

## Review Article

# Perspectives for Titanium-Derived Fillers Usage on Denture Base Composite Construction: A Review Article

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Poly(methyl methacrylate) (PMMA) is an extensively used material in dentistry because of its aesthetics, processability, and reparability. However, PMMA is still far from being ideal in fulfilling the mechanical requirements of prosthesis. PMMA-based denture base polymers exhibit low fracture resistance and radiopacity behavior. Efforts to improve the mechanical and radiopacity properties of denture base materials through inclusion of silica-based fillers are ongoing. Although silane-treated siliceous fillers are commonly used, they are not sufficiently strong. They also exhibit cracks, which either cut through the glass fillers or propagate around the filler particles. This defect occurs when the dental composites are placed in aqueous oral environment because of the hydrolytic degradation of silica-based fillers and silane-coupling agents. The clinical problem of using silanes in adhesion promotion is bond degradation over time in oral environment. In addition, silanes do not bond effectively to nonsilica-based dental restorative materials. This review presents titanium-derived fillers as alternatives to siliceous fillers. Titanate-coupling agents are found to be effective couplers in treating Ti-based fillers because of their chemical compatibility and relatively high stability in aqueous environment.

## 1. Introduction

Polymers are important in dentistry because their distinctive properties allow a range of clinical applications, which are impossible with the use of other types of materials. The most widely used impression materials (alginates, polyethers, polysulfides, and silicones) are polymers. Further applications include denture bases, artificial teeth, cements, dies, provisional crowns, endodontic fillings, tissue conditioners, and pit and fissure sealants. Poly(methyl methacrylate) (PMMA) is extensively used as a denture base material [1]. However, this material is not ideal in every aspect, particularly in satisfying the mechanical requirements of prosthesis. Fracture of acrylic resin denture base occurs frequently because of fatigue and chemical degradation of base material [2].

Polymeric matrices with silane-treated silica-based fillers are commonly used in dental restorative materials [3, 4]. However, these fillers do not exhibit sufficient strength to reinforce the resultant composites [4] and they leach in

aqueous oral environment [5, 6]. Siliceous filler treatment with silane-coupling agents provides bond between two components in dental composites, but this bond can be degraded by water absorbed by the composites [4, 6], thereby adversely affecting the mechanical properties of the materials and decreasing their longevity. Thus, incorporation of alternative fillers should be considered, in which a suitable coupling agent is used to achieve an acceptable mechanical behavior of the dental composites. This narrative review aims to evaluate the effectiveness of inclusion of titanium-derived fillers in dental composites and denture bases. Such fillers should be treated by a titanate-coupling agent because of its relatively good hydrolytic stability compared with that of silanes and the inefficiency of silanized nonsilica-based fillers [7, 8].

## 2. A Brief Historical Review

Early prostheses were fashioned by carving denture bases from naturally occurring materials, such as wood, bone,

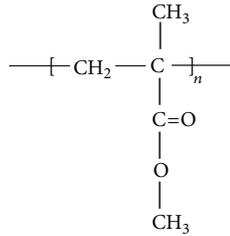


FIGURE 1: Chemical structure of PMMA.

and ivory; however, aesthetics and hygiene became the main concerns. In 1788, a porcelain complete denture was fabricated. Although this material was stable with minimal water absorption and solubility, as well as low porosity, it was brittle and difficult to grind and polish. During the middle of the 19th century, vulcanized rubber (vulcanite) was introduced as a denture base material. The main disadvantage of these denture bases was their dark red color, which was difficult to pigment, and absorption of saliva, making them unhygienic [1]. Moreover, vulcanite exhibited inherent massive volume shrinkage because of the vulcanizing techniques used at that time [3]. This material was eventually displaced by another polymer, PMMA (Figure 1), which displays improved physical, aesthetic, and handling properties [9]. The adoption of the dough technique first described in the mid-1930s enabled the use of acrylics in dentistry. In the dough technique, a liquid component (monomer) is mixed with a powder component (polymer). The monomer wets the polymer to a dough-like consistency, which is packed into the mould prior to polymerization. Adoption of the new denture bases was rapid in America. However, in Europe, change was forced upon the profession by rubber shortage during World War II. By the end of the war, the use of vulcanite for dentures had almost ceased. After the war, resins developed for aircraft production and the burgeoning plastics industry were offered for use as denture base materials; the simplicity of the dough technique and the lifelike results have sustained acrylics as the market leader to the present day [3].

### 3. PMMA as a Denture Base Material

Acrylic polymers were utilized as denture base materials since 1937 [9]. They were so well received by dental professionals that, by 1946, approximately 98% of all denture bases were based on PMMA. The cured polymer should be stiff enough to hold the teeth in occlusion during mastication and to minimize uneven loading of mucus under the denture. The denture material should not creep under masticator loads for long-term use if good occlusion is to be maintained and potential irritant effects are kept at minimum [10]. Such material should also have sufficient strength and resilience to withstand normal masticator forces; withstanding sudden shock caused by impact forces is an important property. The material should not deteriorate in the aqueous environment of the mouth, and craze formation caused by solvents present in food, drinks, or medicaments should be absent or minimal [11].

TABLE 1: Composition of denture base materials (heat curing).

