

Effects of Filler Size on the Mechanical Properties of Polymer-filled Dental Composites: A Review of Recent Developments

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ABSTRACT: Resin composites are widely used in esthetic restorative dentistry. Since their introduction in the mid-1960s, these composites made steady gains in popularity. Their increased use is attributed to their excellent biocompatibility, absence of taste, odour, tissue irritation and toxicity, insolubility in body fluids, easy operation, excellent aesthetic properties, stable colours, optical properties, easy pigmentation, low cost and repairability. The composite resins in current use still suffer from several shortcomings such as poor mechanical properties. In order to improve these properties, microparticles have been used as fillers for a long time. However, the inadequate mechanical properties of resin composites remain problematic. Recently, researchers have utilised nanoparticles as dental composite fillers. This article reviews the relevant literature on the mechanical properties of polymer dental composites filled with micro- and nano-scale particles. The effects of particle size on fracture toughness, flexural strength, and hardness were examined with emphasis on other important factors for improvement. The second section focused on the toughening mechanisms of particulate-polymer composites.

Keywords: Polymer dental composites, particle size, nanoparticles, mechanical properties, toughening mechanisms

1. INTRODUCTION

Polymer-based composites have been widely used in dentistry since their introduction in the late 1950s. Recently, nano-composites were introduced as dental polymers.^{1,2} Resin composites are widely used in dentistry as restorative materials, cavity liners, pit and fissure sealants, cores and buildups, inlays, onlays, crowns, veneers, denture teeth, provisional restorations, cements for single or multiple tooth prostheses and orthodontic devices, endodontic sealers, root canal posts, structured scaffolds, and plates and screws.³⁻⁵ Excellent biocompatibility, superior aesthetic qualities as fillings, moderate cost compared with ceramics, and strong bonding ability to the tooth structure, make resin composite the preferred material in dental restorative applications.^{1,6,7} Most dental composites consist of an organic matrix (polymer phase), inorganic fillers (dispersed phase) and interphase (coupling agent).⁸ Usually, the organic matrix is based on methacrylates, epoxy and polyethylene.⁹⁻¹¹ The filler is added to enhance polymer properties and usually consists of different compositions, sizes and size distributions of glass or ceramic particles, nanotubes, whiskers, fibres and nanoclusters.^{12,13}

The coupling agent such as silane is designed to strongly bond the matrix to the filler, thus improving composite performance. The most commonly used silane in dental restorative composites is 3-methacryloxypropyltrimethoxysilane (γ -MPS). Filler content, type, shape, size and morphology are important factors enhancing the desirable mechanical properties of dental composites.¹⁴ Multiple fillers have been employed in dental composites to improve strength, toughness and durability. However, some problems continue to persist, such as inadequate mechanical properties, water uptake, polymerisation shrinkage, and poor wear resistance of large occlusal restorations during use.^{1,15,16} Dental composites fail because of surface and/or bulk cracks, degradation of the matrix and fillers, water uptake, and insufficient mechanical properties.¹⁴ The degradation of the bond between the fillers and resin after long-term water absorption is the main reason for the failure of dental composites.¹⁷

Adding filler nanoparticles to the resin matrix of dental composites improves aesthetic, optical and mechanical properties, such as tensile strength and resistance to fracture, as well as reduces polymerisation shrinkage.¹⁸ Moreover, nanoparticles enhance wear resistance and gloss retention and also improve the fatigue properties of dental composites.⁷ Reduced interparticle spacing may increase obstacles for dislocation motions and decrease strain localisation.¹⁹ However, nano-composite properties are significantly affected by various factors, including the degree of conversion of the polymer matrix and interphase, which requires a high level of silanisation because of the high surface area of nanoparticles.^{19,20} This review

focuses on several mechanical properties of dental composites, namely fracture toughness, flexural strength and hardness. However, the effect of particle/matrix interface adhesion and particle loading on the mechanical properties of polymer dental composites are not covered here. Fracture toughness strongly depends on toughening mechanisms, such as crack deflection, crack pinning, matrix-filler interactions and crack bridging, which increase crack propagation resistance.

