Three-Dimensionally Printed Versus Conventionally Cured Polymer-Based Material for Interim Restorations.
Doaa Al-Jubouri, Mohammad Saad

Master thesis, 30 hp
Tandläkarprogrammet/ Examensarbete, 30 hp
Autumn term 2021
ABSTRACT

Background: Three-dimensional (3D) printing is a manufacturing technique, based on building objects layer by layer. It has received more attention lately especially in the medical and dental fields.

Aim: To investigate two mechanical properties of three-dimensionally printed polymer-based materials and compare them with conventionally cured polymer-based material.

Methods: Samples of four 3D-printed polymer-based materials (NextDent C&B MFH; NextDent Denture 3D+; NextDent Ortho Rigid and Freeprint® temp) and a conventionally cured and hand-mixed polymer-based provisional material (Luxatemp star) were investigated. Flexural strength and Vickers hardness were analyzed. Before the tests were carried out, all samples were placed in water in 37°C for at least 24 hours.

Results: The flexural strength results showed that there was statistically significant difference between Luxatemp star, NextDent C&B MFH and Freeprint® temp. Both 3D printed materials had a higher flexural strength than the conventionally cured material (Luxatemp star). At the same time, there was no statistically significant difference between Luxatemp star, NextDent Denture 3D+ and NextDent Ortho Rigid. The hardness values showed no statistically significant difference between the conventionally cured material (Luxatemp star) and the 3D printed materials. Furthermore, no statistically significant differences could be seen between the different 3D printed materials.

Conclusions: NextDent C&B MFH and Freeprint® temp had higher flexural strength than the conventionally cured material. NextDent Ortho Rigid and NextDent Denture 3D+ had a flexural strength comparable to the conventionally cured polymer-based material. 3D printed materials had a hardness comparable to the conventionally cured ones.
BACKGROUND

Three-dimensionally printing (3D), which is also known as additive manufacturing, has become increasingly used across the healthcare industry. This term is used to describe the process of building objects using a layer by layer (multiple layers) technique. 3D printing methods have been used since the late 1980s and 1990s. However, the use of the term 3D printing is relatively new (Bahargav et al. 2017; Dawood et al. 2016). And nowadays this technology is gaining an extraordinary increase throughout multiple biomedical disciplines. Even though creating 3D printed organs is still a faraway goal into the future, dentistry and maxillofacial surgery have been already applying 3D printing in many significant ways (Dawood et al. 2016).

3D printing is typically practical in medical uses because of its high build resolution, smooth surfaces, and the capability of a fast building-process, in addition to its solid structure at the Z axis caused by strong chemical bonds among its layers (Stansbury and Idacavage, 2015).

Computer-Aided Design and Computer-Aided Manufacturing (CAD and CAM) software is used in 3D printing. CAM can be classified based on the production process into three main types: forming, subtractive or additive manufacturing. The Forming part includes an alteration in the shape of demanded pieces without removing or adding any materials, vacuum forming moulding is such example. On the other hand, subtractive manufacturing uses a cutting tool to dispose of the unwanted material (Stansbury and Idacavage, 2015). Whereas additive manufacturing creates a final product by adding materials to it rather than removing them and that gives the ability to design a complex structure when it is required (Dawood et al. 2016; Stansbury and Idacavage, 2015).

Additive manufacturing has various techniques such as Stereolithography (SLA), Digital light projection (DLP), Selective laser sintering, Fused deposition modeling, Multi jet fusion, etc. (Stansbury and Idacavage, 2015). Yet most of the 3D printers used in dentistry depend on SLA or DLP (Reymus et al. 2019).

In SLA, the 3D structures can be built by a laser light beam directed by a Galvano mirror, that induce a polymerization of material monomers, which in return will form the final structure (Scotti et al. 2020). In this technique the z axis is defined by the depth of the cure which is decided by the photo initiator in addition to the conditions of exposure (wavelength, intensity, and time of exposure/velocity). UV absorbers help forming transparent parts. The photo-induced layer has a thickness of 50 to 200 µm (Stansbury and Idacavage, 2015).

