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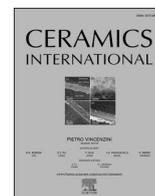
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# Influence of filler characteristics on the performance of dental composites: A comprehensive review

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## ABSTRACT

In restorative dentistry, dental composites have become a popular material of choice due to the increasing aesthetic demands and address challenges like recurrent cavities and restorative bulk fracture, which are the most common causes of dental composite failure. To address these issues, various types and shapes of reinforcement fillers were researched to enhance the mechanical properties of composite formulations over conventional composites. Furthermore, antibacterial agents and ion-releasing fillers are used to prevent secondary caries and promote the remineralisation of dental tissue. This review article aims to review the literature of dental resin composites, focusing on various filler categories and their impact on the materials' performance, to aid future development of dental resin composites for clinical applications with optimal properties that can overcome current limitations.

## 1. Introduction

Composite filling materials have superior aesthetic properties over silver amalgam restorations; mostly because they can be customised to match the colour of a patient's teeth, and this adaptability is one of the key elements in its efficiency [1]. Additionally, the use of composites is more conservative to the tooth structure due to its adhesive system where composites bond to the tooth structure without needing extensive tooth preparation. According to the Minimata convention and calls to reduce the use of mercury-containing products, Composites have recently emerged as the best viable replacement for amalgam as a direct restorative material [2]. Although amalgams have shown outstanding clinical performance for up to twenty years after placement compared to other types of direct tooth filling materials [3]. However, owing to the toxicity of mercury which makes up about 50% of the total composition in commercially available amalgam fillings, clinicians and dentists have raised concerns as it can be difficult to isolate the cause when people develop health problems such as an increase in the risk of tremors in practicing dentists [4]. Dental composites consist of two main components: (organic resin) matrix and (organic/inorganic) filler in composites. Organic resins are made of a blend of multifunctional monomers

and initiators, while the fillers can be organic or inorganic in nature with a varying size range (from nanometer to micrometer), shapes and functions.

Although the current restorative composites have superior mechanical and physical properties compared to classic composites [5–7] they have an average duration of just under ten years [8], after which professional intervention may be required [1,9–14]. The common causes of clinical failure are recurrent caries and restorative bulk fracture. According to meta-analyses of resin composite restorations, at least 5% of these restorations were anticipated to experience bulk fracture during 10 years, while 12% will exhibit significant wear [9,12]. From the standpoint of material properties, the multifactorial interaction of inadequate degree of conversion [15], stresses resulting from the polymerisation shrinkage [16,17], high surface affinity to bacterial biofilm formation [18], low fracture toughness [19,20], and high-water sorption and solubility [21–24], affect the longevity of dental resin composites.

Therefore, to address above mentioned challenges, various developments in dental resin composites have been presented and investigated to improve the qualities of dental composite materials, including the production of low shrinkage monomers, to meet the issues [25,26], monomers with antibacterial activity [27], and different mechanisms of

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free radical chain developing polymerisation [28]. However, the most significant enhancements and changes have been in the fillers such as size reduction, shape enhancement (platelike, rods, nanoparticles), functionalisation [29–32], and bioactive ability [33] to suit the demands of dentists. This review article aims to present the evolution of dental resin composites, with a focus on the several ceramic filler categories that have been added (Fig. 1), and their impact on the performance of the materials according to their specific purpose. An analysis of recent research on the use of ceramic fillers as additives would aid researchers and practitioners in determining future research areas and assisting in the appropriate selection of dental materials. With optimum properties that can overcome the current limitations.

## 2. Composition of dental composites

Fig. 1 summaries the contents of this review paper in which focus is the different types of traditional or untraditional fillers used to discuss their associated effect on the overall properties of the dental composites. It is pertinent to mention here that in literature, the term Dental Composite is commonly referred as Resin Based Dental Composites, Composite Resin and/or Polymer Dental Composites [34]. The following section briefly touches upon the Organic matrices as they make backbone of the dental composites before moving onto the prime focus of the paper.

### 2.1. Organic resin matrix (monomers)

Organic resins form the backbone of the dental composites and are frequently used in dentistry for cosmetic purposes. They are manufactured using free radical polymerisation, which is initiated by visible light in modern materials. Monomers are viscous, bulky compounds that react to form an organic matrix that is robust and long-lasting in clinical use.

The organic matrix the dental resin composites consist of photopolymerised three-dimensional system that contains and bonds the fillers. Aromatic monomer Bisphenol A glycidyl methacrylate (BisGMA) is the main constituent of most composite resins used in dentistry in its linear form. BisGMA is a strong monomer with high mechanical properties, and low polymerisation shrinkage. However, it has a high viscosity which lowers the degree of conversion [35], and also as a result of this high viscosity of BisGMA, incorporating fillers to reinforce or enhance physical and mechanical properties proves to be difficult [36, 37]. Monomers with lower viscosity, such as triethyleneglycol dimethacrylate TEGDMA, are added to BisGMA as diluents to attain appropriate handling and degree of conversion. TEGDMA increases the reactivity and the percentage of the degree of polymerisation [38]; However, this dilution has the unintended outcome of enhancing polymerisation shrinkage, as it has been proven that increasing the concentration of TEGDMA causes greater polymerisation shrinking and higher contraction stress which could be due to adding lower molecular weight monomers leading to a greater conversion per unit volume [39–41]. Urethane dimethacrylate (1,6-bis(methacryloyloxy2-ethoxycarbonylamino)-2,4,4-trimethylhexan) UDMA (Fig. 2) have been also explored for dental composites. This UDMA has similar molecular mass as BisGMA (470 g/mol), but it has lower viscosity and synthesised either singularly or blended with other monomers. This makes UDMA based materials potentially superior to a BisGMA and TEGDMA mixtures because of lower polymerisation shrinkage and a higher degree of conversion which directly enhance the mechanical properties of the composites [17,34,42]. To achieve a balance in viscosity, mechanical characteristics, polymerisation shrinkage, and other features of dental composites, it is required to balance the composition and ratio of resin monomers.

Many derivatives and several new monomers groups of the above-mentioned resins have been developed to substitute bisphenol A-

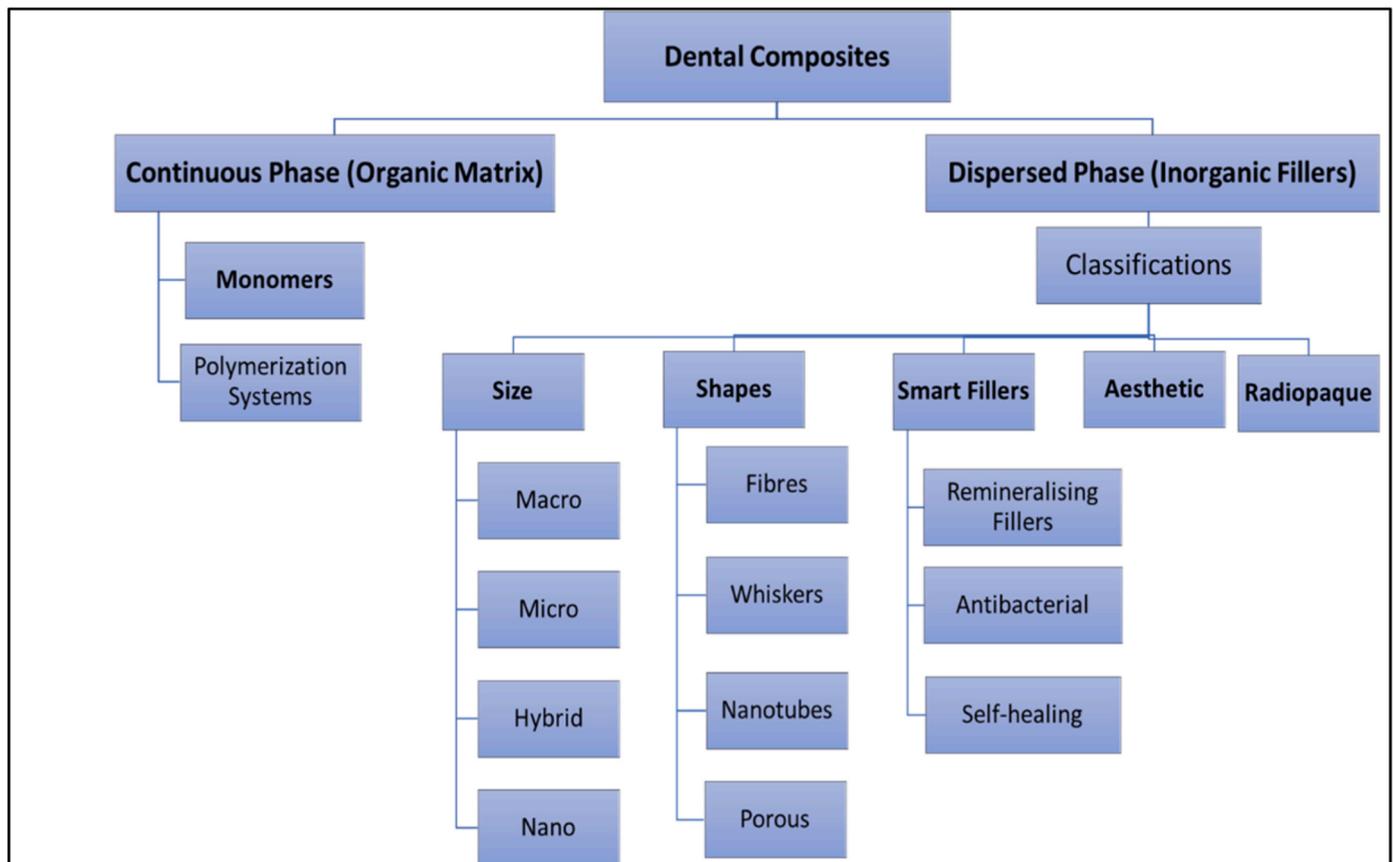


Fig. 1. Graphical summary of the general composition of dental resin composite with different types of fillers added.

