# **ORIGINAL ARTICLE**

# THE EVOLUTION OF DENTAL RESTORATIONS: 3D PRINTING RESINS VS. METAL-CERAMIC – ADVANTAGES AND LIMITATIONS

Marina Olimpia Amărăscu<sup>1</sup>, Adrian Daniel Târtea<sup>2,\*</sup>, Silviu Vîrvoreanu<sup>3</sup>, Simina Găman<sup>4</sup>, Antonia Samia Khaddour<sup>1</sup>, Alexandru Andrei Iliescu<sup>2</sup>, Iulia Roxana Marinescu<sup>2</sup>

<sup>1</sup> Department of Oral Morphology, University of Medicine and Pharmacy of Craiova, 200349 Craiova, Romania <sup>2</sup> Department of Oral Rehabilitation, University of Medicine and Pharmacy of Craiova, 200349 Craiova, Romania <sup>3</sup> Dentist with private practice, Craiova, Romania <sup>4</sup> Department of Prosthetics Dentistry, University of Medicine and Pharmacy of Craiova, 200349 Craiova, Romania

All authors contributed equally to this work

\* Corresponding author: **Adrian Daniel Tartea** Email: daniel.adrian.tartea@gmail,com

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Abstract: With the development of nanotechnology, nanomaterials have been increasingly used in dentistry in recent years. Among them, graphene and ceramics its derivatives have attracted great attention due to their excellent physicochemical properties. (1) Background: The present study aimed to compare technological aspects related to the fabrication of prosthetic crowns from a new material made from reinforced resins in comparison to the most commonly used crowns currently, metal-ceramic crowns. (2) Methods: 54 prosthetic restorations were performed for 45 patients using Exocad software for the digital design, 3D printing for metal framework and long term printable resins with two different printing technology. (3) Results: The prosthetic restorations were performed on both arches, both on the frontal and lateral areas, those made of reinforced resin being obtained by 3D printing, and the metal-ceramic ones by the classical method. (4) Conclusions: The use of CAD/CAM technology allows the processing of new composite materials such as those reinforced with a significantly longer lifespan.

**Keywords**: 3D printing, composite materials, prosthetic restorations, CAD/CAM

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# 1. Introduction

PMMA has gained popularity for various dental applications due to its excellent which include low density, properties, esthetics. cost-effectiveness, ease of handling, and adaptable physical and mechanical properties [1]. Although there are a number of concerns related to the use of PMMA, such as fracture of dentures due to water absorption and poor impact and flexural strength, ongoing research has introduced a variety of modifications to overcome and improve its properties (such as conductivity, water absorption, solubility, impact and flexural strength). For example, studies several have reported the improvement of PMMA materials by reinforcing them with a variety of fibers [2-7], nanoparticles [8-15] and nanotubes [16-20]. Similarly, PMMA-based biocomposites with the addition of epoxy, polyamide, or styrene butadiene resins have been reported to improve the impact resistance of PMMA [21].

With development the of nanotechnology, nanomaterials have been increasingly used in dentistry in recent years. Among them, graphene and its derivatives have attracted great attention due to their excellent physicochemical properties, morphology, biocompatibility, multidifferentiation and antimicrobial activity. The challenges and prospects of graphenebased nanomaterials in dental applications have begun to be discussed more and more in recent years. Among various nanomaterials, graphene, as a two-dimensional (2D) carbonbased nanomaterial, is the thinnest and strongest material. In 2004, it was first isolated by Novoselov and Geim using mechanical exfoliation with an adhesive tape and they won the Nobel Prize in 2010 [22]. Graphene-based materials can be divided into four categories: single-layer graphene, fewlayer graphene, graphene oxide, and reduced graphene oxide [23].

Graphene compounds are obtained by oxidation (graphene oxide) or reduction (reduced graphene oxide) and have applications in science, technology, biomedicine and dentistry, through metal functionalization, organic binders and polymer matrix to improve its properties [24-26].

Graphene oxide is obtained by the oxidation of graphite, with hydrophobic and hydrophilic parts of the molecule [27,28] and oxygen functional groups that facilitate the chemical association of graphene with other compounds [29]. Graphene oxide is soluble in water, has a large contact surface, electrical and optical properties and chemical reactivity, which allows its multifunctionality and wide technological applicability [30]. Reduced graphene oxide, obtained by the reduction of graphene oxide, begins to exhibit free radicals that decrease the presence of oxygen, which makes it more stable due to the higher amount of carboncarbon bonds. In addition, this process considerably improves the electrical conductivity of the material [28,31]. However, the reduction of oxygen functional groups can lead to a decrease in the surface potential and a decrease in the solubility of the reduced compound [32].

Graphene nanoplatelets are obtained by exfoliating graphite, exhibit high electrical conductivity and are formed from one to two layers of the exfoliated compound, containing exclusively carbon bonds, with lateral dimensions in the order of nanometers and thin thickness [33].

