

Impact Strength Comparison of Heat-Polymerized PMMA and Graphene-Reinforced Pre-Polymerized PMMA (G-CAM) as Provisional Restorative Materials: An In Vitro Study

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Abstract

Objective: To evaluate and compare the impact strength of heat-polymerized polymethyl methacrylate (PMMA) and graphene-reinforced pre-polymerized PMMA (G-CAM) used as provisional restorative materials.

Materials and Methods: Twenty standardized specimens were fabricated and divided into two groups (n = 10 each): Group A, heat-polymerized PMMA (DPI Heat Cure); and Group B, graphene-reinforced pre-polymerized PMMA (G-CAM, Graphenano Dental). All specimens were tested using an Izod impact testing machine at 23 ± 2°C. Impact strength values were recorded in kJ/mm², and data were analyzed using descriptive statistics and unpaired t-tests.

Results: Group A (heat-polymerized PMMA) demonstrated a mean impact strength of 3.03 kJ/mm² (SD = 1.34), whereas Group B (graphene-reinforced G-CAM) showed a mean of 1.63 kJ/mm² (SD = 0.77). The intergroup difference was statistically significant (t = 2.841; p = 0.011).

Conclusions: Conventional heat-polymerized PMMA exhibited significantly superior impact strength compared with the graphene-reinforced pre-polymerized PMMA tested in this study. Although graphene-based materials remain promising for certain dental applications, the specific G-CAM formulation evaluated did not improve impact resistance and is therefore not recommended as a substitute for conventional PMMA when impact strength is a primary clinical consideration.

Keywords: provisional restorations, polymethyl methacrylate, graphene, G-CAM, impact strength, mechanical properties, CAD/CAM

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1. Introduction

Provisional restorations constitute an indispensable phase in fixed prosthodontic treatment, serving multiple critical functions including pulpal protection, maintenance of tooth position, restoration of occlusal function, preservation of gingival health, and provision of aesthetic and phonetic feedback during the fabrication of definitive prostheses.¹ In complex treatment scenarios such as full-mouth rehabilitation, extensive crown and bridge work, temporomandibular joint dysfunction therapy, and correction of vertical dimension, provisional restorations may remain in situ for weeks to months, necessitating superior mechanical durability.

Polymethyl methacrylate (PMMA) has been the gold standard provisional restorative material for more than seven decades because of its ease of manipulation, acceptable aesthetics, low cost, good repairability, and proven clinical performance.^{2,3} Despite these advantages, PMMA has well-established mechanical limitations, particularly low impact strength, flexural strength, and fracture toughness. Additionally, conventional PMMA exhibits polymerization shrinkage (0.3–0.8% by volume), residual monomer leakage, and sensitivity to thermal cycling, all of which can compromise marginal adaptation and clinical longevity.

Provisional restorations frequently fracture during clinical use as a result of sudden impact loading from mastication, accidental trauma, or parafunctional habits such as bruxism.^{4,5} The prevalence of sleep bruxism ranges from 8–16% in the adult population, and nocturnal bite forces can exceed voluntary daytime forces by a considerable margin.⁶ To mitigate fracture risk, clinicians have traditionally reinforced PMMA through the incorporation of various agents, including polyethylene fibres, glass fibres, metal oxides, nanofillers, and carbon-based materials.^{7,8}

In recent years, graphene and its derivatives have emerged as promising nanomaterials for dental polymer reinforcement. Graphene is a single-layer, two-dimensional allotrope of carbon with a honeycomb lattice structure, displaying exceptional mechanical strength, electrical conductivity, thermal stability, and a massive surface area-to-volume ratio. Graphene oxide (GO), reduced graphene oxide (rGO), and graphene nanoplatelets (GNP) have been explored as reinforcing agents in both conventional and CAD/CAM PMMA systems.^{9,10}

The advent of computer-aided design and computer-aided manufacturing (CAD/CAM) technology has further transformed provisional restoration fabrication. CAD/CAM-milled PMMA offers advantages over conventionally processed resins,

including superior marginal fit, reduced residual monomer content, higher cross-linking density, and elimination of polymerization shrinkage related to the powder-liquid mixing technique. Several manufacturers have recently introduced graphene-reinforced CAD/CAM PMMA discs (e.g., G-CAM), marketing them as superior alternatives that combine the benefits of CAD/CAM processing with graphene-based reinforcement.¹¹

