ABSTRACT
Extensive studies have been undertaken to improve dental composites with advances in filler compositions and resin chemistry. The unique nature of the filler particles of nanocomposites provides mechanical strength and wear resistance similar to hybrid composites, and superior polish and gloss retention similar to micro fill composites. The polymerization shrinkage in composites depends on the chemistry of the organic matrix. The flexural strength depends on the filler content and the filler chemistry. The nanometric particles and nanoclusters in the nanocomposites improve mechanical properties such as compressive strength, flexural strengths, and wear resistance of several nanocomposites were as good as those of universal hybrid composites. They provide high esthetics, hence they can provide optimal optical characteristics since the size of the nanometric particle is below the wavelength of light. This is relevant because the size is not measurable by the refractive index that can result in formulations having a broad spectrum of shade and opacity. Nanocomposite denture teeth composites of poly-methylmethacrylate, and uniformly dispersed nano-sized filler particles. Their advantages are: - highly polishable, stain and impact resistant material; - lively surface structure; - superior surface hardness and wear resistance.

Key words: nanodentistry, dental restorative materials, nanocomposites, physical properties, nanocomposite denture teeth

INTRODUCTION
Extensive studies have been undertaken to improve dental composites with advances in filler compositions and resin chemistry. The unique nature of the filler particles of nanocomposites provides mechanical strength and wear resistance similar to hybrid composites, and superior polish and gloss retention similar to micro fill composites. The polymerization shrinkage in composites depends on the chemistry of the organic matrix. The polymerization shrinkage in composite resin is reported to be 1.4% to 1.6%. Nanocomposites are with low shrinkage value due to the low shrinkage epoxy resin and strong interfacial interactions between resin and nanoparticles. The volumetric shrinkage depends on the total content of organic matrix of composites. Nanohybrid composites (Grandio) showed least amount of organic matrix (13.0 wt-%) and least shrinkage when compared to nanofilled composites (Filtek Supreme Translucent), which had 30.0 wt-% organic matrix [1-3].

A low shrinkage light curable dental nanocomposite was prepared by using an epoxy resin 3,4-epoxycyclohexymethyl-(3,5-epoxy)cyclohexane carboxylate matrix with 55 wt% of 70-100 nm nanosilica fillers through ring opening polymerization. γ-glycidoxypropyl trimethoxysilane was used to modify the surfaces of silica nanoparticles. The developed epoxy resin based nanocomposite demonstrated low shrinkage and high strength and is suitable for dental restorative material applications [4].

The flexural strength depends on the filler content and the filler chemistry. The flexural strength of nanocomposites was found to be equivalent or higher than those of the hybrid or microhybrid composites and significantly higher than those of the microfill composites. Nanofill composites, which have higher filler loading, show greater flexural strength than nanohybrid composites with lesser filler loading [5].

REVIEW ON LITRRATURE
Tanimoto et al (2006) observed progressive decrease in flexural strength as the mean filler-particle diameter increased. This investigation was limited to silica fillers from 3.3 to 15.5 µm - considerably above the maximum range of nanohybrids or nanofills particle size [6]. Turassi et al (2006) found considerable variation among different nanocomposites in a threebody wear test conducted in an oral wear simulator, as well as flexural fatigue limit analysis by the staircase method. Of these materials, a micro fill control (Heliomolar®; Ivoclar Vivadent), a nanohybrid (Grandio®; Voco GmbH, Cuxhaven, Germany) and an agglomerated cluster/fine-particle nanofill (Filtek™ Supreme) showed significantly higher flexural fatigue limit than either an ormocer-based resin-based composite (CeramXTM monor; Dentsply International, York, PA, USA), or another nanohybrid (Premise™; Kerr Corp., Orange, CA, USA) [7].

Beun et al. (2007) compared the physical proper-
ties of three nanofilled composites (Supreme, Grandio and Grandio Flow) four universal hybrid (Point-4, Tetric Ceram, Venus, Z-100) and two micro filled composites (A110, Durafill VS), and observed a higher elastic modulus of the nanofilled resin-based composite than most of the hybrids tested. While all materials tested exhibited similar flexural strengths, microfills showed the poorest physical properties overall [8].

