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DEPARTMENT I MD

MODIGA CRISTINA

PhD THESIS

ASSESSMENT OF POLYMERS AND POLYMER PROCESSING PROCEDURES IN DENTAL TECHNOLOGY

ABSTRACT

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Following over thirty years of dedicated service in the Department of Prostheses technology and Dental Materials at the University of Medicine and Pharmacy "Victor Babeș" in Timișoara, my journey has been one of profound transformation and growth. Beginning as a dental technician and evolving into a Doctor of Dental Medicine, I have been privileged to witness the remarkable advancements within our field. As the world of dentistry has transitioned from traditional methods to the digital era, the landscape of dental materials and their applications has been revolutionized. The once limited options for creating complete dentures have expanded into a sophisticated array of digital techniques, including CAD/CAM systems, which offer remarkable precision and esthetics. This thesis is driven by the motivation to explore and understand the most widely used polymers and their processing technologies. The investigations aim to illuminate the strengths and limitations of these materials and techniques, offering insights into their performance and potential for future development. Hopefully this research will contribute to the ongoing evolution of dental prosthodontics, ensuring that the advancements we make continue to enhance the quality of care we provide to our patients.

Given the widespread use of PMMA and its proven durability over time, this material will be the focus of the investigation from the perspective of its mechanical performance. This focus aims to ensure that the results of the study are applicable to as many practitioners as possible.

Since the treatment of both edentulous (partially or completely) and dentulous patients requiring crowns relies heavily on the use of polymers, it is of great interest to investigate these materials. Understanding their properties will allow for improved patient care, the correct application of current technologies, and the development of well-informed practitioners.

The studies were carried out with the help of the Department of Prostheses Technology and Dental Materials, Faculty of Dental Medicine, the research Center in Dental Medicine Using Conventional and Alternative Technologies, the Department of Prosthodontics, Faculty of Dental Medicine, University of Medicine and Pharmacy "Victor Babeș" in Timișoara, in collaboration with the Department of Mechanics and Strength of Materials, “Politehnica” University of Timisoara, and the Research Institute for Biosafety and Bioengineering, Faculty of Agriculture, The King Michael I University of Life Science. The interdisciplinary collaborations allowed for insights into the vast field of polymers to come to fruition. The mechanical strength (both flexural and compressive force tests were carried out) of the dentures made by means of the injected technology were found to show far better mechanical performance than the traditional packing-press, the CAD/CAM (both additive and subtractive) methods. This same manufacturing process, however, showed far greater variability in the results and less predictability, even though the mean result was performing better compared to the other methods.

The comparison of the polymers processed by different technologies is also carried out on temporary crows. The findings indicate that the milled and injected interim restorations show less of a cytotoxic effect, which is associated with less free monomer residuals.

Along with the cytotoxic effect of interim restorations, their clinical performance was also evaluated using OCT technology. These show satisfactory results in terms of esthetics and functional performance for short to medium term use. The marginal fit is suitable, the esthetics are pleasing if not used for long durations and its ease of use makes it easy to polish.

The general part is comprised of two chapters that analyse the relevant literature. These chapters are essential for understanding the significance of the studies conducted in the specialized section.

Chapter 1 pertains to **Polymers used in dental technology**, particularly Polymethyl methacrylate (PMMA), are extensively used in dental technology for various applications, including denture repair, relining, and prosthetic teeth creation. PMMA is favored for its biocompatibility, aesthetics, and ease of manipulation. It is typically provided as a powder-liquid mixture, where the powder consists of PMMA with added colors and fibers, and the liquid contains methyl methacrylate monomer, inhibitors, and cross-linking agents. Polymerization of PMMA can be initiated by heat, light, or chemical means, resulting in different types of PMMA materials.