In DLP the 3D structure is built by flashing a light through the whole layer from a digital projector screen (Lin et al. 2019).
The use of 3D printing in dentistry has the advantage of fitting the various needs of patient-customized model implant, crowns and bridges. (Stansbury and Idacavage, 2015). It supports the fact that each patient has his/her own distinctive procedures of restoration or reconstruction that can be achieved precisely by 3D printing. Additionally, by transferring a patient’s data through the internet and designing his/her smile with a CAD-software we can save a lot of time and effort (Dawood et al. 2016).

Nowadays, it is increasingly common for temporary constructions to be made by using CAM, for example for temporary prosthetic constructions. In 2020 there were 155 790 crowns placed in Sweden, (Försäkringskassan 2020). Therefore, it is important to analyze and improve the mechanical properties of materials in temporary constructions.

For temporary restorations polymethyl methacrylate (PMMA) and bis-acrylic resins are among the most used materials as they are cost efficient and adequate for clinical use. However, they still lack the aspect of digital modification and can only depend on free-hand fabrication (Lin et al. 2019). Ultimately, between milling and 3D printing, 3D printed restorations have the advantage of improving the acceptance of the patient, by providing sufficient marginal and internal fits, and having lower cost (an average of 300 tooth crowns can be printed using 1 liter of resin) (Lin et al. 2019). Additionally, the increased orientation towards intraoral scanners opens the way for 3D printing to be used for creating a physical model of a patient’s scanned jaw. Even though printing a master model is not common nowadays, it still can be used for conventional purposes, such as adding a veneering material. It can be more convenient to see those restorations exhibited on a model even if it has already been designed digitally (Dawood et al. 2016).

There is a long way to go before putting 3D printed polymer-based materials into further use in dental practices. We can see that 3D printed ceramic and metallic constructions are already used as materials for implants, bridges and crowns and other types of dental applications. Although the use of 3D printed polymer-based materials has spread significantly in a lot of dental aspects (Stansbury JW and Idacavage MJ, 2015). Literature about mechanical properties of 3D printed materials in dental use is rare, so more research in vitro as well as in vivo is obligatory (Reymus et al. 2019). It is still in continuous need for development, especially in processing technologies and the materials being used (Stansbury JW and Idacavage MJ, 2015).
Interim restorations are important for protecting the dental pulp, protecting against sensitivity pain and patient comfort. Since interim restorations may get damaged in real life for various reasons, it is essential for the material to have a high flexural strength. Therefore, mechanical properties such as hardness and flexural strength are some qualities to consider before choosing the 3D material (Scotti et al., 2020). Vickers hardness test and flexural strength (three-point bending test) are commonly used tests for studying mechanical properties. Therefore, the aim of this project was dedicated to compare the mechanical properties hardness and flexural strength of 3D printed and conventionally manufactured polymer-based materials for interim use.

According to Scotti et al. (2020), the 3D printed resin had better mechanical properties than bis-acrylic resin. This result was achieved by using 3-point bend test and Knoop hardness test. Another study, (Reymus et al. 2019) showed that the 3D printed restorations for interim use are comparable to milled and conventionally fabricated restorations and can be an alternative for them.

The null hypothesis for this study is that there is no major difference between 3D printed materials and the tested resin-based materials regarding mechanical properties flexural strength and hardness.
METHODS

Specimen design and fabrication
The in vitro study involved five polymer-based materials. Four of these materials were 3D printed. The following materials for 3D printing were used: NextDent C&B MFH, Freeprint® temp, NextDent Denture 3D+ and NextDent Ortho Rigid. The conventionally cured material (bis-acrylic resin based) was Luxatemp star. The manufacturing technique, manufacturer and the composition of each material are presented in Table 1.

