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3D printed dental materials - nano-mechanical properties and biochemical interactions in the oral environment

PHD THESIS ABSTRACT

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Background and importance of research

In recent decades, three-dimensional (3D) printing technology has revolutionized many fields, including medicine and dentistry. In dentistry, 3D printing offers innovative solutions for various applications, from creating precise and customized dental models to making prosthetic restorations (crowns, bridges), orthodontic appliances - mouth guards, retainers, aligners, surgical guides and rigid occlusal sleeves for muscle relaxation. This technology allows a high level of precision, reduced treatment time and lower costs.

CAD/CAM (Computer-Aided Design/Computer-Aided Manufacturing) technology was introduced to dentistry in the 1980s and has brought significant improvements in the design and fabrication of dental restorations. It allowed crowns, bridges and other prosthetic devices to be made with high precision by subtractive processes using milling cutters to carve materials from solid blocks. CAD/CAM has rapidly become an established technology in dentistry due to its ability to produce high-quality restorations in a relatively short time.

In contrast, 3D printing is a relatively recent technology that has only started to be widely applied in dentistry in recent years. Unlike the subtractive process of CAD/CAM, 3D printing is an additive process, in which material is added layer by layer to build complex structures. This method not only reduces material waste, but also offers greater design flexibility, allowing the creation of shapes and structures that would be impossible or impractical with traditional technologies.

In modern dentistry, there is a constant need for dental materials that offer superior performance, biocompatibility and durability in the oral environment. Acrylic resins, used in 3D printing as well as in CAD/CAM technologies and classical fabrication methods, are an important focal point due to their properties suitable for dental applications.

The relevance of 3D dental materials in modern dentistry

Dental materials used in 3D printing play a crucial role in the success of clinical applications. Specifically, acrylic resins are among the most widely used materials due to their properties suitable for dental use, such as biocompatibility, ease of handling and relatively low cost. These materials are used for a wide range of applications, including mouth guards, temporary crowns and surgical guides, providing customized and precise solutions for patients.

A significant advantage of 3D printed acrylic acrylic resins is the ability to create complex tooth structures with high precision and in a short time. This not only improves clinical efficiency, but also patient comfort and satisfaction.

However, the interactions of these materials with the oral environment, including saliva and the oral microbiome, is an essential area of research to ensure their durability and safety over time. The oral environment is complex and dynamic, containing a variety of chemicals and microorganisms that can affect dental materials. Understanding these interactions is crucial for the development of dental materials that not only stand the test of time, but also maintain patients' oral health.

This research focused on evaluating the nanomechanical properties (hardness, elasticity and stiffness), micro-porosity, biocompatibility and biochemical interactions of 3D printed acrylic resins in comparison with materials made by CAD/CAM and classical methods.

Working hypothesis and general objectives

The working hypothesis underlying the present research was that three-dimensionally printed acrylic resins for dental applications, including gums, temporary crowns and surgical guides, exhibit physical, chemical and biological properties comparable or superior to materials made by CAD/CAM technology and the classical fabrication method, demonstrating high biocompatibility and adequate durability in the oral environment, despite the challenges presented by biochemical interactions with saliva and the oral microbiome.

The overall objectives identified from the working hypothesis of the thesis were:

1. To characterize the nanomechanical properties of 3D printed acrylic resins: to measure and compare the nanomechanical properties (hardness, elasticity and stiffness) of 3D printed acrylic resins with those obtained by CAD/CAM technology and the classical method of obtaining dental devices.
2. Evaluation of the porosity of 3D printed acrylic resins: micro-CT analysis of the porosity of 3D printed acrylic resins in comparison with CAD/CAM and conventional materials by in vitro studies.
3. Investigation of biochemical interactions in the oral environment: To study the interactions between 3D printed acrylic resins and artificial saliva components in order to evaluate the degradation processes and their impact on the performance and durability of the materials.
4. Comparison of the performance of 3D printed dental materials with CAD/CAM and conventional dental materials: To evaluate and compare the biochemical interactions of 3D printed, CAD/CAM and conventional acrylic resins in dental applications including gums, temporary crowns and surgical guides by in vitro testing.