Heat-cured PMMA is the most common, requiring a water bath for activation, while microwave-cured PMMA offers faster curing times but requires specific equipment. Cold-cured PMMA, also known as chemically cured, uses a chemical initiator and does not need heat, though it has lower polymerization degrees and potential residual monomer issues. Light-cured PMMA uses visible light to activate a photo-sensitive initiator, allowing precise control over the curing process but is less commonly used due to cost and technical challenges.

Polyaryletherketone (PAEK) and its derivatives, including Polyetheretherketone (PEEK), are also gaining attention in dentistry due to their excellent mechanical properties, biocompatibility, and resistance to corrosion and wear. PEEK is particularly valued for its

lightweight nature, high toughness, and compatibility with 3D printing, making it suitable for various dental prostheses and frameworks. However, PEEK's inert surface poses challenges for bonding with other materials, necessitating surface treatments to enhance adhesion.
Studies have shown that PEEK can be effectively used for temporary crowns, inlay-retained fixed dental prostheses, posts, and cores, offering comparable or superior performance to traditional materials like PMMA and metal alloys. However, the mechanical strength of PEEK needs further enhancement through hybrid reinforcement for long-term applications. PEEK's potential in removable partial dentures and telescopic crown dentures is also notable, providing adequate retention and aesthetic benefits while reducing stress on abutment teeth compared to traditional metal clasps.

Overall, while PMMA remains a staple in dental technology, advancements in PEEK and other polymers are expanding the possibilities for durable, biocompatible, and efficient dental restorations and prostheses. Dental practitioners must consider the unique properties and suitability of each polymer type to optimize patient outcomes.

Chapter 2 discusses various **Polymer processing procedures used in dental technology**. The traditional packing-press technique for fabricating complete dentures involves several precise steps. First, impressions of the edentulous arches are taken to capture the 3D conformation of oral structures. Preliminary casts are poured using the box-in method. Custom trays are then made on these diagnostic casts, ensuring all anatomical landmarks are clear. A final impression is taken with a more precise material like silicone. The spatial relation of the mandibular and maxillary ridges in centric relation and vertical dimension of occlusion are determined using rims. The final cast is used for a provisional try-in with wax-up and artificial teeth fitting. The wax-up is then flasked, filled with PMMA, and pressed to conform to the mold. After pressing, the denture base is removed, polished, and finished for use.

Injection-molding technologies for denture fabrication address the drawbacks of traditional methods like PMMA dosage errors and incomplete polymerization. This method uses specialized equipment to inject chemo- or thermoplastic polymer into a gypsum mold. It ensures better fit and suction by applying pressure during injection, compensating for polymerization shrinkage. Systems like SR-Ivocap use continuous high-pressure injection, improving accuracy and requiring less post-processing. Thermoplastic injection methods, such as those by Girrbach-Dental and If Dental, use high temperatures and pressures to mold denture bases efficiently, though they require expensive equipment and have mixed results compared to chemoplastic methods.

3D printing methods for denture fabrication start with capturing a digital impression of the patient's oral cavity using an intraoral scanner, ensuring high accuracy and comfort. The digital data is used to create detailed models of the patient's dentition and oral anatomy, which guide the design and customization of dentures, including the vertical dimension of occlusion (VDO). Advanced software like 3Shape helps in precise tooth selection and placement. The digital designs are optimized for 3D printing and printed using high-resolution printers with dental-grade photopolymerizable resins. Post-processing includes washing, curing, and polishing to ensure quality and fit.

The CAD/CAM milling procedure for dentures begins with capturing a detailed digital impression of the patient's oral cavity using an intraoral scanner. The acquired data is then imported into CAD software, where the dental technician designs the dentures, including virtual wax rims for the initial vertical dimension of occlusion (VDO). Denture teeth are selected from a digital library and precisely positioned. Once the design is complete, the digital files are prepared for milling. A CAM milling machine then precisely cuts the denture components from a solid block of dental material. Post-processing includes surface finishing, polishing, and trimming. The dentures are then assembled, adjusted for fit and occlusion, and undergo a final inspection before being provided to the patient with follow-up care instructions.

