An Updated Review on the Properties of Graphene Nano Filled Composites and Their Applications in Dentistry

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ABSTRACT

Researchers looking for innovative nanomaterials to be used in dentistry have recently been attracted to graphene nanofillers which demonstrate exceptional biological, chemical and mechanical characteristics over other nanofillers. Even though literature contains data for implementing graphene in different areas of medicine like utilization of their tissue regenerative potentials and antibacterial activities; only small numbers of studies are focused on their applicability in dental nanocomposites. This literature review aims to summarize current information and the latest progress made relating to graphene properties, synthesis and use as fillers for dental nanocomposites. Reports included in this review showed that graphene as well as its derivatives have recently turned into promising tools to be used in the biomedical field. These nano-size-materials exhibit great versatility and peculiar properties like huge surface area and impressive thermal stability, electrical conductivity and mechanical strength. Moreover, these nanomaterials can be incorporated into other materials for improvement in their bioactivity and optimization of their mechanical, physical and chemical characteristics. Accordingly, this indicate the potential utility of graphene for several different dental applications. Thus, it is highly recommended that more studies must be conducted for investigating the advantages and the utility of graphene nanomaterials in dental applications. This review would give valuable data toward new material fabrication and practical application of graphene nanofilled composite.

KEY WORDS: GRAPHENE, NANOFILLER, COMPOSITE, NANOCOMPOSITE, DENTISTRY.

INTRODUCTION

Graphene is one of the allotropes of elemental carbon. It is a one-atom-thick, sp2 hybridised, two-dimensional sheet of carbon atoms arranged in a honeycomb lattice, with 0.142 nm carbon-carbon bond length and with individual graphene sheets of 0.34 nm thickness, (Papageorgiou et al., 2017). Since (Novoselov et al., 2004) succeeded in identifying single-layer graphene at Manchester University in 2004, graphene has attracted enormous scientific attention in recent years, due to its unique electrical, thermal, and mechanical properties. In particular, it has many interesting characteristics, including unprecedented mechanical properties: modulus of elasticity about one TPa; tensile strength of 130GPa which can be considered as the strongest material ever discovered, remarkable thermal conductivity (5300 Wm-l.K-1), (Jun Han et al., 2013, Erol et al., 2018), and high electron mobility at room temperature (250,000 cm2/Vs)(Novoselov et al., 2012, Zhao et al., 2017). However, the properties of graphene depend on the perfection of

its structure, which is significantly influenced by the methods of its synthesis (Skoda et al., 2014, Erol et al., 2018).

Graphene Synthesis And Production Methods: The Graphene nanofillers are produced with lightweight, high performance, low cost, and have a wide range in biomedical applications,(Zhang et al., 2012, Erol et al., 2018). However, large scale production of graphene has been a challenge although much research has been done to produce high quality sheets of graphene (Amiri et al., 2018). Hence, it has created more research and understanding of the graphene nanofilled composites. Enhancement of various properties like physical and mechanical will increase the suitability of graphene nanofilled polymers in many technological fields, (Zhang et al., 2012, Wang et al., 2016). Consequently, graphene can be synthesised by employing various methods such as; deposition of chemical vapor, growth of the epitaxial, exfoliation of compounds intercalated with graphite, and methods that include the oxidation and reduction of chemicals, (Lee et al., 2017, Lin et al., 2018).

In addition, high quality graphene can be produced through the micromechanical cleavage method that is more reliable and effective. However, the technique experiences a draw back since it produces very low yields and, thus, cannot be applied for large scale production of graphene. (Novoselov et al., 2004) Moreover, graphite precursors are the most suitable polymer for the extraction of graphene since they are considered to be relatively cheaper than other polymers. Consequently, the thorough analysis of different techniques of graphene synthesis is highly applicable to the current world of science (Verdejo et al., 2011, Lee et al., 2017).

