

## Review of titanate coupling agents and their application for dental composite fabrication

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Silane is a dominant coupler that is widely used in dentistry to promote adhesion among the components of dental composites. Silica-based fillers can be easily silanized because of their similarly ordered structure. However, silane is hydrolytically degraded in the aqueous oral environment and inefficiently bonds to non-silica fillers. Thus, the development of hydrolytically stable dental composites is an important objective in the research on dental materials. Titanate coupling agents (TCAs) exhibit satisfactory interfacial bonding, enhanced homogeneous filler dispersion, and improved mechanical properties of the composites. Titanates also provide superior hydrolytic stability in wet environments, which should be considered in fabricating dental composites. The addition of a small amount of titanates can improve the resistance of the composites to moisture. This paper reviews the effects of the instability of silanes in moisture on the performance of dental composites and presents TCAs as alternative couplers to silanes for fabricating dental composites.

**Keywords:** Titanate coupling agent, Silane coupling agent, Aqueous oral environment, Hydrolytic degradation, Dental composite

### INTRODUCTION

Polymeric composite materials are extensively used in dental applications. Inorganic filler particles form bonds to the organic resin matrix during setting through coupling agents, such as silane<sup>1</sup>. A coupling agent resembles a molecular bridge between the interface of the inorganic filler and organic polymer matrix. Interfacial bonding is important for load transfer from the polymer matrix to the reinforcing fillers; this interaction significantly influences the mechanical properties of particulate-reinforced systems. Coupling agents are used to enhance the dispersion of fillers throughout the matrix, prevent aggregation, and reinforce interfacial coherence with the resin<sup>2</sup>. Thus, durable adhesion between the filler and matrix is important to improve the mechanical performance and longevity of restorative dental materials.

Coupling agents should be polyfunctional or possess specific hydrophobic moieties to become hydrolytically stable<sup>3</sup>. The coupled interface can reduce water sorption and enhance property retention and stability under humid and wet conditions<sup>4</sup>. Organofunctional silanes and organotitanates are commonly used coupling agents. Moreover, organozirconates are a type of less readily available coupling agents because of their high production cost<sup>5</sup>.

Titanate coupling agents (TCAs) are organometallic interface chemicals that contain titanium. These compounds are usually employed in the polymer industry to strengthen polymeric composites by improving the

affinity of the particles to the matrix<sup>6,7</sup>. TCAs can overcome the limitations of incompatible polymers and inorganic fillers and provide good chemical bonding and dispersion<sup>8</sup>. The molecular formula of TCAs is  $XO-Ti-(OY)_3$ , where  $XO-$  is the alkoxy group that reacts with the inorganic substrate and  $-OY$  is the organofunctional fragment. The  $Y$  portion typically contains different groups that interact with the polar and nonpolar thermoplastics (such as benzyl and butyl), thermosets (such as amino and methacryl), and binder groups (such as pyrophosphate or carboxyl). These components perform additional functions in the composite<sup>9</sup>. Titanates can also be used to couple interfaces that are nonreactive with silane, such as calcium carbonate ( $CaCO_3$ ), graphite, aramid, and carbon black. Silane forms a chemical bond by reacting with oxides or hydroxyl groups on the particle surface but not on the surface of other fillers, such as  $CaCO_3$ <sup>10</sup>. Adding a small amount of titanates can improve bond strength and moisture resistance<sup>11</sup>.

Resin composites are widely used in restorative dentistry, and satisfactory clinical performance is largely determined by their resistance to degradation in the oral environment<sup>12,13</sup>. The mechanical properties of resin composites are influenced by their chemical composition and type of environment that they are exposed to. These materials are hydrolytically degraded mainly because of water accumulation at the filler/matrix interface, which promotes the displacement of inorganic particles or slow down the development of superficial flaws related to preexistent corrosive processes<sup>14-16</sup>. Thus, the stability of coupling agents in moisture is important to improve the clinical

Color figures can be viewed in the online issue, which is available at J-STAGE.

Received Jan 15, 2016; Accepted Jan 16, 2017

doi:10.4012/dmj.2016-014 JOI JST.JSTAGE/dmj/2016-014

performance of resin-based restorative composites.

The development of hydrolytically stable dental resin composites is an important objective in dental materials research. The stability of the interface in the oral environment and its ability to transfer stresses between the matrix and filler phases during mastication are particularly significant properties of dental composites. Although silane is a coupling agent that is conventionally used in dentistry, its hydrolytic breakdown and the inefficiency of silanized non-silica-based fillers remain challenging<sup>13,15-17</sup>. These limitations cause failure at the interface and the dissolution and leaching out of components, such as unreacted monomers or fillers, because of hydrolytic instability of the siliceous filler and silanes, thereby leading to inferior mechanical properties and shortened service life of dental restorations<sup>16,18,19</sup>. Therefore, alternative couplers are extremely needed. This study aims to review the effects of the instability of silanes exposed to moisture on the performance of dental composites and presents TCAs as alternative coupling agents to silanes for the construction of dental composites.

## MATERIALS AND METHODS

This paper presents a review of the effects of moisture exposure and hydrolytic instability of dental composites used in dental treatment and prosthodontics on functional properties and clinical longevity. An electronic search was performed for data published until May 2016 by using PubMed, Web of Science, Google Scholar, and Science Direct database. Search terms included titanate coupling agent, titanates, silane coupling agent, silanation, silanized interfaces, aqueous oral environment, hydrolytic degradation, and dental composite. In addition, a reference list of previous reviews was checked to find additional studies. Every article indicating a possible match or could not be excluded based on the information provided in the title was considered and evaluated. Only studies published in English were viewed. A total of 89 studies

were included in the final selection. No additional manual search was performed.

## SILANE COUPLING AGENTS

Coupling agents serve as a highly important ingredient in numerous high-performance polymer composites. Silane coupling agents are a unique class of organic silicon compounds containing a hydrolytically active silicon-based functional group. For more than 50 years since their first introduction in dentistry, silanes have been applied to promote the bonding between inorganic fillers and organic polymer materials. A widely known silane is 3-Methacryloyloxypropyltrimethoxysilane (3-MPS; Fig. 1). This monofunctional silane is less stable at the interface compared with bifunctional silanes<sup>20</sup>. Silica and siliceous fillers are the commonly used fillers in dental composites<sup>21-26</sup>. These additives can be easily functionalized by silanes because of their similarly ordered structure. In particular, silanes chemically bond the silica present in silica-based fillers (such as quartz, silicon dioxide, silicate glasses, and electrical glass; Table 1) to the organic matrix of resin by siloxane and hydrogen bonds<sup>27</sup>. Figure 2 presents a schematic of the surface modification of ceramic filler by MPS grafting. A layer of siloxane is formed on the surfaces through condensation. Excellent matrix-to-filler adhesion is important for the favorable mechanical behavior and longevity of dental composites<sup>28</sup>.

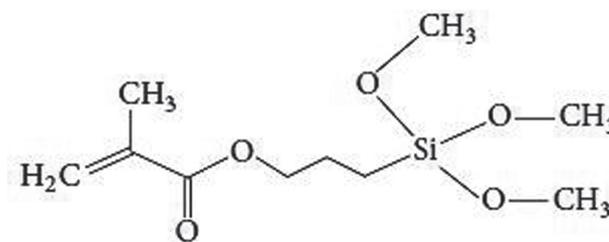


Fig. 1 3-MPS, a silane coupling agent.

