An Introduction to Silanes and Their Clinical Applications in Dentistry

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Purpose: This overview presents a description of organofunctional trialkoxysilane coupling agents (silanes), their chemistry, properties, use, and some of the main clinical experiences in dentistry. ***Materials and Methods:*** The main emphasis was on major dental journals that have been reviewed from 1958 up to the latest research news from 2002. A MEDLINE search with the key words "dental silanes" was used. Special silane literature and journals outside dentistry were also cited. ***Results:*** The main emphasis is on the use of silanes in prosthetic and restorative dentistry. Clinical relevance was based mainly on either short- or long-term tests. The interpretation of various results is not given, mainly because of controversial observations that may be very difficult to explain. Nevertheless, the majority of the clinical results pointed to silanes playing a significant role in the adhesion process. Silane reaction mechanisms were not entirely understood, and there exist several theories for bonding mechanisms for silanes and substrates. ***Conclusion:*** Dental materials offer a continuously challenging forum for silanes, and silanes will play an essential role in material development. *Int J Prosthodont 2004;17:155–164.*

Study of organofunctional trialkoxysilane coupling agents (also, briefly, silanes) has generated many scientific publications. This overview aims at giving an introduction to silanes in dentistry; it is not a systematic review because of the overwhelming amount of material over about 50 years. The articles and other literature were cited more or less randomly.

Silanes form a large group of organic compounds that essentially contain a silicon (Si) atom or atoms. Silanes resemble orthoesters, and they can be bifunctional, ie, they have a dual reactivity. The organic functional part (eg, vinyl $-CH{=}CH_2$, allyl $-CH_2CH{=}CH_2$, amino $-NH_2$, isocyanato $-N{=}C{=}O$) can polymerize with an organic matrix. The alkoxy groups (eg, methoxy $-O-CH_3$, ethoxy $-O-CH_2CH_3$) can react with an inorganic substrate, in both cases forming covalent bonds between the matrices (see below). Generally, silanes may or may not contain reactive groups. A reactive group can also be, eg, chloride ($-Cl$). There can be a propylene link ($-CH_2CH_2CH_2-$) between Si and the organic functionality, especially when the silane is used for metal pretreatment.[1–3]

Silanes may be monofunctional (when there is one Si atom with three alkoxy groups in the molecule) or bisfunctional, ie, there are two Si atoms, each with three alkoxy groups, eg, bis(3-trimethoxysilyl)propyletylenediamine. Trisfunctional silanes with three Si atoms (and respectively each of them with three alkoxy groups) also exist, eg, tris(3-trimethoxysilylpropyl)isocyanurate. Vinyltriethoxysilane is an example of a monofunctional silane (Fig 1).

Silanes, hybrid organic-inorganic compounds, can function as mediators and promote adhesion between

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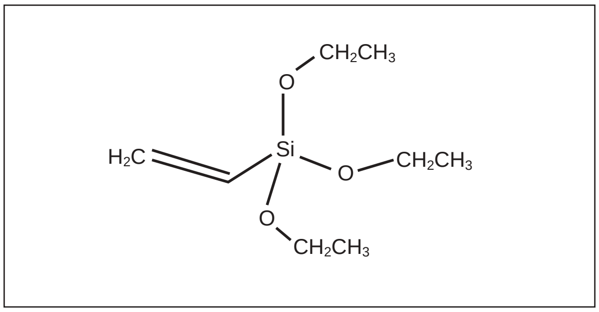
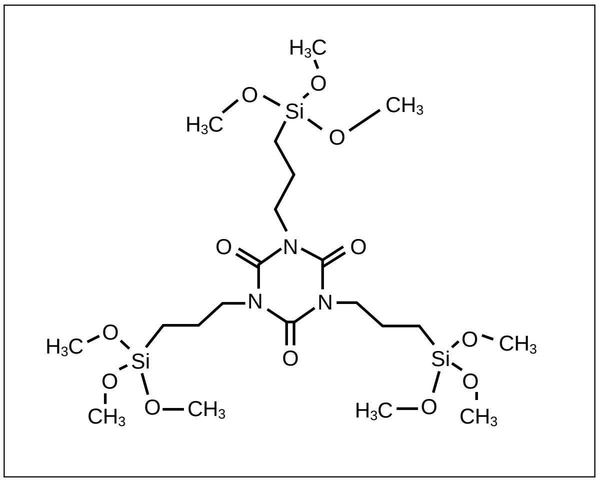


Fig 1a Monofunctional silane, vinyltriethoxysilane.