The **special part** features four studies that aim to provide insights into the polymers used in dentistry and their properties, with the hope of enabling the formulation of appropriate treatment plans.

The **first study** of the PhD thesis, presented in the **third chapter**, focuses on the **Impact of fabrication methodologies on the flexural strength of complete dentures: an investigation into technological influences.**

The hardness of denture bases is crucial for ensuring that chewing pressure is evenly distributed to the bone, mucosa, and remaining teeth. Materials with a low modulus of elasticity are unsuitable as they lack resistance to bending forces and are prone to elastic deformation. Conversely, excessively strong materials can shatter easily and lack the impact resistance required to prevent prosthesis bases from breaking. The forces applied during chewing and swallowing can cause prostheses to bend while maintaining occlusal contact. Over time, repetitive bending can lead to fractures or breaks in the prosthesis, affecting its adaptation to ongoing changes in the prosthetic field.

This study evaluates the flexural strength of specimens fabricated using three different methods from the same thermopolymerizable PMMA material. The flexural strength tests were conducted in collaboration with the Department of Strength of Materials at Timisoara's Faculty of Civil Engineering and Architecture. The results were published in the Romanian Journal of Oral Rehabilitation, No.1, 2024.

Specimens were created, each measuring 40 x 40 x 3 mm, using three fabrication methods: Suction-injection process (vacuum-pressure alternation) with continuous pressure polymerization, SR-Ivocap (IVOCLAR) injection technology with polymerization under constant pressure, classical technology using the manual packing-press method and traditional hot polymerization.

All specimens were made from the same material: SR-Ivocap "Plus" High Impact (IVOCLAR), consisting of a PMMA and copolymer powder with dibenzoyl peroxide liquid. The specimens underwent heat polymerization as per the prescribed regimes.

After embedding, the specimens were treated and completed using standard techniques, then left for a week at 37°C in distilled water. They were subjected to a 3-point bending test using a hydraulic press to determine the force applied until the specimen yielded. The flexural strength was calculated using the formula:

Rf=(3*Pmax*L)/2BH^2

where Rf is the flexural strength, Pmax is the maximum force at yield, L is the length, B is the width, and H is the thickness of the specimen. Statistical analysis was conducted using SPSS and Microsoft Excel, with significant differences evaluated using Mann-Whitney and Kruskal-Wallis tests.

All 24 specimens fractured under stress rather than yielding via flow, indicating brittleness regardless of the fabrication method. The flexural strength values ranged from 69.28 to 103.92 N/mm² for the classical method, with a mean value of 86.6 ± 12.62% N/mm². For the SR-Ivocap method, the values ranged from 110.08 to 140.11 N/mm², with a mean of 125.1 ± 11.93% N/mm². The suction-injection method showed values ranging from 114.67 to 145.93 N/mm², with a mean of 130.3 ± 12.30% N/mm².

The suction-injection method produced flexural strength values slightly higher than the SR-Ivocap method and significantly higher than the classical method. The Kruskal-Wallis test indicated significant differences among the three methods. Post hoc comparisons using Mann-Whitney tests showed statistically significant differences between the classical method and both injection methods, but not between the two injection methods.

The study concludes that the suction-injection method yields flexural strength values similar to, but slightly higher than, the SR-Ivocap method and significantly higher than the classical method. The classical method results in lower flexural strength values and greater variations under bending conditions. The superior performance of the suction-injection method is attributed to controlled thermobaropolymerization, involving vacuuming of the mold cavity, polymer injection under pressure, and continuous thermal monitoring.

