

Nanocomposites and nanoionomers for orthodontic bracket bonding

10

Prabhat Kumar Chaudhari*, Lata Goyal[†], Shailendra Singh Rana*, Kunaal Dhingra[‡], Nandita Kshetrimayum[§]

*Division of Orthodontics and Dentofacial Deformities, Centre for Dental Education and Research, All India Institute of Medical Sciences, New Delhi, India, [†]Department of Dentistry, All India Institute of Medical Sciences, Rishikesh, India, [‡]Division of Periodontics, Centre for Dental Education and Research, All India Institute of Medical Sciences, New Delhi, India, [§]Department of Public Health Dentistry, Regional Institute of Medical Sciences, Imphal, India

10.1 Introduction

In the history of orthodontic bonding, the concept of acid etching techniques to bond restorative materials with the tooth's surface was a breakthrough. It is of paramount importance to have good bond strength between adhesive material and the tooth surface, so that masticatory forces and pressure exerted by wires can be well tolerated. With advances in materials and technology, orthodontic bonding has become predictable, simpler, and less time consuming. Earlier restorative materials consisting of diglycidylether methacrylate, coupling agents, and a high amount of inorganic fillers (quartz and silica) have been used [1]. Inorganic fillers are known to improve the physical properties such as abrasion resistance, shear strength, and the coefficient of thermal expansion. If the size of filler particles is reduced, more filler overload is achieved that in turn, improves the physical and mechanical properties of restorative material.

In the conventional dental composite, the filler particle size ranges from a few micrometers to millimeters. Nanotechnology is the production and manipulation of materials in the range of 0.1–100 nm by various methods [2]. When the inorganic filler particle size in a composite resin becomes nano-sized, the particles are called nanocomposites (Table 10.1). Nanofilled composites have a filler size ranging from 5 to 100 nm. Nanocomposites have been reported with a good marginal seal [3]. When the filler content of resin-modified glass ionomer cements (RMGIC) is replaced with the formulation based on bonded nanofiller technology, it is called a nanoionomer. Based on bonded nanofiller technology, a nanoionomer, Ketac N100, has been developed [4]. This light-curing nanoionomer consists of fluoroaluminosilicate glass and nanofillers. It shows improved mechanical properties and high fluoride release. This chapter addresses the physical, mechanical, and clinical applications of nanocomposites and nanoionomers in relation to orthodontic tooth bonding.

**Table 10.1 Showing classification
of composites based on filler sizes**

S. No.	Filler category	Filler size
1.	Megafill	0.5–2 mm
2.	Macrofill	10–100 µm
3.	Midifill	1–10 µm
4.	Minifill	0.1–1 µm
5.	Microfill	0.01–0.1 µm
6.	Nanofill	0.005–0.01 µm

10.2 Development of composite resin from restorative applications to orthodontic bonding

Modern dental composites started their journey long ago, back in the 1960s. Over the past 55 years, resin-based composite materials continue to evolve, with better handling characteristics, finer filler particle size, and better bonding and curing systems (Fig. 10.1). A typical dental composite consists of a triad of a synthetic polymeric matrix (bisphenol A diglycidylether methacrylate: BIS-GMA), inorganic fillers (quartz, silica), and a coupling agent (silane) to bind the matrix and filler together