	Polymer	PMMA
Powder	Initiator	Benzoyl peroxide (BPO) (0.5%)
	Pigments	Salts of cadmium or iron or organic dyes
	Monomer	MMA
Liquid	Crosslinking agent	Ethylene glycol dimethacrylate (EGDMA) (10%)
	Inhibitor	Hydroquinone (>1%)

Acrylic resin is extensively used in denture construction. This material exhibits various desirable attributes and handling characteristics, such as low cost, lightweight, easy handling and processing, easy polishing, excellent aesthetics, lack of toxicity, and biocompatibility in the oral environment [12, 13]. It is normally supplied in powder and liquid forms; details of its composition are given in Table 1. The major components of the powder are PMMA beads with diameters of up to 100  $\mu\text{m}$ . These beads are produced by suspension polymerization, in which the methyl methacrylate (MMA) monomer containing an initiator is suspended as droplet in water. The temperature is then increased to decompose the peroxide and induce MMA polymerization to form PMMA beads that form a free-flowing powder at room temperature after drying. In addition, crosslinking molecules are added to reduce the formation of small surface cracks in the denture when it is allowed to dry. an inhibitor (hydroquinone) is used to prolong the shelf life of the liquid component.

**3.1. Classification of Denture Base Polymers.** Denture bases can be typically classified according to the activation method, which has a significant effect on the resultant material properties. During fabrication, the cure condition and method affect the physical and mechanical properties of the denture [14].

**3.1.1. Heat-Cured PMMA.** Table 1 summarizes the composition of heat-cured denture base. The powder supplied has significantly high molecular weight. The highest molecular weight distributions and lowest plasticizer content are favored because they produce better physical and mechanical properties in the cured denture base [3]. BPO is added as an initiator, which decomposes rapidly to form free radicals at  $>65^\circ\text{C}$ . Once polymerization commences, the temperature of the resin may become considerably higher than the temperature of the water bath. the increase in the curing temperature enhances the mechanical and chemical properties of acrylic resins. The heat-cured PMMA is the strongest material for denture base fabrication [15, 16]. In addition, this material has more color stability and less residual monomer level than light and autopolymerizing acrylic resins [17, 18]. The heat-activated denture base can be modified with the inclusion of a rubber phase into the beads during polymerization, producing a high-impact acrylic denture base.

**3.1.2. Cold-Cured PMMA.** Cold-cured or self-curing PMMA is referred to as “pour risen” because it is poured into a processing mould made of agar hydrocolloid to form

a denture base. The composition of this material is the same as that of the heat-cured version, with the following two differences: the powder contains polymer beads with lower molecular weight than those of the heat-cured material; the liquid contains a chemical activator (an amine molecular), which initiates the reaction. Self-curing or autopolymerizing denture bases are processed quickly at room temperature. They have more residual monomers (1% to 4%) but lower dimensional changes (0.2%) than heat-cured dentures [19].

The poured-type mould itself has design weaknesses. The gelatinous agar cannot grip the teeth as easily as does the rock-hard plaster mould. Thus, teeth displacement during acrylic pouring is likely to occur. In addition, prior to being placed in the mould, the teeth themselves are part of the wax-up. Thus, any wax remaining on the teeth prevents the monomer from wetting their surfaces. This problem is far less common when solution and diffusion of the wax can occur at elevated temperature of the heat-curing process.

**3.1.3. Light-Activated Polymer.** Light-activated polymer is a composite of a paste urethane dimethacrylate (UDMA) monomer with fillers. Although most of the light-curing composites are employed as direct filling materials [20], they could also be used as repair materials for prosthodontics and custom tray material. However, their application in denture construction is restricted when a patient has hypersensitivity to PMMA [21]. Some studies have shown that the properties of these denture polymers are slightly lower than those of the conventional PMMA materials and they produce slightly rougher surfaces that seem to stain more readily [19]. In addition, the adhesive strength of denture teeth to the light-curing denture base is less than that of heat-curing denture base resins [22].

Light-cured materials are comparable with conventional heat-cured materials in terms of impact strength and hardness, but they have considerably lower elastic modulus. Thus, a denture based on light-cured material deforms elastically to a greater extent than a heat-cured denture under the forces of mastication. However, the transverse strength of light-cured material, which is a measure of the total force required to fracture a thin strip of material in a transverse direction, is just slightly lower than that inherent in conventional materials.

**3.1.4. Microwave-Polymerized Polymers.** The resins used with microwave-polymerized polymers have the same composition as those used with conventional material. The properties of the microwave resins are optimal when a special liquid is substituted for the normal monomer liquid. Although the denture base cures well in the special polycarbonate (instead of metal) flask with the use of normal monomer liquid, higher level of porosity is found compared with dentures processed with the use of special liquid. The properties and the accuracy of these materials are as good as or better than those of the conventional heat-cured material, and the processing time is significantly shorter (4 min to 5 min) [19]. Lai et al. [23] concluded that microwave energy can efficiently polymerize denture base resin. High statistical differences are found in

terms of morphology and flexural properties in favor of the water-bath method. In addition, the selection of appropriate microwave power and curing time is vital in reducing the porosity to a minimum level.

