact angle of 0 ($\cos \theta_e = 1$) (Figure 2). The critical surface tension is unique for any solid, and is determined by plotting the cosine of the contact angles of liquids of different surface tensions and extrapolating to 1 (Table 3). The contact angle is given by Young's equation:

$$\gamma_{sv} - \gamma_{sl} = \cos\theta_e$$

where γ_{sl} = interfacial surface tension, γ_{lv} = surface tension of liquid, and ($\gamma_{sv} = \gamma_l$, when $\gamma_{si} = 0$ and $\cos \theta_e = 1$).

Silane treatment has allowed control of thixotropic activity of silica and clays in grease and oil applications. In the reinforcement of thermosets and thermoplastics with glass fibers, one approach for optimizing reinforcement is to match the critical surface tension of the silylated glass surface to the surface tension of the polymer in its melt or uncured condition. This has been most helpful in resins with no obvious functionality such as polyethylene and polystyrene. Immobilization of cellular organelles, including mitochondria, chloroplasts, and microsomes, has been effected by treating silica with alkylsilanes of C_8 or greater substitution. The organelles can be adsorbed from solution by such surfaces.
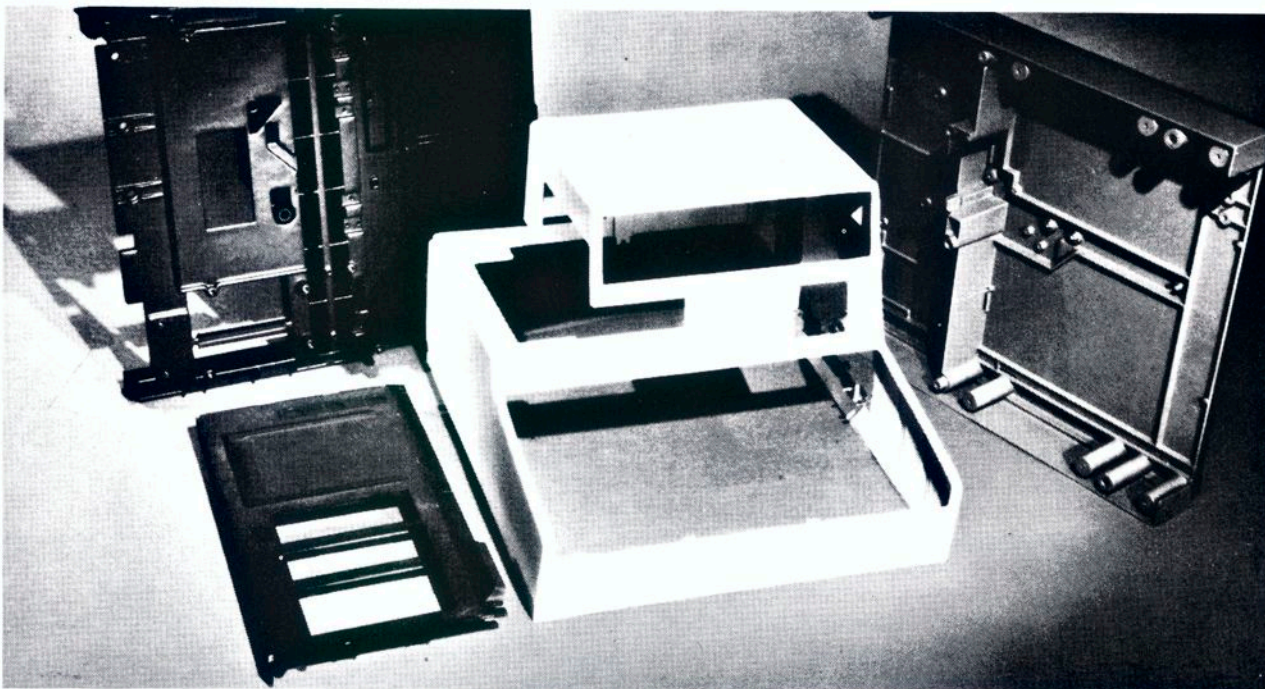
Complex ribs, bosses, and stiffness in NCR 250 base and housing assembly permit direct attachment and support of electronic and mechanical components. The parts are made from glass fiber/polyester composite sheet molding compounds. (Courtesy Owens-Corning Fiberglass)
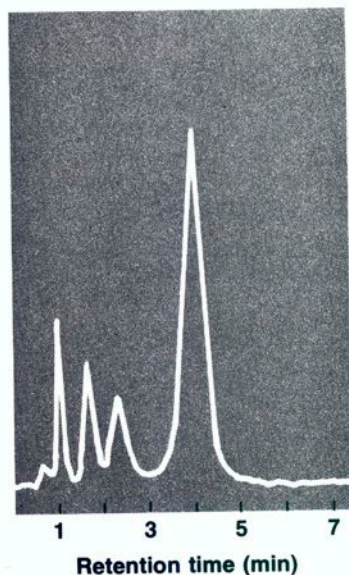
Figure 3. Liquid chromatography, using octadecylsilylated porous silica support

Mobile phase, 60:40 acetonitrile: 0.01 M ammonium carbonate; peaks, ϕ_3COH, ϕ_3CH, ϕ_3SiH, $1,3,5\phi_3C_6H_3$. From Gilpin

