Comparison of the mechanical properties of 3D-printed, milled, and conventional denture base resin materials

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Directed by Professor Jee-Hwan Kim

A Master's Thesis
Submitted to the Department of Dentistry
and the Graduate School of Yonsei University
in partial fulfillment of the
requirements for the degree of
Master of Dental Science

Hyeong-Ju Yu

December 2023

This certifies that the Master's Thesis
of Hyeong-Ju Yu is approved.

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December 2023

감사의 글

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Abstract

Comparison of the mechanical properties of 3D-printed, milled, and conventional denture base resin materials

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(Directed by Professor Jee-Hwan Kim, D.D.S., M.S.D., PhD.)

Objectives: This study aimed to evaluate the mechanical properties of three-dimensional (3D)-printed resin materials for denture bases by conducting a comparative analysis with dental resin materials for denture bases separately fabricated using conventional methods and computer-aided design/computer-aided manufacturing milling.

Methods: Sixty rectangular specimens were fabricated and divided into before and after thermocycling groups for a three-point flexural test. Single rectangular and single disc specimens from each group were fabricated for dynamic mechanical analysis (DMA) and nanoindentation experiments, respectively.

Results: Regardless of thermocycling, the 3D-printed denture base resin group exhibited a significantly higher flexural strength ($p < 0.05$). Before thermocycling, the flexural modulus of the 3D-printed and milled denture base resin group were significantly higher than that of the conventional denture base resin group ($p < 0.05$). After thermocycling, the 3D-printed denture base resin group exhibited the highest flexural modulus, followed by the milled denture base resin group, and then the conventional denture base resin group. Significant differences were observed between the groups ($p < 0.05$). The 3D-printed denture base resin

group exhibited a higher storage modulus than the other groups in the DMA at 0.1 Hz. The 3D-printed denture base resin group exhibited a higher resistance to nanoindentation deformation and better ability to recover its original shape after the applied force was removed than the other groups.

Conclusion: Regardless of thermocycling, the 3D-printed denture base resin group exhibited higher flexural strength and modulus than the groups fabricated using the other methods, demonstrating excellent mechanical properties. In addition to the flexural test, the 3D-printed denture base resin group also demonstrated superior mechanical properties in all other tests. The 3D-printed denture base resin group exhibited suitable mechanical properties for use in hard denture applications.

Keywords: 3D printing resin, CAD/CAM, denture base, flexural strength, dynamic mechanical analysis, nano-indentation, thermocycling

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I. Introduction

Dentures are effective treatment options for edentulous patients. Among the various materials used for fabricating dentures, poly methyl methacrylate (PMMA) has several advantages in terms of economic feasibility, physicochemical properties, and aesthetics; therefore, it has been actively used in denture manufacturing since the 1930s (Zarb GA, 2012). However, several characteristics of traditional PMMA fabricated using conventional methods, such as insufficient resistance to fracture or deformation from polymerization shrinkage and complex processing procedures, require improvement (Infante et al., 2014; Rodriguez et al., 2013).

Recent advancements in the field of digital dentistry have significantly increased the use of digital technology for denture fabrication (Bidra et al., 2013; Fang et al., 2018). This innovative approach is under active implementation and application in clinical settings as it can replace traditional methods, reducing the drawbacks of polymerization shrinkage, labor, and working time, and improving the accuracy of processing through simplified fabrication procedures (Fiore et al., 2022; Granata et al., 2020).

Computer-aided manufacturing (CAM) involves subtractive machining in which PMMA blocks are milled. Consequently, wear and tear of the milling machine during the cutting process are unavoidable, and

the process is limited to the use of only approximately 90% of the PMMA block (de Oliveira Limírio et al., 2021; Strub et al., 2006). In contrast, additive manufacturing methods, such as three-dimensional (3D) printing, enable the fabrication of more complex structures. Additive manufacturing also allows for a reduction in material consumption of nearly 40% and eliminates concerns about milling machine wear and tear (Alharbi et al., 2017).

Denture bases are susceptible to fracture owing to prolonged exposure to physical stresses caused by mastication. Therefore, denture bases must possess sufficient strength and resilience to withstand such forces without fracturing (Kelly, 1969). Flexural strength refers to the maximum bending stress at the point of fracture, and dentures with higher flexural strength exhibit better resistance to fracture (Zappini et al., 2003). Sustained flexural stress caused by mastication can lead to creep, resulting in a damping effect and potential deformation. To prevent this, the denture bases should exhibit appropriate elasticity and stiffness (Vaidyanathan and Vaidyanathan, 1995). Additionally, a humid oral environment can accelerate moisture absorption of acrylic resin and deteriorate its mechanical properties (Ayaz et al., 2015). Therefore, additional research is needed that includes an artificial aging process that reproduces the oral environment.

Numerous comparative studies on the mechanical properties of 3D-printed, computer-aided design (CAD)/CAM milling and conventional denture base resin materials focusing on strength have been reported. To fully exploit the advantages of digital technology, it is necessary to conduct comparative studies on the mechanical properties from various perspectives.

The aim of this study is to evaluate the mechanical properties of 3D-printed resin materials for denture base by conducting a comparative analysis with dental resin materials for denture base separately fabricated using conventional and CAD/CAM milling methods and to compare changes in flexural strength through a thermocycling process that reproduces the long-term oral environment.

The first null hypothesis of this study states that 1) there will be no significant difference in the mechanical properties between denture base resin materials fabricated by 3D printing and denture base resin materials fabricated by conventional methods or by CAD/CAM milling. The second null hypothesis states that 2) thermocycling will not have any significant effect on the mechanical properties of denture base resin materials

II. Materials and methods

A flowchart describing the experimental procedure is presented in Figure 1.

1. Specimens preparation

Three groups of acrylic denture base resin materials were used in this study, namely, a conventional injection-type resin (Ivocap, Ivoclar Vivadent, Schaan, Liechtenstein), a CAD/CAM milling resin (Vipi Block Gum, VIPI, São Paulo, Brazil), and 3D printing resin (TDD-80, Graphy Co., Seoul, Korea) (Table 1).