Fig 1b *(right)* Bisfunctional silane, bis(3-trimethoxysilyl)propyl-etylenediamine.



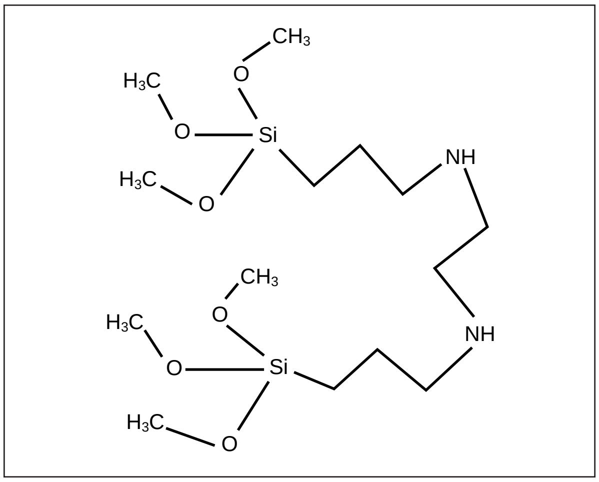
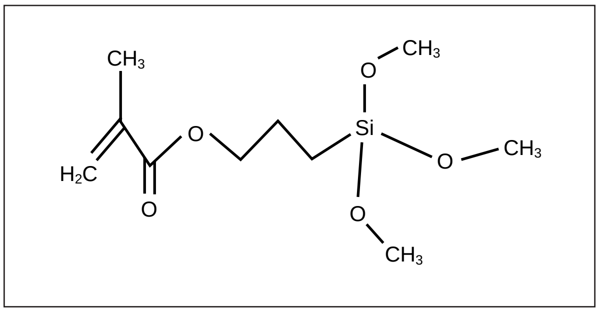


Fig 1c *(left)* Trisfunctional silane, tris(3-trimethoxysilyl-propyl)isocyanurate.

Fig 1d *(below)* Monofunctional silane, γ-methacryloxypropyl-trimethoxysilane (or 3-trimethoxysilylpropyl methacrylate).



dissimilar, inorganic and organic, matrices through dual reactivity. They are called primers, coupling agents, or sizes, depending on their function and substrates. They can also be used as filler surface treatment agents. Silanes have been widely used in various industrial fields during approximately the last 40 years. Basically, organosilanes are either hydrophilic or hydrophobic; they can also be anionic or cationic.[2,4]

There exist a few silane chemistry reviews: a comparison of silicate, aluminate, borate, etc, filler surface treatments with especially different vinylsilanes[5]; a technologic review of the history and industrial-scale use of silanes[4]; a review of dental materials and related techniques[6]; and a review of the studies on molecular and microstructure of silane coupling agents and their functions in composites.[7] Tetraalkoxysilanes (eg, tetraethoxysilane) are widely applied in the so-called sol-gel technique for synthesizing SiO_2 coatings.[8] A novel application in steel manufacturing is a silane pretreatment for corrosion inhibition. The environmentally harmful and toxic traditionally used chromates could be substituted by certain silanes.[9–12]

Chemical Reactions of Silanes

To be able to act as coupling agents in the interface between organic-inorganic substances, silanes must first be hydrolyzed (activated) and condensed. In an aqueous solution, their alkoxy groups react with water to form reactive, hydrophilic, acidic silanol groups, Si–OH, and release free alcohols as side products. The acidity of the silanol groups depends upon the organofunctional group of the silane. The simplified chemical reactions are described as:

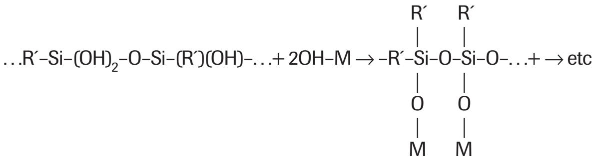
$$R'\text{–}Si(OR)_3 + 3H_2O \rightarrow R'\text{–}Si(OH)_3 + 3R\text{–}OH$$

