



## Review Article

# Silane Coupling Agents and Their Clinical Application in Oral Health Care

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Received: 27 October 2025

Accepted: 19 June 2026

Published online: 30 June 2026

**Keywords:** adhesion, bonding, coupling agent, oral health science, silane, surface adhesion

Silane coupling agents play a pivotal role in modern dental biomaterials due to their ability to modify and enhance the surface properties of a wide range of substrates. Functioning as molecular bridges, silanes facilitate adhesion between inorganic surfaces and organic resin matrices, thereby improving the performance and longevity of restorative systems. Traditionally, their application has focused on silica-based ceramics and fillers; however, growing interest has shifted toward their use to modify non-silica substrates, including metals such as titanium and its alloys. This expansion reflects the increasing demand for durable and reliable bonding across diverse dental materials. The incorporation of silane coupling agents into adhesives, composites, and surface treatments has been shown to improve critical properties such as bond strength, resistance to hydrolytic degradation, biocompatibility, and aesthetic outcomes. Collectively, these enhancements contribute to the functional stability of the stomatognathic system and positively influence patient-centered outcomes, including quality of life (QoL). In this context, the present review aims to provide a comprehensive overview of silane coupling agents, with emphasis on their chemistry, mechanisms of action, and evolving applications in contemporary dental biomaterials.

## Introduction

Over the past few decades, oral health care has undergone a significant transformation, with an increasing emphasis on patient-centered approaches and the use of biomaterials that closely mimic the properties of natural dental tissues. Contemporary dental materials are expected to exhibit a combination of mechanical, physical, rheological, chemical, and biological characteristics that align with those of hard and soft oral tissues [1]. Although numerous materials have been developed to enhance clinical outcomes, many have failed under clinical conditions, while others have required substantial modifications to improve their compatibility and performance; only a limited number have remained in use without major alterations.

The oral cavity presents a particularly challenging environment for restorative materials. It is characterized by constant moisture from saliva and dietary intake, frequent temperature fluctuations, variable pH

levels, and a complex and dynamic microbial ecosystem [2-4]. These factors collectively contribute to the degradation of dental materials over time. Consequently, many conventional materials are unable to withstand these hostile conditions, leading to compromised performance and eventual failure. Such failures can adversely affect treatment outcomes and diminish the patient's quality of life. One effective approach to enhance the performance of dental materials is the incorporation of organic and inorganic components, which are integrated using coupling agents [5]. Coupling agents are chemical intermediaries designed to improve adhesion between dissimilar materials by promoting interfacial bonding [6]. They function as molecular bridges, facilitating chemical interaction between the inorganic filler particles and the organic resin matrix.

The use of coupling agents for surface modification of filler materials dates back to the early 1950s, marking a significant advancement in material science. These agents are inherently bifunctional, possessing

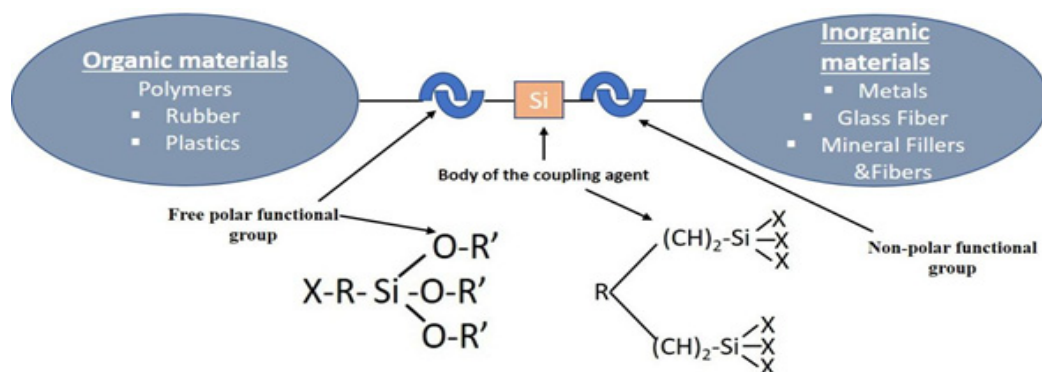
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<https://doi.org/10.65795/a2w4w044>

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**Figure 1: Schematic of a silane coupling agent showing three components: (a) a polar hydrolyzable group ( $-OR$ ) for bonding to inorganic substrates; (b) the silane backbone acting as a molecular bridge; and (c) a non-polar organofunctional group (e.g., methacrylate/vinyl) that bonds with the resin matrix, enabling adhesion between dissimilar materials**

two distinct reactive groups: one with affinity for the organic phase and the other for the inorganic substrate (Figure 1). This dual reactivity enables effective stress transfer across the interface and enhances the overall mechanical integrity of composite systems. Historically, coupling agents were developed by the United Carbide Corporation in the context of glass-reinforced plastics [7]. The concept originated even earlier, in the 1940s, with the introduction of glass fibers as reinforcement for polymeric resins in industrial applications [7]. Among various coupling systems, organosilanes have gained particular importance. These compounds, often regarded as hybrid materials, exhibit both organic and inorganic characteristics, allowing them to interact with resin matrices and silica-based surfaces. Their amphiphilic nature underpins their effectiveness in improving adhesion and durability in composite materials used in dentistry [7,8].

Silane coupling agents exhibit a broad spectrum of applications owing to their ability to chemically link polymers with dissimilar substrates, particularly inorganic oxides such as silica and alumina [9-11]. The covalent bonds formed at the interface provide strong and durable adhesion, even under challenging environmental conditions. A wide range of organic polymers, including both thermoplastic and thermosetting resins, have been shown to be compatible with silane-based systems [10,12]. In clinical and material applications, silanes may be applied as a surface pre-treatment or incorporated directly into resin formulations. In the latter approach, they can migrate toward the substrate during mixing and placement, facilitating interfacial bonding. This versatility has expanded their use across multiple dental materials and techniques. The presence of silane coupling agents enhances adhesion and contributes to improvements in mechanical strength, thermal stability, physical integrity, and biological performance [10,11]. Among available coupling systems, organosilanes are the most extensively utilized in oral health sciences due to their effectiveness and compatibility with commonly used dental substrates. In contrast, alternative agents such as titanates and zirconates have seen relatively limited application [13,14]. This review aims to provide a comprehensive overview of the chemistry, mechanisms, and clinical applications of silane coupling agents in dentistry.

## Chemistry of Silane

Organo-functional coupling agents, particularly organo-silanes and organo-titanates, are widely employed across multiple fields, including rubber technology, pharmaceutical sciences, dental composites, agriculture, and polymer engineering [13,15-17]. Another class, organo-zirconates, is also available; however, their use remains limited, largely due to higher cost (table S1) [18].