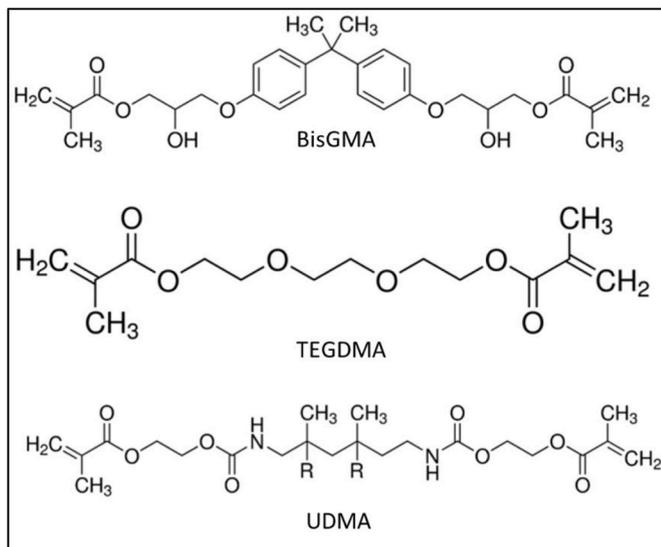


Fig. 2. The basic monomers for resin dental composite. Reproduced with permission from Merck KGaA, Darmstadt, Germany and/or its affiliates [45].

containing BisGMA such as oxiranes [43], dendrimers, isorsorbides and more [44]. Wherein alternative polymerisation chemistries have been suggested. Accordingly, several research investigated variety of monomers to enhance polymerisation kinetics, rheology, biocompatibility, and mechanical properties to address the limitations of the conventional dimethacrylate based monomers. Those studies classified the monomers according to their chemistry as methacrylate, vinyl, click chemistry and ring opening polymerised monomers [28].

## 2.2. Inorganic fillers (dispersed phase)

Fillers, also known as the dispersed phase of the composites and is primarily responsible for providing mechanical reinforcement. Different types of inorganic fillers are used such as glass, quartz and/or silica. Previously, strontium, quartz or barium glasses were the most used fillers in composites [31], however, quartz was replaced by glass particles which offer higher optical properties, accessibility, and acceptable mechanical properties, however, due to its hardness which proved to produce high wear of antagonist teeth. Existing composites contain silicate particles derived from barium oxide, strontium oxide, zinc oxide, aluminium oxide, or zirconium oxide, with typical filler percentage in the range of 50–80% by weight and particle size varies in the range of 5 nm to 85  $\mu\text{m}$  [46,47]. Parameters linked to fillers, such as filler loading, size, shape, and particle distribution, impact the physical and mechanical characteristics of composites, with several studies indicating a relationship between filler parameters and mechanical properties [17, 25,30,48–53], increased radiopacity [54], enhanced aesthetics [55], and improved handling [56].

In addition to the reinforcement function of the fillers that enhance the mechanical properties of dental composite materials, other types were added to address the restoration failure caused by recurrent caries such as fillers with bioactive properties. The following section presents a classification of filler systems and the relationship between filler characteristics and their impact on the physical, chemical, Biological and mechanical properties of dental composites. The summary of main mechanisms and general trends of results regarding the effect of various filler characteristics on the properties of dental composites are provided in Table 1.

### 2.2.1. Particle size

Varieties of dental composites are traditionally distinguished by the characteristics of their reinforcing fillers, and in particular their size as

Table 1

A summary of different fillers and their influence on the properties of the dental composites.

Filler category	Type	Influence on properties of dental composites
Filler Size	Large filler size	<ul style="list-style-type: none"> <li>The size of the filler influences its refractive index and degree of light scattering in the matrix phase, which can alter DC and depth of cure. When the filler size is nearly half the wavelength of the visible light curing unit, maximum light scattering of fillers is produced, which is linked with the lowest DC. Poor wear resistance due to crack propagation at the filler/resin interface, and loss of filler particles, resulting in poor polishability, as well as early discolouration and staining due to roughness.</li> </ul>
	Reduced filler size	<ul style="list-style-type: none"> <li>diminishes interparticle spacing, limiting the development of localised nanogel in the matrix and resulting in decreased DoC.</li> <li>Filler size reduction reduces particle projection at the surface which improves wear resistance. Furthermore, increases matrix viscosity and limits the total polymerisation which adversely affects the mechanical properties.</li> </ul>
Filler Shapes	Fibres	<ul style="list-style-type: none"> <li>Nano-sized electrospun fibres were found to improve composite properties such as flexural strength, and modulus [93,94].</li> <li>Micron-sized fibres showed deterioration in materials properties [93,94].</li> </ul>
	Whiskers	<ul style="list-style-type: none"> <li>Silicon nitride whiskers showed better strength and toughness, hardness and modulus of dental resin composite compared to the silicon carbide whiskers [99–101].</li> <li>Silica fused whiskers showed improved wear resistance and flexural strength [98].</li> </ul>
Filler Shapes	Nanotubes	<ul style="list-style-type: none"> <li>Silanated carbon nanotubes enhanced the flexural strength of the composite resin by 23% and adversely affected the optical properties due to their dark colour [55].</li> <li>Adding TNTs as fillers to flowable dental composite improved the composites' strength and the elastic modulus [105,106].</li> </ul>
	Porous fillers	<ul style="list-style-type: none"> <li>Composite resins enforced by porous fillers showed better wear resistance [109–113].</li> <li>Porous glass ceramic fillers enhanced the flexural strength and modulus of dental resin composites, with no effect on the tensile strength [113,114].</li> <li>Inadequate infiltration of the resin matrix into the filler porosity results in deterioration in the flexural strength of the composite resin [115].</li> <li>Wrinkled mesoporous silica fillers significantly increased the mechanical properties of dental resin composites compared to the conventional silica fillers of the same size [103].</li> </ul> <p>Mesoporous silica-filled composites demonstrated superior transparency,</p>

(continued on next page)

Table 1 (continued)

Filler category	Type	Influence on properties of dental composites
Smart (multifunctional) fillers	Bioactive glass	<p>higher glass transition temperature, and increased adhesive strength [113, 119].</p> <ul style="list-style-type: none"> <li>45S5 bioglass caused swelling and cracking upon immersion of the resin matrix due to its hydrophilicity [121].</li> <li>BRP composites showed improved mechanical properties as well as water sorption and solubility compared to typical BAG-based composites [29,138].</li> <li>Replacement of sodium with <math>F^-</math>, <math>Mg^{2+}</math>, <math>Zn^{2+}</math>, and <math>Sr^{2+}</math> in BAG fillers added to the composites' ultimate features. Low sodium BAG showed a comparable neutralizing effect with conventional 45S5 [128].</li> <li>Amorphous <math>Ca_3(PO_4)_2</math> nanoparticles filled composites could be recharged with <math>Ca^{2+}</math> and <math>PO_4^{3-}</math> to maintain a continual ion release.</li> <li><math>Ca_3(PO_4)_2</math> results in a reduction in the strength of the composite. This was resolved by adding a co-filler with <math>Ca_3(PO_4)_2</math> filler such as nano silica fused silicon carbide whiskers and Dimethyl tetrachloroterephthalate (DCPA) nanoparticles [143,144].</li> <li>The flexural strength was twice higher in the filler mixture compared to the composite contained <math>Ca_3(PO_4)_2</math> filler only [143,144].</li> <li>CaP enhances the material's water sorption, which speeds up the breakdown of the resin matrix [122].</li> <li>Composites with crystalline calcium phosphate have lower translucency and aesthetics due to the difficulty in manipulating their refractive indices.</li> <li>A new <math>Ca_3(PO_4)_2</math> nanocomposite showed inhibition in bacterial biofilm and did not show any effect on the release and recharge of <math>Ca^{2+}</math> and <math>PO_4^{3-}</math>, while it has no significant effect on mechanical properties [122].</li> </ul>
	Calcium phosphate	<ul style="list-style-type: none"> <li>HA in dental restorations assist in the remineralisation of collagen of the natural dental tissue [147]</li> <li>HA whisker (HW) and nanofibres showed superior reinforcing properties compared to particulate HA [143].</li> <li>urchin-like HA (UHA) was used as a dental filler with silica nanoparticles, and demonstrated higher flexural strength, modulus, and compressive strength [88].</li> <li>UHA filled composites showed decreased degree of conversion and depth of cure due to the mismatch in the refractive index of the UHA with the matrix [88].</li> </ul>
	Zinc oxide particles	<ul style="list-style-type: none"> <li>Adding zinc oxide (0–5%) in composites, inhibited bacterial growth while maintaining strength [150].</li> <li>ZnO composites showed reduced depth of cure due to the opacity of ZnO.</li> <li>Resin composites comprising 7 wt% ZnO@m-SiO<sub>2</sub> nanoparticles showed</li> </ul>