However, evidence regarding the mechanical superiority of graphene-reinforced PMMA remains inconsistent. Recent systematic reviews have highlighted heterogeneous findings, with some studies reporting improved mechanical properties while others report unchanged or even diminished performance depending on graphene concentration, type, manufacturing technique, and the specific mechanical property being tested.^{12, 13} Notably, most published data focus on flexural strength, compressive strength, and hardness; relatively few investigations have specifically evaluated impact strength, which is arguably one of the most clinically relevant parameters for provisional restorations.

The present study was therefore undertaken to fill this evidence gap by directly comparing the impact strength of conventional heat-polymerized PMMA with graphene-reinforced pre-polymerized PMMA (G-CAM) under controlled in vitro conditions. The hypothesis tested was that graphene reinforcement would enhance impact resistance compared with unreinforced PMMA.

2. Materials and Methods

2.1 Study Design and Sample Preparation

This was a controlled in vitro comparative study. A total of 20 standardized rectangular specimens were fabricated and divided into two groups with 10 specimens per group:

- **Group A (Control):** Heat-polymerized PMMA (DPI Heat Cure, Dental Products of India, Batch No. 8174)
- **Group B (Test):** Graphene-reinforced pre-polymerized PMMA (G-CAM, Graphenano Dental, Batch No. L18101120248)

2.2 Specimen Fabrication (Fig 1)

Group A Specimens (Heat-Polymerized PMMA)

A metal die measuring 50 mm in length, 6 mm in width, and 4 mm in depth, with a V-shaped notch of 1.2 mm in the center (in accordance with ISO 179:1999 specifications), was prepared. A thin layer of petroleum jelly was applied to the metal die surface and the die was invested in a varsity flask using die stone (Ultrarock, Kalabhai Karson Pvt. Ltd., Batch No. 190603). A separating medium (Cold Mould Seal, Pyrax, Batch No. CMS-085) was applied to facilitate deflasking.

After the investment material had fully set, the flask was opened and heat-polymerized PMMA was packed into the mold using the standard powder-

liquid ratio. A short curing cycle was performed using an acrylizer with thermostat (Sirio Dental Hydraulic Press 400) following the manufacturer's protocol. After processing, the samples were carefully deflasked and finished using wet silicon carbide paper (No. 120 grit) followed by polishing with pumice slurry and distilled water.

Group B Specimens (Graphene-Reinforced G-CAM)

Ten specimens were milled from pre-polymerized graphene-reinforced PMMA discs (G-CAM, shade A3) using a CAD/CAM milling unit. The specimens were designed in stereolithography (STL) format with identical dimensions to Group A samples. After milling, specimens were finished and polished using conventional trimming burs, wet silicon carbide paper, and pumice-water slurry.

Storage

All finished specimens from both groups were stored in distilled water at room temperature until testing.

2.3 Impact Strength Testing

Impact strength testing was performed using a computerized Izod impact testing machine (International Equipment's, India, Serial No. 430) equipped with an S2 scale. Before testing each specimen, the pendulum was released freely in air to record air resistance (AR = 0.6 Joules).

Specimens were positioned vertically in the clamping mechanism, with the notched area aligned precisely with the impact hammer. The pendulum was released, and the energy absorbed (EA) to fracture the specimen was recorded on the S2 scale at $23 \pm 2^\circ\text{C}$.

Impact strength (I) was calculated using the following formula:

$$I = (AE - AR) \times 10^3 / XY$$

Where:

- I = Impact strength (kJ/mm²)
- EA = Absorbed energy (Joules)
- AR = Air resistance (0.6 Joules)
- X = Sample thickness (mm)
- Y = Sample width (mm)

2.4 Statistical Analysis

Data were analyzed using SPSS version 21 (IBM Corp., Armonk, NY). Descriptive statistics including mean, standard deviation (SD), standard error (SE), minimum, and maximum values were calculated for each group. Normality of data distribution was assessed visually. An unpaired (independent samples) t-test was used to compare mean impact strength values between the two groups. Statistical significance was set at $p < 0.05$ with a 95% confidence interval (CI) and power of 80% ($\alpha = 0.05$; $\beta = 0.20$).