This reaction is the oxonium ion [H_3O^+] (ie, in acidic solution) catalyzed. At about pH 4 (for organotrialkoxysilanes), the rate of condensation between silanol groups of monomeric silane molecules to larger oligomers is at the minimum, and the silane solutions have the highest stability. Acetic acid is often used for the pH adjustment. The hydrolysis time varies depending on the silane concentration, solution, and temperature, but usually 0.5 to 2.0 hours is enough. Aminosilanes in which the organofunctional group is $-NH_2$ are usually stable as such.[3–5,13]

During the condensation reaction, silane molecules react with each other, forming dimers:

$$R'\text{–}Si(OH)_3 + R'\text{–}Si(OH)_3 \rightarrow$$
$$R'\text{–}Si(OH)_2\text{–}O\text{–}Si\text{–}(R')(OH)_2 + H_2O$$

Then, dimers condense to form siloxane oligomers. Also, hydrogen bonding between the siloxane monomers and oligomers occurs in the solution. Silane oligomers react with each other, forming branched hydrophobic siloxane bonds, –Si–O–Si–, and with an inorganic matrix (eg, silica, metal oxides that contain hydroxyl –OH groups) they can form –Si–O–M– bonds (M = metal). Fresh metal surfaces have very high surface energies. In air, the surfaces are oxidized and become covered by hydroxyl groups. The acidic silanol groups then can react with the OH– groups on the metal. The basicity of the metal surfaces depends upon, eg, the metal itself and the pretreatment before the silane treatment. On the inorganic substrate (metal), thus will be formed siloxane bonds of both types, –Si–O–M–, and above and between them, –Si–O–Si–. According to the latest theories, there will be a film, a hydrophobic and branched polysiloxane layer that may also contain free hydrogen-bonded oligomers. Also, free water molecules can appear in the film. If the substrate is silica (quartz, SiO_2) or silicate, only a siloxane layer, –Si–O–Si–, will be formed. A simplified schematic equation for the reaction of silanols with the metal surface reaction can be presented as:



$$\ldots R'\text{–}Si\text{–}(OH)_2\text{–}O\text{–}Si\text{–}(R')(OH)\text{–}\ldots + 2OH\text{–}M \rightarrow \text{–}R'\text{–}\overset{\substack{R'\\|}}{\underset{\substack{|\\O\\|\\M}}{Si}}\text{–}O\text{–}\overset{\substack{R'\\|}}{\underset{\substack{|\\O\\|\\M}}{Si}}\text{–}O\text{–}\ldots + \rightarrow \text{etc}$$

The branched siloxane layer (film) thickness is dependent on the concentration of the silane solutions. Theoretically, it should be a monolayer, but in practice it is essentially thicker, eg, 50 to 100 nm, and the silane molecules are likely randomly oriented.[14] If the substrate is aluminum, –Si–O–Al– bonds seem to have poor hydrolytic stability. Numerous factors affect the adhesion of silanes to metals (eg, isoelectronic point of the metal oxide, chemical character of oxide bond, metal hydroxide solubility in water), but they are beyond the scope of the present review.[10,12,15]

In prosthetic and restorative dentistry, high bond strength between material phases is essential. The silane most commonly applied in dental laboratories and chairside is a monofunctional γ-methacryloxypropyltrimethoxysilane (or 3-trimethoxysilylpropyl methacrylate [MPS]), usually dilute, often less than 2 wt% in water-ethanol solution, with its pH of 4 to 5, adjusted with acetic acid, being prehydrolyzed. More concentrated solutions are also known and in use. MPS is used to optimize and promote the adhesion, through chemical and physical coupling, between metal-composite, ceramic-composite, and composite-composite. Any composite material that contains methacrylate groups in the molecules can be used, since the methacrylate end copolymerizes better to the composite than acrylate.[16]

Silanes are applied in polar aqueous alcohol solutions (eg, ethanol, isopropanol) and in ethyl acetate, but nonpolar solutions (eg, n-pentane, n-hexane) have also been investigated.[17] The silanes used in dentistry are usually in 90% to 95% ethanol or isopropanol solutions, but more dilute alcohol solutions, about 20% or even 40% to 50%, are also used. Acetone-ethanol mixture is also known. Numerous silane products are available for professional dental use (Table 1).

