Silane coupling agents and surface conditioning in dentistry

In dental restorations, it is desirable to have durable and strong bonding between resin composite and dental restorative materials. Weak bonding at the interface can be dramatically enhanced with a coupling agent.

Silane coupling agents, which are synthetic hybrid inorganic-organic compounds, are used to promote adhesion between dissimilar materials. They are good at promoting adhesion in silica-based materials such as porcelain. However, adhesion in non-silica-based restorative materials such as zirconia, metals and metal alloys is not satisfactory.

A solution to this problem may be surface conditioning of the restorative materials. Currently, a widely used surface-conditioning method in dentistry is tribochemical silica coating. After this treatment, a silica layer is formed on the surface so that the silane coupling agent can react chemically to form a durable bond with non-silica-based materials. Moreover, this treatment increases surface roughness, which will enhance micromechanical interlocking for bonding.

This review will discuss surface-conditioning methods and some new surface-conditioning techniques, silane chemistry, silane application in dentistry, and the limitations of silanes in adhesion promotion.

The silane monomer most commonly used in clinical commercial products is 3-methacryloxypropyltrimethoxysilane. This is pre-hydrolysed in a solvent mixture usually consisting of ethanol and water that is acidified with acetic acid.

The shelf life for a single-bottle silane solution is relatively short. The solution will turn cloudy over time and cannot be used for adhesion. Two-bottle silane systems have been developed to offer a more stable system. One bottle contains an unhydrolysed silane in ethanol and the other one contains an aqueous acetic acid solution. The two solutions are mixed for silane hydrolysis before use.

Surface-conditioning methods

The surface conditioning of restorative materials is an important preliminary step in clinical practice to modify surface properties for durable and hydrolytically stable adhesion. The surface pretreatment methods widely used in dental technology are grit blasting, tribochemical silica coating and hydrofluoric acid etching, which will be discussed briefly in the following section.

Grit blasting

The surface of materials such as metals, alloys and some ceramics is sand-blasted with alumina particles of 110 µm in size at a perpendicular dis-
tance of 10 mm under an air pressure of 380 kPa for ten to 15 seconds. This process is intended to increase the surface roughness of the materials. It also enhances micromechanical retention for bonding.

**Pyrochemical silica coating**

Over the years, several silica-coating systems have been used in dental laboratories. Briefly, they are Silicoater Classical, Silicoater MD and Sililoc (all Heraeus Kulzer) and PyrosilPen (SURA Instruments). In these systems, a tetraethoxysilane solution is injected into a flame and burned with butane in oxygen. The silane decomposes and forms reactive SiOx-C fragments, which are deposited on the substrate surface. A glass-like silica layer is thereby formed on the surface. The use of this surface treatment is not popular in clinical practice.

**Tribochemical silica coating**

The tribochemical Rocatec system (3M ESPE) that uses silica-coated alumina particles was introduced in 1989. It is indicated for silica coating of ceramic and metal surfaces. It enhances the adhesion of a silane coupling agent to a silica-coated material by forming a durable siloxane Si-O-Si bond. This surface treatment also increases the surface roughness that provides micromechanical retention for resin bonding, that is, for the resin to penetrate pores on the surface.

**Hydrofluoric acid etching**

Hydrofluoric acid is normally used to etch porcelain veneers and for intra-oral repair of fractured porcelain restorations before cementation. Low concentrations of 4 to 10% hydrofluoric acid are used in clinical practice. When a porcelain surface is etched with hydrofluoric acid etching gel, the acid dissolves the glassy matrix of the porcelain. A microscopically porous and micro-retentive surface is thus produced and micromechanical interlocking for resin bonding is enhanced.

**New surface-conditioning methods**

The quest for enhanced and durable bonding continues. Several new surface-conditioning methods are currently under investigation globally. These include laser surface treatment, selective infiltration etching, nanostructured alumina coating, internal coating, chemical vapor deposition and plasma fluorination.

**Laser surface treatment**

Laser stands for light amplification by stimulated emission of radiation and the technology was introduced in the 1950s. Er:YAG, Nd:YAG, and CO₂ lasers are used in dentistry for soft-tissue surgery and hard-tissue treatment and surface treatment. Laser irradiation of a ceramic surface produces irregularities on the surface, which increase the surface roughness for mechanical retention. The main problem, however, of this surface treatment method is the formation of surface cracks owing to thermal effects of laser irradiation at high power settings. Therefore, appropriate laser settings for different ceramic surfaces is important to prevent formation of surface cracks.