Table 1 Chemical composition of some siliceous fillers

| Siliceous fillers        | Composition   | Description  |
|--------------------------|---|--|
| Feldspar                 | $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (Albite) and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (Potassium-aluminum silicate) | It is naturally occurring material.  |
| Quartz                   | $\text{SiO}_2$  | Quartz is naturally occurring substance.   |
| Silicon dioxide (Silica) | $\text{SiO}_2$  | Silica is an entirely synthetic material.  |
| Silicate glasses         | Such as barium-aluminosilicates $\text{BaAl}_2\text{Si}_2\text{O}_8$ strontium silicates $\text{SrSiO}_4$   | Commonly used in dental composites fabrication   |
| E-glass fibers           | Alumino-borosilicate Glass  | “E” stands for electric.   |
| Bioactive glass          | $\text{P}_2\text{O} \cdot 8\text{CaO} \cdot 16\text{SiO}_2$   | Bioactive glass is a highly biocompatible material because of its bioactivity and osteoconductivity. |

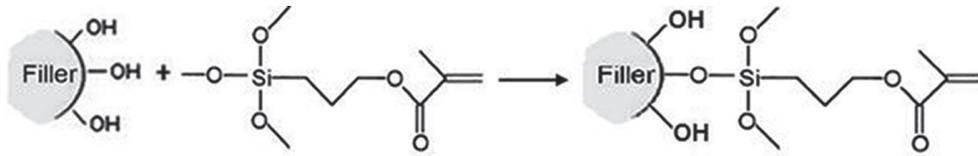


Fig. 2 Schematic diagram of surface modification of ceramic filler.

Xavier *et al.*<sup>26)</sup> evaluated the influence of silane concentration and filler size distribution on the mechanical properties of experimental composites; they found that silanation increased the fracture toughness of both the 1 and 3 wt% groups because of good bonding between the silanized nano-silicon dioxide (SiO<sub>2</sub>) and the polymer material. Another study<sup>29)</sup> was performed to investigate the mechanical and thermal properties of denture polymethyl methacrylate (PMMA) reinforced with aluminum borate whiskers (ABWs). To improve the bonding between ABWs and the PMMA matrix, the surface of ABWs was modified using a silane coupling agent. This coupler acts as a “molecular bridge” to establish chemical bonding between ABWs and the PMMA matrix. Consequently, the flexural strength of ABW/PMMA composites is enhanced because more energy is needed to break the strong chemical bonds between both materials. Naveen *et al.*<sup>24)</sup> found that PMMA reinforced with silanized glass fibers exhibit markedly enhanced flexural strength. Although an improved silane bond was fabricated by hydrosilylation after silanation<sup>30)</sup> or application of an acetone primer to the glass prior to silane treatment, such procedures do not solve the problem of slow silane degradation in oral fluids<sup>31,32)</sup>.

#### Limitation of silane treatment

Silanes are suitable coupling agents used to modify the siliceous filler surface. However, silane coupling agents exhibit several limitations. For a reaction to occur, silanes require active sites, preferably hydroxyl groups, on the filler surface. Inefficient reaction could occur because of the absence of these functional groups on the surface of various fillers such as metal powders. Accordingly, silanes do not bond to the metal surface as they do with ceramic<sup>20,33)</sup>. Other substrates that are not readily compatible to the usual silane coupling agents include graphite, aramid, carbon black, calcium salts (such as oxides, carbonates, and phosphates), and alkali glasses (such as sodium glasses)<sup>21)</sup>.

Although silanation is commonly employed to promote dental resin matrix/filler adhesion, silane coupling agents form aggregates on the filler surface because of incomplete coating, thereby leading to unstable bonding between fillers and resin<sup>14,34)</sup>. Filler/polymer interaction is not extremely strong probably because of the chemical structure of the silane and the insufficient surface coverage by silanes. A no-step-based experiment is available to predetermine the optimal dosage of filler treatment. The effect is also not

proportional to the coupling agents.

#### Hydrolytic degradation of silane

Although the use of silane coupling agents to enhance the bond of resin composites to Si-based fillers is well accepted in dental literature, most of these studies were conducted in dry environments<sup>22–25)</sup>. The warm, wet nature of the mouth entails filled-resin restorative materials and all other dental restorative materials to maintain reasonable stability in such an environment. The oral cavity is a harsh environment because of its wetness, temperature stresses from drinking and eating, and mechanical stress caused by dental occlusion. Therefore, the enhancements are more apparent when dental composites are exposed to high humidity. However, exposing dental composites to an aqueous environment degrades their mechanical properties<sup>14,35–37)</sup> because of the failure of the polymer-filler bond<sup>38–40)</sup>. The absorbed moisture hydrolyzes the silanized interfaces and opens an extra pathway for water diffusion. This deterioration leads to stress and crack growth, thereby resulting in a rapid increase in the amount of water absorbed by the composite material due to silane hydrolysis and degradation<sup>20,36)</sup>.

Cilli *et al.*<sup>12)</sup> found that water uptake by filled specimens is approximately twice that in an unfilled resin. This behavior is attributed to an accumulation of water between the filler/matrix interfaces because of the slow development of superficial flaws related to preexistent corrosive processes. This path of facile diffusion leads to the hydrolytic degradation of silane couplers and fillers. Other researchers<sup>35)</sup> concluded that composites reinforced with silanized glass fibers exhibit decreased mechanical properties after prolonged storage in water. The flexural strength and modulus decreased by 66 and 60%, respectively, after being soaked in water for three months. Another study was performed to measure the interfacial bond strength at the glass fiber-resin interface; a positive correlation was observed between the amount of silane on the filler surface and property loss after soaking because of the hydrolytic cleavage of the siloxane interfacial layer<sup>41,42)</sup>. These outcomes agreed with the findings of other researchers who inferred that high (3 wt%) silane content enhances the initial biaxial strength but increases the vulnerability to the deleterious effects of prolonged water storage<sup>26)</sup>.

Furthermore, the artificial aging of silanized filler surfaces can break siloxane bonds and induce the debonding of filler particles<sup>16)</sup>. The hydrolyzed silane

molecules adversely affect cell morphology at high concentrations and induce cell damage. Owing to the adverse biological activity of leached products, the high stability of the silane coating on the filler surface must be guaranteed<sup>43</sup>. In this regard, the coupling agent should be changed to promote good adhesion in an aqueous environment, thereby improving the clinical performance of resin-based composite restorative materials. Titanates are introduced as alternatives to silanes because of their moisture resistance and greater affinity for filler protons compared with that for water molecules.

