



NANOMATERIALS AND THEIR APPLICATION IN PROSTHODONTICS: A REVIEW

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ABSTRACT

Objectives: The objective of this paper is to review the available literature on the novelties and applications of nanomaterials in Prosthodontics.

Data and Sources: 125 articles were retrieved which included reviews and studies on various nanomaterials used in Dentistry especially Prosthodontics after Gray literature search, cross references and electronic database search in PubMed, MedLine and Google search using the following key words- Nanomaterials, Nanotechnology, Prosthodontics, Dentistry, Applications

Study selection: 74 articles were selected and reviewed as they met the selection criteria.

Conclusion: Within the scope of this review, reported literature showed that the emerging science of nanotechnology in Dentistry especially in the field of Prosthodontics has triggered growing interest in the potential applications and benefits compared to the conventional materials in use. The latest research progress on the applications of nanomaterials used in Prosthodontics was reviewed with detailed description, keeping in mind the limitations like challenges faced and the health implications.

KEYWORDS: Nanomaterials. Nanotechnology. Prosthodontics. Dentistry. Applications.

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INTRODUCTION

'Nano' is derived from the Greek word which means Dwarf. Nanotechnology is the art and science of material engineering at the nanoscale size (1-100nm).¹ In 1959, famous American Physicist, Dr Richard Feynman seeded the concept of Nanotechnology. However, in 1974, Taniguchi was the first to use the word and in 2002, Filtek

Supreme first introduced Nanocomposites.²⁻⁴

The ongoing research in the realm of nano is due to the unique structure and properties of nanoparticles thus gaining high impetus in their application. There are more atoms on the surface of the nanoparticle which present with unbound surfaces compared to the core of the nanoparticle. This gives them a potential to create new and strong

bonds and makes them more reactive when compared to macro or micro particles which have more core than surface atoms and are easy to manipulate and use.⁵ In prosthodontics, nanoparticles are added to ceramics, acrylic resins, composites, dental adhesives, dental cements, implants and maxillo-facial prosthesis since modulating these materials to nanosize

has given greater efficacy and durability.^{6,7}

The aim of this paper is to give the readership a comprehensive review mainly on the nanomaterials and their up to date applications in Prosthodontics, the challenges faced and the health implications.

SEARCH STRATEGY

125 articles were retrieved which included reviews and studies on various nanomaterials used in Dentistry especially Prosthodontics after Gray literature search, cross references and electronic database search in PubMed, MedLine and Google search using the following key words- Nanomaterials, Nanotechnology, Prosthodontics, Dentistry, Applications. Articles which were duplicated and not related to Dentistry were excluded. 74 articles which fulfilled the inclusion and exclusion criteria were selected.

Inclusion criteria:

1. Peer reviewed articles in English only.
2. Full text articles-Reviews and studies.

Exclusion criteria:

1. Abstracts only on the Databases searched.
2. Nanomaterials used in fields of Dentistry other than Prosthodontics.

SYNTHESIS OF NANOPARTICLES

The three approaches in the synthesis of Nanoparticles are:

1. Bottom up: This approach includes miniaturization of material components up to atomic level with further self assembly process leading to the formation of nanostructures. It starts with atoms or molecules to

build up Nanostructures. For e.g. Nanodentifrices, tooth repair, diagnosis of oral cancer.^{8,9}

2. Top down: This approach uses larger initial structures which can be externally controlled in the processing of nanostructures. For e.g. Nanocomposites, impression materials, nanoneedles, nanosolutions.¹⁰
3. Functional: This approach does not give importance to the method of production of nanoparticles. Its objective is to produce nanoparticle with a specific functionality.⁴

NANOMATERIALS IN PROSTHODONTIC APPLICATIONS

POLY METHYL METHACRYLATE (PMMA)

PMMA resin has been widely used as a denture base material and in making orthodontic appliances. However owing to the surface porosities they have been prone to plaque accumulation, thus increasing the cariogenic oral flora.^{11,12}

Inclusion of carbon nanotubes into heat cure monomer has decreased polymerization shrinkage and has enhanced the mechanical properties.¹² Similarly incorporation of nanoparticles like silver, platinum, titanium and iron have shown increase in flexural strength, antimicrobial properties, surface hydrophobicity, viscoelasticity, decrease in porosity and biomolecular adherence.¹³⁻¹⁵