Scanning electron micrograph of a broken gear tooth from a non-coupled glass fiber/acetal composite. Note that cleavage occurred between fibers (author's work)
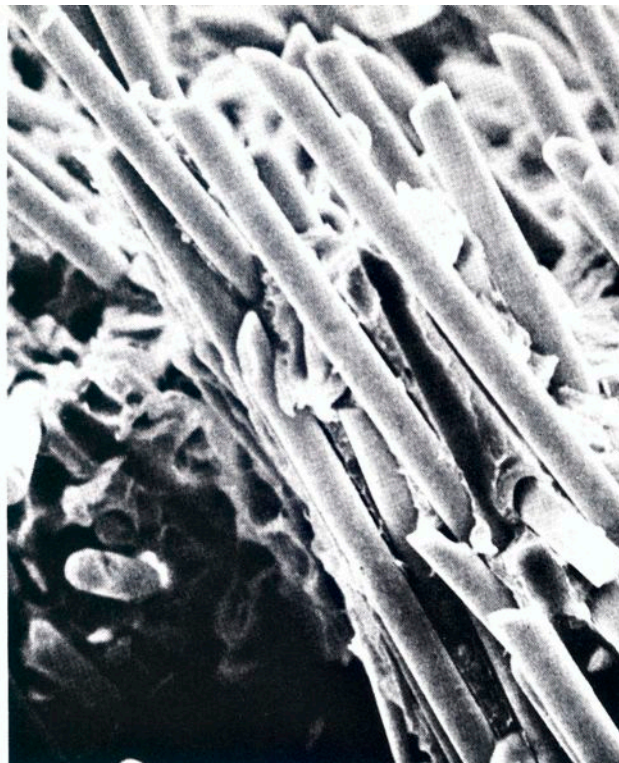
Chromatography

Octadecyl, and cyanopropyl silanes provide bonded phases for gas and liquid chromatography (Figure 3). Reverse-phase thin-layer chromatography can be accomplished by treating plates with dodecyltrichlorosilane.

By forming complexes of copper ions with aminoalkylsilylated surfaces, an interphase results that can selectively adsorb ethylene, propylene, and other gases.
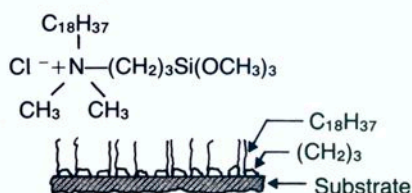
Liquid crystals

The geometry of the interphase can also impose orientation on the bulk phase. In liquid crystal displays, clarity and permanence of image are enhanced if the display can be oriented parallel or perpendicular to the substrate. The use of surfaces treated with octadecyl(3-(trimethoxysilyl)propyl) ammonium chloride (perpendicular) or methylaminopropyltrimethoxysilane (parallel) has eliminated micromachining operations (Figure 4). The oriented crystalline domains often observed in reinforced nylons have also been attributed to orientation effects of the silane in the interphase.

The substituted aminosilanes described above, although not functional in the organic phase, are an example of mixed function with the substrate. The substrate silanol groups will hydrogen bond to the amine groups. Another example of mixed-function substrate interaction is silane derivatives of ethylenediamine-type compounds. These are utilized for treating metal substrates because the amines chelate metal atoms. The aminoalkylalkoxy silanes also have the unique feature of hydrolyzing immediately in water solutions and slowly condensing to oligomers. The speed of hydrolysis has been attributed both to the basicity of the group and to the internal chelation of the amine function with its silanolate. The extent of internal cyclization is strongly dependent upon pH. Near pH 7 silica is above its isoelectric point (2.2) and surfaces are rich in silanol anions. If the organic substitution contains a cationic group initially, the silane will tend first to orient with the silanol anions on the substrate followed by hydrolysis of the alkoxy groups. It is the initial anionic substrate that is exploited for deposition of silanes used in orientation of liquid crystals.

(a) N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP)

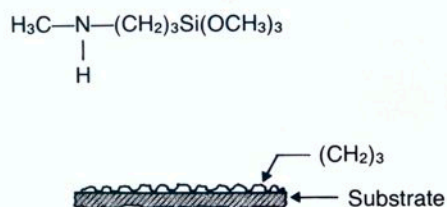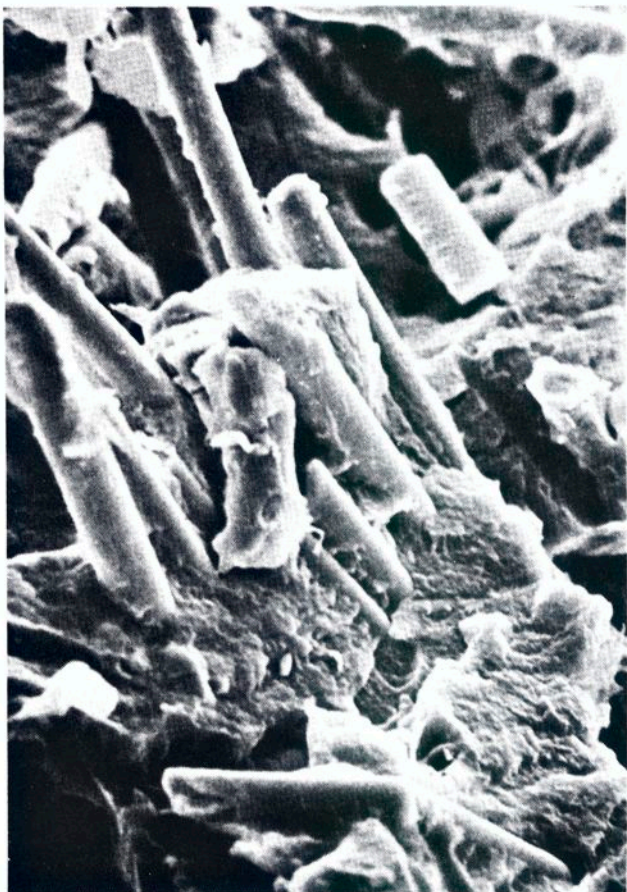(b) N-methyl-3-aminopropyltrimethoxysilane (MAP)

