



## Review Article

# Surface Conditioning and Silanization for Ceramic Adhesion

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## Introduction

Bonding of two dissimilar materials require the substrate and adherent to have a clean surface for maximum bond strength. Removal of impurities from the surface results in, increase in surface energy and wettability of the surfaces to be bonded. The process of removing impurities and increasing the surface area is known as surface conditioning. Several surface conditioning techniques exist, namely acid etching, air abrasion, tribo chemical coating, grit blasting, etc. However, conditioning alone did not result in sufficient bond strengths between composites and metals/ceramics. A chemical component was required in the bonding process to enhance bond strengths.

The chemicals that promote adhesion between two dissimilar molecules are called coupling agents. Most widely used coupling agents are organo metallic compounds such as organosilanes, titanates, zirconates and thiones. Coupling agents played a vital role in adhesion of matrix (resin) and fillers (silica) to form dental composites. This provides composites the necessary physical properties to withstand the adverse oral conditions. Organosilanes are the most commonly used coupling agent in dentistry. Silanes are derivatives of silicon compounds that contain Si-C and Si-H bond(s). The silanes are of two main types: functional silanes and non-functional silanes. the former contains two functional groups that can react with both organic and inorganic surfaces. Silica based ceramic and resin composites (an organic substrate), are unified by silanes showing that they can bring about adhesion of two chemically different materials while the non-functional Silanes that are not intended to impart chemical reactivity to the substrate used for surface modification. Non-functional silanes have only one reactive group which is capable of reacting with the hydroxyl groups of the inorganic substrate only.

The main aim of this article is to discuss about the different methods of surface conditioning and the mechanism of how a silane modifies the surface of a substrate.

## Methods of Surface Conditioning

1. Tribo-chemical silica coating 2. Pyro-chemical silica coating 3. Acid etching and electrolytic coating 4. Grit blasting 5. Selective infiltration etching 6. Nano-structured alumina coating 7. Chemical vapor deposition 8. Internal coating method 9. Gel-sol form 10. Plasma fluoridation 11. Nano silica coating 12. Silicon based coating

### *Surface conditioning:*

Conditioning of the surface increases the critical surface energy for adhesion. when surface tension of a liquid is less than the surface energy of particular surface, the contact angle is 0° degree and therefore the liquid can spread immediately. Adequate wetting of the substrate with bonding agent is essential for micro-mechanical retention, resistance to fatigue and stress relief. <sup>(6)</sup>

### *Tribochemical silica coating:*

This method was introduced in 1989 as an improvement of the pyrochemical silica coating. A tribochemical Rocatec System (3M ESPE, Seefeld, Germany) was designed for surface conditioning of dental restorative materials like ceramics, metals and metal alloys. The substrate surface is grit-blasted under compressed air using silica-coated alumina powder (alumina particles act as the carrier) and this causes the melting of the surface microscopically. The impact of the powder particles changes the surface topography and then the powder particles also gets embedded onto the substrate surface. A silica coated surface is then subjected to follow silanization. The produced bond strength is affected by the blasting pressure applied.

Recently it was reported that the grit blasting angle might be one of the cause which can affect the resin bonding. However, no significant effect with the change of angle or distance during sandblasting is provided.

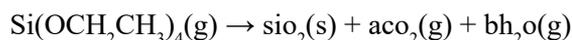
Currently, the widely used surface-conditioning method is Tribochemical silica coating in which, a layer of silica is created on the surface so that the silane coupling agent will re-join chemically to make a strong bond with non-silica-based materials. Due to the increased surface roughness there will be improved micro-mechanical retention. Silanes were used as adhesion promoters in ceramic restorations and their repairs with resin composites \glass fibre, reinforced polymer composites, glassy fillers in resin composite to form durable bonds between resin composite to silica-coated metal and metal alloys. Silanes lack intrinsic toxicity.<sup>(7)</sup>