**Selective infiltration etching**

In this method, a thin layer of a glass conditioning agent is coated onto the zirconia surface and is then heated to above the glass transition temperature. The molten glass particles infiltrate between the surface grains. After this process, the specimens are allowed to cool at room temperature. The conditioning agent is then removed by applying hydrofluoric acid and rinsing it off. This creates a new retentive surface for resin–zirconia bonding.

**Nanostructured alumina coating**

In this coating method, the zirconia is immersed in a suspension of aluminium nitride. Aluminium nitride undergoes hydrolysis to form boehmite, which is deposited onto the zirconia surface. A heat treatment at 900 °C is carried out. Boehmite undergoes a phase transition to d-alumina. Through this treatment, a micro-retentive surface area is created that may increase mechanical interlocking for resin bonding.

**Internal coating with porcelain**

The zirconia surface is sand-blasted with alumina particles of 70 µm in size. Then, the surface is coated with high fusing porcelain, which is prepared by stirring the porcelain powder into an excess amount of distilled water. The porcelain is fired at
Silane chemistry

Functional and non-functional silanes

Functional silanes contain two different functional groups that can react with inorganic matrices, for example ceramics, and organic materials, for example resins. Therefore, they can be used as coupling agents to connect dissimilar materials.

There is also a group of silanes called the non-functional silanes. They contain one reactive functional group that can react with inorganic materials. They are widely used for some specific surface modification of materials. In addition, there are bifunctional/cross-linking/dipodal silanes that possess two silicon atoms with three hydrolysable alkoxy groups. Cross-linking silanes are used in the steel and tyre industries. Such silane is also incorporated with functional silane to increase the bonding and hydrolytic stability of resin composite to titanium.

Silane activation mechanism

Silanes can create a bond between inorganic and organic materials. A general formula for a functional silane coupling agent is $Z-(\text{CH}_2)_n-\text{Si}(\text{OR})_3$, $Z$ is an organo-functional group that reacts with organic resin, $(\text{CH}_3)$, is a linker group, and $\text{OR}$ is an alkoxy group. The alkoxy groups are activated by hydrolysis ($\text{SiOR}$ $\rightarrow$ $\text{SiOH}$) before they react with the surface hydroxyl groups of the substrate.

The first step of silane hydrolysis is the fast and reversible protonation of the alkoxy group at a low pH (3–5). Next, a bimolecular nucleophilic substitution ($\text{SiO}_2$) reaction at the silicon atom takes place. A nucleophile, a water molecule, attacks backside to the silicon atom, an electrophile, to form a pentacoordinate transition state. A new bond is formed between the silicon and the nucleophile, and a bond is cleaved between the silicon and the leaving group, alcohol. This yields the product with an inversion of the configuration. A suggested mechanism for silane hydrolysis is shown in Figure 1.

The silane hydrolysis rate depends on the steric (size) and inductive (electronic) effects of alkoxy groups on the silane. The steric effect is the dominant factor that affects the silane hydrolysis rate. This effect is best illustrated using a ball-and-stick model (Fig. 2).

As shown in Figure 2, the steric repulsion increases when the size of the alkoxy group is changed from a methoxy to butoxy group. The approach of a water molecule, a nucleophile, to the silicon atom is more difficult for the bulky butoxy groups. This may explain why ethoxy silanes are employed in commercial dental products because of fast hydrolysis of small ethoxy groups. Methoxysilanes are not used, as the by-product methanol is very toxic.

The organo-functional groups of silane coupling agents consist of, for example, $\text{C}=\text{C}<$, a vinyl double bond that can react with the functional groups of resin composite consisting of $\text{C}=\text{C}<$ bonds. The reaction is initiated by the initiators in the resin composite, which are decomposed by visible blue light to form free radicals. These free radicals react with the $\text{C}=\text{C}<$ bond in the resin composite monomer or in the silane molecule to generate another free radical species. The reaction of these free radicals with resin composite monomers and silane molecules forms new C-C single bonds. Therefore, the silane coupling agents connect the resin composite and the inorganic substrate surface.

