

POST-GEL SHRINKAGE STRAIN AND DEGREE OF CONVERSION OF NANOHYBRID RESIN COMPOSITE CONTAINING GRAPHENE OXIDE NANOPARTICLES

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ABSTRACT

Objectives: This study evaluated the effect of incorporating Graphene oxide nanoparticles on the post-gel shrinkage strain and degree of conversion of resin composite restorative material.

Materials and methods: Graphene oxide nanoparticles was synthesized and incorporated within a nanohybrid resin composite (Filtek™ Z250 XT). 20 specimens (7x4x2 mm) were fabricated for polymerization shrinkage and divided into 2 equal halves. 10 specimens were fabricated without incorporation with Graphene oxide nanoparticles (the control group; group 1), while the other half was incorporated with 2% concentration by weight and referred to group 2. The post-gel shrinkage strain was measured by strain gauge technique. The degree of conversion was measured using a Fourier Transform Infrared (FTIR) spectrometer. Similar groups specimens were prepared by polymerizing the material in a disc-shaped split white Teflon mold 2 mm thick and 4 mm in diameter. Ten disc-shaped specimens were prepared for each experimental condition. The resultant data were subjected to independent T-test ($P \leq 0.05$) to reveal the statistically significant difference.

Results: The incorporation of Graphene oxide nanoparticles significantly reduced the post-gel shrinkage strain. On the other hand, the degree of conversion reported no significant difference between the two groups.

Conclusion: Addition of Graphene oxide nanoparticles to resin composite restorative material positively affect the polymerization shrinkage while maintaining the degree of conversion.

KEYWORDS: Graphene oxide NP, resin composite, polymerization shrinkage, degree of conversion.

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INTRODUCTION

Resin composite is a reliable aesthetic restorative material with a good clinical performance. However, the clinical longevity of the restoration is affected by many factors such as development of secondary caries, marginal adaptation, fracture and degradation of the surface finish¹. Polymerization shrinkage is an inherited property of the polymerization process. This shrinkage impairs the marginal adaptability of the restorations and subsequently leads to lower survival rate². Polymerization shrinkage is affected by many factors such as the chemistry of the organic matrix and the fillers of the resin composites. Modifications of the fillers shape, size, distribution and composition had been advocated as these modifications showed a significant control of the polymerization shrinkage³.

All contemporary resin composite restorative materials shrink during polymerization, resulting in a volumetric reduction ranging from 1.5% to 5%, depending on the molecular structure of the monomer, the amount of filler, rate of cure and degree of conversion of the resin matrix. The total shrinkage can be divided into two components: the pre-gel and post-gel phases. During pre-gel polymerization, the composite is able to flow, which relieves stresses within the structure. After gelation, flow ceases and cannot compensate for shrinkage stresses. Post-gel polymerization, therefore, results in clinically significant stresses in resin composite-tooth bond and the surrounding tooth structure⁴⁻⁷.

Furthermore, the degree of conversion affects the longevity of the resin composites. Degree of conversion could be defined as the number of monomers changed to polymers². Therefore, lower degree of conversion means more unreacted monomers that are more susceptible to release, hydroxylation and oxidation in addition to their plasticizing effect, that resulted in lowering the mechanical and biological properties of the restorations^{2,3,8-10}.

In the attempts of improving the properties of the resin composites, modifications in the resin com-

posite fillers reserved its unique place in this revolution against resin composite limitations. From the newly introduced materials in the dentistry, the graphene, graphene oxide and reduced graphene oxide. Graphene formed of sp²-bonded pure carbon atoms that arranged in a 2D monolayer with a honeycomb crystal lattice. Graphene oxide contains oxygen atoms bonded to carbon atoms and contains many functional groups at its surface such as oxygen, epoxide, carbonyl, phenyl and hydroxyl groups. However, reduced graphene oxide can be considered as an intermediate structure between the purely-carbon graphene and highly-oxidized graphene oxide^{11,12}.