Table 1 (continued)

Filler category	Type	Influence on properties of dental composites
Self-healing fillers	Polymer nanoparticles	<p>improved interfacial bonding which resulted in improved compressive strength, flexural strength, and modulus [122].</p>
	Antimicrobial treated fillers	<p>Un-leachable, long-lasting antibacterial effects.</p> <ul style="list-style-type: none"> <li>Drug-coated copper nanoparticles filled composite showed a persistent release of antimicrobial particles and enhanced hardness with increasing coated fillers fraction [158].</li> </ul>
	Piezoelectric bio-ceramics	<ul style="list-style-type: none"> <li>Piezoelectric BaTiO<sub>3</sub> nanoparticles demonstrated a considerable decrease in bacterial growth and the production of calcium phosphate minerals [160].</li> <li>Sodium Potassium Niobate (NKN) composites had a combination of both antibacterial and remineralising activity [160].</li> <li>TEGDMA was added in PU microcapsules shells with a combination of DHEPT as a healing liquid, an effective self-healing mechanism was observed with no determinantal effect on the mechanical properties [166].</li> </ul>
Radiopaque fillers		<ul style="list-style-type: none"> <li>Adding Heavy atoms such as BaSO<sub>4</sub>, TiO<sub>2</sub>, or ZrO<sub>2</sub> as opacifying components [172].</li> <li>Adding SiO<sub>2</sub>-ZrO<sub>2</sub>-SiO<sub>2</sub> (SZS) as secondary fillers in composite resulted in an improvement of the radiopacity as well as it showed lower shrinkage and enhanced mechanical properties [176].</li> </ul>
		<ul style="list-style-type: none"> <li>ZrO<sub>2</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, modify the translucency of dental composites [177–179]</li> <li>Eu2O3, Tb4O7, Dy2O3 are used to enhance the fluorescence of the dental materials [181].</li> <li>Replacing the particles with smaller size spherical particles (100 nm in diameter) results in achieving the appropriate level of opalescence [180].</li> </ul>

shown in (Fig. 3), as they are classified based on the average particle size of filler particles and has been widely used and investigated.

**2.2.1.1. Macro filled composites.** Also known as conventional or traditional composites. Fillers made of inorganic particles larger than 1  $\mu$ m. These particles were introduced to the BisGMA/TEGDMA resin matrix at a concentration of around 55–65 (vol%) to create a paste that, after chemical polymerisation, had flexural strengths of 110–135 MPa [57]. Traditional resin composites included Concise (3 M, St. Paul, MN, US) and Adaptic (Johnson & Johnson, Windsor, NJ, US) which contained a particle size range of 1–40  $\mu$ m [58]. The addition of these fillers resulted in a significant enhancement in properties when compared to unfilled acrylic materials, especially improved compressive strength, hardness, and elastic modulus, and noticeable declines in polymerisation shrinkage and thermal expansion [59]. However, due to the large filler size many drawbacks were reported such as poor wear resistance due to crack propagation at the filler/resin interface, and loss of filler particles, resulting in poor polish-ability, as well as early discolouration and staining due to roughness. Ground quartz, strontium, or heavy metal glasses containing barium, are the fillers most commonly used in this type of composite [60,61].

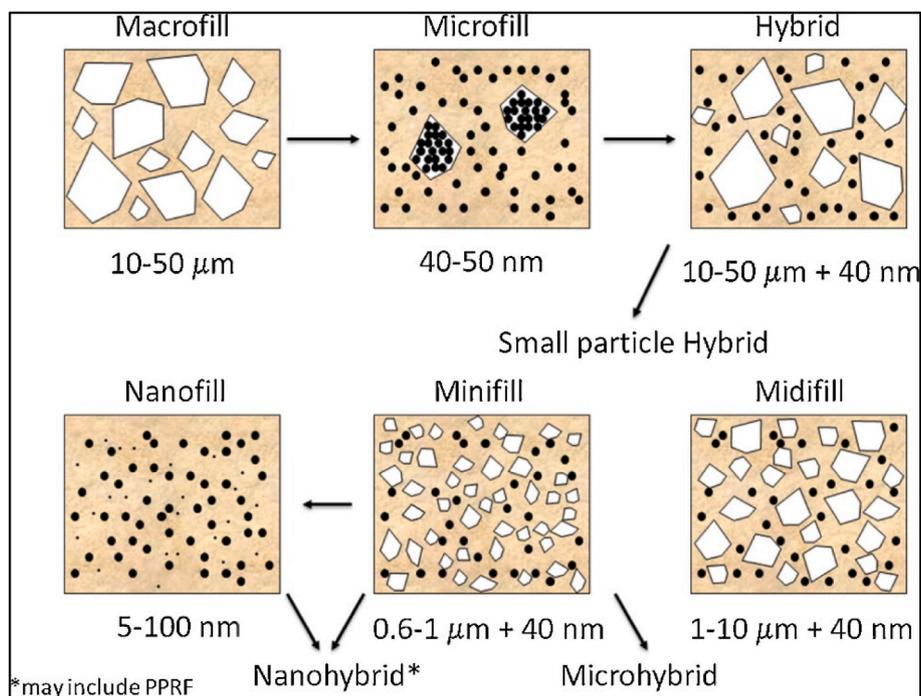


Fig. 3. The classification of dental composite formulations based on filler particle size. Reproduced with permission of the rights holder, Elsevier [59].

**2.2.1.2. Micro filled resin composites.** Micro-filled resin composites were introduced to overcome the macro filled disadvantages and to comply with the aesthetic needs for polishable composites. The name was not precise as it was to express the fact of the microscopical size of the particles, as the size of the amorphous spherical silica was around 40 nm. Fine filler particles of silica have a massive effect on the polymer rheology (increases the viscosity) [59]. Nevertheless, the very large surface area of the particles considerably restricts the volume of filler that can be incorporated accordingly they have a large volume of the polymer. This would lead to a greater water absorption, a higher coefficient of thermal expansion and decreased elastic modulus compared to macro-filled composites. Compared to macro-filled resin composites, they have also been shown to have lower fracture resistance, stiffness, and fatigue strength compared with heavily filled composites [62–64]. To overcome this drawback, pre-polymerised fillers (PPRF) were introduced which are larger in size to improve the filler volume fraction. PPRFs are processed using ground-cured composite containing a variety of submicron particles. The addition of PPRF also decreases the polymerisation shrinkage and improves polish ability when compared to conventionally filled resin composites [65,66]. However, PPRF lack the active binding sites for surface coupling which results in reduced bonding to the resin matrix and consequently compromised mechanical properties [30,67].

**2.2.1.3. Hybrid resin composites.** These materials consist of both micro- and nano-fillers, and therefore share the characteristics of them both. They were introduced to solve the mechanical and the shrinkage problems, also finishing problems, of macro filled composites [59]. The first introduced hybrid resin composites contained large filler particles, of a size of 10–50  $\mu\text{m}$ , as well as colloidal silica of particle size of 40 nm. Hybrid composites are therefore ideal for use as universal composites as they are supposed to combine the advantages of macro-filled with its high mechanical properties enable the material to withstand masticatory forces as in posterior filling these properties related to the large filler size, and at the same time it has excellent optical properties and acceptable polish ability acquired from the small particles' fillers, to be used for anterior teeth restorations. However, they do not have the final finish and translucency of micro-filled resin composites [60,61].

**2.2.1.4. Nanocomposites.** Nanocomposites are a recent development which has been introduced with nano-sized filler particles. These nanoparticles are either individually dispersed with an average diameter of 5–100 nm or agglomerations of these particles described as nanoclusters [68], of overall size 0.6–1.4  $\mu\text{m}$  respectively. Also, they show high translucency, and due to the small size of the particles, these dental nanocomposites possess higher surface quality and superior ability to retain polish compared to conventional composites. When compared to micro fill or nanohybrid systems, nanoclusters provide a unique reinforcing mechanism, resulting in considerable enhancement in strength [69]. They have similar mechanical, physical, and wear resistance as hybrid composites. As a result, they may be applied in both load-bearing and aesthetic essential areas [68,70].

The addition of fillers to the polymer matrix improves fracture toughness, elastic modulus, and tensile strength [30,51,71,72]. The mechanical characteristics of particle-filled polymer composites are significantly influenced by the size of particles [48]. Fracture toughness in particular was proved to be significantly affected by the particle size added [73]. As it was found that resin composites with 1.9  $\mu\text{m}$ -sized glass particles, comprising 78 wt % of the material, had greater fracture toughness of 1.41 MPa than resin composites with smaller particles of 0.5  $\mu\text{m}$  of 1.24 MPa [74]. This improvement was related to crack deflection [75]. In dental restorative materials, filler particles improve fracture toughness by improving crack propagation resistance through a variety of toughening processes, including crack deflection, crack pinning/bowing, matrix–filler interactions, and crack bridging.