Silicatization provides a chemical basis to enhance composite bonding since silica rich surface is required for strong organic matrix to make bond with resin composite filling materials<sup>(8)</sup> These days, dental resin composites are composed of a resin matrix that contain monomers and cross-linking monomers, a free-radical initiator, colouring pigments such as glass, silica, hydroxyapatite and a silane coupling agent. The latter improves the bonding between the filler particles and resin matrix. The filler particles which are added to the resin matrix also recover the physical and mechanical properties of the resin composite. Additionally, the incorporation of fillers reduces the volume shrinkage after polymerization and improves the radio-opacity, aesthetic appearance. Also, this treatment will increase surface roughness, which will improve micromechanical interlocking for bonding.<sup>(8)</sup>

### ***Pyrochemical silica coating***

This technique is done based on the utilization of elevated temperatures eg: silicatermd, silicoater tm classic. The surface of the substrate is sandblasted and introduced into flame. A pyro-chemical silica coating is thus obtained of roughly 0.1-1.0  $\mu$  thickness. The coating solution consists of tetra-ethoxysilane.<sup>(6)(9)</sup>

The basic principle of the pyro-chemical silica-coating is the chemical reactions of silane at high temperature to form silica. Silicoater Classical, Silicoater MD and Siloc (heraeuskulzer, Wehrheim, Germany) systems were used since 1984. Base metal alloys, noble metal alloys and porcelain had been silica-coated by this method. In the Silicoater system, tetraethoxysilane,  $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ , TEOS, is injected into a flame. A series of pyrochemical reactions take place which can be summarized as follows



The processing temperature is 150–200°C. The reactive silane intermediates,  $\text{Si}(\text{OH})_m\text{C}$  (where  $m = 1, 2, 3$ ) deposits on the substrate surface. After cooling, a silane coupling agent is applied onto the silica coating to react. This method is however, no longer used in dental technology.

A modification of the Silicoater technique was introduced later on as Silano Pen or pyrosil Pen (Bredent, Senden, Germany) for extra-oral use in dental laboratories. It is applied by a hand-held device with a flame treatment.

Traditional surface treatment methods discussed above are applied in dental laboratories. Researches on other surface treatments is in progress in an attempt to improve adhesion and its durability in the oral cavity.<sup>(2)</sup>

### ***Acid etching and electrolytic coating:***

Acid etching of ceramic restorations prior to bonding is important to create the appropriate surface structure needed to maximize retention of the resin cement. This method involves etching of the surface with hydrofluoric acid (5%HF), lithium disilicate (e.max): 20 second etch with 5% HF..Leucite ceramic (Empress Esthetic, Authentic, etc.): 60 second etch with 5% HF.Feldspathic ceramic (d.SIGN, Ceramco, etc.): 120 second etch with 9% HF

Base metal alloy of fixed partial denture is electrolytically etched to reinforce the adhesion of resin composite luting cements by creating irregularities on the metal surface. The etched surface is difficult to assess with the naked eye. Another modification is that the electrolytical tin plating is done before veneering metal crown followed by which sandblasting is completed and this enhances micro-mechanical retention<sup>(6)</sup>

### ***Ceramic restorations and repairs:***

Silane coupling agents are used for dental re-establishments, like ceramic repairs of on-lays, in-lays, crowns and bridges. Mostly the repair is less expensive and time-saving unless the damage due to fracture is beyond repair. The clinical procedure for mending ceramic restoration sometimes involves the subsequent steps<sup>(1)</sup>

- Roughening the surface with diamond burs
- Sand-blasting the surface
- Acid etching, silanization
- Finally bonding to resin composite

### ***Grit blasting***

In dental laboratory the routine procedure for surface pre-treatment of some indirect restorative materials is grit blasting with aluminum oxide powder with particle size of eg: 110 $\mu$  under a constant pressure of 380 k pa, this cleansing action will increase the surface roughness that enhances the bonding by micro-mechanical interlocking (retention). However, the surface is also contaminated with aluminum oxide powder particles throughout grit blasting. A thin layer of aluminum oxide coating is also formed onto the substrate surfaces during grit-blasting. The quantity of aluminum oxide deposited is directly proportional to the blasting pressure applied. Al- O -Si linkages is also formed The linkages are rather weaker than -Si-O-Si- and are more susceptible to hydrolysis. A drawback of this method is an induction of sub-surface damage causing surface micro-cracks due to the impact of the powder particles. This would possibly compromise the mechanical strength at the surface layer that successively affects the long run clinical performance.<sup>(10)</sup>