Fillers with smaller particle sizes can improve flexural strength because of increased particle surface area, which results in a high surface energy at the filler-matrix interface. Hardness is readily improved by adding either micro- or nanoparticles because rigid inorganic particles generally have considerably higher stiffness than polymer matrices. The novelty of the present paper is that, no review has been done on the effects of different scales of fillers (i.e., nano- and microfillers) on the mechanical properties (fracture toughness, flexural strength and hardness) of polymeric dental composites. It elaborates on the effects of toughening mechanisms in improving the mechanical properties of particulate-polymer composites at these two scales. This review article aims to present the results of recent efforts to improve the mechanical properties of polymer-filled dental composites, compare and discuss in depth the reinforcing effects of nano- and micro-particles, as well as provide some basic understanding of the toughening mechanisms of these composites. To our knowledge, no review papers on these topics have been published yet.

2. THE EFFECT OF PARTICLE SIZE ON MECHANICAL PROPERTIES

2.1 The Effect of Particle Size on Fracture Toughness

Fracture toughness is a fundamental property of material to predict the strength of material when a crack is present.²¹ It is expressed with the critical stress intensity K_{IC} .²² The crack driving force and critical value (fracture toughness) are equated, to obtain the relationship between applied load, crack size and structure geometry which provide the necessary information on structural design.²³ The units of K_{IC} are units of stress (force/length²) × units of length^{1/2}, or force × length^{-3/2} and are often reported as MNm^{-3/2} or MPa m^{1/2}.²⁴ The measurement of this fracture mechanics was applied to a number of problems associated with dental materials. It analysed the behaviour of materials containing cracks or flaws. These flaws and cracks may grow naturally or nucleated after a time in service, and sudden fractures can occur at stresses below the yield stress. Such fractures exist in brittle materials that are unable to plastically deform and redistribute stresses. The fracture mechanics analyses are performed during these types of failures.⁵ In the neat resin, there is

a high stress concentration in front of the notch. Whereas composites with well-distributed nanoparticle have more uniform stress distribution, thus enhancing the toughness.²⁵

Incorporating fillers in the polymer matrix increases fracture toughness, elastic modulus and tensile strength.^{5,26} Particle size has a distinct effect on the mechanical properties of particulate-polymer composites.^{27,28} Fu et al. reported that particle size significantly affected the fracture toughness of particulate-filled polymer composites.²⁷ According to Tanimoto et al., increasing filler particle size increased the fracture toughness of resin-modified glass ionomers.²⁹ Ornaghi et al. also found that the fracture toughness of resin composite containing 78 wt% glass particles with a size of 1.9 µm was higher than that of resin composites containing smaller particles; they attributed the increase in fracture toughness to crack deflection.³⁰ Asar et al. found that adding Al₂O₃, TiO₂ and ZrO₂ fillers with average sizes of 12.4, 9.6 and 8.6 µm, respectively, at different percentages (1% TiO₂ and 1% ZrO₂, 2 wt% Al₂O₃, 2 wt% TiO₂ and 2 wt% ZrO₂) significantly increased the fracture toughness of poly(methyl methacrylate) (PMMA) denture base composites.³¹ In the study, the fracture toughness of the test groups was significantly higher than that of control group ($p < 0.05$). The test group containing 2 wt% ZrO₂ had the highest fracture toughness among all groups ($p < 0.05$) and increased fracture toughness by 30% compared with the control group.³¹

Alhareb et al. reported an improvement in the fracture toughness of PMMA denture base reinforced with nitrile-butadiene rubber (NBR) particles, Al₂O₃ and yttria-stabilised zirconia (YSZ) fillers with average particle sizes of >150, 4.4 and 1.05 µm, respectively.³² In another study, adding up to 50 wt% glass particles with average sizes of 105–210 µm to acrylic bone cement significantly increased fracture toughness.³³ Dental composites filled with nanoparticles showed enhanced fracture toughness.³⁴ Nanoparticle fillers can be dispersed uniformly in polymer matrix, which increases fracture toughness compared with micro-filled polymer composites.^{35,36} Theoretical results obtained by Chan et al. indicated an increase in fracture toughness of dental composites because of silanisation and nanoparticle loadings.³⁷ Ahmed and Ebrahim concluded that adding nano-sized ZrO₂ particles significantly increased the fracture toughness of PMMA denture base.³⁸ The fracture toughness of PMMA resin for provisional restorations, increased remarkably with addition of 0.25 wt% of SiO₂ nanoparticles with average size of 12 nm.³⁹