Figure 4. Orientation effects of silanes for liquid crystal displays From Kahn

Non-covalent functional interaction

Hydrogen bond and dipole interaction of organofunctional substituents has been applied to the binding of resins. Polyamides, thermoplastic and polyesters, polycarbonates, and polyphenylene oxides are typically reinforced with glass fibers treated with aminofunctional silanes. The silanes may contain single or multiple functionality, for example the n-trialkoxysilylpropyl derivatives of ammonia, ethylene diamine, diethylenetriamine, and polyethyleneimines. The aminosilanes often lend an undesirable yellow-brown coloration to composites and urea, urethane, or amide compounds are sometimes used to reduce coloration.

The strong hydrogen bonds formed by these silanes are also used to bind dyes to both glass and cellulosic fabrics. In these cases, however, one of the alkoxy groups is often substituted with a methyl group to retain flexibility of the cloth.

Ionic and polar interaction of silane-modified surfaces has been adapted to ion-exchange columns and liquid chromatography. (Chloromethyl) phenylalkylsilanes have been reacted with silica surfaces and then treated to form benzylic sulfonate and carboxylate salts for cation exchange. Quaternary ammonium salts are used as anion exchangers in phosphate-buffered butanol-water. Cyanopropyl and polyethylene oxide substituted alkylsilylated stationary phases have satisfied the requirements for liquid chromatography separations of amino acids and many steroids.

Coupling agents

One can form covalent bonds between an organic moiety and a substrate through an intermediary functional silane, called a *coupling agent*. Coupling agents are used in enzyme immobilization, solid state synthesis, as antimicrobial agents and dye-fixing agents in textiles, organic surface coatings, and polymer composites and bulk interfaces. In most cases the substrate is pretreated with the silane-coupling agent, but integral blending accomplished by simple mixing of all the reactants at once, particularly for coatings and composites, is frequently used.

There are several limitations on the functionality that may be introduced in a silane-coupling agent. Silicon is less electronegative than carbon. Consequently, introduction of electronegative substitutes on the alkyl portion of a coupling agent has a considerable influence on the reactivity of the Si—C bond. Electronegative substitution on the β carbon always has the greatest effect. The Si—C bond is readily accessible to nucleophilic or electrophilic attack as well as subject to thermal decomposition. Nucleophilic attack also takes place on the α carbon, although susceptibility to electrophilic attack is reduced. Most silane-coupling agents introduce functionality at the γ carbon where these effects are far less significant. Certain functional groups like the carboxylate are eliminated because they react with the alkoxy portion of the silane.

Polymer applications

Coupling agents find their largest application in the area of polymers. Since any silane that enhances the adhesion of a polymer is often termed a coupling agent, regardless of whether or not a covalent bond is formed, the definition becomes vague. In this discussion the parochial outlook will be adopted, and only silanes that form covalent bonds directly to the polymer will be considered. The covalent bond may be formed by reaction with the finished polymer or copolymerized with the monomer. Thermoplastic bonding is achieved through both routes, although principally the former. Thermosets are almost entirely limited to the latter. The mechanism and performance of silane coupling agents is best discussed with reference to specific systems. The most important substrate is E-type fiberglass, which has 6–15 silanol groups per $m\mu^2$.

Thermoset composites

Polyesters. Unsaturated thermoset polyesters, owing to their facility for undergoing free-radical polymerization, can be modified by copolymerization with reactive monomers. These resins, usually of loosely defined structure, often have had their viscosity reduced by addition of a second monomer, typically styrene. The usual coupling agents for thermoset polyesters undergo radical copolymerization in such systems. Vinylsilanes have achieved widest use. Vinyltrichlorosilane is used less often than vinyltrialkoxysilanes or vinyltriacetoxysilanes because of both the first's corrosive nature and reluctance to undergo free-radical additions. Methacrylyl and styryl functional silanes undergo addition much more readily than vinylsilanes.

In general, better reinforcement is obtained when the silane monomer matches the reactivity of the styrene rather than the maleate portion of the polyester.