To improve the mechanical properties of resin-based composites Xia et al. (2008) used TiO$_2$ nanoparticles (with diameter <20nm) treated with the organosilane allyltriethoxysilane (ATES). TiO$_2$ nanoparticles were sonically dispersed in an ethanol solution containing ATES. The modified particles were washed in pure ethanol and dried before being used as filler. By spaltation TiO$_2$ particles were manually blended with a resin monomer consisting mainly of UDMA. The particles were then manually added to Z100 dental composite and the mixture was blended. Surface modification by the organosilane ATES influences the dispersion and linkage of TiO$_2$ nanoparticles within a resin matrix and the modified particles were found to improve the microhardness and flexural strength of dental composites [9].

Tian et al. (2007) studied the reinforcement of electrospun nylon 6/fibrillar silicate nanocomposite nanofibers on Bis-GMA/TEGDMA dental composites. The hypothesis was that uniform distribution of nano-scaled and highly aligned fibrillar silicate single crystals in electrospun nylon 6 nanofibers would improve the mechanical properties of the resulting nanocomposite nanofibers and would lead to the effective reinforcement of dental composites. The nylon 6/fibrillar silicate nanocomposite nanofibers were crystalline, structurally oriented and had an average diameter of approximately 250 nm. To relatively well distribute nanofibers in dental composites the nanofiber containing composite powders with a particle structure similar to that in interpenetration networks were prepared first and then used to make the dental composites. The results indicated that small mass fractions (1% and 2%) of nanofiber impregnation improved the mechanical properties substantially while larger mass fractions (1% and 2%) of nanofiber impregnation resulted in less desired mechanical properties [10].

Hosseinalipour et al. (2010) aimed to investigate the mechanical properties of experimental composites containing various mass fractions of silica nanoparticles. Experimental composites were composed of a visible-light-curing monomer mixture (70 wt% Bis-GMA and 30 wt% TEGDMA) and silica nanoparticles of a size ranging from 20 nm to 50 nm modified with gamma-methacryloxypropyltrimethoxysilane (MPS). The total amount of silane used was kept constant at 10 wt% relative to the filler weight to ensure the complete silanization of nanoparticles. Then the silanized nanoparticles (55 wt%) were mixed with a photoactivated Bis-GMA/TEGDMA (50/50 wt/wt) matrix. The static flexural strength and flexural modulus were measured using a three-point bending set up. The dynamic thermomechanical properties were determined by dynamic mechanical analyzer (DMA). Sorption, solubility and volumetric change were determined after storage of composites in water or ethanol/water solution 75 vol% for 30 days. As the average silica particle size decreases, the percentage amount of MPS attached on the silica surface increases. However, the number of MPS molecules attached on the silica surface area of 1 nm$^2$ is independent of filler particle size. As the average filler particles size decreases a progressive increase in the degree of conversion of composites and an increase in the amount of sorbed water is observed. The prepared composites containing different amount of silica filler, with different particle size, but with the same amount of silanized silica and organic matrix showed similar flexural strength and flexural modulus, except composite with the lowest filler particle size, which showed lower flexural modulus [12].

Atai et al. (2012) evaluated the properties of an experimental dental composite consisting of a porous thermally sintered nano-silica as filler. The properties were compared with those of an experimental composite containing micro fillers and a commercially available nano-composite, Filtek Supreme® Translucent. Different models are used to predict the elastic modulus and strength of the composites. Nano-silica with primary particles of 12 nm was thermally sintered to form nanoporous filler particles. The experimental composites were prepared by incorporating 70 wt.% of the fillers into a mixture of Bis-GMA and TEGDMA as matrix phase. Having added photoinitiator system the composites were inserted into the test molds and light-cured. The microfiller containing composites were also prepared using micron size glass fillers.
Diametral tensile strength (DTS), flexural strength, flexural modulus and fracture toughness were measured.

The results from the study showed improvements in flexural modulus and fracture toughness of the composites containing sintered filler. AFM revealed a lower surface roughness for sintered silica containing composites. No significant difference was observed between DTS, DC%, and flexural strength of the sintered nanofiller composite and the Filtek Supreme®. The results also showed that the modulus of the composite with sintered filler was higher than the model prediction. The thermally sintered nano-porous silica fillers significantly enhanced the mechanical properties of dental composites introducing a new approach to develop materials with improved properties [13].