On the other hand, the flexural strength of dental composites was improved by more than 100% when 50 wt%  $\text{Al}_2\text{O}_3$  (10  $\mu\text{m}$ ) was added. It was reported that dental composites' flexural strength was raised when 70 wt%  $\text{SiO}_2$  (3.3  $\mu\text{m}$ ) was added to 174.2 MPa, however, it was decreased when bigger microparticles (4.3, 7.9, and 15.5  $\mu\text{m}$ ) were added 129.3, 110.4, and 102.2 MPa, respectively [74]. The reduced particle size of the filler particles increases their surface area, which generates high surface energy at the filler-matrix contact and accounts for the gain in flexural strength. However, the decrease in flexural strength can be due to the higher stress concentration at the filler-polymer matrix contact as a result of bigger particles, poor interaction between the matrix and filler or the presence of interfacial flaws,

inadequate stress distribution caused by the formation of the stress concentration points resulted from the filler clusters [76].

Comparatively to conventional micro-composites, dental composites incorporating nanoparticles offer better mechanical characteristics, such as flexural strength, compressive strength, and wear resistance. Foroutan et al. found that dental nanocomposites strengthened with various loadings of Al<sub>2</sub>O<sub>3</sub> (25–40 nm) (10, 20 and 30 wt %) had a considerably higher flexural modulus of 1157.23, 2221.57 and 2894.76 MPa respectively [77]. Additionally, Hosseinalipour et al. evaluated the mechanical properties of Bis-GMA/TEGDMA dental composite reinforced with various loadings of SiO<sub>2</sub> nanoparticles (20–50 nm) at 20, 30, 40, and 50 wt%. At a loading of 40 wt%, they discovered a considerable improvement in flexural strength (149.74 MPa) [78]. However, SiO<sub>2</sub> (20 nm) was added to micro-filled composite resin by Garoushi et al. at different loadings of 10, 15, 20, and 30 wt%. Their findings demonstrated that plain resins have superior flexural strength (123.7 MPa) to nanocomposites (84.8, 71.1, 71.2, 84.4 MPa) [72]. The increase in flexural strength was explained by the high specific surface area of the nanoparticles, and strong interfacial bond formation. While the low flexural strength results can be attributed to the nanosized oxides which act as impurities inside the polymer structure in addition to the insufficient matrix wetting of the filler. Furthermore, the dispersion of the nanoparticles restricts the degree of monomer conversion and results in the entrapment of unreacted monomers that can act as plasticisers [76].

### 2.2.2. Filler shapes

Fillers come in a wide range of chemical compositions, but they are most easily identified by their diverse shapes and aspect ratio [79]. Conventional dental fillers are usually spherical, irregular granules or particles and can detach from the resin matrix during long-term service [80]. Fibre-reinforced polymers composites have widespread applications in other sectors such as aerospace, automotive, space, construction to name a few [81–84]. The superior properties of fibre reinforced polymers composite prompted their use in dental composites. Whisker/fibre pin the pull out, crack deflection, and bridging resulting in enhanced lifetime of the composite. Fibres are known to have a relatively high aspect ratio (20–500) and are flexible. The impact of fibre/nano-fibres [79,82,84], nanotubes [85,86] and whiskers [87,88] on the efficiency of dental composites has been widely studied in literature and known to have enhanced mechanical properties. Nanotubes are slightly different from fibres as they too have a high aspect ratio but possess hollow centres giving them a tubular shape. Whiskers on the other hand have the lowest aspect ratios within fibrous fillers and are generally rigid [29,31,89]. Although fibrous fillers enhance mechanical properties of the matrix, they produced inferior aesthetics due to the mismatch in the refractive index.

**2.2.2.1. Fibres.** Fibres are elongated homogeneous materials having a transverse cross sectional diameter or thickness of less than 250 µm, and with an aspect ratio that is often more than or equal to 100, i.e., the ratio of length to cross-sectional diameter or thickness [90]. However, there are several situations when the aspect ratio of the fibres might be less than 100, for as with short fibres, chopped fibres, whiskers, or staple fibres. The mechanical characteristics of the fibre resin composite are influenced by the fiber's type, length, orientation, and volume percentage [82]. Glass fibres are the most common fibres used in dental composites as they share comparable refractive index to silica. They also share similar chemical composition to silica as well as being inexpensive, they show high mechanical properties and excellent bonding to the polymer matrix compared to other types of fibres such as Carbon/epoxy, polyaramide and ultrahigh molecular weight polyethylene [79,82]. A study investigated the mechanical characteristics of short glass fibre resin composite structures made as temporary dental crowns and bridges. It discovered that these structures had higher flexural strength (117 MPa) and compressive load bearing capacity (730 MPa) than those

made of temporary crowns and bridges that were more commonly used [84]. Another research looked at the features of bio ceramic (nHA) and high-strength (E-glass fibre) materials coupled in a unique way to amalgamate reinforcing agents in dental resin-based composites. The values for the DC were all satisfactory (65) compared to the control group (50) [91]. However, the higher loading of nHA/E-glass fibre declined the resin-filler adhesion and impacted the water sorption behaviour. Accordingly, the experimental composites' results for hardness and flexural strength were at opposition with one another. With an increase in the concentration of reinforcing elements (40%,50%,60%), the hardness values increased (52.06, 56.78, 61.89), but the flexural strength declined (126.12, 107.61, 98.4 MPa). According to ISO 4049, all experimental composites demonstrated the flexural strength needed for resin-based materials (flexural strength over 80 MPa) [92]. When fibres were incorporated in low weight fractions (1–5%) with spheroidal silica fillers, nano-sized electro-spun fibres were found to improve composite properties such as flexural strength, and modulus, unlike micron-sized fibres which deteriorate materials properties [93,94], as they tend to aggregate and create voids into the matrix upon addition in large quantities. Nanofibers as a co-filler can give a unique packing architecture by forming a protective system around other particle fillers, resulting in higher wear resistance and reduced polymerisation shrinkage. During fibre pull-out, nanofibers elevate modulus and strength through crack bridging and energy adsorption. The most used glass fibres in dentistry are E-glass and S-glass such in Vectris Pontic and FiberKor [79](Fig. 4). S-glass is more expensive and has a shorter life-span than E-glass, and it also has higher tensile strength (4700–4800 MPa) and elastic modulus (86–93 GPa) compared to E-glass of tensile strength (1950–2050 MPa) and elastic modulus (72–85 GPa) [79,90,95].

**2.2.2.2. Whiskers.** Recently ceramic whiskers have been used in dental composites to enhance flexural strength and fracture toughness of composites. Whiskers are structurally flawless, as they have no grain boundaries, dislocations, or other crystallographic imperfections. As a result, whiskers have known to improve mechanical characteristics by an order of magnitude [31]. Materials such as ceramics and glasses were used in dental composites to enhance mechanical properties [31]. Various whiskers with a diameter ranging from 5 nm to 1 µm and length in the range of 10–200 µm have been used [97]. Some of these will be discussed in the upcoming sections (zinc oxide, hydroxyapatite). Xu investigated Silicon nitride and silicon carbide whiskers by incorporating them with silica particles at different whisker/silica mass ratios in a matrix of BisGMA and TEGMA, and the results showed that the mechanical properties of dental resin composites are significantly influenced by the type of the whiskers and to the ratio of the whiskers to silica particles [98]. The inclusion of silicon nitride whiskers showed better strength and toughness of dental resin composite compared to the silicon carbide whiskers, Silicon carbide whiskers, on the other hand, improved modulus and hardness more than silicon nitride, The silicon nitride whisker composite reached a strength of 246 ± 33 MPa at whisker/silica of 1:1, while the silicon carbide whisker composite reached 210 ± 14 MPa at 5:1. The brittleness of the silicon carbide was explained due to the morphology of the silicon carbide as they are significantly longer with twisted forms compares to silicon nitride making them readily fractured during crack bridging and whisker pull-out [99–101]. Whisker composites outperformed glass-particle-filled composites in thermal cycling, long-term water ageing [100], and three-body wear [101]. In vitro, the whisker composites were biocompatible and promoted cell proliferation and survival [102].

With the improvement in the mechanical properties of whiskers filled composites however, they still lack the ability to prevent secondary caries. Further study utilised nano-sized dicalcium phosphate anhydrous particles (DCPA) as fillers with whiskers in resins to release large quantities of Ca and PO<sub>4</sub>, which are required for remineralisation [98].

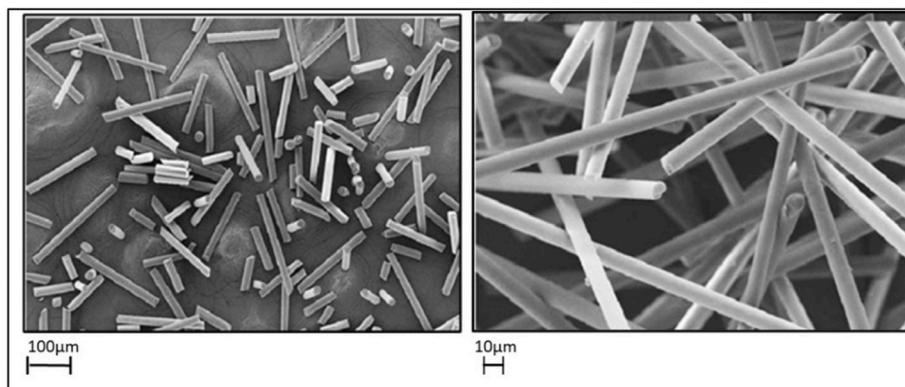


Fig. 4. SEM micrographs showing E glass fibres (1003). Reproduced with permission of the rights holder, John Wiley and Sons [96].

