Bonding Dissimilar Materials in Dentistry: A Critical Review

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Abstract: Bonding of dental restorative materials to tooth tissues is one of the most important aspects in dentistry. Adhesion at the interface has been the topic of never-ending and growing discussion in the research field of adhesive dentistry for quite some time. Prosthetic materials have to be cemented in the moist oral cavity either to the remaining tooth structure or to another prosthetic dental material. The affinity of most of the dental materials to each other is inherently inadequate. Thus, to meet this harsh oral environment many so-called coupling agents are used after the surface modification to further enhance the adhesion between different materials. There has been considerable research on coupling agents, with most of it focusing on silane coupling agents as compared to studies on some other coupling agents. One of the main problems with silanes is their susceptibility to humidity, and thus other coupling agents have been investigated to provide a more hydrolytically stable bonding agent. Some phosphate, zirconium and titanium based inorganic-organic hybrid compounds are also actively being investigated for the purpose. This review is focused on the coupling agents used in the contemporary adhesive dentistry including silanes which have and are being extensively studied. This review starts briefly from the history of the coupling agents and finally moving on to the current trends in research on coupling agents. This review is aimed to give better view and understanding of the different coupling agents and how these can be used in adhesive dentistry in the future.

Keywords: Silane coupling agents, zirconates, phosphate coupling agents, sulfur-based coupling agents, adhesion, hydrolytic stability, titanate coupling agents, zircoaluminate coupling agents

1 Introduction

One of the main clinical aspects in any field of dentistry is durable adhesion, and it is of critical importance in the fields of aesthetic, conservative, orthodontic and prosthetic dentistry. Modern adhesive dentistry is conservative, *i.e.*, it preserves tooth tissues as much as clinically possible. According to the Oxford Dictionary of Dentistry, "Adhesion is the sticking of two surfaces together" or according to ISO Dental Terminology, adhesion can be defined as "A state in which two surfaces are held together by chemical or physical attraction or both with or without the aid of a substance formulated for coating one or two surfaces for the purpose of holding or intend to be held by another body". In general, adhesion has been explained as coming together or sticking of two dissimilar surfaces together. It is simple to understand that two dissimilar surfaces may not have natural affinity for each other. Adhesion in dentistry can be described as connecting or joining of two dissimilar surfaces to obtain the optimal result for the particular purpose and it is different from cohesion which is the union of two similar surfaces. Adhesion can be broadly divided into two main categories: mechanical and chemical adhesion. Mechanical adhesion is the one in which the substrate surface is subjected to surface conditioners thus forming irregularities on the surface, and when the restorative material is placed on the substrate it penetrates into these irregularities. These small surface irregularities enable mechanical locking (interlocking) between the surfaces and provide good bonding as compared to the bodies without any irregularities. Dental silver amalgam restorations and resin composite restorations are good examples of mechanical adhesion. Chemical adhesion does not involve any surface treatment but only an adhesive which has affinity for both substrates when placed between them, thus increasing the bonding and giving good, adequate, and durable adhesion. Examples of this include adhesive resin bonded ceramic (porcelain).

Adhesion in dentistry is promoted by many factors such as clean surfaces, increased wettability (low contact angle) and absence of biofilms on the substrates. One of the main problems encountered and which is still of main concern is the adhesion property of dental materials when placed in the harsh and hostile oral environment. The materials in the oral cavity have to bear varying masticatory forces, changes in temperature (ca. + 5°C to + 55°C), varying pH, saliva, bacteria, fungi, proteins *etc.* [1, 2]. This limits the options for different types of adhesives which can be used in dentistry as compared to the adhesives being used in numerous industrial applications. In the 1950's acid etching technique was introduced to create mechanical retention on dental ceramics and thus giving birth to the concept of mechanical adhesion. In the 60's resin composite materials were developed with further modification of the composite material components to be used *e.g.*, with acid etching techniques to bond orthodontic brackets to the tooth structure. Since then acid etching of tooth tissues has been used in adhesive dentistry. In the 1970's the so-called polycarboxylate cements were introduced and subsequently

followed by the introduction of glass ionomer cements (GICs) by Wilson and Kent [3, 4], thus giving rise to the concept of chemical adhesion.

In general, coupling agents are synthetic, functional compounds and conditioning agents used to increase the bond strength between e.g., various oxide-based dental materials and tooth structures with resin based composite luting cements. The coupling agents may be used for the bonding of resin composites to the tooth, bonding resin composites to surface-treated base or noble metal alloy frameworks or bonding resin composites to silanized silica and non-silanized non-silica based permanent ceramic crowns/inlays/onlays to be placed in the oral cavity. Coupling agents basically act as adhesives providing adhesion between dissimilar materials which without coupling agents would not bond or adhere to each other. Silane coupling agents were the first coupling agents to be introduced. The developments of other coupling agents such as zirconates, titanates and phosphates have been of increasing interest.

In this critical review we discuss all the currently used coupling agents or those which have a potential to be used and drawing the attention to their reactivity and molecular structure and the how they can be applied to benefit clinical dentistry.

2   Silane Coupling Agents

There has been a great deal of research in the field of silanes during the last six decades to promote adhesion between dissimilar materials, ranging from glass fiber lamination to building material coatings, mineral surface treatments, optical coatings, glass fillers in resin composites for high-tech applications, such as in dentistry. In dentistry silanes are also used in the bonding of porcelain with resin composites, repair of ceramics and metals, bonding of metals and ceramics to resin composites and a number of other applications [5-7].

Silanes are derivatives of silicon compounds and they contain Si-C and Si-H bond(s). Si and C are interestingly from the same periodic element group 14 (previously IV A) which includes carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Out of which carbon and silicon are the two most important elements for living things [8]. Silanes are, in general, synthetic organic-inorganic silicon compounds which have the synergic property of bi-functionality which enables promotion of adhesion between two chemically dissimilar materials [9-12]. Silanes are also of two main types, *viz.* functional and non-functional silanes. Functional silanes contain two functional end groups that can react with organic and inorganic surfaces, respectively. Silica-based ceramics are one of the most utilized (inorganic) substrates and resin composites are the (organic) material, which are unified to each other by the use of silanes, leading to the adhesion of two chemically different materials [8, 9]. Non-functional silanes have only reactive groups which react with the hydroxyl groups of the inorganic substrate. These types of silanes are used for special purposes, *e.g.,* coatings. Other types of silanes include the so-called bis-functional silanes (also known as bis-silanes) or cross-linking
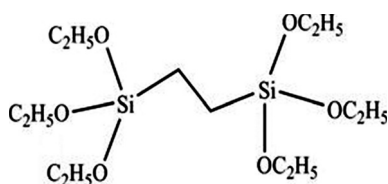
**Figure 1** Example of bis-silane, bis-1, 2-(triethoxysilyl) ethane [1].
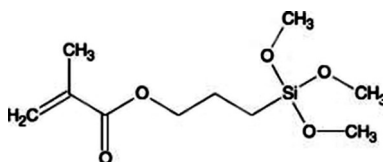
Figure 2 Molecular structure of 3-methacryloxypropyltrimethoxysilane [1].

silanes. They can have *e.g.,* two Si atoms in the molecular backbone and with three hydrolysable alkoxy groups (usually ethoxy) as shown in Figure 1 [8, 9].