To fabricate specimens using conventional injection molding-type resins, rectangular wax duplicates were first flasked and invested in dental stones. Gypsum was poured into a flask and wax duplicates were placed inside the flask. After the gypsum was set, the wax was completely removed and the mold was coated with a separator (Separating Fluid, Ivoclar Vivadent, Schaan, Liechtenstein). The pre-measured resin and monomer capsules (SR Ivocap High Impact, Ivoclar Vivadent, Schaan, Liechtenstein) were mixed using a cap vibrator (Ivoclar Vivadent, Schaan, Liechtenstein) for 5 min before being injected into the flask. The injection process was performed at a pressure of 6 bar according to the injection molding system. The SR Ivocap assembly was polymerized at 100 ℃ for 35 min, and then immersed in cold water for 30 min. Finally, the specimens were removed from the flasks and polished according to the instructions of the manufacturer.

The CAD/CAM specimens were prepared using CAD/CAM denture base-resin blocks. The CAD/CAM milling blocks were cut using a diamond disc and polished to obtain rectangular blocks with set dimensions.

The 3D-printed samples were designed using 3D modeling software (Tinkercad, Autodesk, San Rafael, CA). The design was saved as a standard tessellation language (STL) file, which were used to manufacture specimens using denture base materials. The specimens were fabricated using a 3D printer (Sprint Ray Pro 95, Sprint Ray, Los Angeles, CA) employing the digital light processing technique according to the parameters recommended by the manufacturer. The 3D-printed specimens were cleaned in an ultrasonic bath (UCS-20, Lab Companion, Billerica, MA) using isopropyl alcohol (Samchun Pure Chemical, Pyeongtaek,

Korea), and then cured for 25 min using a curing machine (Cure-M 102H, Graphy, Seoul, Korea) according to the recommendations of the manufacturer.

The specimens for three-point flexural strength test were fabricated in accordance with the international standard ISO 20795-1:2013. The specimen dimensions were 64 mm × 10.0 mm (± 0.2 mm) × 3.3 mm (± 0.2 mm) (length × width × height). A single specimen for each group with the dimensions of 30 mm × 10.0 mm × 3.3 mm (length × width × height) was prepared for the dynamic mechanical analysis (DMA) test. A single 20 mm-diameter and 2 mm-high disk specimen from each group was fabricated for nanoindentation tests.

Sixty specimens (20 from each group) were prepared for the three-point flexural strength tests. Half of the specimens from each group were stored in distilled water for 50 ± 2 h at 37 ℃. The other half of the specimens were subjected to an aging treatment of 10,000 thermal cycles at 5–55 ℃ in distilled water.

Table 1 : Materials of denture base resin and fabrication type

Group	Product name	Manufacturer	Fabrication method
Group C	Ivocap	Ivoclar Vivadent, Schaan, Liechtenstein	Conventional
Group M	Vipi Block Gum	VIPI, São Paulo, Brazil	Milling
Group P	TDD-80	Graphy Co., Seoul, Korea	3D printing

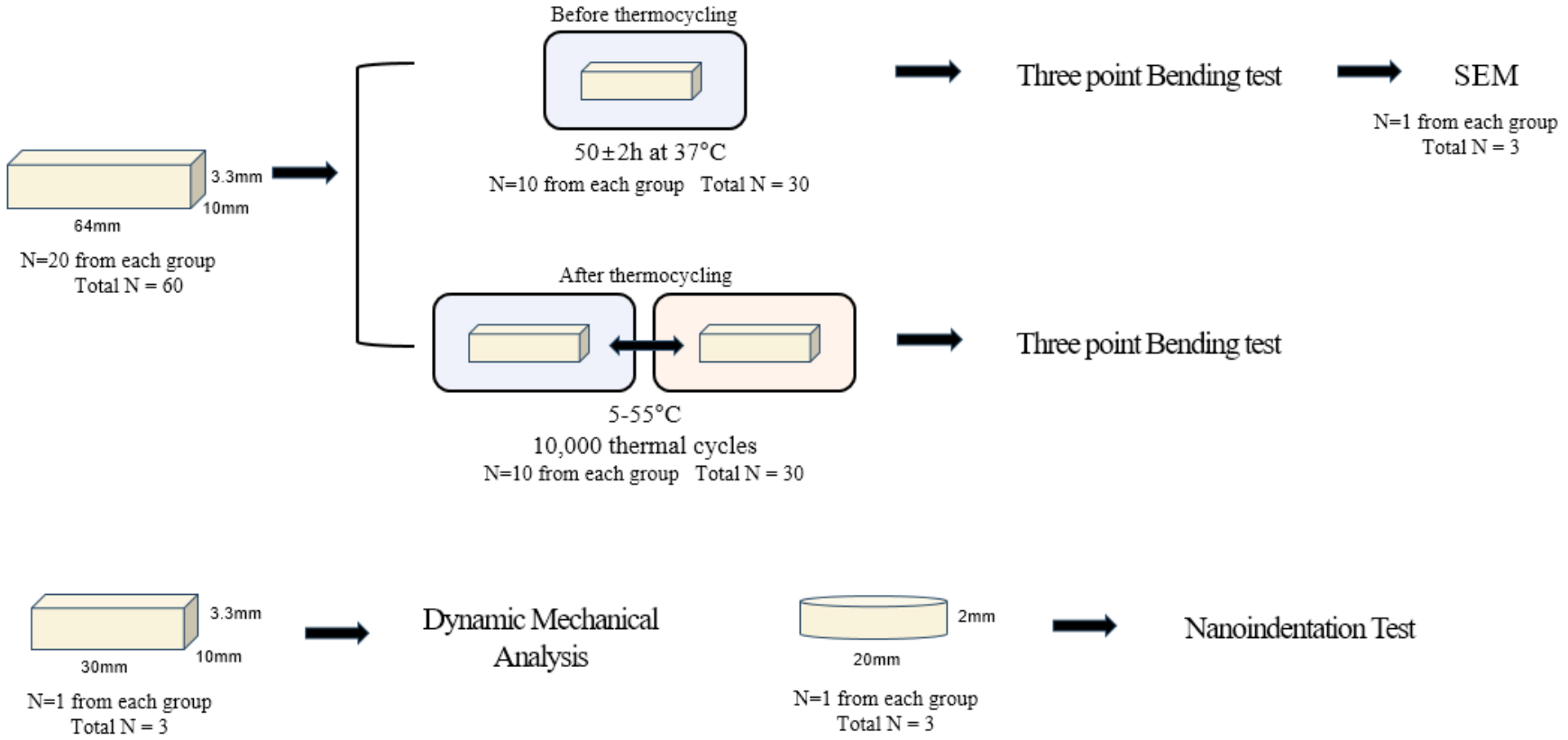

Figure 1 : Flowchart of the experimental procedure.