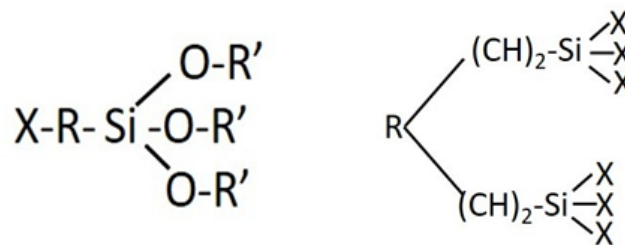
Among these, silane coupling agents are especially valued for their ability to establish strong bonds between inorganic dental substrates, such as glass, filler particles, metals, and metal oxides-organic resin systems [19,20]. This effectiveness arises from their bifunctional structure:

one end of the molecule interacts with inorganic surfaces, while the other can be chemically tailored to bond with organic components, including polymeric resins and functional groups such as vinyl, amino, or epoxy moieties [6,20].

Owing to this dual reactivity, silanes are often regarded as hybrid compounds that serve as molecular intermediaries, promoting adhesion between chemically dissimilar phases (figure 1). Their capacity to bridge organic and inorganic materials underpins their widespread application in enhancing the performance and durability of dental biomaterials [5,6].

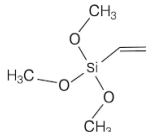
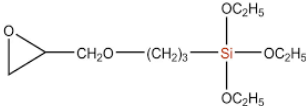
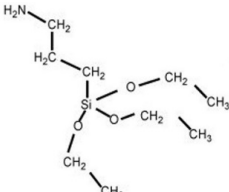
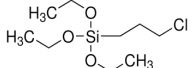
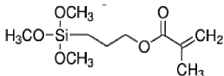
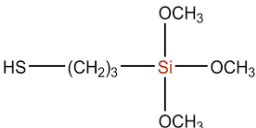
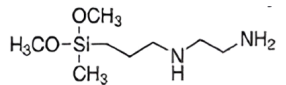
Silanes constitute a class of organosilicon compounds characterized by the presence of one or more silicon (Si) atoms within their structure (table 1). Chemically, they are analogous to orthoesters and are typically monomeric species with a general formula of  $R_nSi(OR')_{4-n}$  where the substituent groups may be non-reactive, organofunctional, or inorganically reactive (figure 2) [21,22]. The organofunctional component is capable of polymerizing with the organic resin matrix, thereby contributing to interfacial bonding. The reactivity of silanes is defined by their bifunctional nature. The alkoxy groups ( $-OR'$ ) undergo hydrolysis and subsequently react with inorganic substrates, forming stable covalent siloxane ( $Si-O-Si$ ) linkages. This inorganic reactivity enables strong bonding with surfaces such as glass, silica-based fillers, and metal oxides [20,23]. In contrast, the organic functionality of the molecule interacts with the resin phase without direct involvement of the silicon atom, facilitating integration with polymeric systems [22].

As a result, silanes are capable of forming durable covalent bonds between inorganic materials and organic matrices. Silicon exhibits strong affinity for inorganic substrates such as glass and metals (e.g., titanium and steel), ensuring robust interfacial adhesion [23]. For metal surface modification, silane molecules can be structurally tailored—for example,



**Figure 2: Chemical structure of silane. a) Schematic sketch of an organosilane compound. (X: Organic moiety, such as amino, alkyl, vinyl; R': methyl, ethyl, isopropyl; R: aryl or alkyl  $(CH_2)_n$  with  $n=0,1$  or  $3$ ), b) Dipodal structure of silane.**

**Table 1: Representative commercially available silane coupling agents and their key chemical characteristics**

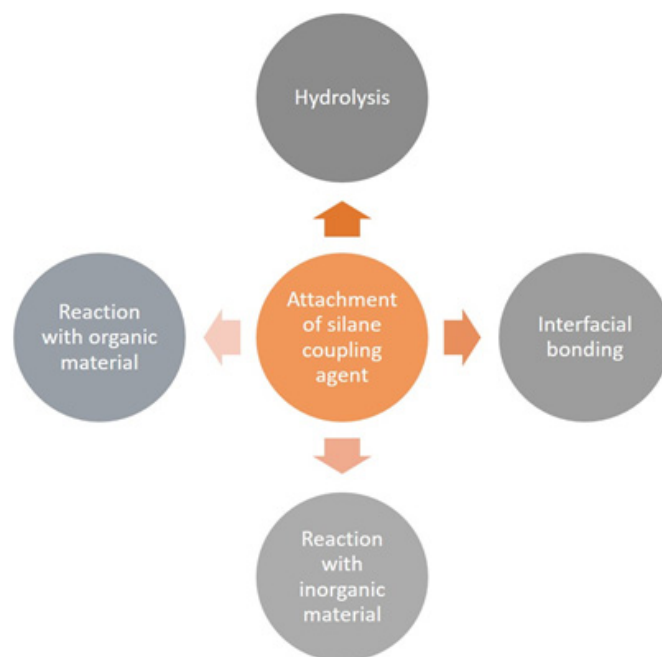
| Organofunctional group | Structural formula, and/ or Chemical structure                                                                                                                                                                   |
|------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Vinyl                  | $\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$<br>                                                                                   |
| Epoxy                  | $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{OCH}_2\text{CHOCH}_2$<br>                                          |
| Primary amine          | $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$<br>                                                     |
| Chloropropyl           | $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$<br>                                                   |
| Methylacrylate         | $\text{H}_3\text{CO}-\text{Si}(\text{OCH}_3)_2-\text{CH}_2\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2$<br> |
| Mercapto               | $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$<br>                                                            |
| Diamine                | $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$<br>                           |
| Cationic styryl        | $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3=\text{HCl}$                                                                              |

by incorporating a propylene spacer ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ) between the silicon atom and the organic functional group to optimize bonding performance. Furthermore, the introduction of functional groups such as aminopropyl enhances interaction with organic polymers, reinforcing the coupling between the two phases [24,25].

Silane coupling agents demonstrate significant structural versatility, as they may lack inherent reactive groups but can be functionalized to impart specific chemical properties. This adaptability enables the development of diverse silane variants with tailored characteristics, facilitating their interaction with a wide range of carbon-based systems. Moreover, silanes are typically low-molecular-weight compounds with relatively high volatility, factors that influence their handling and application in material systems.

### Adhesion with Silane Coupling Agents

Adhesion is a process of bonding between two distinct atoms/mol-

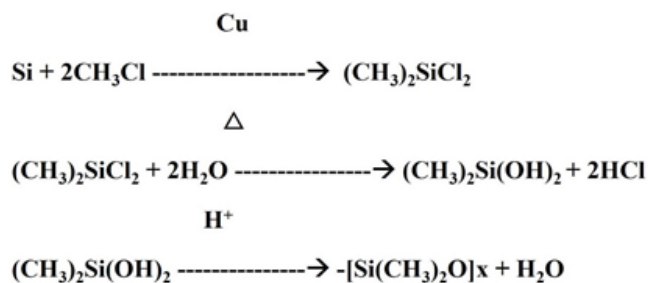


**Figure 3: Schematic illustration of the sequential stages of silane coupling agent interaction with a substrate, including hydrolysis, condensation, and formation of a stable interfacial bond**

ecules/substances. Adhesion with silane coupling agents takes place through hydrolysis, interfacial bonding, reaction with inorganic material, and reaction with organic material (figure 3).