Such silanes are mainly used in steel and tire industry and also a few laboratory research studies have shown them to increase the adhesion of resin composites to titanium and zirconia substrates [9, 13, 14]. As most of the coupling agents are not completely reactive as such, they need to be activated by the process of hydrolysis before they can adsorb on the surface of the substrate. One of the most commonly used silane is 3-methacryloxypropyltrimethoxysilane (MPS) and its structure is shown in Figure 2 [1]. This molecule has a very reactive methacrylate group at the end of the backbone, which provides good chemical reactivity in particular with other acrylic based dental materials [15-17].

MPS has to be pre-hydrolyzed before use. It should be noted that these silanes may have a relatively shorter shelf-life if they are kept in a pre-hydrolyzed form. But this pre-hydrolyzed form of silane has a very short shelf-life and should not be used after becoming milky, so now the silanes are also supplied as two-bottles systems commercially. When needed, the unhydrolyzed silane dissolved in ethanol is mixed with water and some acetic acid solution is added to hydrolyze it before its application (normally one coat) on the substrate (Figure 3) [8, 9]. Nevertheless, there is no international standard about the shelf-life after acid mixing or even after opening the bottle. Every company has its own indication of usage and thus should be followed accordingly by each user, be it in dental laboratories or at chair-side. Further research in this regard is necessary.
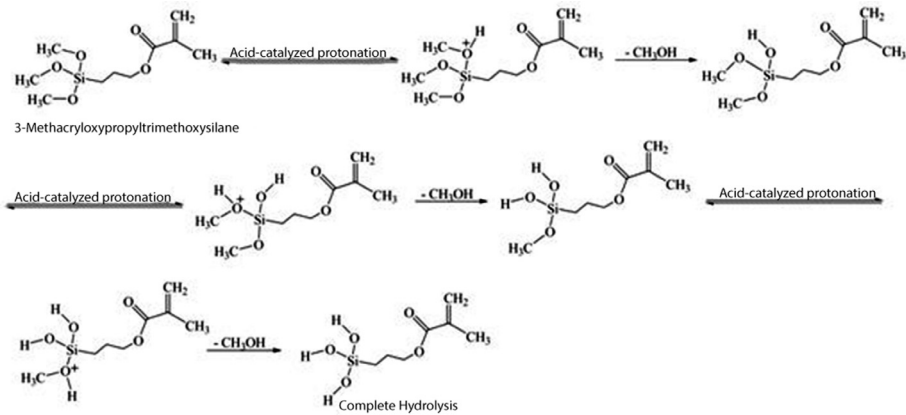
Figure 3 Silane hydrolysis reaction mechanism in an acidic medium, using 3-methacryloxypropyltrimethoxysilane as an example.

Silanes which intrinsically are nontoxic have a wide range of uses in dentistry, biomedicine and other fields. This said, the main function of silanes remains the promotion of union of dissimilar materials together.

In dentistry the silanes find their use in bonding the resin based composites to silica coated zirconia, acid-etched porcelain, other silica-coated substrates such as base metal and noble metal alloys, titanium and even Ag-amalgam [11, 12, 16, 17]. Another use in dentistry is the application of silanes for bonding glass-based fillers of various sizes to a resinous matrix to form the resin composites used in restorative dentistry (filling materials) and luting cements. Thus, the mechanical properties, such as fracture toughness and hardness of the material are significantly enhanced. As a relatively new group of dental materials, silanized E-glass fibers are being used to increase the strength of fiber reinforced resin composites (FRCs), and are mainly used in removable prostheses, periodontal splinting and in some new filling materials [8, 18-21]. Silanes are also used in the intraoral repair of fractured/chipped ceramics, composite veneers, and Ag-amalgam [11, 12, 22, 23]. In another study, rebonding of resin cement to ceramic brackets (mainly zirconia) was found to have higher shear bond strength but high ceramic fracture rates after storage and thermocycling were observed because of the hydrolytic instability of silanes [24]. Using a new commercial silane primer containing three components, namely methacrylate silane, phosphoric acid methacrylate and sulfide methacrylate, the authors [24] tried to explain the higher adhesion between alumina brackets and adhesive, by the presence of lowly soluble phosphate layer on the bracket. This can be attributed to the phosphoric acid methacrylate present in the commercial silane. Despite silane being a conventional coupling agent used in dentistry, the nomenclature of silanes should not be confused with the new generation of coupling agents, in which [24] the "silane" should be referred to a coupling agent

mixture that contains MPS and a phosphate monomer. Essentially the authors [24] are wrong and confusing the scientific community. Therefore, a generalized (re) definition about the terminologies is necessary.

A particular group of novel dental materials are E-glass fiber reinforced composites (FRCs). E-glass fibers are fibrous materials containing very thin silanized fibers embedded into a resinous matrix to form a composite material. These materials have a high fracture resistance because of the high amount of fibers present in them and thus it is difficult for the crack to propagate through them and these fibers act as reinforcing agents in the material. Such materials have a wide range of applications in dentistry especially the novel resin composite materials and also in prosthetic dentistry where they are used as denture base polymers and the multi-directional fibers present in them can help eliminate fractures and these materials are also used to make dentures. In addition, E-glass fibers are hydrolytically stable because they do not practically dissolve in water in observable quantities. Various silane coupling agents have been screened and evaluated by Matinlinna and co-workers [25, 26] in FRCs to adhere the glass fibers to the polymer matrices and it was concluded that the mechanical properties of the materials weakened after aging in water storage, this may be because silanes are unstable in aqueous media. Some other coupling agents which are more hydrolytically stable might be incorporated into E-glass fibers to provide better mechanical properties and durable adhesion of dissimilar materials.