## 4. Alternative Polymers

Although PMMA has been commonly utilized in the fabrication of removable denture bases, a number of polymeric materials, such as high-density polyethylene (HDPE), polyamide (PA), and poly(L-lactide) (PLLA), have been studied for their prosthodontic applications. Furthermore, polystyrene polyvinyl acrylic and light-activated UDMA have also been used in the construction of denture bases. These materials must be durable and strong enough to withstand masticatory forces, particularly for patients with parafunctional habits. However, none of these polymers provides the unique combination of physical and aesthetic properties exhibited by PMMA. Thus, PMMA remained a main component of denture base polymer for many years because it is hard, rigid, and easy to repair and can be color-matched to the patient's teeth and gum tissue [13, 24]. Moreover, Yilmaz and Korkmaz [25] stated that PMMA displays advantage for long-term fixed provisional restorations; it has higher fracture toughness values than poly(ethylene methacrylate) (PEMA) before and after reinforcement. In 2010, a comparative study between denture bases made from conventional PMMA and polyurethane denture base materials was performed by Young [26]. This study determined that samples of the alternative denture base material had relatively poor mechanical strength compared with the PMMA-based samples, which were all fabricated in accordance with the manufacturers' instructions. As a result, PMMA remained the dominant denture base material for >50 years, and a suitable alternative material has yet to be discovered.

Despite these excellent properties, improvement in the fracture resistance of PMMA is needed. Most denture fractures occur inside the mouth during service, primarily because of resin fatigue [13, 27]. The denture base resin is subjected to various stresses, including compressive, tensile, and shear forces, during function. Some of the factors responsible for denture fracture include stress intensification, increased ridge resorption leading to an unsupported denture base, deep incisal notching at the labial frenum, sharp changes at the contours of the denture base, deep scratches, and induced processing stresses. A modified PMMA that includes poly urethane (PU) rubbery particles shows higher fracture toughness than unmodified PMMA; however, its transparency is reduced [28]. Jagger et al. [2] conducted a study to strengthen and modify the acrylic resin by using graft copolymerization with high-impact resins. The resultant material was not generally evaluated because of flexural property deterioration of the resin. Moreover, resistance to functional loads and removal forces, which are mechanical factors, must be considered in choosing a provisional restorative material for clinical use [25]. Such properties can be developed effectively by creating a composite material.

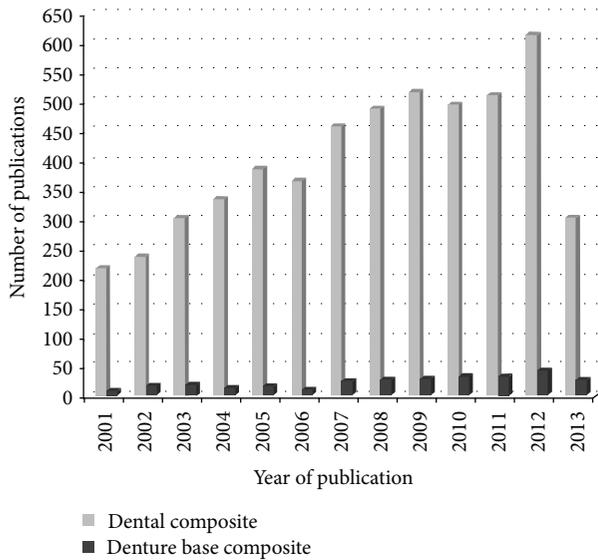


FIGURE 2: Increasing significance of dental composites compared with that of denture base composites. (Search keywords: dental composite and denture base composite in ISI Web of knowledge until October 2013).

## 5. PMMA Composite as a Denture Base

Polymeric composites are expansively utilized as dental filling and they have gained more significant attention than denture base composites (as shown in Figure 2). These materials are becoming increasingly popular for the treatment of small- and medium-sized defects in the posterior region because of their favorable physical properties. Composite filling materials were first developed in the early 1960s, and they provided materials with higher mechanical properties than acrylics and silicates, lower thermal coefficient of expansion, lower dimensional change on setting, and higher resistance to wear, thereby improving clinical performance [29]. The organic matrix employed is usually based on methacrylate chemistry, particularly crosslinking dimethacrylates, such as 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (Bis-GMA), ethoxylated Bis-GMA, 1,6-bis-[2-methacryloyloxyethoxycarbonylamino]-2,4,4-trimethylhexane (or UDMA), dodecanediol dimethacrylate, and triethylene glycol dimethacrylate [20]. Although Bis-GMA is used in most of the resin composite systems because of its superior aesthetic quality, simple operation technique, enhanced mechanical strength, less shrinkage, higher modulus, and reduced toxicity because of its lower volatility and diffusivity into the tissue, Bis-GMA still has some shortcomings, thereby limiting its application [30, 31].

In addition to the use of polymeric composite as dental filling material, PMMA composite is also used as bone cements [32–34], artificial teeth [35], and denture bases [13–15, 24, 35–37]. The differences in applications depend on the varying required characteristics. For instance, a significant development in dental filling composites is the ability to bond materials to tooth structure, whereas this property is not a requisite for materials used in removable

prosthodontic construction. In other words, properties of denture base composites should be more related to their application, which make these two composites completely different. discrimination between them has been already stated in a previous study [38], in which a remarkable increase in fracture toughness with high pressure and temperature is shown in dental composite, whereas their effect on the mechanical properties of the PMMA denture base resin is unknown. Denture base composites have been developed to overcome the neat PMMA drawbacks, such as poor strength, polymerization shrinkage, and radiolucence. The denture base material should possess a desired balance of stiffness and toughness. The stiffness of the commercial denture base materials seems satisfactory; however, the inherently low fracture toughness of PMMA is a major shortcoming of its corresponding resins. Despite satisfying aesthetic demands, the mechanical requirements of prosthesis are unsatisfactory [37].