Since they do not have the presence of oxygen, they are not soluble in water, but they have a large surface area due to the dispersion of nanoparticles [34, 35]. The particle size of the compounds can influence their functionalization, since when they are larger they tend to agglomerate more easily [36]. The particle size of graphene oxide and reduced graphene oxide varies depending on the production method and synthesis conditions, their dimensions ranging from nanometer to micrometer [32, 37]. On the other hand, graphene nanoplatelets have nanometric dimensions, with thicknesses ranging from 0.34 to 100 nm and lateral diameters ranging from 5 to 500 nm [35, 38]. Graphene compounds, when added to dental polymers, provide antimicrobial efficacy [39] and increase mechanical properties [33, 40], such as wear and fracture resistance [34, 39, 41-43]. Polymers with dental applications must be biomechanically resistant to masticatory forces and parafunctional habits that occur in the oral cavity [44]. These forces are usually evaluated by flexural, tensile, compressive, and hardness tests [41].

To develop the application of graphenebased materials in dentistry, it is necessary to evaluate the biocompatibility and cytotoxicity of graphene-based materials [45].

With the development of CAD/CAM, a number of 3D printing technologies and systems have emerged in the dental field. The digital workflow in dental laboratories offers the possibility of much faster and lower-cost design and production of dental restorations using 3D printing, as opposed to the more expensive milling method. Currently, 3Dprinted provisional restorations are part of the daily workflow, but 3D printing of longlasting, definitive dental resin restorations is not widely used due to the fact that there is too little clinical data on printable materials considered definitive. As 3D printing technology and printable materials continue to advance, it is possible to produce longlasting final restorations that can withstand both high occlusal stress and various chemical processes present in the oral cavity, while meeting safety requirements [46].

The present study aimed to compare technological aspects related to the fabrication of prosthetic crowns from a new material Tera Harz BR 23 (Graphy Inc., Seoul, South Korea) made from reinforced resins in comparison to the most commonly used crowns currently, metal-ceramic ones.

# 2. Materials and method

Between 01.06.2023 and 01.04.2024, 54 prosthetic restorations were performed for 45 patients, the age of the patients ranged from 20-70 years, involving patients of both sexes. The prosthetic restorations were performed on both arches, both on the frontal and lateral areas, those made of reinforced resin being obtained by 3D printing, and the metalceramic ones by the classical method. Before starting the treatment, the patients were informed about the objectives of the study, the clinical procedure, the materials used, the risks and benefits of metal-ceramic restorations and those printed from reinforced resin the and therapeutic alternatives. All patients signed an informed consent to participate in the study. Ethics Committee Opinion, 65/29.01.2024.

In the case of metal-ceramic restorations, after preparing the teeth requiring restoration, the impression stage was performed by the classical three-step method, using synthetic elastomers. After obtaining the impressions, class aIVa plaster working models were made, subsequently these were scanned using the laboratory scanner and using the ExoCAD software, the digital design of the metal components of the future prosthetic crowns was performed (Figure 1a). These components were obtained by laser-sintering (Figure 1b). The metal components received in the laboratory were then plated with ceramic masses on all surfaces according to the instructions received in the laboratory sheet (Figure 1c).





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Figure 1. Reduced head design (A), laser sintering (B), ceramic layering (C).

In the case of reinforced resin restorations, they were obtained by 3D printing, after preparing the teeth that required restoration, the impression stage was performed by the classic three-step method, using synthetic elastomers. After obtaining the impressions, class aIVa plaster working models were made, which were subsequently scanned using the laboratory scanner and using the ExoCAD software, the digital design of the future prosthetic restorations was made (Figure 2a). These restorations were obtained by 3D printing (Figure 2b). The 3D printed restorations were then individualized with photopolymerizable colored pigments on all surfaces according to the instructions received (Figure 2c).



Figure 2. DentalCAD with digital impression (A) and design model of a dental restoration (B).

## 3. Results

The study group consisted of 45 patients, 17 women and 28 men (Figure 3), aged between 20 and 70 years (Figure 4). The 45 patients included in the study received prosthetic restorations made of reinforced resins (8) and metal-ceramic restorations (Figure 5).



Figure 3. Gender distribution of patients.



Figure 4. Age distribution of patients.



**Figure 5**. Frequency of stress on composite resin crowns compared to metal-ceramic crowns.

The two types of restorations were performed in both the maxilla and the mandible. At the level of the maxillary arch, the 36 prosthetic restorations were distributed across the three areas as follows: the molar area was restored with metal-ceramic crowns only, on the premolar area there were 7 crowns, 6 metal-ceramic and 1 reinforced resin crown, and at the level of the frontal area, there were 10 metal-ceramic crowns and 5 reinforced resin crowns (Figure 6).



**Figure 6**. Frequency of stress on composite resin crowns compared to metal-ceramic crowns depending on location on the maxillary dental arches.



**Figure 7**. Frequency of stress on composite resin crowns compared to metal-ceramic crowns depending on location on the dental arches in the mandible.



**Figure 8**. Frequency of demand for composite resin crowns compared to metal-ceramic crowns according to the requested execution time.