Exfoliation: It refers to the process of separating layered materials into single sheets in order to make them thin due to the high demand of very thin nanomaterials. Thin graphene nanofillers are very beneficial since they have enhanced electrical conductivity, thermal stability, and reduced gas permeability than bulk materials(Rao et al., 2009). Moreover, graphite oxidation is a good approach of separating bulk materials into single layers and involves various techniques such as; stirring, shaking, and ultra-sonication. The process of oxidation is normally done in water by a sonication process since the polar functional groups are present in water. However, the exfoliation process can be done in an organic solvent which is much easier than in water because of the hydrophobic nature of sheets. Also, the thermal exfoliation process is also employed in exfoliation and produces single layer graphene in gaseous media in a relatively shorter time as compared to graphite oxidation, (Dimiev and Tour, 2014).

When the exfoliation process is done under heat, it leads to the production of gases from the functional groups which increase pressure thereby leading to disruption of molecular forces of association which exist between the layers hence causing separation. Moreover, the strategy is employed in large scale production since it

produces high quality graphene with a perfect structure. This method, however, has limitations since it produces multilayered sheets because it allows the restacking of graphene sheets even after de-intercalation.(Verdejo et al., 2011, Shang et al., 2019).

Chemical Vapor Deposition: Chemical Vapor Deposition (CVD) process is normally used to produce high quality graphene which is achieved by using substrates of transitional metals like copper and nickel, which are used as a catalyst (Seah et al., 2014). This process is cheaper compared to others and requires the addition of the polycrystalline nickel films to a mixture of methane and hydrogen at a very high temperature. Once methane gas decomposes, it produces carbon atoms that react with nickel and solidifies in the presence of argon which decreases its solubility, and removes carbon atoms, and precipitates on the nickel film leading to the formation of graphene films. In addition, copper can alternatively be used as a catalyst in the formation of single layered graphene (Zhang et al., 2013). Moreover, another method used to produce single layered graphene is the Plasma-enhanced chemical vapour deposition which is a promising method, and it is likely to be used in large scale production. The process is flexible of various substrates, and it is achieved at a very low temperature and pressure which allows the generation of reactive species in the plasma. However, the process needs to be modified to control the graphene thickness, (Chan et al., 2013, Lin et al., 2018).

Chemical Oxidation–Reduction Methods: The reduction of graphite oxide is currently considered the most reliable route of producing graphene in considerably large quantities (Dreyer et al., 2010). The method involves the employment of oxidizing agents, and even strong mineral acids for the oxidation of graphite through the treatment with potassium permanganate and sulfuric acid as per hummer's method (Hummers and Offeman, 1958). As opposed to pristine oxide, the graphite oxide oxygenated heavily with its carbon atoms at the basal plane decorated with groups such as hydroxyl and epoxide. Moreover, its edge atoms are also decorated with carboxyl and carbonyl groups, and, thus, making graphite oxide extremely hydrophilic. The presence of the functional groups within the graphite oxide decreases the forces between the planes as the interaction of faces between polymers and the graphite oxide reduces, and thereby leading to the state of separation of the graphite oxide element, (Potts et al., 2011).

However, the chemical treatment during oxidation openly yields defects of the structures such as; multiple and single vacancies, defects of dislocation, chemical groups accessory and the defect type known as Stone- Wales. Subsequently, the structural defects affect the mechanical functionality of graphene in a great way. In addition, these defects of the structure lead to the interruption of the electronic framework of graphene and, thus, change its conductivity effect. Also, the graphite oxide that is insulated can be transformed into conductive graphene by the employment of procedures such as chemical

reduction with low temperatures and thermal annealing with high temperatures, (Verdejo et al., 2011).

Moreover, there are two reducing methods employed which include the chemical reduction process which involves the use of reducing agents of chemical nature in the graphite oxide chemical reactions (Park et al., 2009) and the thermal reducing process which is normally conducted by the intense heating of a vacuum or inactive environment to temperatures of the range between one thousand and fifty to two thousand degrees Celsius per minute, (Schniepp et al., 2006). Besides, there are various chemical reducing agents that are employed on graphite oxide reduction including hydroquinone, metal hydrides, hydro iodide, and p-phenylene diamine among others, (Galpaya et al., 2013, Singh et al., 2012).

