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EVALUATION OF THE MICROHARDNESS OF DIFFERENT 3D PRINTING RESINS FOR DENTURE BASE

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Abstract. *The main material used for the manufacture of complete dentures is a heat-curing acrylic resin. The technological and scientific evolution in all areas of knowledge allows dentistry to absorb technologies such as additive manufacturing, ensuring that the clinical results obtained are safer and more predictable. However, because these materials are recent in use in dentistry, there are no reports on their mechanical properties such as Microhardness, directly related to wear resistance, which is important in complete dentures. To evaluate the Knoop Microhardness of two 3D printing resins for complete denture base in comparison with the heat-curing acrylic resin. Sixty circular specimens (20.0 x 3.0 mm) were made using two 3D printing resins (BioDenture and BB Base) and a heat-curing acrylic resin as control. The printed specimens were designed in the software Rhinoceros 6 and exported in .stl format to the software CHITUBOX Basic 1.9.1. In CHITUBOX the positioning of supports and slicing of the samples were performed, according to manufacturer's instructions. After the impression procedure, the specimens were washed in isopropyl alcohol. The post-curing process for complementary photopolymerization was performed with a specific post-curing booth, according to manufacturer's instructions. The heat-curing acrylic resin specimens were made from a teflon matrix to obtain wax patterns, subsequently included in metal muffles, using stone gypsum and solid Vaseline. Gypsum/resin insulator was applied over the gypsum. The heat-curing acrylic resin was manipulated, placed in the muffle, pressed, and polymerized according to the manufacturer's instructions. All specimens were sanded with a horizontal polisher in a sequence of sandpapers (320, 600, 1200, 2000). For the final polishing, the Alumina (1 µm) in suspension and then with calcium carbonate water solution were used. Five indentations per specimen were made using a Knoop diamond penetrator in the microhardness test. The applied load was 245.2mN for 5 seconds. The data were tested for normality and the one-way ANOVA and Tukey post-test were performed ($\alpha = 0.05$). Statistically significant difference was observed among all resins ($p < 0.001$). The highest values (mean; standard deviation) were observed for the heat-curing resin (18.8; 0.5), followed by BB base (17.7; 1.8) and the lowest values for Biodenture (12.5; 1.2). In conclusion, Heat-curing acrylic resin shows higher Knoop microhardness than 3D printing resins. The use of these new 3D printing resins can decrease the durability of the complete denture.*

Keywords: *Knoop Microhardness, 3D printing resins, heat-curing acrylic resin, denture*

1. INTRODUCTION

In a research conducted in 2010, SB Brazil highlights that 32.8% of adults need some type of dental prosthesis, in the case of the elderly, the number increases to 63.1%. These results show that despite advances in preventive dentistry, the number of partial or total edentulous people in Brazil is still large. The use of dental prosthesis is necessary not only for aesthetic reasons, but also for the maintenance of the stomatognathic system, which influences the masticatory function, phonetics, deglutition and quality of life of the individual (Olchik et al., 2013).

Currently, polymethylmethacrylate (PMMA)-based acrylic resin is the most commonly used material for denture base production, and it can be thermo- or self-curing (Al-Dwairi et al., 2019). This is due to its ease of manipulation, repair and polishing, besides being an aesthetic and low-cost material. However, PMMA presents limitations such as dimensional alterations, susceptibility to fracture and presence of residual monomer (Quezada et al., 2022).

The advent of digital equipment and technologies, such as CAD/CAM, has enabled the development of 3D printing resins for the manufacture of denture bases (Prpić et al., 2020). New 3D printing resins enable shorter production time, better adaptation in support tissues, more stability and greater production economy (Al-Qarni et al., 2020). However, the technology demands well-trained operators and specific technological equipment (Tian et al., 2021).

CAD/CAM technology is based on digital designs created by using software that will be processed in a computer and used for the manufacture of specific 3D structures using the material of interest (Barazanchi et al., 2017). Subtractive and additive techniques are production methods covered by CAD/CAM technology. The subtractive technique is based on the elimination of unwanted parts of a block by means of cutting tools and has as main disadvantages the wasting of material, the high production of waste and the inability to reproduce complex shapes (Braian et al., 2018).