For the mandibular arch, the 18 prosthetic restorations performed were distributed across the three areas as follows: the molar area was restored only with metal-ceramic crowns, on the premolar area there were 4 crowns, 3 metal-ceramic and 1 crown made of reinforced resin, and at the frontal area level, there were 2 metal-ceramic crowns and 1 crown made of reinforced resin (Figure 7).

Execution times varied greatly, with reinforced resins having a much shorter execution time (1-2 days) compared to metalceramic restorations, whose execution interval can range from 6 days to 10 days (Figure 8).

# 4. Discussion

In recent years, the use of 3D printing systems for the production of dental restorations has become favorable and reliable. Therefore, when using graphenebased nanomaterials in dental restorations, it is necessary to observe and evaluate its inflammatory effect on the tissue with which it comes into contact.

For a biomaterial to be considered excellent in dentistry, it is necessary to have low cytotoxicity, multidifferentiation ability, and antibacterial properties. The antibacterial effect of graphene-based materials was first discovered by Hu et al. [47]. After this study, several researchers confirmed the antibacterial effect.

For example, Gholibegloo et al. found that the bacterial survival rate of Streptococcus mutans treated with graphene graphene oxide, oxide-carnosine, and graphene oxide-hydroxyapatite can be reduced by 67%, 86.4%, and 78.2%, respectively [48]. Many composites have been fabricated to study its antibacterial property, and some researchers have fabricated graphene-based materials in glass ionomer cements, polymethyl methacrylate (PMMA), and dental adhesive [49,50].

Biomaterials, when used in high reinforcement concentrations as for polymeric structures, easily agglomerate and modify the material performance, as they form stress concentration points, which favors fracturing and deformation of the devices [34,51]. Incorporation of graphene oxide in high concentrations (1 and 2 wt%) caused a reduction in the flexural strength and hardness of PMMA, forming agglomerates that led to a high viscosity of the mixture [39]. The authors reported that the initial dispersion of graphene oxide in water was homogeneous, however, when incorporated into the PMMA liquid and subsequently into the powder, the graphene oxide particles did not disperse properly [39]. To overcome this challenge, the study recommends silanization of graphene oxide particles or incorporation of carboxylic groups [39].

Graphene synthesized in the form of nanoplatelets has a structure that favors polymer reinforcement due to the lower number of layers, which allows better dispersibility and insertion of the compound between the polymer chains, thus increasing the rigidity of the material [40].

Recently, the graphene family has shown good mechanical properties and desirable antibacterial properties in various forms in other fields. Due to the mechanical effect of graphene on PMMA, Azevedo et al. performed the definitive rehabilitation of the complete maxillary arch by incorporating graphene oxide into PMMA resin [52]. After 8 months later, no mechanical, aesthetic and other complications were found, indicating that the addition of graphene oxide to PMMA resin would be a good choice for prosthetic rehabilitation.

Bacali et al. reported PMMA with graphene-silver nanoparticles, and the mechanical properties, hydrophilic capacities and morphology of the composites were subsequently evaluated [52].

The results showed that the compression, bending and tensile strength parameters of the graphene-silver fillings were significantly higher than the pure PMMA group, indicating that the addition of graphene-silver improved the mechanical properties of the PMMA resin. In addition, Bacali and his collaborators also evaluated the antibacterial properties of graphene-silver modified PMMA, and the results confirmed that the graphene-silver modified groups exhibited an inhibitory effect in all Gram-negative strains, Staphylococcus aureus, E. coli, and Streptococcus mutans [53].

Therefore, graphene-based materials may be an ideal solution for promoting the physicomechanical and antibacterial properties of PMMA.

# 5. Conclusions

Mixed metal-ceramic crowns remain a basic option in prosthetic crown restorations because they offer resistance through the metal component and special aesthetics through the ceramic component. However, these metal-ceramic restorations still require a lot of time for their execution. Although the metal component can be obtained today even faster and more precisely by using CAD-CAM technologies, the application of ceramic masses must be done manually which involves time, skill and availability on the part of a trained dental technician.

Modern manufacturing technologies such as three-dimensional printing allow the precise and rapid realization of resin crowns offering efficient and personalized solutions for dental restorations. At present, they are more related to the obtaining of temporary or long-term provisional prosthetic structures.

However, these technologies also allow the processing of new composite materials such as those reinforced with a significantly longer lifespan. As research continues, it is expected that the use of graphene in dentistry will become increasingly widespread, offering new prosthetic treatment possibilities for patients.

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# Author contributions

All authors read and approved of the final manuscript. All authors have equally contributed to this work.

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## **Conflict of interest statement**

There are no potential conflicts of interest concerning this study.

## Data availability statement

Will be provided on request.

## **Ethics statement**

Approved by the Scientific Ethics and Deontology Commission of UMF Craiova (no. 65/29.01.2024).

## ORCID

Marina Olimpia Amărăscu: <u>https://orcid.org/0000-0002-3394-1486</u> Daniel Adrian Târtea: <u>https://orcid.org/0009-0004-8015-0275</u>

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