### TCAs

Although silanes are the most commonly used coupling agents, numerous other classes of materials, including titanates and zirconium compounds, have been used to promote adhesion. Coupling agents, such as silanes and titanates, can function as adhesion promoters, but the reverse is not applicable<sup>44</sup>. Titanium-derived coupling agents (such as KR 12; Fig. 3) chemically bridge two dissimilar species, such as an inorganic filler/particulate and an organic polymer, consequently improving bonding and enhancing mechanical properties. Potentially, the alkoxide group of the titanate can react with the hydroxyl groups on the filler

surface to form covalent bonds, whereas the aliphatic chain can mix well with polymers because of their high compatibility with the organosilanes<sup>7</sup>. As shown in Fig. 4, the presence of OH<sup>-</sup> on the filler surface enables the reaction with titanate after the release of alcohol. This reaction results in the formation of an organic titanium monolayer on the filler surface to increase the compatibility of the filler/matrix interface. The nature of the interlayer between the filler and polymer matrix introduced by titanate treatment is important in improving the mechanical properties of the composite<sup>45</sup>.

New-generation TCAs are reportedly user-friendly, easy to incorporate with high-aspect ratio fillers, and eliminate filler pretreatment during processing. Thus,

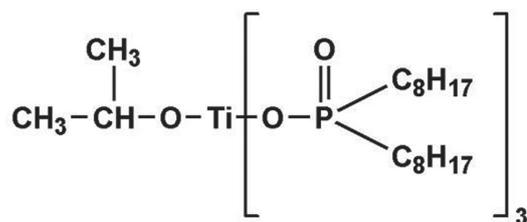


Fig. 3 Isopropyl tri[di(octyl) phosphato] titanate; KR 12; as an example of TCA.

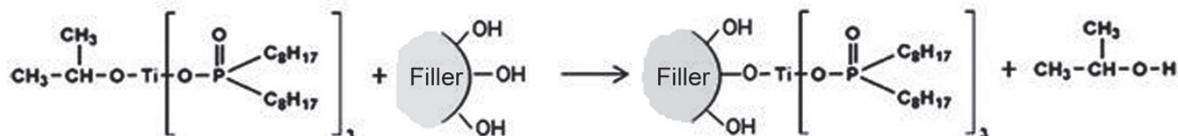


Fig. 4 Reaction scheme of TCA (KR 12).

Table 2 Chemical description of some TCAs

| Type                 | Trade name   | Chemical description  |
|----------------------|--|---|
| Monoalkoxy titanates | KR <sup>®</sup> TTS  | Titanium IV 2-propanolato, tris isooctadecanoato-O                                  |
|                      | KR 7   | Titanium IV bis 2-methyl-2-propenoato-O, isooctadecanoato-O 2-propanolato           |
|                      | KR 9S  | Titanium IV 2-propanolato, tris(dodecyl)benzenesulfonato-O                          |
|                      | KR 12  | Titanium IV 2-propanolato, tris(diocetyl)phosphato-O                                |
|                      | KR 33DS  | Titanium IV, tris(2-methyl)-2-propenoato-O, methoxydiglycolylato                    |
|                      | KR 38S   | Titanium IV 2-propanolato, tris(diocetyl)pyrophosphato-O                            |
|                      | KR 39DS  | Titanium IV, tris(2-propenoato-O), methoxydiglycolylato-O                           |
|                      | KR 44  | Titanium IV 2-propanolato, tris(3,6-diaza)hexanolato                                |
| Neoalkoxy titanates  | LICA 01  | Titanium IV 2,2(bis 2-propenolatomethyl)butanolato, tris neodecanoato-O             |
|                      | LICA 09  | Titanium IV 2,2(bis 2-propenolatomethyl)butanolato, tris(dodecyl)benzenesulfonato-O |
|                      | LICA 12  | Titanium IV 2,2(bis 2-propenolatomethyl)butanolato, tris(diocetyl)phosphato-O       |
|                      | LICA 38  | Titanium IV 2,2(bis 2-propenolatomethyl)butanolato, tris(diocetyl)pyrophosphato-O   |
|                      | LICA 44  | Titanium IV 2,2(bis 2-propenolatomethyl)butanolato, tris(2-ethylenediamino)ethylato |
| LICA 97              | Titanium IV 2,2(bis 2-propenolatomethyl)butanolato, tris(3-amino)phenylato |   |

KR # = Ken-React titanates; Liquid monoalkoxy  
LICA # = Liquid coupling agent, (titanate coupler)

these materials are more cost-effective compared with early TCAs<sup>46)</sup>. Various types of titanates are introduced. However, alkoxide titanates (Table 2) are mostly used in fabricating polymer composites (Table 3). These

types of titanates are employed based on the polymer and its properties. The new neolkoxy titanates differ from their monoalkoxy titanate analogs only in the substrate-reactable side of the coupling agent molecule,

Table 3 Types of TCAs used in composite fabrication

| Material                                       | Type of TCA        | Comments   | Ref.   |
|--|--------------------|--|--------|
| Nylon 6/mica                                   | TPT                | Improved impact and tensile strength   | 2,9)   |
| PP/RHA   | LICA 38            | Enhanced impact strength   | 5)     |
| Surface modification of TiO <sub>2</sub>       | TCA                | Low viscosity and good dispersivity  | 6)     |
| PE/metal powder                                | LICA 12            | Improved bonding between the metal powder and the binder   | 7)     |
| PBT/TiO <sub>2</sub>                           | NDZ-102            | Good dispersion  | 8)     |
| PVC/CaCO <sub>3</sub>                          | CAPOW L38/H        | Improved fracture toughness and strong interfacial bonding   | 10)    |
| Nylon 6/fly-ash                                | TPT                | Enhanced tensile and impact strength   | 45)    |
| PP/talc  | LICA 12            | Increased impact strength and improved filler dispersion   | 46)    |
| PVC/TiO <sub>2</sub> , CaCO <sub>3</sub> , ZnO | TCA                | Improved compatibility, enhanced thermal stability, and improved impact strength and toughness   | 50)    |
| PMMA/HA  | KR TTS             | Enhanced thermal and mechanical properties   | 52)    |
| PP/fly-ash                                     | LICA 38            | Enhanced thermal and mechanical properties   | 53)    |
| Epoxy/TiO <sub>2</sub>                         | KR-38S             | Significant improvement in flexural properties was observed for titanated TiO <sub>2</sub> .   | 56)    |
| Polyamide/Coal                                 | CAPOW KR 12/H      | Higher mechanical properties   | 58)    |
| PP/CaCO <sub>3</sub> and talc                  | LICA 12            | Improved mechanical properties   | 59,67) |
| PP/CaCO <sub>3</sub>                           | LICA 12            | Improved mechanical properties and good dispersion of treated filler   | 60,61) |
| Polybutylene/clay                              | LICA 01            | Improved tensile strength and enhanced polymer-filler adhesion   | 63)    |
| HDPE/talc                                      | KR 12/H            | Reduced void content, increased stiffness and tensile strength   | 64)    |
| Chloroprene rubber/fly-ash                     | LICA 01            | Improved tensile strength, hardness, and Young's modulus   | 65)    |
| Surface modification of TiO <sub>2</sub>       | TCA                | Reduced aggregation  | 75)    |
| Surface modification of SiO <sub>2</sub>       | KR TTS and KR 33CS | Change the surface from hydrophilic to hydrophobic   | 76)    |
| Kevlar/Phenolic                                | TPT                | Good water resistance, improved flexural properties  | 78)    |
| PP/bentonite                                   | LICA 12            | Lowest water absorption characteristic, improved tensile strength, elongation at break, and Young's modulus  | 79)    |
| Ethylene vinyl alcohol/HA                      | TCA                | Non-cytotoxic behavior was found.  | 85)    |
| Polymethacrylate/ TiO <sub>2</sub>             | KR 33DS            | Titanated TiO <sub>2</sub> could prevent the leaching process of the TiO <sub>2</sub> composites in oral environments as does silane treatment in SiO <sub>2</sub> composites. | 87)    |

TPT=Tetra isopropyl titanate

RHA=Rice husk ash

PBT=Polybutylene terephthalate

NDZ-102= Titanate coupler

CAPOW=Coupling agent powder (titanate coupler)

in which solvolysis occurs to form an organofunctional monolayer on the substrate<sup>47,48</sup>.