The fracture of acrylic resin dentures is still a common clinical occurrence. Attempts to analyze and determine the causes of such fractures have received considerable attention in recent years. These notable efforts have been conducted to solve this problem and to strengthen the dental polymer by incorporating various types of fibers [10, 13, 39–43] and fillers [24, 44–46] (Table 2), but it has not been solved [40]. In addition, denture breakage can also be caused by faulty design and/or faulty fabrication, such as severe frenal notch, prominent torus palatinus, poor fit of denture base, and also insufficient mechanical properties of the denture base resin, which lead to failure during service [27]. Denture fracture outside the mouth occurs from impact caused by accidents as a result of expelling the denture from the mouth while coughing or dropping the denture. Inside the mouth, excessive biting force may also cause fracture [47]. Although a strong positive association is found between fracture toughness and impact strength of PMMA bone cement [48], the fracture toughness method is more suitable than impact strength measurements in demonstrating the effects of resin modifications [49].

Furthermore, denture bases constructed from pure PMMA are not radiopaque, and thus they are not detectable on radiographs. This means that should such denture be accidentally inhaled or swallowed, it cannot be detected by radiographic means; any delay in localizing or removing the foreign body may be life threatening. Therefore, radiopacity in denture bases is a desirable attribute. Many attempts to incorporate a degree of radiopacity into acrylic denture base materials have been performed. Some radiopaque additives are mentioned in Table 2 accompanying remarkable comments according to the related references. Atoms with higher atomic number than C, H, and O, which compose the acrylic resin, have been incorporated. A commercially available product contains 8% BaSiO<sub>4</sub>, which did not produce sufficient levels of radiopacity. Increasing the BaSiO<sub>4</sub> content to 29% produces sufficient radiopacity but shows deleterious effect on the mechanical properties of the resin; no additive has been proved to be satisfactory [26].

During clinical use, the denture base materials are immersed in saliva and, when not in use, may be soaked

TABLE 2: Some of the components added into dental polymers.

Additives	Comments	References
Glass fibers, particles or whiskers, quartz, and silica	Decreased mechanical properties after storage in water	Guo et al. 2012 [72]
	Not strong enough	Lin et al. 2008 [64] and
	Not radiopaque and not strong enough	Mirsasaani et al. 2011 [4]
	Reduced radiopacity	Cruvinel et al. 2007 [117]
Polyethylene fibers	Poor interaction between the fibers and the matrix	Geerts et al. 2008 [10] Alla et al. 2013 [13]
Ultrahigh molecular weight polyethylene fibers	Impractical for the dental laboratory practice	Uzun et al. 1999 [42]
Nylon fiber	Fiber pullout from the matrix	Lin et al. 2008 [64]
Carbon and Kevlar fibers	Aesthetic unsatisfactory and poor adhesion with acrylic resin	Tandon et al. 2010 [1] and Alla et al. 2013 [13]
	Complicated etching process required to improve their incorporation into PMMA	Uzun et al. 1999 [42]
Metal wires and metallic fillers	Poor adhesion between wires and the acrylic resin	Mowade et al. 2012 [37] and Alla et al. 2013 [13]
	Aesthetic unsatisfactory	Young 2010 [26]
PA and sapphire whiskers, fibers	Break up the homogeneity of acrylic resin	Mowade et al. 2012 [37]
ZrO <sub>2</sub>	Not compatible with the matrix	Kitayama et al. 2009 [7]
	Insufficient radiopacity	Carrodeguas et al. 2003 [33]
BaSO <sub>4</sub>	Adverse effect on mechanical properties and color instability	Young 2010 [26]
	Increased cost	Mowade et al. 2012 [37]
Comonomers containing rubber phase	Deterioration of flexural properties	Jagger et al. 1999 [2]
	Reduction of the resin's translucency	Jung et al. 1998 [28]
Comonomers containing heavy metals	Poor mechanical properties and aesthetic unsatisfactory	Young 2010 [26]

in water or cleansing agents. When immersed in such solutions, plasticizers and other soluble components may leach out over extended periods, whereas water or saliva is absorbed. The loss of plasticizer may cause brittleness and increased hardness. The effects of water on the bond strength of acrylic materials can have a detrimental effect on bond strength to acrylic resin. Furthermore, exposure of restorative materials to an aqueous environment is known to degrade their mechanical properties and resistance to wear. These deteriorations have been attributed to the hydrolytic degradation of the polymer matrix and filler, as well as to the water-induced filler-matrix bond failure [50, 51]. In other words, the used coupling agent is unaffected by an aqueous oral environment. Numerous studies [4–6, 52] have indicated that the high water sorption and solubility of restorative resins produce decreased mechanical properties and reduced longevity of composite restorations.

## 6. Interfacial Phase and Coupling Agents

For a composite to have effective clinical performance, a good bond must form between the inorganic filler particles and the organic resin matrix during setting. This phenomenon is achieved through the use of coupling agents, such as

silane [30]. This interfacial bonding is important to transfer load from the polymer matrix to the reinforcing fillers. The general principles of adhesion are mechanical interlocking and chemical bonding through ionic or covalent bonds, at the interface of composite's phases. However, if the adhesion is not durable enough and if any voids appear between the fiber and the matrix, then these voids may act as initial fracture sites in the composite, thereby facilitating material breakdown. Thus, durable adhesion between the fiber and the matrix is significant for the mechanical performance and the longevity of restoration in dental applications [53]. The most common types of coupling agents are organofunctional silanes and organotitanates, which are used to improve filler dispersion in matrix, prevent aggregation, and reinforce the interfacial coherence with resin [54].