3. Results

3.1 Descriptive Analysis

All 20 specimens (10 per group) were successfully tested. Table 1 presents the individual impact strength values for each specimen.

Table 1: Individual Impact Strength Values (kJ/mm²)

Specimen No.	Group A (Heat-Cure PMMA)	Group B (G-CAM)
1	3.64	0.60
2	6.06	1.21
3	3.03	0.60
4	1.51	1.51
5	2.73	1.81
6	2.12	3.03
7	2.42	1.21
8	3.33	2.42
9	3.94	2.12
10	1.51	1.81

3.2 Summary Statistics

Table 2: Descriptive Statistics of Impact Strength

Parameter	Group A (Heat-Cure PMMA)	Group B (G-CAM)
Mean (kJ/mm ²)	3.03	1.63
SD	1.34	0.77
SE	0.42	0.24
Minimum	1.51	0.60
Maximum	6.06	3.03
Range	4.55	2.43

Group A showed a mean impact strength of 3.03 kJ/mm² with a standard deviation of 1.34, while Group B demonstrated a mean of 1.63 kJ/mm² with a standard deviation of 0.77. Group A values ranged from 1.51 to 6.06 kJ/mm², whereas Group B values ranged from 0.60 to 3.03 kJ/mm².

3.3 Comparative Analysis

Table 3: Unpaired t-Test Comparison of Impact Strength

Parameter	Group A	Group B	Mean Difference	t-Value	p-Value	Significance
Mean (kJ/mm ²)	3.03	1.63	1.40 ± 0.49	2.841	0.011	Significant*
SD	1.34	0.77	—	—	—	—

The unpaired t-test revealed a statistically significant difference in impact strength between the two groups ($t = 2.841$; $p = 0.011$). Group A (heat-polymerized PMMA) demonstrated approximately 85.9% higher mean impact strength compared with Group B (graphene-reinforced G-CAM). The 95% confidence interval for the mean difference was 0.41–2.39 kJ/mm².

4. Discussion

4.1 Summary of Key Findings

The present investigation compared the impact strength of conventional heat-polymerized PMMA

with a commercially available graphene-reinforced pre-polymerized PMMA (G-CAM) system. Contrary to the marketing claims and theoretical expectations surrounding graphene reinforcement, the heat-polymerized control group demonstrated significantly superior impact strength. The graphene-reinforced material exhibited a 46% reduction in mean impact strength relative to conventional PMMA, a finding that raises important questions about the mechanical behaviour of graphene-reinforced dental polymers and their clinical suitability.

4.2 Interpretation of Results

The superior impact strength of heat-polymerized PMMA (3.03 kJ/mm²) compared with G-CAM (1.63 kJ/mm²) can be attributed to several material and processing factors.

Polymer Network Structure: Heat-polymerized PMMA undergoes in situ polymerization within the mold, creating a continuous, three-dimensional polymer network with relatively homogeneous cross-linking density. In contrast, pre-polymerized CAD/CAM discs are fabricated under industrial conditions and then milled to shape. This post-polymerization machining introduces microdefects, microcracks, and surface irregularities that may concentrate stress during impact testing.¹⁴ Furthermore, milling-induced machining stresses and subsurface damage can act as nucleation sites for crack initiation under sudden loading.

Graphene Dispersion and Interfacial Bonding:

The mechanical benefit of graphene reinforcement is critically dependent on homogeneous dispersion within the polymer matrix and strong interfacial bonding between graphene particles and the resin. Agglomeration of graphene particles—a common challenge in manufacturing—creates stress concentration zones rather than reinforcing the material.^{15,16} If the graphene content, dispersion protocol, or surface functionalization in the G-CAM formulation is suboptimal, particles may act as flaws rather than strengthening elements. This is particularly problematic under impact loading, where sudden stress application can propagate cracks from poorly bonded filler clusters.