General research methodology

The general methodology involved the sample preparation stage, in which the indications for the use of acrylic resin in different dental applications were considered, taking into account processing methods such as 3D print, CAD/CAM - milled PMMA, and traditional method:

1. *Temporary crowns*: Temporary use in dental restorations to protect and maintain the integrity of the tooth structure until the final restoration is completed, regardless of the processing method chosen.
2. *Guards* (bruxism, orthodontic): Manufactured using CAD/CAM or 3D printing technology to protect teeth against the damaging effects of bruxism or in orthodontic treatments, ensuring a precise and comfortable fit.
3. *Surgical guide*: 3D or CAD/CAM fabricated device used during the insertion of implants into the bone structure of the jaw.

Obtaining samples by *additive manufacturing* (3D Printing)

In our study, the discoidal samples were fabricated using the digital light processing (DLP) technique and liquid acrylic resin specifically for provisional crowns and guthera. This method resulted in specimens with well-defined morphological and structural characteristics, essential for further evaluations.

Materials and equipment used:

- liquid acrylic resin;
- DLP 3D printer;
- construction platform;
- cleaning equipment;
- post-polymerization system.

Stages of Dental Technique

1. Digital Model Preparation
2. 3D Printing
3. Removing excess material
4. Post-polymerization

Obtaining samples by the *traditional method*.

In our study, we obtained discoidal samples using the traditional dental laboratory method. The samples were fabricated from Superpont C+B acrylic resin, supplied by Spofadent, with dimensional specifications of 12 ± 2 mm in diameter and 3 ± 1 mm in thickness. The fabrication process involved several critical steps, each of which contributed to the high quality samples essential for further evaluation.

Acrylic resin used Superpont C+B:

- Powder: 100 g bottle
- Liquid: 250 ml bottle

The last method of obtaining samples was *subtractive manufacturing*.

Subtractive manufacturing is a manufacturing process in which material is removed from a solid block to obtain the desired shape of the final part. This is the opposite of additive manufacturing, where material is added layer by layer to create an object. In the context of dentistry and prosthodontics, subtractive manufacturing is used to create precise and customized components such as crowns, bridges and discs from biocompatible materials.

The samples were milled from industrially prefabricated HUGE PMMA BLOCK HUGE PMMA industrial prefabricated disks.

The manufacturing process was realized using the innovative CORiTEC 350i machine.

The design of the discoidal samples was realized using CAD (Computer-Aided Design) and CAM (Computer-Aided Manufacturing) software. CAD software allows the creation of an accurate digital model of the desired part, while CAM translates this model into a set of instructions for the milling machine. The wheels were designed with a diameter of 12 ± 2 mm and a thickness of 3 ± 1 mm.

Sample finishing was an important step in the fabrication process of dental components as it significantly influences their esthetic and functional quality. The procedure described involves several grinding and polishing steps to achieve a high gloss and smooth surface, essential for patient comfort and component durability.

1. Sanding

Material used - corundum sandpaper

Procedure: Manufactured disks are initially sanded using corundum sandpaper to remove coarse imperfections and smooth the circular surface. This step prepares the surface for subsequent polishing steps.

2. Rubberizing

Three types of acrylic-specific polishers, each with a different grit and hardness, are used to refine the surface and prepare the material for polishing.

- First step - use a coarse-grit polisher to remove large debris and smooth the surface.
- Second step - medium grit polisher to further refine the surface.
- Third step - fine-grit polish to provide additional smoothness and prepare the surface for final polishing.

3. Pre-polishing

Material used - synthetic brush and pumice powder.

