

Nanocomposites: Past, present, and future of dentistry

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The recent advent of nanotechnology has enabled manipulation of the conventional dental composites at a nanoscale level, resulting in newer and advanced materials called nanocomposites. Thanks to their light weight, efficient mechanical properties, and light-conducting properties, nanocomposites can be used in many ways.

Restoration is one of the vital specialties of dentistry. In spite of improvements in materials used for restorative dentistry, there is no material that is ideal for this dental application. The conventionally used silver amalgam comes with issues of toxicity and poor esthetics. The conventional composite restorative materials have better esthetics, but lack adequate strength; hence, they cannot be used in posterior areas of dentition, and are highly technique-sensitive. In addition, there are issues of wear resistance, polymerization shrinkage, and microhardness, which are essential in posterior occlusal restorations. Hence, there is a need for dental materials with properties that are better suited for restorative dentistry.

Conventional dental composite resins, due to their superior esthetics and shade-matching properties, have been widely used as the material of choice for restoring anterior teeth. However, their application in the posterior stress-bearing areas has remained questionable due to the lack of adequate physical and mechanical properties. In these composites, the resin matrix is reinforced with nanosized filler particles, resulting in significantly improved mechanical properties. The resultant improvement in physical properties, coupled with superior esthetics, has made nanocomposites the material of choice in anterior, as well as posterior, class I and II restorations.

The emergence of nanocomposites has enabled the use of a single restorative material, universally, in various areas of the oral cavity, as these composite materials possess not only favorable esthetic properties, such as high initial polish and polish retention, but also excellent mechanical properties and improved handling characteristics.

11.1 Development of composites

Conventional dental resin-based composites (RBC) were plagued by the issues of shrinkage, viscosity, moisture contamination, and changes with aging. The composition largely included the two polymers triethylene glycol di-methacrylate (TEGDMA) and 2, 2'-bis glycol methacrylate (Bis-GMA). Later, the Bis-GMA was replaced with other dimethacrylates to overcome the issues associated with conventional compositions.

In the development of the composites, the three main components, which can be modified, are the inorganic fillers, the organic resin matrix, and the silane coupling agents. For increasing the mineral content of the tooth, calcium and phosphate

ion-releasing composites and fluoride-releasing nanocomposites were developed. For enhancing mechanical properties, nanocomposites reinforced with nanofibers or nanoparticles were investigated. For reducing polymerization shrinkage, investigators modified the resin matrix by using methacrylate and epoxy functionalized nanocomposites based on silsesquioxane cores, or epoxy-resin-based nanocomposites.

- Johnson and Johnson (Langhorne, PA, United States, 1970) brought in the two composite materials: 3M's composite, Concise™, and a resin matrix filled with ground quartz particles, Adaptic. Although these were effective anterior restorative materials, the presence of quartz in them resulted in the drawback of surface discoloration.
- Use of microfills began in 1973, and around this time the amalgam was replaced by RBCs with improved filler-matrix technologies. The prepolymerized organic fillers were added with silicon dioxide filler particles (<100 nm in diameter), although these restorations were deficient in the high strength of amalgam.
- Simultaneous with microfills, nanomaterials were made available that included various oxides (aluminum, silica, titanium) in a proportion of 1%–5%. Later, the nanoparticle phase was added to these oxide products, introducing a methyl silane (Ox-50) to develop the restorative materials Isopast® and Heliomolar® by Dentsply International, York, PA, United States and Ivoclar Vivadent.
- The microhybrids and nanohybrids are the most commonly used RBCs nowadays (filler particle size <100 nm to 600+ nm), which surmounts most of the strength issues. The nanofills and microfills (<100 nm) offer better smoothness, but lack strength.

The use of nanofillers for posterior restorative material has greatly increased over the past two decades. The nanofilled restoratives contain mainly nanocluster particles with a particle size of 2–20 nm. By creating a smaller particle size, a material's desirable performance, such as esthetics and optical properties, can be optimized.