In the medical field, silanes can be used to provide longevity to the hip replacement prostheses, when the head and neck of the femur are formed from a base metal alloy (Co-Cr or $TiAl_6V_4$). The neck part can be silica-coated and can be silanized for adhesion to the socket of the hip bone by bone cement. These two parts are to be cemented by bone cement, but this raises an issue due to the hydrolytic environment. This can either be prevented by pre-coating the metal with *poly*(methyl methacrylate) as reported with various studies [8, 27, 28]. Another way of doing this is to first coat the metal with a silica layer and then silanize it as reported in [8]. Interestingly, silanes may also prevent the formation of biofilms which reduce the adhesion of the biomedical implants to the body tissues, and in addition, silanes have also been used as carriers in the field of drug delivery [8, 29-33]. Industrial uses of silanes include significantly enhanced mechanical properties of fiber reinforced resin composites by promoting adhesion. Such composites are used in the construction of spaceships, automobiles, aircraft, construction materials and different electronic products and even to prevent corrosion of certain metals and alloys [8, 25, 34]. The toxic hexa-valent chromium based coupling agents (*i.e.* chromates) were replaced by biocompatible and non-toxic silane coupling agents in the steel and tire industry as reported by van Ooij *et al.* [34]. Silanes are not only biocompatible in the oral environment but are also found to be non-toxic by different laboratory experiments [35]. Thus, silanes have a large application in the field of biomedicine and biomedical materials.
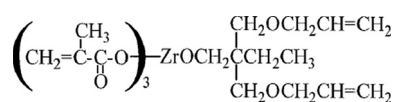
One of the main drawbacks when resin composites are bonded to prostheses is the loss of adhesion or degradation of bonding under aging. This indicates hydrolytic instability of commercial silanes (*e.g.,* MPS) [8, 36]. The silane coupling agents have been found to be very good for silica based (or hydroxyl groups containing surfaces) materials but the adhesion for non-silica based materials or some metals (*e.g.,* Mg, Ca) has not been found to be adequate at all. A solution to this has been found by conditioning the surface of the material by adding silica content, *e.g.,* by tribochemical silica coating after which the rough surface is wetted with the silane solution resulting in a more durable bonding of the materials by combined chemical and micro-mechanical adhesion [9].

Development of a hydrolytically stable silane material is the direction for the ongoing research and it may increase the durability of adhesion between dental materials in the oral environment.

Ceramic restorations are bonded to the tooth or other dental materials after surface treatments, such as either by the chemical action of hydrofluoric acid (HF) for silica-based ceramic materials and lately very commonly used method of tribochemical silica-coating method for non-silica based ceramics like zirconia. As the next step, they are treated with silane for the bonding (cementation) step. However, the main shortcoming is the hydrolytic instability of silane-based bonding in the harsh oral environment [37]. Due to this the failure takes place at the interface and leads to clinical problems, such as marginal leakage and secondary caries. This is why the quest for more hydrolytically stable coupling agents is ongoing. Zirconate, phosphate, thiol, titanate based coupling agents which may have the potential to be more hydrolytically stable and thus they are being investigated to provide a durable bonding between the resin cements and the metal/ceramic indirect restorations.

3   Zirconate Coupling Agents

Zirconate coupling agents, *i.e.,* organozirconium compounds, have been studied extensively for coupling zirconium and ZrO_2. They increase bonding between the zirconia substrate and resin composite in the same manner as silanes by bonding with their hydroxyl groups to ZrO_2 [37-40]. Zirconate coupling agents are considered to be more hydrolytically stable and have been used to increase the adhesion between the two dissimilar components in the composite material. Also, zirconates have been found to be non-toxic to the osteoblasts and, therefore, can be considered for bonding of zirconia to resin composite materials [38]. The chemical modifications of the ceramic surfaces are mainly focused on the application of zirconate coupling agents with resin composites, which give a good, stable bond by association of chemical bonding with mechanical bonding when compared with only chemical bonding [41]. Zirconate coupling agents along with phosphate adhesives are also said to have good chemical bonding property with metal oxides

$$\left(CH_2=\overset{CH_3}{\underset{O}{C}}-\overset{}{\underset{}{C}}-O \right)_3 -ZrOCH_2\overset{CH_2OCH_2CH=CH_2}{\underset{CH_2OCH_2CH=CH_2}{CCH_2CH_3}}$$

Figure 4 General structure of zirconate coupling agent [39].

and react well with hydroxyls at the surfaces and thus can create durable adhesion with luting cements [41, 42]. Some of the pioneering studies using zirconate coupling agents were their use as a coupling agent between dental enamel and polymer filler [39] and between zirconia and resin cement by Cheng *et al.* [38]. Also, a very low weight percentage of zirconate in the resin composite material has shown to increase the adhesion between the inorganic and organic phases of dental composite material [40] and thereby reducing the amount of resin and being cost effective as well. Zirconates can be combined with polymers to obtain thereby materials with increased hydrolytic stability. Zirconates can be used for surface modification and thus can also be considered to not only increase the mechanical properties but also to reduce the moisture uptake [42].

Although zirconate coupling agents as shown in Figure 4 [38] increase the bond strength of the resin cements to zirconia, highly decreased bond strength was observed after thermo-cycling the test specimens [37]. Nevertheless, some studies have found that a mix of the acidic 10-methacryloxydecyl dihydrogen phosphate (MDP) and a zirconate coupling agent (2,2-di(allyloxymethyl) butyl trimethacryloyl zirconate) primer increased the bond strength between the resin cement and the zirconia substrate and was clinically found to be quite effective and durable [39, 40]. The ratio of such a mix is unknown, but the blend of various functional and non-functional coupling agents might be a good strategy for a synergistic effect and thus to improve the bonding performance.

In biomedicine, zirconate coupling agents have been found to increase adhesion in biodegradable implants by acting as an adhesive between hydroxyapatite crystals and the polymer matrix. During the last few years, hydroxyapatite incorporated into high density polyethylene has been used in the orthopedics. The incorporation of hydroxyapatite is obviously for biointegration and could also be used as a filler for improvement of mechanical properties. When the fillers were treated with a zirconate coupling agent at a particular weight ratio it increased the mechanical properties of the composite materials through better adhesion between the polyethylene matrix and the filler particles [43]. Hence, as in dental resin composites, if zirconia is used as a filler material, zirconate could be used as a coupling agent between the resin and zirconia which might possibly increase the strength of resin composites. More testing is necessary in this regard.

In industry, zirconate coupling agents find numerous applications such as in printing inks, lithographic printing plates, aluminum beverage cans, pigment coatings on titanium materials, and enhancement in the toughness of thermoplastics [42].

In dentistry, zirconate coupling agents have been studied and investigated only very sparingly so far. The zirconates can be modified according to their requirement in dentistry to increase the adhesion of organic and inorganic phases in the dental materials but can also help in increasing the adhesion of the ceramic prosthetic dental materials to metal prostheses. Zirconates possess the potential to provide the restorations a longer clinical service life by being hydrophobic under natural aging in the oral cavity.