Application of silanes in dentistry

Ceramic restorations and repairs

Silane coupling agents are used in dental restoration, such as ceramic repairs of onlays, inlays, crowns and bridges. For most patients, repair is more economical and time-saving than the fabrication of new restorations, unless damage due to a fracture is beyond repair. The clinical procedure for repairing ceramic restoration usually involves the following steps: roughening the surface with diamond burs, sand-blasting the surface, acid etching, silanisation and finally bonding to resin composite.
Glass fibre-reinforced composites

A relatively new group of dental biomaterials, the glass fibre-reinforced composites, is used in fixed partial dentures, removable prosthodontics, periodontal splints and retention splints. The adhesion between the glass fibre and resin composite is improved by adding a silane coupling agent. The silane forms siloxane linkages with the surface hydroxyl groups of glass fibre. The organo-functional groups of silane react with the functional group in the resin composite. Thus, the bonding strength is increased between resin composite and glass fibre.

Resin composite filling materials

Nowadays, dental resin composites are composed of a resin matrix that contains monomers and cross-linking monomers, as well as a free-radical initiator, an inhibitor, colouring pigments, filler materials such as barium glass, silica, apatite and a silane coupling agent. The latter enhances the bonding between the filler particles and the resin matrix. The filler particles added to the resin matrix also improve the physical and mechanical properties of the resin composite. Moreover, the addition of fillers reduces volume shrinkage after polymerisation, and improves the aesthetic appearance and radiopacity.

Titanium, noble metal and base metal alloys

Titanium, noble metals and cobalt–chromium (base metal) alloys are commonly used for removable partial and complete dentures with a metal frame incorporated and metal–resin cement restorations. For these metal and metal alloys, surface conditioning by sand-blasting using silica-coated alumina particles produces a silica-coated layer on the surface. Application of a silane coupling agent to the silica-coated surfaces forms a durable siloxane linkage. This is followed by cementation.

Limitations of silanes as adhesion promoters

Silanes are good at promoting adhesion between resin composites and dental restorative materials but there are some limitations to silane coupling agents.

The adhesion of silane coupling agents and non-silica-based restorative materials such as alumina, zirconia or metals is weaker than the silica coating of these materials. Therefore, a surface pretreatment with silica coating is required so that durable bonds (siloxane bonds) are formed between silane and silica-coated restorative materials. For noble metals or noble metal alloys, thione or thiol-based coupling agents are used to promote adhesion.

These coupling agents have different bonding mechanisms with various dental restorative materials.

Current trends and future development of coupling agents in dentistry

Nowadays, other coupling agents (such as phosphate ester) are added to self-adhesive resin cements and adhesive primers, metal and alloy primers, and carboxylic acid primers used in dental restoration. Phosphate esters can bond directly to non-silica-based ceramics such as zirconia. It has been reported that using this phosphate ester can enhance the hydrolytic stability of bonding more than using silane coupling agents can.

The main problem of resin composites bonded to silica-coated restorative materials with the application of commercial silane coupling agents is the bond degradation over time under artificial ageing. In order to increase the hydrolytic stability of the bonding at the interfacial layer, novel surface treatments of restorative materials and the design of novel silane monomers can solve this problem. Silane coupling agents with long hydrocarbon chains are more hydrophobic than those with short hydrocarbon chains. The bonding at the interfacial layer is more resistance to water ageing. These two approaches could resolve the problem.

It could be said that silane coupling agents can fulfil the clinical requirements for dental restorations. Nowadays, a standard laboratory protocol for dental restorations entails surface conditioning of dental materials, silanisation 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 addressed. It is not an exaggeration to claim that silane coupling agents have wide application in industry, dentistry and medicine and will play an important role in biomaterials science.

This review is based on the article “Aspects of silane coupling agents and surface conditioning in dentistry: An overview”, Dental Materials, 28 (2012): 467–77. A complete list of references is available from the publisher.

About the author

Dr Christie Lung Ying Kei is a postdoctoral fellow in Dental Materials Science at the Faculty of Dentistry at the University of Hong Kong. He can be contacted at cyklung@hku.hk.