Chen et al. (2011) investigated the properties of high aspect-ratio hydroxyapatite (HAP) nanofibers and the reinforcing effect of such fibers on bisphenol A glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA) dental resins (without silica microparticle filler) and dental composites (with silica microparticle filler) with various mass fractions (loading rates). The HAP nanofibers with aspect-ratios of 600 to 800 can be successfully fabricated with a simple wet-chemical method in aqueous solution. Impregnation of small mass fractions of the HAP nanofibers (5 wt% or 10 wt%) into the BisGMA/TEGDMA dental resins or impregnation of small mass fractions of the HAP nanofibers (2 wt% or 3 wt%) into the dental composites can substantially improve the biaxial flexural strength of the resulting dental resins and composites. A percolation threshold of HAP nanofibers, beyond which more nanofibers will no longer further increase the mechanical properties of dental composites containing HAP nanofibers, was observed for the dental composites with or without silica microparticle filler. The authors tested the biaxial flexural strength (BFS) of the HAP nanofibers reinforced dental resins without any microsized filler and dental composites with silica microparticle filler and examined the morphology of fracture surface of tested dental composite samples. Their results indicated that the relatively good dispersion of HAP nanofibers at low mass fraction is the key reason for the significantly improved biaxial flexural strength, while higher mass fraction of HAP nanofibers tends to lead to bundles that cannot effectively reinforce the dental resins or composites and may even serve as defects and thus degrade the resulting dental resin and composite mechanical properties. According to this study, the incorporation of small mass fraction of HAP nanofibers with good dispersion can improve the mechanical property of dental resins and dental composites [2].

Xia et al. (2008) reported that surface modification by the organosilane of TiO2 nanoparticles within a resin matrix was found to improve the micro hardness and flexural strength of dental resin based composites [9]. Andrade et al (2011) tested fragments of nanofiller (mean particle size of 80 nm and 1.508 refractive index containing aluminoisilicate - 1:4 M ratio of alumina to silica) powder. The nanfill/nanohybrid composite has been found to show acceptable clinical performance in restorations of occlusal cavities of posterior teeth [14]. Moreover, the application of alumina-whisker-reinforced composites in dental applications might be promising for increasing hardness and fracture toughness compared with other materials [15]. Dental resin nanocomposites containing CaF2 nanoparticles that were developed with relatively high strength as well as sustained release of fluoride ions yielded restorations that reduce the occurrence of both secondary caries and restoration fracture. Nanocomposites show better hardness, superior flexural modulus, modulus of elasticity, and translucency, superior handling properties, and display a 50% decrease in filling shrinkage [16].

In a most recent study Wang et al. (2014) stated that organic-inorganic hybrid materials, such as polyhedral oligomeric silsesquioxanes (POSS) have the potential to improve the mechanical properties of the methacrylate-based dental composites and resins. They investigated nanocomposites of methacryl isobutyl POSS (MI-POSS - bears only one methacrylate functional group) and methacryl POSS (MA-POSS - bears eight methacrylate functional groups) to determine the effect of structures on the properties of dental resin. Monofunctional POSS showed a strong tendency toward aggregation and crystallization, while multifunctional POSS showed higher miscibility with the dimethacrylate monomer. The mechanical properties and wear resistance decreased with increasing amounts of MI-POSS, indicating that the MI-POSS agglomerates act as the mechanical weak point in the dental resins. The addition of small amounts of MA-POSS improved the mechanical and shrinkage properties. However, samples with a higher MA-POSS concentration showed lower flexural strength and flexural modulus, indicating that there is a limited range in which the reinforcement properties of MA-POSS can operate. This concentration dependence is attributed to phase separation at higher concentrations of POSS, which affects the structural integrity, and thus, the mechanical and shrinkage properties of the dental resin (fig 1.).

Fig 1. POSS (polyhedral oligomeric silsesquioxanes) distribution in the polymer matrix shown
as (A) polymer matrix with MA-POSS (methacryl polyhedral oligomeric silsesquioxanes) and (B) polymer matrix with MI-POSS (methacryl isobutyl polyhedral oligomeric silsesquioxanes) (Wang et al. 2014).