The **second study,** presented in the **fourth chapter**, undertakes to shed light on the **Mechanical Assessment of Denture Polymers Processing Technologies.**

With the global elderly population expected to surpass 2 billion by 2050, the demand for removable prostheses is increasing, particularly in regions with lower economic status. Removable dentures are vital for those unable or unwilling to undergo dental implants, but they are susceptible to damage from accidental drops, highlighting the need for durable and resilient denture materials. Polymethyl methacrylate (PMMA) is the primary material used for denture bases due to its versatility and beneficial mechanical properties, which arise from addition chain reaction polymerization. Despite its advantages, PMMA exhibits limitations such as weak flexural strength, fracture susceptibility, and shrinkage during polymerization. Recent research has focused on improving PMMA through copolymers, fiber reinforcements, and advanced processing techniques like CAD/CAM manufacturing to overcome these drawbacks.

The study compared the compressive strength of complete dentures made from PMMA using four different processing techniques: traditional packing presses, thermoplastic injection molding, 3D printing, and subtractive CAD/CAM technology. Each technique produced eight pairs of dentures, totaling 16 dentures per method. The dentures were tested using a Universal Testing Machine to replicate compressive pressures similar to those experienced in the mouth.

Traditional Dentures: Fabricated using a conventional wax-up method, where artificial teeth are set in wax, which is then flasked and replaced with acrylic resin. The dentures are polished before testing.

Thermoplastic Injected Dentures: Made using an injection molding system which involves forcing molten acrylic into a mold. This method produces denser and more fracture-resistant dentures.

3D Printed Dentures: Created from digital models and printed using photopolymerizable resins. This method allows for precise customization but the printed dentures showed lower performance in preliminary results.

CAD/CAM Technology: Utilizes monolithic PMMA discs to create dentures with both the base and teeth machined in a single process. This technology reduces manual bonding and allows for highly accurate and consistent production.

Mechanical testing involved immersing dentures in distilled water at 37°C for 24 hours, then subjecting them to compressive forces until failure. The force-displacement curves were analyzed, and fracture energy was calculated based on the area under the curves. The study found significant differences in the mechanical properties of dentures based on the processing method used:

Traditional Dentures: Showed fracture forces ranging from 2.25 kN to 7.89 kN, with a mean of 4.54 kN, and fracture energy between 1.16 kJ and 6.79 kJ, with a mean of 3.58 kJ.

Thermoplastic Injection Molding: Demonstrated superior performance with fracture forces ranging from 14.14 kN to 28.17 kN (mean: 19.67 kN) and fracture energies between 17.71 kJ and 88.37 kJ (mean: 49.47 kJ). This method produced the highest force and energy values, indicating superior toughness.

CAD/CAM Technology: Resulted in fracture forces between 3.73 kN and 6.28 kN (mean: 5.09 kN) and fracture energies from 3.34 kJ to 6.03 kJ (mean: 4.63 kJ). These results show a good balance of performance and stability.

3D Printed Dentures: Had the lowest values, with fracture forces between 0.72 kN and 2.23 kN (mean: 1.51 kN) and fracture energies ranging from 0.28 kJ to 1.35 kJ (mean: 0.81 kJ). This method exhibited poor force and energy performance.

Statistical analyses using Kruskal-Wallis and Dunn's tests revealed significant differences between the methods, with thermoplastic injection molding outperforming others in both fracture force and energy. The 3D printed dentures showed the least performance, while CAD/CAM technology demonstrated consistent results.

The study concluded that denture processing technology significantly affects the mechanical properties of dentures. Thermoplastic injection molding provided the highest fracture force and energy, making it the most robust option. CAD/CAM technology also showed good results but with less variability. In contrast, 3D printed dentures performed poorly, indicating the need for further improvement in 3D printing techniques for denture fabrication. These findings emphasize the importance of selecting appropriate processing technologies to enhance the durability and performance of removable prostheses. Future research should explore additional mechanical properties and clinical relevance to fully understand the impact of different manufacturing methods on denture performance.

The **fifth chapter** contains the **third study**, which represents an **Evaluation of various processing technologies of polymers for provisional prostheses.**

Provisional dental restorations, essential for diagnosis and treatment planning, can be produced using both traditional and modern techniques such as CAD/CAM technologies. The advancement of polymer processing methods—including additive, subtractive, and CAD/CAM systems—has improved the quality and efficiency of these temporary restorations.