Hydrolysis is the initial step in silane activation and is generally rapid and reversible, occurring preferentially under mildly acidic conditions. It proceeds via a bimolecular nucleophilic substitution at the silicon atom, wherein water attacks the alkoxy groups, forming a transient pentacoordinate trigonal bipyramidal intermediate [19]. This intermediate subsequently decomposes, leading to the formation of silanol ( $-\text{Si}-\text{OH}$ ) groups. The reaction continues until most or all alkoxy substituents are hydrolysed (figure 4).

The rate of silane hydrolysis is influenced by several factors, including the molecular structure of the silane, its concentration, temperature, pH, and the nature of the solvent system [25]. The type of alkoxy substituents present on the silane significantly affects its reactivity; hydrolysis rate decreases with increasing alkoxy group size, following the order: methoxy > ethoxy > propoxy > butoxy. The pH of the medium is a



**Figure 4: Schematic representation of hydrolysis and activation reactions of silane coupling agents, leading to formation of reactive silanol groups for subsequent bonding**

critical determinant, with hydrolysis proceeding more rapidly under acidic conditions compared to alkaline environments. Temperature also plays a direct role, as an increase in temperature accelerates the reaction rate. In addition, the solvent system influences hydrolysis kinetics; greater hydrophilicity of the medium enhances the reaction. Ethanol-based aqueous mixtures are among the most commonly employed solvent systems for silane coupling agents due to their effectiveness in facilitating controlled hydrolysis.

At a fundamental level, adhesion arises from intermolecular interactions, primarily van der Waals forces, between the adhesive and the substrate. In addition to these forces, adhesion may be influenced by a combination of physical, chemical, and biological interactions. Several mechanisms have been proposed to explain adhesion, including mechanical interlocking, diffusion, adsorption, and chemical bonding. Coupling agents, owing to their bifunctional nature, play a crucial role in enhancing interfacial adhesion. They facilitate the formation of chemical bonds across the filler–resin interface, thereby strengthening the interaction between inorganic and organic phases. This improved interfacial coupling contributes to enhanced mechanical properties, stability, and overall performance of the composite material.

Silane adhesion strength with different substrates shows a wide variation. It shows strong adhesion with silica, glass, quarts through siloxane bond, and condensation with surface hydroxyl groups [19]. On the other hand, it shows mild adhesion with pure metal and/ or alloy surfaces [19].

## Glass-fiber Adhesion with Silane Coupling Agents

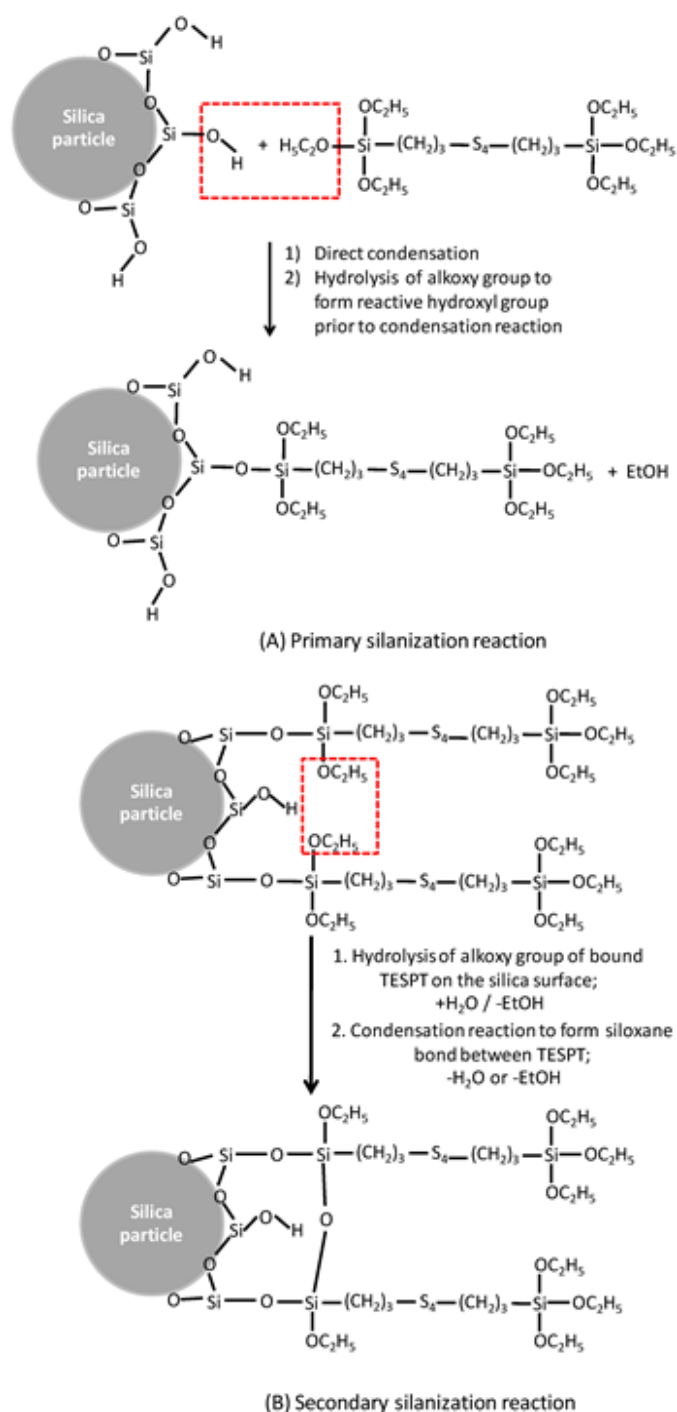
Silanes, by virtue of their chemical structure, are capable of forming covalent bonds with silanol groups present on glass and silica-based substrates through condensation reactions involving reactive groups such as  $-Cl$ ,  $-OH$ , or  $-OR$ . In the presence of moisture, the alkoxy groups of silanes undergo hydrolysis to generate silanol ( $-Si-OH$ ) groups, which subsequently condense with hydroxyl groups on the filler or fiber surface. However, it has been observed that silanol groups of adjacent silane molecules may preferentially react with each other rather than with surface silanol groups, leading to self-condensation. To minimize this effect, silanes with a limited number of hydrolysable groups per silicon atom have been suggested, as excessive self-condensation can result in the formation of di- or polysiloxane structures with reduced bonding efficiency to the substrate under normal conditions.