Unlike silanes, TCAs react with free protons on the inorganic interface and form organic titanium monomolecular layers on the inorganic surface without water for condensation. The coupling of titanate to the inorganic/organic substrate in atomic monolayers allows the elimination of air voids, hydrophobicity, and a complete continuous phase for stress/strain transfer<sup>49</sup>. The absence of a multi-molecular layer at the interface and the titanate chemical structure modify the surface energy of filler particles, thereby causing the melt viscosities of polymers to decrease compared with those of the other coupling agents<sup>50</sup>. A theoretical monolayer of phosphato titanate on a filler surface is presented in Fig. 5. Table 2 provides the chemical description of common TCAs along with their commercial names. Table 3 presents particular types of TCAs used in composite fabrication with related comments and references. The commercial names of the substances were used for brevity.

#### Functions of TCAs

As mentioned, the coupling agents must be polyfunctional or possess particular hydrophobic moieties to be hydrolytically stable. TCAs enhance the functionality of the fillers in plastics. The different mechanisms by which these additives function in filled polymers can be explained by breaking down the various mechanisms of the titanate molecule into six distinct functions. Monte<sup>49</sup> proposed six functional sites of titanates relative to the di-functional silane (Table 4). The TCA holds six functions in accordance with the relevant parts on its molecular structure. Their performance differences are explained as follows:

- (1) Coupling function (RO)<sub>n</sub>=hydrolyzable or substrate-reactive group with hydroxyl or protons. Function (1) is concerned with filler-substrate reaction mechanisms, whereas functions (2) to (6) are polymer-reactive. Silane function 1, the silanol-siloxane water condensation mechanism, limits the reactions of silane to temperature environments below 100°C. This attribute eliminates the possibility of in situ reaction in the thermoplastic or elastomer melt above 100°C. This reaction is possible with titanates.
- (2) Catalysis function (Ti)=tetravalent titanium or non-catalytic silicon (Si). The Ti–O bond is capable of disassociating, thereby allowing transesterification, transalkylation, and other catalytic mechanisms such as repolymerization.
- (3) Hetero-atom function (X)=binder functional groups, such as phosphate, sulfonyl, carboxyl, and other groups that may impart intumescence, burn rate control, anticorrosion property, quaternization sites, and dissociation rate/electron transfer control.
- (4) Thermoplastic function (R')=thermoplastic functional groups, such as aliphatic and non-

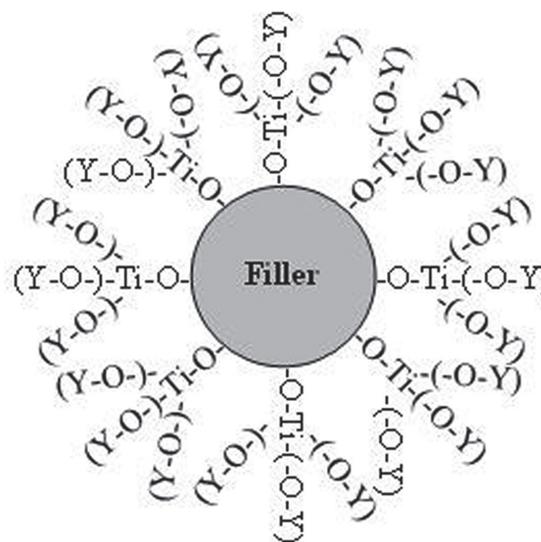


Fig. 5 A nanometer atomic monolayer of phosphato titanate on an inorganic filler surface.

Table 4 The number of functional sites of titanates, as compared with silanes

| Titanates  |     |     |     |     |     | Silanes          |     |
|--|-----|-----|-----|-----|-----|------------------|-----|
| (1)  | (2) | (3) | (4) | (5) | (6) | (1)              | (5) |
| [RO-] <sub>n</sub> -Ti-[O X R' Y] <sub>4-n</sub> |     |     |     |     |     | [RO-]-3Si-[R' Y] |     |

polar isopropyl groups, butyl groups, or aromatic benzyl groups that provide entanglements with long hydrocarbon chains and bonding by van der Waals forces.

- (5) Thermoset function (Y)=thermoset functional groups, such as acryl, methacryl, and amino groups that provide thermoset reactivity and chemically bond the filler to the polymer.
- (6) 4–*n*=mono-, di-, or tri-organofunctional hybrid titanates are possible forms.

Therefore, function (1) relates to filler/fiber substrate reaction mechanisms, whereas functions (2) to (6) are polymer-reactive.

#### Filler/coupling agent interaction

Titanates preferentially produce organic titanium monomolecular layers on the inorganic surface without water for condensation<sup>49</sup>. In general, coupling the entire filler surface is crucial to resist the worsening of mechanical properties in reinforced compositions caused by chemical, corrosive, and moisture attacks. Interestingly, evidence confirmed that different from silanes, TCAs form thin interfaces. For instance, a 5–8 nm coating layer is formed after the silanation of nanobarium titanate (NBT) (Fig. 6a). However, NBTs are not fully coated. Thus, agglomeration and inadequate adhesion to the matrix occur and adversely affect the

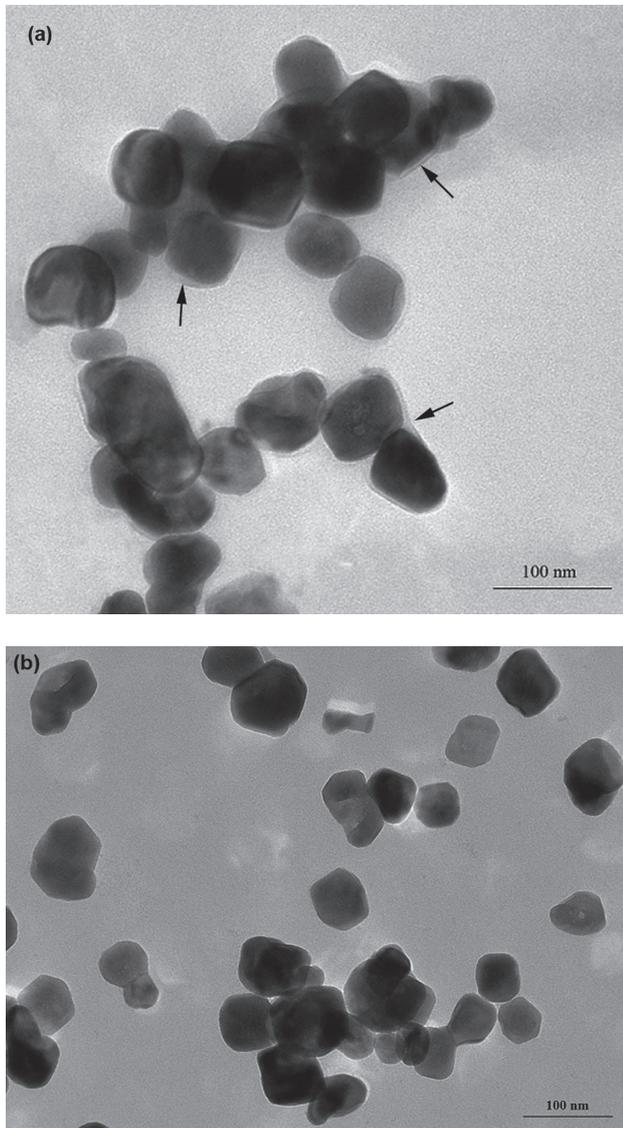


Fig. 6 TEM images of NBT; (a) silanized NBT, (b) titanated NBT.