The graphene and its derivatives reported an improvement in the modulus of elasticity, surface hardness, compressive strength and flexural strength^{13,14}. Moreover, graphene and its derivatives showed an antibacterial effect after their integration with different materials¹¹⁻¹⁴. As a result of these unique properties, they were tested by adding to many materials such as poly methyl methacrylate, resin composites, glass ionomer cement, orthodontics adhesives and dentine adhesives^{14,15,17-22}.

The antibacterial effect of graphene oxide nanoparticles (GO NPs), especially on dental pathogens, has been discovered recently, and it has been shown that GO NPs displays the highest antibacterial effect in comparison to other graphene-based materials such as graphite, graphite oxide, graphene oxide, and reduced graphene oxide^{11,14,15,17}.

Therefore, the aim of the current study was to evaluate the effect of incorporation of graphene oxide nanoparticles on the post-gel shrinkage strain and degree of conversion of a nanohybrid resin composite restorative material.

MATERIAL AND METHODS

Preparation of Graphene Oxide Nanoparticles

A 9:1 mixture of concentrated sulfuric acid/Phosphoric acid (H₂SO₄/H₃PO₄) (360:40 mL) was introduced to a mixture of graphite flakes (3.0 g)

and Potassium permanganate (KMnO_4) (18.0 g). The liquid was heated to 50°C for 12 hours while stirring, then cooled to room temperature before being poured onto ice (-400 mL) with 30% Hydrogen peroxide (3 mL). The filtrate was centrifuged for 4 hours at 4000 rpm. The solid substance that remained washed in a series of washes.

Characterization of Graphene Oxide Nanoparticles:

A. Visible Near Infra-Red (Vis-NIR) Spectroscopy:

Visible Near Infra-Red (Vis-NIR) Spectrophotometer was used to monitor the absorption rate of the graphene nanoparticles (Fathy & Riad (2019)²³ and Prabhu & Poulouse (2012)²⁴). Data was recorded using a special computer software and the absorption rate curve was drawn.

B. Transmission Electron Microscope Imaging (TEM Imaging):

The transmission electron microscope was used to record size, shape and particles' distribution (Fathy & Riad (2019)²³, Pérez-Díaz et al. (2015)²⁵ and Espinosa-Cristóbal et al (2009)²⁶).

C. X-Ray diffraction (XRD) analysis:

The crystallite size is usually determined and calculated from the broadening of the reflection profile of the XRD pattern and the interlayer spacing from the corresponding position of the peaks (Aidaros & Kamh²⁷).

An XRD pattern has been performed using XPERT-PRO Powder Diffractometer system, with 2 theta ($20^\circ - 80^\circ$), with Minimum step size 2Theta: 0.001, and at wavelength ($K\alpha$) = 1.54614° .

Calculation of Graphene Oxide Nanoparticles volume and resin composite mass:

Split Teflon mold was used to prepare standardized resin composite specimens (7mm length x 4mm width x 2mm height). Mold was placed on

a glass slide, and then the Filtek™ Z250 XT resin composite (Table 1) was packed into the mold hole by a gold-plated instrument and covered with Mylar strip. Resin composite was then polymerized using light emitting diode (LED) (3M ESPE Elipar Deep Cure-S) Light-Curing Unit of wavelength range (λ) = 430–490 nm, and maximum light intensity $I \approx 500 \text{ mW/cm}^2$, for 20 seconds according to manufacturer instructions. The excess material was removed and discarded. The resin composite specimen was removed from the mold and weighted using a Sukot® sensitive digital balance and it was found to be 0.3 gm. Weight calculation of graphene oxide powder as follows: Graphene oxide was tested in 0.2% per weight concentration. Concentration per weight * actual weight of the specimen. Concentration: $0.2\% * 0.3 = 0.0006 \text{ gm}$.

According to the previous calculations, each 0.3 gm of resin composite needs 0.0006 gm graphene oxide to achieve the 0.2% concentration. In order to prepare 2 ml graphene oxide in ethanol with concentration 0.03 gm/ml, a weight of 0.06 gm of graphene oxide was added to 2 ml of absolute ethanol and stirred for 15 minutes with a glass stirring rod then sonicated for 10 minutes in ultrasound bath then the mixture was stored in dark and sealed container (Luceño-Sánchez et al., (2018)²⁸).