11.2 The various phases of composites

The structure of a composite resin basically includes a combination of materials with mechanical and physical properties differing from each other; and the product formed out of the combination of these materials has better characteristics than each of the individual components.

Similar to any other composite, dental composites have three basic phases:

1. The first phase (organic phase) consists of the resin matrix, or body of the material. This is the chemically activated component of the composite, which undergoes polymerization.
2. The second phase (dispersed phase) is constituted by the filler material, which is embedded in the matrix. This phase provides the bulk and overall strength to the composite material.
3. The third phase (interfacial phase) involves the coupling agent, which forms a bond between the matrix and the filler.

Nanotechnology works in the various phases to improve the characteristics of the final product.

4. Contemporary nanorestorative research is heading toward:
 - (a) Nanocomposites with anticaries' applications, such as composites with fluorides, calcium, and phosphates.
 - (b) Nanomolecular assembly of recombinant amelogenins based on biomimetic processes mimicking the natural dental enamel formation processes.

11.3 Approaches in production of nanomaterials

There could be three possible approaches, as follows [1]:

Option	Description
Material synthesis	Producing synthetic materials matching the morphology and properties of natural dental tissues
Biomimetic approaches	Replacing lost dental tissues by producing biomaterials that resemble the natural properties very closely
Tissue engineering	Use of regenerative medicine and tissue engineering approaches for replacing the lost dental tissues by regeneration

These approaches need the intervention of nanotechnology. Dental hard tissue is made of natural nanoscale units forming various tissues such as dentin, enamel, and cementum; and artificial nanomaterials are needed that resemble the properties of the natural dental tissues. The basic components such as cells, biomolecules, tissue engineering scaffolds, and signals will be needed to create such nanomaterials.

11.4 Combined manufacturing approach of nanomaterials

In the conventional approach, the larger particles of glass, quartz, or ceramics are milled or grinded into smaller particles; however, the manufacture of particles of less than approximately 100nm in diameter needs the bottom-up approach. Thus, nanocomposites are being produced using a combination of top-down versus bottom-up manufacturing approaches.

The composite resins produced from the bottom up-approach of nanotechnology involve 2 types of nanofillers; namely nanomeric particles and nanoclusters. The nanoclusters (0.6µm) contain zirconia silica and pure silica embedded in a resin matrix, and nanomers contain nanosilica particles with an average diameter of 20–75 nm. These composites are better for maintaining smoothness, as the matrix and fillers wear out at the same rate.

The Filtek supreme XTE universal restorative composite resins have 3 M Adper as a bonding agent, with silica nanoparticles that allow superior bonding with reduced degradation of composite materials in the oral cavity.

The various nanostructures used in composite restorations are as follows:

Nanoparticles

Currently, the focus is on the reformulation of interfacial silanes that bond the inorganic fillers present in nanocomposites. The 3-methacryloxypropyltrimethoxysilane enhances the dispersion of silica nanoparticles (5–25 nm) within the restorative resin matrix, and allyl-triethoxysilane has demonstrated compatibility with titanium dioxide.

Nanorods

Using nanorods, Chen and colleagues have shaped enamel prism-like nanorods of hydroxyapatite with self-assembly properties to resemble artificial enamel.

Nanospheres

Natural tooth development can also be explored using an amelogenin nanochain and nanosphere assembly to evaluate the calcium phosphate deposition in a restorative context.

Nanotubes

The flexural strength of RBCs have been enhanced using carbon and titanium oxide nanotubes, along with organosilane bonding agents, which have silicon dioxide applied to them.

Nanofibers

Nanofibers are being used to produce ceramics containing hydroxyapatite and fluor-hydroxyapatite with improved physical properties. Additionally, silicate crystals can be used to reinforce the nanocomposites; specifically, a combination of the triethylene glycol dimethacrylate (TEGDMA), a thinning agent, and 2, 2'-bis glycol methacrylate.