Scanning electron micrograph at a broken gear tooth from an aminosilane-coupled glass fiber/nylon 6/6 composite. Note how fibers have broken as well as matrix (author's work)
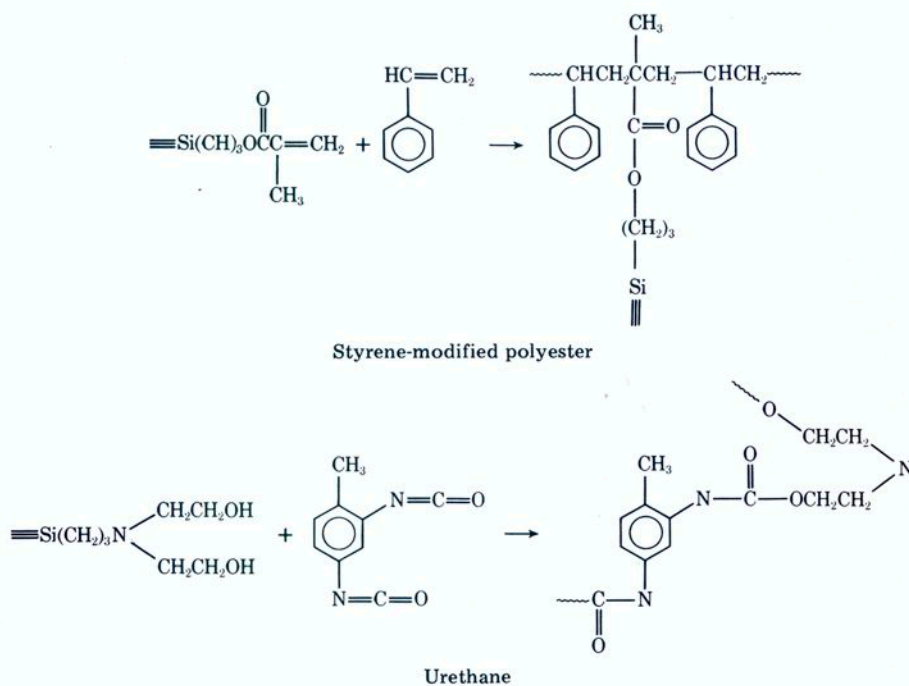
Figure 5. Thermoset—silane model reactions

A direct approach to selecting the optimum silane uses the e and Q parameters of the Alfrey-Price treatment of polymerization. Here e indicates the polarity of the monomer radical that forms at the end of a growing chain, while Q represents the resonance stabilization of a radical by adjacent groups. Optimum random copolymerization is obtained from monomers with similar orders of reactivity.

Apart from copolymerization, a second route is available for silane coupling. A typical formulation contains propylene glycol, maleic anhydride, and phthalic anhydride with excess glycol to drive the reaction to completion. The excess alcohol groups can be reacted with epoxy or isocyanate functional silanes. The situation is parallel to alkyds used in paints and protective coatings. These resins are synthesized from polybasic acids and polyols, usually phthalic anhydride and glycerol. As with polyesters, the alcohol function is in excess, so the epoxy and isocyanate silanes are also used. Adhesion of polyesters is enhanced not only with silane coupling agents but with silane hydrogen-bonding agents, i.e., the amino silanes.

The unsaturated polyesters represent the largest use area for organosilanes. Fiberglass lay-up and spray-up for large structural parts such as boats and car bodies are well-known applications. In lay-up applications, glass cloth is impregnated with resin, while in spray-up applications a mixture of polyester and unoriented long glass fibers are sprayed onto a mold or a base structure. Volume

usage of sheet molding compound (SMC) for smaller parts like business machine housings is also expanding. SMC is prepared by blending polyesters and unoriented fiberglass into sheets and partially curing the system. Final cure is accomplished by heat and pressure in the molding step.

Urethanes. Thermoset urethane can be effectively coupled with two types of silanes. The first type, including isocyanate and isothiocyanate functional silanes, may be used to treat the filler directly or integrally blended with the diisocyanate (TDI, MDI, etc.) prior to cure. Amine and alkanolamine functional silanes, on the other hand, are blended with the polyol rather than the diisocyanate. Isocyanate functional silanes couple with the polyol. Alkanolamine functional silanes react with the isocyanate to form urethane linkages, while amines silanes react with the isocyanates to yield urea linkages.

A typical application for a coupled urethane system is improving bond strength with sand in abrasion-resistant, sand-filled flooring resin.

Epoxies. Epoxy resin systems are treated much as urethanes. Thus epoxycyclohexyl and glycidoxy functional silanes are used to pretreat the filler or blended with the glycidylbisphenol-A ether. Amine functional silanes can likewise be used to pretreat the filler or blended with the hardener portion. Treatment of fillers in epoxy adhesives improves their dispersibility and increases the mechanical

$\equiv$Si(CH$_2$)$_3$NHCH$_2$CH$_2$NH$_2$
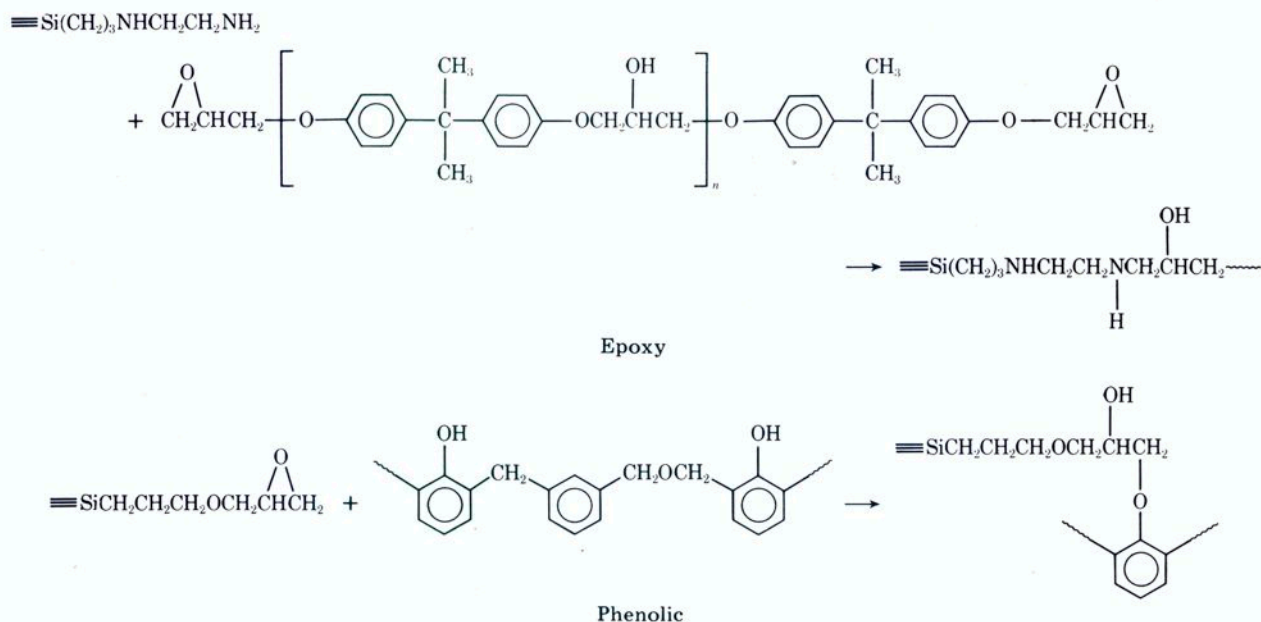
Epoxy