The test groups consisted of beams with a dimension of $25 \pm 2 \times 2.0 \pm 0.1 \times 2.0 \pm 0.1$ mm that were produced according to the Swedish standard SS-EN ISO 4049: 2009. Beams of Luxatemp star, were manufactured by hand following the manufacturer’s recommendations. The involved components were blended and inserted into a customized mould of silicon (Provil NOVO Putty, Kulzer GmbH, Hanau, Germany), that have the previously mentioned dimensions.

The rest of the specimens were ordered and manufactured with the same dimensions according to the Swedish standard SS-EN ISO 4049: 2009.

Additionally, all specimens were then ground to their final dimension with a grinding machine (LaboPol-30, Struers ApS, Ballerup, Denmark) by using SiC coated (P1200) abrasive paper.

For an illustration of the workflow see Fig 1.
In the present study, all the materials above were assessed for their flexural strength and hardness. That’s by applying 11 specimens of each material on the flexural strength test and 4 specimens of each material on the hardness test.

Flexural strength
The 3-point bending test was carried out after water aging, where all specimens were placed in tap water for at least 24 hours in $37^\circ$ according to the ISO 4049: 2009. After that, the test was completed using a testing machine (Tinius Olsen H10KT, Horsham, PA, USA) that had a crosshead speed of 0.75 mm/min after aging. The force-load was increased until the specimen cracked.

To calculate flexural strength (MPa) from the load till fracture the following formula was used:

$$\sigma = \frac{3FL}{2Wh^2}$$
σ stands for flexural strength [MPa].
F stands for the maximum force applied to the test sample [N].
L is the length of the sample [mm].
W is the width of the sample [mm].
h is the height/thickness of the test specimen [mm].

Vickers Hardness
The Vickers hardness test method involves making indentations on the specimen by using a Vickers diamond, built in a testing machine (Zwick hardness tester Z 3.2A, Ulm, Germany). The measurement for the length of the diagonals (mm) of the impression was done by using a built-in microscope. Before the test, all specimens were placed in water for at least 24 hours in 37°C according to ISO 4049: 2009.
Fractured fragments from the flexural strength tests were used for the hardness tests. The load 0.5 Kg was applied for 15 seconds on the largest fractured fragment n=4 for each material on the same specimen after performing a flexural strength test. One measurement was performed on each specimen. Thereafter the Vickers Hardness was calculated using the following formula:

\[ HV = 1.854 \frac{F}{d^2} \]

HV stands for Vickers Hardness, [MPa].
F is the force load applied to the specimen, [Kgf].
d is the mean of the two diagonals, \(d_1\) and \(d_2\), [mm].

Statistical analysis
Hardness test and Flexural strength test were done on several different days. All data has been saved and analyzed by Microsoft Office Excel 2021 in addition to IBM SPSS Statistics version 27. Mean values were calculated by Microsoft Office Excel 2021. Group comparison was done by IBM SPSS Statistics by Crosstabs. A p value of < 0.05 was considered as statistically significant.

Literature
The literature used in this study was found by using free term searching on PubMed. Only publications with full text available in English were included. Literature was also obtained by Google scholar web engine in addition to articles provided by the tutor of this study. No filter for excluding articles was used, but the focus was on the newest studies with the latest updates. Free terms used for the literature search, were “3D printing in dentistry”, “flexural strength”, “Vickers hardness”, “mechanical properties of interim restorations”, “3D printed
vs. conventionally cured” and “additive manufacturing”. Google search terms; “3D-printed material”, “3 punkts böjhållfasthetstest” and “hårdhetstest”.

**Ethical Approval**  
This project does not involve any human participants or animal experiments.  
Beneficial implications of this project, by doing this study we hope that we will get an overview of how close we are to be able to replace the conventionally cured polymer-based materials with the 3D printed materials in clinical use.
RESULTS

The 3D printed beams had flexural strength values ranging between 76.2 and 120.8 MPa, as shown in Fig 2. The hand manufactured beams (Luxatemp star) ranged between 60.3 and 97.8 MPa. Both of the NextDent C&B MFH and the Freeprint® temp specimens had the highest flexural strength from 92.9 to 120.8 MPa and 100.4 to 120.7 MPa, respectively. NextDent Ortho Rigid specimens ranged from 82.9 to 110.2 MPa. NextDent Denture 3D+ had the lowest median flexural strength among the five materials tested with a range from 76.2 to 94.6 MPa.