The organic functional end of the silane molecule copolymerizes with the organic matrix. A polymer-silica interface study concluded that a silane with two Si functional groups (ie, two Si atoms, each with three alkoxy groups) is more stable at the interface than silanes with mono- or trisilicon functional groups. The generation of a water-resistant, cross-linking siloxane phase that forms an interpenetrating, covalent polymer network polymerized into the matrix resin is crucial.[18] After having synthesized nine silane oligomers, with both mercapto (–SH) and alkenyl groups, the research group tested the bond strength of silanized steel substrates to resin. They concluded that the formation of a rigid siloxane film increases the bond strength. However, they proposed that a very high degree of three-dimensional siloxane structure formation could be a disadvantage to adhesive ability. Organofunctional groups should be flexible at the boundary of two phases to enhance the adhesion.[19] One suggestion was that there should be a monolayer of MPS, rather than a loosely adsorbed layer against a polymethyl methacrylate (PMMA) matrix.[20] When adhering glass plates to methacrylic resin, bond strengths and water resistance are excellent when using a mixture of bisfunctional silanes (that do not contain double bonds). A mixture of such a silane and MPS could be suggested for high durability.[21]

The latest theories discussing what could happen at the interface during silane reactions include ideas of: *(1)* ionomer bonding, interpenetration, and both soft and rigid layer theories[22]; and *(2)* the silane modifying the substrate surface oxide layer and forming a conversion

Table 1 Commercial Dental Silanes*

Trade name, manufacturer	Purpose, substrates	Effective silane	pH	Solution	Date of information
Monobond-S, Ivoclar Vivadent	Porcelain, composites	MPS 1.0%	4	Ethanol 52%, distilled water 47%	May 2001
Vectris Wetting Agent, Ivoclar Vivadent	Crowns, fixed partial dentures	MPS 1.0%	4	Ethanol 50%–52%	Jan 2001
ESPE Sil, 3M/ESPE	Metals, ceramics, composites	A silane (%NA)	NA	Ethanol > 90%	Jan 2002
RelyX Ceramic Primer, 3M/ESPE	Ceramics	A silane < 1%	NA	Ethanol 70%–80%, water 20%–30%	Dec 2001
Porcelain Repair Primer, Kerr	Porcelain	A silane 15%–20%	NA	Ethanol 80%–85%	Dec 1998
Pulpdent Silane Bond Enhancer, Pulpdent	Porcelain, composites	A silane (%NA)	NA	Ethanol 92.6%, acetone 7.4%	April 2001
Silicoup A and B (two-bottle system), Heraeus Kulzer	NA	MPS (%NA) (Silicoup B)	NA	Ethanol 25%–50%, ethylacetate 25%–50%, acetic acid 5%–10%	Nov 2001
Ultradent, Ultradent	Resin coupling agent	MPS (%NA)	NA	Isopropanol 92%	May 1998
Bisco Porcelain Primer, Bisco	Porcelain, composites	Silane with methacrylate (MPS?)	NA	Alcohol	July 1998
Clearfil Porcelain Bond Activator, Kuraray	Porcelain	MPS (%NA)	NA	Bisphenol-a-polyethoxy-dimethacrylate	Nov 1998
Quadrant Porcelain Coupling Agent (Liquid A), Cavex	Porcelain, composites	Based on 4-methacryloxy-ethyltrimellitate anhydride 10% (4-META); no silane	NA	Methyl methacrylate (MMA)	Sept 2002
Quadrant Porcelain Coupling Agent (Liquid B), Cavex	Porcelain, composites	MPS 5%	NA	Methyl methacrylate (MMA), water	Sept 2002
Bifix DC, Voco	Porcelain, composites	MPS (%NA)	NA	Alcohol, water	May 2003

*Information based on available material safety data sheets, technical data sheets, and instruction sheets issued by respective manufacturers. pH is set by acetic acid unless otherwise noted. Products are in arbitrary order; to the best of the authors' knowledge, all exist on the current market.

