The Effect of Different Post-Curing Methods on Chemical Properties of 3D Printed Resin

by

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Abstract

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Purpose: To investigate the effects of different post-curing units on chemical properties (degree of polymerization) of 3D printed resins to determine whether less expensive alternative post-curing units can be a viable alternative to the manufacturer's recommended units.

Methods: Forty-five samples were fabricated with an LCD printer (Phrozen Sonic Mini, Phrozen 3D, Hsinchu City, Taiwan) using MSLA Dental Modeling resin (Apply Lab Work, Torrance, CA, USA). These samples were divided randomly into four different groups for post-curing by four distinct curing units, the Phrozen Cure V2 (Phrozen 3D, Hsinchu City, Taiwan), a commercial acrylic nail UV LED curing unit (SUNUV, Shenzhen, China), a homemade curing oven fabricated from a readily available UV LED light source (FastToBuy, Shenzhen, China) and the Triad® 2000™ tungsten halogen light source (Dentsply Sirona, York, Pennsylvania, USA). The degree of conversion was measured by FTIR spectroscopy using a Nicolet 6700 FTIR Spectrometer (ThermoFisher Scientific, Waltham, MA, USA).

Results: The Phrozen Cure V2 had the highest overall mean degree of conversion value, 69.6% with a 45-minute curing time. The Triad® 2000 VLC Curing Unit had the lowest mean degree of conversion value at the 15-minute interval with 66.2% and tied the lowest mean degree of conversion at the 45-minute interval with the Homemade Curing Unit, both with 68.2%.

Conclusion: The type of light-curing unit did not yield statistically significant differences in the degree of conversion values. There was a statistically significant difference in the degree of conversion values between the 15-minute and 45-minute curing interval. When comparing individual light-curing units there was a statistically significant difference in the degree of

conversion for the Phrozen Cure V2 between the 15-minute and 45-minute curing time ($p = 0.029$).

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Dedication

This thesis is dedicated to my wonderful wife Monica, my mother Debbie, and stepfather David. Your unwavering support and love throughout residency and life, in general, have made me the person I am today and I cannot thank you enough.

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Chapter 1

Introduction and Background

Digital dentistry has become ever increasingly popular in recent years among private practitioners, researchers, and educational institutions alike. At the heart of digital dentistry, a significant amount of attention has been focused on computer-aided design and computer-aided manufacturing, commonly referred to as CAD/CAM. The computer-aided design (CAD) side of the workflow in dentistry initially involves a method of digitizing data, such as a desktop or intraoral scanner to capture a digital impression, and software to manipulate that data and design a myriad of different restorations or appliances (Beuer, Schweiger, and Edelhoff 2008). The computer-aided manufacturing (CAM) portion of the workflow can be broken down into two basic processes including subtractive manufacturing and additive manufacturing (Sulaiman 2020).

Subtractive manufacturing is the process by which the design data is transformed into the physical world by milling that object from a prefabricated blank of material in a CNC milling machine (Bae et al. 2017). Many dental materials are currently available to be milled with the subtractive manufacturing process such as metals, waxes, polymethyl methacrylates, ceramics, composite resins, and many more hybrid materials that are beyond the scope of this review (Sulaiman 2020). Inherently, this process is quite wasteful because in many scenarios the material debris from the milling process cannot be reprocessed or reused (Bae et al. 2017). In addition, the remaining material in the blank may not be sufficient in size to mill another object, leaving the economic burden to be a significant disadvantage of the subtractive manufacturing process. Additive manufacturing, commonly known as 3D printing, has become an extremely popular topic of interest in recent years, especially within the dental community. There are currently seven main categories of additive manufacturing techniques which include: vat photopolymerization, material jetting, material extrusion or fused deposition modeling, binder jetting, powder bed fusion, sheet lamination, and direct energy deposition (ASTM International 2013). Within dentistry, the most commonly used methods of additive manufacturing are vat photopolymerization and material jetting (Sulaiman 2020). Many of the same materials used in a subtractive manufacturing process can also be used in an additive manufacturing fashion but the nature of 3D printing lends itself to be less wasteful due to the fact that the only material used is the material needed to produce the object (Bae et al. 2017).

