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The Science of Carbon Nano-Tubes and Graphene Influencing the core of PMMA: A Review

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Abstract

Throughout the years acrylic resin has been the foremost choice of material for removable prosthetics due to its many favourable properties. Over the years there have been a number of alterations to its chemical as well as physical properties by filler particles which helps it to enhance its strength and biomimetic properties. Many recent scientific accreditation have laid grounds for using materials from the carbon family especially carbon nanotubes and grapheme to influence the properties of acrylic resin. This particular piece of literature will talk through the properties of PMMA and the need to reinforce this material with the advantages and disadvantages of addition of carbon nanotubes and graphene. Hybrid reinforcements will also be discussed to draw certain conclusions.

1. Introduction

PMMA, the most largely used material in acrylic denture fabrication, has many favourable characteristics, but also several disadvantages, regarding its physical, chemical, biological and mechanical properties. The denture or rather the material used to fabricated a denture is a part and parcel of the oral cavity throughout a patient's life. This undergoes various interactions with the oral cavity in the form of masticatory forces, numerous fluids interact with the denture material and hence it needs to have properties which allows it to sustain as well exhibit biomimetic properties. From the past to

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the present acrylic resin has been the top notch used material for fabrication of denture base. Although exhibiting many favourable properties, it cannot be considered an ideal material. Complete dentures have been fabricated from various materials namely wood, bone, rubber, plastics and what not; as its history is dated back to 700 BC. Several attempts have been made with time improving the properties of acrylic materials used for denture fabrication with different newer fillers and materials. There are numerous kinds of fillers which have been used to improve properties of resin material namely: glass, aramide, metal inserts, meshes, fibres and a lot more.[1-5]

Certain drawbacks such as low flexural strength, residual monomer allergy, porosity, polymerisation shrinkage, poor conductor of heat, poor adhesion to metal, high coefficient of thermal expansion, low impact strength, crazing, warpage all of these lead to experimenting and creating newer or chemically changed materials which could avoid these drawbacks in the most possible manner.[7,8] With the passing years and today in the decade of millennials extensive research has been done, in order to improve PMMA mechanical properties, by changing its chemical structure, material reinforcement using fibres or fillers of different types, sizes, shapes, in different concentrations, or by obtaining hybrid materials.[9]The stream of Nanosciences is vast and research done is quite little hence newer opportunities are created with each passing year. With various advents in the field of Macro to Nano science opens doors to materials which can enhance PMMA properties to an innovative approach.

In the year 1991 Iijima was the person to discover carbon nanotubes and to enhance its properties there are numerous on going researches of incorporating it with PMMA to enhance its properties. Belonging to the genre of fullerenes, Cnts is a form of allotropic carbon of third group which is man-made fiction nano substance. These are fine and lengthy graphite cylinders, here the atoms of carbon are designated in a sextuplet form lattice. [10,11]

CNT's are usually having a wall of either one or multi nanotubes (SWNTs and MWNTs). Arranged in the form of a beehive, Graphene, being a 2D filler has a single atom with broad planar sheet of SP2 bonded atoms.[12,13]

Even with this advent and improvement in designs of graphene and multi-walled carbon tubes there are not much studies availed of the use in heat polymerized resin.

2. Need for Reinforcement:

Even though PMMA was considered to be the ideal material[2] for denture base resin it has its own drawbacks hence the material needs enhancement in the form of reinforcements at different levels for changes in Physical, Mechanical as well as Chemical properties[4]:

	Drawbacks of PMMA
1.	Low flexural strength
2.	Residual monomer allergy
3.	Low Modulus of Elasticity
4.	Poor conductor of heat
5.	Polymerisation Shrinkage
6.	Warpage
7.	Crazing & Porosity

Hence after keeping in mind these properties newer materials and fillers were added and tried to overcome certain drawbacks and to bring about changes with these reinforcements. Several attempts have been done in time at improving the properties of acrylic materials used for denture fabrication.

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The properties of PMMA so far have been modified by various methods such as[5]:

i) Chemical modification

ii) PMMA reinforcement at Macro & Micro Scale

iii) PMMA reinforcement at Nano scale

iv) Hybrid Reinforcement

Carbon based materials due to its tangible properties are now preferred for reinforcements of PMMA in various forms. This is made possible due to its very specific mechanical and structural properties.

Carbon black, carbon nanotubes (CNTs), carbon nanofibers. Carbon fiber composites are among the most popular ones, due to their excellent and specific mechanical and structural properties. CNTs (both single and multi-walled) find multiple applications, due to their extraordinary properties.

Why Nano-particles over micro-particles?

The headway in nano-science and nano-tech gives an establishment to newer materials of nano spectrum, which possess unique properties from those of the original materials. Smaller in size but highr active surface is what brings the utility in them. Various Studies have efficiently proved that nanofillers addition is more efficient than that of microfillers in improving the properties of composites.[14]

Nanoparticles addition to PMMA follows:

1. Better mechanical properties
2. Extremely high surface-to-volume ratio of the additives

3. Area of the interface between the matrix and the reinforcement phase

All these enhances the interfacial interactions and can improve the mechanical, physical, chemical and biological properties.[14,15]

Carbon Nanotubes

Carbon based nanotubes have a sextuplet arrangement of columnar (Barrel-shaped) atoms which are hybridized in nature. Sheets folded into nanometer created from metric linear unit are upholded onto with sphere shaped fullerenes. Carbon nanotubes have peculiar properties of electrical nature. Thus being put into two forms according to their thickness.[16]

MWCNTs – multifaceted furled sheets

SWCNTs –nanostructures of columnar one sheet

These nanotubes are very firmly spiralled in nature due to the forces of vander walls and frail inside planar interactions of graphene sheets. These result in a firm accumulation and regulations of dimensions and shape and also surface area.[17,18]

Altered properties due to CNTs are Mechanical, Electrical and Thermal conductivity.