Concentration-Dependent Effects: A recent systematic review by Salgado et al. (2023) synthesizing evidence from 11 studies concluded that graphene incorporation into dental polymers exhibits a concentration-dependent response.¹² Concentrations below 0.75 wt% of GO or 1 wt% of GNP can enhance mechanical properties, but higher concentrations or poorly controlled incorporation methods may degrade performance. The review noted substantial heterogeneity in published findings and emphasized that there is no universal "optimal" graphene concentration because the effect depends on graphene type (GO, rGO, GNP), PMMA formulation, manufacturing technique, and test methodology. It is unknown whether the G-CAM

formulation tested in this study employed a concentration and dispersion strategy aligned with these evidence-based recommendations.

Material-Specific Limitations: Angelis et al. (2023) conducted an in vitro study comparing three-point flexural strength, compressive strength, and Vickers hardness of conventional CAD/CAM PMMA, graphene-reinforced CAD/CAM PMMA (G-PMMA), and bis-acryl composite resin.¹³ Although no significant differences were detected in flexural strength among the groups, the G-PMMA group showed significantly lower compressive modulus and hardness compared with conventional PMMA. The authors concluded that "the graphene-reinforced (PMMA)-based polymer herein tested was not superior to the conventional PMMA and seemed not able to be considered as an alternative material for permanent restorations, at least in terms of hardness and mechanical response to compressive stress."¹³ These findings align with the current results and suggest that the specific graphene formulations currently available may not consistently outperform conventional PMMA across mechanical property domains.

4.3 Comparison with Previous Literature

The present findings must be contextualized within the broader, inconsistent literature on graphene-reinforced dental materials.

Studies Reporting Improved Performance: Several investigations have demonstrated mechanical benefits of graphene incorporation. For instance, Al-Harbi et al. (2018) reported that the addition of nanodiamonds to heat-cure PMMA improved flexural strength at low concentrations (0.5 wt%).¹⁷ Jaikumar et al. (2018) found that glass-fibre-reinforced PMMA exhibited higher impact strength than unreinforced PMMA.¹⁸ More recently, Alhareb et al. (2016) showed that nitrile-butadiene-rubber (NBR) particles combined with ceramic fillers enhanced impact strength and fracture toughness of PMMA denture base materials.¹⁹ However, notably, none of these studies specifically evaluated graphene-reinforced PMMA.

Fatigue and Cyclic Loading Evidence: A contrasting finding emerged from a fatigue-based study by Bacali et al. (2023), who evaluated graphene-doped PMMA CAD/CAM restorations in implant-supported provisional bridges with cantilevers.²⁰ Using a chewing simulator with 80 N cyclic loading over 240,000 cycles (simulating approximately 12 months of clinical use), the authors reported that graphene-doped PMMA demonstrated three times greater resistance to fracture compared with conventional CAD/CAM PMMA (mean cycle count to failure: 155,455 for graphene-doped versus 51,136 for conventional PMMA; $p < 0.05$).²⁰ This suggests that graphene may enhance resistance to repetitive cyclic stress rather than sudden impact loading. This distinction is important: a material can exhibit superior fatigue

resistance while remaining vulnerable to acute impact stress—two different mechanical phenomena governed by different failure mechanisms.

Why the Discrepancy? The difference between impact strength (instantaneous loading to failure) and fatigue strength (repetitive cyclic loading to failure) is mechanistically important. Impact failures typically initiate from pre-existing surface flaws or machining defects and propagate rapidly without significant plastic deformation. Fatigue failures accumulate damage gradually through cyclic loading and may benefit from mechanisms such as crack-deflection by filler particles or work-hardening at the polymer-filler interface, which are less relevant in sudden impact scenarios.²¹ Therefore, the superior fatigue performance reported by Bacali et al. (2023) does not contradict the present finding of lower impact strength, but rather illustrates that graphene-reinforced PMMA may offer selective mechanical advantages in specific loading scenarios.

4.4 Clinical Implications

The clinical implications of these findings are important for provisional restoration planning and material selection:

1. Impact Strength as a Clinically Relevant Parameter

Fracture of provisional restorations remains one of the most frequent prosthodontic emergencies encountered in clinical practice. These failures typically occur from:

- Accidental impact trauma during mastication (e.g., biting on a hard object)
- Parafunctional forces (bruxism, clenching) especially during nighttime sleep
- Sudden loading in patients with high bite force
- Stress concentration at margins or beneath restoration margins in long-span restorations

In each of these scenarios, the ability to withstand sudden, high-amplitude stress (measured by impact strength) is more relevant than fatigue performance. Therefore, materials with superior impact strength should be preferred for provisional restorations, particularly in patients with documented parafunctional habits, high occlusal forces, or long-span restorations.