The silica and dicalcium phosphate nanoparticles fused whiskers showed improved wear resistance and flexural strength ranged from  $(148 \pm 9)$  MPa to  $(167 \pm 23)$  MPa, compared to control groups of  $(103 \pm 32)$  MPa (Fig. 5) [98] (see Fig. 7) (see Fig. 8).

The nano DCPA whisker composites had double the strength compared to the conventional calcium and phosphate releasing composites. They release equivalent or greater number of ions, suggesting that these high-strength composites may offer a unique combination of stress-bearing and caries-inhibiting properties.

**2.2.2.3. Nanotubes.** Nanotubes are hollow fibrous fillers with a high aspect ratio and provide similar toughening and strengthening mechanisms as fibres in a composite. There are several chemical compositions of nanotubes such as Kaolinite nanotubes [93], and carbon nanotubes were the most widely explored [31]. Salinized methacrylate groups on the carbon nanotube surface enhanced the flexural strength of the composite resin by 23%, notwithstanding its dark unpleasing appearance [55].  $\text{TiO}_2$  nanotubes (as shown in Fig. 9) displayed several impressive qualities such as a significant increase in the surface area while also being biocompatible, nontoxic, and having excellent mechanical and photo catalytical characteristics [103]. Alkaline hydrothermal synthesis is often used to produce  $\text{TiO}_2$  nanotubes (TNTs) [104] and adding TNTs as fillers to flowable dental composite improved the composites' strength and the elastic modulus. The highest elastic modulus, 16.8 GPa, was found in composites reinforced with n- $\text{TiO}_2$  functionalized with 3% methacrylic acid. While the elastic moduli were 16.1 GPa and 15.5 GPa, respectively, for composites reinforced with 3% silane-functionalized n- $\text{TiO}_2$  and 3% non-functionalized n- $\text{TiO}_2$  [103]. It is well established that homogeneous nanotube dispersion in the resin matrix is crucial when loading exceeds 5%. As a result, nanotube clusters or aggregates may impair the mechanical characteristics of nanoscale reinforcement [105,106].

**2.2.2.4. Porous fillers.** As a result of continuous exposure to oral humidity during long-term clinical service, conventional silane coupling agents degrade over time compromising the interfacial matrix-filler coupling [107,108]. Porous fillers are a more stable form of micro-mechanical interlocking with the resin matrix [109–113]. In contrast to dense fillers, porous fillers may be infiltrated by liquid resin to strengthen the bonding between the matrix and the fillers and increase the mechanical characteristics of dental resin composites. Additionally, composite resins enforced by porous fillers showed better wear resistance due to the strong micro-mechanical bond between the resin and the fillers which prevent the filler detachment. Porous glass-ceramic fillers enhanced the flexural strength and modulus of dental resin composites but did not affect the tensile strength [113,114].

The maximum filler loading of dental composites was up to 50% and this was due to the high surface area of mesoporous  $\text{SiO}_2$ . Although the filler loading of composites may be enhanced by combining nano-porous and mesoporous silica, the mechanical characteristics remained unsatisfactory, as the final composite's flexural strength with the improved filler mix was  $68 \pm 9$  MPa, which was insufficient to fulfil the ISO 4049–2009 criterion (minimum 80 MPa) [92]. As the presence of the filler surface porosity itself is not a determining factor that affects the mechanical properties as much as the degree of penetration of the resin into the pores [89]. Inadequate infiltration of the resin matrix into the filler porosity results in poor mechanical properties especially flexural strength compared to the conventional silica filled composites [115], as the unfilled porosity behave as voids resulting in weak zones in the structure of the composite. This could be challenging for dental composites to maintain the performance to ensure maximum micro-mechanical interlocking, and this theory was validated by Ruddle [115]. The issue of resin penetration was addressed using two ways. The first featured vacuum-assisted mixing of porous fillers and resin [116], while the second required adding solvents to lower resin viscosity facilitate

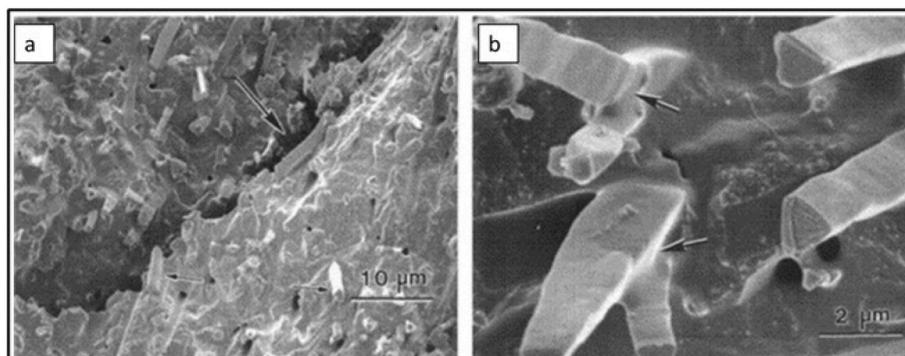


Fig. 5. Rough fracture surfaces of composite containing silica-fused whiskers (a), with large fracture steps (large arrow in (a)) and pulled-out whiskers (small arrows). The arrows in (b) show the whisker–resin interfaces of whiskers bonded with the matrix resin. Reproduced with permission of the rights holder, Elsevier [100].

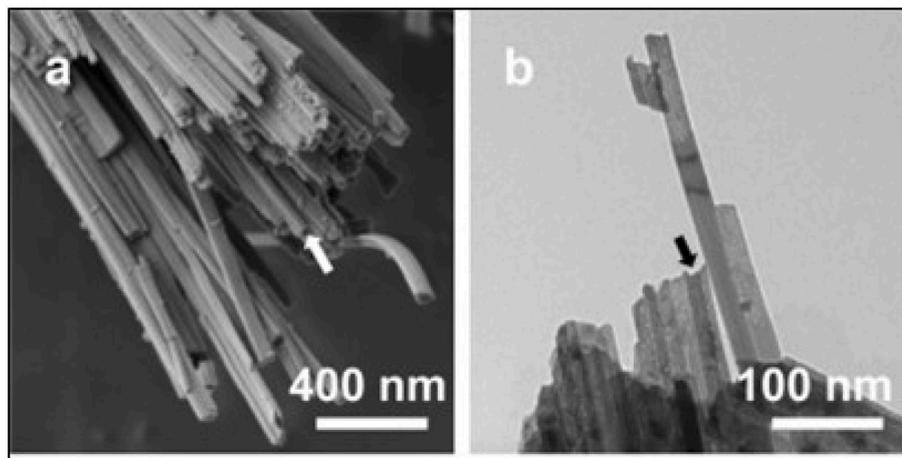


Fig. 6. (a) SEM of n-TiO<sub>2</sub> and (b) TEM of n-TiO<sub>2</sub> following alkaline hydrothermal reaction and calcination. Arrows indicate the hollow tubular structure of TiO<sub>2</sub> nanotubes, *Reproduced with permission of the rights holder, Elsevier [103]*.

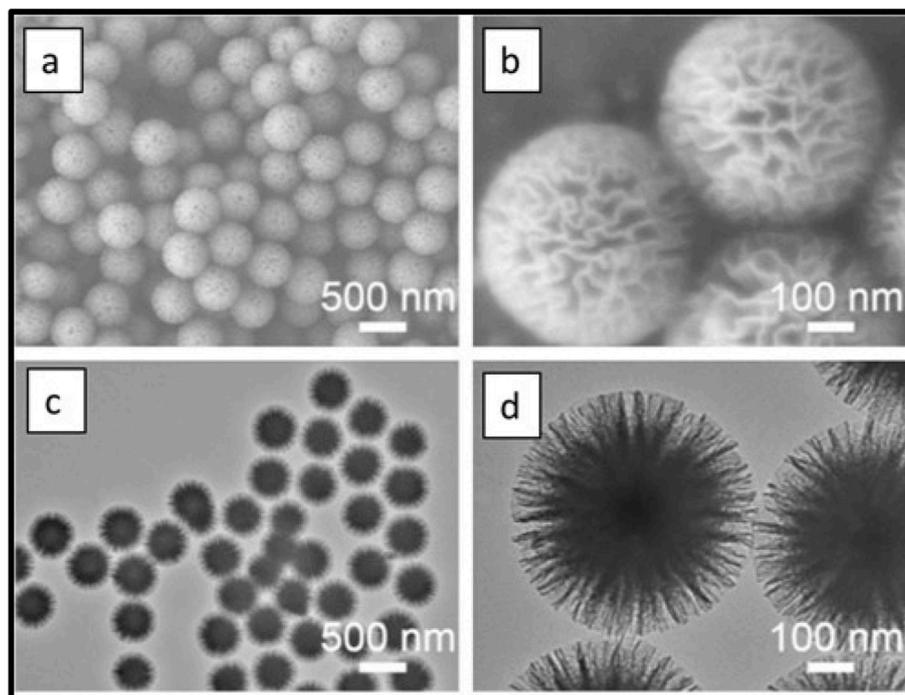


Fig. 7. FE-SEM images (a and b) and TEM images (c and d) of different magnifications of wrinkled mesoporous silica fillers, *Reproduced with permission of the rights holder, Elsevier [118]*.

infiltration [117]. Moreover, wrinkled mesoporous silica (WMS) fillers with size  $\sim 500$  nm as shown in Figure 10 were synthesised to control the size of the pores and the uniformity [118]. They exhibited a micro-mechanical bond with the resin matrix and significantly increased mechanical properties of dental resin composites namely flexural strength (78.5 MPa) compared to the conventional silica fillers (62.6 MPa) of the same size and loading of 77 wt% in both groups [103,113]. This indicates an increased filler matrix bonding due to the mechanical interlocking and was confirmed by the investigating the fractured surface of the WMS composite and exhibited a small number of detached particles compared to the conventional filled composite. Moreover, mesoporous silica-filled composites demonstrated superior transparency, a higher glass transition temperature, and increased adhesive strength, compared to composites filled with conventional glass-ceramics making mesoporous silica a possible filler for anterior composites [113,118–120].