Dendritic copolymers and dendrimers

Dendrimers and dendritics are also being studied in relation to dental composites; combining these with other nanostructures is known to optimize the performance of nanocomposites.

The production of material at the nanoscale level increases the surface area of the nanomaterial enough that the quantum effect can make the most of the advantageous properties of materials. In this scenario, the characteristic particulate nature of fundamental matter emerges to result in composite materials with improved physical, chemical, and biological properties.

Nanocomposites have three different filler components, namely: prepolymerized fillers, silica nanoparticles, and barium glass. When comparing the Filtek Ultimate Body and Filtek Ultimate Translucent nanofilled composites, with GC Gradia Direct Anterior (microfilled) and Filtek Z250 (micro-hybrid composites), the nanofilled composites were found to have properties that were superior to more traditional composite resins. The aluminosilicate powder used as a nanofiller (80 nm) has a refractive index of 1.508, and the ratio of 1:4 M of alumina to silica.

11.5 A shift of nanofillers to clusters to hybrids

In the evolution of dental composites, two materials evolved as nanohybrid and nanofilled composites through manipulation of the morphology and loading efficiency of the fillers. Their inability to scatter or absorb visible light has a role in creating excellent esthetic properties for their use as anterior restorative materials.

The predominant size of nanofills is 1 to 100 nm-sized particles, and that of nanohybrids ranges from 0.4 to 5 μm ; hence, they are not truly nanofilled. The wettability of fillers is influenced by the surface area of filler particles and their loading. The presence of nanosized fillers and nanoclusters results in a composition that can tailor the bulk and surface properties of composites as appropriate for the site of application.

The inclusion of nanofillers in the composite has the following advantages:

- Nanofillers are undetectable in composites, owing to their particle size being smaller than that of the wavelength of visible light
- Improved optical properties
- Polishability
- Aesthetic properties
- Increase in the precision of shade characterization and color stability
- Excellent finish and gloss retention in the final product
- Higher translucency
- Possess a higher modulus of elasticity
- Greater flexural, compressive, and tensile strengths
- Improved hardness and fracture toughness
- Wear resistance
- Decreased inter-particle distance between the nanofillers, which reduces the tendency for crack formation and propagation
- The smooth and rounded edges of the spheroidal nanoparticles tend to distribute stress more evenly throughout the composite resin
- The increased filler loading, decreased overall content of the soft organic matrix, and strong interfacial interactions between the resin matrix and filler particles result in reduced polymerization shrinkage
- Reduced tendency for appearance of micro-fissures, resulting in a better marginal seal
- High polish retention after toothbrush abrasion, as only the nanosized particles are removed
- Decreased water sorption and solubility
- Decreased disparity of coefficient of thermal expansion

11.6 The observations of the studies conducted using various nanocomposites

Recently, several clinical studies have been published that have tested various nanocomposites clinically. These materials, with filler-particle sizes of $\leq 100\text{nm}$, offer the advantages of esthetics and strength over conventional microfilled and hybrid resin-based materials, mainly in terms of smoothness, polishability, precision of shade characterization, flexural strength, and microhardness.

Nanocomposites that are being used today are a blend of hybrid and microfilled composites, in which the properties of both are used to enhance the utility of the resultant combined product. The mechanical features of the hybrid composites and the esthetics of microfilled composites are retained to the maximum.

Nanohybrid and nanofilled RBCs are advantageous over their predecessors' microhybrids and microfilled RBCs in terms of particle size combinations and distribution; the particle size in them may vary greatly.

The Filtek™ Supreme has better wear patterns and a smoother surface, with a particle size of 2 and 75 nm from the bottom-up designed larger clusters (0.6–1.4 μm). Nanomaterials with this cluster structuring have been reported to have superior preservation of flexural strength in water immersion for 6 months, as compared with other composites.