**6.1. Silane-Coupling Agents.** Silanes are commonly used in dentistry in different applications to provide the opportunity for chemical bonding. They can bond both inorganic and organic dissimilar materials together. They typically contain two functional parts. One end contains an organic group that can polymerize with the adhered resin system. The other end contains groups that can react with inorganic groups of substrate, which means that silanes can function as mediators

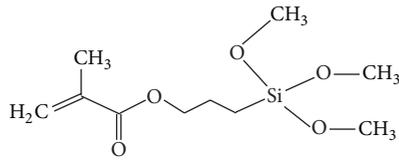


FIGURE 3: 3-Methacryloyloxypropyltrimethoxysilane silane-coupling agent.

between dispersed and organic phases. The most common silane, 3-methacryloyloxypropyltrimethoxysilane (MPS, or 3-MPS; Figure 3), has been evaluated as filler particles of resin composites and in lamination of glass fibers [55]. Silica and Si-based fillers are commonly employed fillers in dental composites [4, 26, 39] and biomaterials [56]; these additives can be easily functionalized by silanes because of the similarity in their ordered structure. Thus, silane-coupling agents chemically bond the silica, present in silica-based fillers such as porcelain, quartz, pyrogenic silicon dioxide, and silicate glasses [31, 57], to the organic matrix of resin by means of siloxane bonds and hydrogen bond [55, 58]. Although the filler-matrix interphase is the least abundant phase of the composite material, it has significant effects on the physicochemical properties of the composites [59, 60].

Good bond strength is found between a dental leucite-based glass ceramic and resin cement generated after functionalizing the ceramic filler with the use of silane-coupling agent [61]. Other studies [62, 63] demonstrated that flexural properties of PMMA containing silanized siliceous fillers could be improved effectively. The use of silane-treated silica fillers is an effective method of reinforcing PMMA resins. Despite the popularity of silica and glass fillers, they are not strong enough or they may create stress concentration points throughout the matrix caused by their irregular shapes, and then composites exhibit cracks, which either cut through the fillers or propagate around the filler particles [4, 26, 56, 64, 65].

However, for nonsilica-based restorative materials, such as zirconia, metals, or metal alloys, the adhesion performance achieved with the use of silanes only is unsatisfactory [8]. These techniques do not improve the bond strength of zirconia and alumina ceramics because the suitable chemical reaction is impossible with these ceramics [7]. Approaches to solve this problem have been focused on surface conditioning. A currently used method is tribochemical silica coating. A silica-coated layer is anchored to the substrate surface such that silane-coupling agents can form durable bond with nonsilica-based materials through this layer [8]. Nevertheless, the qualitative and quantitative changes in the surface through these procedures are not fully known. In addition, failures are partly or mostly adhesive; that is, the failure is observed in the interface between resin composite and zirconia surface [66]. Kitayama et al. [7] reported that a tribochemical silica coating might be less effective for densely sintered ceramics than for glass-infiltrated ceramics. Moreover, a tribochemical silica coating cannot cover the entire abraded surface with silica. Therefore, long-term studies of the effects of various surface treatments are needed

to improve our understanding of the bonding mechanisms and failure modes involved.

Dental restorative composites can serve in a wet environment, but they exhibit less stability in oral fluids. Although marked improvements have been noted in terms of physical and mechanical properties during the last two decades, various molecules, such as enzymes and alcohol, present in the oral cavity can degrade the composite and deteriorate the interfacial bond among the composite phases [4, 5, 67]. Thus, silane-coupling agents provide the bond between two components in dental composites, but this bond can be degraded by water absorbed by the composites. Hence, the improvements are more apparent when composites are exposed to high humidity and high temperature. In addition, the interface among composite constituents should not be degraded by the oral environment [67–69]. Some studies revealed that composites based on silane-coupling agents rapidly lose strength and stiffness when exposed to aqueous environment [70, 71], which could be attributed to tendency of silane-coupling agents to form aggregates on the filler surface, thereby resulting in an unstable bond between fillers and resin; this bond can be degraded by water absorbed by the composites [62]. Thus, their hydrolytic instability and longevity in oral conditions are a continuous concern for clinicians [69].

Guo et al. [72] reported that composites reinforced with silanized glass fibers exhibit decreased mechanical properties after prolonged storage in water. For example, the flexural strength and modulus of a commercial dental composite, which contains 38% short glass fibers, decrease by 66% and 60%, respectively, after storage in water for three months. The flexural strength after dehydration did not recover to the same level as that in the dry group. Although some studies showed improved silane bond by applying an acetone primer to the glass prior to the silane treatment, this has not solved the problem of slow silane degradation in oral fluids [73, 74]. Accordingly, silanes should be replaced by one of other different kinds of coupling agents, particularly when nonsiliceous fillers are impregnated. For instance, zirconia ceramics are not silica based and thus they present a physicochemical challenge for reliable and durable resin bonding because chemically stable silica-silane bonds cannot be directly established [75]. Moreover, some composites cannot be light-cured, thereby limiting their application, because the mismatch of the refractive indices between the whiskers ( $\text{SiC}$  2.65 and  $\text{Si}_3\text{N}_4$  2.2) and polymer resin (1.53) causes high opacity of the whisker-reinforced composites. Therefore, alternative reinforcing elements for dental composites are also needed [72].