Descriptive statistics for hardness values are presented in Fig 3. The values of Vickers hardness of the 3D printed beams ranged between 13.1 and 20.1 HV while Luxatemp star beams ranged between 17.5 and 23.4 HV.

All the materials were compared with each other in Table 2 and 3 in terms of flexural strength p-value and hardness p-value. The flexural strength result shows that there is a statistically significant difference between Luxatemp star and NextDent C&B MFH (P=0.000) and between Luxatemp star and Freeprint® temp (P=0.001). NextDent C&B MFH and Freeprint® temp had higher median flexural strength values than the conventional material. At the same time, there was no statistically significant difference between Luxatemp star and NextDent Denture 3D+ (P=1.000) and between Luxatemp star and NextDent Ortho Rigid (P=1.000).

When it comes to flexural strength comparison within different 3D-printed materials as it is seen in Table 2, there is no statistically significant difference between NextDent C&B MFH and Freeprint® temp (P=1.000), NextDent Denture 3D+ and Nextdent Ortho Rigid (P=1.000) and between Nextdent Ortho Rigid and Freeprint® temp (P=0.166). On the other hand, there were statistically significant differences between NextDent C&B MFH and NextDent Denture 3D+ (P=0.000), NextDent Denture 3D+ and Freeprint® temp (P=0.001) and between NextDent Ortho Rigid and NextDent C&B MFH (P=0.046).

The hardness P-value (Table 2) showed no statistical significant difference between the conventionally cured material (Luxatemp star) and the 3D printed materials (p >0.05). The same result showed within different 3D printed materials, that is no statistical difference appeared between them (p>0.05).
DISCUSSION

The study was performed using 3D printed beams ordered from two different labs and the control group (Bis-acryl methacrylate) Luxatemp star beams were clinically produced at the lab at University Hospital of Umeå.

As the present results show, two of the 3D printed materials NextDent C&B MFH and the Freeprint® temp had higher flexural strength values in comparison with the control samples. The other two 3D printed materials NextDent Ortho Rigid and NextDent Denture 3D+ had comparable values to the control.

The control group, the bis-acryl methacrylate-based material (Luxatemp Star) had a mean value of 83.4 MPa. The flexural strength of the 3D printed material NextDent C&B MFH for example, had a mean value of 111.5 MPa. That means the result of flexural strength coincides with previous studies (Chen et al.2020; Takamizawa et al.2014; Tahayeri et al.2017) and the Nextdent product brochure. NexDent specification brochure shows that the 3D printed material NextDent C&B MFH had a mean-value between 100-130 MPa. According to Takamizawa et al. (2014), the Bis-acryl methacrylate-based material Luxatemp Automix Plus has a mean-value of 87.7 MPa.

Accordingly, the null hypothesis of the flexural strength in the present study was rejected for the following materials: NextDent C&B MFH and Freeprint® temp. The statistical analysis showed significant differences between Luxatemp star and those materials. On the other hand, NextDent Denture 3D+ and NextDent Ortho Rigid showed a kind of similarity with Luxatemp star considering the mean-values, 86.9 MPa for NextDent Denture 3D+, 96.6 for NextDent Ortho Rigid and 83.4 MPa for Luxatemp, unlike other 3D printed materials.