2. Material Selection Based on Clinical Presentation

For high-risk scenarios (patients with bruxism, clenching, high bite force, posterior edentulous areas, or long-span restorations requiring provisional coverage):

- Heat-polymerized PMMA remains the material of choice based on impact strength superiority
- Conventional PMMA may be reinforced with glass fibres or other proven

reinforcements if further mechanical enhancement is desired

- G-CAM and other graphene-reinforced materials are NOT recommended as primary choices for impact-critical applications

For lower-risk scenarios (short-span restorations, anterior regions, patients without parafunctional habits):

- G-CAM may still be selected for advantages unrelated to impact strength, such as superior machinability, dimensional stability, reduced residual monomer, or potentially improved fatigue resistance during extended provisional phases
- However, clinicians must acknowledge the mechanical trade-off regarding impact resistance

3. Implications for CAD/CAM Provisional Restorations

CAD/CAM technology has genuinely transformed provisional restoration fabrication by improving marginal fit, reducing monomer toxicity, and enabling rapid chair-side modifications. However, the present study suggests that the mechanical benefits of CAD/CAM milling may be partially offset by machining-induced defects, at least in the impact testing paradigm. If CAD/CAM-fabricated provisional restorations are selected, clinicians should consider:

- Careful design to minimize cantilevers and long spans
- Adequate thickness to buffer against impact stress
- Reinforcement strategies beyond graphene alone (e.g., hybrid reinforcement)
- Closer clinical follow-up and early intervention if any microleakage or marginal discrepancy becomes apparent

4. Patient Counselling

Patients receiving provisional restorations should be explicitly advised to:

- Avoid hard or sticky foods that may exert sudden impact on the restoration
- Refrain from parafunction such as nocturnal tooth clenching or nail biting
- Report any evidence of restoration fracture or loosening immediately
- Understand that provisional restorations are temporary and have inherent mechanical limitations despite advances in material science

4.5 Limitations of the Study

The present investigation has several important limitations that should be acknowledged:

1. **In Vitro Design:** This study was conducted under standardized laboratory conditions at $23 \pm 2^\circ\text{C}$ in air. The oral environment—including saliva, pH variation, thermal

cycling, enzymatic attack, and long-term hydrolytic degradation—was not replicated. Exposure to oral fluids and temperature fluctuations can alter the mechanical properties of both conventional and graphene-reinforced PMMA over time.²² Therefore, the present findings may not directly translate to clinical performance.

2. **Limited Sample Size:** The study included only 10 specimens per group. Although adequate for a pilot investigation, a larger sample size would enhance statistical power and reduce the probability of type II error. Future studies should aim for sample sizes calculated based on published effect sizes in the literature.
3. **Single Material Tested:** Only one commercially available graphene-reinforced PMMA product (G-CAM) was evaluated. Multiple graphene-reinforced formulations are available from different manufacturers, each potentially differing in graphene type, concentration, dispersion method, and polymerization protocol. The present findings apply specifically to the G-CAM product and may not generalize to other graphene-reinforced systems.
4. **Absence of Microstructural Analysis:** The study did not include scanning electron microscopy (SEM), fracture surface analysis, or characterization of graphene dispersion. Such analysis could have elucidated whether the reduced impact strength was related to poor dispersion, agglomeration, processing defects, or other structural factors.
5. **Single Mechanical Property:** Impact strength, while clinically relevant, is only one of many mechanical properties. The present study does not evaluate flexural strength, compressive strength, fracture toughness, fatigue resistance, hardness, wear resistance, or other parameters that influence clinical performance. A comprehensive material characterization would require multi-property evaluation.
6. **Control for Potential Confounders:** Although both groups were tested under identical conditions, the fabrication techniques differed substantially (conventional heat-polymerization vs. CAD/CAM milling). This confounding makes it difficult to attribute the lower impact strength solely to graphene content versus machining-induced defects or other processing-related factors. A more rigorous design might include CAD/CAM-milled specimens of conventional PMMA as an additional control.