Although silver nanoparticles have antibacterial activity, their incorporation in acrylic resin have shown a colour change in concentrations above 80 ppm and cytotoxicity in concentrations more than 40 ppm.¹⁵ Addition of zirconium dioxide nanoparticles in heat cure PMMA has increased abrasion resistance, tensile and fatigue strength, decrease in water

sorption, solubility and porosity. However, the translucency has decreased with the increase in nano zirconium oxide.^{16,17} The results of the study by Ahmed et al using heat cure PMMA with 7% nano zirconium oxide has shown enhanced hardness levels, flexural strength and fracture toughness.¹⁸ According to Gad et al, 2% or 5% nano zirconium oxide has increased the transverse strength of repaired dentures with auto polymerized resin.¹⁹ Addition of 0.4% TiO₂ nanoparticles into 3D printed PMMA denture base has shown significant antibacterial effects especially against Candida species and has also improved mechanical properties.²⁰

COMPOSITES

- Nano Filled Composites

Nano fillers of 1-100nm have been incorporated into the resin matrix to produce nanocomposites. The two types of nanoparticles that have been used are nanomers and nanoclusters.²¹

NANOMERS: They are mono dispersed, non-aggregated and non-agglomerated particles of silica treated with 3-methacryloxy-propyltrimethoxysilane (MPTS). MPTS has helped in chemical bonding of the nanomer filler to the resin whilst curing.²²

Advantages: Good optical properties, Good dispersion rate, High polish and polish retention, Superior hardness, Flexural strength and Good esthetics
Disadvantages: Poor rheological and handling properties.⁷

NANOCLUSTERS: Nanocluster fillers range from 2-20 nm. They have been formed by lightly sintering nanomeric oxides to form clusters of a controlled particle size distribution. Nanoclusters of

silica sol exclusively and mixed oxides of silica and zirconia have been synthesized.^{23,24} They have shown the same advantages as nanomers with better rheological properties but the disadvantage of poor handling has still persisted.²³

- Nanohybrid Composites

Pre-polymerized organic fillers have been incorporated in nanomers to improve the desirable rheological properties of composites.²⁵

Advantages: Improved esthetics and rheological properties.

Disadvantages: Decreased polish retention and surface gloss.²⁶

- TiO₂ Reinforced Resin Based Composite:

Titanium dioxide nanoparticles treated with organosilaneallytriethoxysilane (ATES) have been used to improve microhardness and flexural strength of composites.²⁷

- Nanocomposites With Alumina Nanoparticles

Alumina nanoparticles have shown increased hardness, strength and modulus of elasticity of the nano composites.²⁸

- Calcium Phosphate And Calcium Fluoride Nanoparticles Based Composites

Materials that release Calcium phosphate and calcium fluoride have shown remineralization of tooth structure and hence have been incorporated in composites.^{29,30} They have also maintained the level of Calcium (Ca) and Phosphate (P) ion release

through recharge and release and hence has been called a “smart” material whereby it has inhibited secondary caries.³¹ Nanohydroxyapatites (HAP) of 20 nm size has mimicked natural building blocks of human enamel and shown anti caries repair effect.³²

- Ormocers (Organically Modified Ceramics)

These nanoparticles consist of a polysiloxane backbone used for glass and ceramics. Iron oxide, titanium oxide and aluminium sulfo silicate pigments have been added for shade. These nanoceramic particles have prevented the micro crack propagation. It is commercially available as Ceram X mono (DENTSPLY).³³

- Nano-Composite Denture Teeth

Nanocomposite denture teeth have homogenously distributed nanofillers and polymethyl methacrylate. They have shown high durability and polishability, increased shear strength, superior esthetics and higher abrasion resistance.³⁴

DENTAL ADHESIVES

Dental adhesives are materials that have been used to enhance adhesion and cohesion of two different substances or between a material and natural tooth structure. Polymerizable silane has been added to increase the cohesive strength. Discrete silane treated 5-7 nm size nanoparticles of silica and zirconia have been added to overcome the inconsistency in their performance due to settling of the filler particles during storage.³⁵ Zirconia has shown an added advantage of giving radiopacity to the adhesive. Nano adhesives have increased

the bond strength to enamel and dentine, have longer shelf life, no separate etching required and has shown durable marginal seal.³⁵ Trade names: Adper Single Bond 2, Adper Single Bond Plus (3M ESPE).³⁶ Nano-amorphous calcium phosphate has shown a significant remineralization ability for up to 3 weeks without affecting the bond strength to dentine.³⁷