Other Methods: There are other mechanisms that can be employed in the synthesis of graphene such as the conversion of carbon nanotubes to graphene nanoribbons by the unzipping process which includes the use of a mixture of potassium permanganate and concentrated sulfuric acid (Rafiee et al., 2010, Shukla et al., 2016). The unzipping procedure is possible since carbon nanotubes are normally considered as a roll of graphene sheets, and thus the process of unzipping them will reduce the thickness and increase the quality and demand of the sheets. However, the technique has a challenge of defecting sites which will hamper the properties of graphene, (Wei et al., 2013, Lee et al., 2017).

Preparation Of Graphene–Nanocomposites: The dispersion of nanofillers is a very critical step in the preparation of polymer nanocomposite. The properties of a whole matrix are equally improved by a good dispersed state that ensures a maximum reinforced surface area that affects other polymer chains. There are certain strategies that have been used in the preparation of graphene polymer nanocomposites and they include the process of melting, solvent processing, and in situ polymerization (Galpaya et al., 2013, Papageorgiou et al., 2017).

Solvent Processing: The graphite-oxide is scrubbed into single sheets of graphene oxide by the chemical processing or treatment using heat as previously mentioned. Moreover, the solvent process involves the partial oxygenation of graphene layers that allow dispersion in polar solvent, which is a preferred method of preparation of graphene composites through the process of solvent blending technique (Verdejo et al., 2011, Sharma et al., 2018). In addition, the procedure involves three primary steps that include; the dispersion by ultra-sonication in a preferable solvent, followed by the addition of polymers and finally the removal of the solvent through evaporation or distillation. The solvent processing technique is typically simple and, thus, more of graphene polymers are developed using it. However, the procedure has its disadvantage such as the permanent adsorption of organic solvents on the graphite oxide (Galpaya et al., 2013, Ahmad et al., 2018).

In situ polymerization: This is a procedure that involves the use of the chemically modified graphene which are combined with monomers in the existence of a selected solvent, thereby allowing polymerization response by regulating both temperature and time parameters. The chemically modified graphene (CMG) contains minute molecules that are employed in covalent bonding or during grafting of polymer chains via atom polymerization by transferring of radicals (Lee et al., 2010, Ahmad et al., 2018, Sreenivasulu et al., 2018). A good example of the in situ polymerization is epoxy, polymethylmethacrylate (PMMA) and polydimethylsiloxane (PDMS) foams (Chhetri et al., 2018, Zhang et al., 2018, Yang et al., 2018). However, despite the findings generated regarding the technique, there is still need for more research to be done on curing reaction so as to enhance the understanding and discovering of the consequence of nanofillers in the morphology of polymer matrix and its properties and curing reaction (Verdejo et al., 2011, Sharma et al., 2018).

Studies have shown that the polymerization reaction rate of PDMS decreases by the addition of graphene which has been exfoliated by thermal treatment, and leads to robust relations between the matrix of polymer and the incorporated particles that facilitate stress transfer (Verdejo et al., 2009). Moreover, the in-situ polymerization method also leads to a homogenous and an exceptional dispersion. The limitation of this strategy is that it is accompanied by increased viscosity that prevents loading and manipulation fraction (Papageorgiou et al., 2017, Varenik et al., 2017).

Melt process: This process is the most useful technique employed commercially as compared to in situ polymerization and solvent process, in particular for thermoplastic composites (Galpaya et al., 2013). The melt-process involves direct incorporation of the CMGs into the selected polymer which has been melted by the use of an extruder (twin screw) and the regulation of speed, time, and temperature (Verdejo et al., 2011). Moreover, for exfoliated graphene nanofillers that are prepared thermally, most available strategies are developed by using various polymers like polycarbonate, isotactic polypropylene, and polystyrene-co-acrylonitrile, (Kim and Macosko, 2009, Ajayan and Tour, 2007). The limitation of this method is the inadequate dispersion at a high level of fillers loading and increased viscosity, in addition to that graphene sheets are prone to rolling or folding during the blending procedure leading to a lower dispersion degree which consequently, resulted in poor mechanical properties, (An et al., 2010, Ji et al., 2016, Sreenivasulu et al., 2018).

Mechanical and physical properties of graphene–polymer–nanocomposites: Properties of Polymer-Nanocomposites are classified into mechanical and physical properties. There are variations between the mechanical features of the chemically exfoliated graphene and the thermally exfoliated graphene (Jang and Zhamu, 2008). The mechanical properties of nanocomposite include features such as raise in modulus as a loading fraction function.