Phenolic

properties of the cured resin. A large application area is glass cloth-reinforced epoxy laminates and prepregs in aerospace and electrical circuit board applications.

Phenolics. Phenolic resins are divided into base catalyzed *single-step* resins called *resols* or better known acid catalyzed *two-step* systems called *novolaks*. Although some foundry sand molds are formulated with resols and silanes, the commercial utilization of silanes in phenolic resins is largely limited to novolak/glass fabric laminates and molding compounds. The phenolic hydroxyl group of the resins readily react with the oxirane ring of epoxy silanes to form phenyl ether linkages. When phenolic resins are compounded with rubbers, as is the case with nitrile/phenolic or vinylbutyral/phenolic adhesives, or impact-resistant molding compounds, additional silanes, particularly mercaptofunctional silanes, have been found to impart greater bond strength than silanes that couple to the phenolic portion (Figure 5).

Thermoplastic composites

Thermoplastics provide great synthetic challenge in promoting adhesion through silane coupling. The silanes must react with the polymer and not the monomeric precursors, which not only limits avenues for coupling, but also presents additional problems in rheology and thermal properties during composite formulation. Moreover mechanical requirements here are stringently determined.

Most thermosets are either reinforced with continuous fiber mat and roving or they are simply filled. Although fillers are used in thermoplastics, the thrust is toward discontinuous fiber reinforcement. The discontinuous glass fiber-reinforced thermoplastics have formed a major industry serving the injection molding and extrusion market.

Thermoplastics with discontinuous reinforcement were developed from observations made on continuous fiber-reinforced thermosets. Composites with broken glass fibers were found to maintain much of the tensile strength of composites with unbroken strands. Moreover, reinforcements made of chopped fibers laid end-to-end gave similar results. In thermoplastics, like thermosets, the fibers are the principal load-bearing component. The matrix transmits the load to the fibers. Load is transferred into the fiber from the matrix through shear action. The shortest fiber that permits stress build-up to a level where tensile fracture occurs in the fiber is termed the critical length (l_c). (The *critical aspect ratio* for a glass fiber is 20:1.) With a composite made up of fibers of critical length, the average stress in the fiber is half the tensile strength of the fiber. In fiber longer than l_c a greater portion of the fiber can be stressed to the tensile limit so that a discontinuous fiber is ten or a hundred times l_c, the stress that can be realized in the fiber is 95% and 99.5% of that using continuous fibers, respectively.

Polymers that contain regular sites for covalent reactiv-

ity either in the backbone or in a pendant group include polydienes, polyvinylchloride, polyphenylene sulfide, acrylic homopolymers, maleic anhydride, acrylic, vinyl acetate, diene-containing copolymers, and halogen or chlorosulfonyl-modified homopolymers. A surprising number of these are coupled by aminoalkylsilanes. Chlorinated polymers readily form quaternary compounds while the carboxylate and sulfonate groups form amides and sulfonamides under process conditions. At elevated temperatures, the amines add across many double bonds although mercaptoalkylsilanes are the preferred coupling agents. Although the most widely used coupling agents, the aminoalkylsilanes are not necessarily the best. Epoxysilanes for example are frequently used with acrylics, whose properties vary widely. Reinforcement of PVC enhances its dimensional stability and increases its resistance to deformation at increased temperature. Polyphenylene sulfide (PPS) can be utilized at temperatures up to 500 °F while under compressive loads. Both are used in pump housings and impellers while polypropylene/maleic anhydride or acrylic-reinforced copolymers are used in automotive fan shrouds.

A challenge

The group of polymers that most closely approaches theoretical limits of strength does not appear to contain regular opportunities for covalent bond formation to substrate. Most of the condensation polymers including polyamides, polyesters, polycarbonates, and polysulfones are in this group. Adhesion is promoted by introducing high energy groups and hydrogen bond potential in the inter-

Figure 6. Thermoplastic—silane model reactions

A Hewlett-Packard portable printing calculator demonstrates a wide variety of composite applications. *a,* carbon fiber—PTFE/polyphenylene sulfide; *b, d,* glass fiber/polycarbonate; *c, e, f,* glass fiber/PTFE/polycarbonate. (Courtesy LNP Corp.)

phase area or by taking advantage of the relatively low molecular weight of these polymers, which results in a significant opportunity for end-group reactions. Aminoalkylsilanes, chloroalkylsilanes, and isocyanatosilanes are the usual candidates for coupling these resins. This group has the greatest mechanical strength of the thermoplastics, allowing them to replace the cast metals in such typical uses as gears, connectors, and bobbins.