### 2.2.3. Smart (multifunctional) fillers

Smart materials are those having the ability to express an alteration in their characteristics in a regulated behaviour when they are exposed to specific external stimuli. Temperature, pH or moisture fluctuations, mechanical stress, and electric or magnetic fields are examples of such stimuli. In dental composites, this function was utilised to react against the following sections different types of smart fillers well be discussed according to their responses, such as remineralising, antibacterial, and self-healing activity.

Conventionally, the introduction of fillers in dental composites is to enhance their mechanical and physical properties, however, these fillers did not contribute to the bioactivity of the composites and prevention of second caries [121]. Secondary or recurrent caries corresponds to dental decay that affects the area between the tooth structure and the pre-existing filling and is one of the major causes of composite restoration failure [122]. Acidic by-products from bacterial metabolism of

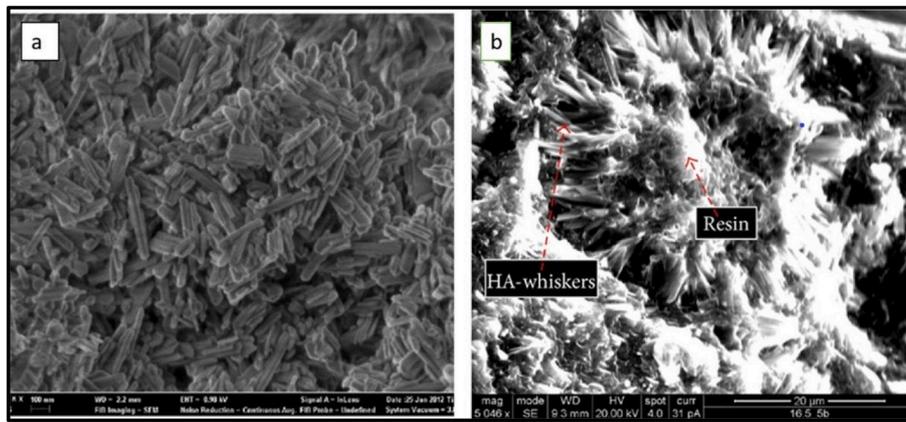


Fig. 8. SEM images of (a) synthesised whiskers, (b) high magnification of the composite resin reinforced with hydroxyapatite whiskers *Reproduced with permission of the rights holder, Hindawi [143]*.

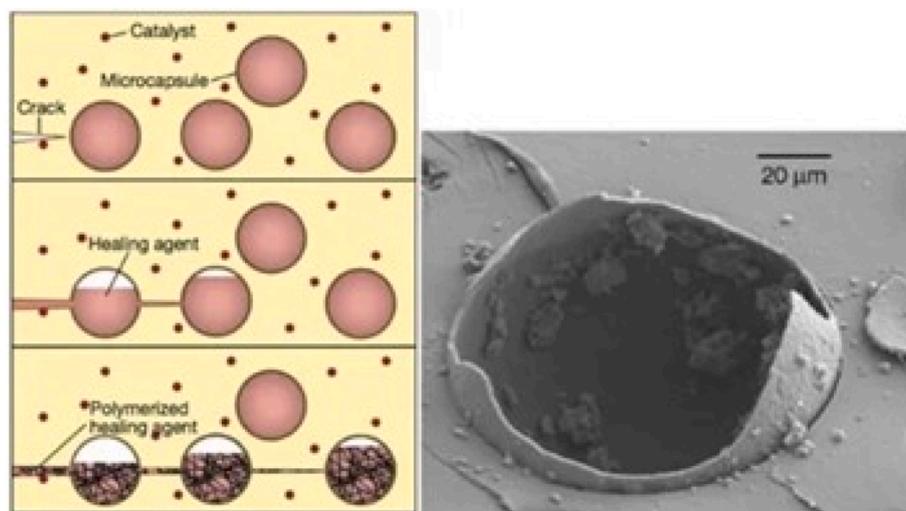


Fig. 9. Representative mechanism of microcapsules function (Left), SEM image showing ruptured microcapsule (Right). *Reproduced with permission of the rights holder, Elsevier [170]*.

dietary carbohydrates, predominantly produced by *S. mutans*, are the primary cause of dental caries [123,124]. *S. mutans* are cariogenic bacteria that are responsible for dental caries as they adhere to tooth surfaces and restorations and develop a biofilm. Oral biofilm consists of colonies of different microbial species incorporated in a medium of microbial components, salivary proteins, and food debris [125]. The structural integrity of biofilms is kept by bacterial by-products such as polysaccharides, proteins, nucleic acids, and lipids, these together are known as extracellular polymeric substances. Oral biofilm is responsible for causing different types of infections in the mouth such as dental caries [125], gingivitis and periodontitis, and candidosis [126]. To control the growth of oral biofilms and prevent the formation of plaque, traditional mechanical oral hygiene measures such as tooth brushing, mouth rinsing, and flossing are required [127].

Dental composites tend to accumulate a greater biofilm thickness than other types of restorative filling materials such as glass ionomers and amalgams [128]. This could be due to the cariostatic ions released from glass-ionomer and amalgams. However, some studies reported that bacterial growth was increased with composite restorations, which could be an intrinsic characteristic adversely affecting the ecosystem of the dental plaque biofilm [129,130]. The increased levels of biofilm accumulation could have an impact on more caries development [18, 130]. Anti-caries composites were developed with antibacterial and remineralising activities to control oral biofilm formation and prevent

recurrent caries [122,131–136]. Antibacterial composites were produced by blending anti-bacterial particles with resin matrix. Several types of anti-bacterial particles were examined such as bioactive glass BAG, metal/metal oxide, and polymer nanoparticles, some of which are overviewed below.

#### 2.2.3.1. Fillers with re-mineralising activities

##### 2.2.3.1.1. Bioactive glass (BAG).

Although the word “bioactive” has several meanings, a substance that develops a connection with a tissue [137] and promotes the creation of hydroxyapatite (HA) when it meets physiological fluids [33,137]. In restorative dentistry, a material can also be bioactive if it can dissolve or leach components that have anti-microbial activity (including the increase in pH) [137]. BAG is an extensively investigated biomaterial for restoration of both soft and hard tissues and has been added to dental composites for various purposes such as minimising the marginal gap penetration by bacteria, dentin remineralisation, and bacterial acid neutralisation. It has also been tested for applications in restorative dentistry such as adhesives, pulp capping, and implants [33,137].

L. Hench produced the first BAG in 1969, Bioglass 45S5, which was a blend of 46.1 mol% SiO<sub>2</sub>, 26.9 mol% CaO, 24.4 mol% Na<sub>2</sub>O, and 2.6 mol % P<sub>2</sub>O<sub>5</sub> [33]. The antibacterial properties of BAG are mostly owing to its alkaline pH and osmotic qualities, which are induced by the presence of silica, salt, and calcium ions in glass [112]. When dental composites

containing BAGs are exposed to a moist environment, their mechanical properties can be compromised as BAGs tend to cluster in the hydrophobic resin matrix due to their hydrophilicity resulting in swelling and cracking [121]. To address this issue, amphiphilic bioactive raspberry-like composite particles (BRP) were synthesised, and incorporated into dental composites as fillers [29,138]. The BRP was based on two active components: a hydrophobic polymer component (resin matrix) and a hydrophilic bioactive component to enhance mineral precipitation within the composite. The BRP composites outperformed typical BAG-based composites in terms of mechanical properties as well as water sorption and solubility [128]. Additionally, a dense layer of minerals was observed when BRP composite was applied on a demineralised dentin, compared to a few micro particles were found with composites containing BAG. The rich mineral layer was caused by the ion released from the BRP [139].

Because sodium in BAG is hydrophilic which weakens the composite and lowers its mechanical characteristics, approaches to alter and substitute its composition have been made. As a result, most BAG fillers are now low in sodium [140]. Additionally, ion replacements such as  $F^-$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ , and  $Sr^{2+}$  are frequently substituted with sodium, and each adds to the composites' ultimate characteristics. A recent study compared the acid neutralizing ability of a novel low sodium, fluoride containing BAG experimental composite with the conventional 45S5 composition, after being immersed in hydrochloric acid and lactic acid of pH 2.6 and 4.5 respectively over 1-h immersion and showed comparable results to the conventional BAG without reducing the degree of conversion caused by the decreased resin mobility related to the filler size. The novel bioactive composites containing 40 wt% of BG fillers after 28 days of PBS immersion showed the ability to form fluorapatite in the calcium phosphate precipitated on the composite surface, unlike conventional BAG composite [132]. In comparison to the precipitate generated by standard BAG, fluoride-modified BG may provide a more stable marginal gap repair.