2. Three point flexural test

The flexural strength and modulus were measured in accordance with the international standard ISO 20795-1:2013 by conducting three-point flexural strength tests using a jig in a universal testing machine (3366 Series; Instron Engineering, Norwood, MA). Immediately prior to testing, the specimens were removed from the water bath and placed in the jig. The distance between the specimen supports was 50 mm and a loading force was applied to the specimens at a crosshead speed of 5 mm/min until they fractured. The maximum flexural strength (σ; MPa) was calculated using Equation (1):

$$\sigma = \frac{3Fl}{2wh^2} \quad (1)$$

The flexural modulus (*E*; MPa) was calculated using Equation (2):

$$E = \frac{Fl^3}{4wh^3d'}, \quad (2)$$

where *F* is the fracture load (N), *l* is the distance between supports (mm), *w* is the specimen width (mm), *h* is the specimen height (mm), and *d* is the deflection (mm) under load *F*.

3. Dynamic Mechanical Analysis

To measure the mechanical dynamics and rheological properties of the materials, DMA (Q800, TA Instruments) was performed at a mechanical dynamic analysis frequency of 0.01–1000 Hz. In single cantilever mode, the strain rate was 0.1%, and the strain rate was automatically calculated by DMA software considering the length and width of the specimen. The chamber was maintained at 37 ℃ and atmospheric pressure during the experiment.

4. Nanoindentation test

Nanoindentation tests were conducted to determine the microscopic surface properties. An Anton Paar GmbH (Graz, Austria) STeP4 MCT3 equipped with a Vickers diamond indenter was used to perform the nanoindentation tests. The applied test conditions were a loading time of 10 s, dwell time of 5 s, and unloading time of 10 s using indentation loads of 2, 4, 6, 8, and 10 N.

5. Scanning electron microscopy (SEM)

Fracture surface images of each group were obtained at magnifications of ×40 using SEM (S-300N, Hitachi, Tokyo, Japan). One representative specimen per group was used, and all specimens were coated with a 100 nm-thick platinum coating using an ion sputter coater (E-1010, Hitachi, Tokyo, Japan) to prepare the samples for SEM analysis.

6. Statistical analysis

Statistical analyses were performed using SPSS software (SPSS 25.0, SPSS Inc., Chicago, IL). The normality of all data was assessed using the Shapiro–Wilk test. For the analysis of flexural strength and flexural modulus data according different fabrication methods, a one-way analysis of variance (ANOVA) was conducted for data following a normal distribution, followed by post-hoc tests using Bonferroni correction. Data that did not follow a normal distribution was anaylzed Kruskal-Wallis test, with post-hoc tests performed using the Mann-Whitney U test. Regarding the comparison between before and after thermocycling process, the data following a normal distribution were analyzed using independent sample t-tests, while data not following a normal distribution were analyzed using the Mann-Whitney U test. All analyses were conducted at a confidence level of 95% ($\alpha = 0.05$).

III. Results

1. Flexural strength

The flexural strength results showed that Group P exhibited the highest flexural strength (119.11 ± 9.29 MPa), followed by Group C (95.28 ± 5.59 MPa) and Group M (93.01 ± 6.27 MPa). Regardless of thermocycling, Group P exhibited a statistically significant higher flexural strength ($p < 0.05$) than Groups M and C. After thermocycling, the mean flexural strength of Groups P and M decreased to 117.62 ± 9.81 and 89.62 ± 8.60 MPa, respectively, and Group C slightly increased to 96.08 ± 4.13 MPa. Despite these changes, no group exhibited statistically significant differences before and after thermocycling ($p > 0.05$) (Table 2 and Fig. 2).

Table 2 : Mean and standard deviation values of flexural strength among the materials and thermocycling groups (unit: MPa).

	Group C	Group M	Group P	*P*-value
Before thermocycling	95.28±5.59[a]	93.01±6.27[a]	119.11±9.29[b]	<.001
After thermocycling	96.08±4.13[a]	89.62±8.60[a]	117.62±9.81[b]	<.001

Different lowercase letters in each column indicate statistically significant differences ($P<0.05$).