The ethanol solution containing graphene oxide nanoparticles were applied by micropipette into amalgam capsule and then left for 5 minutes to allow complete evaporation of ethanol. Then, a weight of 0.3 gm of resin composite was taken into the amalgam capsule. The capsule was mounted on the amalgamator and mixing was done for 10 seconds (Aref et al., (2015)²⁹). The resin composite was then packed again into the Teflon mold and covered with a mylar strip to prepare 10 specimens. Another 10 specimens were prepared from resin composite only (control group). Resin composite specimens were then polymerized for 40 seconds.

TABLE (1) Material used, specification, composition, lot number and manufacturer

Material/ Specification	Composition	Manufacturer	Lot number
Filtek™ Z250 XT Nano-hybrid composite (Z250)	<u>Matrix:</u> Bis-GMA ¹ , UDMA ² , BIS-EMA ³ , PEGDMA ⁴ & TEGDMA ⁵ . <u>Fillers:</u> (82% by weight) Surface-modified zirconia/silica with a median particle size of approximately 3 microns or less and non-agglomerated/non-aggregated 20-nanometer surface-modified silica particles.	3M ESPE, Dental Products, Saint Paul, MN,USA https://www.3mespe.com	NC07012

1-Bis-GMA: Bis-phenol A glycol di-methacrylate

3-Bis-EMA: Ethoxylated bisphenol A glycol methacrylate,

5-TEGDMA: Triethylene glycol di-methacrylate

2-UDMA: Urethane dimethacrylate

4-PEGDMA: Poly ethylene glycol di-methacrylate

Post-gel shrinkage strain measurement:

A foil electrical resistance strain gauge (Kyowa Electronic Instruments Co, LTD, Tokyo, Japan, Lot #Y4683M) was used to measure the post-gel shrinkage strain of the resin composite specimens. The head of an electrical resistant strain gauge was fixed to a flat glass slab using a sticky tape and the hole of the Teflon mold was centralized and fixed over the strain gauge. The other side of the strain gauge was then connected to the strain monitoring device (Strain-Meter PCD-300A Kyowa-Electronic Instruments Co, LTD, Tokyo, Japan).

Degree of conversion measurement:

Degree of conversion of the tested resin composite specimens was measured using Fourier transform infrared spectroscopy (FT-IR) (VERTEX 70, Bruker, Germany). From each group, 10 specimens were packed inside a disc-shaped Teflon mold (2 mm in thickness and 4 mm in diameter). The resin composite was packed inside the mold against glass slap using a gold-plated instrument then tested by a spectrum from 400 to 4000 cm^{-1} for measuring the absorbance peak of aliphatic C=C at 1637 cm^{-1} (polymerizable) and aromatic C-C absorbance peak at 1607 cm^{-1} (unpolymerizable) as a reference peak. Each specimen was cured as discussed before and the same absorbance peaks were measured again. The degree of conversion was measured by baseline technique from the following equation:

$$DC (\%) = [1 - (A_{1637}/A_{1608})_{\text{cured}} / (A_{1637}/A_{1608})_{\text{uncured}}] \times 100$$

Statistical analysis

Data was analyzed with IBM® SPSS® Statistics Version 25 for Windows. The mean and standard deviation values were calculated for each group. Normality test was performed using Kolmogorov-Smirnov test and revealed normal distribution between values of each group. Homogeneity test was performed using Levene's test and revealed homogenous distribution between all variables. Therefore, independent T test was performed (with significance level was set at $P \leq 0.05$) to reveal the statistically significant difference between the variables.

RESULTS

Post-gel shrinkage strain:

The results of the current study revealed that the incorporation of nano graphene oxide particles resulted in a significant decrease in the post-gel shrinkage strain (p-value = 0.000) from 1978 $\mu\text{m}/\text{m} \pm 300.51$ for control group to 501 $\mu\text{m}/\text{m} \pm 163.18$ for the graphene incorporated group.

