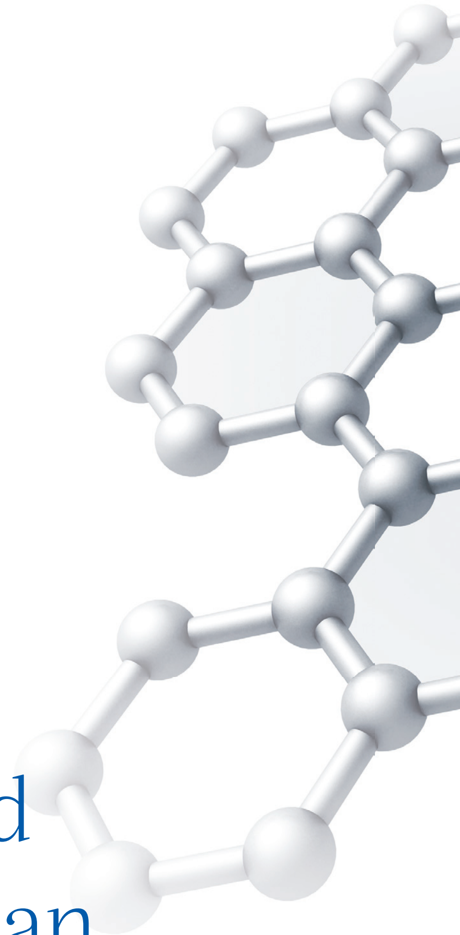

The effect of thermocycling on surface microhardness of PMMA doped with graphene: an experimental in vitro study

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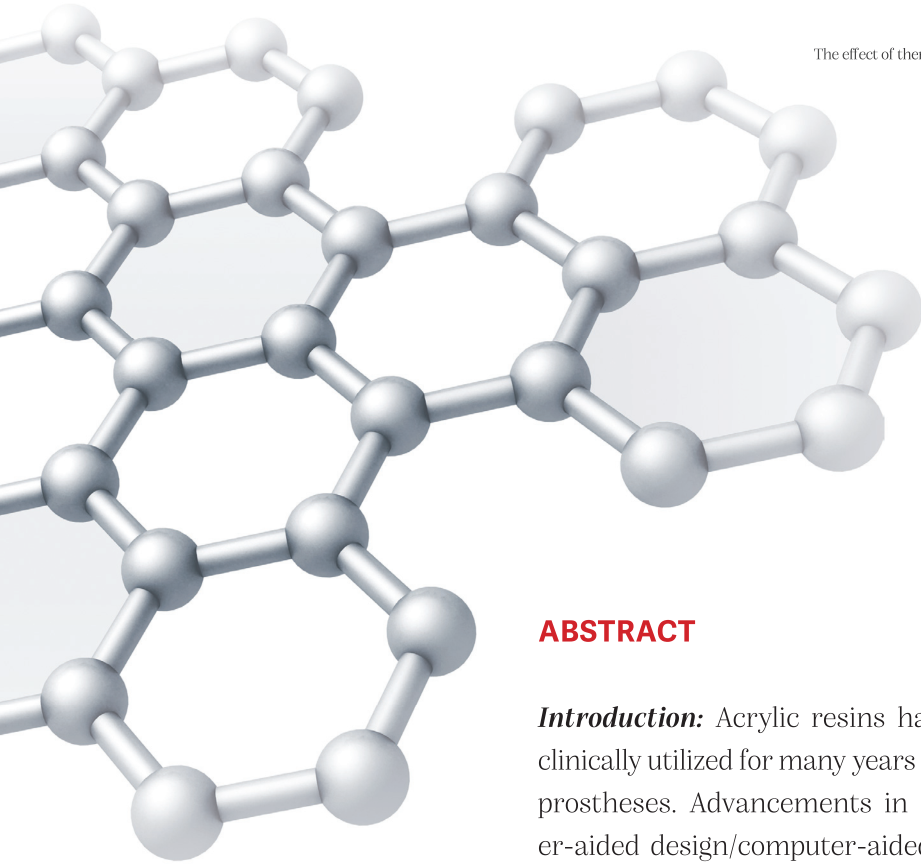