**2.2.3.1.2. Calcium phosphate (CaP).** Calcium phosphate ( $Ca_3(PO_4)_2$ ) particles was reported to release  $Ca^{2+}$  and  $PO_4^{3-}$  ions as a method of caries inhibition involved remineralisation under an acidic environment [122,128]. In addition to their ability to remineralize, nanoparticle amorphous  $Ca_3(PO_4)_2$  nanoparticles filled composites could be recharged with  $Ca^{2+}$  and  $PO_4^{3-}$  to maintain a continual ion release which is considered a beneficial quality that helps to keep their characteristics and, as a result, improves their long-term capacity to prevent caries [122,128]. Amorphous  $Ca_3(PO_4)_2$  is known for its water solubility than other  $Ca_3(PO_4)_2$  forms, making it easier to discharge ions in the oral cavity. Because it is metastable and can spontaneously convert to hydroxyapatite (HA),  $P_2O_4^{4-}$  is added as a stabiliser during synthesis [141, 142].  $Ca_3(PO_4)_2$  fillers, however, have poor mechanical strength which results in a reduction in the strength of the composite. This can be resolved by adding a co-filler with  $Ca_3(PO_4)_2$  filler such as nano-silica fused silicon carbide whiskers and Dimethyl tetrachloroterephthalate (DCPA) nanoparticles [143,144]. The flexural strength was twice as higher in the filler mixture compared to the composite containing  $Ca_3(PO_4)_2$  filler only. Also, the ion release matched or slightly exceeded the  $Ca_3(PO_4)_2$  filled composite. Another drawback of CaP is that they enhance the material's water sorption, which speeds up the breakdown of the resin matrix, which causes a significant reduction in the mechanical properties of the composite [144]. An optimal quantity of  $Ca_3(PO_4)_2$  fillers added was used to sustain ion release without jeopardizing the material's mechanical properties. Also, composites with crystalline calcium phosphate have lower translucency and aesthetics due to the difficulty in manipulating their refractive indices [122]. A new  $Ca_3(PO_4)_2$  nanocomposite having antibacterial activity and recharging ability was synthesised by adding dimethylaminohexadecyl methacrylate (DMAHDM) to the Sodium cyclopentadienide (NACP). The novel composite showed an inhibition in bacterial biofilm and did not show any effect on the release and recharge of  $Ca^{2+}$  and  $PO_4^{3-}$ . While the tested mechanical properties did not show significant changes compared

to the control group [122]. This innovative CaP rechargeable composite, which has long-term remineralisation and antimicrobial capabilities, shows promise as a caries-inhibiting tooth filling material.

**2.2.3.1.3. Hydroxyapatite.** As a common bioactive material, hydroxyapatite (HA), with chemical formula  $Ca_{10}(PO_4)_6OH$  has the potential to be used in biomaterials especially in dental implants and bone replacement materials [88,145,146]. In principle, HA could be a promising bioactive filler for dental resin composites since it is the main biological constituent of dentin and enamel giving the best radiopacity and mechanical strength to the hard tissues [81]. Furthermore, in dental restorations may remineralize neighbouring collagen, possibly allowing the sealing of small gaps between dental composites and natural dental tissue, reducing the risk of recurrent caries over time [147]. Mechanical characteristics, biological qualities, and stability of dental composites are all influenced by the shape and size of HA particles [81,146]. Particulate HA was originally utilised as a filler in dental resin composites; however, it did not exhibit sufficient strengthening properties. On the other hand, resin composites purely filled with nano HA proved their inefficiency for practical application and this is related to their significant water solubility and inadequate mechanical properties. However, to overcome this shortcoming a mixture of micro and nano particle HA was used to enhance the total filler loading and the mechanical properties [148].

Recently, innovative dental fillers such as HA whisker (HAW) as shown in Figure 11 [143] and nanofibres showed improved reinforcing properties when they are added in a hybrid mixture with conventional silica particles where the flexural strength, flexural modulus, compressive strength were 36.1%, 61%, and 50.1% respectively higher compared to the materials filled solely with HAW [146]. However, owing to the unfavourable filler–matrix interfacial characteristics of these high aspect ratio fillers (with or without silane treatment), they tended to clump in the resin matrix, resulting in poor filler distribution and lower strength of the composites, as the agglomerated fillers have unbonded loose internal structure which would interfere with the stress transfer and lead to a weak point formation that fails and eventually reduce the mechanical properties [88]. Using microwave irradiation, a unique urchin-like HA (UHA) was recently synthesised and used as a dental filler with silica nanoparticles. It demonstrated higher flexural strength, elastic modulus, and compressive strength [88]. However, its main disadvantage is the mismatch in the refractive index with the matrix which leads to a lower degree of conversion and depth of cure.

### 2.2.3.2. Fillers with antimicrobial activities

**2.2.3.2.1. Zinc oxide (ZnO).** The electronic band structure of ZnO comprises a valence band and a conduction band. Upon exposure to ultraviolet or a visible light, the electrons in the valence band absorb energy and transfer to the conduction band. This jump results in the development of holes (positively charged) in the valence band and free electrons in the conduction band (negatively charged) resulting in the semiconducting ability of ZnO. The positive holes in the valence band oxidise  $H_2O_2$  resulting in the formation of HO. The electrons in the conduction band on the other hand, can reduce  $O_2$  to form a series of intermediates such as  $O_2$ ,  $HO_2$ ,  $H_2O_2$ , and HO. These are known as reactive oxygen species (ROS) which play a significant role in ZnO antibacterial activity [29,149]. In a recent study the findings revealed that the addition of zinc oxide nanoparticles (0–5%) to matrices, successfully inhibited bacterial growth while the compressive strength of the group that included 1% ZnO nanoparticles was significantly greater than that of the unmodified control group. However, the opacity of zinc oxide resulted in a drastically reduced curing depth as the fraction of ZnO nanoparticles increases, both flexural and compressive strength decrease [150].

Chen developed ZnO@m-SiO<sub>2</sub> nanoparticles by coating ZnO particles with mesoporous SiO<sub>2</sub> [122]. An improved interfacial bonding between the matrix and fillers in relation to the mesoporous structure of

these particles was reported which resulted in improved compressive strength (32.5%), flexural strength (121.2%), and modulus (67.1%) of dental resins composites comprising 7 wt% ZnO@m-SiO<sub>2</sub> compared to the control filler with SiO<sub>2</sub>. An effective antibacterial rate of more than 99.9% was reported with no major changes in other properties of the composite. Similar results were obtained when regular-shaped SiO<sub>2</sub>-ZnO complex clusters (CCs) synthesised by spray-drying technology were used. The overall performances of composites containing SiO<sub>2</sub>-ZnO CCs were further improved, and the composites filled with 70 wt% Si<sub>66</sub>Zn<sub>4</sub> exhibited greater antibacterial ability (antibacterial ratio >99.9%) and satisfactory depth of cure, degree of conversion, and biocompatibility [151]. Because of the antibacterial effect and satisfactory properties of ZnO, it proved to be an effective antibacterial filler that could be used in dental composites as secondary fillers in minimal amount [149,150,152].

**2.2.3.2.2. Polymer nanoparticles.** The introduction of polymerisable antibacterial monomer particles into a dental composite was used to overcome the porosity and poor mechanical properties by introducing un-leachable antimicrobial age. When the antibacterial monomer is copolymerized with the resin, it prevents the bacterial growth on the composite surface during contact [153]. Methacryloyloxydecyl pyrimidinium bromide (MDBP) has received the most attention among antibacterial quaternary ammonium (QA) compounds [27,154,155] and because of the colour instability of MDBP, it is often used for repairs when appearance is not a factor. For the first time in 2012, ionic dimethacrylates (IDMAs) were registered and suggested to be used in dental applications [156]. When integrated into Bis-GMA/TEGDMA matrices, IDMA's antibacterial activity was similar to that of MDBP [157]. One of the disadvantages of immobilisation of polymerisable agents, is their action is limited only when the bacteria is in contact with the surface [154].

**2.2.3.2.3. Anti-microbial treated fillers.** Traditionally, nanoparticles are coated with phenols or antibiotics to improve their performance [118] which prompted the coating of antibiotics to readily penetrate the bacterial cell membrane, exerting a strong and sustained inhibitory impact on bacterial growth. This procedure significantly minimises the likelihood of antibiotic resistance and systemic toxicity. A study investigated the anticariogenic efficacy of drug-coated copper nanoparticles used as an antibacterial filler in a light cures resin composite [158]. Which demonstrated that the experimental material had a greater antibacterial impact in the contact test when compared to the control groups. Additionally, the material demonstrated a persistent release of antimicrobial particles for up to 28 days. Furthermore, the material demonstrated enhanced hardness when the coated fillers fraction was increased.

