Applications of Nano Graphene Oxides in Prosthodontics and Implant Dentistry- Current Trends and Future Outlook

Blessy Susan Bangera[1]
MDS, Reader, Department of Prosthodontics,
A J Institute of Dental Sciences, Mangalore, India.

Dr. Prajna K S[2]
Post Graduate at the Department of Prosthodontics,
A J Institute of Dental Sciences, Mangalore, India.

Dr. Vidya Shenoy[3]
Professor and Head of the Department of Prosthodontics,
A J Institute of Dental Sciences, Mangalore, India.

Abstract:- The world of Material Science has constantly evolved with newer materials being introduced constantly. One such material is Graphene which possessed excellent electrical, mechanical, thermal, optical, and biological properties due to which it has been used extensively in the fields of Optoelectronics, Energy harvesting, Films and Coatings, Water Filtration, Structural Engineering applications, Thermal management Devices and Sensors. Graphene-based Nanoparticles have also shown promising results in biomedicine, Tissue engineering scaffolds, Biomarker detectors, Biosensors, and Drug Delivery systems. Furthermore, extensive investigation is being performed on graphene-based Nanomaterials for their use in Dentistry, as it is shown to have promising results when incorporated into various Dental Restorative and Prosthetic Materials. This narrative review aims to give an overview of the application of graphene derivatives in dentistry, particularly on their application in Prosthodontics and Dental Implantology based on available research data and clinical studies.

Further research is imperative to fully explore the potential of graphene to ensure its safe usage in dental practice.

Keywords:- *Nano Particles, Graphene Oxide, Prosthodontics, Implant Dentistry.*

I. INTRODUCTION

The oral cavity has always been an area that demands high settings for its smooth functioning and esthetics which directly impact the quality of life. [1] To meet these demands, a plethora of dental materials have been advocated and a current trend has been set for constant advancement and research involving these materials. With the discovery of fullerene in 1985 and carbon nanotubes in 1991, carbon-based nanomaterials have been sought after and highly merited on the scientific stage. Graphene is one such derivative. Upon its discovery, Graphene in its various forms has been widely tested and its use in the field of dentistry is being looked upon. Graphene was discovered by Andre Geim and Konstantin Novoselov in 2004 where they used mechanical exfoliation technique to isolate a single layer of Graphene, that is considered one of the thinnest and strongest materials. [2] Due to its outstanding physical properties, electrical conductivity, and excellent biocompatibility, graphene and its derivatives have gained attention in the field of medicine and dentistry particularly with the advent of graphene base scaffolds in tissue engineering, as dental implant coatings, bone cements, resin additives, and in tooth whitening.[1,2] The content for this narrative review has been collected from various databases with emphasis on papers published in the last 5 years. Articles focussed on Graphene in Dentistry particularly in Prosthodontics and Implant Dentistry have been selected for review. Hence, based on the present data available, this article aims to provide an overview of the applications and future prospects of Nano graphene oxides in the field of prosthodontics and implant dentistry.

II. PROPERTIES OF GRAPHENE OXIDES

Graphene is a product obtained by chemical vapour deposition of Graphite. It is hydrophobic because of missing oxygen groups. [3] Graphene is available in various forms like graphene nanoplatelets, powder, Nano flakes, sheets, and foam. It is also categorized as reduced graphene oxide, single-layered graphene, multilayered graphene, and graphene oxide.[2] Few of its outstanding properties include: light weight in nature, Ultra-thin in cross section, strongest material known with strength up to 42 N/m in monolayer form., exceptional impermeability, high stiffness, high transparency (absorbs only 2.3% of light), good electrical conductivity, large surface area (-2600m2g"i), most stretchable crystal (20% elasticity), chemical stability (S000W/m.k), high intrinsic mobility (100 times more than in Si), biocompatible, antibacterial. high intrinsic mobility (100 times more than in Si) and mechanical strength (1.0 TPa-young's modulus). [4,5,6,7,8]

Due to its outstanding properties, Graphene has a plethora of applications in various fields such as [7,9,10]:

Table 1: Applications of Graphene

General applications of Graphene	**Biomedical applications of Graphene**
Nano-scale transistors.	Gene transportation.
Energy storage and Water filtration devices.	Anticancer drug release.
Ultra-thin batteries and High sensitivity touch screens.	Photo thermal and photodynamic therapies.
Thermo conductive lubricants.	Biosensors.
Nano-scale transistors.	Tissue engineering.