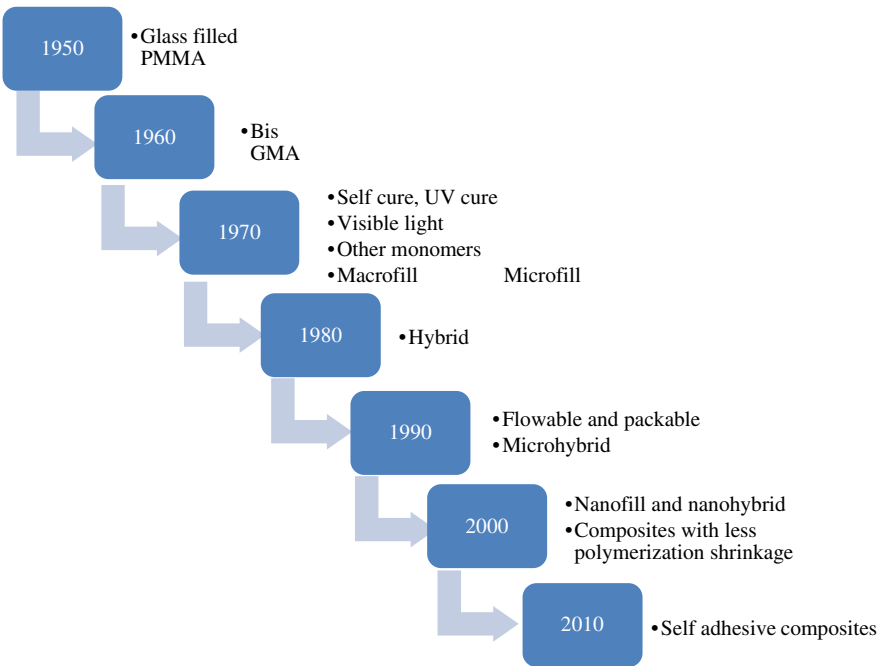


Fig. 10.1 Showing evolution of dental composites in last six decades.

[5]. It also contains visible light initiators and activators that initiate the polymerization processes; the most common one being camphoroquinone, which is accelerated by amines.

Light-cure materials are gaining acceptance and popularity in orthodontic practices because of their efficient working time, better handling characteristics, and high early bond strength after their placement on the orthodontic bracket, followed by polymerization. In routine orthodontic practice, it is essential to obtain a reliable adhesive bond between an orthodontic attachment and tooth enamel. Filled dental restorative materials have been used as orthodontic adhesives [1]. Based on consistency and filler content, composite materials range from flowable to packable composites. Flowable composites have a lower viscosity, either due to reduced filler content, or due to the addition of surfactants, which increases fluidity of material without compromising filler content. They have main advantages of injectibility and nonstickiness. With better flowing characteristics, they can easily flow into the bracket base, and better mechanical retention can be achieved.

Moreover, flowable resin reduces the filler load, so it is expected that it will adversely affect the physical properties of the material, such as wear strength, abrasion resistance, microhardness, and polymerization shrinkage. Inorganic filler also decreases the coefficient of thermal expansion, affecting long-term micro-leakage [6]. To have practical application in orthodontics, it should have sufficient bond strength so that it can withstand forces of mastication. But evidence supports the fact that flowable resin can be used as an orthodontic adhesive, although bond strength is low compared with conventional composites, but it still exceeds the minimal acceptable value of bond strength required for orthodontic bonding [7].

Based on particle size, composites can be further distinguished [8] as [Fig. 10.2]:

Conventional: Particle size is more than 1 μm . These are very strong, but difficult to polish, and surface smoothness is difficult to attain.

Microfill: Particle size is approximately 40 nm. These are developed to overcome limitations regarding aesthetics of conventional composites. They are polishable, but lack strength.

Hybrid: When the particle size of a conventional composite is further reduced to provide strength, the resultant composite is called a hybrid. Hybrid composites are categorized as midfill (average particle size greater than 1 μm , and a portion of 40 nm sized silica microfillers), and minifill/microhybrid (particle size 0.4–1 μm).

Nanofill/nanohybrid: Microhybrid with more nanoparticles of size 5–100 nm, and also containing prepolymerized resin.

10.3 Nanocomposites and nanoionomers for orthodontic bonding

When inorganic phases in a composite become nanosized, they are called nanocomposites. As the filler particle size decreases, there is an increased filler load, along with reduced polymerization shrinkage. In nanocomposites, extremely small filler particle has dimensions below the wavelength in the visible light range, thus offering better optical properties and aesthetics. When the filler content of resin-modified glass