**2.2.3.2.4. Piezoelectric bio-ceramic.** A piezoelectric material generates an electric charge when subjected to mechanical stress [138]. This material category has been effectively used in a variety of biomedical applications, including bone regeneration, tissue engineering, and drug delivery, however, in the field of dentistry, the use of piezoelectric materials is still in its infancy. Some piezoelectric materials can maintain electrical charges for over 12 million mechanical loading/unloading cycles, equating to a little more than two decades of clinical operation [159]. Piezoelectric barium titanate (BaTiO<sub>3</sub>) nanoparticles demonstrated a considerable decrease in bacterial growth of up to 90% in the experimental dental composites' groups containing 10% piezoelectric fillers exposed to cyclic loading of 3-point bending at 2 Hz (~40 MPa) and a stress ratio of R = 0.1.41 The stress amplitude ( $\sigma_a$ ) was set to 2 MPa, which is 25% of the endurance limit (6.5 MPa). The test was working in concert for 6 days conducted for ~1 M cycles, resembling the magnitude of stress range available in clinical settings [160]. Furthermore, a significant production of rich and heavy layers of calcium phosphate minerals in mechanically stimulated for up to 7 days in piezoelectric groups. Moreover, the antibacterial activity of BAG-(10, 20, and 30% vol) Sodium Potassium Niobate (NKN) composites against *S. aureus* and *E. coli* bacterial cells was enhanced on poled composite

samples at 20 kV for 30 min at 500 °C [160,161]. This combination of both antibacterial and remineralising activity of piezoelectric materials is ideal to enhance composite restoration by resisting pathogenic bacterial species and developing a new mineral layer at restoration margins for long periods [159,162]. However, despite the advantages that could be gained from the piezoelectric fillers as they offer longstanding therapeutic results without affecting the bacterial-drug resistance, and lack of ion release which could enhance the biocompatibility, however, their effect should only impact the pathogenic bacteria where some investigations indicated that non-pathogenic species and mammalian cells might be negatively affected leading to inflammatory reactions [163].

**2.2.3.3. Fillers with self-healing ability.** Repeated mechanical loading in the oral environment can develop micro-cracks in dental composites. Crack formation is a form of structural damage that might occur in composites. The progression of these micro-cracks might ultimately result in material failure [13,164]. This issue led researchers to develop smart self-healing resin-based composites that can detect and restore damage on their own improving the long-term mechanical performance of dental composites. Poly-urea-formaldehyde (PU) microcapsules filled with dicyclopentadine and Grubb's catalysts (as a healing agent) in epoxy matrix [165] to create self-healing capsules. When a crack appears in a composite bulk, the crack propagation will trigger the break of the microcapsule, releasing the dicyclopentadine. When the dicyclopentadine contacts the catalyst distributed in the matrix, the polymerisation process occurs as a result of capillary action and the dicyclopentadine's penetration along the crack [166]. Further crack propagation will be controlled until the healing liquid has fully polymerised. Following that, a polymer layer serves as an adhesive, reattaching the split regions [167-169]. With the potential toxicity and the expensive cost of the dicyclopentadine and Grubb's catalysts systems, attempts to replace these were made [169]. A more biocompatible system was developed where TEGDMA was used as a healing agent, benzoyl peroxide (BPO) was used as an initiator, and N, N-dihydroxyethyl-p-toluidine (DHEPT) as a co-initiator. Because of its low viscosity, TEGDMA could flow into the crack and fill it resulting in a self-healing composite. TEGDMA was also investigated in PU microcapsules shells with a combination of DHEPT as a healing liquid [169]. It was observed that the inclusion of PU microcapsules resulted in efficient self-healing with no determinantal influence on the mechanical properties [166]. In another approach, encapsulated silica microcapsules containing a combination of an aqueous solution of polyacrylic acid, (as a healing liquid), with strontium fluoroaluminosilicate particles (as healing powder) was used. The interfacial bond between the capsules and the matrix was achieved by salinisation, to ensure the rupture of the microcapsule successfully during the fracture of the composite. As soon as the liquid was released from the micro capsule and encountered the healing powder, the crack was restored through the formation of a glass ionomer cement.

#### 2.2.4. Radiopaque fillers

The radiopacity of composite fillings is an important property to help dentists detect and diagnose recurrent caries or the presence of any defect in the restoration. In dental composites, the radiopacity is directly proportional to composition, thickness, and materials density [171, 172]. Several types of elements with heavy atoms are added as opacifying components such as BaSO<sub>4</sub>, La<sub>2</sub>O<sub>3</sub>, or ZrO<sub>2</sub>, where these atoms can enhance the radiopacity by absorbing and then scattering the X-ray [171,173]. Objects with high atomic numbers show as white in the x-ray while low atomic number objects show as a black shadow. However, excessively adding radiopacifying fillers in the dental composite can adversely affect the translucency of the material and affect the mechanical properties [172,174,175].

Amirouche investigated the radiopacity of materials by comparing the effect of different types of radiopacifying ceramic fillers namely BaO,

BaSO<sub>4</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and SrO, their loading, and the composition of monomer [172]. The radiopacity of pure resin matrix was low compared to enamel and like dentin since it is composed entirely of organic components with low atomic numbers. While radiopacity levels somewhat higher than enamel was attained with ZrO<sub>2</sub> starting at 30 wt% [17]. A recent study in which a unique radiopaque filler structure was created and called Core-shell structured SiO<sub>2</sub>-ZrO<sub>2</sub>-SiO<sub>2</sub> (SZS) microspheres [176]. These fillers were added to the composite in different ratios as secondary fillers and resulted in a great improvement of the radiopacity at 20% SZS with 52% silica which exceeded the radiopacity of the enamel as well as showed lower shrinkage and enhanced mechanical properties compared to the composites filled with mono-dispersed silica microspheres [176].

### 2.2.5. Aesthetic fillers

Dental resin composites with the ideal translucency should resemble human enamel. Certain oxides, such as ZrO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, can be used to modify the translucency of dental composites. The opacity and size of materials is affected by the difference in refractive indices between the opacifying agent (such as ceramic fillers) and the resin matrix. ZrO<sub>2</sub> absorbs minimal incident light and backscatters most of the incident light which makes ZrO<sub>2</sub> translucent, like tooth dentine. Additionally, ZrO<sub>2</sub> also has outstanding biocompatibility physical and mechanical properties making it a widespread an excellent choice in the field of dental materials [177–179]. Another important aesthetic property is fluorescence [180] which occurs when an object is exposed to light and after 10–8 s, it spontaneously produces a longer-wavelength light. Both dentin and enamel exhibit this phenomenon, with dentin exhibiting a stronger fluorescence owing to its structure's higher collagen content. The fluorescence of dental materials can be defined by the colour difference during and after the exposure to UV light [181], and it can be measured using spectrophotometer. Certain dental composites lack this feature, resulting in a colour match with the teeth during the day, however, a mismatch under UV light. Some rare earth oxides can be used to overcome this mismatch such as (Eu<sub>2</sub>O<sub>3</sub>, Tb<sub>4</sub>O<sub>7</sub>, Dy<sub>2</sub>O<sub>3</sub>), in addition to quantum dots and fluorescence whitening agents [181].

Opalescence is another phenomenon that can affect the aesthetics of composite resin. This is caused by the light scattering, which occurs due to the variation in the refractive indices of both the resin matrix and fillers. It results in a blue object in the reflected light but orange/brown in transmitted light [16,179]. By adjusting the refractive index and adding ceramic fillers such as ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, the opalescence of the dental resin composite can be obtained [179,180]. This can be achieved by several methods such as, adding organic groups to the silica filler resulting in an inorganic-organic hybrid filler, increasing monomer to filler ratio, or reducing the particles size (100 nm in diameter) to achieve the appropriate level of opalescence [180].

### 3. Conclusion and future prospective

In conclusion, it is established that contrary to structural and functional composites, dental composites are a complex system as they must survive within the harsh oral environment and need to keep up with their structural, aesthetic, chemical, and biological properties. The complexity stems from the fact that dental composites must have a combination of so-called 'desired' properties which are essential for their usage in dentistry. However, a 'right combination' of fillers and resin that must be designed to avoid the contrasting nature of the individual properties of the raw materials.

One of the main challenges for dental composites during their life is their failure. The development of recurrent caries is the primary reason for the failure of dental composites. Recurrent caries is induced indirectly by polymerisation shrinkage leading to restorations fracture, the two most difficult challenges to solve in dentistry. Modifying the matrix of a dental composite has a major effect in reducing polymerisation

shrinkage than changing the filler's properties. Furthermore, monomers with novel structures and various chemistries have been created to replace traditional monomers such as TEGDMA and BisGMA to overcome their shortcomings. On the other hand, the filler phase has a major impact on the improvement of the mechanical properties of dental composites through factors such as the filler loading, size, shape, porosity, and surface modification of filler particles to enhance the interfacial bonding between the matrix and fillers. With the development of new types and forms of fillers to improve their mechanical and physical properties, however, these fillers didn't extend to the composites' bioactivity or the control of recurrent caries. There are several opportunities for the advancement and development of fillers in dental composite resins that may increase the durability, function, and aesthetics of restorations. Future research will focus on the creation of long-lasting and stable dental materials with enhanced biocompatibility and additional functionality that do not undermine the other qualities.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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