Degree of conversion:

The results of the present study showed no statistically significant difference (p-value = 0.217) between the control group (61.44% \pm 15.56) and after incorporation of nano graphene oxide particles (46.91% \pm 18.64).

TABLE (2) The mean and standard division of post-gel shrinkage strain ($\mu\text{m/m}$) and Degree of conversion (%) of the tested materials.

	Post-gel shrinkage strain ($\mu\text{m/m}$) Mean \pm SD	Degree of conversion (%) Mean \pm SD
Control	1978 \pm 300.51	61.44 \pm 15.56
Composite containing Graphene oxide NP	501 \pm 163.18	46.91 \pm 18.64
P-value	0.000*	0.217

*: indicates significant difference between variables ($p\leq 0.05$) by independent T test.

Figure (1) represents the absorbance peaks before and after curing of both groups. There is a marked reduction in the C=C absorbance peak of both groups after curing indicating conversion of C=C bond to C-C.

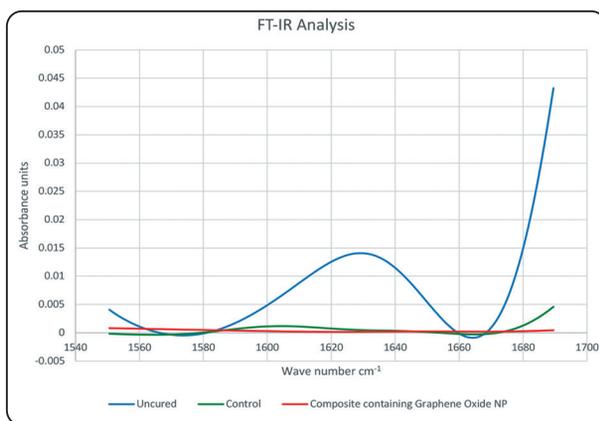


Fig. (1) The FT-IR spectra of uncured, control and composite containing graphene oxide specimens represent the decrease in the absorbance peak of C=C after curing in both groups.

DISCUSSION

Light curing of resin composites results in their polymerization shrinkage. Unfortunately, this polymerization shrinkage results in stresses that can be transferred to the bonding interface and the remaining tooth structure, leading to interfacial adhesive failures, cuspal deflection, and/or enamel microcracks, post-operative sensitivity and recurrent caries¹⁻³. During polymerization, the double carbon-carbon bonds are broken down and

shorter single carbon-carbon bonds are formed. This rearrangement of the reacted monomers shortens of the intermolecular distances between the reacted monomers resulting in what is called polymerization shrinkage³⁰.

The polymerization process could be classified by two macroscopic stages; gel stage followed by vitrification stage. The former stage is characterized by incipient gel formation while the later stage is characterized by formation of a glassy structure and increase in the modulus of elasticity. The polymerization stresses could be classified by pre-gel and post-gel stages. During the pre-gel stage, the developed stresses can be relaxed by the flow of the material while the stresses developed at post-gel stage can't be relaxed as the material flow is ceased. Therefore, the post-gel stresses persist and are the stresses of clinical importance³¹.

The polymerization stresses are also affected by the degree of conversion which is the percentage of carbon-carbon double bonds that is transferred to single bonds. Increasing the degree of conversion improves the mechanical and biological properties of the resin composite restorations and subsequently their clinical reliability^{3,31}.

The polymerization shrinkage and degree of conversion are multifactorial properties. They related to matrix chemistry, fillers size and shape and percent, photoinitiator chemistry and concentration and light curing unit type^{32,33}.

Many trials have been suggested in order to decrease this polymerization shrinkage such as incremental packing of the resin composite restorations, soft-start light curing method, changing in the chemistry of the resin matrix, incorporation of higher fillers content and using of indirect resin composite restorations^{2,3}. One of the newly introduced nanofillers in the medical and dental field is the graphene oxide¹¹⁻¹³. Graphene oxide reported an improvement in the mechanical properties of polymeric materials^{13,14}. Moreover, the antibacterial effect of GO NPs has been reported by many authors¹³⁻¹⁶. Therefore, this study was conducted to evaluate the effect of GO NPs on the polymerization shrinkage and degree of conversion of methacrylate-based resin composite material.