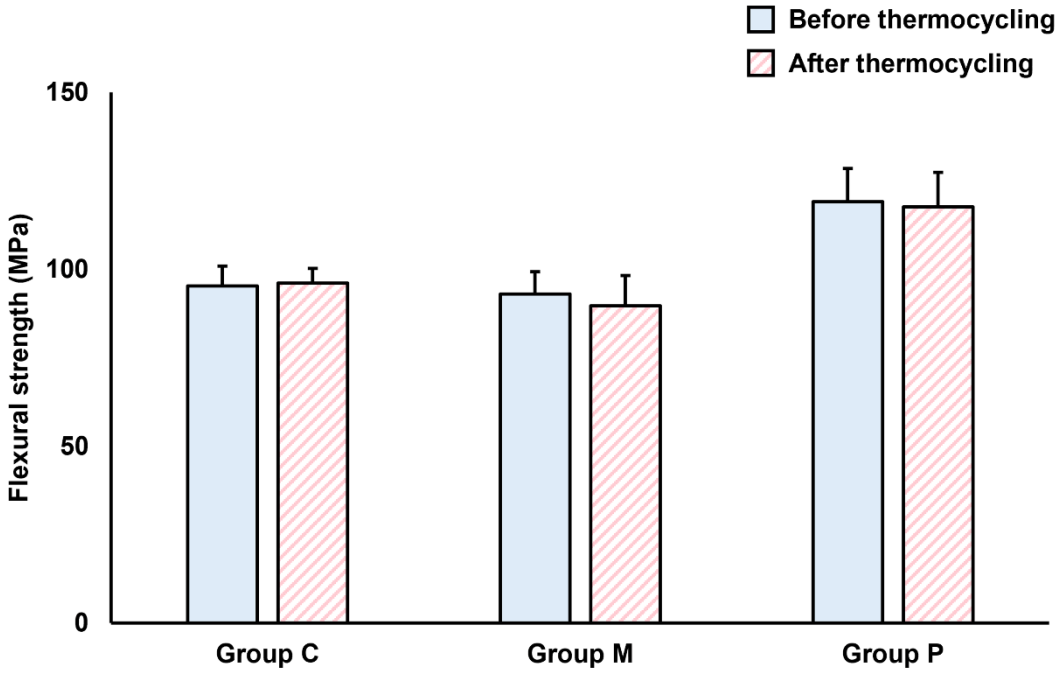

Figure 2. Comparison of the flexural strength for the three specimen groups before and after thermocycling. Groups C, M, and P represent the conventional, milling, and 3D printing fabrication methods.

2. Flexural modulus

The flexural modulus results showed that Group P exhibited the highest flexural modulus (2.38 ± 0.19 GPa), followed by Group M (1.92 ± 0.18 GPa) and Group C (1.42 ± 0.20 GPa). The flexural modulus of Groups P and M were significantly higher than that of Group C ($p < 0.05$). After thermocycling, the flexural modulus of all groups increased. Groups P, M, and C exhibited post-thermocycling flexural modulus of 4.06 ± 0.15, 2.18 ± 0.14, and 1.79 ± 0.14 GPa, respectively. Statistically significant differences were observed between the groups ($p < 0.05$) (Table 3 and Fig. 3).

Table 3 : Mean and standard deviation values of flexural modulus among the materials and thermocycling groups (unit: GPa).

	Group C	Group M	Group P	*P*-value
Before thermocycling	1.42±0.20[a]	1.92±0.18[b]	2.38±0.19[b]	<.001
After thermocycling	1.79±0.14[a]	2.18±0.14[b]	4.06±0.15[c]	<.001

Different lowercase letters in each column indicate statistically significant differences ($P<0.05$).

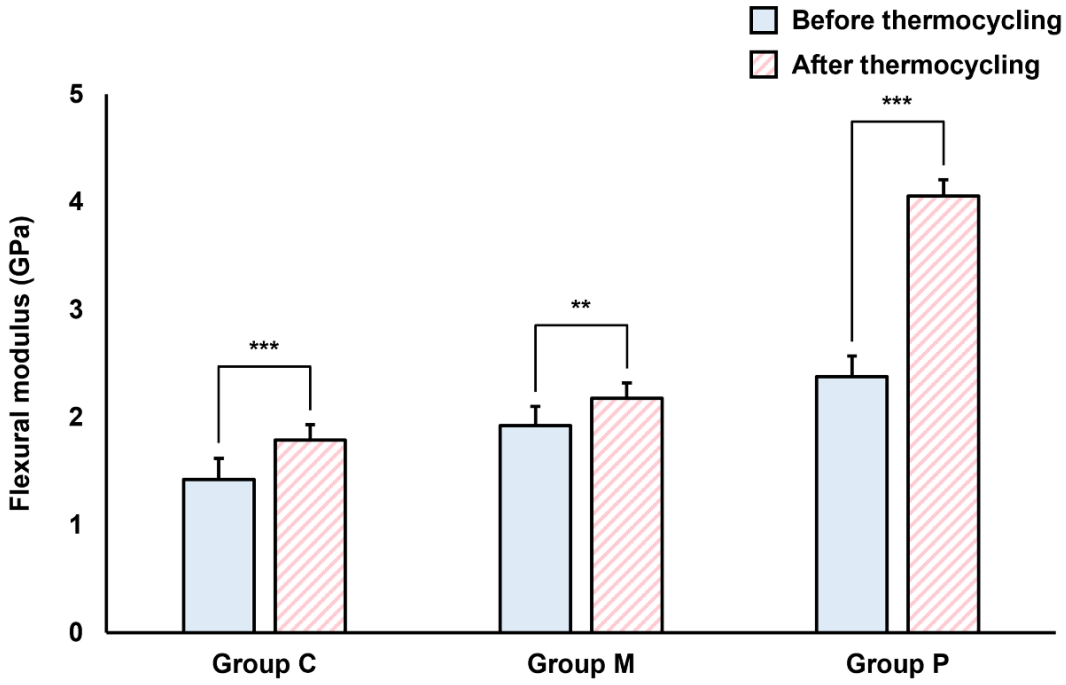

Figure 3. Comparison of the flexural modulus for the three specimen groups before and after thermocycling. Groups C, M, and P represent the conventional, milling, and 3D printing fabrication methods. Comparison among groups is expressed as *P < .05, **P < .01, ***P < .001, asterisks and horizontal bars indicate statistically significant differences before and after thermocycling.

3. Dynamic Mechanical Analysis

DMA was used to evaluate the mechanical properties of the polymer materials under dynamic conditions. The storage and loss modulus of each material were measured at various frequencies (Fig. 4). Groups C, M, and P exhibited storage modulus of 1814 and 2522, 3001.5 and 4307, and 3940 and 5707 MPa at 0.1 and 63 Hz, respectively (Fig. 4a). The storage modulus of all three groups increased with an increasing frequency, indicating a stiffer material response at higher frequencies. Group P exhibited a higher storage modulus at 0.1 Hz than the other materials, which is consistent with the results from the other tests.