ABSTRACT

Introduction: Acrylic resins have been clinically utilized for many years in dental prostheses. Advancements in computer-aided design/computer-aided manufacturing (CAD/CAM) materials and recent developments in nanotechnology have enabled the use of graphene as reinforcement phase in polymethyl methacrylate (PMMA) for CAD/CAM restorations with promising results. ***Material and Methods:*** 96 samples from monochrome G-CAM discs (G-MONO) and multichrome G-CAM discs (G-MULTI) were equally divided into 4 groups (n = 24): group 1 (G-MONOc) and group 2 (G-MULTIc) served as a control and was not thermocycled, group 3 (G-MONOt) and group 4 (G-MULTIt) were subjected to thermocycling. Measurements were made using a digital Shore A durometer and values were statistically analyzed using 1-way ANOVA followed by Tukey's test. ***Results:*** The results were very similar for G-MONO thermocycled and not thermocycled; the one-way ANOVA revealed no significant differences between group 1 (G-MONOc) and group 3 (G-MONOt) and between group 2 (G-MULTIc) and group 4 (G-MULTIt). All paired Tukey test comparisons were also not significantly different ($\alpha < 0.05$). ***Conclusions:*** CAD/CAM poly (metilmethacrylate) PMMA doped with graphene has successfully passed the aging process based on 10,000 thermal cycles maintaining its surface microhardness values. Maintaining the surface microhardness will allow less wear and greater longevity of the restoration, which opens up the possibility of using PMMA doped with graphene in permanent restorations. Further investigations are needed to establish mechanical properties of PMMA doped with graphene.

KEYWORDS

Graphene. PMMA resin. Computer-aided design. Thermocycling.

INTRODUCTION

Acrylic resins have been clinically utilized for many years in dental prostheses, including complete or removable partial dentures, provisional fixed restorations, and implant-supported prostheses. Most prosthetic acrylic resins consist of polymethyl methacrylate (PMMA) resin and additional copolymers[1] due to its high availability, low cost, acceptable aesthetics, easy fabrication and biocompatibility.[2] The addition of reinforcement fillers (such as glass, silica, carbon fiber, steel wires, and polyaramid)[3] and advancements in computer-aided design/computerized manufacturing (CAD/CAM) materials, CAD/CAM poly(methyl methacrylate) (PMMA)-based polymers in our case, has improved the mechanical properties of PMMA resins for provisional fixed restorations.[3,4,5] However, poly(methyl methacrylate) (PMMA) based resins still have moderately low mechanical properties that prevent their use for permanent restorations.[6]

Although metal-ceramic restorations are clinically successful, the metal-free restorations have become more popular in last years for supplying the disadvantages in its esthetic appearance and biocompatibility of metal-ceramic restorations.[7] Recent developments in nanotechnology have enabled the use of graphene as reinforcement phase in polymethyl methacrylate (PMMA) for CAD/CAM restorations with promising results.[8,9]

Graphene is a single atomic sheet of conjugated sp2 carbon atoms arranged in a honeycomb pattern. It possesses exceptional physicochemical and optical properties with extremely high mechanical strength and modulus of elasticity. Graphene has an enormous potential in new therapeutic strategies in dental field (potential applications of graphene are being studied in tissue engineering, dental implants, endodontics, restorative dentistry or periodontology).[10]

Oral thermal changes oscillate between minimum temperatures of 0º C and maximum of 67º C.[11]

Thermocycling is an in vitro process used to simulate the extreme conditions of thermal variation in the oral environment produced from eating, drinking and breathing that can cause damage in the surface and mechanical properties of dental materials.[12,13] Different thermocycling regimes have been proposed, the temperature range used widely is 5º C for cold provocation, and 55º C for hot provocation[13,14,15].

The purpose of this study was to evaluate the impact of thermocycling on surface microhardness of CAD-CAM poly (metilmethacrylate) PMMA doped with graphene. The null hypothesis was that there would be no significant difference in the surface microhardness before and after thermocycling.

MATERIAL AND METHODS

The selected materials included C2 monochrome G-CAM discs (G-MONO) (LOT: L19091120053) and C2 multichrome G-CAM discs (G-MULTI) (LOT: L18091120131) provided by Graphenano Nanotechnologies (Paterna, Valencia ,Spain).

A total of 96 samples (n= 48 G-MONO and n= 48 G-MULTI) were designed and manufactured by CAD-CAM in a rectangular shape (64 x10 x 3,36 mm) (Fig 1).

Once all the samples were milled, all samples were taken in an incubator in a 100% wet condition at 37º C for 24 hours to be treated.

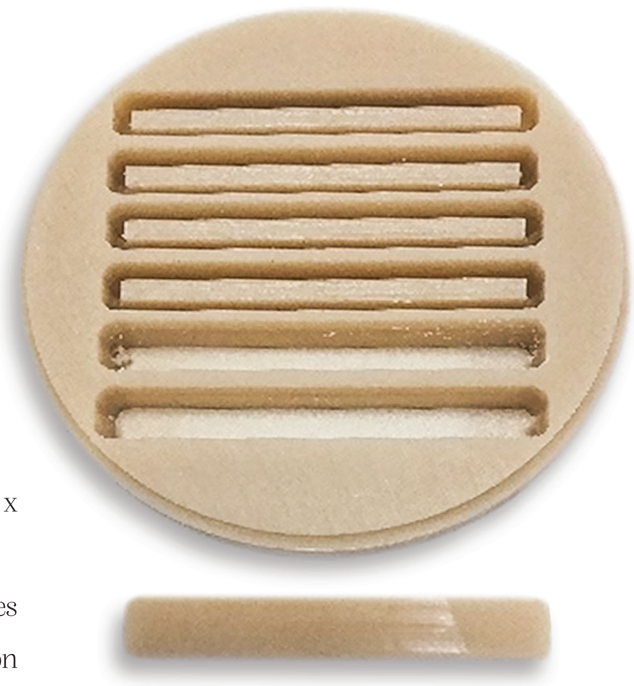

Figure 1: Samples designed by CAD/CAM.