Procedure: The disk surface is pre-polished using a synthetic brush in combination with pumice powder

4. Final polishing

Products used: Abraso Star Glaze polishing paste and Polirapid fine cotton Polirapid disk

Procedure: Discs are polished to a high gloss using Abraso Star Glaze polishing paste. The fine Polirapid cotton polishing disk is used to apply the paste and ensures even distribution and efficient polishing of the surface.

After polishing, the disks are cleaned using a steam jet to remove any residues of polishing paste and other impurities. The samples are then subjected to an ultrasonic bath, which provides a deep cleaning by using high-frequency sound waves to dislodge and remove fine particles from the surface and interior of the samples.

Summary of the chapters

The PhD thesis contains a part which is describing the current state of knowledge, *Chapters 1 and 2*, and a part highlighting personal contributions, *Chapters 3-8*.

In the general part the contextual framework is discussed and the molecular interactions between saliva and dental resins are described, but also a comparison of the methods to obtain dental devices: 3D printing, CAD/CAM and traditional methods.

Chapter 1 explores the molecular interactions between saliva and dental resins used in dentistry. It begins with an introduction to the complex chemical background of modern resins, discussing their chemical composition and how they interact with saliva components. The chapter highlights elements of the chemical landscape of dental resins, emphasizing recent changes in the formulation of these materials to improve their strength and biocompatibility properties. In the final part, future research perspectives and directions are presented, emphasizing the need to better understand these interactions to optimize the clinical performance of dental materials.

Chapter 2 focuses on the comparison of different methods of manufacturing dental devices, including 3D printing, CAD/CAM technology and traditional methods. The chapter starts with a general introduction about these techniques and their fields of application. It then specifically discusses polymethylmethacrylate temporary crowns, surgical guides, and orthodontic and bruxism guards, outlining the advantages and disadvantages of each method. Introductory terms on the nano-mechanical properties and micro-porosity of the materials obtained by these methods are also provided. The chapter con concludes with a discussion on the sustainability of these technologies and future prospects in the fabrication of dental devices, suggesting directions for further research to optimize these processes.

Part II of the paper - Personal Contributions - sets out the *main hypothesis* and overall *objectives* of the thesis (*Chapter 3*). The main hypothesis states that 3D printed acrylic resins for dental applications, such as dental guards, temporary crowns and surgical guides, have physical, chemical and biological properties comparable or superior to materials made by CAD/CAM technology and the classical method of fabrication. These materials are considered to have high biocompatibility and adequate durability in the oral environment, even in the face of biochemical challenges such as interactions with saliva and the oral microbiome. The overall research objectives are also mentioned, which include detailed characterization of the nano-mechanical properties, porosity evaluation, analysis of biochemical interactions and comparison of the performance of 3D printed dental materials with those obtained by other methods.

Chapter 4 describes the *general methodology* used to test the hypothesis and achieve the set objectives. Three material processing methods are presented: additive manufacturing (3D printing), traditional method and subtractive manufacturing (CAD/CAM). Each method has detailed specifications and procedures for the fabrication of dental specimens such as temporary crowns, mouth guards and surgical guides. For example, additive manufacturing involves the use of Digital Light Processing (DLP) technology to three-dimensionally print liquid acrylic resin samples. The traditional method and subtractive fabrication are described in terms of specific processes and characteristics of the resulting materials. The chapter emphasizes the importance of sample finishing, an important step in ensuring the accuracy and reliability of experimental results. Each processing method has been evaluated to ensure that the materials produced meet the standards required for dental applications.

Chapter 5: Study 1 - Nano-mechanical properties of acrylic resin based materials for dental restorations processed by milling, 3D printing and traditional method. This chapter of your thesis is dedicated to an in-depth analysis of the nano-mechanical properties of acrylic resin-based materials used in dental restorations, comparing three distinct processing techniques: CAD/CAM milling, 3D printing and the traditional casting method. The *introductory* part of the chapter starts from the premise that dental restorations must fulfill rigorous criteria of mechanical strength and durability, being constantly subjected to occlusal forces and complex chemical exposures in the oral environment. In this context, the question arises to what extent new processing technologies, such as milling and 3D printing, can improve these properties compared to traditional methods. It is *hypothesized* that materials processed by 3D printing and milling will exhibit nano-mechanical properties at least comparable to those obtained by classical methods, with the potential to surpass them in some aspects.