The various commercially available brands of nanocomposites include Filtek Supreme XTE Universal Restorative (3M ESPE), Premise (Kerr/Sybron, Orange, CA), IPS Empress Direct, and Tetric N-Ceram (both Ivoclar Vivadent). The translucent and nontranslucent shades of Filtek™ Supreme Plus have a particle size range of 75 nm and 5–20 nm, respectively. The NANOSIT™ composite has inorganic particles averaging 7 nm, together with larger glass particles averaging <2000 nm.

A study by Turssi and colleagues conducted three-body wear tests, and a flexural fatigue limit analysis revealed that a microfill control (Heliomolar®; Ivoclar Vivadent), and a nanofill (Filtek™ Supreme) and a nanohybrid (Grandio®; Voco GmbH, Cuxhaven, Germany) showed a significantly higher flexural fatigue limit than either an ormocer-based RBC, or another nanohybrid.

A comparative study by Yap and colleagues demonstrated that materials based on ormocer and nanomer technology were significantly smoother than those based on microfillers and nanoclusters with reduced roughness values. In an *in vitro* study by Oxman and colleagues, Ketac™ Nano showed significantly higher gloss and lower wear rates than the other fluoroalumosilicate RMGIs.

Ormocers correspond to a composite technology based on a sol-gel synthesis of particles comprised of silicones, organic polymers, and ceramic glasses. Some ormocers (such as CeramX™, Dentsply International) have a smaller particle size (2–3 nm in diameter). Moszner and colleagues observed that the alterations in ormocers using organic moieties such as methacrylate-substituted ZrO₂ or SiO₂ organosol nanoparticles enhanced the mechanical properties of RBCs. The *in vitro* studies described ormocers as being more biocompatible with decreased surface roughness after polishing with a variety of techniques.

Beun and colleagues; Terry, Senawongse, and Pongprueksa, Tanimoto, and colleagues; and Milnar and Ernst and colleagues conducted studies in regards to the esthetics of nanocomposites, which resulted in similar observations.

The various authors Ergucu and Turkun, Efes, and colleagues; and Mahmoud and colleagues conducted and published approximately 2 years of comparative follow up of the clinical performance of the various nanocomposites and other resin-based composite restoratives, such as Filtek™ Supreme, Grandio® (Voco GmbH), Admira, an ormocer® RBC; Tetric EvoCeram®, and Tetric Ceram®. The results were similar and consistent across the studies, indicating that the nanocomposites are being used often in clinical practice. Although the studies could not reveal clear advantages of nanofills against other nanocomposites and older hybrids, the continued comparative studies are essential for any such advantage to be noted; still, the low failure rates and increasing clinical acceptability are encouraging.

Nanocomposite denture teeth are also being prepared, which are made up of polymethylmethacrylate and uniformly dispersed nanosized filler particles. These teeth have superior surface hardness, wear resistance, lively tooth surface structure, high polishability, and are composed of stain- and impact-resistant material.

Various nanocomposite materials being used [1,2]:

Restorative dentistry	Ketac™ (3M ESPE, St. Paul, MN, United States), Ketac N100; Nano-ionomers (3M ESPE), Filtek Supreme XT (3M ESPE), Fuji IX GP (GC, Leuven, Belgium), Nano-primer, Premise™ (Kerr/Sybron, Orange, CA, United States), Adper™ Single bond plus Adhesive (3M ESPE), Ceram X™ (DENTSPLY International, Milford, CT, United States)
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11.7 Additional in vitro nanotechnologic dental research

Recently, titanium oxide has been used as a nanofiller, with superior results. The porous nanostructured filler particles are in the experimental stage, which will allow the penetration of the resin matrix to produce mechanical interlocking materials, and may eliminate the need for a coupling agent. Xu and colleagues and Chan and colleagues reported that silanization augments the fracture toughness and strength of an ion-releasing calcium phosphate composite. A study by Karabela and Sideridou observed varied effects on solubility and sorption of the RBC when the diverse silane compositions are used to bind silica-containing composites.

11.7.1 Nanofibrillar reinforcement

Tian and colleagues have added data about nanocrystals and nanofibers, revealing that nanofibrillar silicate crystals alone, or with nanofibers, reinforce the bis-GMA or TEGDMA-based nanocomposites.