In contrast to subtractive technology, additive technology uses the successive addition of layers of material, in this case liquid 3D printing resin, to build a complex object (Ligon et al., 2017). Light-curing of the liquid resin layers can be done using high power LEDs (DLP process) or a single laser beam (stereolithography - SLA process) (Park et al., 2020).

The additive technology presents advantages over subtractive technology, such as: reproduction of complex parts, lower waste production, lower energy consumption and lower cost, besides dispensing the use of cutting materials. However, it presents as disadvantages the need for additional work after the end of the printing and longer production time (Park et al., 2020; Rahman et al., 2023)

In the first production step, the digital design, in STL format, is imported into a software that makes the slicing of the object of interest, the placement of temporary supports and the printing information is inserted according to the printer to be used (Ligon et al., 2017). The production information will be used by the printer to direct the light beams, responsible for stimulating the photopolymerization of the resin at specific points for the formation of the final object. After printing is necessary a isopropyl alcohol or tripropylene glycol monomethyl ether (TPM) bath for the removal of any potential residue. The final step is post-curing, which consists of using UV light to increase the conversion of polymers present in the printing resin (Stansbury; Idacavage, 2016).

Prpić et al. (2020) and Al-Dwairi (2019) indicate that the physical and mechanical characteristics, such as microhardness and roughness, of 3D printing resins vary significantly by brand and manufacturer, with no standardization. Thus, Steinmassl et al. (2018) conclude that differences in the mechanical characteristics of 3D printing resins are due to composition rather than industrial processing.

Srinivasan et al. (2021) found a strong preference for conventional dentures when compared to 3D printed dentures in terms of aesthetics. Furthermore, the researchers report the need for additional studies with long-term follow-up to completely evaluate the characteristics of 3D-printed resins.

Thus, we can realize that we still have a great demand for the use of dentures in Brazil, requiring an evolution in their production methods to attend to the current needs. Despite the increasing use of CAD/CAM technology in dentistry, studies on the intrinsic physical-mechanical properties of the materials used for 3D printing are still necessary to ensure a quality end product. Therefore, the present study evaluated the microhardness of two 3D printing resins used for making denture bases available in Brazil. The null hypothesis is that there is no difference between the 3-D impression resins and the heat-curing resin used to make dentures.

2. MATERIALS AND METHODS

Twenty circular specimens (Ø20 mm x 3 mm) were made of each 3D-printed resin (Table 1) totalling 40 printed specimens. As control, 20 specimens were obtained in heat-cured acrylic resin.

Table 1 - Information about manufacturers and composition of the materials tested.

Resin	Manufacturer	Type	Composition
Bio Denture	Smart Dent, Brasil	3D-printed resin	Methacrylic ester monomers with stabilizers, initiators and accelerators
BB Base	Printax, Brasil		Monomers, stabilizers, pigments and photoinitiators
Clássico	Artigos Odontológicos Clássico Ltda, Brasil	heat-cured acrylic resin	Copolymer, methyl ethyl methacrylate, DBP, pigments and peroxide, monomer

2.1 Obtaining 3D-printed specimens

To obtain the 3D-printed resin specimens, a three-dimensional object drawing of the specimen (Ø20 mm x 3.5 mm) was generated in the Rhinoceros program and exported in .STL (Standard Triangle Language) format. The object drawing was 3.5 mm thick so that it was possible to polish the specimen and obtain the final dimension with 3 mm thickness. The .STL file was exported to the program CHITUBOX Basic 1.9.1 (CBD Technology Co., Shenzhen, China) for support positioning and slicing of the .STL file in layers for printing (Figure 1). Slicing was performed according to the different 3D printing resins (Table 2).

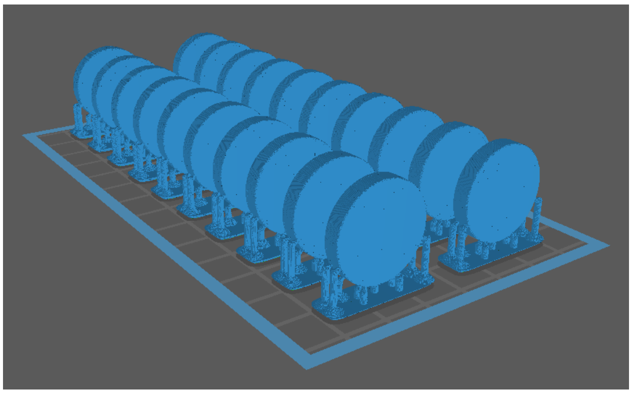

Figure 1. Image of the specimen design with the supports positioned and sliced, ready for printing.