According to the authors, resin with 3% MA-POSS is a potential candidate for resin-based dental materials [17]. In a review article, Li et al. (2014) demonstrated the efforts to reinforce mechanical performances of dental composites using nanofibers and nanotubes, including polymeric nanofibers, metallic nanofibers or nanotubes, and inorganic nanofibers or nanotubes. They confirm the enhancement of nanofibers or nanotubes’ reinforcement on the mechanical performances of dental restorative composite and make a general description about the reinforcement mechanism of nanofibers and nanotubes, especially, the impact of formation of interphase boundary interaction and nanofibers themselves on the advanced mechanical behaviors of the dental composites. By means of the formation of interface interaction and poststretching nanofibers, reinforced effect of dental composites by sorts of nanofibers/nanotubes has been successfully obtained (fig. 2, fig. 3) [18].

Water uptake in the polymeric phase of composites causes two opposing processes. The solvent extracts unreacted components, mainly monomer, resulting in shrinkage, loss of weight, and reduction in mechanical properties. Conversely, solvent uptake leads to a swelling of the composite and increase in weight. The solvent diffuses into the polymer network and separates the chains creating expansion [19]. Since the polymer network contains microvoids created during polymerization and free volume between chains, a part of the solvent is accommodated without creating a change in volume. Thus the dimensional change of a polymer composite in a solvent is complex and difficult to predict and depends on the chemical structure of the polymer matrix. In general, nanohybrid composites show less water sorption than nanofill composites.

Mayworm et al. (2008) discovered that the wear resistance of nanoparticles containing dental composites increases after its storage in artificial saliva. The storage of artificial saliva increases the material’s wear resistance, signifying that material bulking post-cure takes place and saliva absorption occurs only on the surface of the composites. Surface microhardness of the composites decreases after storage in artificial saliva whereas bulk microhardness of the materials increases [20]. Moreover, it has been reported that radiopaque Ta2O5/SiO2 filler nanoparticles dispersed in a methacrylic matrix results in adhesives with radiopacity higher than dentin and enamel and excellent adhesive strength [21].

Curtis et al. (2008) compared the influence of short- and medium-term immersion on water uptake and mechanical properties of nanofilled (Filtek Supreme in body and translucent shades, FSB and FST; 3M ESPE, St. Paul, USA) and a conventional (a microhybrid, Filtek Z250, FZ) resin-based composite. For each material mean bi-axial flexure strength was determined following 24 h ‘dry’ and 24 h, 3, 6 and 12 months in a water-bath maintained at 37 ± 1°C prior to testing. The extent of water uptake following each storage regime was determined using a near-infrared spectroscopy (NIRS) technique. No significant difference in bi-axial flexure strength was identified for each material stored dry or wet for 24 h whilst bi-axial flexure strength decreased following 3, 6 and 12 months. A significant decrease in bi-axial flexure strength of FZ was observed following 3 and 6 months with no further reduction following 12 months. In contrast, no significant decrease in bi-axial flexure strength of FSB and FST was recorded following 6 compared with 3 months immersion. Storage for 12 months resulted in a further significant strength reduction of FSB and FST. Water uptake of FZ and FSB increased up to 3 months before equilibrating, whereas water content of FST increased following all storage periods. The authors concluded that water uptake and mechanical properties of test materials were influenced by the size and morphology of the reinforcing particulate...
phase. The use of nanoparticles and associated agglomerates in modern RBCs exhibit distinct mechanical and physical properties compared with a conventional resin based composite type [22].

The nanometric particles and nanoclusters in the nanocomposites improved mechanical properties such as compressive strength, flexural strengths, and wear resistance of several nanocomposites were as good as those of universal hybrid composites. However, the worn surfaces of the nanocomposites were smoother, the translucency and the gloss retention after tooth brushstrokes was higher, compared with those of hybrid composites [23]. They also provide high esthetics [8, 24], hence they can provide optimal optical characteristics since the size of the nanometric particle is below the wavelength of light. This is relevant because the size is not measurable by the refractive index that can result in formulations having a broad spectrum of shade and opacity [25].