**6.2. Titanate-Coupling Agents.** As stated previously, the interfacial bond between dispersed and polymer composite phases should not be deteriorated by the oral cavity moisture. In addition, silane provides chemical coupling by reacting with oxides or hydroxyl groups available on the particle surface, which are not available on the surface of other fillers [76]. Thus, a substitute for silane-coupling agents is necessary. Accordingly, titanate-coupling agents have important role in achieving durable bonding between ceramic filler and

polymer matrix. They can modify the surface characteristics of filler and improve the interfacial bonding with the matrix. The nature of the interlayer between the filler and the polymer matrix, introduced by the titanate treatment, is significant in improving the mechanical properties of the composite [77]. Unlike silanes, titanium-derived coupling agents react with free protons at the inorganic interface, resulting in the formation of organic titanium monomolecular layers on the inorganic surface without water for condensation. The absence of a multimolecular layer at the interface and the chemical structure of titanates modify the surface energy of filler particles in such a way that the melt viscosities of polymers are lower than those of other types of coupling agent [78]. Titanate-coupling agents can also provide good interphase bonding, improve mechanical properties, enhance filler homogenous dispersibility, and modify the rheological behavior of the composites [22]. Titanates can also be used to couple interfaces, which are nonreactive with silane, such as calcium carbonate, graphite, aramid, and carbon black. They overcome many of the limitations of incompatible polymers and inorganic fillers [79].

Titanate-based coupling agents have been successful in providing chemical bonding and dispersion. The molecular formula is described as  $XO-Ti-(OY)_3$ , where  $XO-$  is the alkoxy group capable of reacting with the inorganic substrate and  $-OY$  is the organofunctional fragment. The  $Y$  portion typically contains several different groups to provide interaction with polar and nonpolar thermoplastics (e.g., benzyl and butyl), thermosets (e.g., amino and methacryl), and binder groups, such as pyrophosphato or carboxyl, which can introduce additional functions to the composite [76]. These coupling agents should protect the interface from hydrolytic deterioration. Hence, the coupling agents should provide water-resistant bonds at the interface. Organotitanates offer enhanced stability in wet environment. The hydrolytic stability of titanate coupler has been evaluated by a previous study, which stated that composite samples treated with titanates exhibit greater resistance to moisture-ingress than the untreated composites. Recovery in strength on reconditioning was also higher for treated samples than the control [80].

Tham et al. [24] reported that titanate-coupling agents can provide good interphase bonding, improve mechanical properties, enhance filler homogenous dispersibility, and modify the rheological behavior of the composites. In addition, titanate-coupling agents can be used to induce the hydrophobic property of filler surface characteristics and distribute the smaller particle size uniformly in polymer matrix [79]. When used in polymers, titanates can increase adhesion, impact strength, and mechanical properties [81]. An investigation of the effect of different coupling agents on the mechanical properties of the  $TiO_2$  particulate filled epoxy composite shows the mechanical properties enhanced with the use of titanate-coupling agent because of the formation of a strong interface or adhesion between the filler and matrix [82]. Titanate coupler is found to be more effective than silane-coupling agent, and it modifies the surface characteristics of filler and improves the interfacial bonding with the matrix [76, 82–84].

## 7. Titanium-Based Fillers in Dentistry

Titanium (Ti) and Ti-based alloys are preferred materials in the production of implants for medical and dental applications. These biomaterials have relatively poor tribological properties owing to their low degree of hardness. One approach to altering the biological properties of Ti alloys is by modifying its chemical composition. Another method is to produce a composite that exhibits the favorable mechanical properties of Ti and the excellent biocompatibility and bioactivity of a ceramic [56]. Furthermore, the introduction of Ti fillers as an added component can potentially enhance the mechanical strength and radiopacity of the dental filling composites [85]. Abdelaziz [86] reported that the type of the filler used significantly influences the properties of the composite restoratives. Although the improvement of the properties of dental composites has received considerable attention, the available information on the usage of Ti-derived fillers remains limited.

In general,  $TiO_2$  particles are preferred in dentistry because of their pleasing color and high biocompatibility [44].  $TiO_2$  nanoparticles ( $n-TiO_2$ ) also have excellent mechanical properties; for example, the elastic modulus of  $n-TiO_2$  is approximately 230 GPa, and it is inexpensive with titanium being the fourth most abundant metal on earth, following aluminum, iron, and magnesium [87]. Other characteristics such as white color, low toxicity, and high stability and efficiency, as well as availability and low cost, have made  $TiO_2$  an appropriate antimicrobial additive for dental materials [88]. Considering that titania is stable in the body and does not degrade, bone cements that contain bioactive titania filler can thus be stable in the body. Subsequently, composite bone cement that contains  $n-TiO_2$  was developed. Studies have shown that certain compositions of the cement have good mechanical strength [32, 89].