Experimental studies have provided insight into the nature of silane–substrate interactions. Vapor-phase chemisorption studies have confirmed the formation of siloxane bonds between chlorosilanes and E-glass fibers [27]. Infrared spectroscopic analyses have further indicated that silane adsorption may initially involve reversible physical interactions at ambient temperatures, which can transition to irreversible chemisorption at elevated temperatures [28,29]. Additionally, investigations on silane-treated glass fibers have demonstrated that, despite partial removal of surface treatments during extraction processes, the integrity of the silane–glass bond remains largely preserved, indicating strong and stable interfacial bonding.

A well-known example is bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT), widely used in silica-based systems (figure 5). Its effectiveness arises from dual reactions involving silanization of the silica surface and subsequent coupling interactions that establish chemical bridges between the filler and the matrix. The silanization process includes primary reactions, either direct condensation with surface silanol groups or prior hydrolysis followed by condensation—both releasing ethanol as a byproduct. Secondary reactions may occur between adjacent silane molecules, further contributing to the formation of a stable, cross-linked siloxane network [30,31].

## Resin-matrix adhesion with silane coupling agents

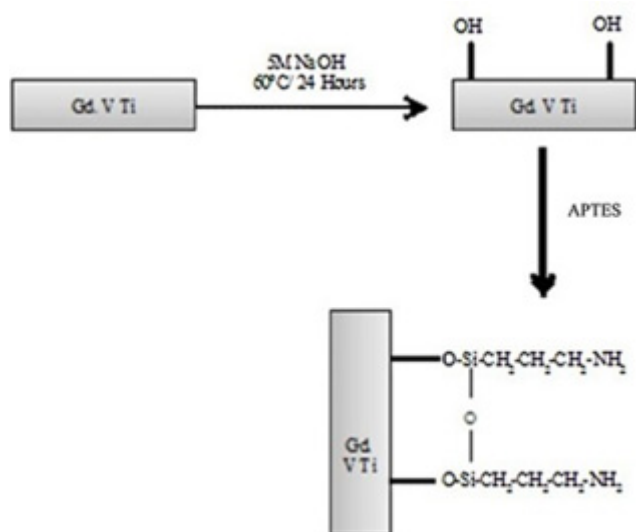
Silane coupling agents enhance adhesion within resin-based systems by acting as molecular bridges between inorganic fillers and the organic resin matrix. Initially, the hydrolysed silane forms silanol ( $-Si-OH$ ) groups that react with hydroxyl groups on the inorganic surface, establishing



**Figure 5. Schematic representation of primary and secondary silanization reactions on a silica surface using bis(3-triethoxysilylpropyl) tetrasulfide (TESPT).** Reprinted with permission from [30], Hayichelaeh C, et al. Polymer.10, (2018). ©2018, MDPI

stable siloxane linkages. Subsequently, the organofunctional group of the silane interacts with the resin matrix, typically through covalent or, in some cases, ionic bonding, resulting in a durable and integrated interface.

The effectiveness of this coupling mechanism is highly dependent on the compatibility between the organofunctional group of the silane and the chemistry of the resin system. Therefore, the selection of an



**Figure 6: Schematic illustration of covalent attachment of 3-aminopropyltriethoxysilane (APTES) to an alkali-treated Grade V titanium alloy surface. Reprinted with permission from [6], Sharan J, et al. *Appl Surf Sci* 412, (2017). ©2017, Elsevier**

appropriate silane is critical to achieving optimal bonding performance. A wide range of organofunctional silanes is currently available, offering reactivity with various thermosetting resin systems. Consequently, the chemistry and performance of silane coupling agents are best understood when considered in relation to specific resin matrices and their corresponding interaction mechanisms.

Resin matrix bond formation with silane coupling agent involves two stages: silane and substrate bond formation (figure 6), and resin and silane bond formation (figure 7).

Upon acid activation, silane undergoes hydrolysis to form silanol ( $\text{Si-OH}$ ) groups, which subsequently react with hydroxyl groups on the treated substrate via condensation reactions, establishing siloxane linkages. During polymerization, photoactivation of the resin matrix generates reactive free radicals that initiate bonding between the organofunctional groups of the silane and the functional groups of the resin monomers (figure 7). This sequence of reactions results in the formation of stable covalent bonds, effectively linking the resin composite to the substrate surface through the silane coupling agent.

### Applications of Silane Coupling Agent

An appropriate and suitable method for application of the silane coupling agent [32-38] is very crucial as it determines the covalent attachment of two different molecules. This is mainly decided by type of resin,

its filler content, and the substrate to which it is attached. The use of silane coupling agent mainly includes, surface pre-treatment method and direct addition method.

The surface pre-treatment method is used to treat the surface of the filler with diluted coupling agent, on the other hand in the direct addition method solution of coupling agent is directly added into the resin and filler matrix. Two more methods are also used for silane application: water-soluble silane coupling agent (fiberglass surface treatment agent) and bottom method of silane coupling agent.

Dispersion of the silane coupling agent on the material surface is enhanced by preparing its solution. Most commonly used media/solvent for making up the solution of the silane coupling agent is water and/or alcohol (most commonly ethanol, isopropanol). As discussed earlier, the hydrolysis of the silane is related to the pH value, temperature of the solution/media. Higher temperature and low pH generally enhance the silanization reaction. Silane usually hydrolyses quickly, and cannot be stored for a longer duration. Due to this reason the silane solution is always prepared fresh and used within an hour.

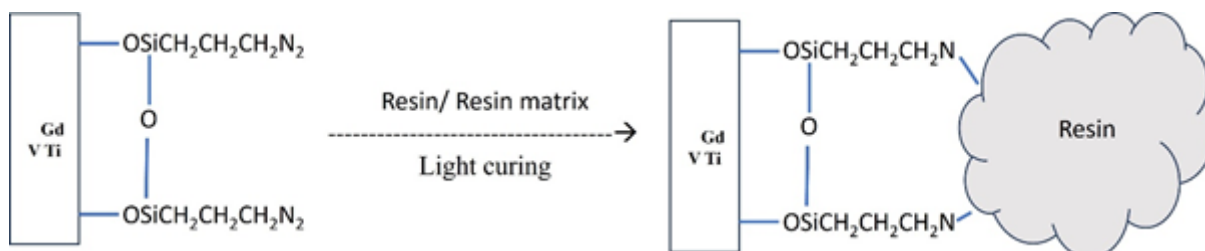
Pre-mixing silane with resin, as seen in one-bottle adhesive systems, compromises the stability and functional efficacy of the silane component [39,40]. Once activated in the presence of water and acid, silane undergoes hydrolysis followed by self-condensation, forming siloxane oligomers that are ineffective in establishing durable chemical bonds with substrates. Although the resin phase may remain relatively stable, the reactive capacity of silane declines over time [39].

The acidic environment of many universal adhesives further accelerates silane degradation, leading to a time-dependent reduction in bonding performance [30-41]. Evidence suggests that while some pre-activated formulations may retain partial activity for several months, significant deterioration can occur as early as days to weeks [41,42].

