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# NANO COMPOSITES

<sup>1</sup> Sridhar Reddy M

<sup>1</sup> Professor

<sup>1,</sup>Department of Conservative Dentistry and Endodontics, Narayana Dental College, Nellore, Andhra Pradesh, India.

**ABSTRACT:** Nanotechnology was first described in 1959 by physicist Richard P Feynman, who viewed it as an unavoidable development in the progress of science, and has since been part of mainstream scientific theory with potential medical and dental applications since the early 1990s. Nanotechnology's most tangible contribution to dentistry to date has been the restoration of tooth structure with Nanocomposites. Nanocomposites are characterized by filler-particle sizes of <= 100 nm, which offer these materials aesthetic and strength advantages over conventional microfilled and hybrid resin-based composite (RBC) systems. They offer advantages primarily in terms of the smoothness, polishability and precision of shade characterization, notwithstanding the flexural strength and microhardness they offer similar to those of the better-performing posterior RBCs. The strength and aesthetic properties of the resin based Nanocomposite makes it possible for it to be used for both anterior and posterior restorations. This article aims to address the current major uses of practical nanotechnology in dentistry, mainly the restoration of tooth structure with RBCs that make use of nanoparticles.

KEYWORDS: Nanotechnology, Nanocomposite, Polymerization shrinkage, Resin based composites, Flexural strength, Wear

# INTRODUCTION

Composite resins were introduced into the field of conservative dentistry to minimise the drawbacks of the acrylic resins that had replaced the silicate cements in the 1940s. Buonocore used orthophosphoric acid, in 1955, to improve the adhesiveness of acrylic resins to the surface of the enamel. Bowen developed the Bis-GMA monomer in 1962 in an attempt to improve the physical properties of acrylic resins, since their monomers only allowed linear chain polymers to be formed. These early composites, which were chemically cured, required that the base paste be mixed with the catalyst, leading to problems with proportions, with the mixing process and colour stability. However since the 1970s, composite materials polymerised by electromagnetic radiation have done away with mixing and its drawbacks.<sup>1</sup>

Initially, an ultraviolet light source at 365 nm was used to provide the required light energy, but due to its shallow polymerisation and iatrogenic side-effects it was replaced by visible light (427 - 491 nm). This is currently in use and is undergoing further development. The field of composite development has been witnessing continuous development since its advent, which makes it necessary for practitioners to keep abreast continually.

The physical, mechanical and aesthetic properties of composites and their clinical behaviour depend on their structure. Dental composites are basically composed of three chemically different materials: 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. Research and Development of resin based composites during the last decade has generated different subspecies of restorative materials like the hybrid resin composites, the fine hybrid resin composites, and the microfill composites.<sup>2</sup>

While some studies demonstrated that hybrid and microfilled composites have similar performance in aesthetic cavities, others concluded that microfilled composites are the best option for anterior cavities because of their high translucency, high polish, and polish retention. Hybrid and microhybrid composites have traditionally been used for posterior restorations due to their high strength. However, no one composite material has been able to meet both the functional needs of a posterior Class I or Class II restorations. To this end, a new category of resin composites were developed and named Nanocomposites.

### NANO TECHNOLOGY

Nanotechnology, also commonly referred to as molecular nanotechnology or molecular engineering, is the production of functional materials and structures that fall in . the range of 0.1 to 100 nanometres (the nano scale) by various physical or chemical methods. When inorganic phases in an organic/inorganic composite become nanosized, they are called Nanocomposites. The intense interest in using these nanomaterials stems from the idea that they can be used to manipulate the structure of materials to provide dramatic improvements in electrical, optical. chemical and mechanical properties. available as nanohybrid types Nanocomposites are containing milled glass fillers and discrete nanoparticles (40 - 50 nm) and as nanofill types, containing nano-sized filler particles, called nanomers and agglomerations of these particles described as nanoclusters.

Nanofillers are very different from traditional fillers and require a shift from a top-down to a bottom-up manufacturing approach. Various techniques are used to prepare nanofillers, like flame pyrolysis, flame spray pyrolysis, and sol-gel processes. To reduce the filler particle size below 100 nm, synthetic chemical processes were used to produce building blocks on a molecular scale. There are 2 kinds of nanofiller particles – nanomeric particles (NM) and nanoclusters (NC). The nanomeric particles are monodisperse non-aggregated and non-agglomerated silica nanoparticles.<sup>4</sup>

There are 2 types of nanocluster fillers. The first type consists of zirconia-silica particles synthesized from a colloidal solution of a zirconyl salt and silica. The primary particle size of this NC filler ranges from 2-20 nm, while the spheroidal agglomerated particles have a broad sized distribution with an average particle size of 0.6  $\mu\text{m}.$  The second type of nanocluster filler, which was synthesized from 75 nm primary particles of silica, has a broad secondary particle size distribution with a 0.6 µm average. These silica particles were treated with 3methacryloxypropyltrimethoxysilane (MPTS), as coupling agent that contains a silica ester functional group on one end for bonding to the inorganic surface, and a methacrylate group on the other to make the filler compatible with the resin before curing to prevent any aggregation or agglomeration.4

Extremely small filler particles have dimensions that are below the wavelength of visible light (0.4 - 0.8  $\mu m),$ and hence they are unable to scatter or absorb visible light. Thus, nanofillers are usually invisible and render the advantage of optical property improvement. Additionally, due to their small particle sizes, nanofillers can increase the overall filler level. More filler can be accommodated if smaller particles are used for particle packing. Theoretically, with the use of nanofillers, filler levels could be as much as 90 - 95% by weight. However, the increase in nanofillers also increases the surface area of the filler particles that limits the total amount of filler particles, because of the wettability of the fillers. Since polymerization shrinkage is mainly because of the resin matrix, the increase in filler level results in a lower amount of resin in Nanocomposites and will also significantly reduce polymerization shrinkage and dramatically improve its physical properties.