III. APPLICATIONS OF GRAPHENE OXIDES IN PROSTHODONTICS

Since its properties are manifold, graphene has been incorporated as a Nano filler into a plethora of dental materials. Polymethylmethacrylate (PMMA) is a commonly used denture base material and the incorporation of graphene into the material has resulted in enhanced mechanical, thermal, electrical and antimicrobial properties as listed below.

Table 2: Graphene in PMMA

Sl no	**Author**	**Structure and form**	**Inclusion method into PMMA**	**Parameters tested**	**Analysis**	**Outcome**
1	Ramanathan et al. (2008) [11]	Functionalized graphene sheets (FGS) and Expanded graphite (EG).	Nano filler was initially scattered in Tetrahydrofuran (10 ml) by bath sonication at room temperature. The solutions were then mixed with enough of a solution of PMMA in THF (10–30 ml) to yield a total composite mass.	Tensile strength and elastic modulus.	Atomic Force Microscopy, Scanning Electron microscopy, Transmission Electron Microscope, and X-ray diffraction.	The incorporation of 1% graphene into PMMA showed a hike in Elastic modulus by 80% and tensile strength by 20%
2	Yang et al. (2012) [12]	Graphene Oxide(GO) and graphene sheets using the modified Hummers method	Different concentrations of GO were incorporated into PMMA emulsions and mixed at room temperature for 2 h. GO sheets were reduced with hydrazine. Later the samples were centrifuged, washed with distilled water, and dried at 70^o C.	The glass transition temperature of PMMA.	SEM, XRD, TEM, Differential Scanning Calorimetry.	Improvement in glass transition temperature (Tg).
3	Heo et al (2012) [13]	The graphite powders were oxidized and exfoliated to GO using a modified Hummers method.	GO content varied from 1 to 3 wt%.	Thermal reinforcing effects.	Thermogravimetric analysis, Differential Scanning Calorimeter(DSC), and Thermal Conductivity meter.	With the addition of 3 wt% of GO, the PMMA/GO nanocomposite showed an increase in the glass transition temperature by more than 7^0C, and the thermal conductivity also increased 1.8 times.
4	An et al and Song et al. (2013) [14]	GO obtained by Hummer's method.	Ultrasonic dispersion of GO was done in the liquid phase after which mechanical milling was done.	Surface resistivity, Volume resistivity, Frictional coefficient, Surface	High-resolution SEM, Vickers micro-hardness meter.	Increase in surface resistivity and volume resistivity with an increase in GO content. Decrease in frictional coefficient thereby

				smoothness, and Wear resistance.		improving the wear resistance of PMMA.
5	Alamgir et al. (2018) [15]	GO is produced by modified Hummer's method.	PMMA Nanocomposites (PNCs) were prepared by melt processing using a twin-screw extruder machine at a processing temperature of 270o C and screw rotation of 10rpm.	Young's modulus and deformation.	X-ray diffraction, differential scanning calorimetry, Thermogravimetric analysis, Micro Indentation test, and scratch analysis.	More resistant to deformation. The value for Young's modulus was more than PMMA.
6	Khan et al. (2018) [16]	GO Nanosheets.	GO was incorporated into the MMA monomer and sonicated using a probe-type sonicator for 15 min. Then powder of PMMA was mixed with monomer with a 1.3:1.0 P/M ratio.	Bending strength and wear resistance.	Scanning Electron Microscope, Transmission Electron Microscopy, XRD, TGA, Bending test, Fourier Transform Infrared Spectroscopy (FTIR),.	Significant increase in wear resistance and bending strength in comparison to original PMMA.
7	Lee et al. (2018) [17]	nGO (graphene oxide Nano sheets).	nGO was added in 0.25%, 0.5%, 1.0%, and 2.0% by weight relative to PMMA powder. nGO was homogeneously dispersed in MMA under sonication for 1 h.	Flexural strength, Elastic modulus, Hardness, Anti-adhesive effect.	3-point flexural test and hardness machine. The anti-adhesive property was investigated by nonthermal oxygen plasma treatment.	0.5 wt% of nGO into PMMA increased the FS significantly; more than 0.5 wt% nGO increased the surface hardness significantly. Specimens with nGO had more anti-adhesion properties and sustained anti-adhesive effects against microbial species for up to 28 days after incorporating GO into PMMA.
8	Gamal et al. (2019) [18]	nGO.	Nano graphene oxide in five different concentrations 0 %, 0.05 %, 0.1 %, 0.15 %, and 1 % by weight was added to PMMA.	Antibacterial effect, Thermal expansion.	Minimal Inhibitory Concentration (MIC), agar well diffusion test, linear coefficient of thermal expansion.	The growth of Streptococcus mutans can be inhibited by the addition of 0.5% of GO into PMMA. There is an inverse relation between the concentrations of GO and the Coefficient of Thermal Expansion.
9	Carlo Di et al. (2020) [19]	Graphene.	G-PMMA was obtained by milling "G-CAM" polymeric disc.	Flexural strength (FS), Elastic Modulus (EM).	3-point bending test.	Improved flexural strength and elastic modulus. Resulted in greater homogeneity of the mechanical behavior during the bending test.