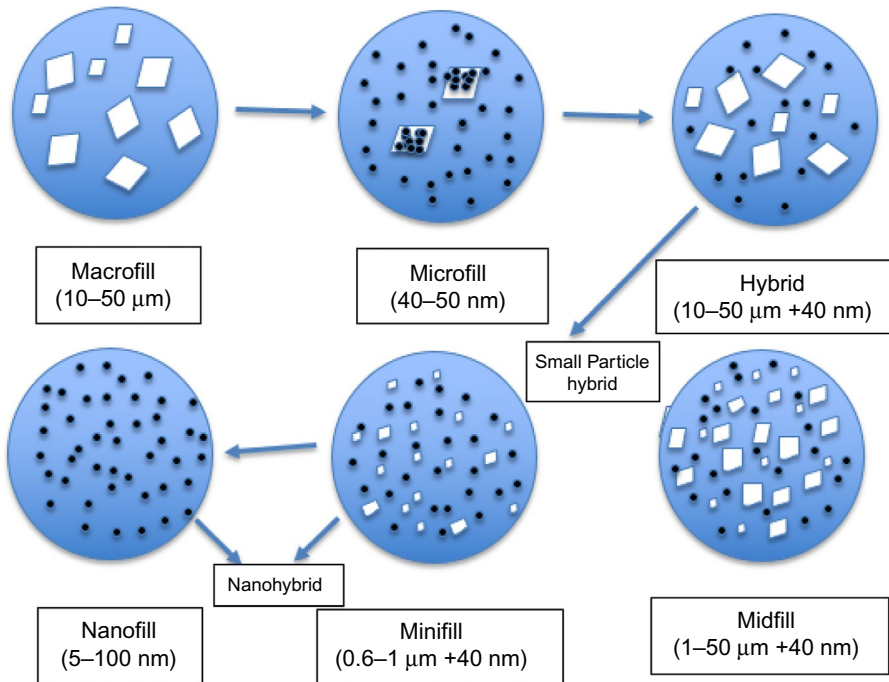


Fig. 10.2 Showing dental composites based on filler sizes.

ionomer cements (RMGIC) is replaced with the formulation based on bonded nano-filler technology, it is called a nanoionomer. Among various formulations of nanocomposites and nanoionomer available in the market, the most common commercially available formulations of nanocomposites include Filtek Supreme, Premise, Ceram X, and the nanoionomer Ketac N 10 [5]. A brief description of each of these is presented as follows, and has been summarized in Table 10.2.

- Filtek Supreme* is a nanofilled composite containing nanomers and nanoclusters. Nanomers contain silica particles of 20 and 75 nm in diameter, and are monodispersed, nonagglomerated, and nonaggregated. Nanoclusters (NC) contains nanosized fillers and loosely bound agglomerates. Two types of NCs have been synthesized. The first type of NCs are made of zirconia-silica particles of 2–20 nm with agglomerated particle size of less than 0.6 μm. The second type consists of silica particles of 75 nm with an agglomerated particle size of 0.6 μm. The filler content is about 58%–60% by volume and 78.5% by weight.
- Premise* is a nanohybrid composed of three different types of fillers, such as prepolymerized fillers (PPF) 30–50 μm, barium glass fillers (0.4 μm), and nonagglomerated “discrete” silica nanoparticles of 20 nm. This combination of fillers allows for increased filler loading of 69% by volume and 84% by weight. These nonagglomerated nanoparticles are so well dispersed in the matrix that they allow increased filler loading, as well as flowability of nanocomposites desired for orthodontic bonding.
- Ceram-X* is an ormocer-based nanoceramic composite having glass fillers (1.1–1.5 μm) and methacrylate modified silicon-dioxide-containing nanofillers of a particle size of 10 nm. “Ormocer” is an acronym for “organically modified ceramic technology” and ormocer materials contain inorganic–organic *co*-polymers in addition to the inorganic silanated

Table 10.2 Showing most common commercially available nanocomposites and nanoionomers