This study assessed four types of polymer processing for temporary fixed partial prostheses: fiberglass-reinforced thermoplastic polymers, injected polymers, milled polymers, and printed polymers. Each group was compared to a control group using traditional self-curing acrylic resin. Methods involved thermoplastic polymers BioHPP and Pekkton® Ivory for injection, PMMA for milling, and Detax Freeprint temp UV resin for printing. Key techniques included the use of specialized curing ovens, milling machines, and UV light for polymerization.

Evaluation involved radiographic analysis and Optical Coherence Tomography (OCT) to detect air inclusions and defects in restorations. Microscopic analysis was also performed to measure cervical adaptation errors, showing variations in fit across different methods. Results indicated that milled PMMA restorations exhibited superior optical qualities and mechanical resistance compared to other methods. Injected polymers demonstrated promise for long-term use in complex cases. CAD/CAM technologies offered enhanced precision but required careful management to avoid design errors. Additive and subtractive technologies each had specific advantages and limitations in terms of biocompatibility, adaptation accuracy, and ease of use.

In conclusion, the choice of polymer processing method significantly impacts the success of temporary restorations. Milled and injected polymers are effective, with advantages such as reduced monomer residue and improved fit, while CAD/CAM technologies enhance precision. Comprehensive material testing and consideration of processing techniques are crucial for optimal prosthodontic outcomes.

In the **sixth chapter**, the **fourth study** is presented, focusing on **Non-invasive defectoscopy and the evaluation of the fit on the abutment, and the marginal adaptation of polymeric provisional prostheses.**

The study aims to address two key aspects of provisional prostheses: detecting internal defects and assessing the precision of fit on dental abutments. Provisional prostheses are essential in dental treatments, as they provide temporary solutions while permanent restorations are being prepared. Ensuring their optimal fit and functionality is crucial for the overall success of dental treatments.

Non-invasive defectoscopy techniques are employed to identify internal defects within the provisional prostheses without the need for destructive testing. These techniques include advanced imaging technologies like Optical Coherence Tomography (OCT) and X-ray radiography.

Optical Coherence Tomography (OCT): This imaging method provides high-resolution cross-sectional images of the prosthesis, allowing for the detection of internal inclusions and voids. OCT is particularly useful for evaluating the interface between the polymer and reinforcing materials, such as fiberglass. The study utilized Time Domain Mode OCT to assess the quality of the polymer-fiberglass interface, revealing potential defects that could compromise the prosthesis's mechanical properties.

X-ray Radiography: Radiographic analysis was used to detect air inclusions and other defects within the provisional prostheses. X-rays were taken from both buccal and occlusal perspectives, highlighting the presence of air bubbles in self-curing resins. These defects can reduce the mechanical strength and longevity of the prostheses.

Evaluating the fit of provisional prostheses on abutments is critical to ensure proper occlusion and function. The study employed several methods to assess marginal adaptation:

Microscopic Analysis: A digital microscope was used to measure the cervical adaptation of the prostheses. The resolution of the microscope allowed for detailed examination of the spacing between the crown margin and the marginal preparation. Measurements of cervical adaptation errors were recorded for both printed and milled restorations, providing insights into the precision of different manufacturing techniques.

Comparison of Techniques: The study compared various methods of producing provisional prostheses, including traditional techniques using self-curing resins, milled PMMA, and 3D printed polymers. Each method was evaluated for its ability to produce restorations with accurate marginal adaptation and minimal defects.

The study highlighted several key findings:

Internal Defects: OCT and X-ray analyses revealed that air inclusions and gaps at the polymer-fiberglass interface could weaken provisional prostheses. Identifying these defects early allows for improvements in material and manufacturing processes.

Marginal Adaptation: Milled PMMA demonstrated superior fit and marginal adaptation compared to other methods. The precision of milling technology resulted in fewer adaptation errors, making it a viable option for creating high-quality provisional restorations.