properties of resultant composites<sup>51</sup>). This behavior is due to the lack of hydroxyl groups in the filler surface. Hydroxyl groups are necessary for the coupling of the silanes to the additives. Monte<sup>49</sup>) pointed out one major difference, that is, silanes work on the hydroxyl (OH<sup>-</sup>) group of various substrates through water condensation-related siloxane-forming mechanisms, whereas titanates function *via* proton (H<sup>+</sup>) coordination mechanisms and do not need condensation water. Although atomic monolayers formed by titanates were not observed in titanated NBT (Fig. 6b), the formation of these layers was confirmed by energy-dispersive X-ray spectroscopy (Fig. 7). The presence of Ti was clearly noted in the filler and TCA. However, the P peak demonstrates the deposition of a monolayer of phosphorus on the particle surface. Therefore, improved distribution

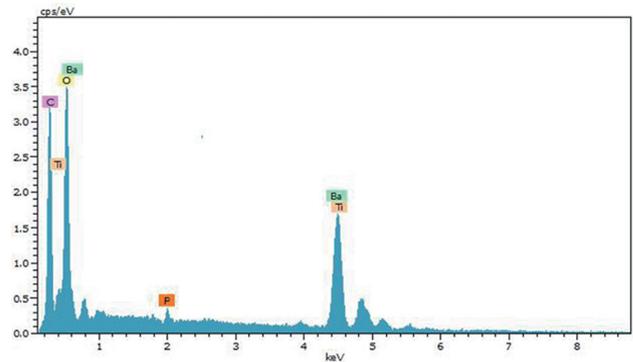


Fig. 7 EDX analysis showing the deposition of a monolayer of phosphorous on the surface of NBT after titanation by KR 12 phosphato titanate.

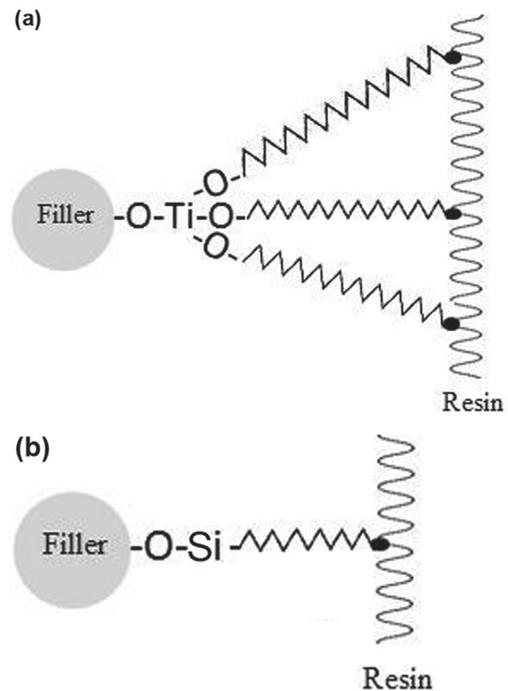


Fig. 8 Reaction mechanism for different coupling agents. (a) Titanate-treated showing three reaction sites, (b) Silane-treated showing one reaction site.

with less agglomeration was observed after titanation because of the hydrophobicity of the induced particles. Moreover, a distinct property of titanates is their ability to be coupled in the phase of the matrix resin because of the three functional radicals of the coupling agent and transesterification reaction (Fig. 8a). By contrast, the silane coupling agent creates only one functional radical (Fig. 8b). Consequently, the chemical bonding between the filler and TCA strengthened compared with that in silane.

In addition, the amount of TCAs incorporated does

not depend on the surface area of the fillers. Importantly, selected titanates should be examined in a range of concentrations from 0.1 to 2.0% by mass in a filled system and an even lower range for unfilled systems. Most polymers exert balanced property effects at 0.2–0.6 wt% titanate dosages. Petrie<sup>11)</sup> defined the typical dosage of 0.2% by weight of the polymer. However, excess titanate results in unreacted alkoxy groups on the surface and leads to loss of adhesion of the polymer. This finding can be misinterpreted to denote that a particular titanate is unsuitable or even harmful<sup>44)</sup>. Thus, the amount of titanate to be utilized is an important parameter. The effects of different TCA concentrations (that is, 2–8 wt%) on the mechanical and morphological properties of PMMA denture base filled with 5 wt% hydroxyapatite (HA) were investigated<sup>52)</sup>. Although good interfacial bonding with increasing fracture toughness was observed, the flexural properties slightly decreased at high TCA concentrations (6 and 8 wt%). This increment is attributed to the plasticizing effects caused by excessive concentrations of the coupling agent. Thus, the intermolecular forces in the matrix reduced and enhanced the flexibility of the composites. When a load transfers from the PMMA to the HA filler, the lubricating effect of TCA cannot confine the segment, and the chains may slip easily. However, this adverse effect can be avoided by increasing the filler load, as proven by Kulkarni and Mahanwar<sup>53)</sup>. The tandem evaluated the influence of TCA concentrations on the mechanical and thermal properties of polypropylene (PP) filled with various concentrations of fly ash. Fly ash is obtained from thermal power plants as a by-product of the burning of pulverized coal. The material is a fine powder that is mainly composed of substantial amounts of SiO<sub>2</sub>, aluminum oxide, and calcium oxide. The study results showed that the use of 0.5 and 1.5 wt% TCA improves the performance at lower loadings of fly ash, whereas 2.5 wt% TCA showed enhanced performance at increased loadings of fly ash. Overall, fly ash dispersion and interfacial adhesion were significantly affected by the amount of coupling agent.