layer. The metallo-siloxane layer's electrochemical properties are different from those of the silanes and metal oxide.[12,14]

Silane Studies in Dentistry

The resin development of bis-GMA (bisphenol-α-glycidyl methacrylate or 2,2-bis(4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl)propane) gave rise to the use of silanes in dental materials. The earliest silane studies were performed with vinyltrimethoxysilane.[23,24] The effects of silane and their significance were also evident in reviews that will be mentioned briefly: a study about posterior resin composite restorations[25]; a study of different surface conditioning methods[26]; a material survey on dental composite and glass-ionomer[27]; silane reactions on alternative alloys (other than Ni-Cr-Be)[28]; a review of porcelain-to-composite silanization[29]; the use of silanes in porcelain veneer technology[30]; and the effects of fluorocarbon silanes on plaque formation.[31] Silane applications are not restricted to prosthetic dentistry. Numerous investigations have been made into the silanization of orthodontic brackets[32–42]; silanized ceramic root canal posts in endodontics[43]; glass fiber and silane applications, especially in periodontal cases[44]; and the effect of silanization of ceramic repairs in crowns with varied surface treatments.[45,46]

Vinylsilanes proved to be useful, but in time, MPS was synthesized and widely tested, first with glass fibers,[2,13] and its excellent copolymerization property was observed with radioactive-labeled silanes.[47] MPS became of interest for coupling porcelain teeth to acrylic denture resin.[48,49] The first results were encouraging; however, the sensitivity of silane treatment became understood.[50] Silane and fumed silica form a water-repellent matrix, and in vitro studies observed good saliva and water repellency.[51] Subsequently, vinylsilane has been of interest, especially in conjunction with PMMA.[52–54] Mercaptosilanes (–SH functional groups) were synthesized and compared with vinylsilanes.[54] Vinyltriethoxysilane treatment of fillers enhanced the hydrolytic stability of certain composites.[52]

Experience with Dental Materials and Silanes

Ceramic Restorations and Repairs

In earlier studies, the bonding between gold alloys and porcelain was based on roughening the contact surfaces and applying hot temperatures, ie, mainly micromechanical attachment techniques.[55] Later, a technique for the ceramic part, which was baked on a gold framework matrix and then resin bonded to the silane-treated ceramic, was presented.[56] The advantage of bonding resin composite to dental porcelain by MPS solution became apparent, although difficulties were caused by the instability of the silane solutions used to prepare the ceramic surface.[57] Evaluation of silanes establishing bonds to metal or ceramics showed that silanes do not bond to the metal surface as they do with the ceramic.[58] Silane coupling agents improve the bond of resin composite to ceramic by about 25%.[58] Three commercial silane-based porcelain-to-resin bonding agents were tested. The use of these porcelain repair materials was suggested mainly as a temporary clinical procedure.[59] Glazed ceramic surfaces need etching before silanization. It was indicated that the use of silane is necessary in ceramic restorations. However, various composite systems yield different bond strength values. This idea was supported with long-term water storage test results.[60]

Good results for the use of silane in porcelain-fused-to-metal restorations have been presented.[61] The findings clearly support the idea of using silanes to improve the strength and quality of the bond. It was also emphasized that the siloxane bonds are sensitive to moisture between the resin and the ceramic matrix.[62] A further development step was presented in a study where intraorally fractured porcelain facings were repaired successfully. The bonding system consisted of MPS, ferric chloride ($FeCl_3$), and an adhesive opaque resin.[63] Three of four commercially available organosilanes meant for bonding composite to porcelain showed equally acceptable flexural strengths in the tests.[64] All dry specimens showed, however, higher bond strengths than the water-treated ones, with all products. In a subsequent study, four silane products showed different bond strengths when silanized specimens were thermocycled.[65] Also, later studies confirmed that the use of silane increases the bond strength of resin composite to hydrogen fluoride (HF)–etched porcelain.[66]