“Graphene has an enormous potential in new therapeutic strategies in dental field.”

Samples from G-MONO and G-MULTI were equally divided into 4 groups (n = 24): group 1 (G-MONOc) and group 2 (G-MULTIc) served as a control and was not thermocycled, group 3 (G-MONOt) and group 4 (G-MULTIt) were subjected to thermocycling for 10,000 cycles in distilled water between 5° C and 55° C with a dwell time of 30 seconds.

Shore A hardness measurements

The hardness measurements of the samples were made using a digital Shore A durometer (Sauter HD, Balingen, Germany). This method is based on the penetration of a needle on the surface of the material. The digital durometer was placed in a vertical position, and the presser foot was applied perpendicular to the surface of the samples as rapidly as possible without shock. Three hardness measurements were taken from each sample and the average values were calculated as the final Shore A value. The hardness values are expressed in Shore A units, and the reading ranges from 0 to 100 Shore. Hardness is inversely proportional to the penetration of the needle; that is, the greater the penetration, the lower the value indicated in the scale.

Statistical analysis

The hardness values were statistically analyzed using 1-way ANOVA followed by Tukey’s test. The level of significance was fixed at p=0.05. All statistical analyses were performed using Statistix 2020 Analytical Software (Tallahassee, USA).

RESULTS

The mean values of surface microhardness for all groups are shown in Figure 2 and Table 1.

The results were very similar for G-MONO thermocycled and not thermocycled; for G-MULTI thermocycled a small decrease in the surface hardness was found. The one-way ANOVA revealed no significant differences between group 1 (G-MONOc) and group 3 (G-MONOt) and between group 2 (G-MULTIc) and group 4 (G-MULTIt). All paired Tukey test comparisons were also not significantly different ($\alpha < 0.05$).

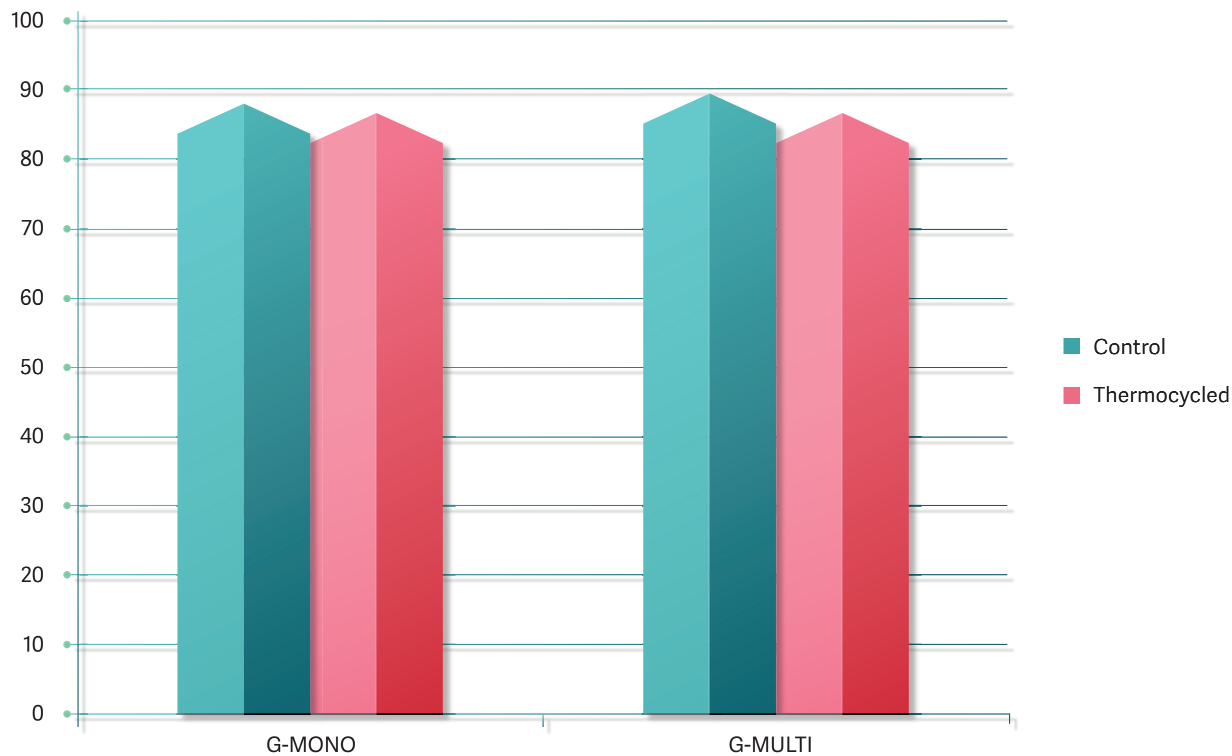

Figure 2: Comparison of mean values of surface microhardness for G-MONO (control and thermocycled) and G-MULTI (control and thermocycled).