Moreover, the graphite nanoplatelets have seen to reduce crack propagation in epoxy polymer. Thermally exfoliated graphene has been shown to have a larger interfacial area and aspect ratio. Subsequently, one of the limitations of thermal exfoliation is causing defects and wrinkles on the single layered sheets rather it has been seen to increase mechanical reinforcement,(Galpaya et al., 2013).

In addition, the wrinkles increase surface roughness which enhances the interlocking and mechanical properties of the graphene nanocomposite. Chemically and thermally exfoliated graphene has been seen to increase tensile modulus. Ultimately, it is important to note that, the tensile strength, toughness of the fracture, and the modulus of elasticity increase significantly in graphene based nanocomposite. Moreover, it is also interesting to note that plasticity decreases as compared to other pure polymers. The mechanical characteristics' improvement in graphene polymer nanocomposites is due to various key factors such as the fillers have a high surface area, homogenous scattering experienced within the matrix of the polymer and due to the binding strength between the polymer matrix and graphene nanofillers, (Mogharabi and Faramarzi, 2015).

Thermal Properties: Polymers are sensitive and are degradable at low temperatures, and considered as a limitation since they cannot be used at high temperatures. This degradation behavior of polymers is due to three parameters that include: the onset temperature which starts to degrade them, the degradation temperature, where maximum degradation takes place and the rate of degradation. Moreover, thermal stability has been seen to be increased in graphene that is exfoliated both thermally and chemically based nanocomposites. The increased area of the surface and excellent dispersion in graphene nanocomposites have been demonstrated as a contributing factors of thermal stability. Besides, thermally exfoliated graphene based nanocomposites have also been shown to have a radical raise in the glass-transition-temperature, (Singh et al., 2012, Galpaya et al., 2013, Ji et al., 2016).

Graphene nanofillers have been reposed to reduce gas permeability of polymer based nanocomposites, whereas reduction of gas permeability and water vapour permeation are a great enhancement to increase potential applications in various fields. Moreover, the elevated surface area of graphene is a factor, which attributes to the improvement of both physical and mechanical properties which make the graphene based nanocomposite very useful for the application in biomedical research and development (Mogharabi and Faramarzi, 2015, Sharma et al., 2018).

Biocompatibility of Graphene–Based Nanocomposite: There is recent research and interest geared towards the understanding and exploitation of graphene nanocomposite because of its significant contribution to the use of graphene in the field of biomedical research.

These applications include important techniques such as bio imaging, bio sensing, drug delivery, cancer therapy, and antibacterial materials, (Pinto et al., 2013, Kuila et al., 2012). Moreover, graphene materials have a high surface area that absorbs many molecules that yielding a negative health concern in human and environmental ecosystem. In microbiology research, the graphene based composites has been shown to be of great significance because of its antimicrobial effect to suppress the growth of E coli and different types of bacteria, (Lim et al., 2012, Some et al., 2012, Panda et al., 2018) and also common oral pathogens such as S. mutans, F. nucleatum and P. gingivalis , (He et al., 2015), hence showing promising results of production of antibacterial composites (Pinto et al., 2013). In genetic engineering, the graphene nanocomposite has shown promising results because of its advantageous interaction with the nucleic acids, (Wang et al., 2014). This biocompatibility will be of use in diagnostic purposes and also in development of recombinant DNA vaccines, (Yang et al., 2010, Kuila et al., 2012, Erol et al., 2018).

The graphene based nanocomposite applications in tissue engineering have been reported, though faced with limitations of toxicity related to fibroblasts, epithelial cells of the lungs among others. The toxicity levels are attributed to reactive oxygen species which are known to induce oxidative stress (Pinto et al., 2013). However, this cytotoxicity can be related to the use of graphene oxide in graphene based nanocomposite since studies on graphene oxide showed that it is cytotoxic to cells (Sasidharan et al., 2011), while exfoliated graphene from liquid media does not have cytotoxic effects which emphasizes the importance of graphene, not its derivatives in fabrication graphene based nanocomposite since it will be more useful especially in biomedical applications. In the research findings from (Fan et al., 2010), it showed conclusive evidence that graphene based nanocomposites have good biological safety since it displayed almost non cytotoxic effects. In addition, research conducted recently showed that the toxicological and biological activity of a material was dependent on size, quality, state, and oxygen threshold, (Singh et al., 2012).