10	Bacali et al (2020) [20]	The graphene silver nanoparticles (G-AgNp) composite was synthesized through the Radio-Frequency Catalytic Chemical Vapor Deposition (RF-CCVD) method.	Graphene silver nanoparticles (1 wt% and 2 wt%) was added to resin powder using a lab vibrator.	antibacterial activity, cytotoxicity, and monomer release.	Agar Disk Diffusion Test, 3-point bending test. MMA monomer release analysis was evaluated using a high-performance liquid chromatograph.	PMMA resin mixed with G-AgNp exhibited promising antibacterial activity associated with minimal toxicity to human cells, in vitro, as well as improved flexural properties.

Table 3: Graphene in Resilient Denture Liners and Tissue Conditioners

Sl no	Author	Structure and form	Inclusion method	Parameters tested	Outcome
1	Dr. Swapnil Shankar gouda, et al (2020) [21]	Nano graphene oxide	nGO powder was incorporated in 1%, 3%, and 5% by weight relative to the acrylic-based tissue conditioner (GC Soft liner) powder and mixed properly.	Antifungal susceptibility.	The antifungal activity against Candida albicans was increased. The acrylic-based tissue conditioner with 5% Nano graphene oxide exhibited the highest diameter of inhibition zone followed by the addition of 3% nanographene oxide and the least with 1% nanographene oxide concentration both after 1 day and 7 days.
2	Khan AA et al in (2022) [22]	GO Nanosheets	nGO powder incorporated by 0.1%(G_1), 0.3% (G_2) and 0.6%(G_3) by wt into acrylic-based Resilient Denture liner (RDL	Surface roughness, water contact angle, Shore A hardness, water sorption, and solubility parameters	Reduced hardness without change in surface roughness of GO incorporated RDL was noted. Statistically decreased water solubility and sorption values were seen in G_1 group as compared to G_2 and G_3 groups.

Table 4: Applications of Graphene oxides in Implantology:

Sl no	Author	Structure and form	Inclusion method	Parameters tested	Analysis	Outcome
1	Kulshrestha et al (2014) [23]	Graphene/Zinc oxide Nanocomposite(GZNC).	Graphene oxide was prepared Hummers and Offman method.	Antimicrobial, anti-biofilm and anti-adherence activity.	Microscopic studies and Anti-Biofilm assays	The results showed the potential of GZNC as an effective coating agent for dental implants by efficiently inhibiting S. mutans biofilms.

2	Jung et al (2015) [24]	Reduced graphene oxide (RGO).	4 mg/mL of graphene oxide (GO) solution with a size of 0.3-2 µm was spin-coated on the Multi-pass caliber-rolling Ti13Nb13Zr (MPCR-TNZ) surface at 100 rpm for 5 sec following 2,000 rpm for 30 sec to obtain GOcoated MPCR-TNZ with a uniform thickness. RGO-MPCR-TNZ was obtained by reducing in hydrazine vapor for 24 h	The Dynamic Fatigue Experiment.	Alizarin red staining, Alkaline phosphatase activity test, Immunocytochemistry, and Real-Time Polymerase Chain Reaction (RT-PCR).	Superior fatigue resistance of the implant prototype, enhanced mechanical stability, high mechanical strength, and prolonged product lifetime. The drug-loaded implant materials can stimulate and facilitate cellular response around the implant surface to reduce the osseointegration time.
3	Jin et al (2017) [25]	Graphene oxide.	Ti substrate surface was modified by graphene oxide (GO) thin film and silver (Ag) nanoparticles via electroplating and ultraviolet reduction methods.	antimicrobial activity and cytotoxicity.	Field emission scanning electron microscopy observation, RT-PCR assay, Fluorescence staining, and Flow cytometry testing.	GO-Ag-Ti multiphase nanocomposite exhibited excellent antimicrobial ability and anti-adherence performance.
4	Li et al (2019) [26]	Graphene oxide	GO dispersed solution was spun down at 12000 rpm for 20 min, washed three times with water, and redispersed into the Tannic Acid (TA) solution (1 mg/ mL). After another three cycles of spin down and washing, the TAGO was obtained. GO was redispersed into the water by sonicating for 10 min with a concentration of 1 mg/mL.	Antibacterial and osteogenesis property.	LIVE/DEAD BacLight kit, RT-PCR analysis.	The coatings showed a synergic effect on the killing bacteria, both Gram-negative bacteria and Gram-positive bacteria represented by E. coli and S. aureus, respectively, and enhanced osteogenesis of Dental pulp stem cells (hDPSCs).
5	Zhang et al. (2020) [27]	Graphene oxide sheets.	3Y-ZrO2/GO composite ceramics with different graphene oxide contents (0–0.2 wt%) were hot pressed.	The relative density, the mechanical properties including Vickers hardness, Flexural	Multi-function Vickers Digital Micro Hardness Tester, Universal Testing Machine, Vickers Indenter.	Compared to raw 3Y–ZrO2, the incorporation of GO sharply enhanced bending strength and