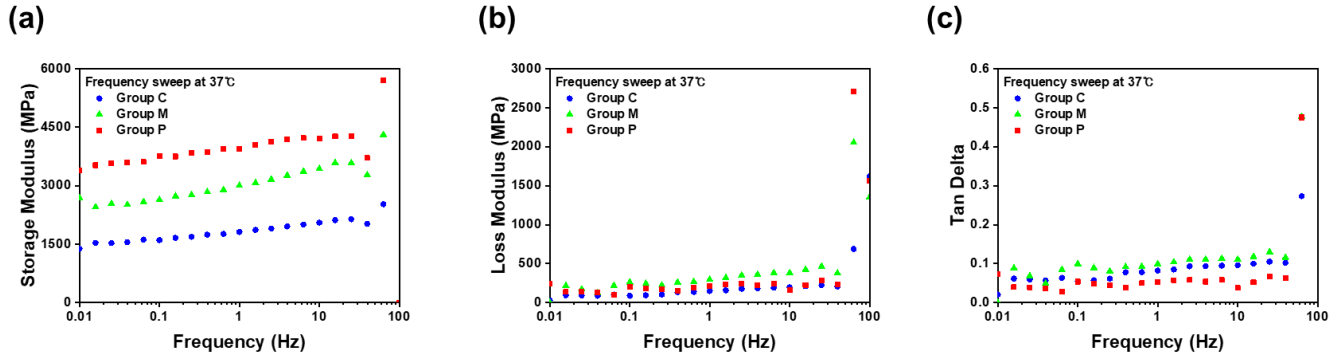

Figure 4 : Dynamic rheological properties as a function of the frequency for Groups C, M, and P at 37 ℃.

(a) Storage modulus, (b) loss modulus, (c) and loss tangent change graphs.

4. Nanoindentation

The applied nanoindentation force was increased from 2 to 10 N in 2 N increments. Group C exhibited indentation depths of 26.7, 38.4, 47.5, 54.2, and 58.3 μm, respectively. After the applied force was removed, the recovered indentation depths were 15.2, 22, 27.5, 31.2, and 32.9 μm, respectively (Fig. 5a). The Group M indentation depths were 23.8, 33, 40.1, 46.5, and 51.8 μm, respectively, and the recovered indentation depths were 15.8, 20.8, 25, 28.5, and 31.8 μm, respectively (Fig. 5b). The Group P indentation depths were 22.8, 30.7, 37.5, 42.5, and 48 μm, respectively, and the recovered indentation depths were 14.5, 18.1, 21.7, 24.1, and 27.1 μm, respectively (Fig. 5c). A comparison of the force-depth curves under a 10 N load revealed that Group P exhibited the lowest deformation and strongest resilience (Fig. 5d). This indicates that Group P exhibited a higher resistance to deformation and a better ability to recover its original shape after the applied force was removed than the other materials.

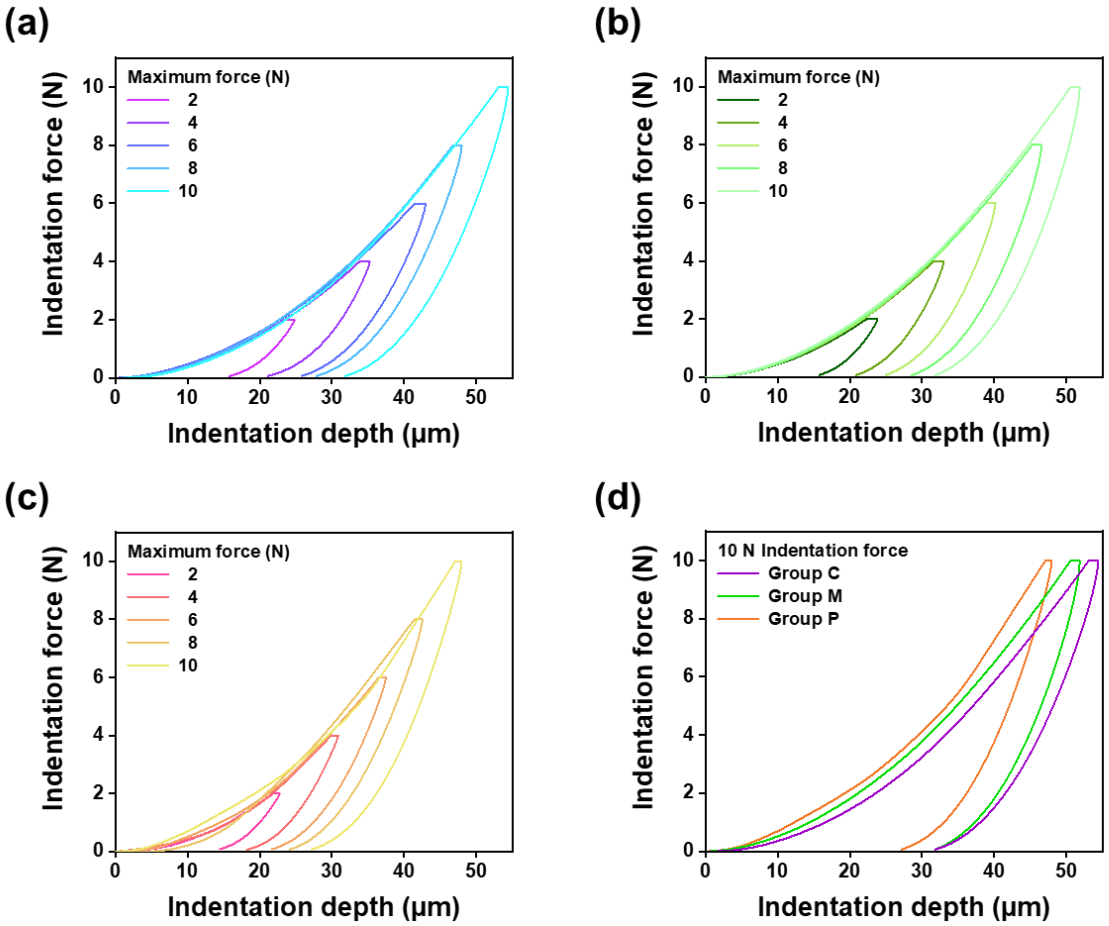

Figure 5 : Pressure-indentation characteristics in the nanoindentation tests. Indentation deformation behavior of the resins as a function of various indentation loads of 2–10 N (a) Groups C, (b) M, and (c) P. (d) Comparison of the force-depth curves of Groups C, M, and P at an indentation load of 10 N.