The design with the supports was transferred to the printer (Phrozen Sonic 4K, Odontomega, Ribeirão Preto - SP, Brazil) and the specimens were obtained. The specimens, still on the printing table, were cleaned by isopropyl alcohol baths under agitation (Tornado 3D Cleaning System, Odontomega, Ribeirão Preto - SP, Brazil), with exchange of isopropyl alcohol between baths and drying at room temperature. The post-curing process for complementary photopolymerization was performed with a specific post-curing cabin, with wavelengths of 365nm, 385nm and 405nm (Photo Phrozen Cure Oven V2, Odontomega, Ribeirão Preto, Brazil). The post-curing times varied among the resins. The parameters that were used after the calibrator test are described in Table 2.

Table 2 - Parameters used to print the specimens.

Resin	Impression					Post-cure
	Layer height mm)	**Exposure time (s)**	**Number of base layers**	**Exposure time base (s)**	**Lifting / retracting speed (mm/min)**	**cycles / minutes**
Bio Denture	0,05	4,50	10	35,0	65,0	1/9
BB Base	0,05	3,80	8	35,0	60,0	5/1

2.2 Obtaining the specimens in heat-cured resin

Wax patterns (Ø20 mm x 3.5 mm) were obtained from a Teflon matrix. The patterns were included with gypsum in a metal muffle (Figure 2) for making the specimens in heat-cured resin (control group). The heat-cured resin (Classico) was manipulated in the proportions indicated by the manufacturer, placed in the spaces inside the muffle, which was closed and pressed for 1 hour in a hydraulic press. After pressing, the muffles were placed in a manual press and submitted to a thermal cycle of heating at 1.5 °C/min to 72 °C remaining 1.5 h at this temperature, heating at 1.5 °C/min to 94 °C remaining 1.5 h at this temperature for complete polymerization of the resin.

Figure 2: Metal muffle with the wax patterns in place.

2.3 Polishing procedures

All specimens were immersed in distilled water and placed in an oven at 37 °C for 24 hours to eliminate the residual monomer after completion of the impression and heat-curing.

The remaining resin was removed with a fine cutter and polished with a horizontal polisher. All specimens were sanded with sandpaper sequence (120, 240, 400, 600, 1200 and 2000) and polished with polishing cloth with 1µm alumina suspension and subsequently in polishing cloth with calcium carbonate solution and water.

2.4 Knoop microhardness test

Microhardness was evaluated using a microhardness tester (HMV-2, Shimadzu Corp., Japan) and Knoop penetrator. The applied load was 245.2mN for 5 seconds (Pisani et al., 2012). Five indentations were made per specimen and the values obtained after the quantification of the diagonal of the market rhombus on the surface were calculated by the equipment. The final value attributed to each specimen was the result of the average of the five indentations made.

2.5 Statistical analysis

The data were tested for normality (Shapiro-Wilk) and homogeneity of variance (Levene). As the data presented normal distribution and homogeneity of variance, ANOVA and post-test of Tukey with Bonferroni adjustment were performed. The significance level was 5%.

3. RESULTS

Figure 3 presents the microhardness mean values and standard deviation obtained.