In contrast, two-bottle systems that separate silane from its activator demonstrate superior shelf life and maintain higher reactivity at the time of application [39,43]. To preserve stability, silane-containing materials should be stored under controlled conditions, ideally in cool, dry, and light-protected environments [43]. For optimal clinical outcomes, the use of freshly mixed silane or dedicated silane primers immediately prior to application is recommended, particularly in ceramic bonding procedures [43].

### Application of Silane Coupling Agents in Oral Health Sciences

Commercially available dental silanes are primarily employed to improve the adhesion between resin-based materials and inorganic substrates, particularly silica-containing surfaces such as porcelain and lithium disilicate ceramics, as well as silica-coated metals and resin composites (table 2). Their effectiveness is largely attributed to their bifunctional structure, which enables simultaneous interaction with both inorganic and organic phases, thereby promoting durable interfacial bonding. In clinical practice, silanes are most commonly applied as a surface pre-treatment following procedures such as acid etching or airborne-particle abrasion. These surface treatments increase surface roughness and expose reactive hydroxyl groups, facilitating the formation of siloxane bonds between the silane and the substrate. This chemical coupling enhances



**Figure 7: Schematic representation of covalent bonding between the resin matrix and a silanized titanium surface following light curing**

Table 2: Commercially available silane coupling agents used in dental applications with their key composition and clinical indications

| Commercial Name                    | Manufacturer                    | Key Active Silane (%)                                    | pH         | Solution                                 | Application/ Indication             |
|------------------------------------|---------------------------------|----------------------------------------------------------|------------|------------------------------------------|-------------------------------------|
| Bisco porcelain primer             | Bisco, USA                      | Unspecified silane/ 1-5%                                 | 5.9        | Ethanol and acetone                      | Porcelain, composite bonding        |
| Bisco bis silane                   | Bisco, USA                      | 3-trimethoxysilylpropyl-2-methyl-2-propenoic acid/ 5-10% | 4          | Ethanol based                            | Porcelain, composite repair         |
| Bifix DC                           | VOCO, Germany                   | 3-trimethoxysilylpropyl-2-methyl-2-propenoic acid/ NA    | close to 7 | Alcohol based                            | Porcelain, composite                |
| Cimara                             | VOCO, Germany                   | 3-methacryloxypropyltrimethoxysilane/ 3%                 | 5.5        | Propan-2-ol                              | Repair of ceramic and metals        |
| Clearfil ceramic primer            | Kuraray, Japan                  | 3-methacryloxypropyltrimethoxysilane / < 5% + MDP        | 3          | Ethanol based solution                   | Porcelain, ceramic, resin materials |
| Calibra silane coupling agent      | Dentsply                        | Silane/ NA                                               | 5.5        | Acetone                                  | Repair of ceramic and metals        |
| Ceramic bond                       | VOCO, Germany                   | Silane/ NA                                               | 5.5        | Acetone                                  | Repair of ceramic and metals        |
| Clearfil porcelain bond activator  | Kuraray, Japan                  | 3-methacryloxypropyltrimethoxysilane/ 40-60              | 2.3        | Hydrophobic dimethylacrylate formulation | Porcelain repair                    |
| ESPE Sil                           | 3M/ ESPE                        | 3-methacryloxypropyltrimethoxysilane/ <3%                | 4.5        | Ethanol, Methyl ethyl ketone             | Metals, ceramics, composites        |
| ESPE RelyX ceramic primer          | 3M/ ESPE, USA                   | 3-methacryloxypropyltrimethoxysilane/ <2%                | 4.6        | Ethanol and water-based                  | Ceramic primers, laminates          |
| Fusion liquid surface primer       | George Taub Products, USA       | 3-methacryloxypropyltrimethoxysilane/ 12-15%             | 4.7        | Two-part silanol system                  | Porcelain, alloy priming            |
| Monobond-S                         | Ivoclar Vivadent, Liechtenstein | $\gamma$ -methacryloxypropyltrimethoxysilane/ 1%         | 4          | Ethanol solution                         | Porcelain, composite                |
| Porcelain repair primer            | Kerr                            | A silane/ % NA                                           | NA         | Ethanol                                  | Porcelain                           |
| Pulpdent silane bond enhancer      | Pulpdent, USA                   | A silane/ % NA                                           | 6.3        | Ethanol + Acetone                        | Porcelain, composite                |
| Quadrant porcelain coupling agent  | Cavex, The Netherlands          | 3-methacryloxypropyltrimethoxysilane/ 5%                 | NA         | Alcohol + water                          | Porcelain, composite                |
| Silicoup A & B (Two bottle system) | Heraeus Kulzer, Germany         | 3-methacryloxypropyltrimethoxysilane/ % NA               | NA         | Ethanol+Ethylacetate+Acetic acid         | Porcelain, metal alloy bonding      |
| Silanit                            | Ivoclar Vivadent, Liechtenstein | $\gamma$ -methacryloxypropyltrimethoxysilane/ % NA       | 4.6        | Two component silane formulation         | Porcelain repair                    |
| Ultradent silane                   | Ultradent, USA                  | 3- methacryloxypropyltrimethoxysilane/ <10%              | 5.3        | Isopropanol based                        | Resin, porcelain bonding            |
| Vectris wetting agent              | Ivoclar Vivadent, Liechtenstein | 3- methacryloxypropyltrimethoxysilane/ <1%               | 4          | Ethanol based                            | Crown, fixed partial denture        |
| Vitasil                            | VITA Zahnfabrik, Germany        | 3- methacryloxypropyltrimethoxysilane/ <2.5%             | NA         | Ethanol based                            | Ceramic and resin composite         |

the wettability of the surface and promotes more intimate contact with the resin matrix, resulting in improved bond strength and reduced interfacial defects. The use of dental silanes contributes to enhanced mechanical performance, improved resistance to hydrolytic degradation, and increased longevity of restorative materials, making them indispensable in contemporary adhesive dentistry.

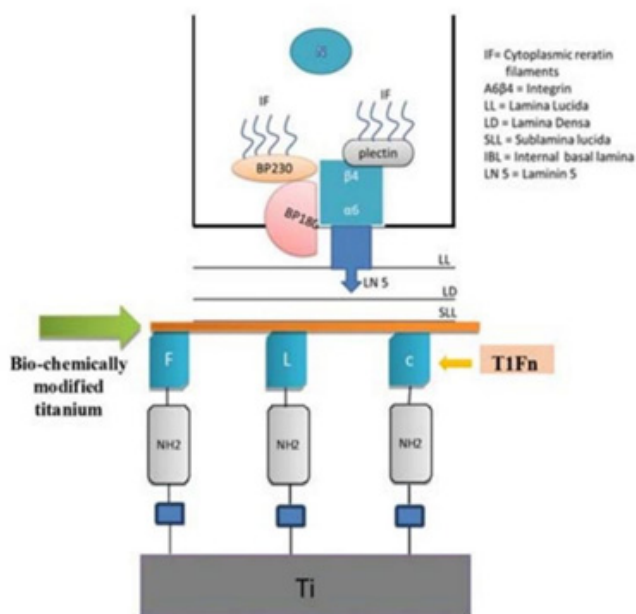
### Dental ceramics

In oral health sciences, a wide range of ceramic materials has been employed as indirect restorative options due to their excellent biocompatibility, favorable esthetics resembling natural dentition, and precise marginal adaptation. Commonly used ceramics include glass-infiltrated alumina, leucite-reinforced ceramics, tetragonal zirconia polycrystals (TZP), and feldspathic porcelain. To enhance the durability of resin-ceramic bonding, these materials typically undergo surface pretreatment procedures such as airborne-particle abrasion (grit blasting),

followed by the application of a silane coupling agent [44,45].