5. Scanning Electron Microscopy

After the three-point flexural strength test, the fractured section of the specimen was examined using SEM. Group C exhibited a relatively smooth fracture cross-section (Fig. 6a). Group M exhibited an irregular, grooved, and rough surface with a partially torn cross-section (Fig. 6b). Group P resisted the applied force and exhibited a sagging torn cross-section (Fig. 6c).

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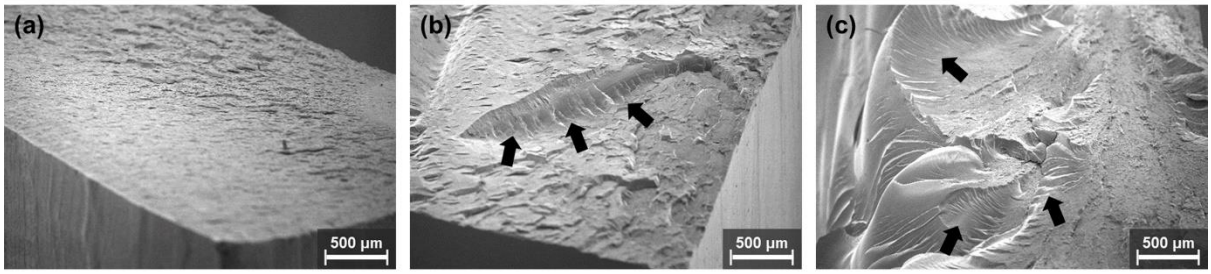

Figure 6 : SEM images (×40 magnification) of the fracture surfaces of each material. (a) Group C. The smooth and even surface. (b) Group M. Arrows indicate the jagged, rough appearance, and partially torn aspect. (c) Group P. Arrows indicate stretching and tearing features.

IV. Discussion

This study aimed to evaluate the mechanical properties of dental resins for denture base fabricated using three different manufacturing methods by employing three-point flexural strength tests before and after thermocycling, and DMA and nanoindentation analyses. The results showed that the Group P exhibited the highest flexural strength and modulus, as compared with the other groups, and the first null hypothesis was rejected. Although there was no significant difference in the flexural strengths before and after thermocycling, there was a significant difference in the flexural modulus. Therefore, the second null hypothesis was partially rejected.

Flexural strength refers to the maximum stress experienced by a specimen during the flexural strength test immediately before it fractures. The flexural strength indicates the mechanical strength of the material (Pacquet et al., 2019; Steinmassl et al., 2018b). The flexural modulus is a strength property calculated as the ratio of stress to strain and indicates the resistance of the material to bending (Ayman, 2017; Meng and Latta, 2005). These mechanical properties are important for dental prosthetic materials because they experience various forces in the oral environment (Gharechahi et al., 2014). Fiore et al. reported that CAD/CAM resin exhibited the highest flexural strength (110.23 ± 4.71 MPa) among the different fabrication methods (Fiore et al., 2022). The CAD/CAM resin was followed by 3D-printed (87.34 ± 6.19 MPa) and heat-polymerized resins (80.79 ± 4.37 MPa). In a review, de Oliveria Limirio et al. reported that several experimental studies have shown that CAD/CAM resins exhibit superior flexural strengths and modulus (de Oliveira Limírio et al., 2021). The excellent mechanical properties of the CAD/CAM resin blocks have been attributed to their high polymerization rate and the resulting improvement in their mechanical properties under high-temperature and high-pressure polymerization conditions (Infante et al., 2014; Steinmassl et al., 2018a). However, Prpic et al. found that experimental groups of heat-polymerized denture base resins exhibit higher flexural strength than CAD/CAM denture base resins (Prpic et al., 2020). They also observed that the experimental groups of heat-polymerized denture base resins exhibited similar levels of strength to CAD/CAM denture baes resins. Additionally, Lee et al. observed that experimental groups of 3D-printed and heat-activated denture base resins exhibited higher flexural strengths and flexural modulus than

CAD/CAM denture base resin (Lee and Lee, 2020). The differences in the resin polymerization method and the degree of polymerization resulting from the fabrication method are important factors that can affect the material properties, but relying solely on the fabrication method to determine the strength of the material has limitations. Lee et al. argued that factors beyond the fabrication method, such as the polymeric composition of the material and the unique fabrication techniques proposed by manufacturers, also play significant roles in determining the material properties (Lee and Lee, 2020). In this study, the 3D-printed denture base resin exhibited excellent flexural strength (119.11 ± 9.29 MPa), as compared with the other denture base resins. Moreover, the CAD/CAM (95.28 ± 5.59 MPa) and heat- polymerized denture base resins (93.01 ± 6.27 MPa) exhibited similar strengths with slight differences. The 3D-printed denture base resin exhibited the highest flexural modulus (2.38 ± 0.19 GPa), followed by CAD/CAM denture base resin (1.92 ± 0.18 GPa) and heat-polymerized denture base resin (1.42 ± 0.20 GPa). In all groups flexural strength met the ISO standards(65Mpa) (ISO 20795-1, 2013). Although flexural modulus fell short of the ISO standards (2Gpa) in groups C and M, the group P met the standard. These results are consistent with previous studies (ISO 20795-1, 2013; Lee et al., 2012; Ucar et al., 2012). The 3D-printed material, which exhibited lower strength in previous studies, exhibited superior physical properties in this study. These experimental results suggest that the 3D-printed material possesses sufficient strength to be used as a hard denture material. These results could be attributed to the unique material characteristics and manufacturing methods employed by the manufacturers, as mentioned by Lee et al. (Lee and Lee, 2020). Additionally, it is possible that post-processing techniques aimed at increasing the polymerization degree of the printing resin may also be associated with these findings.