The second test in this study was Vickers Hardness, which is about measuring the resistance to a localized plastic deformation made by mechanical indentation. As seen in Table 2, the p-value for hardness test exceeds 0.05 for each material compared to the Luxatemp star, which supports the null hypothesis. Statistical analysis showed, therefore, no statistically significant differences between study material group of 3D printed materials and the control group (Luxatemp star) concerning hardness. In this study, the control (Luxatemp star, Fig 3) had the highest median Vickers hardness value of 21.1. At the same time the mean Vickers hardness value is comparable to a previous study by Lenglerphol et al. (2019), the Luxatemp had mean Vickers hardness value 22.9. Thereafter comes NextDent Denture 3D+, Freeprint® temp, NextDent Ortho Rigid and NextDent C&B MFH with mean-values of (17.1, 15.7, 15.7 and 15.1 respectively).
Although the Vickers hardness test is a valid method, some factors can affect the measurements, for example the resolution of the optical system, the elastic recovery of the material and the operator's perception (Farina et al, 2012). In some studies, the Vickers hardness test was not possible to accomplish on 3D printed resins (Berli et al, 2020). Because of the previously mentioned factors and the complexity of micro-measurements, the sample size was limited to four samples of each material, instead of eleven as it was planned at first. In addition, three indentations should be performed on each specimen, but the fractured fragments were too small to accommodate three indentations. To get a better overview of material’s hardness, more samples are suggested to be investigated in the future. Furthermore, new specimens that have not been fractured in a flexural strength test should be used since the test might alter the hardness values.

As it is shown in the results of the present study, Luxatemp star had a wider range of measuring values compared to 3D printed materials in both tests, Vickers Hardness values between 17.5 and 32.0 MPa for Luxatemp Star while the flexural strength values ranged between 60.3 and 97.8 MPa. This probably depends on the production procedure of Luxatemp specimens. The hand mixing causes a higher risk for inhomogeneous specimen – the use of conventional auto-mixing tips might increase the risks for porosities and incomplete polymerization.

The reason why the mechanical properties differed between the 3D-printed materials could be due to the different chemical compositions of the materials. That is also reported in a previous study (Revilla-León et al. 2019). The sample size was relatively limited in this study especially for the hardness tests. Therefore, in future research, mechanical properties of 3D printed materials still need to be investigated and the development of new and improved materials is fast.
CONCLUSION
Based on the findings of the present in vitro study, bearing the given limitations in mind, the following conclusions were drawn:

1. NextDent C&B MFH and Freeprint®temp had a significantly higher flexural strength than the conventionally cured polymer-based material. NextDent Ortho Rigid and NextDent Denture 3D+ had a flexural strength comparable to the conventionally cured polymer-based material.

2. The 3D-printed materials tested had a hardness comparable to that of the conventionally cured material. More research is needed.

ACKNOWLEDGMENTS
The specimens were kindly provided by Forstec and we would like to express special thanks to them. We would also like to acknowledge and thank for the appreciated guidance and motivation from our tutor Wen Kou.
REFERENCES


Försäkringskassan. (2020). Antal utförda tandvårdsåtgärder. https://www.forsakringskassan.se/statistik/statistikdatabas/!ut/p/z1/04_Sj9CPykssvoxPLMnMzovMAfljo8ziLQi8TDv8Dlx8Ddv8jQwCfZ3dLUxDPY1dnE30w8EKDHAARwP9KGLo41EQh4cPoosBITDxdnQ3dnA293Lo83A8eQIDqTTvNfQ4NgY6gCPGYU51ZGGGQ6KgIAcdXorg!!/#/tand/tand-atgard. (2021-11-21)


Stansbury JW, Idacavage MJ. 2016. 3D printing with polymers: Challenges among expanding options and opportunities. Dent Mater. 32:54-64.


Figure 1. Flowchart of the workflow for this study.
Figure 2. Median values and ranges of flexural strength of the conventionally cured polymer-based beams and the 3D printed beams
**Figure 3.** Median values and ranges of Vickers hardness of conventionally cured polymer-based and 3d-printed beams.
**Table 1:** Type, name, manufacturer, and composition of the resin materials tested.