Watanabe et al. demonstrated that hybrid and nanoparticle composites had significantly higher fracture toughness compared with micro-filled composites, particularly at high-volume fractions.⁴⁰ Hosseinalipour et al. investigated the mechanical properties of bisphenol A-glycidyl methacrylate/triethylene glycol

dimethacrylate (Bis-GMA/TEGDMA) dental composites reinforced with SiO_2 nanoparticles with sizes of 20–50 nm. Their results showed significantly increased mechanical properties compared with a conventional composite control containing SiO_2 particles with sizes of 10–40 μm . The fracture toughness of GMA/TEGDMA dental composite remarkably increased compared with that of the control when the weight fraction of the filler increased to 40 wt%, indicating the significance of the filler weight fraction in determining the mechanical properties of composites.⁷ However, Elsaka et al. reported that glass ionomer filled with 3 wt% and 5 wt% TiO_2 nanoparticles with average sizes of 21 nm had improved fracture toughness compared with the unmodified glass ionomer.⁴¹ These findings are supported by Protopapa et al., who observed a significant increase in the fracture toughness of PMMA dental composite filled with a low-volume fraction of nanodiamond particles.⁴² Table 1 shows the effects of filler size on the fracture toughness of dental composites.

Table 1: The effect of filler size on fracture toughness of dental composites.

Author (year)	Average particle size	Effect on fracture toughness
Alhareb et al. (2015) ³²	NBR (>150 μm), Al_2O_3 (4.4 μm), YSZ (1.05 μm)	Significant increase
Asar et al. (2013) ³¹	ZrO_2 (8.6 μm)	Significant increase
Hosseinalipour et al. (2010) ⁷	SiO_2 (20–50 nm)	Significant increase
Watanabe et al. (2008) ⁴⁰	SiO_2 (5–20 nm)	Significant increase
Ahmed and Ebrahim (2014) ³⁸	ZrO_2 (5–15 nm)	Significant increase
Protopapa et al. (2011) ⁴²	Diamond (4–6 nm), clusters (20–60 nm)	Significant increase
Topouzi et al. (2017) ³⁹	SiO_2 (12 nm)	Significant increase
Ornaghi et al. (2014) ³⁰	Glass (1.9 μm)	Increase
Chan et al. (2007) ³⁷	SiO_2 (40–120 nm)	Increase
Elsaka et al. (2011) ⁴¹	TiO_2 (21 nm)	Increase
Balos et al. (2014) ¹⁰³	SiO_2 agglomerates (50 nm)	Increase

As shown in Table 1, incorporating a low content of large microparticles and a high content of smaller microparticles can increase fracture toughness. In addition, the fracture toughness of nano-composites depends on loading. Composites filled with low concentrations of nanoparticles have high fracture toughness, whereas composites filled with high loadings have low fracture toughness. Filler particles in dental restorative materials substantially enhance fracture toughness by increasing crack propagation resistance via several possible toughening mechanisms, such

as crack deflection, crack pinning/bowing, matrix–filler interactions and crack bridging.^{26,43–46} Silanisation and nanoparticles improve the fracture toughness of dental polymer nano-composites through a combination of enhanced interface toughness through silanisation, crack deflection and crack bridging.³⁵ The fracture toughness of dental composites can be increased by improving the interfacial bond between the nanoparticles and matrix through a larger surface area-to-volume ratio and high particle strength.³⁷ Du et al. illustrated that Al₂O₃ nanoparticles (8 nm) with fixed filler content (1 wt%) were well dispersed in polyester resin and promoted crack front trapping that increased fracture toughness.⁴⁷ The increase of volume-specific debonding energy also increases crack resistance with reduced particle size. Particles near the crack plane under high stresses are too small to be debonded from the matrix, indicating the importance of particle size distribution.⁴⁸ To summarise, filler particle size significantly affects the fracture toughness of polymer dental composites. This property of dental composites can be improved by incorporating nanoparticle fillers at low concentrations, in addition to several factors.

2.2 The Effect of Particle Size on Flexural Strength

The addition of ceramic fillers to dental composites improves flexural strength.^{49,50} The particle size of fillers significantly affects the mechanical properties of particulate-polymer composites.^{28,51} Incorporating 50 wt% Al₂O₃ (<10 µm) in dental composites increased flexural strength by more than 100%.⁵² Tanimoto et al. reported that adding 70 wt% SiO₂ (3.3 µm) increased the flexural strength of dental composites, whereas adding larger microparticles reduced flexural strength (4.3, 7.9 and 15.5 µm).²⁹ Two similar studies also reported that adding HA (18.1 µm) to PMMA denture base reduced flexural strength.^{53,54} According to Oral et al., the flexural strength of groups reinforced with large microparticles (>315 µm) decreased.⁵⁵ Table 2 shows the effect of microparticles on the flexural strength of dental composites.