Carbon nanotubes incorporated in PMMA determined better mechanical and electrical properties, and also a higher thermal conductivity.[19] Surface functionalization of CNTs is an effective method to improve their dispersion, as a result of the strong interfacial interactions.[20] CNT sponge, or CNT foam can find applicability in modern composites, due to its high porosity and very low density.[21,22]

To increase the flexural and impact strengths of heat polymerized resin, 1.5% single walled nanotubes can be incorporated as a filler but it might cause decrease in hardness.[23]

Astudywas conducted and it was proposed that 2 wt% carbon nanotubes can improve properties of impact strength and flexural strength. This can be done by the use of a technique assisted with ultrasound. The sample can be produced by heat induced processing of acrylic resin.[24]In 2019, a study was conducted which deduced that the flexural strength of PMMA acrylic was ot altered with the incorporation.[25]

Talking about multi-walled CNT's Kim and fellows probed about the incorporation into resin to form antimicrobial bonding characteristics. In their study, the adherence of staphylococcus aureus, candida albicans and streptococcus mutans were tested on keratinocytes in 1wt% in comparison to PMMA. They concluded that CNTs influenced both resilience and flexural strength.[25]

Wang explored a study into understanding and assessing the modification with multi-wall carbon nanotubes of acrylic resin in the possibilities of flexural strength, resilience and its resistance to

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fatigue.[26]They concluded by its results that 0.5 wt% and 1 wt% were useful as filler particles. Whilst, 2 wt% were not that useful due to lesser dispersion of MWCNTs in the resin matrix. Hence more studies need to be deduced.

Disadvantages

Maybe owing to its cytotoxicity and also poor results in aesthetics nano-carbon are lesser used substances for strengthening of acrylic resin. Whereas handling the material for polishing too causes a drawback.The varying amount of percentage difference being added to PMMA brings about all the more changes in the properties. Some working in the favour whilst other against the very system. If more studies are conducted by altering and hybridizing the properties it can overcome these and be a boon to the drawbacks of PMMA.

Material	Enhances	Drawbacks /No effect
Nano Carbon	"Flexural strength & Impact strength"	"Hardness, Cytotoxicity and Biomedical issues, Poor aesthetics attribute"
SWCNTs	"Impact strength & Transverse strength"	"Hardness"
MWCNTs	"Flexural strength and resilience"	"No effect"

3. Graphene

The unique and attributes mechanical properties of graphene has given its well deserved title as "the thinnest material in the universe" since 2004. The varied properties have created a space for unique and diverse role in research fields not just in dentistry but every aspect.[27] Consisting of a bee-hive like structure (hexagonal) , with one atom thick sheet of sp2, this is a carbon allotrope which are densely packed crystal structure.[28]With a wide range of apllications, groups which contain epoxy, hydroxyl and carboxyl are Graphene oxide and reduced graphene oxide.[29,30]

Studies enable their use in a couple of different polymers. Many studies conducted conclude that incorporation in acrylic resin materials enhance the surface interaction of graphene and the polymer core. This transits the load to the filler instead of the polymer. 1% incorporation was considered to be improving the compression parameters.[31]

Graphene, an easy-to-obtain and cheap material, but having exceptional thermal, mechanical, chemical and electrical properties, was combined with various metals, carbon materials or polymer materials, inducing improved properties of the obtained composites.[32] Reinforcement of PMMA using graphene or graphene oxide leads to a higher impact strength. The higher functionalization of GO, compared to G, determines better results, as it facilitates the interfacial interactions between PMMA and GO.

4. Disdvantages

Independently graphene likes the rise of the residual monomer amount at higher concentrations of G and GO, and a delay in the polymerization reaction because of graphene interference – are also possible.[32]

Hybrid Reinforcement

Hybrid reinforcement, obtained by combining different types of additives, shows significant improvements with the mechanics and properties of acrylic resin. Acrylic resin with carbon fiber coated by graphene oxide showed better mechanical performances than the PMMA carbon fiber composite.[33] A graphene and CNTs hybrid material can also be an efficient solution for multi-functional interfacial nano reinforcement, improving the mechanical and electrical properties in carbon fiber and epoxy composites . A combination of graphene oxide and silver nanoparticles showed favorable effects on several mechanical, chemical and physical properties of a PMMA denture resin.[34,35,36]

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5. Conclusion

A broken prosthesis, not taking into consideration its design is always an inconvenience to the patient as well as the operator. With the advent in processing and material science of resins and digitally driven processed PMMA blocks if we think about micro additions of nano particles it can enhance in the glory of acrylic resin.

With the different percentages of incorporation of fillers, the rate of fracture of prosthesis declines. Properties like flexural strength, ease and effectiveness all of it can be altered to a beautiful extent with various different addition on the bases of quantity of incorporation.

Acrylic resin with Graphene or Carbon Nanotubes need to be studied with severe concentration to obtain a stable dispersion of filler with the core. Superior mechanical properties and many other additional properties can be used to bring about a change in the strengthening effect.

Thus, more and more research can bring about a great transition in the material science of denture base resins.

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