#### *Effect of chain length of the coupling agent*

The strength of the particulate-treated composite system with the use of a coupling agent depends on the type of coupling agent used. The increase in interfacial adhesion can be explained by the reaction of the organofunctional group of the coupling agents with the chain-end hydroxyl groups of the polymer. Evaluation of the chain length factor is beneficial to clarify the mechanism by which the performances of the composites are improved after filler surface treatments. Lung and Matinlinna<sup>42)</sup> stated that coupling agents with long hydrocarbon chains are considerably more hydrophobic than those with the short hydrocarbon chains. In principle, bond hydrolytic stability should be enhanced. The effect of chain length on the interfacial performances of the carbon-fiber-reinforced polymer composites was investigated<sup>54)</sup>. The results depict that chain lengths significantly influence interfacial

adhesion in composites. Long chains on the fiber surface also augment the interfacial shear strength. The chain interaction is caused by molecular-chain movements and entanglements. The two molecular chains are entangled with the movement of polymer chains and chains of coupling agents on the fiber surface. These entanglements are fixed by polymer-resin curing. As a result, long chains on the fiber surface produce strong chain interactions at the composite interface<sup>55)</sup>. Hussain *et al.*<sup>56)</sup> demonstrated that the hydrocarbon chains plasticize and improve the compatibility of the inorganic particle to the epoxy when titanate is bonded to an inorganic filler. The interfacial adhesive effects arise from the attachment of a large number of organic groups to the surface of the inorganic filler. This occurrence allows the chemical interaction and/or the formation of a strong van der Waals attraction between the short organic chains of titanate and the long chains of the polymer. As shown in Figs. 1 and 3, the chemical structure of TCA contains a relatively long hydrocarbon chain, which could result in superior performance.

#### *Surface modification of various fillers with TCAs*

TCAs play an important role in achieving a durable bond between the ceramic filler and polymer matrix. The organometallic monolayer-covered filler surface becomes a catalysis support bed for the “repolymerization” of the surrounding polymer phase, thereby allowing fillers to function as mechanical property enhancers. Furthermore, the *in situ* monomolecular deposition of titanate on the surface of a particulate, such as a nanofiller, renders the particulate as hydrophobic and organophilic. Under melt-compounding shear conditions, titanate assists in the removal of air voids and moisture from the particle surface; this activity results in complete dispersion and formation of a true continuous phase, thereby optimizing filler performance<sup>57)</sup>. Accordingly, these couplers can be used effectively to coat inorganic fillers of dental materials to improve dispersion and bonding to the resin matrix<sup>52)</sup>. Regardless of the filler type, titanates can then modify the surface characteristics of a filler. Interfacial bonding with the matrix is thereby improved.

#### 1. Ceramic fillers

Numerous studies indicate that TCAs provide good interfacial bonding, improve mechanical properties, enhance homogeneous filler dispersion, and modify the rheological behavior of composites<sup>2,9,45,46,56-60)</sup>. Thus, titanate adhesion promoters allow higher filler loading of particulate matter to either improve the properties or decrease the cost of the system without adversely affecting its viscosity. Bose and Mahanwar<sup>45)</sup> conducted a study to determine the effect of the TCA on the properties of fly-ash-filled nylon 6. Their group concluded that the increase in viscosity with the increase in filler content is due to the restricted molecular motion in the matrix caused by the agglomeration of the particles. However, with TCA treatment, the particles are well-dispersed and decrease the viscosity because of the

free motion of the chains. The group also evaluated the effect of the surface modification of ceramic fillers on the interfacial adhesion and dispersion of filler particles in the polymeric matrix. The use of titanate-treated fillers increased the amount of filler incorporated into the polymeric matrix. Mechanical properties, such as tensile and flexural stresses, elongation at break, modulus, and impact strength, were also improved. Micrographic analyses confirmed the efficiency of surface treatment of the filler on its dispersion<sup>61,62</sup>.

Similarly, Alkadasi *et al.*<sup>63</sup> explored the effect of TCA treatment on clay/polybutadiene composite. They reported that filler treatment enhances the polymer-filler adhesion and accordingly improves mechanical properties. Other researchers<sup>64</sup> concluded that the addition of TCA to resultant composites increases the stiffness and tensile strength of composites. This result verifies that such an agent is effective at low filler concentrations. A different study demonstrated a substantial enhancement in the mechanical properties of composites derived from chloroprene rubber and titanate-treated fly ash. The tensile strength was improved by 1,365%, the modulus at 400% increased by 1,410%, and Young's modulus was enhanced by 1,216%<sup>65</sup>. The effect of treatment involving different percentages of liquid coupling agent (LICA) 38 on the various properties of fly-ash-filled PP composites was also investigated. The fly ash dispersion and interfacial adhesion were significantly affected by the amount of LICA 38. Thus, the treatment improved the mechanical and thermal properties of the composites compared with the untreated fly-ash filling. These findings were consistent with those of another work<sup>66</sup>; the result reveals the effectiveness of TCA in improving the compatibility and interfacial bonding between carbon fiber and epoxy resin.

Meanwhile, mechanical and thermal properties between treated and untreated hybrid-filler PP composites were compared. The impact strength value of a LICA 12-treated hybrid composite was the highest for all the composites studied. Treatment with LICA 12 can induce good filler orientation, dispersion, and interaction with the PP matrix<sup>59,67</sup>. Coupling agents, such as LICA 09, LICA 01, and 1:1 mixture of LICA 12 and LICA 01, have been used in blends of PP/high-density polyethylene (HDPE) (80/20 weight ratio) with a filler percentage of up to 30%. These coupling agents improve the mechanical properties of PP/HDPE/CaCO<sub>3</sub> composites. Each coupling agent is responsible for a specific action. LICA 01 improves Young's modulus (0.7 wt%). Considerable improvement in impact strength was observed with the LICA 12 and LICA 01 (1:1) mixture<sup>68</sup>. Another study<sup>59</sup> described the effects of applying titanate, zirconate, and silane coupling agents to rice husk ash in PP composites. Findings show that the impact properties of the PP composites are enhanced by TCA, whereas silanes improve the tensile strength of the composites. A study<sup>59</sup> investigated the effect of silanes and TCA on the mechanical properties of titanium dioxide (TiO<sub>2</sub>)/epoxy composite.

The investigation revealed that the chemical bonding between the filler and TCA is strengthened with that with silane and contributes to increased flexural strength. A similar finding was reported by Kamal *et al.*<sup>69</sup>, who stated that titanate exhibits the best mechanical properties compared with silane because of the efficient bonding between nano-CaCO<sub>3</sub> and PP matrix in the former case. Therefore, the TCA used was more effective than the silane coupling agent<sup>56,58,69</sup>.

## 2. Metal powders

The surface modification of metal powders with TCA offers superior performance, including improved dispersibility, increased compatibility between the metal powders and resin, and augmented adhesion strength between the metal particles and polymer matrix, which is contributed by TCA grafting into the metal powder surface. A previous study<sup>7</sup> added LICA 12 to the binder system to determine whether the action provides a bridging effect between the polymer and the metal powder. Findings show that the presence of TCA enhances the bonding between the metal powder and the binder. The bridging effect of LICA 12 between the metal powders and polymers also reduces the amount of swelling of the green part during solvent debinding. This effect is also beneficial in reducing distortions and cracking. Hsiang and Tsai<sup>70</sup> investigated the TCA effects on a nonaqueous ferrite (Fe) suspension dispersion and observed that the Ti–O–Fe covalent bond is formed through the interaction of the Ti–O bond in the TCA and Fe–OH onto the surface of ferrite powders. TCAs also altered the ferrite powder surface from hydrophilic to hydrophobic by the interaction of the Ti–O bond of the titanate with the Fe–OH bond, thereby forming a hydrophobic Ti–O–Fe layer on the surface and increasing the adhesion between the hydrophobic resin and ferrite powders<sup>71</sup>.