NANO-CERAMICS

Nano-ceramics have shown improved toughness, ductility, toughness and strength as compared to conventional ceramics.⁶ NanoGlass ceramics have exhibited good translucency, excellent corrosion resistance, higher hardness and low modulus of elasticity when produced with sol-gel method of zirconia-silica system.³⁸ NanoTiO₂ ceramics have shown higher toughness and hardness as compared to traditional TiO₂ ceramics.³⁹ C.H Li et al concluded in their study that nanozirconia ceramics have improved fracture toughness and hardness with addition of up to 20% nanoZrO₂.⁴⁰ According to results from an in vitro study ceramics with upto 4% carbon nano tubes (CNT) have significantly improved wear and mechanical properties.⁴¹ Lava Ultimate Resin Nano Ceramic (RNC) blocks (3M ESPE) are innovative new CAD/CAM materials with superior esthetic results, durability and fracture resistance.^{42,43}

TISSUE CONDITIONERS AND SOFT LINERS

Addition of silver nano-particles in these materials have displayed antimicrobial properties against *S.mutans* and *S.aureus* at 0.1% and *C.albicans* at 0.5% after 24 hours incubation period.⁴⁴

Solutions of chlorhexidine mixed with sodium triphosphate (TP), trimetaphosphate (TMP) or Hexametaphosphate (HMP) were investigated for antifungal property on silicone soft liners and obturators and Chlorhexidine-HMP coating has been proved to be the most effective antifungal agent thus enhancing the life of the prosthesis.⁴⁵

DENTAL CEMENTS

Innovations and modifications by incorporating nanoparticles as fillers have enhanced the properties of cements. Glass ionomer cement with up to 5% w/w TiO₂ nano particles have shown increased fracture toughness, flexural strength, compressive strength and antibacterial activity.⁴⁶ Also addition of 5% TiO₂ nanotubes has significantly increased the noncollagenous composition of extra cellular matrix which has improved the micro hardness and fluoride release without influencing the surface roughness, hence it could be considered for restorations in higher stress bearing sites.⁴⁷ Nano light cure Glass ionomer cement has hydroxyapatite/fluoro-alumino silicate technology and has been used for core build up in Prosthodontics owing to its significantly high compressive, tensile and biaxial flexural strength. Commercially available as Ketac N100 light curing nano-ionomer (3M ESPE).^{33,48} Poly quaternary ammonium salt containing Glass ionomer cement has shown significant antibacterial activity and high strength.⁴⁹ A new Nanofilled Resin Modified Glass Ionomer with 65% nanofillers has been used to restore primary teeth and small cavities in permanent teeth.⁵⁰ Silver nano particles in Resin luting cements have shown long term inhibitory effect against *S. mutans*

and favourable mechanical properties.⁵¹ Hybrid Resin luting cements with less than 2.5% of 7 nm silica nanofillers have also shown improved properties.⁵² TiO₂ nanotube reinforced self adhesive resin cement has been used in luting indirect dental restorations as it has exhibited superior physicochemical and biological properties compared to the unreinforced cements without cellular viability compromise.⁵³ Nanoparticle impregnated luting cements have increased the bond strength to enamel and dentine. Compressive and tensile strength of Zinc Polycarboxylate has been enhanced with addition of ZnO and MgO nanoparticles.⁵⁴

IMPRESSION MATERIALS

Impression materials are available now with nanomaterials. Nanofillers in Poly Vinyl Siloxane (PVS) have shown good flow, improved hydrophilic properties and superior detail precision. Trade name Nano Tech Elite HD+(Zhermack).⁵⁵ These nanofilled silicone impression materials have shown a high degree of fluidity compared to from the original viscosity. It has been designed to give a snap set with less errors caused by micromovements.⁵⁶