In a study conducted by Olteanu et al., (2015), they assessed the cytotoxic effects of three graphene based materials: graphite oxide (GO), thermally reduced graphene oxide (TRGO) and N-doped graphene (N−Gr), on stem cells obtained from the human dental follicle. The study was conducted in vitro and they evaluated cell viability, damage of the cell membrane, mitochondria properties and its effect on cytoskeleton. They also evaluated the oxidative stress induced by the graphene derivatives. From this study, it was shown that GO had the lowest cytotoxic effects compared to the other two. It further showed that GO induced oxidative stress without causing damage to the cell membrane which is a very important property in drug studies since it will not affect the host's cell membranes. The biocompatibility evidence on graphene based nanocomposite determined

that it can be very useful in biomedical applications and development, (Erol et al., 2018).

Graphene In Dental Nanocomposites: In research by Nuvoli et al., (2013), Bis-GMA/TEGDA was the polymer system selected for the experiment, instead of the commonly used Bis-GMA/TEGDMA polymer system. TEGDA is a copolymer of TEGDMA, with similar structures, and TEGDA was selected for the experiment because it is one of the best graphene exfoliation media. During the research, in the experimental section, the dispersion of graphene in TEGDA with graphene nanofiller loadings were acquired by distributing graphite flakes in the TEGDA and ultrasonicating for enabling graphite flakes exfoliation find then centrifuging for letting the un-exfoliated graphite flakes precipitating and recovering liquid-phase that contain graphene. Additionally, it was diluted with appropriate amounts of liquid monomer to obtain the required concentration (0.003, 0011, 0.053 and 0.27 wt.%) and the actual graphene content was checked using UV -Vis and Raman spectra. Thereafter, the right amount of Bis-GMA was applied to obtain 1:1 w/w mixture. Also, 1 wt.% of Benzoyl peroxide was added and the mix homogenized and further poured into silicon molds for polymerization at 80 degrees for 24 hours.

The results of this study showed that this synthesis technique reduced the phenomena of re-aggregation at the time of recovery of graphene nano- filler during solid state. As graphene concentration increases, a rougher surface was observed with the SEM results. Also, the increase of graphene content in the polymer relates to better mechanical reinforcement of the polymer in a proportional manner. Also, due to the presence of graphene in low amounts, the modulus of elasticity and hardness of the surface increased significantly in comparison to the absence of graphene, but glass transition temperature in nano-filled composites was independent of the filler content. The significant result of the study was that the graphene obtained by direct exfoliation is a good and safe alternative to carbon oxidized forms, due to the non-involvement of chemical manipulation in the synthesis.

The research done by Sava et al., (2015) is based on the efficiency and viability of the graphene- silver nano-particles used for the purpose of dental restoration. The aim of the research was to analysis an experimental composite material's mechanical properties, prepared both with and without, graphene-silver nano-particles. The materials used in the composition were monomer mixture with BIS-GMA/TEGDMA, as a matrix, in addition to hydroxyapatite along with silica and bioglasses in addition to graphene-silver nano-particles (0, 5, 10 wt.°/c) forming the reinforcing components in the mixture. During the experimentation section of the study, a total of 10 different composite samples were prepared from each group for each test. Tests for flexural strength of the specimens, diametrical tensile strength, and compressive strength test were performed, as was modulus of elasticity test.

The result revealed that when 5- 10 wt.% of graphene-silver nanoparticles, mixed with hydroxyapatite, silica, and bio-glass, was added to unfilled monomer mixtures of BIS-GMA and TEGDM A, then compressive strength, modulus of elasticity, surface hardness, and flexural strength increased significantly. Thus, the research empirically measures the effects regarding the mechanical properties when graphene-silver nanoparticles were added, and thus, it acts as nanofiller reinforcing material for resin-based dental composite. Recently, Lee et al., (2018a) found when 0.5% of graphene oxide nanosheet (nGO) was added to PMMA, the Vickers micro hardness and resistance to 3-point flexural bending were significantly increased in comparison to control specimens. Furthermore, (Alamgir et al., 2018) added GO and TiO2 to PMMA for reinforcement. The researchers synthesized two types of nanocomposites (PMMA / GO + TiO2 and PMMA / GO).