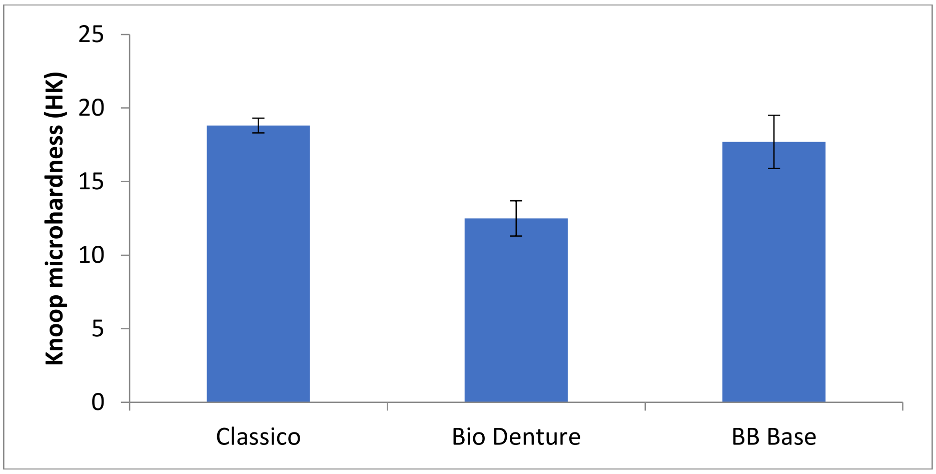

Figure 3 - Graph of the average values of microhardness presented by the groups (n=10).

Statistically significant difference was observed among all resins ($p < 0.001$). The highest mean values (standard deviation) were observed for the heat-curing resin 18.8(0.5), followed by BB base 17.7(1.8) and the lowest values for Biodenture 12.5(1.2).

4. DISCUSSION

The null hypothesis was rejected once 3D printing resins showed lower microhardness than heat-curing resin.

The Knoop microhardness test is most frequently used to evaluate dental materials as it represents the viscoelastic characteristics and provides notions of durability, strength and clinical applications (Shahdad et al., 2007; Schoeffel et al., 2019). Indirectly, the test indicates the degree of polymer conversion, which directly influences the mechanical properties (Shafeeq et al., 2016). Microhardness is directly associated with the abrasion resistance of acrylic resins, thus, higher microhardness values are associated with lower wear of dentures submitted to brushing (Campanha et al. 2005).

Melo et al. (2021) reported that the effectiveness of mechanical and/or chemical biofilm control is related to the longevity of the prosthetic device. However, Sartori et al., 2008 reported that the methods of cleaning and disinfection of full dentures performed by the patient could cause changes in the microhardness of the material. Thus, materials with lower microhardness are more prone to surface degradation and dimensional changes during brushing and also masticatory efforts (Al-Dulaijan et al., 2022).

The wear of prostheses from the brushing process may bring problems such as increased surface roughness and the consequent favoring of microorganism adhesion that may be precursors of prosthetic stomatitis. Prosthetic stomatitis consists of inflammation of the intraoral mucosa in contact with the prosthesis. It is related to the presence of *Candida* *ssp*, mainly *Candida albicans* (Araújo et al. 2022). In addition, the wear from brushing can result in displacement of some areas of the adjacent tissues, causing disadaptation and instability (Mangal et al., 2020). Thus, the materials used to make prostheses must allow an adequate finish, as well as resistance to the occurrence of grooves caused by brushing for a better longevity of the rehabilitation.

Facing the development of 3D printing processes and the recent large distribution of materials for 3D printing, studies in the field are becoming more necessary to provide dental professionals with information about the performance and durability of these materials. The application of 3D printing resins in the base of dentures is recent and the information made available on the properties of these materials is scarce. In the present study it was possible to observe that the printed resins showed lower microhardness than the heat-cured acrylic resin, in agreement with previous results, where the 3D printing resin showed lower microhardness values than the PMMA-based resins (Fouda et al., 2022; Gad et al., 2021; Lourinho et al., 2022; Prpić et al., 2020; Valenti et al., 2022). Despite the lower statistical value observed by the BB Base printed resin (17.7 MPa), the values are close to those observed in the heat-cured resin (18.8 MPa). The other tested printed material, Bio Denture, showed lower microhardness results. The results of the present study show that printed resins have potential for application under the same conditions as heat-cured resins, but they need improvement. Particles can be incorporated into the original composition of a 3D printing resin improving its microhardness (Mangal et al., 2020; Aati et al., 2021), which could contribute to the development of these materials over time.

With the rapid adaptation of CAD-CAM methods to 3D printing and development of new polymeric materials, even though still with limitations, the indications are that 3D printing has an increasing participation in dentistry. In view of this reality, studies are still needed to indicate the behavior of these materials in the oral environment under pH, temperature and bacterial colonization changes. The results shown so far and the simplification in the processes of obtaining prostheses show that with the development of materials for 3D printing the proposed uses can be applied safely and successfully. However, the 3D printing resins showed higher microhardness values than the heat-curing resin, which may affect the durability and maintenance of the health of the supporting tissues of the denture.

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