<table>
<thead>
<tr>
<th>Manufacturing technique</th>
<th>Name</th>
<th>Manufacturer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>Luxatemp star</td>
<td>DMG Chemisch-Pharmazeutische Fabrik GmbH, Hamburg, German</td>
<td>Acrylic resin, glass powder and silica. Contains urethane dimethacrylate, aromatic dimethacrylate, glycol methacrylate.</td>
</tr>
<tr>
<td>3D-printed</td>
<td>Freeprint® temp</td>
<td>Detax GmbH &amp; Co, Ettlingen, Germany</td>
<td>Mixture of acrylic/methacrylic resins with auxilliary matters</td>
</tr>
<tr>
<td>3D-printed</td>
<td>NextDent Denture 3D+</td>
<td>NextDent BV, Soesterberg, Netherlands.</td>
<td>Ethoxylated bisphenol A dimethacrylate 7,7,9(or 7,9,9)-trimethyl-4,13-dioxo-3,14-dioxo-5,12-diazahexadecane-1,16-diyl bismethacrylate 2-hydroxyethyl methacrylate Silicon dioxide diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide Titanium dioxide</td>
</tr>
<tr>
<td>3D-printed</td>
<td>NextDent Ortho Rigid</td>
<td>NextDent BV, Soesterberg, Netherlands.</td>
<td>Ethoxylated Bisphenol A Phosphine oxide</td>
</tr>
</tbody>
</table>
Table 2. Flexural strength P-value between Luxatemp star and 3D-printed materials and between different 3D-printed materials

<table>
<thead>
<tr>
<th></th>
<th>NextDent C&amp;B MFH</th>
<th>NextDent Denture 3D+</th>
<th>NextDent Ortho Rigid</th>
<th>Freeprint® temp</th>
<th>Luxatemp star</th>
</tr>
</thead>
<tbody>
<tr>
<td>NextDent C&amp;B MFH</td>
<td>–</td>
<td>0.000</td>
<td>0.046</td>
<td>1.000</td>
<td>0.000</td>
</tr>
<tr>
<td>NextDent Denture 3D+</td>
<td>0.000</td>
<td>–</td>
<td>1.000</td>
<td>0.001</td>
<td>1.000</td>
</tr>
<tr>
<td>NextDent Ortho Rigid</td>
<td>0.046</td>
<td>1.000</td>
<td>–</td>
<td>0.166</td>
<td>1.000</td>
</tr>
<tr>
<td>Freeprint®temp</td>
<td>1.000</td>
<td>0.001</td>
<td>0.166</td>
<td>–</td>
<td>0.001</td>
</tr>
<tr>
<td>Luxatemp star</td>
<td>0.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.001</td>
<td>–</td>
</tr>
</tbody>
</table>

Statistically significant difference (P <0.05).
No statistically significant difference (P > 0.05).
Table 3. Vickers hardness P-value between Luxatemp star and 3D-printed materials and between different 3D-printed materials

<table>
<thead>
<tr>
<th></th>
<th>NextDent C&amp;B MFH</th>
<th>NextDent Denture 3D+</th>
<th>NextDent Ortho Rigid</th>
<th>Freeprint® temp</th>
<th>Luxatemp star</th>
</tr>
</thead>
<tbody>
<tr>
<td>NextDent C&amp;B MFH</td>
<td>-</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.079</td>
</tr>
<tr>
<td>NextDent Denture 3D+</td>
<td>1.000</td>
<td>-</td>
<td>1.000</td>
<td>0.000</td>
<td>0.393</td>
</tr>
<tr>
<td>NextDent Ortho Rigid</td>
<td>1.000</td>
<td>1.000</td>
<td>-</td>
<td>1.000</td>
<td>0.131</td>
</tr>
<tr>
<td>Freeprint® temp</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>-</td>
<td>0.136</td>
</tr>
<tr>
<td>Luxatemp star</td>
<td>0.079</td>
<td>0.393</td>
<td>0.131</td>
<td>0.136</td>
<td>-</td>
</tr>
</tbody>
</table>

Statistically significant difference (P <0.05).
No statistically significant difference (P > 0.05).