The chapter details *the methodology* used to evaluate the nano-mechanical properties of the samples. The materials tested are acrylic resins, which were selected due to their widespread use in dentistry for temporary restorations and dental devices. The sample preparation procedures for each processing method are described: CAD/CAM milling, 3D printing and traditional casting. The resulting samples were subjected to nano-hardening tests to determine hardness, modulus of elasticity and stiffness.

The experimental results are presented in a systematic manner, comparing the performance obtained for each machining method. The data show differences between the three methods in hardness and elasticity of the materials. The resins processed by 3D printing showed better uniformity of nano-mechanical properties and comparable hardness to those obtained by milling, outperforming the results of samples made by the traditional method. These observations suggest that 3D printing not only meets the required standards, but could also become a viable alternative for permanent restorations.

In the *discussion section*, the author interprets the results in the context of the clinical applicability of these materials. It is argued that the uniformity and consistency of the nano-mechanical properties obtained by 3D printing may contribute to a more predictable clinical performance and increased durability of dental restorations. The potential impact of these findings on how materials and technologies are selected for dental restorations in everyday practice is also discussed. It is emphasized that CAD/CAM milling continues to be a robust technology, but 3D printing could offer superior economic and customization advantages in some cases.

The chapter *concludes* with conclusions emphasizing the relevance of these findings for the evolution of dental restorations. It is proposed that 3D printing should be considered as a future technology for processing dental materials, due to its ability to produce restorations with optimized mechanical properties tailored to individual patient needs. However, it is recognized that further clinical studies are needed to validate the long-term performance observed in the laboratory.

Overall, this chapter makes a valuable contribution to the understanding of how emerging technologies can influence and improve dental practice, providing a sound basis for the adoption of new quality standards in the fabrication of dental restorations.

Chapter 6: Study 2 - Quantitative morphological characterization of porosity in acrylic resin samples obtained by 3D printing and CAD/CAM milling using computerized micro-tomography. This chapter of your thesis is dedicated to a detailed study of the porosity of acrylic resin-based dental materials, comparing two modern processing techniques: 3D printing and CAD/CAM milling. By using computerized micro-computed tomography (Micro-CT), this chapter explores the internal morphological characteristics of the materials, with a particular focus on the distribution and impact of porosity on the clinical performance of dental restorations.

In the *introduction* the chapter describes the importance of porosity in dental materials, emphasizing its impact on the mechanical properties, biocompatibility and durability of restorations. It is hypothesized that modern processing technologies, such as 3D printing and CAD/CAM milling, may generate materials with distinct levels of porosity, thereby influencing clinical performance. In this context, computed micro-computed tomography is presented as an essential tool for the detailed and non-invasive characterization of the internal structures of dental materials.

The methodological section describes in detail the sample preparation procedures and settings used for micro-tomography. Acrylic resin samples were obtained by 3D printing and CAD/CAM milling, each method being optimized to reflect actual clinical conditions. Computerized micro-computed tomography was used to capture high-resolution three-dimensional images of the samples, allowing quantitative porosity analysis. Parameters analyzed included pore size, pore distribution, pore volume, and material density.

The results obtained reveal differences between the samples produced by the two processing methods. The micro-CT images showed a lower porosity and a more uniform pore distribution in the CAD/CAM milled samples compared to the 3D printed ones. This difference may be attributed to the distinct manufacturing processes, where CAD/CAM milling involves removing material from a solid block, while 3D printing adds material layer by layer, possibly favoring pore formation. It was also observed that porosity may negatively influence the mechanical properties of the material, such as fracture toughness and durability over time.