4   Phosphate Coupling Agents

The first study in dentistry showing the durability of the shear bond strength between phosphate containing resin composites and ZrO_2 was done by Kern and Wegner [44]. 10-Methacryloxydecyl dihydrogen phosphate (MDP) shown in Figure 5 [45] has been widely studied and considered to be a very promising primer for the bonding of ceramic substrates to resin composites. The functional group of the MDP bonds with the metal oxide surfaces by chemical bonding mechanism along with secondary forces (or hydrogen bonds) at the interface between the ceramics and resins [46-48]. It was further established that the MDP-based resin cements could be used for the final cementation of the ZrO_2-based restorations in clinical practice [49]. The recent research has focused on improving bonding with MDP-based monomers as they are very stable in hydrolytic environment over long periods [37].

With the good chemical bonding of 10-methacryloxydecyl dihydrogen phosphate coupling agent to zirconia substrate there have been a few studies which have shown adhesion failure [22, 41, 49, 51]. It has been suggested that the possibility of using zirconate coupling agents instead of silanes and 10-methacryloxydecyl dihydrogen phosphate might be worth further studies [38, 42].

10-Methacryloxydecyl dihydrogen phosphate coupling agent has also been found to enhance the bonding of different alloys, such as chromium-titanium, nickel-chromium and cobalt-chromium alloys with resin composites. Thus, it can have a high potential in increasing the bonding between zirconia and resin composites [38]. Ikemura *et al.* explained the hypothetical bonding mechanism of phosphate monomers by stating that phosphonic acid monomer 6-methacryloxyhexyl phosphonoacetate (6-MHPA) (Figure 6) [51], and 6-methacryloxyhexyl 3-phosphonopropionate (6-MHPP) (Figure 6) [51] ionize by the water present on
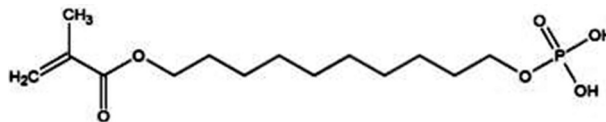
Figure 5 Chemical structure of 10-methacryloxydecyl dihydrogen phosphate (MDP) [45].
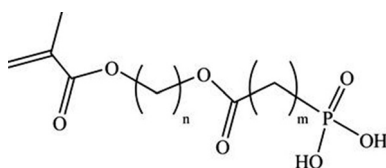
**Figure 6** General structure for both MHPA and 6-MHPP molecules [51].

the surface of the ceramic and then penetrate into the micro-spaces in the substrate. Next, chemical bonds form first via hydrogen bonds and with the polymerization of resin composites with light irradiation, forming stronger bonds at the interface of resin composite and substrate [52]. Two primers were recently introduced in the dental market out of which one primer was methacrylate with a thiophosphoric acid moiety (MEPS) and the other primer was a combination of 10-methacryloxydecyl dihydrogen phosphate (MDP) and 6-(4-vinylbenzyl-n-propyl)-amino-1,-3,-5-triazine-2,-4-dithiol (VBATDT) which showed in the infrared spectroscopic studies that the phosphate groups of the MDP were adsorbed on the silver substrate thus giving quite a strong bonding. These types of coupling agents can provide good bonds between noble metal alloys and polymeric materials [53].

10-Methacryloxydecyl dihydrogen phosphate coupling agent even with high hydrolytic stability has been considered to be unstable under artificial aging [48, 54-56]. This is because its hydrolytic stability has been found to be less than the baseline which has been set up by silane coupling agents. Therefore, these bonding agents have to be looked into more detail and extensive study is necessary.

5 Thione/thiol Coupling Agents

Primers containing thione/thiol monomers form chemical bonds with precious (noble) metals and have the tendency to form a good bond to gold, gold alloys, silver alloys and gold-silver-palladium alloys. The methacrylate based monomers with sulfur atoms in the backbone are also used as primers for bonding noble metals and their alloys [52, 57]. When the sulfur based primers are combined with some other acidic monomers they impact positively the bonding efficacy of that substrate to resinous materials.

Bonding by sulfur containing primers to some noble metals may be due to the formation of a monolayer by self-assembly of thiol (-SH) groups. A recent study carried out on a thiol-based primer stated that the application of the mixture of 6-(4-vinylbenzyl-n-propyl)-amino-1,-3, 5-triazine-2,4-dithiol (VBATDT) as shown in Figure 7 [58] and 10-methacryloxydecyl dihydrogen phosphate even after thermocycling exhibited good bond strength between a gold-palladium-copper-silver alloy and titanium [52]. This observation was further confirmed by a study using
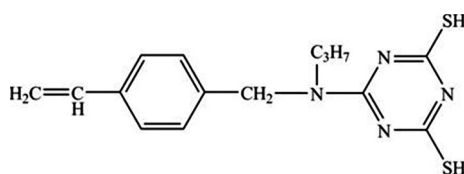
Figure 7 Structural formula of VBATDT [58].

a commercially available primer containing 6-(4-vinylbenzyl-n-propyl) amino-1,-3,-5-triazine-2,-4-dithiol and MDP which showed increased bond strength of not only precious metals but also non-precious metals [57, 59].

It has also been reported that the effect of sulfur-based primers on the enhancement of the bond strength to the metals is not as much as that of phosphates [56]. In addition, some studies have reported a high percent loss of bond strength after artificial aging and the increase in bond strength can vary depending on the substrate (adherend) [59-61]. Thus, further work is required on this topic as sulfur-based primers look favorable in the future to potentially act as good coupling agents.

6   Titanate Coupling Agents

Coupling agents form an interfacial unifying layer between two dissimilar materials. They promote the adhesion between the organic matrix and filler particles in dental resin composites. In addition, the biomechanical properties of the dental composites mainly depend on how the masticatory forces are transferred through the matrix to the reinforcing filler particles and thus, the bonding of the resin and filler particles is of primary importance and can be provided only by appropriate coupling agents [62]. As mentioned above, the coupling agents should be hydrolytically stable, should not deteriorate in an aqueous environment, and provide a waterproof bond at the interface of the two dissimilar materials [63]. In some commercial products, titanium dioxide has been incorporated as a filler material and it seems that titanate could bond dissimilar fillers and resins. However, very limited information is available about the titanates and more extensive investigations are needed.

The titanate coupling agents *i.e.,* tetravalent organo-titanium compounds, may form an organic reactive monomolecular layer on the inorganic surface of the substrate by reacting with the free protons of the hydroxyls at the inorganic interfacial surface. Ti at the molecular center undergoes reorganization and reshuffling enabling itself to act either as a proton donor or acceptor [64, 65], thus when introduced into a polymeric system it not only increases the bonding but also reduces the brittleness of the material [44]. The formation of -Ti-O-Ti-O- bonds leads to hydrophobicity of the substrate material. The chelate titanates, as the name

implies, have a chelating function, attract filler protons more than water and are more hydrolytically stable than the alkoxide titanates which are more reactive in a moist environment and undergo hydrolysis quickly [63].