## 3. Nanoparticles

In recent years, polymer nanocomposites have attracted considerable attention. Nanosized particles markedly tend to agglomerate because of their large surface areas and surface energies. Interactions between particles are affected by attraction and repulsion resulting from van der Waals and electrostatic forces. As the particle size decreases, the reduction in repulsive electrostatic forces is considerably more significant than the reduction in attraction because of van der Waals force. Thus, attractive forces dominate the interface and induce particle agglomeration. Titanates not only aid the mixing of two phases but also help improve the particle dispersion because of the hydrophobic particle surfaces. This phenomenon enables the elimination of water and air voids from the particle surface, ultimately resulting in deagglomeration. Kemal *et al.*<sup>10</sup> evaluated the mechanical properties and microstructure of polyvinylchloride (PVC)/CaCO<sub>3</sub> composite; their group reported that the scanning electron micrographs of the impact fracture surface of the composites with titanate markedly show strong particle-matrix adhesion. In

addition, cavitation is limited compared with the composites without a coupling agent. This result suggests that the *in situ* addition of TCA generates composites with combined strong and intermediate interfacial bonding. Other researchers<sup>50</sup> explored the effect of TCA and particulate nanoscale particles, such as TiO<sub>2</sub> and CaCO<sub>3</sub>, on the thermal and mechanical properties of emulsion PVC. These scholars posited that titanate functions as a compatibilizer and increases the tensile strength and modulus of the samples by improving the compatibility of the polymer and nanoparticles. PP nanocomposites filled with titanated NBT were also prepared to improve their electrical and dielectric properties<sup>72</sup>. Enhanced compatibility between NBT and polymer matrix was observed after treatment with TCA, thereby corroborating the results of other studies<sup>51,73</sup>.

However, specific interfacial failures have been attributed to the chemical incompatibility between the composite phases and the coupler<sup>74</sup>. Therefore, chemical compatibility between the dispersed phase and the coupling agent should be considered. Titanium-based fillers serve as suitable candidate fillers to enhance the performance of composites when TCAs are used. Li *et al.*<sup>5</sup> modified the TiO<sub>2</sub> surface with TCA and inferred that TiO<sub>2</sub> exhibits a desirable, modified surface when TiO<sub>2</sub> is treated with TCA. Their group also stated that the surface characteristics of TiO<sub>2</sub> change from hydrophilic to hydrophobic. Furthermore, the TiO<sub>2</sub> particles show good dispersion in liquid paraffin. The results indicate that the treated TiO<sub>2</sub> particles enhance the binding force of the samples and the dispersion in the polymer matrix. Another study<sup>56</sup> investigated the effects of different coupling agents on the mechanical properties of the TiO<sub>2</sub> particulate-filled epoxy composite. The study results reveal that the mechanical properties of the epoxy composite were enhanced using TCA through the formation of a strong interface or adhesion between the filler and matrix. Yu *et al.*<sup>75</sup> evaluated the effects of modifying the surface of TiO<sub>2</sub> nanoparticles with TCA and verified the interactions between nano-TiO<sub>2</sub> and TCA. Moreover, the modification caused the large aggregation of nanoparticles to disintegrate into fine particles. As inorganic filler candidates, titanate fillers are a suitable material of choice for titanation because of their homogeneity. Under these circumstances, TCA can be used as an alternative to silanes.

#### *Hydrolytic behavior of TCAs*

Coupling agents should be hydrolytically stable, should not deteriorate in an aqueous environment, and should provide a waterproof bond at the interface of the two dissimilar materials. Under humid conditions, water can initiate corrosion and aging mechanisms in inorganic material-filled organic composites. Moisture resistance can be improved by adding a small amount of titanates to the composites<sup>11</sup>. Typically, titanate-treated inorganic fillers are hydrophobic, organophilic, and organofunctional<sup>65</sup>. Hydrophobicity is a desirable property of fillers and other functional particulates and

fibers to provide long-term-aged mechanical properties. Krysztafkiewicz *et al.*<sup>76</sup> modified hydrated silica with silane and TCAs. The degree of hydrophobicity of the silica surface was determined based on the heat of immersion of this surface. Silanol groups were identified by infrared spectroscopy. The modification with silane and TCAs leads to an increase in the chemical affinity of silica to the polymer. Application of these agents resulted in changes from a hydrophilic to a hydrophobic character. Moreover, the highest degree of hydrophobicity was observed for silicas modified with titanates, whereas hydrophobicity slightly decreased after modification with silane. Water is also necessary for the coupling of silane to silica but is not needed for titanate. The absence of the need for condensation water to affect TCAs offers possibilities for *in situ* coupling in the thermoplastic or thermoset elastomer melt. This phenomenon is not possible with silanes. Another study was conducted to investigate the effects of TCA on the mechanical properties and stability of wet CaCO<sub>3</sub>-filled blend films. When the TCA content was 0.5 wt%, the film achieved good membrane formation property and augmented the tensile strength, elongation at break, mechanical properties, and stability of the wet state of the blend films<sup>77</sup>. Similarly, Menon *et al.*<sup>78</sup> evaluated the hydrolytic stability of a titanate coupler. The composite samples treated with titanates exhibited higher resistance to moisture ingress than the untreated composites. Recovery in strength on reconditioning was also higher in the treated samples compared with that in the control samples. These results are consistent with other findings that PP/bentonite (aluminum phyllosilicate) treated with LICA 12 exhibits a high impact value and tensile strength<sup>79</sup>. The lowest water sorption characteristic was also observed. Therefore, given the high hydrolytic stability of numerous TCAs, such agents could serve as a candidate substitute for silanes.

#### *TCAs in dental application*

Dental composites are required to possess long-term durability in the oral cavity. The oral cavity is a complex environment that subjects the material to challenges, such as contact with saliva and a variety of inorganic and organic compounds, as well as microorganisms. However, the clinical performance of these materials over time is frequently correlated with degradation characteristics that can directly affect their mechanical properties. The deterioration over time is attributed to chemical reactions that are naturally accelerated by heat. In the oral environment, the degradation of resin composite restorations that are located in areas not exposed to abrasive and compressive forces suggests the occurrence of chemical degradation. Water is directly related to organic matrix deterioration of the resin-based materials because the sorption of the liquid results in diffusion in the matrix, thereby causing its degradation and decreasing the mechanical properties<sup>80</sup>. Among these properties, the hardness of the polymers is compromised by the hydrolytic degradation of

methacrylate monomers at high temperature. Thus, substances such as saliva, food, and beverages exert deleterious effects on the restorations containing resin-based materials because of their intermittent or continuous sources of chemical degradation<sup>81</sup>. These deteriorations are attributed to the hydrolytic degradation of the polymer matrix and filler, as well as water-induced filler-matrix bond failure<sup>39,42,82</sup>. Therefore, a decrease in mechanical properties is expected after storage in water because of water sorption. The action of the water molecules inside the polymeric structure described as plasticizing effect is the separation of the polymer chains by a molecule that does not form primary chemical bonds with the chain. This effect simply serves as a space occupier. Thus, the main effect of the water is to reduce interchain interactions such as entanglements and secondary bonding. This behavior creates more volume in the matrix and enhances the movement of the chain segments, thereby resulting in the decrease of the stiffness of the material<sup>83</sup>. A previous study<sup>84</sup> inferred that storage of composites in water and artificial saliva caused plasticization and degradation of the polymer matrix and degradation of the bond between the filler and coupling agent.