Polymerization shrinkage of dental resin composite could be measured by many ways such as strain gauges, dilatometer, bonded disc-based Watts method, scanning laser beam, video imaging, linear displacement and force and by using fiber-optic sensors. However, strain gauge recorded only the post-gel deformation and neglect the pre-gel deformation which gives a more reliable results as the post-gel deformation is the more clinically related deformation^{31,34}.

Degree of conversion of resin composite could be measured by many equipment such as Fourier transform infrared spectroscopy, Raman Spectroscopy, electron paramagnetic resonance, nuclear magnetic resonance, differential scanning calorimetry and differential thermal analysis. However, FTIR is the most frequently used technique by authors^{31,35}.

The results of the current study revealed that incorporation of the GO NPs into the resin composite leads to a significant decrease in the post-gel shrinkage strain that is means a decrease in the polymerization shrinkage of the tested material. Polymerization shrinkage predominantly is affected by the resinous matrix². Therefore, increasing the filler percentage results in decrease

the polymerization shrinkage and subsequent developed shrinkage strain.

Moreover, filler size affects this shrinkage strain in two ways. The first one is the surface area of the fillers (with a constant filler load). The higher surface area of the smaller fillers exerts more constrains on the matrix that increases resultant strain. The second way is the translational movements of the fillers which enhance the stress relaxation of the matrix³.

Many authors investigated the effect of incorporation of different filler materials and evaluated their effect over the polymerization shrinkage. **Lin** et al., (2020)³³ studied the effect of addition Zirconia and rice husk silica as fillers in resin composite and reported a decrease in the polymerization shrinkage with an increase in the filler percent. Similarly, **Par** et al., (2020)³⁶ reported a decrease in the polymerization shrinkage of an experimental resin composites with the increase in concentrations of unsilanized bioactive glass fillers. Moreover, **Kumar** et al., (2016)³⁷ incorporated silane-modified nanosilica particles with different concentrations in to an experimental resin composite and found that increasing fillers amount leads to decrease in polymerization shrinkage.

The results of the present study exhibited that the incorporation of 0.2% of GO NPs resulted in a statistically non-significant difference in the degree of conversion compared with control group. This insignificant difference may be referred to the inversely proportional relation between the degree of conversion and fillers size as the smaller filler size exhibited a limited light scattering and reflection³⁸. Moreover, the limitation of the FT-IR in measuring only the superficial surface of the tested specimens which is well irradiated compared with deep layers³⁵.

In accordance with the present study, **Velo** et al., (2022)³⁹ reported a non-significant difference after incorporation of GO to experimental resin composites with a percent of 0.3% and 0.5% compared to control group. Moreover,

Tsagkalias et al., (2017)⁴⁰ reported that addition of 0.1% of GO on poly methyl methacrylate showed a similar polymerization conversion as control group. However, the increase amount of GO to 0.5% and 1% reported a decrease in the polymerization conversion. They claimed that decrease in polymerization conversion to the inhibitory effect of GO on the initiator system which is not significant with small amount 0.1%. However, in the present study, GO was added with 0.2% to resin composite that was too small to inhibit degree of conversion.

On the other hand, **Bin-Shuwaish et al.**, (2020)²² reported a decrease in degree of conversion after addition of 2% GO to an experimental adhesive. They claimed that decrease due to the increase of the GO percent results in their agglomeration and hindering the passage of curing light through the material.

Furthermore, **Alrahlah et al.**, (2020)⁴¹ reported an increase in the degree of conversion of dental resin composites after addition of silanized GO fillers. This contradiction was clarified by the silanization of the GO fillers results in interaction between the GO fillers and the resin matrix. Moreover, the silanized GO may decreased the inhibitory effect of GO over the initiator system. In addition, **Sarosi et al.**, (2016)²⁰ reported an increase in the degree of conversion after addition of graphene–gold nanoparticles. They claimed that the high thermal conductivity of the fillers played an effective role in increasing the degree of conversion. These conflicting results can be referred to the difference in the chemical formula of the used fillers.