The structural, mechanical and thermal characteristics of these nanocomposites were then studied. Microstructural and thermal properties demonstrated by these nanocomposites were quite different from pure PMMA. They also demonstrated higher resistance to localized deformation. In comparison to pure PMMA and PMMA/ GO specimens, the PMMA/GO+TiO2 nanocomposites exhibited greater surface hardness and modulus of elasticity. Impact of addition of graphene nanosheets (GNS) on physical, chemical, mechanical and bioactive characteristics of two different dental cement specimens namely EndocemZr (ECZ) and Biodentine (BIO) was investigated by (Dubey et al., 2017). Different proportions (1,3,5 and 4 wt%) of GNS was added to the cement specimens. It is noteworthy that GNS addition made cement setting quicker and improved the hardness without changing the pH of the two types of cements. However, when GNS was added to ECZ, it resulted in considerable decrease in adhesion strength.

Researchers have also tried to add graphene derived nanomaterials to glass ionomers (GI) for the purpose of reinforcement. Several different clinical applications have made use of GI demonstrating ideal coefficient of linear thermal expansion, dynamic fluoride discharge and capability to attach chemically with the intact tooth structure. Still, the utility of this substance continues to be challenged by unsatisfactory physio mechanical characteristics even though considerable progress has been made relating to GI constituents added with different filler types like hydroxyapatite powders, metallic powders and fibers (Baig and Fleming, 2015). Substantial improvement in physio mechanical characteristics of GIs has been achieved by combining graphene with glass ionomer synthesized from poly (acrylic acid) (Malik et al., 2018).

A GICs/FG composite matrix can be formed by the mechanical blending of glass ionomer with fluoride graphene synthesized from the hydrothermal reaction of graphene oxide. In this way, antibacterial, tribological and mechanical characteristics of glass ionomer can be considerably improved (Sun et al., 2018). It has been

reported that increment in proportion of FG in glass ionomer results in increment in antibacterial activity, reduction in micro cracks and pores and reduction in vulnerability to microbial attack and erosion. Moreover, surface characteristics and degree of conversion has been reported to be improved with reinforcing resin polymer matrices containing graphene gold nanoparticles as fillers. It can, therefore, be considered as a good approach for improving the physicochemical characteristics of dental nanocomposites (Sarosi et al., 2016).

The development of antibiofilm adhesives has become a necessity because of the existence of micorgaps between tooth healthy tissues and dental restoration resulting in microbial invasion (Ferracane and Hilton, 2016). Considering the antibacterial characteristics of graphene, utilization of GFNs as antibiofilm filler and antimicrobial filler for dental adhesives has been suggested by (Bregnocchi et al., 2017). GFNs modified dental adhesives were shown to cause inhibition of growth and adhesion of S. mutans with no effect on adhesion properties and mechanical efficiency. In another study, (Lee et al., 2018b) have investigated the biological and mechanical characteristics of orthodontic bonding adhesive (Transbond XT (LV) enriched in GO and bioactive glass mixture (BAG) in a proportions of 1,3 and 5% (BAG+GO). In comparison to LV, improved microhardness has been demonstrated by the adhesive containing 3% and 5% by wt. of GAG+GO. However, the shear bond strengths of all specimens were found to be statistically indifferent. Also, anti-demineralization and antibacterial action of the BAG+GO group were found to be superior.

CONCLUSION

Owing to their impressive structural and other characteristics, graphene as well as its derivatives have recently turned into promising tools to be used in the biomedical field. These nano-size-materials exhibit great versatility and peculiar properties like huge surface area and impressive thermal stability, electrical conductivity and mechanical strength. Moreover, these nanomaterials can be incorporated into other materials for improvement in their bioactivity and optimization of their mechanical, physical and chemical characteristics. Reports included in this review indicate the great utility of graphene for several different dental applications. Accordingly, it is highly recommended that more studies must be conducted for investigating the advantages and the utility of this nanomaterials in dental applications.

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