MAXILLO-FACIAL PROSTHESIS

Maxillofacial prostheses have been made of artificial substitutes like silicones. They replace the tissues lost due to trauma or disease, restore and maintain the health of the tissues and enhance the aesthetics. But contamination and infection have given these materials varied clinical results with regards to quality and stability and so nanoparticles have been added to enhance the properties.^{57,58} Addition of silver nanoparticles to these materials

has prevented adherence of *Candida albicans* to the surface of these prostheses with no toxic effect to the human dermal fibroblast cells.⁵⁹ Titanium dioxide, Zinc oxide and Cerium dioxide nano particles have been added as opacifiers for silicone elastomers and Titanium dioxide and Cerium dioxide nano particles have exhibited the least colour instability.⁶⁰ Addition of surface treated Silicone dioxide nano particles in 3% concentration have improved the mechanical properties, especially the tear strength.⁶¹

IMPLANTS

A lot of research has been conducted to improve the making of implants as a high end treatment modality. The common problems that have been encountered were bacterial biofilm formation on the implant surface which has led to infection, inflammation and implant rejection. Nanotechnology has been widely used for surface modifications of dental implants as it has altered the implant surface at an atomic level thus changing the chemical composition of the surface. This change in the chemistry and the roughness has aided in good osseointegration.⁶² Nanostructured hydroxyapatite (HA) coating for implants has promoted bone formation around implants and has increased osteoblasts formation such as adhesion, proliferation and mineralization.⁶³ Dual layered Silver-hydroxyapatite nanocoating on Titanium alloy implants has created a surface with antibiofilm properties without compromising the biocompatible HA surface needed for successful osseointegration and accelerated bone healing.⁶⁴ Nanoporous ceramic implant coatings has caused anodization of aluminium.⁶⁵ This non porous alumina

has facilitated osseointegrative activity.⁶³ Calcium phosphate (CaP) coating on implant surfaces has increased the osseointegrative activity of implants and has shown favourable slow delivery systems of growth factors and other bioactive molecules.^{66,67}

The various surface modification techniques are:

1. Chemical modification:^{68,69}

(a) Anodic oxidation: It has created nanostructures with diameter of less than 100nm on Titanium implants. Voltage and direct current (Galvanic current) have been used to thicken the oxide layer of implant surface.

(b) Combination of acid and oxidants : Combination of strong acids have created a thin grid of Nanopits of diameter 20-40nm on the Titanium surface.

2. Physical modification:⁷⁰

(a) Plasma spray- It has created a nano structure less than 100nm and has enhanced osteoblasts density on implant surface.

(b) Blasting- alumina has been used for obtaining microporosities. Bioceramic grit blasting and acid etching has been the improved version of this technology.

CHALLENGES FACED BY NANOTECHNOLOGY^{34,71}

1. Precision positioning & manufacture of nanoscale parts.
2. Cost effective nanorobot mass production techniques.
3. Biocompatibility.
4. Inadequate assimilation of clinical research.
5. Finance and skill.

6. Social issues of public acceptance, ethical implications and human safety.

POTENTIAL HEALTH HAZARDS

Despite various health and health care advances by nanomaterials and nanotechnology, it has been perceived with apprehension for potential risk to human health and the environment. Therefore, it is prudent to elucidate their toxicologic effects to minimize occupational and environmental exposure.

The toxicity of nanoparticles has been due to greater surface area volume ratio leading to increased absorption through skin, lungs and digestive tract. They easily enter the lungs and reach the alveoli causing inflammation, tissue damage and subsequent systemic effects.

⁷² These nanoparticles have been transported through the blood stream to the vital organs or tissues throughout the body resulting in cardiovascular and other extra pulmonary effects.⁷³ their penetration through the skin may cause cell damage due to the production of reactive molecules.¹⁶

The unpredictability of nanomaterials has created an ethical dilemma with a wide selection of materials. For example, hybrid and microfilled composites have long track records to support their clinical use whereas the concepts of nanocomposites are appealing but are backed by only short term clinical studies. Utilitarianism cannot be considered in nanotechnology due to its fast development and uncertain future and hence an indepth knowledge, ethical considerations and safety measures is required.⁷⁴

The future of Nanotechnology is intriguing and is set to revolutionize dental practice. In prosthodontics, it will depend on development of material science thus opening up new avenues for vast and abundant research keeping in mind the safety, efficacy and applicability of these new technologies.

This paper is an attempt to give an overview of Nanomaterials and their applications in prosthodontics.

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CONCLUSION

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