11.7.2 Dental caries prevention

The delivery of nanomolecules to facilitate tooth structure remineralization and prevention of dental caries is an active area of nanostructure-based research, in conjunction with RBC systems. Similarly, Xu and colleagues have evaluated the inclusion of nanosized CaPO_4 particles into composites, anticipating the inhibition of caries and improvement in stress-bearing capacity. Lee and colleagues found good release properties and flexural strength by reduction of the particle size of zirconia-amorphous calcium phosphate RBC. Finally, it has been studied that the nanostructure solubility could be manipulated to produce effective release of fluorine ions from fluor-hydroxyapatite.

11.7.3 Biomimetics: Amelogenins, enamel replication and repair, hydroxyapatite

The formation of dental enamel, perhaps the most appealing area of investigation in the next phase of nanorestitution of tooth structure, involves a nanotechnological assumption to mimic the natural process (biomimetics) of enamel formation.

The in vitro studies by Wang and colleagues, Uskokovic and colleagues, Tarasevich and colleagues, Chen and colleagues, and Du and colleagues has elucidated that the amelogenin has a crucial role in directing apatite crystal growth, and has demonstrated mechanisms of interaction among amelogenin nanospheres and nanorods in the process of enamel formation.

Fan and colleagues added to these observations that the hydroxyapatite crystal growth in enamel remineralization occurred in the presence of a fluoride concentration of 1 mg/L under the direction of rP172 amelogenin (33 µg/mL). Finally, Zhou and colleagues have recently hypothesized that the role of genetically engineered peptides is significant in tooth repair.

11.8 Conclusion

Nanotechnological advances in nanomaterials are of great interest for considerably upgrading the properties of existing composite restoration materials. The most tangible contribution of nanotechnology to dentistry may be the reformulation of composite materials for restoration of tooth structure. It may be anticipated that the continued clinical research in this direction will create newer nanocomposite materials that may render a near-ideal material to augment the quality of life of patients. There are plenty of reasons to believe that nanodentistry will generate materials that will be able to react to external stimuli and respond as natural tissue.

References

- [1] Z. Khurshid, M. Zafar, S. Qasim, S. Sana, N. Mustafa, A. Ammar, *Advances in nanotechnology for restorative dentistry*, *Materials* 8 (2015) 717–731, <https://doi.org/10.3390/ma8020717>.
- [2] S.A. Saunders, *Current practicality of nanotechnology in dentistry. Part 1: focus on nanocomposite restoratives and biomimetics*, *Clin. Cosmet. Investig. Dent.* 1 (2009) 47–61.

Further Reading

- [3] S. Sachadev, P. Kapoor, A. Tamarakar, R. Noor, *Nanocomposite dental resin—an overview*, *Ann. Dent. Spec.* 3 (2) (2015) 52–55.
- [4] A. Colceriu, M. Moldovan, C. Prejmerean, T. Buruaina, E. Buruaina, G. Furtos, et al., *Nanocomposites used in dentistry*, *Eur. Cell. Mater.* 10 (Suppl. 1) (2005) 19.
- [5] M. Lyapina, M. Cekova, A. Krasteva, M. Dencheva, M. Yaneva-Deliversk, A. Kisselova, *The physical properties of nanocomposites in relation to their advantages*, *J. IMAB* 22 (1) (2016) 1056–1062.
- [6] Y. Tanimoto, T. Kitagawa, M. Aida, N. Nishiyama, *Experimental and computational approach for evaluating the mechanical characteristics of dental composite resins with various filler sizes*, *Acta Biomater.* 2 (6) (2006) 633–639. [PubMed].