S. No.	Band name	Type	Filler composition, vol% (wt%)	Manufacturer
Nanocomosites				
1.	Filtek Supreme	Nanofilled	Nanomers and nanoclusters 58%–60% by volume and 78.5% by weight	3 M ESPE, St. Paul, MN, USA
2.	Premise	Nanohybrid	Nonagglomerated “discrete” silica nanoparticles, pre polymerized fillers (PPF), and barium glass fillers 69% by volume and 84% by weight	Kerr/Sybron, Orange, CA, USA
3.	Ceram-X	Nanohybrid ormocer-based, nanoceramic composite	Glass fillers (1.1–1.5 μm) Methacrylate modified silicon-dioxide-containing nanofiller (10 nm) 57% by volume and 76% by weight.	Dentsply DeTrey, Konstanz, Germany
Nanoionomer				
1.	Ketac N 100	Light cure resin modified GIC	Fluoroaluminosilicate glass, nanofillers, nanoclusters	(3 M, ESPE, St. Paul, MN, USA)

filler particles. The filler concentration in ceram X is 57% by volume and 76% by weight. Both nanoceramic particles and nanofillers have methacrylate groups, which are required for polymerization.

- (d) A *nanoionomer* is a resin-modified glass ionomer cement (GIC) developed through nanotechnology. It is composed of fluoroaluminosilicate glass, nanofillers, and nanoclusters combined to improve mechanical properties and fluoride release capacity.

10.4 Properties of nanoparticles' orthodontic adhesive

Properties of composite materials depend basically on the three chemically different components, that is, the organic matrix or the organic phase; the inorganic matrix, which is the filler or disperse phase; and an organosilane, which is a coupling agent to bond the filler to the organic resin. Nanocomposites contain a larger volume of the small-sized filler particles in the resin matrix at a nanoscale level, thus resulting in composite materials with improved physical, chemical, and biological properties [9].

Various properties of the composite materials are as follows.

10.4.1 Bond strength

For routine clinical orthodontic bonding, a bond strength of 5.9–7.8 MPa is adequate [10], and an increase in filler content increases the bond strength of the orthodontic composite. Many modifications have been suggested to improve the bond strength

of orthodontic composites [11]. One is to increase the filler content in nanofillers. A study was conducted to test the commercially available nanocomposite material (Filtek Supreme Plus Universal), nanoionomer restorative material (KetactN100 Light Curing Nano-Ionomer), and conventional light-cure orthodontic bonding adhesive (Transbond XT for orthodontic bracket bonding) [4]. It was concluded that the conventional orthodontic composite had a higher shear bond strength than that of the nanocomposite and the nanoionomer groups; but nanocomposites and nanoionomers may be suitable for bonding, but are inferior to conventional orthodontic composites. Another study showed that there was no significant difference in shear bond strength and the bond failure interface between composite adhesive materials containing silica nanofillers and silver nanoparticles, as well as two conventional adhesives composite and resin-modified glass ionomers [12].

Another researcher found that the bond strength of nanoionomers was adequate to bond to the enamel (14.465.8 MPa) and dentin (12.666.5 MPa) at the same extent as other GICs (enamel: 12.963.3 MPa; dentin: 12.362.9 MPa), but less effectively than conventional RMGIC (Fuji II LC) to the enamel (38.867.4 MPa) and dentin (31.464.3 MPa) [13]. For nanocomposite orthodontic bonding, different surface treatments can be used, but the sandblasting surface treatment has been recommended as a safe and effective method of bonding orthodontic metal brackets to nanohybrid composite resins [14].

10.4.2 Flexural strength

The flexural strength, also known as the modulus of rupture, bend strength, or transverse rupture strength, depends on the filler content and chemistry. Nanocomposites possess a higher modulus of elasticity and greater flexural, compressive, and diametrical tensile strengths, along with improved hardness, fracture toughness, and wear resistance [15]. Nanocomposites have flexural strength statistically equivalent or higher than those of the hybrid or microhybrid composites, and significantly higher than those of the microfill composites. However, nanofill composites, which have a higher filler loading, showed greater flexural strength than nanohybrid composites, which have less filler loading [16].

It was also found that the response of nanocomposites was much better to the functional stresses of mastication as compared with the conventional resins because the smooth and rounded edges of the spheroidal nanoparticles tended to distribute stress more evenly throughout the composite resin [17].