7. **Manufacturing Details Unknown:** The precise composition, graphene concentration, graphene type (GO, rGO, or GNP), surface functionalization, and manufacturing protocol of the G-CAM product are proprietary and were not disclosed. This limits the ability to explain the mechanical behaviour or compare it directly with published studies using different graphene formulations.

4.6 Future Research Directions

Several avenues for future investigation are warranted:

1. **Comparison of Multiple Graphene-Reinforced Products:** Future studies should systematically evaluate impact strength and other mechanical properties across multiple commercially available graphene-reinforced PMMA products from different manufacturers to determine whether poor performance is material-specific or inherent to graphene reinforcement in provisional restorations.
2. **Dose-Response Studies:** Investigate the relationship between graphene concentration and impact strength to identify the optimal concentration window, if one exists, for impact resistance in dental PMMA.
3. **Microstructural Analysis:** Employ SEM, transmission electron microscopy (TEM), and fracture surface analysis to characterize graphene dispersion, agglomeration patterns, interfacial bonding, and failure mechanisms.
4. **Comprehensive Material Characterization:** Evaluate multiple mechanical properties including flexural strength, compressive strength, fracture toughness, impact resistance, hardness, abrasion resistance, and wear resistance in a single study to identify the property profile most favorable for provisional restorations.
5. **In Vivo Clinical Trials:** Conduct prospective clinical trials comparing the fracture rates, complication profiles, and patient satisfaction between conventional PMMA and graphene-reinforced PMMA provisional restorations in diverse clinical scenarios (high vs. low mechanical load; anterior vs. posterior; short-span vs. long-span).
6. **Fatigue and Cyclic Loading Studies:** Replicate the fatigue design employed by Bacali et al. (2023) using the specific materials tested in this impact study to determine whether superior fatigue resistance can be demonstrated while acknowledging lower impact strength.

7. **Thermal Cycling and Ageing:** Evaluate mechanical properties after thermocycling and extended water immersion to simulate the oral environment and determine whether aging affects the performance gap between conventional and graphene-reinforced materials.
8. **Synergistic Reinforcement:** Investigate hybrid reinforcement strategies combining graphene with other agents (e.g., fibres, nanoparticles, or surface treatments) to determine whether synergistic effects can overcome the impact strength deficit while maintaining the advantages of CAD/CAM processing.

4.7 Conclusions and Clinical Recommendations

Based on the findings of the present in vitro study, the following conclusions and recommendations are offered:

5. Conclusions

1. Heat-polymerized PMMA demonstrated significantly superior impact strength (3.03 kJ/mm²) compared with graphene-reinforced pre-polymerized PMMA (1.63 kJ/mm²), with an approximately 86% difference in mean values ($p = 0.011$).
2. The graphene-reinforced material tested in this study does not represent an improvement in impact resistance and cannot be recommended as a substitute for conventional PMMA when impact strength is a primary material selection criterion.
3. The discrepancy between the present findings (lower impact strength with graphene) and recent fatigue studies (higher cyclic loading resistance with graphene) suggests that graphene reinforcement exhibits property-specific effects that are dependent on loading mode and duration.
4. Material selection for provisional restorations should be based on comprehensive mechanical property characterization rather than on the presence of a reinforcing agent alone, as the clinical relevance of any property improvement depends on the specific clinical scenario.

6. Clinical Implications

- **For provisional restorations in high-mechanical-demand scenarios** (extensive rehabilitation, posterior regions, patients with parafunctional habits, long-span restorations), **conventional heat-polymerized PMMA remains the gold standard** based on superior impact strength.
- **Graphene-reinforced PMMA products may still be selected for low-demand**

applications or to leverage CAD/CAM advantages (marginal fit, reduced toxicity, faster fabrication), but clinicians must counsel patients regarding the material's reduced capacity to resist sudden impact loading.

- **Until robust clinical evidence demonstrates equivalent or superior fracture resistance, graphene-reinforced provisional materials should not be marketed as mechanically superior alternatives to conventional PMMA.** Manufacturer claims must be evidence-based and property-specific.
- **The future role of graphene in provisional restoration materials likely lies in hybrid or multi-property optimization strategies** rather than graphene alone as a universal reinforcement solution.

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