Titanates are yet to be extensively used in the dental restoration field. The biocompatibility of TCAs has been reported<sup>85</sup>, but the applications of these coupling agents in dentistry remain limited (Fig. 9). TCAs offer superior hydrolytic stability in a wet environment. This condition is an attribute that must be considered in fabricating dental composites. After exposing a reinforced composite to boiling water, the silanes lose more than 70% of their original strength, whereas titanates maintained more than 80% of their original properties. Titanate proton coordination covers 100% of the surface and resists aging<sup>49</sup>. Furthermore, the enhanced filler/matrix adhesion in moisture is due to the presence of pyrophosphate that acts as a binder group and introduces additional functions to the composites. The pyrophosphate group enables the

coupler that is suitable for the filler system under high moisture contents. As previously reported, phosphate-containing couplers have gained increasing attention as a monomer alternative to silane coupling agents because of the enhanced bonding and hydrolytic stability of the former<sup>17,86</sup>. Accordingly, promising results can be obtained with the application of titanates in dental restoratives. However, the literature has not provided sufficient information on the hydrolytic stability of TCAs. To our knowledge, the stability of these coupling agents after aging in simulated body fluid or artificial saliva has yet to be reported. Previous studies demonstrated that the behavior of dental composites in distilled water varies from that in artificial saliva. Filler leaching was higher in artificial saliva than that in distilled water because of the ion exchange and deterioration of the filler-resin interface<sup>15,37</sup>. Thus, the use of TCAs is viable and feasible in future research. TCAs can help in the development of chemical binding

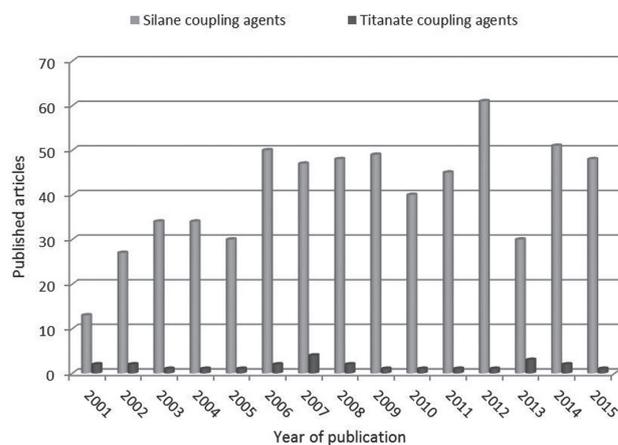


Fig. 9 Popularity of silane coupling agents and the limitation of TCAs as reported in different dental journals.

Table 5 Effects of various coupling agents on the mechanical properties of metal oxide-polymethacrylate composites

| Filler                         | Coupling agent | Compressive and transvers strength   | Conclusion   |
|--------------------------------|----------------|--|--|
| TiO <sub>2</sub>               | TCA            | Diminished strength is observed. Titanated TiO <sub>2</sub> is more stable in moisture than silanized SiO <sub>2</sub> . | TCA enhances the bond between TiO <sub>2</sub> and resin. TCA could prevent the leaching process of the TiO <sub>2</sub> in oral environments. |
| SiO <sub>2</sub>               | Silane         | Reduced strength   | Filler bonding is weakened after one month immersion in water. Filler leachability is induced.   |
| ZrO <sub>2</sub>               | Ziconate       | Decreased strength due to interface failure between zirconated ZrO <sub>2</sub> and the resin                            | Interface may hydrolyze more readily than either titanated TiO <sub>2</sub> or silanized SiO <sub>2</sub> under water immersion.               |
| Al <sub>2</sub> O <sub>3</sub> | 4-META         | Lack of bonding between Al <sub>2</sub> O <sub>3</sub> filler and resin led to lowering the strength.                    | 4-META has no affinitive inorgano-functional groups capable of bonding to metal oxide.   |

Al<sub>2</sub>O<sub>3</sub>=Aluminum oxide

4-META=4-Methacryloxyethyl trimellitate anhydride

between the dispersed phase and the resin composite.

Tham *et al.*<sup>52)</sup> examined the effect of TCA on the mechanical, thermal, and morphological properties of PMMA denture-base composites; their group reported that TCAs provide good interfacial bonding, improve mechanical properties, enhance homogenous filler dispersion, and modify the rheological behavior of the composites. TCAs can also be used to induce the hydrophobic property of a filler surface and uniformly distribute the small particles in a polymer matrix<sup>8)</sup>. Another study<sup>87)</sup> examined the effects of several coupling agents on the mechanical properties of metal oxide-polymethacrylate composites reinforced with several fillers for opaque resins. The results are summarized in Table 5. This particular study concluded that the significant improvement in the mechanical properties of TiO<sub>2</sub>-reinforced polymethacrylate composite achieved with an appropriate TCA is indicative of the potential clinical usefulness of coupling agents as a composite pigment for opaque resin materials. These outcomes are similar to those in other studies<sup>88,89)</sup> that reported high microhardness and mechanical strength in the dental composites filled with TiO<sub>2</sub>. Moreover, the compressive strength of the composites containing titanate-treated TiO<sub>2</sub> was higher than those with untreated TiO<sub>2</sub>. A recent study<sup>73)</sup> investigated the physical properties of denture-base resin filled with titanated NBT. A notable improvement in surface hardness was observed with increasing NBT content in the PMMA matrix. This finding was attributed to the high hardness value of the dispersed phase and the imposed restriction on matrix deformation derived from the uniform distribution of the NBT. In addition, water sorption decreased with increasing filler loading. The presence of TCA induced the hydrophobicity of the NBT and enhanced the adhesion between the filler and the PMMA matrix. As stated in our previous work<sup>13)</sup>, titanated Ti-based fillers are useful reinforcement in dental composites of resin materials. Thus, the chemical compatibility between the dispersed phase and the coupling agent should be considered.

### CONCLUSIONS

The filler-matrix interface is the least abundant phase of a composite material. However, this interface significantly affects the properties of the composite. Concerns regarding the hydrolytic instability and effectiveness of silane coupling agents in an aqueous environment are frequently encountered particularly when non-silica fillers are impregnated in dental restorative materials. Dental composites are used in moist oral environments. Hydration can significantly decrease the mechanical properties of these materials. Specific interfacial failures are attributed to the chemical incompatibility between the composite phases and the coupler. Therefore, the chemical compatibility between the dispersed phase and the coupling agent should be considered. Titanate couplers can effectively be used to coat the inorganic fillers of dental materials

to improve their dispersion and bonding with the resin matrix. As inorganic filler candidates, titanate fillers can be a choice material for titanation because of their chemical compatibility. The notable properties obtained when titanated Ti-based fillers are incorporated into polymeric composites represent a promising direction for the design of ideal materials for dental applications. Previous studies have evaluated the moisture resistance of titanates. However, further investigation is necessary to examine the stability of titanates in simulated body fluid or artificial saliva. Enrichment of the hydrolytic stability of dental composites can help prevent health concerns and promote the longevity of the applications of these materials.

### ACKNOWLEDGMENTS

The authors would like to thank the Department of Mechanical and Materials Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia for supporting this work.

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