The discussions and interpretation of the results emphasize the importance of porosity control in the development of modern dental materials. The high porosity observed in 3D printed samples may pose a challenge for the long-term use of these materials in dental restorations, suggesting the need for adjustments to the printing process to minimize this phenomenon. In contrast, CAD/CAM milling, although more expensive and less flexible in terms of restoration customization, offers an advantage in reducing porosity and thus improving the mechanical properties of the material. The implications of these findings for clinical practice are also discussed, suggesting a rigorous evaluation of processing techniques according to the specific requirements of each case.

The chapter *concludes* that although 3D printing is a promising technology in dentistry, careful control of porosity is essential to ensure the durability and clinical efficiency of dental materials. CAD/CAM milling remains a robust option in terms of nano-mechanical properties and morphological control. The results of this chapter provide a basis for future research, proposing the development of hybrid techniques or the optimization of existing processes to combine the advantages of both processing methods.

In conclusion, this chapter makes significant contributions to the understanding of how processing technologies influence the internal structure and thus the performance of dental materials, highlighting the need for integrated approaches in the development of future dental restorative technologies.

Chapter 7: Study 3 - Analysis of the behavior of gingival fibroblasts in the presence of methacrylate-based dental resins produced by 3D printing versus milling. This dissertation chapter investigates the behavior of gingival fibroblasts when exposed to methacrylate-based dental resins by comparing two manufacturing methods: 3D printing and milling. The study focuses on the cellular responses in the presence of these materials, assessing aspects such as cell adhesion, proliferation and viability, thus providing insight into the biocompatibility of modern dental materials.

The introduction describes the importance of biocompatibility of dental materials, emphasizing that the interaction between dental materials and peri-implant tissues is crucial for the long-term success of dental restorations. The introduction details the need to evaluate the behavior of gingival cells, which are among the first to come into contact with new materials. The hypothesis of the study is that 3D printing technology, through its specific manufacturing characteristics, might influence fibroblast behavior differently compared to CAD/CAM milled materials.

In the following, *the materials and methodologies* used to test the interactions between human gingival fibroblasts and methacrylate resin samples are described. Samples were prepared using 3D printing and milling methods, and gingival fibroblasts were cultured under standardized laboratory conditions. Tests were performed to evaluate cell adhesion to the material, cell proliferation on the surface of the resins and cell viability by various biochemical assays including MTT and adhesion assays.

The results obtained indicate differences in fibroblast response to the materials tested. Fibroblasts exposed to resins produced by 3D printing showed a lower proliferation rate and adhesion compared to those exposed to milled materials. A lower cell viability was also observed on 3D printed materials, which could suggest a higher release of unfixed monomers or other substances that could be toxic to the cells.

In the *discussion* section, potential causes of the different cellular responses observed, such as surface roughness, the presence of pores or differences in the release of compounds from the materials, are analyzed. It is suggested that optimizations in the 3D printing process could improve the biocompatibility of methacrylate resins. The relevance of these results to clinical practice is also discussed, highlighting the need for further testing for the widespread adoption of 3D printing technologies for materials that come into direct contact with gingival tissue.

The chapter *concludes* that although 3D printing offers significant advantages in terms of customization and manufacturing efficiency, it is essential to pay attention to the biocompatibility of the materials used. The potential of 3D printing to revolutionize the fabrication of dental materials is recognized, but the importance of thorough evaluation of cell-cell interactions is emphasized to ensure the long-term success and safety of dental restorations.

Chapter 7 thus makes valuable contributions to the understanding of the interactions between novel materials and dental tissues, highlighting the complexity of biocompatibility assessment in the context of emerging technologies.

Conclusions and personal contributions

Chapter 8 of the PhD thesis is dedicated to the author's personal conclusions and contributions. This chapter is essential as it summarizes the main findings and provides a reflection on the research contributions.