Table 1: Mean values of surface microhardness for all groups.

MATERIAL	CONDITION	SHORE HARDNESS
G-Mono	Thermal Cycling	87.125
	No termal cycling	88.6875
G-Multi	Thermal Cycling	86.875
	No Thermal cycling	89.375

DISCUSSION

The null hypothesis of this study was accepted because tested materials had no significant difference in the surface microhardness before and after thermocycling.

Hardness evaluation has frequently been used to predict dental material wear. The clinical implication of hardness is important, because its resistance to abrasion is directly related to its longevity.[16] Dayan et al.[17] evaluated wear resistance and microhardness of various provisional fixed prosthesis materials and they showed that higher surface microhardness was associated with less wear.

Ayaz et al.[18] evaluated the effects of thermal cycling on surface microhardness of two polymethylmethacrylate (PMMA) denture base resins and they observed an increase of hardness values at both 15,000 and 30,000 thermal cycles may be due to polymerization of residual monomer during thermal cycling by heat. However, Diaz-Arnold et al.[19] in a 14-day storage study observed that hardness of most provisional fixed prosthodontic materials based on conventional resins decreases over time.

Hardness values are directly proportional to the amount of residual monomer content.[16] CAD/CAM poly(methyl methacrylate) (PMMA) based polymers improved structural properties of the conventional resins such as low mechanical stability due to porosity, voids, and polymerization shrinkage, decrease residual monomer release, improve color stability and optical properties[4]. Rayyan et al.[3] compared material properties of provisional CAD/CAM crowns with those of conventional, manually fabricated provisional crowns and they observed that CAD/CAM crowns presented better color stability, higher mechanical properties, and better fit than those fabricated by conventional direct techniques. Al-Dwairi et al.[5] observed higher surface hardness in CAD/CAM PMMA than conventional heat-polymerized PMMA, lower levels of residual monomers in CAD/CAM PMMA may be the reason. CAD/CAM PMMA blocks are industrially polymerized under optimum polymerization conditions with no interference from water, giving adequate time for post-polymerization processes and relaxation phenomena.[6]

Recent developments in nanotechnology have enabled the use of graphene as reinforcement phase into CAD/CAM PMMA resins with promising properties[10]. Agustín-Panadero and cols.[7] analyzed in vitro the mechanical behavior of five types of complete coverage crowns fabricated from different materials and they showed that fracture resistance values of polymethyl methacrylate (PMMA) doped with graphene exceeded maximum mastication forces. Lee et al[9] found that the addition of 0.5 wt% of nGO (graphene oxide nanosheets) into PMMA significantly enhanced the flexural strength and adding more than 0.5 wt% nGO significantly increased the surface hardness. Di Carlo and cols[21] observed a statistically significant difference in the values of flexural strength and elastic modulus and a greater homogeneity of the mechanical behavior during the bending test of PMMA doped with graphene compared with conventional PMMA.

The results of the present study were in line with previous studies, PMMA doped with graphene has successfully passed the aging process of 10.000 thermal cycles maintaining its surface microhardness values which will allow less wear and therefore greater longevity of our restoration.

However, Agarwalla and cols[20] compared translucency, hardness and strength parameters from materials used for CAD/CAM restorations and they showed limited improvements in properties studied, PMMA doped with graphene presented similar properties with unmodified PMMA and other materials used for permanent single tooth restorations.

Although this study was conducted to simulate aging by thermocycling, the effects of beverages, food, mouthwashes, saliva (pH, composition etc.) and the mechanical actions of chewing and brushing in PMMA doped with graphene should be considered in future studies. The performance of PMMA doped with graphene in clinically realistic circumstances and its mechanical properties needs further investigation.

CONCLUSIONS

According to the results obtained, we can conclude that CAD/CAM poly(methyl methacrylate) PMMA doped with graphene like material of reinforcement phase has successfully passed the aging process based on 10,000 thermal cycles maintaining its surface microhardness values. Maintaining the surface microhardness will allow less wear and greater longevity of the restoration, which opens up the possibility of using PMMA doped with graphene in permanent restorations. Further investigations are needed to establish mechanical properties of PMMA doped with graphene.

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