Titania nanoparticles have been used as an additive in dental materials to match the opaque properties of teeth [90] and to enhance the mechanical properties of dental resins. Thorat et al. [91] prepared and characterized bis-GMA resin dental restorative composites with glass, silica, and titanium fillers. The researchers concluded that  $TiO_2$  fillers could be useful in future applications because their photocatalytic effects promote local antibacterial or remineralization reactions. Likewise, other studies have been performed to modify dental composites by incorporating  $n-TiO_2$  into a standard dental acrylic. Such studies have reported that the most available commercial product for dental restorations could be improved through the addition of  $n-TiO_2$  with relatively large particle size [85]. In addition, the mechanical behavior of  $n-TiO_2$  reinforced resin-based dental composites was investigated by Hua et al. [92]. This study demonstrated that the mechanical advantage of nanocomposites over microcomposites could be found in the reinforcing effect of  $n-TiO_2$  with 3% volume fraction on the stiffness, which is the same as a glass fiber with twice the volume fraction. This result is consistent with previous studies, which indicated that dental composites reinforced with 3%  $n-TiO_2$  exhibited superior mechanical properties compared to the control, with minimal effects on flowability and radiopacity. Thus, these reinforced

composites are promising materials for applications in dental restorations [87, 93, 94].

Furthermore, a study [95] investigated the effect of the BaTiO<sub>3</sub> filler on the fracture toughness of PMMA denture base polymer before and after soaking in simulated body fluid (SBF). The researchers concluded that when the composite was exposed to SBF, two detrimental effects occur. First, the liquid destroyed some filler-matrix bonds, resulting in an irreversible reduction in the fracture toughness. Second, the liquid caused the surrounding matrix to swell and plasticize, thus reducing the hoop stress around the filler particles and facilitating filler pull-out. In general, the fracture toughness of denture base materials was significantly changed after immersion in SBF. This change is attributed to the increase in the hydrolytic degradation of the silane-coupling agent, resulting in filler-matrix debonding. This result is consistent with the study of Deb et al. [96], which reported that water uptake can lead to the reduction in polymer strength. Elshereksi et al. [46] examined the thermal characterization of BaTiO<sub>3</sub>/PMMA denture base composites and found that the degradation temperatures of the filled samples were higher compared with that of the PMMA matrix. In addition, increasing filler content from 5 wt% to 20 wt% increased the degradation temperature and thermal stability of the resultant PMMA composites.

Modifying the surface of inorganic filler particles is essential because a durable bond must be created for the composite's phases. In an oral environment, the bonds among the resin composite silanized zirconia and Ti diminish over a long period. This decline may be due to the hydrolytic cleavage of siloxane bond in the siloxane interfacial layer [8]. Titanate couplers can be used to coat the inorganic fillers of dental materials to improve their dispersion and bonding with the resin matrix [5, 24]. Moreover, a dramatic improvement in moisture resistance can be achieved by adding a small amount of titanates [80, 97].

## 8. Titanate-Treated Titanium-Based Fillers

The selection of a proper coupling agent is important in prolonging longevity of the composite. Coupling agents such as phosphates and zirconates have been investigated for resin-to-zirconia bonding as an alternative to silane-coupling agents because of the enhanced bonding. Zirconium oxide nanoparticles are therefore surface functionalized with zirconates (as presented in Figure 4) or aluminozirconates [98]. The application of zirconate coupler and resin bonding agent mixture on the pure zirconium metal surface or zirconia has been shown to be effective in promoting the bonding between zirconium and ZrO<sub>2</sub>, as well as in dual-cured resin-luting cements [98, 99]. Thus, chemical compatibility between the dispersed phase and the coupling agent should be considered. Some interfacial failures have been attributed to chemical incompatibility between the composite phases and the coupler [100]. When titanium-derived fillers are used, the titanate-coupling agent is found to be a better substitute for silane in achieving durable bonding between ceramic filler

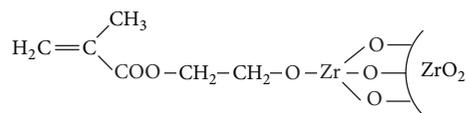


FIGURE 4: Zirconium oxide nanoparticles functionalized with methacryl zirconate.

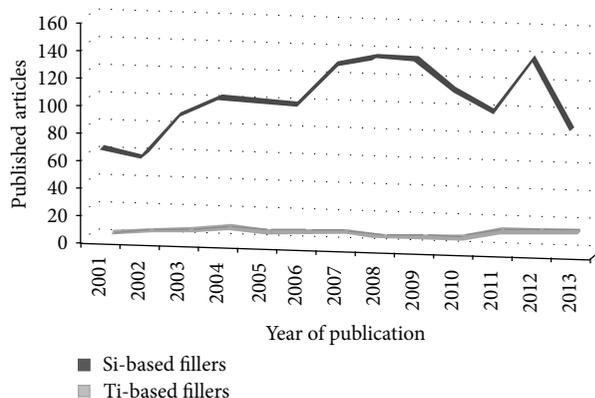


FIGURE 5: Popularity of Si-based fillers and limitation of Ti-based fillers usage in dental composites. (Search keywords: glass dental composite, Si dental composite, and Ti dental composite in ISI Web of knowledge until October 2013).

and polymer matrix. Promising results could be obtained with its application in restorative materials.