A rapid increase in the amount of water absorbed by the composite material that caused hydrolysis and degradation of the silane was observed.[67] Water storage and thermocycling are described as detrimental to the silane-ceramic bond. Silanized interfaces appear to be unstable in humid conditions, and the silane bond deteriorates under atmospheric moisture. Since the resins are permeable to water, the bond between silane and resin composite was expected to deteriorate by hydrolysis over time. In humid conditions, this might lead to stress and crack growth. One other conclusion was that, although the silane coupling agents are capable of forming bonds with both inorganic and organic surfaces, silane itself does not help bonding. Therefore, its use in combination with silica coating was recommended. The bonding strength of the nonsilanized samples was decreased after water storage for 30 days. The data show that when only silane is applied on the ceramic surfaces, the bond strength does not improve because of insufficient mechanical retention.[68] Enhancement of silane solutions was undertaken by incorporating a catalyst and an initiator. The latter results speak for stronger bonding between the studied ceramics and luting agent.[69]

The effects of etching, airborne particle abrasion, and silane primer to bond dual-cured resin cement to glass ceramics were compared. Silane combined with an acidic primer increases the microshear bonds significantly. Glazed ceramic surfaces were proven to be ineffective for adhesion to resin composites with silanes.[70]

Heat treatment for silanized substrates proved to contribute to the bond strength while adhering resin composite to restorative porcelain. The experiments included three commercial silane systems and an experimental laboratory-made one.[71] Bonding inlays and the resin luting cement proved to be most effective when the inlay surface was sandblasted and silanized.[72] A method in which the surface is first silicatized (ie, airborne SiO_2 particle conditioning) and then treated with a silane solution demonstrated promising in vivo and in vitro results.[73] Other research results suggest that restorative porcelain–to–resin composite bonding with a brief HF etching + silanization gives better bonding than silane + acrylic bonding primer, or the latter alone.[74,75] A study to survey improvement to the resin-ceramic (a silica-based ceramic) bond with the aid of silane suggests no need for HF acid etching for the ceramic part when appropriate silane is used; even the siloxane bond was inert against boiling water.[76] An extensive comparison of repair options in combination with silanes has been reviewed.[45]

It should be noted that atmospheric moisture is unfavorable to prehydrolyzed commercial dental silanes. It may accelerate the condensation reactions described above and lead to polymerized siloxane that is clinically useless for adhesion promotion. An indication that this has occurred is an opaque, milky silane solution.

Silanes on Filler Materials

Vinylsilane was one of the first silanes used for silica powder in polymer, and it proved to reinforce the resin material.[24] While the silanization of the filler particle phase yields a better dispersion and wetting for filler particles, it also lowers the viscosity between a filler + liquid resin system, thereby improving the physical properties of composites.[13] The water uptake of two commercial composites, both based on methyl methacrylate (MMA), was compared. Aluminosilicate was used as filler particles in one composite, and glass beads were used in the other. Aluminosilicate filler material primed with silane yielded stronger filler-matrix bonds than nonsilanized glass filler. Also, the water intake of composite with silanized filler was remarkably lower.[77] Silane has found its place as a glass particulate filler treatment medium for restorations.[6] Of chemical and clinical interest was silanization of silica-alumina (SiO_2–Al_2O_3)–coated titania (TiO_2) used as filler in opaque resin composites. It was said to reduce the cure inhibition of the filler.[78,79]

Aging effect tests show that filler materials, either treated with silane or not, in triethylene glycol dimethacrylate (TEGDMA) matrix behave in a similar way in thermal expansion tests.[80] Curing time is needed, and one conclusion is to allow the silane to cure for about 20 minutes and avoid stresses for 24 hours after the use of silane for a reliable adhesion.[81]

Excellent filler-to-matrix adhesion is needed for minimizing wear. A survey of a UEDMA-EGDMA resin with a hybrid-type glass filler proposed that these types of fillers should be silanized to obtain significantly higher flexural strength for the composite.[82]