- [7] C.P. Turssi, J.L. Ferracane, L.L. Ferracane, Wear and fatigue behavior of nano-structured dental resin composites, *J. Biomed. Mater. Res. B Appl. Biomater.* 78 (1) (2006) 196–203.
- [8] W. Wang, X. Sun, L. Huang, Y. Gao, J. Ban, L. Shen, et al., Structure-property relationships in hybrid dental nanocomposite resins containing monofunctional and multifunctional polyhedral oligomeric silsesquioxanes, *Int. J. Nanomedicine* 10 (9) (2014) 841–852.
- [9] S. Beun, T. Glorieux, J. Devaux, J. Vreven, G. Leloup, Characterization of nanofilled compared to universal and microfilled composites, *Dent. Mater.* 23 (1) (2007) 51–59.
- [10] Y. Xia, F. Zhang, H. Xie, N. Gu, Nanoparticle-reinforced resin-based dental composites, *J. Dent.* 36 (6) (2008) 450–455.
- [11] S. Rajan, S. Acharya, V. Saraswathi, Nanodentistry, *Indian J. Sci. Res.* 4 (2) (2013) 233–238.
- [12] A. Nagpal, J. Kaur, S. Sharma, A. Bansal, P. Sachdev, Nanotechnology-the era of molecular dentistry, *Indian J. Dent. Sci.* 3 (2011) 80–82.
- [13] S. Sasalawad, N. Sathyajith, K. Naik, P. Shashibhushan, S. Poornima, M. Shivayogi, N. Hugar, M. Roshan, Nanodentistry: the next big thing is small, *Int. J. Contemp. Dent. Med. Rev.* 2014 (2014), <https://doi.org/10.15713/ins.ijcdmr.12>. Article ID 101114.
- [14] A. Bhardwaj, A. Bhardwaj, A. Misuriya, S. Maroli, S. Manjula, A. Singh, Nanotechnology in dentistry: present and future, *J. Int. Oral Health* 6 (1) (2014) 121–126.
- [15] A.S. Khan, S. Aamer, A. Chaudhry, F.S. Wong, I.U. Rehman, Synthesis and characterizations of a fluoride-releasing dental restorative material, *Mater. Sci. Eng. C* 33 (2013) 3458–3464.
- [16] K.E. Drexler, *Nanosystems: Molecular Machinery Manufacturing and Computation*, John Wiley and Sons, New York, 2006.
- [17] M. Chen, Update on dental nanocomposites, *J. Dent. Res.* 89 (2010) 549–560.
- [18] R. Chandki, M. Kala, K.N. Kumar, B. Brigit, P. Banthia, R. Banthia, Nanodentistry: exploring the beauty of miniature, *J. Clin. Exp. Dent.* 4 (2) (2012) e119–e124.
- [19] H.F. Chen, B.H. Clarkson, K. Sun, J.F. Mansfield, Self assembly of synthetic hydroxyapatite nanorods into enamel prism like structure, *J. Colloid Interface Sci.* 288 (1) (2005) 97–103.
- [20] M. Mikkilineni, A. Rao, M. Tummala, S. Elkanti, Nanodentistry: new buzz in dentistry, *Eur. J. Gen. Dent.* 2 (2013) 109.
- [21] R.K. Saravana, R. Vijayalaksmi, Nanotechnology in dentistry, *Indian J. Dent. Res.* 17 (2) (2006) 62–65.
- [22] S.R. Kumar, R. Vijayalakshmi, Nanotechnology in dentistry, *Indian J. Dent. Res.* 17 (2017) 62.
- [23] D.A. Terry, Applications of nanotechnology, *Pract. Proced. Aesthet. Dent.* 16 (3) (2004) 220–222.
- [24] P.E. Chandra Mouli, S. Manoj Kumar, S. Parthiban, Nanotechnology in dentistry—a review, *Int. J. Biol. Med. Res.* 3 (2) (2012) 1550–1553.
- [25] S. Ozak, P. Ozkan, Nanotechnology and dentistry, *Eur. J. Dent.* 7 (2013) 145–151.
- [26] I.M.F. Abiodun-Solanke, D.M. Ajayi, A.O. Arigbede, Nanotechnology and its application in dentistry, *Ann. Med. Health Sci. Res.* 4 (Suppl. 3) (2014) S171–S177, <https://doi.org/10.4103/2141-9248.141951>.
- [27] S. Das, A.J. Gates, H.A. Abdu, G.S. Rose, C.A. Picconatto, J.C. Ellenbogen, Designs for ultra-tiny, special-purpose nanoelectronic circuits, *IEEE Trans. Circuits Syst.* (11) (2007) 2528–2540.
- [28] S.B. Mitra, D. Wu, B.N. Holmes, An application of nanotechnology in advanced dental materials, *J. Am. Dent. Assoc.* 134 (2003) 1382–1390.