### ***Selective infiltration etching***

This is a comparatively new approach where the zirconia surface is coated with thin layer of a glass-conditioning agent. The coating is fired above the glass transition temperature and also the molten glass particles penetrate into the surface grain boundaries. Surface tension phenomenon is developed which causes the surface grains movements: an inter-grain porosity is formed when treated with acid and the glass particles are removed. Therefore, an extremely reactive and retentive zirconia surface is created. Resin zirconium bonding is considerably improved with the selective infiltration etching treatment followed by a silane application.<sup>(10)</sup>

### ***Nano-structured alumina coating***

Alumina nano-particles are formed by the hydrolysis of aluminum nitride (aln) powder heated at 75°C, resulting in nano-boehmite (alooH) particles deposited on oxide surface. Once the coating is thermally treated in air at 900°C, the boehmite undergoes a series of phase transformation to alumina causing an increase in the surface area enhancing the micro-mechanical interlocking for resin bonding. The improvement in resin zirconia bonding is obtained when water aging process begins even without a silane application<sup>(3)</sup>

### ***Chemical vapor deposition***

In molecular vapor deposition system, a mixture of tetra-chlorosilane ( $\text{SiCl}_4$ ) and water is heated. The vapor is passed onto zirconia surface in a vacuum chamber. Silane undergoes hydrolysis to form hydroxylated silica and HCl gas is produced as a byproduct. A silica seed-layer ( $\text{Si}_x\text{O}_y$ ) is formed on the zirconia surface. The coating thickness can be adjusted by the time of deposition. The silica seed coating is reported to form durable bonding to zirconia with an application of silane coupling agent<sup>(11)</sup>

### ***Laser treatment***

There are three types of laser used in dentistry for clinical use and surface treatment: 1. Erbium: yttrium-aluminum-garnet (Er: YAG), 2. Neodymium: yttrium-aluminum-garnet (Nd: YAG), and 3. Carbon dioxide ( $\text{CO}_2$ ). The substrate surface is irradiated with a laser beam. This laser energy is absorbed and are converted into heat energy which causes the melting of the substrate surface and produces surface irregularities. Surface topography changes take place and enhanced adhesion promotion was observed.<sup>(12)</sup>

### ***Internal coating method***

Silica coating on the zirconia surface is achieved by thermal fusion. Porcelain powder is mainly composed of silica with small percentage of  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ . The zirconia surface is grit-blasted with alumina powder. The porcelain powder is mixed with distilled water to form a paste and is applied onto the grit-blasted zirconia surface. It is then fired at 800°C in vacuum followed by silanization and resin bonding.<sup>(12)</sup>

### ***Sol-gel coating***

The basic principle of this method is the hydrolysis of silicon. Certain precursors, mostly tetra-ethoxy silane form silica sol gel in an acidic or alkaline medium. Hydrolysis of tetra-ethoxysilane produces silica and ethanol as a by-product. The silica sol gel deposits on the substrate surface through the surface hydroxyl groups and forms silica coating

### ***Plasma fluorination***

An extremely reactive coating is created on the zirconia surface by using plasma spray technique. Zirconia surface is exposed to continuous flow of Sulphur hexafluoride ( $\text{SF}_6$ ) gas at a continuous pressure in an inductively

coupled plasma reactor. Under plasma irradiation, the Sulphur hexafluoride molecules are converted to reactive species and they react with zirconia after deposition on the surface. Once silane coupling agent is applied onto the reactive surface, surface silanation happens. <sup>(12)</sup>

### Nano-silica coating

Other silica precursors will react to create silica by chemical reaction however in additional reaction conditions. In a recent study, silica coating was formed on zirconia by the hydrolysis of silicon nitride (sin) under a strong alkaline medium alongside heating. The silicate species are formed from a suspension of silicon nitride nanoparticles in concentrated sodium hydroxide solution and heated to 90°C. The hydrolyzed silicon oxide nanoparticles deposit on the zirconium surface. When drying the coating is heated to 1400°C to create the silica coating by condensation of the hydroxylated silica species <sup>(13)</sup>