Despite their high compressive strength, ceramics are inherently brittle due to their relatively low tensile strength. This characteristic makes them susceptible to the initiation and propagation of microcracks when subjected to repetitive functional stresses, including masticatory forces, parafunctional habits, and occlusal loading. Additional factors such as internal structural defects, impact forces, fatigue loading, and suboptimal restoration design may further contribute to crack formation. Over time, these microcracks can propagate, ultimately leading to fracture of the restoration [46].

Although replacement of the restoration is often the preferred treatment, intraoral repair may be considered in certain situations where economic or time constraints limit full replacement. Repair protocols generally involve surface preparation through polishing and roughening, followed by grit blasting and hydrofluoric acid etching. Subsequent application of a silane coupling agent enhances chemical bonding, after



**Figure 8:** Schematic illustration of biomolecule attachment to a silanized Grade V titanium alloy surface, facilitating soft tissue integration and formation of a gingival seal.. Reprinted with permission from [77], Sharan J, et al. *Trends Biomater. Artif. Organs*, 34, (2020).

which the restoration is re-cemented. This approach can improve the longevity and functional performance of the repaired ceramic restoration [47].

### Resin Composite

Commercial dental resin composites typically consist of a resin matrix, an initiator-inhibitor system, inorganic filler particles, silane coupling agents, and pigments. To improve mechanical properties and reduce polymerization shrinkage, fillers of varying sizes, morphologies, and load-bearing capacities are incorporated into the resin matrix [48]. However, the enhancement in mechanical performance is critically dependent on effective interfacial adhesion between the filler particles and the resin matrix [49,50].

Inorganic fillers are inherently incapable of chemically interacting with the organic resin without prior surface modification. This is achieved through the application of silane coupling agents, most commonly  $\alpha$ -methacryloyloxypropyl trimethoxysilane (3-MPS). During this process, the methoxy groups of the silane undergo hydrolysis and subsequently react with hydroxyl groups on the filler surface, forming siloxane (Si-O-Si) bonds with the release of methanol. Simultaneously, the methacrylate functional group participates in free-radical polymerization with the resin matrix, thereby establishing a covalent linkage between the inorganic filler and the organic phase. This interfacial coupling significantly enhances the mechanical strength and integrity of the composite material [51].

Under clinical conditions, however, the formation of a uniform and stable siloxane layer is challenging and depends on multiple factors, including filler composition, surface characteristics, and processing conditions. 3-MPS, being relatively hydrophilic and exhibiting limited hydrolytic stability, may not achieve complete reaction of all alkoxy groups, resulting in heterogeneous surface coverage.

The hydrolytic stability of silane-treated interfaces remains a subject of debate. While some studies suggest that silanization limits water ingress and enhances durability [43], others report that water can penetrate the interface, leading to hydrolysis of siloxane bonds. This degra-

dation facilitates water diffusion into the interfacial region, ultimately compromising bond strength, water resistance, and long-term durability [52-55].

Additionally, mismatches in the coefficients of thermal expansion between the resin matrix and filler particles can generate internal stresses during thermal cycling, further weakening the composite structure [56,57]. To address these limitations, the incorporation of pre-silanized filler particles has been explored, demonstrating improvements in both mechanical properties and resistance to hydrolytic degradation [58-61].

### Glass fibre-reinforced composite

The incorporation of E-glass fibers into resin composite matrices has been shown to significantly enhance mechanical properties and reduce dimensional changes associated with polymerization shrinkage [62-64]. These reinforcing fibers improve strength, stiffness, and fracture resistance of the composite material. However, effective stress transfer between the fibers and the resin matrix is dependent on strong interfacial adhesion, which necessitates surface treatment of the glass fibers with silane coupling agents [65,66]. Silanization promotes chemical bonding between the inorganic fiber surface and the organic resin matrix, thereby improving the overall structural integrity of the composite.

In addition to enhancing interfacial bonding, the hydrolytic stability of fiber-reinforced composites can be further improved by modifying the silane structure, particularly through increasing the chain length of the linker group, which reduces susceptibility to moisture-induced degradation [67]. Fiber-reinforced composites (FRCs) have found wide-ranging applications in dentistry, including their use as endodontic fiber posts, fixed partial dentures, removable prostheses, periodontal splints, implant-supported restorations, and orthodontic retention devices [68,69].

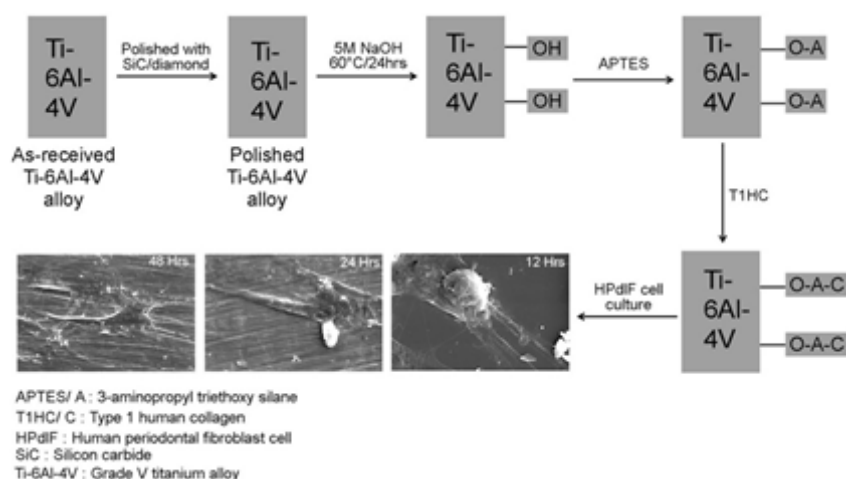
### Titanium, Base Metal and Noble Metal Alloys, Gallium Nitrate Surfaces

Surface pre-treatment of metals and metal alloys is generally required prior to the application of silane coupling agents to facilitate effective bonding with resin composites and biomolecules [70-74]. Following appropriate surface conditioning and primer application, a silica-rich layer may be generated on the metal substrate, particularly when tribochemical or silica-coating techniques are employed. This modification enables the formation of interfacial chemical linkages, typically represented as  $-O-Si-O-M-$  (where M denotes the metal), thereby promoting adhesion between the inorganic substrate and the organic resin phase.