A comparison of MPS and 3-hydroxypropyl methacrylate treatment of glass particle filler blended with bis-GMA and TEGDMA showed the efficacy of silane-treated resin filler.[83] A wide range of tests was performed by silanizing SiO_2 and silica-zirconia (SiO_2–ZrO_2) fillers with 16 silanes to then be dispersed to a bis-GMA monomer matrix. The silanes studied were basic silanes: acrylic, amine, methacrylate, vinyl, phenyl, and aliphatic organofunctional ones. The essential conclusions for the most effective silanes for adhesion were that the silane backbone body should be rather short, the organofunctional part should preferably be methacrylic, hydrolyzable groups should be methoxy, and silane should be applied from ethanol.[84] The conclusion for the amount of alkoxy groups needed was, however, different from the accepted theory.[18] Monitoring the wear performance of restorations for a long period (3 years) showed that silane treatment and filler composition do not significantly affect wear, while urethane-based composites were similar to bis-GMA–based ones.[85] Compared with the acrylic monomer primers, silane gave lower mean bond strengths when bonding a laboratory-made microfilled composite to clinically used resin cements.[86] As far as filler silanization is considered and correlated to monomer leachability, filler composition and silane curing time are significantly affected.[87]

Nanofiller particles were evaluated in a survey. A composite with functionally silanized nanofiller particles showed a higher polymerization stress level that can lead to marginal staining, caries, and sensitivity. This occurs when the strength of the adhesive bond to the surrounding tooth cavity structure is lower than the polymerization stress value.[88] MPS is useful as a sodium fluoride (NaF) regulator from bis-GMA–TEGDMA resin. The hydrophobic siloxane layer formed on the surface of NaF powder results in slow water diffusion to NaF powder.[89] One study proposed that repairing a prosthodonthic composite material (bonding layers of composite material) is successful when combining a silane primer with an unfilled resin bonding agent.[90]

Glass Fibers

Growing interest in glass fiber technology in dentistry is demonstrated by numerous studies of silane treatment. Electrical glass (E-glass) is resistant to chemical attacks and has special electric properties. About 99% of all glass fibers are made from E-glass.[91]

Pretreatment of E-glass fibers by MPS leads to a chemical bond.[92] Scanning electron microscope (SEM) studies show that silanization of E-glass and aramid fibers enhances the adhesion between the fibers and organic acrylic resin in a denture material[93,94] by measuring the effect of curing a silane coupling agent in a PMMA–glass-fiber composite.[95] In vitro cytotoxicity of fiber-PMMA composite when the fibers were sized with a silane and a silane-epoxy solution was studied.[96] Clinical cases using silanized glass fibers with multiphase acrylic resin systems are promising.[97] A contribution to the field of silane glass-fiber technology was made when the interfacial shear strength, with adhesive help of two silanes between dental resin and glass fibers, was tested and good results were obtained.[98] One of the first tests concerning bis-GMA resin–modified composite with silanized short glass fibers as fillers showed better performance than the nonsilanized ones.[99] An oxidative sodium peroxodisulfate ($Na_2S_2O_8$) pretreatment was proposed for E-glass fiber filler material as a step before silanization.[100,101]

A clinically very promising repair quality was observed when a silicate-silane–treated fiber-reinforced composite framework structure and etching the ceramic with HF were combined.[102] Thus, silane coupling agents have been steadily improved, demonstrating higher bond strengths. The main contribution to the values obtained was made not by the solely mechanical interlocking of the resin composite, but also by the formation of covalent siloxane bonds via silane treatment.[103] In a different silane application field, it was also emphasized that silane mixtures must be fresh to be able to produce strong bonding between PMMA and a silicone soft liner.[104] Three bonding agents were used to adhere silicone elastomer to a visible light–activated resin, and one silane proved to be superior despite intensive heat aging.[105] A recent study of cementing computer-aided design/manufacturing (CAD/CAM)–generated composite materials to each other compared silanized and nonsilanized specimens that were attached to each other with dual-cured resin luting agents. All samples had the same failures in adhesion at the bonding interface. Nevertheless, surface-silanized composite materials showed improved shear bond strength in comparison with nonsilanized ones.[105,106]

Base and Noble Alloys, Titanium, and Steel

Studies indicate that silane coupling agents are of importance for the adhesion of resin composite to ceramic/metal. The surface interactions, reactivity, and composition of three MPS-type dental silanes available in the dental market were determined. The hydrolyzed silanol groups of the silane with better orientation toward nickel-chromium (Ni-Cr) alloy sample surfaces were most advanced (compared with the other silanes), since there were thus more bonding sites for silanol groups on the alloy surface, compared with high-palladium (Pd) and gold-palladium (Au-Pd) alloys.[105] However, the silane application reduced the bond strengths of the two chemically adhering resins but increased the bond strength of one mechanically retained resin to Ni-Cr alloy.[107]