Table 2: The effect of microparticles on flexural strength of dental composites.

Author (year)	Average particle size	Effect on flexural strength
Foroutan et al. (2011) ⁵²	Al ₂ O ₃ (<10 µm)	Increase
Tanimoto et al. (2006) ²⁹	SiO ₂ (3.3 µm)	Increase
Lauke (2008) ⁴⁸	HA (18.1 µm)	Decrease
Tham et al. (2010) ⁵⁴	HA (18.1 µm)	Decrease
Oral et al. (2014) ⁵⁵	Bioactive glass (315 to 1000 µm) and biostable glass (915 to 1000 µm)	Decrease

As shown in Table 2, composites reinforced with high-volume fractions of small microparticles have high flexural strength values. The improvement in flexural strength can be attributed to the increased surface area of filler particles because of reduced particle size, which results in high surface energy at the filler-matrix interface. Meanwhile, the reduction in flexural strength can be attributed to the following factors:

1. Increased stress concentration at the interface between the filler and polymer matrix as a result of increased particle size.²⁹
2. Poor interfacial interaction between the matrix and filler. Mechanical interlocking is the only bonding mechanism holding the filler in the matrix because of the cooling shrinkage of the matrix.⁵⁴
3. Agglomerations of the filler act as stress concentration points and lead to inefficient stress distribution; therefore, more stress is concentrated on adjacent particles, causing cracks in the material.^{53,54}
4. Agglomerations restrict molecular motion in the polymer under load-bearing applications, causing deformation.⁵⁴
5. Presence of particle–matrix interfacial defects.⁵³

Dental composites containing nanoparticles have improved mechanical properties, such as flexural strength, compressive strength and wear resistance, compared with traditional micro-composites.^{56,57} According to Foroutan et al., dental nano-composites reinforced with three loadings (10, 20 and 30 wt%) of Al₂O₃ (25–40 nm) had significantly increased flexural strength.⁵² Two similar studies evaluated the effects of adding TiO₂ nanoparticles (<20 nm and 21 nm) to dental composites at different low loadings (<20 nm: 0.5 and 1 wt%; 21 nm: 3, 5 and 7 wt%).^{41,58} Lower filler contents significantly increased flexural strength. Moreover, Hosseinalipour et al. investigated the mechanical properties of Bis-GMA/TEGDMA dental composite reinforced with several loadings (20, 30, 40 and 50 wt%) of SiO₂ nanoparticles (20–50 nm). They found a significant increase in flexural strength at a loading of 40 wt%.⁷ Similarly, Barghamadi et al. incorporated SiO₂ nanoparticles into Bis-GMA/TEGDMA. The first composite consisted of filler (12 nm) with loadings of 15, 20, 25 and 30 wt%, whereas the second consisted of filler (40 nm) with loadings of 25, 35, 45, 50 and 53 wt%. Flexural strength increased at a volume fraction up to 25% and 45% for the first and second composite, respectively.⁵⁹

Many researchers had attempted to enhance the mechanical properties of PMMA denture base. A recent study by Ahmed and Ebrahim evaluated the flexural strength of PMMA denture base reinforced with different low concentrations

(1.5, 3, 5 and 7 wt%) of ZrO_2 nanoparticles (2–15 nm). Their results revealed that flexural strength significantly increased at a filler percentage of 7 wt%.³⁸ In another recent study, researchers used filler mixtures of HA/ Al_2O_3 (30/80 nm). The mixture consisted of HA (5 wt% and 10 wt%) and each percentage was added to 1% of Al_2O_3 (i.e., 0, 3, 6 and 8 wt%). The hybrid nano-composites with 5 wt% and 10 wt% of HA and 6 wt% of Al_2O_3 had the maximum flexural strength.⁶⁰ Two similar studies evaluated the effects of incorporating silver (Ag) particles (38 nm) into PMMA denture base.^{61,62} Ag filler was incorporated at very low loadings (0.5 wt%) and (0.05 wt% and 0.2 wt%). The results showed an insignificant increase in flexural strength. Table 3 shows the positive effects of nanoparticles on the flexural strength of dental composites.