The polyolefins and polyethers present no direct opportunity for covalent coupling. Until recently, the principal approach for composite formulation was to match the surface energy of the filler surface, by treating it with a substituted silane, with that of the polymer. For optimum reinforcement, preferred resins should be of high molecular weight, linear, and have low melt viscosity. Approaches to improved composite strength have been through compatibility with long chain alkylsilanes or aminosilanes. Far more effective is coupling with vinyl or methacryloxy groups, particularly if additional coupling sites are created

in the resin by addition of peroxides. Dicumyl peroxide and bis(*t*-butylperoxy) compounds at levels of 0.15% to 0.25% have been introduced into polyethylene compounded with vinylsilane-treated glass fibers for structural composites or vinylsilane-treated clay for wire insulation. Increases of 50% in tensile and flexural properties have been observed in both cases when compared to the same silane systems without peroxides.

Greater strengths are being achieved by inducing reactivity within the polymer. If polystyrene, for example, is processed at temperatures of 250 °C, it begins to depolymerize to yield free-radical ends. Silanes capable of chain transfer can couple to these radicals. Thus at increased temperature epoxycyclohexylethyl, chloropropyl, phenyl, and substituted silanes couple to polystyrene forming a resin coating that cannot be removed by solvents. The resulting dimensional stability and flexural modulus of styrene, and its copolymers with acrylonitrile, led to opened use in auto housing and dash panel frames.

A second radical-induced method of coupling uses chlorinated alkylaromatics, e.g., bis(trichloromethyl)benzene, which decompose at higher temperatures. The newest and most promising approach for coupling polypropylene and polyethylene is through silylsulfonylazides. Unlike azide bound to silicon, sulfonyl azides decompose above 150 °C to form a molecule of nitrogen and a reactive nitrene that is capable of insertion into carbon-hydrogen bonds, forming sulfonamides, into carbon-carbon double bonds, forming triazoles, and into aromatic bonds, forming sulfonamides. Fillers are treated first with the silane and then the treated filler is fluxed rapidly with polymer melt. Properties of homopolymer composites have approached those of copolymer, leading to use in squirrel cage blowers and timing cams.

The linear ethers, which include polymethylene oxides and copolymers and polyphenylene oxides, have not to my knowledge been coupled directly to substrates. Bonding is primarily the result of electrostatic interaction with the ether oxygens. Amine and cationic substitution are preferred. Indirect coupling through formation of ketals with hexafluoroacetone has met with some success. Glass-reinforced ethers are engineering materials. Acetal composites are frequently found in gears, bearings, valves, and other wear applications. PPO/styrene blends are found in housings for business machines. Long-term exposure to water is an excellent application area for glass reinforced ethers (Figure 6).

The property compromise

Our discussion of coupling agents for fiber-reinforced thermoplastics has oversimplified several aspects of current technology. A thermoplastic composite may have to meet several criteria in a particular application: flexural modulus, resistance to creep, deflection under load at elevated temperature, etc. The most widely applied criterion—toughness—is both the most ill-defined and hardest to meet. Usually the go/no-go test is impact strength. Work-to-break is generally associated with toughness. Increasing the effectiveness of a coupling agent increases tensile strength, but this increase can occur with apparent decreases in impact strength. Usually this dilemma is attributed to loss of elongation. It has been demonstrated that by creating a low modulus interphase without chemical coupling, toughness of a composite can be improved, but other mechanical properties are sacrificed. Elastomers

provide an interesting analogy. Coupling agents that improve dispersion of fillers within the elastomer and maintain impact are hydrophobic, while those that increase stiffness and promote adhesion are reactive with the vulcanizing or crosslinking centers. If the work-to-break is considered a function of the tensile strength (force) and elongation (distance), tougher materials can be produced by increasing their product by any mechanism. In a homologous series of coupling agents, an increase in tensile strength can usually be correlated with an increase in elongation and impact strength. An optimistic view for achieving ultimate composite toughness is through optimizing all mechanical properties. Styrenics and acetals demonstrate overall improved impact strength mechanical properties when compared to their unreinforced counterparts (Table 4).

Another aspect of silane coupling technology that is not straightforward is application of the silane to the glass fibers. Glass fibers must be sized to stop breakage and allow handling. The sizing system contains a binder, usually polyvinyl acetate in older formulations, and in current formulations usually polyester. Specialty binders include propylene-acrylic latices. Lubricants and antistats are also present. The sizing system may be permanent or fugitive. The silane, just one component of the size system, may be interferred with by other components.

Solid-state synthesis

Silane-modified supports including glass and silica are used for the stepwise analysis and synthesis of highly polymeric proteins. The supports are macroscopic, inert structures, usually beads, which have ready access to reactants and yet may be physically confined. Proteins derive their chemical and physical properties from the ordered sequence of many amino acids. In order to clarify the structural and functional mechanisms of proteins, a number of methods of solid-phase analysis have been developed for elucidating the amino acid sequence. They use aminoalkyl and isocyanatoalkyl siliceous supports that are easy to prepare, have great consistency, and are less expensive than modified polystyrenes and polystyrene copolymers. The greater stability of inorganic supports also allows analysis of larger peptides.