- [29] P. Gupta, H. Shetty, Nanotechnology: it's role in restorative dentistry and endodontic, *Res. Rev. J. Pharm. Nanotechnol.* 4 (2016) 19–21.
- [30] D. Fortin, N.A. Vargas, The spectrum of composites: new techniques and materials, *J. Am. Dent. Assoc.* 131 (Suppl) (2000) 26S–30S.
- [31] L. Chen, Q. Yu, Y. Wang, H. Li, BisGMA/TEGDMA dental composite containing high aspect-ratio hydroxyapatite nanofibers, *Dent. Mater.* 27 (11) (2011) 1187–1195.
- [32] 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 (12) (2010) 1144–1150.
- [33] M.H. Chen, C.R. Chen, S.H. Hsu, S.P. Sun, W.F. Su, Low shrinkage light curable nano-composite for dental restorative material, *Dent. Mater.* 22 (2) (2006) 138–145.
- [34] M. Tian, Y. Gao, Y. Liu, Y. Liao, R. Xu, N.E. Hedin, H. Fong, Bis-GMA/TEGDMA dental composites reinforced with electrospun nylon 6 nanocomposite nanofibers containing highly aligned fibrillar silicate single crystals, *Polymer* 48 (9) (2007) 2720–2728.
- [35] M. Atai, A. Pahlavan, N. Moin, Nano-porous thermally sintered nano silica as novel fillers for dental composites, *Dent. Mater.* 28 (2) (2012) 133–145.
- [36] A. Nevarez-Rascon, A. Aguilar Elguezal, E. Orrantia, M.H. Bocanegra Bernal, Al_2O_3 (w)- Al_2O_3 (n)- ZrO_2 (TZ-3Y)n multi-scale nanocomposite: an alternative for different dental applications, *Acta Biomater.* 6 (2) (2010) 563–570.
- [37] H.H. Xu, J.L. Moreau, L. Sun, L.C. Chow, Strength and fluoride release characteristics of a calcium fluoride based dental nanocomposite, *Biomaterials* 29 (32) (2008) 4261–4267.
- [38] X. Li, W. Liu, L. Sun, K.E. Aifantis, B. Yu, Y. Fan, et al., Resin composites reinforced by nanoscaled fibers or tubes for dental regeneration, *Biomed. Res. Int.* 2014 (2014) 542958.
- [39] A.R. Curtis, A.C. Shortall, P.M. Marquis, W.M. Palin, Water uptake and strength characteristics of a nanofilled resin-based composite, *J. Dent.* 36 (3) (2008) 186–193.
- [40] M. Ghazal, Z.S. Albashaireh, M. Kern, Wear resistance of nanofilled composite resin and feldspathic ceramic artificial teeth, *J. Prosthet. Dent.* 100 (6) (2008) 441–448.
- [41] U. Ortengren, H. Wellendorf, S. Karlsson, I.E. Ruyter, Water sorption and solubility of dental composites and identification of monomers released in an aqueous environment, *J. Oral Rehabil.* 28 (12) (2001) 1106–1115.
- [42] M. Ghazal, J. Hedderich, M. Kern, Wear of feldspathic ceramic, nanofilled composite resin and acrylic resin artificial teeth when opposed to different antagonists, *Eur. J. Oral Sci.* 116 (6) (2008) 585–592.