Table 3: The positive effect of nanoparticles on flexural strength of dental composites.

Authors (year)	Average particle size	Effect on flexural strength
Foroutan et al. (2011) ⁵²	Al_2O_3 (25–40 nm)	Significant increase
Elsaka et al. (2011) ⁴¹	TiO_2 (21 nm)	Significant increase
Xia et al. (2008) ⁵⁸	TiO_2 (<20 nm)	Significant increase
Hosseinalipour et al. (2010) ⁷	SiO_2 (20–50 nm)	Significant increase
Ahmed & Ebrahim (2014) ³⁸	ZrO_2 (2–15 nm)	Significant increase
Safarabadi et al. (2014) ⁶⁰	HA/ Al_2O_3 (30/80 nm)	Increase
Barghamadi et al. (2015) ⁵⁹	SiO_2 (12 & 40 nm)	Increase
Sodagar et al. (2012) ⁶²	Ag (38 nm)	Insignificant increase
Kassaei et al. (2008) ⁶¹	Ag (38 nm)	Insignificant increase

However, a few studies had reported a decrease in flexural strength. Sodagar et al. added TiO_2 (21 nm), SiO_2 (20 nm) and TiO_2 with SiO_2 at two concentrations (1 wt% and 0.5 wt%) to PMMA.⁶³ Hamouda and Beyari also incorporated TiO_2 (21 nm) into PMMA denture base with a loading of 5 wt%.⁶⁴ Similarly, Shibata et al. added apatite-coated titanium dioxide ($Ap-TiO_2$) to PMMA denture base at volume fractions of 1, 5 and 10 wt%.⁶⁵ Moreover, Garoushi et al. incorporated SiO_2 (20 nm) into micro-filled composite resin with loadings of 10, 15, 20 and 30 wt%.⁶⁶ The results of these four studies showed that neat resins have higher flexural strength than nano-composites. Table 4 shows the negative effects of nanoparticles on the flexural strength of dental composites.

Table 4: The negative effect of nanoparticles on flexural strength of dental composites.

Authors (year)	Average particle size	Effect on flexural strength
Sodagar et al. (2012) ⁶²	TiO ₂ /SiO ₂ (21/20 nm)	Decrease
Hamouda & Beyari (2014) ⁶⁴	TiO ₂ (21 nm)	Decrease
Shibata et al. (2007) ⁶⁵	Ap-TiO ₂ /TiO ₂ (400 nm)	Decrease
Garoushi et al. (2011) ⁶⁶	SiO ₂ (20 nm)	Decrease

As shown in Tables 3 and 4, composites filled with nanoparticles at low/high loadings exhibit high flexural strength, whereas some composites at low loadings have decreased flexural strength. The increased flexural strength of dental composites reinforced with nano-sized fillers can be attributed to five reasons:

1. Nanoparticle have high-specific surface area and high surface energy that help to grab reactive monomer or polymer segment on their surfaces.^{67–72}
2. Formation of a strong bond between inorganic fillers and organic matrix.^{27,35,72} This bond is formed by covering the fillers with a functional silane coupling agent, such as MPS, to chemically link fillers with the matrix.^{35,73,74} The chemical linkage contains a siloxane bond between the filler and silane, as well as a covalent bond between the reactive groups of the matrix and organofunctional group of silane.⁷⁵
3. Decreased particle size at the same volume fraction results in covalent linkage, strong physical interaction, and increased contact area, which enhance the interfacial adhesion between matrix and nanofiller.^{52,72,76,77} Furthermore, smaller sizes cause more particles to share the applied stress in a specific region.⁷⁷ These factors result in effective stress transfer from the soft resin to the hard nanofiller.^{52,72,76,77}
4. Increased rigidity and decreased ductility of nano-composites result from the addition of highly rigid nanoparticles, such as nano-Al₂O₃ and nano-TiO₂, as well as the capability of these nanoparticles to withstand higher stresses.^{72,78,79}
5. Uniformly dispersed nanoparticles prevent crack propagation and significantly improve flexural strength.^{27,58,72,80}

Flexural strength may decrease because of the following reasons:

1. Nano-sized oxides affect the internal structure of polymerised by acting as impurities.^{60,62,63}

2. Dispersed nanoparticles within the acrylic resin decrease the degree of conversion and increase the amount of residual unreacted monomer that acts as plasticiser.^{63,65}
3. Agglomerated nanofillers in the matrix may enhance crack propagation. Under applied load, slippage may exist within the agglomerate.^{81,82} The surface area for the interaction between nanofillers and matrix decreases and fractures in the agglomerate sites are initiated.^{66,83}
4. Decreased cross-section of the load-bearing matrix.^{60,61,84,85}
5. Changes in the modulus of elasticity of the matrix and crack propagation mode of the sample because of increased filler content.^{60,61,85}
6. Void formation from entrapped air and moisture and from increased filler loading.^{60,61,84–86}
7. Incomplete wetting of the filler by the matrix.^{60,61,84,85}
8. Stress concentration because of higher filler levels.^{60,61,85} However, polymer composition (chemical formulation) also significantly affects flexural strength.⁶² Dental composites showed increased flexural strength when Bis-GMA or TEGDMA was replaced with urethane dimethacrylate (UDMA) and decreased flexural strength when Bis-GMA was replaced with TEGDMA.⁸⁷

To summarise, low contents of nanoparticles and high contents of small microparticle fillers can increase the flexural strength of dental composites. Particle size should be selected based on the properties affected by the filler volume fraction, such as required viscosity and curing shrinkage. Polymer composition is another factor with a marked effect on flexural strength.

2.3 The Effect of Particle Size on Hardness

The presence of filler particles in the resin matrix enhances mechanical properties, such as hardness.^{88–93} The addition of 38.16 micro-sized Nb₂O₅ particles to dental adhesive resin with loadings of 5, 10 and 20 wt% significantly increased hardness at 20 wt%, followed by 10 wt%.⁹⁴ Vojdani et al. incorporated Al₂O₃ with an average particle size of 3 µm into PMMA denture base; they noted that hardness significantly increased at 2.5 wt% and 5 wt%, followed by 0.5 wt% and 1 wt%.⁸⁵ Variance results showed a decrease in the surface hardness of PMMA denture base reinforced with 10 wt% and 20 wt% ZrO₂ with particle sizes of 5–10 µm.⁹⁵ Moreover, filler size affects the hardness of composites.⁹⁶ Dental composites reinforced with nanoparticles displayed high hardness values.^{97–99} Liu

et al. reported a significant increase in the hardness of dental composite reinforced with SiO_2 with a mean size of 30 nm and filler volume fraction of 1.5 wt%.¹ In another study, researchers added modified and unmodified TiO_2 nanoparticles (<20 nm) to dental composite at a filler volume fraction of 0.5% and 1%. Both groups showed increased hardness values.⁵⁸ Moreover, Prentice et al. incorporated YbF_3 and BaSO_4 (25 nm and <10 nm) in glass ionomer cement at loadings of 1 wt% and 2 wt%. Both groups reported insignificant increases in hardness values.¹⁰⁰ Many efforts have been made to improve the mechanical properties of PMMA denture base.^{101,102} Safarabadia et al. evaluated the hardness of PMMA denture base reinforced with hybrid nanofillers consisting of HA and Al_2O_3 (30/80 nm). Their results revealed that HA/ Al_2O_3 (10/8 wt%) significantly increased hardness.⁶⁰ Balos et al. found that using SiO_2 with agglomerate size of 50 nm at very low loading (0.023 wt%) increased the hardness of PMMA denture base composites.¹⁰³ Incorporating ZrO_2 particles with average sizes of 5–15 nm in PMMA denture base at different loadings (1.5, 3, 5 and 7 wt%) significantly increased hardness at 7 wt%.³⁸ Table 5 shows the effects of filler size on the hardness of dental composites.

Table 5: The effect of filler size on hardness of dental composites.