The *general conclusions* summarize the main research findings, highlighting their importance and relevance to the field of dentistry. It is highlighted that 3D printed acrylic resins exhibit physical, chemical and biological properties comparable or superior to materials made by other methods, such as CAD/CAM or traditional methods. The advantages and limitations of each manufacturing method analyzed are discussed, with an emphasis on the potential of 3D printing to redefine dental care standards.

Three-dimensional printing technology has demonstrated the ability to revolutionize various dental applications, from the creation of precise dental models to the fabrication of prosthetic restorations and customized orthodontic devices. It offers significant advantages by reducing treatment time and costs while improving the accuracy and customization of dental treatments.

Unlike CAD/CAM technology, which uses subtractive processes to sculpt materials, 3D printing adds material layer by layer, reducing waste and providing design flexibility. This additive approach allows the creation of complex structures that are difficult to achieve with traditional methods, and contributes to more sustainable dental practices.

The study highlighted the importance of biocompatibility and durability of dental materials in the oral environment. Acrylic resins used in 3D printing have shown superior performance in interacting with saliva and the oral microbiome, which is essential to ensure the long-term success of dental treatments.

Research has shown that 3D printed acrylic resins exhibit outstanding nano-mechanical properties such as hardness, elasticity and stiffness comparable or superior to CAD/CAM materials. The biochemical interactions between these materials and the oral environment are also favorable, contributing to their durability and safety over time.

The study performed a detailed evaluation of the nano-mechanical properties of 3D-printed acrylic resins in comparison with CAD/CAM materials. This analysis identified the advantages and limitations of each technology, providing useful insights for clinical practice.

The biochemical interactions of acrylic resins with saliva and the oral microbiome were investigated, highlighting their behavior in the complex and dynamic environment of the oral cavity. This information is essential for the development of dental materials that maintain patients' oral health.

The role of 3D printing technology in promoting sustainability in dentistry by reducing waste and material consumption, as well as the possibility of local production of dental devices was emphasized. These aspects contribute to greener and more energy-efficient dental practices.

Research *results* have been published in prestigious scientific journals, contributing to the dissemination of knowledge and advancing the field. These publications reflect the research work carried out and the relevance of the results to the scientific community and dental practitioners.

Taking into account the results of the study, the differences observed between the two types of MA-based resin samples can be attributed to the manufacturing method. In general, MA-CAD/CAM materials are often manufactured under controlled laboratory conditions using high quality raw materials, which may reduce the potential for toxicity. In addition, CAD/CAM milling typically involves a subtractive manufacturing process, which generates more waste and emissions compared to 3D printing, which may reduce the environmental impact of the material. In contrast, MA-3D dental materials are typically made using a method called stereolithography, which involves curing a liquid resin using UV light. Samples of dental material made by additive manufacturing affect cell proliferation differently than material made by subtraction, probably due to successive incomplete polymerization reactions. Furthermore, additive manufacturing may generate toxic gases, especially if the material is not fully cured or if the printer is not properly ventilated.

It has been suggested that additional post-processing steps, including additional curing and washing, could improve the biocompatibility of the printed materials, as the printed samples can induce apoptosis, as was also illustrated by the study results.

In the *personal contrib*utions section, original contributions to the field were presented, highlighting innovations or discoveries made during the doctoral research. These include the development of new methods for evaluating dental materials and the integration of advanced manufacturing technologies. The importance of continuous and rigorous evaluation of new technologies to ensure long-term safety and effectiveness is emphasized.

In conclusion, *Chapter 8* serves as a final reflection on the author's work and highlights the potential impact of the research on future dental practice, and the results obtained compel further work to date.

List of published scientific papers

Articles published in extenso as a result of doctoral research

1. **Șaramet V**, Meleșcanu-Imre M, Țâncu AMC, Albu CC, Ripszky-Totan A, Pantea M. Molecular Interactions between Saliva and Dental Composites Resins: A Way Forward. Materials (Basel). **2021** May 13;14(10):2537. https://doi.org/10.3390/ma14102537 . PMID: 34068320; PMCID: PMC8153278.

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