Further research is needed to compare different methods for enhancing the properties of printing resin materials and to investigate the effects of the compositional components on the properties of currently available printing resin materials. Polymeric materials used in dentistry exhibit viscoelastic properties. This implies that the materials can undergo deformation over time and possess both elastic and viscous characteristics. Owing to the different viscoelastic property requirements for different applications, it is necessary to consider these physical characteristics (Braden and Stafford, 1968). Dynamic testing uses frequency to measure the storage modulus, loss modulus, and loss tangent values to evaluate the

viscoelasticity of a material. The storage modulus, derived from the deformation and recovery patterns at a specific frequency, represents the elasticity of the material. In contrast, the loss modulus represents the viscosity of a material. The loss tangent is the ratio between the storage modulus and the loss modulus, and can be used to evaluate the cushioning ability of a material under compressive loads (Braden and Stafford, 1968). Soft liner denture materials require relatively low storage modulus and high loss tangent values to effectively absorb external forces (Murata et al., 2008). In contrast, hard denture materials require high rigidity, making them advantageous due to their high storage modulus values. Additionally, they should exhibit minimal deformation under external forces; therefore, high storage modulus and loss tangent values are preferred (Vaidyanathan and Vaidyanathan, 1995). In this study, Group P exhibited a high storage modulus value, demonstrating its ability to rigidly and elastically resist external forces. Although the differences were not significant, Group P exhibited the lowest loss modulus and loss tangent values, followed by Group M and Group C (Fig. 4 and 4c). The 3D-printed material that exhibited superior strength in the flexural test also demonstrated properties suitable for hard material applications under dynamic testing.

Hardness tests using indentation have been widely used to evaluate the properties of dental materials (O'Neill, 1967). Hardness is typically analyzed by examining the indentation created using Vickers or Knoop tests (Ryge et al., 1961). The applied load in these tests typically range at 10–500 g. The magnitude of the applied load can be considered a macroindentation when compared to the particle size of the resin material to be analyzed (Willems et al., 1992). Nanoindentation tests, as employed in this study, allow the load range to be adjusted between 0.0001 and 5 g. Microindentation can be measured by analyzing the indentation at a scale of 1 μm, allowing for the precise characterization of the properties of the material. In contrast to the conventional method of analyzing hardness using the indentation area, nanoindentation tests allow for continuous observation of the loading and unloading phases of the load using a depth-sensing instrument (Tabor, 1985). This technique enables not only the analysis of hardness, but also the evaluation of the elasticity of the material. In this study, the deformation curves and indentation depths in micrometers were measured using nanoindentation under a loading force range of 2–10 N. When the same load was applied, Group P exhibited the smallest indentation depth. This indicates that Group P exhibited the highest degree of elastic recovery upon release of the load. Furthermore, when comparing the indentation curves of the three

materials under a 10 N load, Group P exhibited a steeper slope. Considering the extent of deformation with an increasing load, it can be inferred that Group P exhibited the stiffest properties based on the slope steepness. The 3D-printed material exhibited excellent elasticity in terms of deformation recovery and stiffness during the deformation process. These experimental results are consistent with the flexural strength and dynamic test results. In addition to analyzing the indentation depth, further research is required to compare the hardness and flexural modulus values obtained from nanoindentation experiments with the hardness values obtained from Vickers experiments and flexural modulus values.

Thermocycling was used to simulate the conditions of constant exposure to moisture and heat in a clinical environment to more realistically mimic experimental conditions (Oliveira et al., 2010; Rinastiti et al., 2010). Thermocycling at 5–55 ℃ in the presence of water is considered appropriate for aging dental materials. Additionally, Gale and Darvell argued that 10,000 cycles of thermocycling are roughly equivalent to one year of intraoral cycling in terms of environmental conditions (Gale and Darvell, 1999). Accordingly, in this study, thermocycling was conducted for 10,000 cycles at 5–55 ℃ to observe the changes in properties. Ghavami-Lahiji et al. determined the flexural strength and hardness as a function of the number of thermocycling cycles (Ghavami-Lahiji et al., 2018). As the number of thermocycling cycles increased, the flexural strength significantly decreased, whereas the hardness exhibited a concurrent trend of decreasing in some experimental groups and increasing in others. Similar to other studies, Ayaz et al. and Machado et al. (Ayaz et al., 2015; Machado et al., 2012) also reported a decrease in the flexural strength with an increasing number of thermocycling cycles. In this study, although no statistically significant difference was detected, a decrease in flexural strength was observed in Group M and Group P after thermocycling. The decrease in flexural strength was attributed to changes in the properties of the polymers. The heat in the thermocycling process increases the water absorption of the resin. Water absorption affects the polarity of the polymer and changes the distance between polymer chains. Additionally, the absorbed water acts as a plasticizer, which induces a slip-over phenomenon in the polymer chains and degrades the properties of the polymer (Machado et al., 2012). Kawano et al. investigated the flexural strength, hardness, and elastic modulus as a function of the number of thermocycling cycles, similar to the aforementioned studies, and reported that the flexural strength of all experimental groups significantly decreased (Kawano et al., 2001). However, the hardness

and elastic modulus exhibited mixed results, with some experimental groups showing an increase and others showing a decrease. In this study, the flexural modulus increased after thermocycling. Chadwick et al. (Chadwick et al., 1990) reported that the hardness and elastic modulus are influenced by the degree of polymerization of the composite resin matrix and the filler volume, which are components of the polymer. Moreover, Ghavami-Lahiji et al. observed an increase in the degree of polymerization with an increasing number of thermocycling cycles (Ghavami-Lahiji et al., 2018). The increase in the degree of polymerization observed during thermocycling can be attributed to the heat-induced polymerization of the residual unpolymerized monomers within the composite resin (Truffier-Boutry et al., 2006). Ferracane et al. stated that the structural deformation of polymers during thermocycling can induce a relative increase in the filler volume, leading to an increase in the elastic modulus of the material (Ferracane et al., 1998). Based on the studies mentioned above, it is possible to infer the causes of the changes in the elastic modulus following thermocycling. However, if the thermal stress continues to increase and causes significant changes and degradation in the polymer properties, both the hardness and elastic modulus are expected to decrease, similar to the decrease in flexural strength.

Owing to the varied forces experienced in the intraoral environment, it is necessary to employ various experimental methods, as attempted in this study, to reproduce different situations to evaluate the material properties. Furthermore, because the 3D-printed material consistently exhibited stiffness and high strength in all three experiments, in contrast to previous research findings, additional investigations are required to re-evaluate the properties of the 3D-printed materials.