Author (year)	Average particle size	Effect on hardness
Leitune et al. (2013) ⁹⁴	Nb_2O_5 (38.16 μm)	Increase
Vojdani et al. (2012) ⁸⁵	Al_2O_3 (3 μm)	Significant increase
Ahmed & Ebrahim (2014) ³⁸	ZrO_2 (5–15 nm)	Significant increase
Liu et al. (2014) ¹	SiO_2 (30 nm)	Significant increase
Balos et al. (2014) ¹⁰³	SiO_2 agglomerates (50 nm)	Increase
Safarabadia et al. (2014) ⁶⁰	HA/ Al_2O_3 (30/80 nm)	Increase
Xia et al. (2008) ⁵⁸	TiO_2 (<20 nm)	Increase
Prentice et al. (2006) ¹⁰⁰	YbF_3 (25 nm) & BaSO_4 (<10 nm)	Insignificant increase
Asopa et al. (2015) ⁹⁵	ZrO_2 (5–10 μm)	Decrease

As shown in Table 5, hardness increased as the filler volume fraction increased. Microparticles improved hardness at relatively higher concentrations than nanoparticles. In addition to particle size, several factors significantly enhance the hardness of dental composites, such as:

1. Inherent properties of some filler particles, such as Al_2O_3 and ZrO_2 . These particles exhibit strong ionic interatomic bonding to confer favourable properties, such as high hardness.^{1,38,60,85} Moreover, SiO_2 , Al_2O_3 and TiO_2 nanoparticles show elastic, rather than plastic, deformation under indentation load.¹⁰⁴

2. Increased filler loading increases hardness values.^{38,44,105–109}
3. Strong interfacial interactions between the modified nanoparticles and polymer.^{45,100,110}
4. Uniform dispersion of nanoparticles provides enough distances between the particles, increasing composite reinforcement and hardness.^{45,96}
5. Harder filler particles exhibit higher surface hardness in the composite.^{111,112} Therefore, filler particle size and filler content, in addition to various factors, can affect the hardness of dental composites.

3. TOUGHENING MECHANISMS

3.1 Crack Deflection

Crack deflection occurs because of the predominant interparticle/intercluster crack growth in the matrix when the crack is forced to move out of its original plane by tilting or twisting.^{113–116} This leads to increased fracture toughness because of non-planar cracks.¹¹⁷ Crack deflection is a shielding mechanism that increases fracture resistance by reducing the stress intensity factor at the crack tip.¹¹³ Schematic drawing of crack deflection is shown in Figure 1.

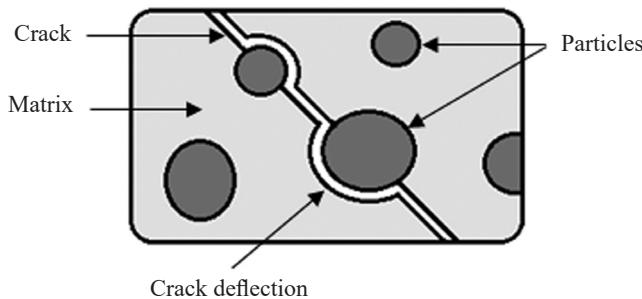


Figure 1: Schematic drawing of crack deflection.

3.2 Crack Pinning

This mechanism suggests that when crack propagation meets inorganic particles, crack propagation becomes pinned and bows out between the filler particles by generating secondary cracks. Crack pinning is a significant toughening mechanism, particularly in rigid particulate-reinforced brittle composites.^{115,117–119} This mechanism has been detected in micro- and nano-composites.^{120,121} It occurs easily

at a nanoscale level, particularly with more reduced interparticle distance resulting from relatively high nanofiller content.¹¹⁹ Medina et al. performed fractography on a nano-composite to illustrate that adding nanoparticles induced crack pinning.¹¹⁵ Moreover, the river-like lines in the nano-composites possibly resulted from crack pinning and the blocking effects of nanoparticles.¹¹⁹ Figure 2 shows a schematic drawing of crack pinning.

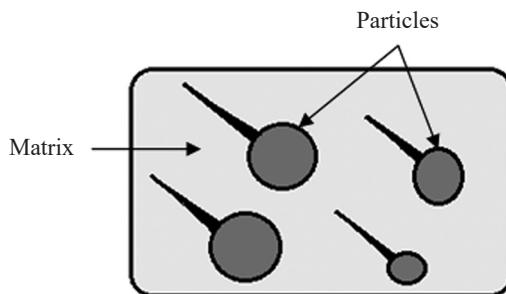


Figure 2: Schematic drawing of crack pinning.

3.3 Matrix–filler Interactions

The strength and toughness of the particulate-filled, polymer micro- and nano-composites are strongly affected by bonding integrity at the filer/matrix interface and thus the stress transfer between the fillers and the matrix.^{51,122,123} Under perfect bonding conditions, a large quantity of energy is consumed at the filler–matrix interface.^{123,124} The existence of a thin and high-strength interphase layer results in effective stress transfer and causes crack deflection and propagation in the matrix. However, a thick and low-strength interphase layer causes crack propagation and crack blunting in the interphase material.¹²⁵ Figure 3 shows a schematic drawing of filler–matrix interphase.