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				strength, and Fracture toughness		fracture toughness, representing a hike of 200% and 41%, respectively. The incorporation of GO decreased the coefficient of friction and wear rate and the surface roughness of 3Y–ZrO2. Obvious signs of cytotoxicity was not seen and GO promoted proliferation, growth, and adhesion of cells. Overall, 3Y–ZrO2/GO composite ceramic with 0.15 wt% GO is promising biomaterial for dental implant applications.
6	Jang et al. (2021) [28]	Graphene oxide.	Zirconia specimens were coated with graphene oxide using an Atmospheric pressure plasma generator. Argon gas (4 L/min) and methane gas (3.5 mL/min) were mixed in a quartz tube and coated on the surface at 240 V at the rate of 10 L/min.	Bacterial adhesion and Osteoblast activation.	Field-Emission Scanning Electron Microscope and Raman Spectroscopy.	GO-coated zirconia showed increased proliferation and differentiation of osteoblasts and inhibition of attachment of S.*mutans*. This can prevent peri-implantitis by preventing bacterial adhesion. Moreover, its osteogenic ability can improve bone adhesion and the success rate of implants.

7	Shin et al (2022) [29]	reduced graphene oxide (rGO).	rGO solution was deposited on each surface via peptide bonds between the carboxyl groups of rGO and terminal amino groups of 3-aminopropyl)triethoxysilane (APTES)	Surface property, in vitro cellular behaviors, and in vivo osseointegration property.	Spectroscopic, diffractometric, and Microscopic analyses.	rGO-coated Ti can accelerate the healing rate with the high potential of osseointegration.

Table 5: Application of Graphene Particles in Maxillofacial Silicone Materials

Sl no	**Author**	**Structure and form**	**Inclusion method**	**Parameters tested**	**Analysis**	**Outcome**
1	Shah et al. (2021) [30]	Graphene oxide.	By stirring thoroughly on a glass slab, silicone was mixed with 5% of nano-graphene oxide into a homogeneous paste.	Antifungal efficacy.	Well diffusion method.	Fungal growth was reduced by adding Graphene oxide into the maxillofacial silicone material

Table 6: Applications of Graphene Oxide Particles in Dental Ceramics

Sl no	**Author**	**Structure and form**	**Inclusion method**	**Parameters tested**	**Analysis**	**Outcome**
1	Li et al. (2014) [31]	Graphene Nanosheets	Using a plasma spraying technique, Zirconia/graphene nanosheets (ZrO_2/GNs) composite coatings were made. (1 wt.%) were anchored at the splat interface	Microstructure and wear behavior	Field-emission scanning electron microscope, Energy Dispersive Spectroscopy, Transmission Electron Microscope, and Micro-Raman spectroscopy.	Microscopic observations exhibited that the GNs additives (1 wt.%) were homogeneously dispersed in the ZrO_2 matrix and most of them were anchored at the splat interface. It also showed increased wear resistance and low friction coefficient with the incorporation of GNs.
2	Su et al. (2016) [32]	Graphene nanosheet (GNS)	Using Spark Plasma Sintering (SPS), GNS-reinforced yttria stabilized tetragonal zirconia polycrystals (TZP) were produced. Various compositions chosen here were pure TZP, 0.5 wt% GNS/TZP, 0.75 wt% GNS/TZP, and 1.0 wt% GNS/TZP composite powders	scratch tests, mechanical properties	Archimedes' method, X-ray diffraction, crack propagation induced by Vickers indenter, Micro scratch tester (MCT).	Compared to monolithic TZP, the elastic modulus and Vickers hardness of a 0.5 wt% GNS/TZP composite exhibit enhanced elastic modulus (*18%), hardness (*13%), and toughness (*36%), respectively. The GNS/TZP composite with improved toughness and scratch resistance might be a potential candidate for engineering and biomedical applications.