The results of the present study found that addition of GO NPs to resin composite decreased the post-gel shrinkage strain with neglectable effect on the degree of conversion. The linear polymerization shrinkage has an independent relation with the degree of conversion as the strain gauge recorded only the post-gel shrinkage strain as the tested material reached a significant rigidity that overcome the resistance of the metallic foil of the

measuring device. However, in the pre-gel stage, the reduction of the specimen in the axial direction can be compensated by shrinkage in the radial direction^{32,37}.

In accordance with the results of the present study, **Lins et al.**, (2019)³⁰, **Yu et al.**, (2017)⁴² and **Kumar et al.**, (2016)³⁷ reported that degree of conversion is directly proportioned to the polymerization shrinkage as the increased number of cured monomers means more approaching of molecules to form single carbon-carbon bond that is has shorter intermolecular distance than van der Waals forces that bonds the precured monomers. On the other hand, **Salem et al.**, (2019)³² found a lower polymerization shrinkage with resin composites with higher degree of conversion after investigating one conventional and four different bulk fill resin composites. They claimed these findings to the difference in the filler's percent and chemistry of resinous matrix of the tested materials that affects the amount of double bonds, viscoelastic properties, flexibility and molecular mass.

CONCLUSION

Within the limitations of the current study, it could be concluded that the incorporation of graphene oxide nanoparticles into resin composite can produce a reliable resin composite restoration with reduced polymerization shrinkage but is not the impact factor on the degree of conversion.

REFERENCES

1. Velo MM de AC, Coelho LVBF, Basting RT, Amaral FLB do, Franca FMG. Longevity of restorations in direct composite resin: literature review. RGO -Rev Gaúcha Odontol. 2016;64(3):320-326.
2. Hamdy T. Polymerization shrinkage in contemporary resin-based dental composites: A Review Article. Egypt J Chem, 2021; 64(6):3087-3092.
3. Aminoroaya A, Neisiany RE, Khorasani SN, Panahi P, Das O, Madry H, et al. A review of dental composites: challenges, chemistry aspects, filler influences, and future insights. Compos B Eng. 2021;216:108852.