Material and Technology Considerations: The study emphasized the importance of selecting appropriate materials and technologies for producing provisional prostheses.

The absence of residual monomers in milled and injected polymers was noted as a significant advantage, reducing the risk of periodontal inflammation and enhancing overall biocompatibility.

In conclusion, the fourth study presented in Chapter Six provides valuable insights into the assessment of polymeric provisional prostheses. By employing non-invasive defectoscopy techniques and evaluating fit and marginal adaptation, the study contributes to improving the quality and effectiveness of temporary dental restorations. The findings underscore the importance of advanced imaging and precision manufacturing in achieving successful dental treatments.

Based on the comprehensive literature review and research findings presented in this doctoral thesis, several final **conclusions** can be drawn, which hold direct practical implications for dental technicians, dentists, and, most crucially, patients. The primary objective of the research was to evaluate the effectiveness and performance of various polymer materials and processing techniques used in temporary and final dental restorations. The study successfully achieved satisfactory and statistically significant results in this regard. However, it also highlighted areas where further research is necessary, particularly concerning the compressive and flexural strength of dentures as indicators of therapeutic success. The analysis encompassed both the materials and processing technologies, revealing opportunities for further refinement and improvement. The study found that 3D-printed dentures, despite their advantages in terms of low manufacturing cost and reduced production time, exhibited the weakest compressive strength. This suggests that additional research is needed to explore more suitable materials for 3D printing and to enhance the characteristics of 3D printers used in dental applications. Although 3D printing offers benefits such as reduced material waste, ease of use, and a streamlined digital workflow, improvements in material strength could significantly enhance its viability for producing durable dental restorations.

In contrast, polymer injection methods demonstrated superior results in terms of the toughness of the final denture, though they exhibited more volatile behavior compared to other techniques. This variability indicates the need for further refinement to achieve more consistent and predictable outcomes. Traditional and milled dentures, while providing consistent material strength, did not perform as well as injected prostheses. Nevertheless, the similar performance of traditional and CAD/CAM (both additive and subtractive) methods suggests that integrating digital workflows in modern dentistry is advantageous. Even if CAD/CAM methods yield slightly lower results compared to injected prostheses, their performance is comparable to that of traditional methods, which have been well-established over time.

The study also revealed that specimens produced using the traditional manual packing-press method generally had lower flexural strength values compared to those made using injection methods. Specifically, the maximum flexural strength achieved with the manual method was lower than the minimum strength obtained with injection methods. Additionally, specimens made using the traditional method showed greater variability in resistance under bending conditions, consistent with findings from compressive strength tests. The suction-injection approach, which involves vacuuming the mold cavity and injecting the polymer under regulated pressure and thermal conditions, outperformed the SR-Ivocap method. This approach provides higher and more consistent flexural strength values due to its controlled thermobaropolymerization process.

Temporary restorations, whether printed, injected, light-cured, or milled, must be designed to closely match the final treatment outcome in terms of size, color, and shape. Cytological testing of new materials is essential to ensure high biocompatibility and resistance to dental plaque adherence before their use in the oral cavity. A significant advantage of milled and injected polymers is the absence of residual monomer, which helps minimize periodontal inflammation and enhances the overall success of temporary restorations.

The study's findings on thermoplastic polymer frameworks for fixed partial dentures highlight their excellent esthetics, resistance to corrosion, and biocompatibility. However, these materials may not be suitable for patients with bruxism, small occlusal spaces, or complex prosthetic needs. They also have a limited usage period of 180 days and require specialized lab space and equipment. Non-invasive imaging techniques such as Optical Coherence Tomography (OCT) and micro-Computed Tomography (microCT) are invaluable for detecting structural flaws before prostheses are placed in the oral cavity, ensuring improved success and longevity. These insights underscore the importance of modern materials and techniques in enhancing dental prosthetics while recognizing their limitations and specific requirements.