Titanates, the general formula of which is shown in Figure 8 [66], when used as a coupling agent in dental composites lead to an increase in their mechanical properties. This has been investigated [67-71], and it has been reported that mainly the increases in the tensile strength and the impact strength of the dental composites by using titanate coupling agents occur. Another study incorporated a titanate coupling agent into a composite which was a blend of polypropylene and two types of calcium carbonates. It was concluded that the titanate coupling agent increased the mechanical properties of the composite material due to the good adhesion between the filler and the matrix. The loading of the coupling agents should be properly investigated to obtain the desired effect of the coupling agent [65]. Different loading ratios of coupling agents can have different effects on the mechanical properties of the materials [62, 64] in that the Young's modulus of the composite increased when two materials were compared, out of which one was treated with the titanate coupling agent and the other not. Along with the increase in the modulus, the dispersion of fillers was better, which was another factor for an increase in the Young's modulus [62]. One more study on a talc-epoxy composite reported an increase in the flexural strength of the composite material when the talc was treated with a titanate as compared to the composite material in which talc was treated with a silane coupling agent [62].

Titanate coupling agents also changed the ferrite powder surface from hydrophilic to hydrophobic by the interaction of the Ti-O bond of the titanate with the Fe-OH bond forming a hydrophobic Ti-O-Fe layer on the surface and thereby increasing adhesion between the hydrophobic resin and ferrite powders [72]. Polybutadiene rubber/clay and nylon 6/mica composites showed superior mechanical properties when the fillers were treated with titanate coupling agents. This was because such titanates increased the adhesion of the matrix to the filler [65].

A definite conclusion has not yet been drawn as to what an optimum loading amount of a coupling agent should be, in order to bring about the required result in the material properties. Therefore, a more systematic approach should be taken for a final say regarding the use of titanates as coupling agents in modern dental applications.
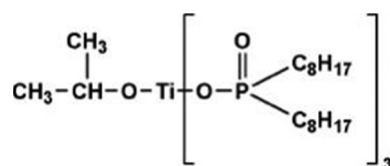

Figure 8 A general titanate structure [66].

7 Zircoaluminate Coupling Agents

Zircoaluminates are low molecular weight compounds and they are more hydrophobic than silanes and titanates [73]. Since their introduction in 1985 by Cohen [74, 75] who studied zircoaluminates as coupling agents and a surface modifier, zircoaluminates have been found to be applicable in different industrial applications as a coupling agent in plastics, rubbers, coatings, pigment and adhesives. They are also used as surface modifiers for certain metal surfaces and as corrosion resistant agents for materials which require a long exposure time to moisture [75-77]. Zircoaluminates are currently being used for enhancing the physical properties of paper and the treatment of TiO_2 with a zircoaluminate coupling agent results in improved optical properties and better print quality in the paper industry [73, 78].

These materials have not yet been studied extensively in the field of dentistry, although this type of coupling agent looks very promising. Nonetheless, nothing can be said until they have been studied thoroughly as to whether they fulfill all the criteria required by the coupling agents.

8 Other Coupling Agents

Lung *et al.* [54] carried out experiments with three different coupling agents, 2-hydroxyethyl methacrylate, oleic acid and itaconic acid (the latter two are carboxylic acids) and compared them with two different types of silane coupling agents. They concluded that even these types of coupling agents did not give better properties to the materials when compared with silane treated materials. However, these coupling agents were hydrolytically more stable, provided mechanical properties in the acceptable range prescribed by ISO standards, had a longer shelf-life and are much cheaper than the competitive silanes. These coupling agents have currently also been found to have a number of applications in different fields/industries. For example, they have been used as a surface modifier in oily wastewater treatment, in contact lenses, in paper industry, and in shampoos and detergents. Some of them are used in a drug delivery system for keloid and hypertrophic scarring, corrosion protection of steel and in many other applications [53]. These cost-effective coupling agents could be further investigated and optimized according to the required applications and modified accordingly for their use.

It cannot be stressed enough how important adhesion is in dentistry, but also in all aspects of life. Virtually all the adhesives or coupling agents which have been used are synthetic. Interestingly, very recently natural marine mussels and their adhering ability are being studied as they have one of the best adhesive qualities and, more importantly, they are from an aquatic environment. This said, they are understood to be hydrolytically very stable and are not vulnerable in the aqueous environment. Hamming *et al.* [79] mimicked the marine mussel's foot protein and carried out the pull-out test between NiTi and Ti-6Al-4V wires and *poly*(methyl methacrylate) using this mussel adhesive. The results indicated an increase in the

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adhesive property [79]. In fact, the mussel adhesive property relies on the repeated 3, 4-dihydroxy-L-phenylalanine (L-DOPA) motif from food protein. Inspired by this, Zhou *et al.* [80] were successful in using the decarboxylated derivative 3, 4-dihydroxyphenethylamine (dopamine, DOPA) to remineralize the human teeth hydroxyapatite *in vitro*. Thus, this material has been found to be one of the best adhesives occurring naturally, also giving the remineralization of the natural tooth and can be further modified and used according to the requirements in dentistry.

Table 1 presents bond strength results obtained using various coupling agents in selected studies.

Table 1 Bond strength results obtained using various coupling agents from selected studies.

Coupling agents	Substrates	Reportedly bonded to	Shear bond strength (SBS) MPa with SD	References
Silane coupling agents				
3-isocyanatopropyl-trimethoxysilane	Zirconia	Resin composite	6.6 (2.6)	14
3-isocyanatopropyl-triethoxysilane	Zirconia	Resin composite	6.6 (2.2)	14
3-methacryloxypropyl-trimethoxysilane	Zirconia	Resin composite	12.1 (2.9)	54
3-acryloxypropyl-trimethoxysilane	Zirconia	Resin composite	14.6 (1.1)	54
3-trimethoxysilylpropyl-trimethoxysilane	Zirconia	Resin cement	16.6 (2.6)	46
3-acryloxypropyl-trimethoxysilane + cross-linking silane	Titanium	Resin composite	14.6 (2.9)	36
3-isocyanatopropyl-triethoxysilane	Titanium	Resin composite	12.5 (5.8)	81
Phosphate coupling agents				
10-methacryloxydecyl dihydrogen phosphate (MDP)	Pure zirconium	Resin luting cement	52.7 (2.7)	39
10-methacryloxydecyl dihydrogen phosphate (MDP)	Zirconia	Resin luting cement	49.2 (4.0)	39

Table 1 cont.