10.4.3 Polymerization shrinkage

The volumetric shrinkage of composite materials depends upon the total organic matrix content. The smaller size of filler particles reduces the organic matrix of composites, enables higher filler packing and distribution in the resin matrix, and also tends to increase the interfacial area between the filler and the matrix, leading to better dispersion and reduced polymerization shrinkage. Nanohybrid composites (Grandio)

showed the least amount of organic matrix (13.0wt%), and the least shrinkage, when compared with nanofill composites (Filtek Supreme Translucent), which had a 30.0wt% organic matrix [18,19].

10.4.4 Water sorption

Generally, nanohybrid composites show less water sorption than nanofill composites. In a nanohybrid composite, there is decreased water diffusion into the polymer network, which prevents the separation of chains. This decreased interparticle distance between the nanofillers reduces the tendency for crack formation, as well as propagation, which results in a better marginal seal and color stability [20].

10.4.5 Cytotoxicity

The orthodontic adhesive containing TiO₂ nanoparticles indicated comparable or even lower toxicity than its nanoparticle-free counterpart, indicating that incorporation of 1 wt% TiO₂ nanoparticles into the composite structure does not result in additional health hazards compared with that occurring with the pure adhesive [21].

10.5 Antibacterial and anticaries activity nanocomposite

Apart from better physical properties, it is also necessary that nanocomposites should have antibacterial and anticaries activities. A study was done to demonstrate the effect of nanoparticles on bacteria. In this study, an experimental composite adhesive material (ECA) containing silica nanofillers and silver nanoparticles was compared with two conventional adhesives (composite- and resin-modified glass ionomers) to evaluate the antibacterial activity against cariogenic bacteria. Bacterial adhesion was measured by incubating the adhesive discs for 6h in a saliva sample. The results of this study showed that the bacterial adhesion and bacterial growth to ECA were less than the conventional adhesives. However, ECA had rougher surfaces than conventional adhesives due to the addition of silver nanoparticles. Finally, it was concluded that nanoparticles can be incorporated into orthodontic adhesive materials to prevent bacterial adhesion during orthodontic treatment [12].

Many types of particles can be added as nanoparticles for antibacterial and anticaries activities, such as silica-based NACP (nanoamorphous calcium phosphate) and TiO₂, which have been very important. The addition of the NACP to the composite caused a significant reduction in the *S. mutans* population around the brackets when compared with the control side at 3 months and 6 months after the initiation of orthodontic treatment [22]. NACP have the advantage of color stability, and have both bactericidal and remineralization effects by releasing calcium and phosphate ions, as compared with nano-Ag, which have only bactericidal action. These silica-based nanoparticles damage bacteria by altering the enamel surface or releasing antimicrobial agents [22].

The flowability of the nanoionomer is higher than composite resin, and thus it is superior to composite resins for penetrating the bracket retention features, and possibly coating the enamel during the bonding procedure. Such an attribute might reduce the possibility of caries forming under brackets during treatment. Fluoride release and recharge might also reduce the possibility of caries formation near the bonding material excess interface between the bonding material/enamel/oral environment lines. From this perspective, nanoionomers should be considered a potentially useful adhesive for bonding orthodontic brackets [23].

10.6 Are nanocomposites and nanoionomers suitable for orthodontic bracket bonding?

Bonding between the enamel surface and orthodontic bracket using an adhesive system is routine practice. Bonding performance depends upon the type of adhesive material used and the interaction between the various interfaces of adhesive material, tooth material, and orthodontic brackets. The maximum bond strength recommended for successful clinical bonding is estimated to be 7 MPa [24]. Reynolds (1975) suggested that a minimum bond strength of 5.9–7.8 MPa is adequate for most orthodontic needs during routine clinical use [10]. Higher stress is expected during mastication. The metal brackets bonded with composite resin have shown a bond strength ranging from 2 to 13 MPa [25].

Evidence supports the finding that nanocomposites and nanoionomers can be used for orthodontic bonding [4]. Due to reduced particle size in nanocomposites and nanoionomers, there is increased filler size and a wider distribution of particles. As a result, more filler load and material with less polymerization shrinkage can be achieved. Uysal T. demonstrated that bond strength of nanocomposites and nanoionomers used was lesser than conventional adhesives, but the range was 1.71 to 20.71 Mpa. For nanocomposites and nanoionomers, it was between 2.43 and 10.00 MPa, which is clinically acceptable [4].