4. Ferracane JL. Developing a more complete understanding of stresses produced in dental composites during polymerization. *Dent Mater.* 2005;21(1):36-42.
5. Braga RR, Ballester RY, Ferracane JL. Factors involved in the development of polymerization shrinkage stress in resin-composites: a systematic review. *Dent Mater.* 2005;21(10):962-970.
6. Davidson CL, de Gee AJ. Relaxation of polymerization contraction stresses by flow in dental composites. *J Dent Res.* 1984;63(2):146-148.
7. Feilzer AJ, De Gee AJ, Davidson CL. Setting stress in composite resin in relation to configuration of the restoration. *J Dent Res.* 1987;66(11):1636-1639.
8. Galvão MR, Caldas SG, Bagnato VS, de Souza Rastelli AN, de Andrade MF. Evaluation of degree of conversion and hardness of dental composites photo-activated with different light guide tips. *Eur J Dent.* 2013;7(1):86-93.
9. Moldovan M, Balazsi R, Soanca A, Roman A, Sarosi C, Prodan D, et al. Evaluation of the Degree of Conversion, Residual Monomers and Mechanical Properties of Some Light-Cured Dental Resin Composites. *Materials (Basel).* 2019;12(13):2109.
10. Al-Rawas M, Johari Y, Mohamad D, Khamis M.F, Ahmad W.M.A.W, Ariffin Z, et al. Water sorption, solubility, degree of conversion, and surface hardness and topography of flowable composite utilizing nano silica from rice husk. *J. Mater. Res. Technol.* 2021;15:4173-4184.
11. Dasari Shareena TP, McShan D, Dasmahapatra AK, Tchounwou PB. A Review on Graphene-Based Nanomaterials in Biomedical Applications and Risks in Environment and Health. *Nanomicro Lett.* 2018;10(3):53.
12. Li X, Liang X, Wang Y, Wang D, Teng M, Xu H, et al. Graphene-Based Nanomaterials for Dental Applications: Principles, Current Advances, and Future Outlook. *Front. Bioeng. Biotechnol.* 2022;10:804201.
13. Nuvoli D, Alzari V, Sanna R, Scognamillo S, Alongi J, Malucelli G, et al. Synthesis and characterization of graphene-based nanocomposites with potential use for biomedical applications. *J Nanopart Res.* 2013;15(3):1512-1519.
14. Gamal R, Gomaa Y, Said A. Incorporating nano graphene oxide to poly-methyl methacrylate; antibacterial effect and thermal expansion. *J Mod Res.* 2019;1(1):19-23.
15. Sun L, Yan Z, Duan Y, Zhang J, Liu B. Improvement of the mechanical, tribological and antibacterial properties of glass ionomer cements by fluorinated graphene. *Dent Mater.* 2018;34(6):e115-e127.
16. Wu R, Zhao Q, Lu S, Fu Y, Yu D, Zhao W. Inhibitory effect of reduced graphene oxide-silver nanocomposite on progression of artificial enamel caries. *J Appl Oral Sci.* 2018;27:e20180042.
17. Lee JH, Jo JK, Kim DA, Patel KD, Kim HW, Lee HH. Nano-graphene oxide incorporated into PMMA resin to prevent microbial adhesion. *Dent Mater.* 2018;34(4):e63-e72.
18. He J, Zhu X, Qi Z, Wang C, Mao X, Zhu C, et al. Killing dental pathogens using antibacterial graphene oxide. *ACS Appl Mater Interfaces.* 2015;7(9):5605-5611.
19. Ardu S, Duc O, Di Bella E, Krejci I, Daher R. Color stability of different composite resins after polishing. *Odontology.* 2018;106(3):328-333.
20. Sarosi C, Biris AR, Antoniac A, Boboia S, Alb C, Antoniac I, et al. The nanofiller effect on properties of experimental graphene dental nanocomposites. *J. Adhes. Sci. Technol.* 2016;30:1779-1794.
21. Lee SM, Yoo KH, Yoon SY, Kim IR, Park BS, Son WS, et al. Enamel Anti-Demineralization Effect of Orthodontic Adhesive Containing Bioactive Glass and Graphene Oxide: An In-Vitro Study. *Materials (Basel).* 2018;11(9):1728.
22. Bin-Shuwaish AM, Al-Hamdan RS, Alresayes S, Ali T, Almutairi B, Vohra F, et al. Influence of graphene oxide filler content on the dentin bond integrity, degree of conversion and bond strength of experimental adhesive. A SEM, micro-Raman, FTIR and microtensile study. *Mat Res Exp.* 2020;7:115403.
23. Fathy HM, Riad M. The effect of silver nanoparticles incorporation in the self-etch adhesive system on its antibacterial activity and degree of conversion: an in-vitro study. *F1000Research* 2019;18:1-8.
24. Prabhu S, Poulouse EK. Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. *Int Nano Lett* 2012;2:1-10.
25. Pérez-Díaz MA, Boegli L, James G, Velasquillo C, Sánchez-Sánchez R, Martínez-Martínez RE, et al. Silver nanoparticles with antimicrobial activities against *Streptococcus mutans* and their cytotoxic effect. *Mater Sci Eng C Mater Biol Appl.* 2015;55:360-366.
26. Espinosa-Cristóbal LF, Martínez-Castañón GA, Martínez-Martínez RE, Loyola-Rodríguez JP, Patiño-Marín N, Reyes-Macías JF, et al. Antibacterial effect of silver nanoparticles against *Streptococcus mutans*. *Mater. Lett.* 2009;63:2603-2606.
27. Aidaros N, Kamh R. Effect of incorporating nano-pearl and nano-seashell particles into fluoride-based pits and fissure