Edman degradations can be accomplished by treating aminopropylsilylated supports (a silica with 10–75 Å pores yields about 2×10^{-7} moles of aminopropylsilane per gram of glass) with the peptide to be analyzed in the presence of dicyclohexylcarbodiimide. 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 repeated with the bound peptide residue.

A variety of alternative immobilization techniques have been developed. For example, aminosilanes are often treated with *p*-phenylene diisothiocyanate. One of the functional groups becomes bound to the silane through a thiourea group, while the remaining isothiocyanate group may be reacted directly with the amine group of a protein (usually from a lysine residue) (Figure 7).

Although (chloromethyl)phenylalkylsilane supports treated with triethylene tetramine adducts are used for sequencing, their more important use is in solid-state syn-

Table 4. Properties of 30% glass fiber-reinforced thermoplastic composites

ASTM test:	Specific gravity D792	Mold shrinkage, In./In. D955	Tensile yield strength, 10^3 psi D638	Flexural modulus, 10^6 psi D790	Impact strength, notched--un-notched		Deflection temp., @264 psi, °F D648	Coeff. of thermal expan., 10^{-5} In./In./°F D696
ABS	1.28	0.001	14.5	1.10	1.4	3–4	220	1.6
	(1.05)	(0.006)	(6.0)	(0.32)	(3.0)		(195)	(5.3)
Acetal	1.63	0.003	19.5	1.40	1.8	8–10	325	2.2
	(1.42)	(0.020)	(8.8)	(0.40)	(1.2)	(1.6)	(230)	(4.5)
Ethylene tetrafluoroethylene	1.89	0.003	14.0	1.10	7.5	17–18	460	1.6
	(1.70)	(0.018)	(6.5)	(0.20)	(>40)		(160)	(4.0)
H.D. polyethylene	1.17	0.003	10.0	0.90	1.1	8.9	260	2.7
	(0.95)	(0.020)	(2.6)	(0.20)			(120)	(6.0)
Nylon 6	1.37	0.004	23.0	1.20	2.3	20	420	1.7
	(1.14)	(0.016)	(11.8)	(0.40)	(1.0)		(167)	(4.6)
Nylon 6/12	1.30	0.004	22.0	1.20	2.3	14	415	1.5
	(1.07)	(0.011)	(8.8)	(0.24)	1.0		(150)	(5.0)
Nylon 6/10	130	0.004	21.0	1.10	24	20	420	1.5
	(1.08)	(0.016)	(8.5)	(0.28)	1.0		(135)	(5.0)
Nylon 6/6	1.37	0.004	26.0	1.30	20	17	490	1.8
	(1.14)	(0.018)	(11.6)	(0.41)	1.0		(170)	(4.5)
Polycarbonate	1.43	0.001	18.5	1.20	37	17–18	300	1.3
	(1.20)	(0.006)	(9.0)	(0.33)	12–17	>40	(265)	3.7
Polyether sulfone	1.60	0.003	19.0	1.20	1.5	10	415	1.8
	(1.37)	(0.007)	(12.0)	(0.37)			(400)	(3.1)
Polyphenylene oxide-base resin	1.27	0.002	21.0	1.30	1.7	10	310	1.4
	(1.06)	(0.005)	(9.5)	(0.36)	1.7		(265)	(3.3)
Polyphenylene sulfide	1.56	0.002	20.0	1.60	1.4	8–9	500	1.1
	(1.34)	(0.010)	(10.8)	(0.60)	0.3		(280)	(3.0)
Polypropylene	1.13	0.004	10.0	0.85	1.6	5–6	295	2.0
	(0.91)	(0.018)	(4.9)	(0.18)	0.5	2.0	(135)	(4.0)
Polystyrene crystal	1.28	0.001	13.5	1.30	1.0	2–3	215	1.0
	(1.07)	(0.004)	(7.0)	(7.45)	0.25	1.0	(180)	(3.6)
Polysulfone	1.45	0.003	18.0	1.20	1.8	14	365	1.4
	(1.24)	(0.007)	(10.0)	(0.40)	1.3		(340)	(3.1)
SAN	1.31	0.001	17.4	1.50	1.4	1–4	215	1.8
	(1.08)	(0.005)	(9.8)	(0.50)	9.50		(200)	(3.4)
Thermoplastic polyester (PBT)	1.52	0.003	19.5	1.40	1.61.8	9–10	430	1.2
	(1.31)	(0.020)	(8.5)	(0.34)	0.8	1.0	(130)	(5.3)
polyvinylchloride	1.34	0.001	13.0	.85	1.2	0.5	155	1.7
		0.003	6.0	0.40			155	5.9
Polyamide-imide	1.60		29.0	1.4	1.8	11	550	1.0
	(1.40)	(0.007)	(27.4)	(0.66)	(2.5)	(19)	(525)	(1.8)

Note: Values in parentheses are the neat base resins.

thesis, where they are rapidly replacing chloromethylated styrene divinylbenzene (Merrifield Resin). Not only are the former easy to prepare, but they also avoid carcinogenic intermediates.

The silylated support is allowed to react with the triethylammonium salt of a protected amino acid. The resulting ester is analogous to the benzyl ester of the acylamino acid. Once the initial amino acid residue has been coupled to the support, a variety of peptide synthesis methods can be used. Automation allows eight synthetic steps daily. At the completion of synthesis the anchored peptide is separated from the support with hydrogen bromide in acetic acid. Such peptides as bradykinin and enzymes as ribonuclease have been synthesized on solid supports.