Coupling agents	Substrates	Reportedly bonded to	Shear bond strength (SBS) MPa with SD	References
Thiol coupling agents				
6-(4-vinylbenzyl-n-propyl)amino-1,3,5-triazine-2,4-dithione tautomer	Ag-Pd-Cu-Au alloy	Resin composite	13.0 (1.4)	59
6-(4-vinylbenzyl-n-propyl)amino-1,3,5-triazine-2,4-dithione tautomer	Stainless steel	Luting cement	33.4 (3.6)	82
Zirconate coupling agents				
2,2-Di(allyloxymethyl) butyl trimethacryloyl zirconate	Zirconia	Resin luting cement	30.7 (3.2)	39
2,2-Di(allyloxymethyl) butyl trimethacryloyl zirconate	Pure zirconium	Resin luting cement	37.4 (3.8)	39

Conclusion

It is fair enough to say that many different coupling agents, especially silanes, have been studied extensively but still at this point we do not have a single coupling agent which can be universally used on all substrates and which fulfills all the criteria which are necessary for a coupling agent to function properly. This can be difficult, so more focus should be on at least finding one coupling agent which is good enough for a single substrate to be used either in restorative, prosthetic or other branches of dentistry but which is hydrolytically stable. A lot has been done but as it is said nothing is ever enough. Therefore, still a lot can be done and should be done to develop much better performing coupling agents. The question may be: How to overcome the detrimental and inevitable effects of water aging?

References

1. J.P. Matinlinna, J.R. Dahl, S. Karlsson, L.V.J. Lassila, and P.K. Vallittu, The effect of the novel silane system on the flexural properties of E-glass fiber-reinforced composites for dental use, in *Silanes and Other Coupling Agents*, Vol. 5, K.L. Mittal (Ed.), pp. 107–121, CRC Press, Boca Raton, FL. (2009).

 2. B.W. Darvell, *Materials Science for Dentistry*, 9th edition, pp. 115–146, Woodhead Publishing Limited, Cambridge, U.K. (2009).
 3. A.D. Wilson and B.E Kent, The glass-ionomer cement: A new translucent dental filling material. *J. Appl. Chem. Biotechnol*. **21**, 313–318 (1971).
 4. A.D. Wilson and B.E Kent, A new translucent cement for dentistry: The glass ionomer cement. *Brit. Dental J*. **132**, 133–135 (1972).
 5. J.P. Matinlinna, M. Özcan, L.V.J. Lassila, and P.K. Vallittu, Applications of trialkoxysilanes in dental biomaterials: A review, in *Silanes and Other Coupling Agents*, Vol. 4, K.L. Mittal (Ed.), pp. 199–215, CRC Press, Boca Raton, FL. (2007).
 6. J.G. Marsden, in *Handbook of Adhesives*, I. Skeist (Ed.), pp. 536–548. Van Nostrand-Reinhold, New York (1990).
 7. B. Arkles, Silane esters, in *Kirk-Othmer Encyclopedia of Chemical Technology*, K. Othmer (Ed.), pp. 69–81. Wiley, London (1997).
 8. C.Y.K. Lung and J.P. Matinlinna, Silanes for adhesion promotion and surface modification, in *Silane Chemistry, Applications and Performance*, K. Moriguchi and S. Utagawa (Eds.), pp. 87–109, Nova Science Publisher, Hauppage, NY. (2013).
 9. C.Y.K. Lung and J.P. Matinlinna, Aspects of silane coupling agents and surface conditioning in dentistry: An overview. *Dental Mater*. **28**, 467–477 (2012).
10. E.P. Plueddemann, *Silane Coupling Agents*, 2nd edition, Plenum Press, New York (1991).
11. G.W. Ho and J.P. Matinlinna, Insights into ceramics as dental materials. Part I: Ceramic material types in dentistry. *Silicon* **3**, 109–115 (2011).
12. G.W. Ho and J.P. Matinlinna, Insights into ceramics as dental materials. Part II: Chemical surface treatments. *Silicon* **3**, 117–123 (2011).
13. U. Gbureck, A. Masten, J. Probst, and R. Thull, Tribochemical structuring and coating of implant metal surfaces with titanium oxide and hydroxyapatite layers. *Mater. Sci. Eng. C* **23**, 461–465 (2003).
14. C.Y.K. Lung and J.P. Matinlinna, Resin bonding to silicatized zirconia with two isocyanatosilanes and a cross-linking silane. Part I. Experimental. *Silicon* **2**, 153–161 (2010).
15. J.P. Matinlinna, J.K-H. Tsoi, J. de Vries, and H.J. Busscher, Characterization of novel silane coatings on titanium implant surfaces. *Clin. Oral Implant Res*. **24**, 688–697 (2013).
16. C.Y.K. Lung, E. Kukk, T. Hägerth, and J.P. Matinlinna, Surface hydroxylation of silica-coated zirconia by various chemical treatments. *Appl. Surface Sci*. **257**, 1228–1235 (2010).
17. J.P. Matinlinna, L.V.J. Lassila, M. Özcan, A. Yli-Urpo, and P.K. Vallittu, An introduction to silanes and their clinical applications in dentistry. *Int. J. Prosthodont*. **17**, 155–164 (2004).
18. F.C. Eichmiller, Titanium applications in dentistry. *J. Am. Dental. Assoc*. **134**, 347–349 (2003).
19. M. Sharma, A.V.R. Kumar, N. Singh, N. Adya, and B. Saluja, Electrochemical corrosion behavior of dental/implant alloys in artificial saliva. *J. Mater. Eng. Performance* **17**, 695–701 (2008).
20. J.H. Lee, C.M. Um, and I.B. Lee, Rheological properties of resin composites according to variations in monomer and filler composition. *Dental Mater.* **22**, 515–526 (2006).
21. M. Zhang and J.P. Matinlinna, The effect of resin matrix composition on mechanical properties of E-glass fiber reinforced composite for dental use. *J. Adhesion Sci. Technol.* **25**, 2687–2701 (2011).

22. M.B. Blatz, A. Sadan, J. Martin, and B. Lang, In vitro evaluation of shear bond strengths of resin to densely sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling. *J. Prosthetic Dentistry* **91**, 356–362 (2004).

23. J.P. Matinlinna and P.K. Vallittu, Silane based concepts on bonding resin composite to metals. *J. Contemp. Dental Pract.* **8**, 1–8 (2007).

24. F. Falkensammer, E. Jonke, M. Bertl, J. Freudenthaler, and H.P. Bantleon, Rebonding performance of different ceramic brackets conditioned with a new silane coupling agent. *European J. Orthodontics* **35**, 103–109 (2013).

25. M. Zhang and J.P. Matinlinna, E-glass fiber reinforced composites in dental applications. *Silicon* **4**, 73–78 (2012).