V. Conclusion

This study aimed to compare and analyze the mechanical properties of 3D-printed, milled, and heat-polymerized denture base resins. The following results were obtained under specific experimental conditions:

1. The 3D-printed resin material exhibited suitable mechanical properties for use in hard denture applications.
2. Regardless of thermocycling, the 3D-printed denture base resin exhibited a higher flexural strength and modulus than the materials fabricated using the other methods, demonstrating excellent mechanical properties.
3. Although there was no significant change in the flexural strength after thermocycling, the flexural modulus showed an increasing trend after thermocycling.

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ABSTRACT (KOREAN)

3D 프린팅 의치상 레진과 열중합 의치상 레진 및 CAD/CAM 절삭 가공 의치상 레진의 물성비교

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유 형 주

PMMA 재료는 경제성, 물리화학적 특성, 심미성과 같은 부분에서 여러 장점을 가지고 있어 1930 년대부터 의치 제작에 활발히 사용되어 왔다. 그러나 기존의 전통적인 가공방식의 PMMA 는 중합 수축에 따른 변형이나 파절에 대한 부족한 저항성, 복잡한 기공과정 등의 개선해야 할 점들이 있다. Digital Dentistry 영역의 발전으로, 디지털 기술을 이용한 의치 제작이 활용 되고 있으며, 이는 기존의 방식을 대체하여 중합 수축의 단점을 줄이고 비교적 우수한 물성을 가지게 한다. 또한 노동력과 작업시간을 줄이고 간편화된 기공과정으로 기공 정확도를 향상 시키는 장점을 가지고 있다.

이에 본 연구는 3D 프린팅 의치상 레진과 기존의 전통적인 방식의 의치상 레진 및 CAD/CAM 절삭가공 의치상 레진의 기계적 물성을 장기간 구강 내의 환경을 재현하는 방식의 Thermocycling 전과 후로 나누어 비교 분석해 3D 프린팅 의치상 레진의 기계적 물성을

검증하고자 한다.

열중합 의치상 레진 시편 제작을 위해, 규격 모형의 왁스를 석고로 플라스킹 후, 왁스를 완전히 소환하고 만들어진 주조모형에 분리재(Separating Fluid, Ivoclar Vivadent AG)를 도포하였다. 레진 캡슐(SR Ivocap High Impact; Ivoclar Vivadent AG)을 Cap vibrator (Ivoclar Vivadent AG)를 이용하여 주입 전 5 분간 믹스하였고, 6bar 의 압력으로 주입을 시행하였다. SR Ivocap 을 100 °C 에서 35 분간 중합을 시행한 이후, 30 분간 찬 물에 보관하였다. 시편을 플라스크에서 분리하고 제조사의 지시대로 polishing 하였다.

CAD/CAM 밀링 블록은 automated cutting machine (Okamoto Slicer; Japan) equipped with a diamond blade (SD400, Noritake; Japan)를 이용하여 기준 규격의 모양에 맞게 절삭하였다.

3D 모델링 소프트웨어를 이용하여, 3D 프린팅 샘플을 디자인하였다. 디자인 파일은 Standard Tessellation Language(STL)로 저장하고, 의치상 레진을 제작하였다. 시편은 3D 프린터 (Sprint Ray Pro95, Sprint Ray)를 이용하여 DLP (digital light processing) 기법으로 제조사의 지시에 맞게 출력하였다. 출력된 시편은 초음파 수조 (UCS-20, Lab Companion, Billerica, MA) 와 isopropanol (IPA, Samchun Pure Chemical, Gyeonggido, South Korea)을 이용해 세척하였고, 20 분동안 curing machine (Cure-M 102H, Grapy, Korea)를 이용해 제조사의 지시에 맞게 중합 하였다

3 점 굽힘 시험을 위해 각 그룹별로 20 개씩 총 60 개의 시편을 국제 표준규격 ISO 20795-1: 2013 기준에 맞추어 길이 64 mm, 너비 10(±0.2) mm, 높이 3.3(±0.2) mm 로 준비하였고, 각 그룹에서 절반의 시편은 37 °C 수조에서 50 ± 2 시간을 보관하였고, 다른 절반의 시편은 5 °C 와 55 °C 사이에서 10,000 회의 thermal cycles 을 시행하였다. (70 s per cycle; dwelling time: 30 s, transfer time: 5 s). Dynamic Mechanical Analysis 를 위해 길이 30 mm, 너비 12.5 mm, 높이 3.3 mm 의 1 개의 시편을 제작하였다. Nanoindentation 실험을 위해 직경 20mm, 높이 2mm 의 디스크 형태의 각 그룹별로 1 개의 시편을 제작하였다.

열처리 여부와 관계없이 3D 프린팅 의치상 레진이 유의하게 높은 굴곡강도를 보였다 ($p < 0.05$). 3D 프린팅 의치상 레진과 CAD/CAM 절삭가공 의치상 레진이 열중합 의치상 레진에 비해 열처리 전 유의하게 높은 굴곡계수를 보였고 ($p<0.05$), 열처리 이후 3D-printed group 이 가장 높은 굴곡계수를 나타내면서, CAD/CAM 절삭가공 의치상 레진과 열중합 의치상 레진이 뒤를 이었다. 각각의 그룹은 유의한 차이를 보였다 ($p<0.05$). 3D 프린팅 의치상 레진이 다른 그룹들에 비해 0.1Hz 에서 높은 저장탄성률을 보였으며, Nanoindentation deformation 에 우수한 저항능력과 복원능력을 나타냈다.

열처리 여부와 관계없이 다른 제작 방식에 의한 의치상 재료들에 비해 3D 프린팅 의치상 레진이 높은 굴곡 강도 및 굴곡계수를 보였다. 굽힘 실험 외에도, 다른 실험에서도 동일하게 3D 프린팅 의치상 레진이 우수한 기계적 물성을 나타냈다. 3D 프린팅 의치상 레진은 Hard denture 용 재료로 사용하기에 적합하다고 사료된다.

핵심 되는 말 : 3D printing 레진, CAD/CAM, 의치상, 굴곡강도, 굴곡계수, dynamic mechanical analysis, nano-indentation