Solid-state catalysis

Use of the ability 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. Such immobilized enzymes serve as models for membrane-bound in vivo enzymes and can be used repeatedly in continuous processes; they can be separated cleanly from products. Their stability to extremes of pH and temperature is enhanced.

Methods of immobilization are divided into two classes; covalent and noncovalent. Silane-modified supports have played roles in both, but emphasis has been on covalent bonding. The most frequently used technique for immobilizing enzymes on a solid support involves reducing N(silylpropyl)-p-nitrobenzamide groups placed on supports to give aniline derivatives, then converting them to diazonium salt and effecting coupling through azo linkage to the tyrosine of the proteins. Isothiocyanate and azido functions on supports have been used as well. Here lysine resi-
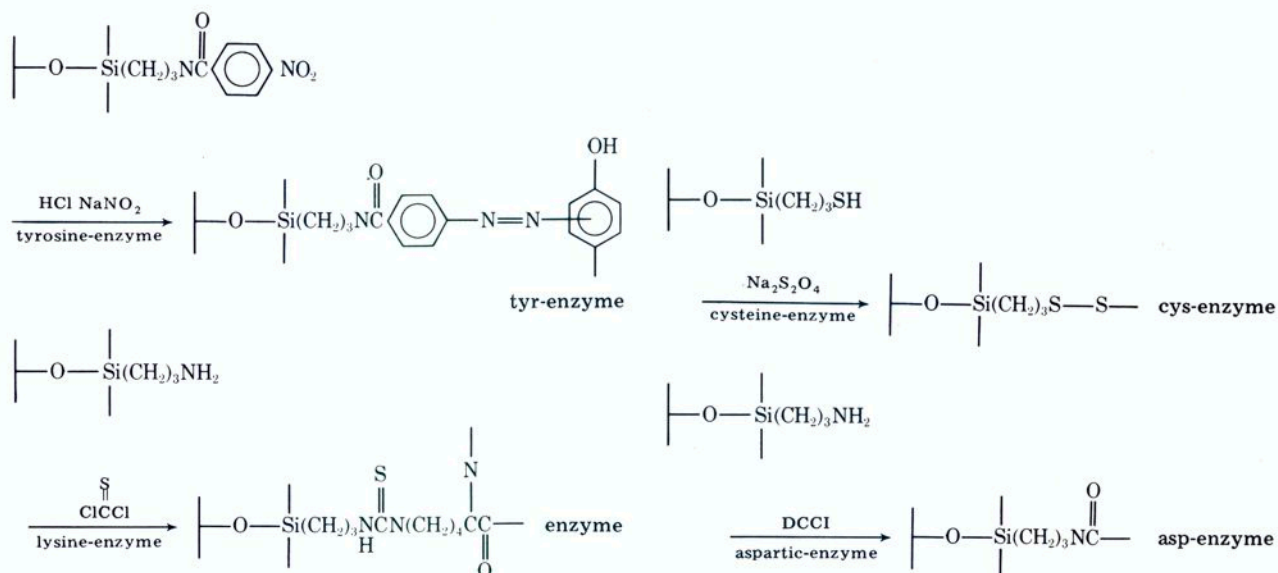
Figure 7. Enzyme immobilization

dues appear to be the more reactive.

Silymercaptans have been used to couple cysteine residues, and amine alklylsilanes have been coupled with aspartic and glutaric acid residues with dicyclohexylcarbodiimide.

Use of immobilized enzymes for production is at the pilot stages with several systems demonstrating sufficient efficiency for final scale-up. Production of glucose and invert sugar are probably the largest applications. Substantial research is being done on glucoamylase, which hydrolyzes the glycolytic linkages of corn starch. Systems that promise to have the most immediate impact are catalase and trypsin treatment of milk, which increases its shelf life and allows higher storage temperature, and amino acid acylase, which can be used to resolve D and L amino acids. Laboratory and clinical applications that have rapidly reached fruition include affinity chromatography and phospohexoseisomerase assays.

Mixed-phase catalysts

Small complexes and molecules can also become useful heterogeneous catalysts when bound to a solid support. Diphenyl(triethoxysilylpropyl)ethylphosphine was bound to silica gel and rhodium with carbonyl ligand introduced to give material that catalyzes the hydrosilylation and the hydroformylation of olefins.

The 2-alkylimidazole silanes have been utilized to accelerate the hydrolysis of model peptide compounds, but this would not be anticipated to be of any great utility. More interestingly, epinephrine bound to a solid support with a silane continues to stimulate chick and dog heart muscle contraction.

As was noted at the outset, siliceous surfaces are ubiquitous. Any reader who has reached this point will certainly agree, and it's our hope that concepts presented here will stimulate ideas he can use in his/her work, whatever that may be.

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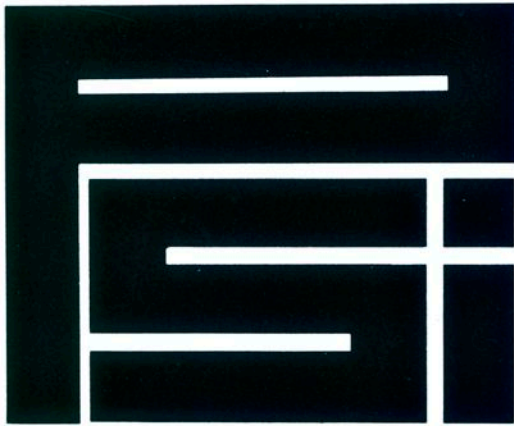
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