Depending on the surface characteristics of the alloy, more complex siloxane-metal covalent networks, such as  $-(Si-O-Si)-O-M-$  linkages, may develop, contributing to improved interfacial stability. However, silane alone may not always provide optimal bonding, especially for non-silica-based metals.

Consequently, alternative or complementary primer systems have been investigated. For base metal alloys, functional monomers such as phosphate esters, carboxylic acids, and acid anhydrides have demonstrated effective bonding through interaction with metal oxide layers. In the case of noble metal alloys, primers containing sulphur-based functional groups, such as thiones or thiols ( $-SH$ ), have shown favourable adhesion characteristics. These bifunctional primer systems can provide bonding performance comparable to or, in some cases, superior to silane-based approaches under in vitro conditions [75,76].

Studies have suggested that various biomolecules (such as human type I collagen, Human fibronectin, Human laminin, Bone morphogenic protein etc.) can be attached to the silanized surface of metal/metal alloy/ gallium nitrate surfaces through stable covalent bond by means of EDC/NHS coupling reaction [6,20,77,78]. The EDC/NHS coupling reaction is a two-step reaction which is used to covalently attach the molecules, typically proteins or peptides, by forming a stable amide bond between a carboxyl group and a primary amine. This will enhance the formation of soft tissue gingival seal like structure with soft tissue, and promote bone growth over the modified surface (Figure 8 and 9) [20,77]. Thus, enhancing the long-term survivability of the implanted metal/ metal alloy in the biological system.



**Figure 9: Silanized titanium alloy biofunctionalized with type I human collagen, demonstrating attachment of human periodontal fibroblasts and formation of a tight seal-like interface. Reprinted with permission from [20], Sharan J, et al. *Colloids Surf. B Biointerfaces*.161, (2018). ©2018, Elsevier.**

## Dipodal Silanes and Hydrophobic Monomers in Dentistry

Dipodal silanes and hydrophobic monomers are increasingly utilized to improve the longevity and hydrolytic resistance of resin-based restorative materials. Their primary role is to counteract water sorption-induced degradation, a major limitation of conventional adhesive systems in the oral environment [78,79].

Compared to traditional monosilanes, dipodal silanes (bis-silanes) provide superior interfacial bonding to silica-based substrates. Owing to their two silicon functional groups, they establish multiple covalent linkages with the substrate, resulting in a compact and highly cross-linked silane layer. This configuration demonstrates significantly enhanced resistance to hydrolytic breakdown, thereby maintaining interfacial integrity in moist conditions and contributing to improved mechanical properties and bond durability [78-83].

Hydrophobic monomers complement this effect by limiting water diffusion into the polymer network. Monomers such as isobornyl methacrylate (IBOMA) function as efficient diluents, reducing viscosity while preserving a relatively high glass transition temperature ( $T_g$ ) and lowering polymerization shrinkage compared to conventional diluents like TEGDMA. In addition, urethane dimethacrylate (UDMA) and Bis-EMA exhibit reduced water sorption relative to Bis-GMA, further supporting material stability [83-86].

The application of an additional hydrophobic resin coating over simplified adhesive systems has also been shown to enhance bond durability by increasing film thickness and minimizing oxygen inhibition. Overall, an effective adhesive design requires an initial hydrophilic phase for adequate dentin infiltration, followed by a predominantly hydrophobic polymerized interface to resist long-term hydrolytic degradation and ensure sustained clinical performance [78-86].

## Bond strength of various substrates used in dentistry after silanization

Silane bonding is most effective with silica-based ceramics due to true chemical interaction (table 3) [87-93]. In contrast, zirconia and titanium exhibit limited bonding with silane alone because of their non-silica surfaces, necessitating additional surface treatments. Combining methods such as air abrasion, silica coating, and MDP-based primers substantially improves adhesion to these substrates.

## Limitations and Failures of Silane Technology

Failures of Silane coupling agents [94-97] used in dentistry are multifactorial in nature which often results from hydrolytic degradation in the wet oral conditions, improper application techniques, inadequate surface conditioning, leading to reduce bond strength between the resin cements and silica-based restorations. The primary causes of silane failure are:

- **Hydrolytic degradation:** Bond formed by the silanes often weakens over time due to water adsorption in the oral environment, leading to the loss of adhesion.
- **Improper application/ Drying:** Drying time affects the life expectancy of the silane bond. If the drying time is kept too short or the layer is too thick, the adsorption becomes inadequate, leading to the weakening of the chemical bond.
- **Substrate incompatibility:** Silanes are usually more compatible with silica-based ceramics i.e, porcelain, on the other hand silanes are less effective on non-silica-based materials such as pure zirconia. Thus, compatibility of the silane with the substrate is very critical and should be assessed for proper comparability.
- **Interaction with dentin:** Any sort of contaminated tooth structure such as dentin with silane during restorative procedures might lead to reduced bond strength.

All these will lead to chain of consequences ultimately leading to adhesive failure between the substrate and restorative materials, reduced bond strength, restoration discoloration, and recurrent dental caries to name a few. Studies have been suggested that to minimized above mentioned failures, proper surface preparation in the form of etching, adequate drying of the surface, and most importantly correct application technique for a durable, long-lasting bond.

## 3-Methacryloxypropyltrimethoxysilane (3-MPS)

3-MPS, is often referred to as MPPTS [98-102], is a widely used bi-functional silane coupling agents in oral health sciences, and polymer filler surface modification. It forms a molecular bridge between the inorganic substrates such as silica, glass, mica, minerals etc. and the organic polymers such as resins, rubbers. It has three methoxy groups, which are hydrolysable, and react with inorganic fillers, apart from a methacryloxy group which reacts with the organic resins. It improves the wettability, reduces particle agglomeration, and at the same time enhances Interfacial adhesion by forming -Si-O- substrate bonds and co-polymerizing

**Table 3: Bond strength values (MPa) of different substrates-ceramic, zirconia, and titanium-following silanization**

| Substrate                                                     | Surface characteristics                      | Effects of silanization                        | Typical bond strength (MPa)  | Key remarks                                                                                |
|---------------------------------------------------------------|----------------------------------------------|------------------------------------------------|------------------------------|--------------------------------------------------------------------------------------------|
| Silica-based Ceramics (e.g., feldspathic, lithium disilicate) | Silica-rich, glassy phase                    | Highly effective (strong siloxane bonding)     | 20-40 MPa                    | Gold standard indication for silane; excellent chemical coupling and durability.           |
| Zirconia (Y-TZP)                                              | Polycrystalline, no silica phase             | Limited effect (requires surface modification) | 5–15 MPa (with silane alone) | Silane alone is insufficient; improved with tribochemical silica coating or MDP primers    |
| Titanium                                                      | Metal oxide surface (TiO <sub>2</sub> layer) | Minimal direct effect                          | 3-10 MPa                     | Bonding relies more on mechanical retention or phosphate monomers (e.g., MDP) than silane. |

with the resin monomers. Studies have been suggested that optimal concentration for maximum bond strength is in the range of 0.5 to 2.0 wt%.