Compared with the use of titanium as dental implant material, the use of its derivatives is limited [101] (Figure 5). Titanium (Ti) is used in odontology because of its excellent characteristics, such as chemical inertia, low density, absence of toxicity, resistance to corrosion biocompatibility, and mechanical resistance. Such metals meet the existing requirements for use in oral defect restoration [102, 103]. Furthermore, TiO<sub>2</sub> can also be utilized as a reinforcing agent in dental and biocomposite fabrication because of its antimicrobial properties and biocompatible features [88, 104, 105]. Khaled et al. [32] enhanced the mechanical properties of commercial acrylic cement by introducing novel nanostructured titania tubes (*n*-TiO<sub>2</sub> tubes) into the cement matrix. The results showed that the treatment with 1 wt% *n*-TiO<sub>2</sub> tubes results in significant increase in fracture toughness of PMMA composite. This increase is attributed to the enhanced interaction and strong interfacial adhesion between the treated *n*-TiO<sub>2</sub> and polymer matrix, thereby allowing external mechanical stress to be more effectively transferred through the filler-matrix interface. These outcomes are similar to those in other studies [44, 106], which concluded that the dental composites filled with TiO<sub>2</sub> exhibit high microhardness and mechanical strength. Moreover, compressive strength of composite with titanate-treated TiO<sub>2</sub> was higher than that with untreated TiO<sub>2</sub>. The results suggested that TiO<sub>2</sub> treated with titanate-coupling agent is useful as a pigment of the opaque material of fixed prosthodontic composite [107]. Regardless of the application, Li et al. [79] inferred that when TiO<sub>2</sub> is treated with titanate-coupling agent, TiO<sub>2</sub> exhibits a good modified surface. The surface characteristics of TiO<sub>2</sub> change from

hydrophilic to hydrophobic and  $\text{TiO}_2$  particles show good dispersion in liquid paraffin. The results indicated that treated  $\text{TiO}_2$  particles enhance binding force with and dispersion in polybutylene terephthalate matrix. Therefore, in such circumstances, titanate-coupling agent could be used as an alternative to the silanes.

In addition, another variety of titanium-derived fillers, such as  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{ZrTiO}_4$ , have not been used in biological application. Although  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  have been evaluated as formulated bone cement composites [33],  $\text{ZrTiO}_4$  is also applicable in bone tissue engineering [108]. These outcomes indicate a significant impact on the nomination of another material, such as  $\text{BaTiO}_3$  to be used as dental filler.  $\text{BaTiO}_3$ , as a class of ceramic systems, possesses interesting features for biological applications because of its favorable mechanical [109], biocompatible [110–112], and piezoelectric properties, which extended the scope of biomaterials because of the stress-generated potential [33, 112]. The piezoelectric effect is a property of certain materials in which an electrical potential is produced by the application of a mechanical stress. These potentials have been linked to the mechanical adaptation of bone in response to loading, thereby indicating that the addition of an electrically active component to an implant material may improve healing and adaptation of the surrounding tissue [113]. Although  $\text{BaTiO}_3$  fillers have repeatedly been shown to be biocompatible, no evidence of their dental applications has been found in literature. In addition, surface modification of  $\text{BaTiO}_3$  fillers by titanates has not been performed.

Radiopacity is another characteristic that should be considered. This feature is now considered as a desirable property of dental and biomaterials. All of the intraoral materials, including denture base materials, denture liners, direct filling restorative materials, and resin cement luting agents, are acknowledged to have desirable radiopacity [114]. As specified by the International Standards Organization (ISO 4049), the radiopacity of dental materials should be equal to or greater than the same thickness of aluminum wedge and should not be less than 0.5 mm of any value claimed by the manufacturer [115]. Radiopacity of composite materials should exceed that of dentin. However, no definitive maximum limit has been identified [93]. Research into radiopaque polymers focuses on developing methods to increase the average electron density and specific gravity of polymers by incorporating heavy elements into these systems. A common practice is to introduce radiopacity via radiopaque additives [116].  $\text{BaTiO}_3$  filler can then be incorporated as a radiopacifier into PMMA matrix because of the relatively high atomic number of its components [95]. In addition, the radiopaque properties of a composite material highly depend upon the size, shape, amount of radiopacifying agent, and crystallinity of the radiopaque material. Thus, the radiopacity degree can vary within the same class of material. For instance, polymer composites intended for use in anterior teeth have filler particles that are smaller in size and lower in concentration than those intended for use in posterior teeth. In addition, the material thickness, the angulation of the X-ray beam, the methodology employed for evaluation, the type of X-ray film, the age of developing and fixing solutions, and

the alteration in the power/liquid ratio can affect material radiopacity [117].

## 9. Conclusions

Although PMMA is far from being a perfect denture base, it is the common material of choice for denture fabrication. PMMA exhibits low fracture resistance, particularly under fatigue failure inside the mouth and impact failure outside the mouth. Different polymers, such as HDPE, PA, PLLA, and PEMA, have been evaluated. However, the tests have not yielded new denture base polymers. Therefore, the expanded use of dental composites in a wide range of applications promotes the demand for the improvement of their properties and performance. This demand requires an ongoing investment in research and improvement. Silane-coupling agents have a critical function as mediators to fulfill the clinical requirements for durable adhesion among the composite phases. However, concerns about the hydrolytic instability and the effectiveness of silane-coupling agents on aqueous environment are frequently encountered, particularly when nonsilica fillers are impregnated in dental restorative materials. Moreover, titanate fillers may be important in enhancing dental composite properties when they are functionalized with the use of titanate-coupling agent.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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