Increasing the filler fraction in a Nanocomposite is a good strategy for manufacturers in aiming for improved mechanical performance. A higher filler fraction helps in increasing the fracture toughness because fillers decrease the volume of the weak polymer matrix and act as toughening sources, besides increasing the elastic modulus. Filler packing is also influenced by the size, arrangement, distribution and shape of the particles.

One of the commercially available nanohybrid composites is composed of 3 different types of filler components: non-agglomerated discrete silica nanoparticles, prepolymerized fillers (PPF), and barium glass fillers. The non-agglomerated "discrete" silica nanoparticles are spheroidal and about 20 nm in size. The prepolymerized fillers are about 30-50  $\mu$ m in size, while the barium glass filler comes with an average particle size of 0.4  $\mu$ m. This combination of three fillers allows for increased filler loading of 84% by weight and 69% by volume. The discrete un-associated nanoparticles that are well-dispersed in the matrix on a nanoscale level allow for

an increased filler loading and reduced viscosity of Nanocomposites, thus resulting in increased hardness, abrasion resistance, fracture resistance, polishability, and in reduced polymerization shrinkage (1.4% to 1.6% by volume) and shrinkage stress. As the inter particle dimension decreases, the load-bearing stress on the resin gets reduced, thereby inhibiting crack formation and propagation. The spheroidal shape of the nanoparticles provides for its smooth and rounded edges, thereby distributing stress more uniformly throughout the composite resin.<sup>6</sup>

Another commercially available Nanocomposite is an ormocer-based, nano-ceramic composite. It contains glass fillers (1.1 - 1.5  $\mu$ m), but differs from the conventional hybrid composites in two main features. A Methacrylate-modified silicon-dioxide-containing nanofiller (10 nm), with a filler concentration of 76% by weight and 57% by volume substitutes for the microfiller that are typically used in hybrid composites (agglomerates of silicon dioxide particles). Most of the conventional resin matrix is also replaced by a matrix that is full of highly dispersed methacrylate-modified polysiloxane particles (2 - 3 nm). These nanoceramic particles are organic–inorganic hybrid particles. Both the nanoceramic particles and nanofillers have methacrylate groups available for polymerization.

A low-shrinkage, high-strength Nanocomposite was developed by using a 4-epoxycyclohexylmethyl-(3,4epoxy) cyclohexane carboxylate (ERL4221) matrix with 55% of 70- to 100-nm nanosilica fillers through ringopening polymerization. γ-glycidoxypropyl trimethoxysilane (GPS) was used to modify the surfaces of γ-glycidoxypropyl the silica nanoparticles. The Nanocomposite exhibited low polymerization shrinkage strain, which was only a quarter of that of currently used methacrylate-based composites. It also exhibited a low thermal expansion coefficient that was comparable with that of methacrylate-based composite. The strong interfacial interactions between the resin and fillers at nanoscale were demonstrated by the observed high strength and high thermal stability of the Nanocomposite.

# PROPERTIES OF NANOCOMPOSITES

The unique nature of the filler particles of Nanocomposites provides it with the mechanical strength and wear resistance similar to hybrid composites, and superior polish and gloss retention similar to microfill composites.

**Polymerization shrinkage:** The polymerization shrinkage in composite resin is reported to be 1.4% to 1.6%. The low shrinkage value of Nanocomposites is 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 nanofill composites (Filtek Supreme Translucent), which had 30.0 wt-% organic matrix. Polymerization shrinkage also depends on the chemistry of the organic matrix<sup>7,8,9</sup>

# Case Reports

Water Sorption: Water uptake in the polymeric phase of composites causes generally two opposing processes. The solvent will extract 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<sup>10</sup>. However, 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.

**Flexural strength:** The flexural strength depends on the filler content and also the filler chemistry. The flexural strength of Nanocomposites were found to be statistically 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, which have lesser filler loading.<sup>11</sup>

Wear and gloss retention: The nano-sized primary particles in the nanoclusters wear by breaking off individual primary particles rather than plucking out the larger secondary particles from the resin. Thus resulting wear surfaces have smaller defects and better gloss retention. Hybrid fillers typically are large dense particles of an average size of about 1  $\mu$ m. Microhybrids are similar and are only slightly smaller than hybrids in average particle size. The SEMs of wear facets of toothbrush abraded surface of hybrid and microhybrid show large particles protruding from the surface, as well as pits where the particles have been plucked from the surface. The resultant surface is not as smooth and glossy as that of a microfill or a Nanocomposite.<sup>12-15</sup>

### CONCLUSION

Nanotechnology has been used to make a dental restorative composites that offers high translucency, high polish and polish retention that are similar to those of microfills while maintaining physical properties and wear resistance equivalent to several commercial hybrid composites. It is expected that with the combination of superior aesthetics, long term polish retention, and other optimized physical and mechanical properties, the Nanocomposite systems would be useful for all posterior and anterior restorative applications.

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# **Corresponding Author**

Dr. M. Sridhar Reddy Professor ,Department of conservative Dentistry and Endodontics Narayana Dental College Nellore, Andhra Pradesh Email:- <u>sree1976@gmail.com</u> Ph: 919849986253