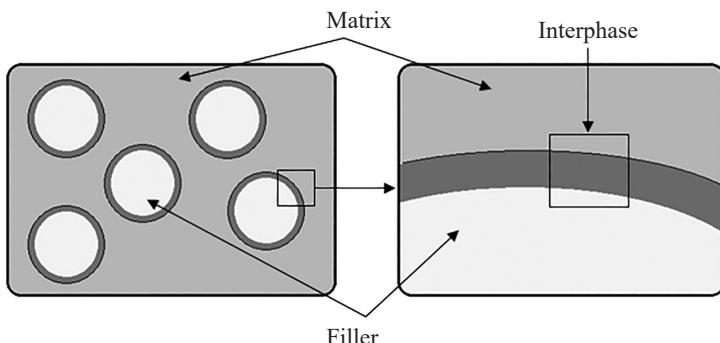


Figure 3: Schematic drawing of filler–matrix interphase.

3.4 Crack Bridging

Crack bridging occurs because of the interparticle/intercluster crack growth when particles connect the crack faces at the crack wake.^{43,113,116} These uncracked bridges sustain part of the load, increasing fracture resistance.^{114,126} Essentially, the crack bridging mechanism minimises the stress concentration at the crack tip and therefore works as an extrinsic toughening source.¹¹⁴ Furthermore, when load is increased, a microcrack is created at some distance from the main crack, and an uncracked bridge exists between the microcrack and the main crack. The microcrack occurs very near to the tip of the main crack and grows in both directions, whereas the main crack stops propagating. Finally, both cracks will meet each other because of the extension of the microcrack. Toughening ceases at this point. However, for small particle-filled composites, crack bridging is not an expected powerful factor enhancing toughness.⁴³ Crack deflection and bridging often work in harmony, given that crack deflection usually leads to crack bridging.^{113,114} Schematic drawing of crack bridging is shown in Figure 4.

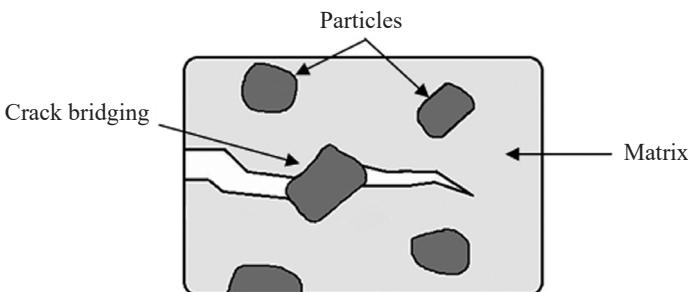


Figure 4: Schematic drawing of crack bridging.

4. CONCLUSION

This review article compares and highlights the effects of micro- and nano-scale particles on the mechanical properties, including fracture toughness, flexural strength and hardness, of particulate dental resin composites. Many types of nanofillers, such as SiO_2 , ZrO_2 , TiO_2 , Al_2O_3 , BaSO_4 , HA, Ag, YbF_3 and nanodiamond, have been used in dental composites. The results of the conducted review showed that the mechanical properties of dental nano-composites with lower filler loadings are superior to microfilled dental composites. The effects of nanoparticles strongly depend on many factors, such as the type and mechanical properties of inorganic nanofillers, uniform dispersal of nanofillers within the polymer matrix, volume fraction of the filler particles, and type of silane used. The key control parameters to enhance fracture toughness are toughening mechanisms (i.e., crack

deflection, crack pinning/bowing, matrix-filler interactions and crack bridging). Good flexural strength requires effective stress transfer from resin to nanofiller, whereas increased filler volume fraction is needed for adequate hardness.

Therefore, future works on this subject demand a proper and systematic investigation on the effects of particle loading, morphology (shape) and particle/matrix interface adhesion that directly contributed to the enhancement of mechanical properties especially fracture toughness and hardness. The reason is obvious since composite strength depends on the load transfer between filler and matrix, and stiffness depends highly on particle loading. However, specific attention should be made on the particle shape of fillers since it has a remarkable effect on some mechanical properties of the dental composites.

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