26. J.P. Matinlinna, J.E. Dahl, L.V.J. Lassila, and P.K. Vallittu, The effect of trialkoxysilane coupling agent coatings on E-glass fibers on the flexural properties of fiber-reinforced composites, in *Silanes and Other Coupling Agents*, Vol. 4, K.L. Mittal, (Ed) pp. 83–97, CRC Press, Boca Raton, FL. (2007).

27. R.T. Muller and N. Schurmann, Shear strength of the cement metal interface: An experimental study. *Arch. Orthopaedic Trauma Surgery* **119**, 133–138 (1999).

28. S. Raab, A.M. Ahmed, and J.W. Provan, Thin film PMMA precoating for improved implant bone-cement fixation. *J. Biomed. Mater. Res.* **16**, 679–704 (1982).

29. H.J. Erli, R. Marx, O. Paar, F.U. Niethard, M. Weber, and D.C. Wirtz, Surface pretreatments for medical application of adhesion. *BioMedical Engineering OnLine* **2**, 15–33 (2003).

30. T. Mumme, R. Marx, R. Müller-Rath, C.H. Siebert, and D.C. Wirtz, Surface coating to improve the metal-cement bonding in cemented femur stems. *Arch. Orthopaed Trauma Surgery* **128**, 773–781 (2008).

31. J.W. Costerton, P.S. Stewart, and E.P. Greenberg, Bacterial biofilms: A common cause of persistent infections. *Science* **284**, 1318–1322 (1999).

32. P.S. Stewart and J.W. Costerton, Antibiotic resistance of bacteria in biofilms. *Lancet* **358**, 135–138 (2001).

33. E. Allemann, R. Gurny, and E. Doelke, Drug-loaded nanoparticles – Preparation methods and drug targeting issues. *Eur. J. Pharm.* **39**, 173–191 (1993).

34. W.J. van Ooij, D. Zhu, S. Prasad, S. Jayaseelan, Y. Fu, and N. Teredesai, Silane based chromate replacements for corrosion control, paint adhesion and rubber bonding. *Surface Eng.* **16**, 386–396 (2000).

35. B. Arkles, Look what you can make out of silicones. *Chemtech* **13**, 542–555 (1983).

36. J.P. Matinlinna and L.V. Lassila, Experimental novel silane system in adhesion promotion between dental resin and pretreated titanium. Part II: Effect of long term water storage. *Silicon* **2**, 79–85 (2010).

37. J.Y. Thompson, R.B. Stoner, J.R. Piascik, and R. Smith, Adhesion/cementation to zirconia and other non-silicate ceramics: Where are we now? *Dental Mater* **27**, 71–82 (2011).

38. H.C.K. Cheng, J.K-H. Tsoi, R.A. Zwahlen, and J.P. Matinlinna, Effect of silica-coating and a zirconate coupling agent on shear bond strength of flowable resin–zirconia bonding. *Intl. J. Adhesion Adhesives* **50**, 11–16 (2014).

39. K. Yoshida, Y. Tsuo, and M. Atsuta, Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler. *J. Biomed. Mater. Res. Part B* **77**, 28–33 (2006).

40. A.N. Cavalcanti, R.M. Foxton, T.F. Watson, M.T. Oliveira, M. Giannini, and G.M. Marchi, Y-TZP ceramics: Key concepts for clinical application. *Operative Dentistry* **34**, 344–351 (2009).

41. J.R. Piascik, S.D. Wolter, and B.R. Stoner, Enhanced bonding between YSZ surfaces using a gas-phase fluorination pretreatment. *J. Biomed. Mater. Res. B* **98**, 114–119 (2011).

42. J.D.C. Wong, C.Y.K. Lung, J.K-H. Tsoi, and J.P. Matinlinna, Effects of a zirconate coupling agent incorporated into an experimental resin composite on its compressive strength and bonding to zirconia. *J. Mechanical Behavior of Biomedical Materials* **29**, 171–176 (2014).

43. A. Carmen, P. Rosestela, K. Arquimedes, G. Gema, D. Nohemy, S. Yanixia, and B.J. Luis, Characterization of HDPE/HA composites treated with titanate and zirconate coupling agents. *Macromol. Symp.* **247**, 190–198 (2007).

44. M. Kern and S.M. Wegner, Bonding to zirconia ceramic: Adhesion methods and their durability. *Dental Mater.* **14**, 64–71 (1998).

45. N. Moszner, U. Salz, and J. Zimmermann, Chemical aspects of self-etching enamel-dentine adhesives: A systemic review. *Dental Mater.* **21**, 895–890 (2005).

46. S. Sanohkan, B. Kukiattrakoon, N. Larpboonphol, T. Sae-Yib, T. Jampa, and S. Manoppan, The effect of various primers on shear bond strength of zirconia ceramic and resin composite. *J. Conservative Dentistry* **16**, 499–502 (2013).

47. M. Kern, A. Barloi, and B. Yang, Surface conditioning influences zirconia ceramic bonding. *J. Dental Res.* **88**, 817–822 (2009).

48. R. Tanaka, A. Fujishima, Y. Shibata, A. Manabe, and T. Miyazaki, Cooperation of phosphate monomer and silica modification on zirconia. *J. Dental Res.* **87**, 666–670 (2008).

49. S.M. Wegner and M. Kern, Long-term resin bond strength to zirconia ceramic. *J. Adhesive Dentistry* **2**, 139–147 (2000).

50. H. Matsumura, H. Shimizu, N. Tanoue, and H. Koizumi, Current bonding systems for resin-bonded restorations and fixed-partial dentures made of silver-palladium–copper-gold alloy. *Japanese Dental Sci. Review* **47**, 82–87 (2011).

51. K. Ikemura, T. Fujii, N. Negoro, T. Endo, and Y. Kadoma, Design of a metal primer containing a dithiooctanoate monomer and phosphonic acid monomer for bonding of prosthetic light-curing resin composite to gold, dental precious and non-precious metal alloys. *Dental Mater. J.* **30**, 300–307 (2011).

52. K. Ikemura, H. Tanaka, T. Fujii, M. Deguchi, N. Negoro, T. Endo, and Y. Kadoma, Design of a new, multi-purpose, light-curing adhesive comprising a silane coupling agent, acidic adhesive monomers and dithiooctanoate monomers for bonding to varied metal and dental ceramic materials. *Dental Mater. J.* **30**, 493–500 (2011).

53. Y. Taira, H. Yanagida, H. Matsumura, K. Yoshida, M. Atsuta, and S. Suzuki, Adhesive bonding of titanium with a thione-phosphate dual functional primer and self-curing luting agents. *Eur. J. Oral Sci.* **108**, 456–460 (2000).