- sealant on enamel remineralization of permanent extracted molars: An In Vitro Study. *ADJ*, 2021;3(4):159-172.
28. Luceño-Sánchez JA, Maties G, Gonzalez-Arellano C, Diez-Pascual AM. Synthesis and Characterization of Graphene Oxide Derivatives via Functionalization Reaction with Hexamethylene Diisocyanate. *Nanomaterials*. 2018; 8(11):870.
 29. Aref A, Riad M, Harhash A. Shear punch strength of resin composite incorporating silver nanoparticles. *CDJ*. 2015;31:1983-1991.
 30. Lins R, Vinagre A, Alberto N, Domingues MF, Messias A, Martins LR, et al. Polymerization Shrinkage Evaluation of Restorative Resin-Based Composites Using Fiber Bragg Grating Sensors. *Polymers (Basel)*. 2019;11(5):859.
 31. Kaisarly D, Gezawi ME. Polymerization shrinkage assessment of dental resin composites: a literature review. *Odontology*. 2016;104(3):257-270.
 32. Salem HN, Hefnawy SM, Nagi SM. Degree of Conversion and Polymerization Shrinkage of Low Shrinkage Bulk-Fill Resin Composites. *Contemp Clin Dent*. 2019;10(3):465-470.
 33. Lin GSS, Abdul Ghani NRN, Ismail NH, Singbal KP, Yusuff NMM. Polymerization Shrinkage and Degree of Conversion of New Zirconia-Reinforced Rice Husk Nanohybrid Composite. *Eur J Dent*. 2020;14(3):448-455.
 34. Rajan G, Raju R, Jinachandran S, Farrar P, Xi J, Gangadhara Prusty B. Polymerisation Shrinkage Profiling of Dental Composites using Optical Fibre Sensing and their Correlation with Degree of Conversion and Curing Rate. *Sci Rep* 2019;9:3162.
 35. Moraes LG, Rocha RS, Menegazzo LM, de Araújo EB, Yukimito K, Moraes JC. Infrared spectroscopy: a tool for determination of the degree of conversion in dental composites. *J Appl Oral Sci*. 2008;16(2):145-149.
 36. Par M, Mohn D, Attin T, Tarle Z, Tauböck T.T. Polymerization shrinkage behaviour of resin composites functionalized with unsilanized bioactive glass fillers. *Sci. Rep.* 2020;10:15237.
 37. Kumar SR, Patnaik A, Bhat I. Analysis of polymerization shrinkage and thermo-mechanical characterizations of resin-based dental composite reinforced with silane modified nanosilica filler particle. *J. Mater. Des. Appl.* 2016;230(2):492-503.
 38. Habib E, Wang R, Zhu XX. Monodisperse silica-filled composite restoratives mechanical and light transmission properties. *Dent Mater* 2017;33(3):280-287.
 39. Velo M.M.d.C, Filho F.G.N, de Lima Nascimento T.R., Obeid A.T, Castellano L.C, Costa R.M, et al. Enhancing the mechanical properties and providing bioactive potential for graphene oxide/montmorillonite hybrid dental resin composites. *Sci Rep*. 2022;12:10259.
 40. Tsagkalias IS, Manios TK, Achilias DS. Effect of Graphene Oxide on the Reaction Kinetics of Methyl Methacrylate in Situ Radical Polymerization via the Bulk or Solution Technique. *Polymers (Basel)*. 2017;9(9):432.
 41. Alrahlah A, Khan R, Al-Odayni AB, Saeed WS, Bautista LS, Vohra F. Evaluation of Synergic Potential of rGO/SiO₂ as Hybrid Filler for BisGMA/TEGDMA Dental Composites. *Polymers*. 2020; 12(12):3025.
 42. Yu P, Yap A, Wang XY. Degree of Conversion and Polymerization Shrinkage of Bulk-Fill Resin-Based Composites. *Oper Dent*. 2017;42(1):82-89.