### Silicone-based coating

Silicone polymers like polydimethylsiloxane that contains a repeating unit of siloxane can form silica upon thermal oxidization and decomposes in air when a thin layer of polydimethylsiloxane gel is applied on to a titanium surface. <sup>(13)</sup>

## How are Surfaces Modified Using Silane?

Most widely used organo- silanes have one organic substituent and three chemical substituents. In majority of surface treatments, alkoxy group of the tri-alkoxysilanes are hydrolysed to form silanol-containing group. The reaction occurs in 4 stages:

- Hydrolysis of the labile groups
- Condensation to oligomers.
- The oligomers and hydrogen bonds with -OH group of the substrate.
- Finally, through drying or solidification, a covalent linkage is made with the substrate with concomitant loss of water. <sup>(3)</sup>

### Coupling mechanism of organofunctional alkoxy silane:

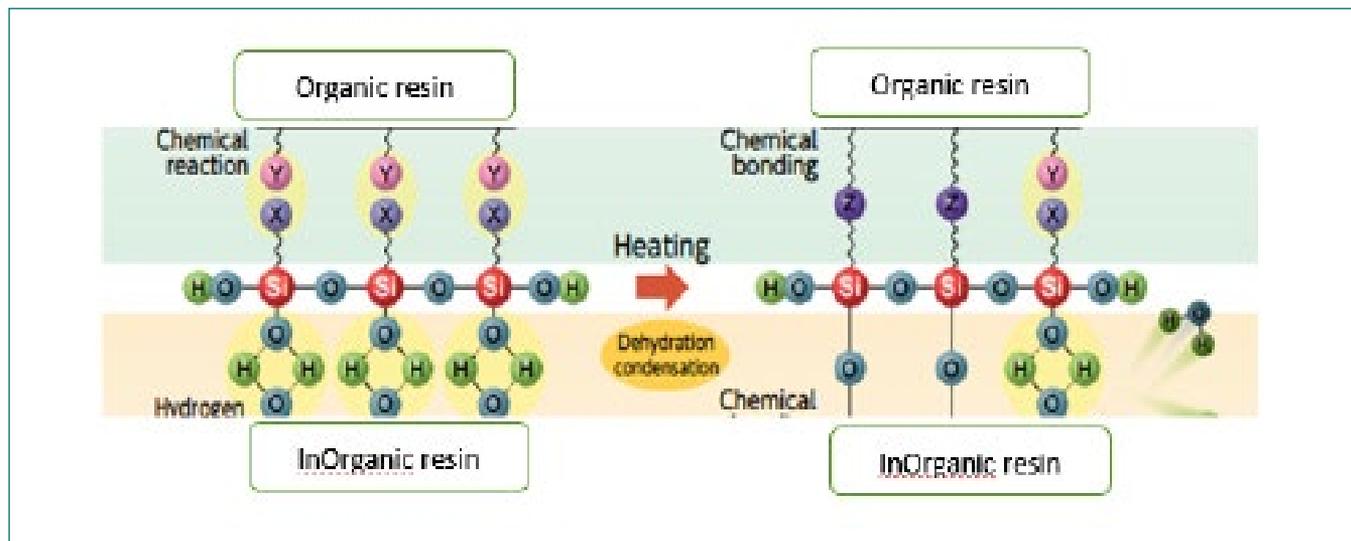
It includes synthetic direct =si-h and =si-c bonds (silicon-hydrogen, silicon-carbon) These are non- functional silanes that have non- reactive group

### hydrolysis reaction is by the removal of organic solvents and water:

Water is the principal product of condensation reaction among silanes and ceramics and therefore the removal of each residual water and organic solvents is very important to enhance the adhesion of resin cement to dental ceramics. Manufacturers have suggested just blowing the air after the application of silane, is not enough to eliminate the residual water and organic solvents in order to reinforce the adhesion between lithium disilicate-based ceramic and resin cement. <sup>(4)</sup>

To achieve adequate cement/ceramic bond strength, numerous treatments on the ceramic surface can be performed. Use of a silane coupling agent is suggested for an adhesive cementation. Silane is a monomer with reactive organic radicals and a hydro-soluble monovalent group that produces bonding between both inorganic phase of the ceramic and the organic phase of the bonding agent and is coupled to the ceramic surface by a siloxane bond. Additionally, the silane agent increases the surface

Figure 1: mechanism of adhesion <sup>(12)</sup>



energy of ceramic substrates and improves the adhesive and/or cement wettability. A suitable silane procedure should be used to assure the bond strength achievement and longevity of the dental restoration.