Adhesion of methacrylate-based polymers to titanium with the support of MPS was studied. Long-term water storage at 37°C reduced the bond strengths. Also, the adhesion between the polymer and titanium was found by infrared spectroscopic measurements to be of a chemical nature.[108]

For an effective bond of resin to feldspathic porcelain and metal, the use of silane in combination with surface conditioning is required. The use of the Rocatec system (3M/ESPE), based on SiO_2 abrasive particles (eg, with 50-μm diameter), is meant for roughening the substrate surface. It increases the bond strength effectively because of the increase in silica content on the substrate surface that provides a basis for silanes to enhance resin bonding. This is called the tribochemical method. The temperature at the surface while the particles are hitting it may momentarily rise up to 1,200°C, and the particles thus will be embedded in the surface. For better clinical success, the use of silane coupling agents is crucial in creating long-term bonds of resin to ceramic or resin to metal. Also, the shear bond between PMMA and the cast alloy was increased.[109]

The use of silanes in combination with different techniques has been reviewed extensively.[45] One such method is Silicoater MD (Heraeus Kulzer), which can be used in an extraoral process to attach resin composite onto metal surfaces. It is based on immediate pyrochemical silica layer formation onto the substrate surface. It was used also for cobalt-chromium (Co-Cr) alloy cast clasps coated with resin. This method did not weaken the clasps after bending tests.[110] Noble alloys roughened by CoJet Sand (3M/ESPE; silica coating) followed by silanization had significantly higher adhesion results to resin composite.[111] The similar tendency for a combination of PMMA and titanium was confirmed.[112] For both a gold-palladium-platinum alloy and feldspathic porcelain, a treatment of Rocatec-Pre abrasion (with alumina particles), followed by an impact alumina-silica coating (Rocatec-Plus), and finally silanization by a commercial MPS silane is effective when bonding a composite to alloys. However, the Weibull moduli were low.[113] Also, steel treated with silane was investigated as a dental material with PMMA matrix; immersion in water reduced the strength of the system.[114]

Some Other Silanes

While amalgam has a shrinkage of around 0.2%, the situation for composites is worse.[115] Comparing nonpolymerized and polymerized composites, a 2% to 3% shrinkage by volume could be detected after curing.[115] Some less-common silanes have also been monitored. Long-range intraoral stain protection was accomplished in a denture when its surface was modified with a fluorocarbon chain containing silane, (1H,1H,2H,2H-henicosafluorododecyl)trimethoxysilane.[116] The same research group found similar effects with another fluoroalkylsilane that was applied onto the denture with a brush and then briefly dried with a hairdryer. The denture also became oil and water repellent.[31] Fluoroalkylethyl silane in dental ceramics reduces stress corrosion.[117] Kappa-methacryloxydecyl triethoxysilane (κ-MDS), which is proposed to adsorb in an ordered fashion on the SiO_2 surface compared with MPS,[18] and 10-methacryloxydecyltrimethoxysilane (ie, a silane with a long carbon chain) show fairly good resistance against degradation by water.[98] MPS was compared with a nonfunctional silane, (3,3,3-trifluoropropyl) trimethoxysilane, in filler surface treatment.[118]

Conclusion

Most clinical results seem to favor the use of silanes. On the other hand, some results exclude the importance of their use. Overall conclusions might be difficult to make. There is continuous discussion as to whether silanization is needed, or, eg, whether acid etching by HF acid is adequate for obtaining clinically relevant attachment of composite to glass ceramics. With ceramics that are not etchable to form a microretentive surface (eg, alumina, zirconia), optimization of silane-promoted adhesion may play a great role in the future. In the authors' opinion, therefore, future research should be concentrated on the interaction of silanes and various nonetchable dental materials.

Also, new dental composite development (eg, ormocers, organically modified ceramics, and certain nanoscale hybrid composites) applies sol-gel technology, and silanes then have a key role.

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