54. C.Y.K. Lung, M.G. Botelho, M. Heinonen, and J.P. Matinlinna, Resin zirconia bonding promotion with some novel coupling agents. *Dental Mater.* **28**, 863–872 (2012).

55. M. Özcan, H. Nijhuis, and L.F. Valandro, Effect of various surface conditioning methods on the adhesion of dual-cure resin cement with MDP functional monomer to zirconia after thermal aging. *Dental Mater. J.* **27**, 99–104 (2008).

56. Y. Taira and K. Kamada. Effect of primers containing sulfur and phosphate monomers on bonding type IV gold alloy. *J. Dentistry* **36**, 595–599 (2008).

57. H. Koizumi, T. Ishii, K. Naito, T. Yoneyama, N. Tanoue, and H. Matsumura, Effects of triazine dithione and hydrophobic phosphate monomers on bonding to Ag-Pd-Cu-Au alloy and titanium with a methacrylic resin-based luting agent. *J. Adhesive Dentistry* **12**, 215–222 (2010).

58. Y. Kadoma, Chemical structures of adhesion promoting monomers for precious metals and their bond strengths to dental metals. *Dental Mater. J.* **22**, 343–358 (2003).

59. H. Matsumura, K. Kamada, N. Tanoue, and M. Atsuta, Effect of thione primers on bonding of noble metal alloys with an adhesive resin. *J. Dentistry* **28**, 287–293 (2000).

60. H. Matsumura, T. Tanaka, and M. Atsuta, Bonding of silver–palladium–copper–gold alloy with thiol derivative primers and tri-n-butylborane initiated luting agents. *J. Oral Rehabilitation* **24**, 291–296 (1997).

61. A.J. Ireland and M. Sherriff, The influence of alloy copper content on the polymerisation of anaerobic adhesives. *J. Dentistry* **27**, 155–161 (1999).

62. M. Hussain, A. Nakahira, S. Nishijima, and K. Niihara, Effects of coupling agents on the mechanical properties improvement of the TiO_2 reinforced epoxy system. *Mater. Letters* **26**, 299–303 (1996).

63. N. Menon, F.D. Blum, and L.R. Dharani, Use of titanate coupling agents in Kevlar/ phenolic composites. *J. Appl. Polym. Sci.* **54**, 113–123 (1994).

64. J. Gonzalez, C. Albano, M. Ichazo, and B. Diaz, Effects of coupling agents on mechanical and morphological behavior of the PP/HDPE blend with two different $CaCO_3$. *European Polymer J.* **38**, 2465–2475 (2002).

65. W.L. Tham, W.S. Chow, and Z.A.M. Ishak, Effects of titanate coupling agent on the mechanical, thermal, and morphological properties of poly(methyl methacrylate)/ hydroxyapatite denture base composites. *J. Composite Mater.* **45**, 2335–2345 (2011).

66. S.J. Monte. Titanates and zirconates in thermoplastic and elastomer compounds, Kenrich Petrochemicals, Inc., Bayonne, NJ (USA), http://www.4kenrich.com/mediashare/5c/ igxaufc6j5ms5r2jci0xliywxyklhc-org.pdf.

67. C.D. Han and R. Shetty, Studies on multilayer film coextrusion II. Interfacial instability in flat film coextrusion, *Polym. Eng. Sci.* **18**, 180–186 (1978).

68. C.D. Han, T. Van Den Weghe, P. Shete, and J.R. Hav, Effects of coupling agents on the rheological properties, processability, and mechanical properties of filled polypropylene. *Polym. Preprints* **21**, 241–242 (1981).

69. P. Bajaj, N.K. Jha, and R.K. Jha, Effect of titanate coupling agent on mechanical properties of mica-filled polypropylene. *Polym. Eng. Sci.* **29**, 557–563 (1989).

70. S.N. Maiti and P.K. Mahapatro, Mechanical properties of i-PP/ $CaCO_3$ composites. *J. Appl. Polym. Sci.* **42**, 3101–3110 (1991).

71. Z.A.M. Ishak, H. Aminullah, H. Ismail, and H.D. Rozman, Effect of silane-based coupling agents and acrylic acid based compatibilizers on mechanical properties of oil palm empty fruit bunch filled high-density polyethylene composites. *J. Appl. Polym. Sci.* **68**, 2189–2203 (1998).

72. W-S. Chen, Y-L. Chang, H-I. Hsiang, F-C. Hsu, and F-S. Yen, Effects of titanate coupling agent on the dielectric properties of Ni-Zn ferrite powders–epoxy resin coatings. *Ceramics Intl.* **37**, 2347–2352 (2011).

73. B. Li, H. Mou, Y. Li, and Y. Ni, Synthesis and thermal decomposition behavior of zircoaluminate coupling agents. *Ind. Eng. Chem. Res.* **52**, 11980–11987 (2013).

74. L.B. Cohen, Aluminum zirconium metallo-organic complexes useful as coupling agents. U.S. Patent 4,539,048, assigned to Jos. Cavedon Company Inc. (1985).

75. L.B. Cohen, Zircoaluminate adhesion promoters. *J. Adhesion Sci. Technol.* **5**, 439–448 (1991).

76. A.R. Marrion, *The Chemistry and Physics of Coatings*, 2nd edition, Royal Society of Chemistry, Tyne and Wear, U.K. (2004).

77. J.I. Melzer and B.P. Gunagan, Process for enhanced drainage of residual aqueous rinse on the external surface of plastic parts. U.S. Patent 5,314,546 (May 24, 1994).

78. B. Li, Y-M. Li, and R-J. Lu, Effect of modified nanoTiO$_2$ on properties of coating and coated paper. *Chemical Industry and Engineering Society of China Journal* **61**, 228–234 (2010).

79. L.M. Hamming, X.W. Fan, P.B. Messersmith, and L.C. Brinson, Mimicking mussel adhesion to improve interfacial properties in composites. *Composites Sci. Technol.* **68**, 2042–2048 (2008).

80. Y-Z. Zhou, Y. Cao, W. Liu, C.H. Chu, and Q-L. Li, Polydopamine-induced tooth remineralization. *ACS Appl. Mater. Interfaces* **4**, 6901–6910 (2012).

81. J.P. Matinlinna, L.V.J. Lassila, I. Kangasniemi, and P.K. Vallittu, Isocyanato- and methacryloxysilanes promote Bis-GMA adhesion to titanium. *Dental Res.* **84**, 360–364 (2005).

82. Y. Ishikawa, Y. Kawamoto, H. Koizumi, M. Furuchi, H. Matsumura, and N. Tanoue, Effect of metal priming agents on bonding characteristics of an acrylic resin joined to SUS XM27 steel. *Oral Sci.* **48**, 215–218 (2006).