### Limitations of 3-MPS as a Silane Coupling Agent

Despite of its widest application in oral health sciences, 3-MPS has several limitations, particularly in the form of durability substrate specificity:

- Hydrolytic instability/ Bond degradation: The siloxane bond (-Si-O-Si-) formed by 3-MPS can degrade in the aqueous media such as oral cavity. Water sorption usually leads to hydrolytic degradation over time, thus weakening the interfacial bond.
- Compromised efficacy on non-silica surfaces: 3-MPS is inefficient when it comes to the bonding to non-silica-based surfaces such as, noble metals, alumina, and zirconia. For such a surface with adequate bonding it needs a surface pre-treatment in the form of silica-coating or sandblasting to be effective on these surfaces.
- Short shelf life: Pre-hydrolyzed 3-MPS solutions have a relatively short shelf life. It has been observed that the silane precipitates out of solution over time, thus making it ineffective. Such a solution turn itself into a hazy or milky appearance.
- Optimum concentration efficiency: The optimum concentration of 3-MPS is in the range of 0.5-2.0 wt%, any concentration above 2wt% might leads to a reduction in bonding performance. This is secondary to the formation of multi-layers, which are often weaker than a monolayer.
- Sensitive application requirements: The activation and condensation of 3-MPS require acidic pH condition in the range of 4-5, and specific hydrolysis time is an ethanol-water solvent to functional optimally.
- Not an ideal coupling agent for all the fillers: Compared to other specialized silanes, 3-MPS might not be the most efficient and effective for specific polymer or filler combinations.

Researchers have suggested that to overcome these limitations of 3-MPS, it is often blended with other compounds such as MDP phosphate monomers. This will improve adhesion to non-silica, non-precious metals, and zirconia.

### Toxicity and the Biological Concerns Regarding use of Silane Coupling Agents

Data regarding the toxicity and biological effects of silane coupling agents remain relatively limited in the literature. In general, silanes and siloxanes (silicones), along with their derivatives, are considered to be well tolerated in humans and are typically regarded as having low toxicity, both biologically and environmentally. These compounds may exist in liquid or gaseous forms, and appropriate safety precautions, including the use of protective equipment, are essential during handling due to their reactive nature.

The biological behaviour of silanes is influenced by their molecular

structure and degree of polymerization. These factors affect their ability to penetrate cellular barriers, undergo systemic absorption, accumulate within tissues, and undergo degradation. Notably, lower molecular weight silanes and siloxanes are more frequently associated with adverse biological effects, and their use should therefore be carefully controlled [103].

Experimental studies provide further insight into their biological impact. Inhalation studies in animal models have demonstrated that controlled exposure to silane may induce mild irritation and inflammation of the nasal mucosa, with occasional evidence of cellular necrosis, suggesting relatively low acute toxicity [104]. In contrast, investigations involving novel antimicrobial quaternary ammonium silane (QAS) copolymers have shown minimal cytotoxic effects in various cell lines, including human dermal fibroblasts (HDF), HaCaT keratinocytes, and HEK293 cells, indicating favorable biocompatibility compared to other QAS systems [105].

At higher concentrations and prolonged exposure durations, silane inhalation has been associated with mild tubulointerstitial nephritis in animal models, although no significant structural alterations in the glomeruli were observed [106]. Chronic exposure may result in the accumulation of silicon-containing particles in organs such as the liver, spleen, lungs, and kidneys. The extent and pattern of such deposition, as well as the associated biological effects, are influenced by factors including the physical form of the silane, particle size, and route of exposure [107,108].

### Future Directions of Silane Coupling Agents in Dentistry

The future of silane coupling agents in dentistry is focused on improving bond durability, simplifying clinical protocols, and expanding their applicability across a broader range of restorative materials. A major limitation of conventional silanes is their susceptibility to hydrolytic degradation in the moist oral environment, which adversely affects long-term adhesion. Recent investigations have therefore emphasized enhancing hydrolytic stability to ensure sustained bond performance despite continuous exposure to saliva, temperature variations, and mechanical stresses [1,2].

Another important advancement is the development of universal or multifunctional primers. These systems combine silane agents with functional monomers such as 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), enabling effective bonding not only to silica-based ceramics but also to non-silica substrates such as zirconia and metals. This integration reduces the complexity of surface treatment procedures and enhances clinical efficiency while maintaining consistent bond strength across diverse restorative materials [3,4].

Progress in formulation strategies has also led to the development of pre-hydrolysed and stabilized silane systems. Conventional silanes are prone to premature hydrolysis and condensation during storage, leading to reduced effectiveness. Newer formulations aim to improve shelf life and ensure optimal reactivity at the time of application, thereby providing more predictable and durable adhesion [2,5].

Furthermore, research is expanding the application of silane chemistry beyond traditional silica-based materials. Novel coupling systems and hybrid primers are being designed to improve adhesion to high-strength ceramics and other contemporary restorative materials that are inherently resistant to conventional silanization techniques. This shift is essential in response to the increasing use of zirconia and other non-etchable substrates in modern restorative dentistry [3,6].

In addition to chemical stability and versatility, future silane systems are expected to enhance the mechanical integrity of the adhesive interface. By strengthening the interaction between restorative materials and resin matrices, these agents can improve resistance to masticatory forces and reduce the likelihood of bond failure, ultimately increasing the longevity of restorations [4,6].

Overall, current advancements indicate a transition toward more durable, versatile, and clinically efficient silane systems, with the ultimate goal of improving the long-term success and reliability of restorative dental treatments.

## Conclusion

Silane coupling agents were introduced into oral health care approximately seven decades ago, initially for use in resin-based composite materials. Since then, their applications have expanded considerably, driven by advances in material science, improved formulation strategies, and ongoing efforts to develop more reliable and durable dental biomaterials. These developments have contributed to enhanced functional performance, improved aesthetic outcomes, and overall better patient quality of life. A key role of silanes lies in their ability to establish strong interfacial bonding between chemically dissimilar materials, particularly inorganic substrates and organic resin matrices. This coupling effect improves critical properties such as mechanical strength, durability, and resistance to degradation, thereby supporting their widespread use in clinical dentistry. More recently, their application has extended into implant dentistry, where silane-based surface modifications are being explored to enhance both hard and soft tissue integration, with encouraging preliminary outcomes. Despite their extensive use and generally favourable biocompatibility, emerging concerns regarding potential adverse effects have been reported. These findings highlight the need for further well-designed studies to better understand their long-term biological behavior and safety profile. Overall, a broad range of silane coupling agents has been investigated, demonstrating significant potential across dental and broader biomedical applications.

## Supplementary Materials

Table S1 provided online as supplementary material.

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