During the application of silane on the ceramic, the surface is dried and an interphase layer is formed. Eliminating the outermost layer of the silane film and leaving the most constant and chemisorbed layer on the ceramic surface improves the bond strength along with the restorative interface.<sup>(1)</sup>

Though described in sequence, these reactions can occur all together after the initial hydrolysis step. Particularly at the interface, there is formation of one bond of each silicon of the organo-silane to the substrate surface. The remaining two silanol groups are present either in condensed or free form. The R group remains available for covalent reaction or physical interaction with other phases.<sup>(4)</sup>

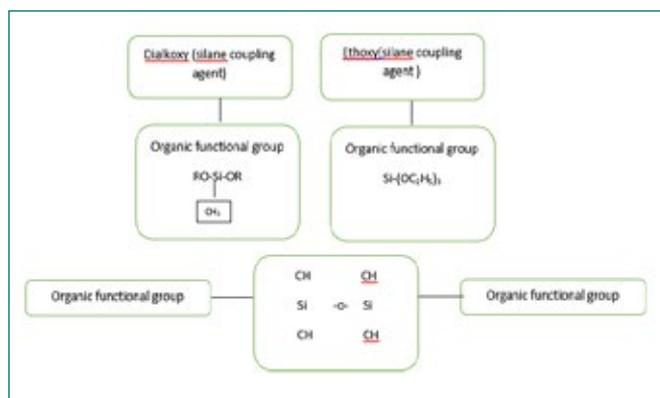
Silanes can modify surfaces in anhydrous conditions by monolayer and vapour phase deposition. Methoxy silanes and cyclic azasilanes are effective devoid of catalysis for vapour deposition.<sup>(5)</sup>

stability of bonding better than using silane coupling agents. The chief problem of resin composites that are bonded to silica-coated restorative materials with the application of commercial silane coupling agents is the bond degradation over time under artificial ageing. To upsurge the hydrolytic stability of the bonding at the interfacial layer, innovative surface treatments of restorative materials and the advanced silane monomers are used. Silane coupling agents by means of extended hydrocarbon chains are more hydrophobic than those with small hydrocarbon chains. The bonding at the interfacial layer is more resistant to thermal and water ageing. These two approaches may decide the problems.<sup>(10)(14)</sup>

## Conclusion

Therefore, it could be said that silane coupling agents can satisfy the clinical requirements for dental restorations. A standard laboratory protocol for dental restorations entails surface conditioning of dental materials, silanization and cementation. The problem of hydrolytic stability of the siloxane linkage formed from silane coupling agents with resin composites and dental restorative materials is currently being hold forth. It is not an overestimation to claim that silane coupling agents have wide application in industry, such as dentistry and medicine and that it will play an important role in biomaterial sciences.

**Figure 2:** Silane coupling agents<sup>(2)</sup>



## 2 Types of Silane Coupling Agents:

### Contemporary Trends and Future Development in Dentistry:

In the recent times, alternate coupling agents (such as phosphate ester) that are used in dental restorations in addition to self-adhesive resin cements are adhesive primers, metal, alloy primers, and carboxylic acid primers. Phosphate esters can bond straight to non-silica-based ceramics such as zirconia. It has been stated that using this phosphate ester one can enhance the hydrolytic

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**How to cite this article :** Nandini Pugal, Praveen Rajesh, Preethe P M, Padhmaraj S N, Dhanavel Chakravarthy. Surface Conditioning and Silanization for Ceramic Adhesion. *Journal of Scientific Dentistry* 2018;8(2):32-7

**Source of support :** Nil, **Conflicts of Interest :** None declared