Bishara in 2007 investigated nanofilled composites (Grandio), and found that bond strength was not significantly different from conventional composites. However, the author found that consistency of these materials was higher during penetration into orthodontic brackets [26].

S.J. Ahen demonstrated that experimental composite material containing silica nanofillers and nanoparticles had less bacterial adhesion than conventional composites, although surface roughness was more in the experimental group. However, there was no difference between shear bond strength between these [12].

10.7 Future trends

Recent developments in this research area are increasing the strength of nanocomposites by reinforcing fillers with nanofibers, *E*-glass fibers (3 nm in length) with BaAlSiO₂ in semi-interpenetrating polymer network (IPN) matrices, and TiO₂ nanoparticles [5].

Another area of research is modification for incorporating antibacterial and caries prevention agents. Scientists have increased the mineral content of dental caries lesions by releasing Ca and PO₄ ions [nano-dicalcium phosphate anhydrous (DCPA) whiskers] [27], or by fluoride release (calcium fluoride (CaF₂, kaolinite). Efforts to modify resin matrices is aimed at reducing polymerization shrinkage by incorporating ring opening resin matrices using epoxy phenols, epoxy resin, or using siloxane. Self-adhesive composites are currently being investigated. Future nanocomposite materials must be modified, so that nanocomposites can bond with the tooth structure through chemical and mechanical retention with antibacterial and anticaries activities.

10.8 Summary

An optimal composite material should bond to the tooth structure to resist the functional forces in the oral environment without affecting oral tissue adversely. Researchers and manufacturers are continuously introducing new adhesives for orthodontics bonding with better properties and handling features. In the future, with the refinement of nanotechnology and nanomaterial science, better filler particles may be synthesized to enhance the bond strength of the nanocomposite. As newly introduced materials and techniques are refined, orthodontists will likely adopt these innovations, and add them to their armamentarium for routine clinical practice.

References

- [1] D.K. Eversoll, R.N. Moore, Bonding orthodontic acrylic resin to enamel, *Am. J. Orthod. Dentofac. Orthop.* 93 (1988) 477–485.
- [2] R.E. Kirk, D.F. Othmer, J. Kroschwitz, M. Howe-Grant, Nanotechnology, in: *Encyclopedia of Chemical Technology*, Supplement Volume, fourth ed., Wiley, New York, 1998, p. 397.
- [3] B.A. Venhoven, A.J. de Gee, A. Werner, C.L. Davidson, Influence of filler parameters on the mechanical coherence of dental restorative resin composite, *Biomaterials* 17 (1996) 735–740.
- [4] T. Uysal, A. Yagci, B. Uysal, G. Akdogan, Are nano-composites and nano-ionomers suitable for orthodontic bracket bonding? *Eur. J. Orthod.* 32 (2010) 78–82.
- [5] M.H. Chen, Update on dental nanocomposites, *J. Dent. Res.* 89 (2010) 549–560.
- [6] S. Geraldeli, J. Perdigao, Microleakage of a new restorative system in posterior teeth, *J. Dent. Res.* 126 (2003). (Abstract).
- [7] S.B. Park, W.S. Son, C.C. Ko, F. Garcia-Godoy, M.G. Park, H.I. Kim, Y.H. Kwon, Influence of flowable resins on the shear bond strength of orthodontic brackets, *Dent. Mater. J.* 28 (2009) 730–734.
- [8] J.L. Ferracane, Resin composite-state of the art, *Dent. Mater.* 27 (2011) 29–38.
- [9] D.A. Terry, Direct applications of a nanocomposite resin system: Part 1—The evolution of contemporary composite materials, *Pract. Proced. Aesthet. Dent.* 16 (2004) 417–422.
- [10] I.R. Reynolds, A review of direct orthodontic bonding, *Br. J. Orthod.* 2 (1975) 171–178.