3	Zeng et al. (2018) [33]	Reduced graphene oxide	Zirconia powders and GO were mixed using a colloidal coating route. Using spark plasma sintering, in situ reduced graphene oxide-toughened zirconia ceramics were made.	microstructure, mechanical properties, toughening mechanisms.	X-ray diffraction, field emission scanning electron microscopy, Vickers hardness tester	The fracture toughness of in situ reduced graphene oxide-toughened zirconia improved by up to 175% (from ~6.07 to ~10.64 MPa·m1/2) at 0.09 wt.% graphene oxide compared to the toughness of 3 mol.% yttria-stabilized zirconia, with a small improvement in hardness

IV. FUTURE OUTLOOK

Promising materials must not exhibit any long-term cytotoxicity both In -vivo or in vitro. Due to a limited knowledge of graphene and its derivatives, a major task in clinical applications is the uncertainty of its cytotoxicity and its potential mechanisms. [34, 35,36,37,38,39] Up to date, there is no agreement on the cytotoxicity and potential hazards of graphene-based materials according to various studies. The introduction of Graphene oxide in the Lungs of mice produced persistent lung injury. It is also known to generate reactive oxygen species hence setting off inflammatory and apoptotic pathways. [40, 41] Since Nanoparticles have a greater potential to interact with individual cells and can traverse through the bloodstream more easily than larger particles, biocompatibility testing for these Nanoparticles may be slightly different from bulk particles. The uncertainty regarding the property of biocompatibility of Nano graphene oxide in the body makes it imperative to carry out further research in this regard. [37,38,39,42]. Biocompatibility testing for in vitro conditions is done using cell viability and proliferation assays, hemocompatibility, genotoxicity, and sensitization tests. [43,44, 45] Cytotoxicity of dental materials is assessed using Colorimetric MTT (3- (4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bro- mide) assays, Lactate dehydrogenase (LDH) assays and Cell counting kit-8 (CCK-8) assays. [46,47] However, while performing these studies it is advisable to consider the conditions of the oral cavity where the dental materials will be of service, unlike the rest of the body which may have a different pH level compared to the saliva. The pH level in the mouth has an average value of 6.7 which is highly variable due to the consumption of various types of food and beverages. The bite force in the mouth while chewing food also needs to be taken into consideration. Taking this factor into consideration, the various biocompatibility tests need to be carried out. [48,49] It has also been noted that the size, structural configuration and concentration of graphene molecules have a direct impact on cytotoxicity. Narrower and smaller particles could easily infiltrate and destroy the cells compared to larger particles. Prolonged exposure to graphene particles has shown evidence of genetic mutations. [50,51,52,53,54,55] Further research needs to be carried out to render the material safe for use in dentistry.

Graphene as a Nano sensor has been studied for intra-oral bacterial detection, and it was found that the sensors had high sensitivity, good biorecognition, and good conformability to the tooth enamel surface due to the graphene and incorporated peptides. [56] Graphene biosensors have been able to detect bacteria and viruses in tooth enamel, saliva, and biological tissues. [57,58,59,60,61] They are being extensively studied for applications in dental adhesives, fillings, and tissue engineering. Graphene-based materials have been shown good antibacterial properties, anti-biofilm properties for dental implants, increased proliferation and differentiation of stem cells in tissue engineering, favorable results when incorporated into dental composites. [34] Though there are studies on invitro biocompatibility testing of Graphene-based materials for dental applications, further long-term effects of these materials and their cytotoxic effects need to be studied.

V. CONCLUSION

The entry of graphene into biomedical field has opened a myriad of possibilities due to its superior physico-chemical properties. Introduction of graphene into dentistry has also received great consideration. Applications of graphene based dental materials require further research and clinical trials for their successful introduction to commercial usage.

- **Conflict of Interest:** None.

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