Nano-composite denture teeth

Wear resistance is the most important physical properties of denture teeth. Porcelain denture teeth are most wear resistant, but they are brittle, lack bonding to the denture base, and difficult to polish. Acrylic resin denture teeth are easier to recontour, but undergo excessive wear. Nanocomposite denture teeth comprises of polymethyl-methacrylate, and uniformly dispersed nano-sized filler particles. Their advantages are: - highly polishable, stain and impact resistant material; - lively surface structure; - superior surface hardness and wear resistance [26].

Suzuki (2004) evaluated the relative wear resistance of several types of denture teeth using an in vitro wear testing device. Four different types of denture teeth [nano-filled (Veracity) and micro-filled composites (SR-Orthosit, Endura, Duradent, Surpass), cross-linked acrylic (SR-Postaris, Genios-P, Creapearl, Vitapan Physiodens, Premium 8, Integral), and a conventional acrylic (Biotone)] were used. The flattened buccal surface of each denture tooth was subjected to the evaluation of Knoop hardness (n=5) and localized wear for 100,000 cycles (n=10). Wear values were determined in micrometers using a profilometer. The data for the hardness, wear depth, and worn surface areas were individually analyzed. Knoop hardness values (KHN) ranged from 28.2 to 29.8 for mini- fillers. Their advantages are: - highly polishable, stain and impact resistant material; - lively surface structure; - superior surface hardness and wear resistance [26].

In conclusion, the nanometric particles and nanoclusters in the nanocomposites improved mechanical properties such as compressive strength, flexural strengths, and wear resistance of several nanocomposites were as good as those of universal hybrid composites. They also provide high esthetics, hence they can provide optimal optical characteristics since the size of the nanometric particle is below the wavelength of light.

Ghazal et al (2008) evaluated the wear of denture teeth and their antagonists produced by two-body and three-body wear tests. Three types of denture teeth, namely feldspathic ceramic (FC), nano-filled composite resin (NCR), and experimental acrylic resin teeth (AR), were tested. For each type two groups of eight upper premolars each were prepared. The first group was tested against cusps from the same material and the second group was tested against human enamel cusps. Each group was loaded with a total of 200,000 chewing cycles (two-body wear, 100,000 cycles and three-body wear, 100,000 cycles). Wear was analyzed by measuring the maximum depth and volume loss of the denture and by measuring the vertical loss of the antagonists. Statistically, there was no significant difference between the following combinations: FC-FC and NCR-NCR regarding the vertical and volume loss; and FC-enamel and NCR-enamel regarding the total vertical substance loss. The combinations AR-AR and AR-enamel showed higher wear values than the other combinations. For complete dentures, composite resin and ceramic teeth showed similar vertical and volume loss, whereas composite resin teeth seemed to be more suitable for partial dentures opposing natural teeth in terms of wear of teeth and antagonists [28].

In a next study, the same authors Ghazal et al. (2008) evaluated the wear resistance of nanofilled composite resin and feldspathic ceramic artificial teeth after simulated mastication against steatite, zirconia, and alumina antagonists. The study evaluated 6 groups of artificial teeth: 3 groups of 8 nanofilled composite resin teeth (Condyloform II NFC) and 3 groups of 8 feldspathic ceramic teeth (Bonartic CT). Three sets of 16 steatite, 16 zirconia, and 16 alumina cusp-shaped antagonist surfaces were fabricated and used to test wear resistance. Each group was loaded for 600,000 cycles. The wear resistance was analyzed by measuring vertical and volume substance lost (microm and mm3, respectively). The influence of the materials tested and antagonists was statistically significant. The composite resin teeth showed significantly higher vertical and volume substance loss than ceramic teeth opposing steatite cusps, while composite resin teeth opposing alumina and zirconia cusps demonstrated less wear than ceramic teeth, but the differences were not statistically significant. The authors established that the wear behavior of nanofilled composite resin and feldspathic ceramic teeth varies according to the type of antagonistic material. However, alumina and zirconia ceramics caused less wear in antagonists than steatite ceramic [29].

In conclusion, the nanometric particles and nanoclusters in the nanocomposites improved mechanical properties such as compressive strength, flexural strengths, and wear resistance of several nanocomposites were as good as those of universal hybrid composites. They also provide high esthetics, hence they can provide optimal optical characteristics since the size of the nanometric particle is below the wavelength of light.
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