- [11] A. Faltermeier, M. Rosentritt, R. Faltermeier, C. Reicheneder, D. Missig, Influence of filler level on the bond strength of orthodontic adhesives, *Angle Orthod.* 77 (2007) 494–498.
- [12] S.J. Ahn, S.J. Lee, J.K. Kook, B.S. Lim, Experimental antimicrobial orthodontic adhesives using nanofillers and silver nanoparticles, *Dent. Mater.* 25 (2009) 206–213.
- [13] E. Coutinho, M.V. Cardoso, J. Munck De, A.A. Neves, K.L. Van Landuyt, A. Poitevin, Bonding effectiveness and interfacial characterization of a nano-filled resin-modified glass-ionomer, *Dent. Mater.* 2 (2009) 1347–1357.
- [14] H.K. Demirtas, M. Akin, Z. Ileri, F.A. Basciftci, Shear bond strength of orthodontic brackets to aged nanohybrid composite resin surfaces using different surface preparation, *Dent. Mater. J.* 34 (2015) 86–90.
- [15] R. George, Nanocomposites-a review, *J. Dent. Oral Biosci.* 2 (2011) 38–40.
- [16] U. Lohbauer, R. Frankenberger, N. Kramer, A. Petschelt, Strength and fatigue performance versus filler fraction of different types of direct dental restoratives, *J. Biomed. Mater. Res. B Appl. Biomater.* 76 (2006) 114–120.
- [17] R.R. de Moraes, S. GonçalvesLde, A.C. Lancellotti, S. Consani, L. Correr-Sobrinho, M.A. Sinhoret, Nanohybrid resin composites: nanofiller loaded materials or traditional microhybrid resins? *Oper. Dent.* 34 (2009) 551–557.
- [18] M.H. Chen, C.R. Chen, S.H. Hsu, S.P. Sun, W.F. Su, Low shrinkage light curable nanocomposite for dental restorative material, *Dent. Mater.* 22 (2006) 138–145.
- [19] L.C. Boaro, F. Goncalves, T.C. Guimaraes, J.L. Ferracane, A. Versluis, R.R. Braga, Polymerization stress, shrinkage and elastic modulus of current low-shrinkage restorative composites, *Dent. Mater.* 26 (2010) 1144–1150.
- [20] S. Mahalaxmi, Composite resins, in: *Materials Used in Dentistry*, first ed., Wolter Kluwer/Lipincott Williams & Wilkins, India, 2013.
- [21] F. Heravi, M. Ramezani, M. Poosti, M. Hosseini, A. Shajiei, F. Ahrari, In vitro cytotoxicity assessment of an orthodontic composite containing titanium-dioxide nano-particles, *J. Dent. Res. Dent. Clin. Dent. Prospects* 7 (2013) 192–198.
- [22] A. Jahanbin, F. Farzanegan, M. Atai, S.A. Jamehdar, P. Golfakhrabadi, H. Shafae, A comparative assessment of enamel mineral content and *Streptococcus mutans* population between conventional composites and composites containing nano amorphous calcium phosphate in fixed orthodontic patients: a split mouth randomized clinical trial, *Eur. J. Orthod.* 39 (2017) 43–51.
- [23] R. Wadenya, J. Smith, F. Mante, Microleakage of nano-particle-filled resin-modified glass ionomer using atraumatic restorative technique in primary molars, *N. Y. State Dent. J.* 76 (2010) 36–39.
- [24] J.I. Lopez, Retentive shear bond strengths of various bonding attachment bases, *Am. J. Orthod.* 77 (1980) 669–678.
- [25] B. Haydar, S. Sarikaya, Z.C. Cehreli, Comparison of shear bond strength of three bonding agents with metal and ceramic brackets, *Angle Orthod.* 69 (1999) 457–462.
- [26] S.E. Bishara, R. Ajlouni, M.M. Soliman, C. Oonsombat, J.F. Laffoon, J. Warren, Evaluation of a new nano-filled restorative material for bonding orthodontic brackets, *World J. Orthod.* 8 (2007) 8–12.
- [27] H.H. Xu, M.D. Weir, L. Sun, Calcium and phosphate ion releasing composite: effect of pH on release and mechanical properties, *Dent. Mater.* 25 (2009) 535–542.