One of the main differences between a subtractive and an additive approach is the rigorous post-processing step that is necessary for 3D printed objects but is generally not required in the subtractive method (Oberoi et al. 2018). Specifically, with polymers, each type of 3D printing technology and individual printer may have their own manufacturer's recommendations for post-processing and post-curing (Revilla-León and Özcan 2019). There appears to be a lack of research examining the impact that correct or incorrect post-processing methods have on the properties of 3D printed materials especially those produced by vat photopolymerization. Given the high expense for dental-specific post-processing units, there is a trend among dentists to approach the post-processing stage with a "DIY" mentality, which includes using less expensive alternative curing units. This off-label use of alternative curing units may not meet the same criteria set by the manufacturer's recommendations for the specific materials used. The degree of polymerization/degree of conversion can be an important factor in achieving sufficient mechanical properties and biocompatibility of photo-polymerized resins (Franz et al. 2009). Therefore, the degree of conversion is an ideal parameter to measure the effectiveness of different post-curing units. The aim of this study will be to investigate the effects of different post-curing units on the degree of polymerization of 3D printed resins to determine whether less expensive alternative post-curing units can be a viable alternative to manufacturer’s recommended units.

Literature Review

Trends in Additive Manufacturing Within Dentistry

Over the past 10 years, there has been a marked increase in the number of publications relating to 3D printing, slightly more in the field of medicine, however, within the field of dentistry, the top two dental specialties responsible for publishing on 3D printing were oral surgery and prosthodontics (Oberoi et al. 2018). Within oral surgery, the application of 3D printing seems endless, whether clinically fabricating surgical guides for implant therapy and orthognathic surgery or in the educational realm by producing highly realistic anatomical models to train students on various maxillofacial procedures (Oberoi et al. 2018). Prosthodontics is an interesting field that can implement and utilize a variety of different 3D printed materials. The most common materials used for additive manufacturing in prosthodontics would be metallic and polymer-based materials for dental prostheses (Sulaiman 2020). Ceramics have been preliminarily studied, specifically printing zirconia crowns with comparable results in trueness values to conventionally milled zirconia (Wang et al. 2019). However, a reduction in equipment and material costs as well as more clinical studies validating accuracy will be needed before additive manufacturing ceramic crowns becomes routine in clinical practice (Wang et al. 2019). The focus of this literature review will be mainly based on polymer materials that can be utilized in the vat photopolymerization category of additive manufacturing.

3D Printing with Photo-Polymerized Polymers

Polymers, especially photo-polymerized resins, are widely used in dentistry for a variety of conventional applications, therefore it not surprising that 3D printing technologies based on similar materials are popular (Stansbury and Idacavage 2020). Applications such as dental models, surgical guides, orthodontic aligners/retainers, resin patterns for cast restorations, and even complex facial prostheses (ears, nose, eyes) are perfectly suited for additive manufacturing using photo-sensitive resins (Oberoi et al. 2018). Photo-polymerized 3D printing is noted to be one of the earliest 3D printing technologies. The overall principle is that a photosensitive resin can be cured only under exposure to light, the areas of resin not exposed to light would stay liquid, therefore allowing the printed object to be easily removed from the remaining uncured liquid resin (Quan et al. 2020). Several techniques involving photo-sensitive resins have been developed including stereolithography appearance (SLA), digital light processing (DLP), liquid crystal display (LCD), among others that will not be touched upon in this review (Quan et al. 2020).

SLA technology is the earliest and most popular technique whereby a laser beam above a resin tank exposes and cures the liquid resin on a platform that lowers to allow curing of each layer until the object is completely formed (Quan et al. 2020). Examples of commercial 3D printers that utilize SLA technology are manufactured by a company called Formlabs which produces the popular Form 3 and previously Form 2 printers. The advantages of SLA technology in the past were that the operator was able to print large objects only limited to the build plate size, but this was met with slow printing rates because the laser had to move around to expose the entire image of each layer (Quan et al. 2020).

Digital light processing (DLP) involves using a projector under a tank of resin to project an image and cure an entire layer at once allowing faster print times compared to SLA where a laser must trace the entire image. The 3D printed object begins to build layer by layer as the build plate raises a pre-determined amount to allow the next layer to cure (Stansbury and Idacavage 2020). However, the size of the projector panels currently limits the size of the objects that can be printed. DLP printers can offer high precision, however, tend to be more expensive than SLA printers available currently (Quan et al. 2020). Examples of commercially available DLP printers that are popular among the dental community are the Nextdent 5100, Moonray and Sprint Ray Pro, and the Asiga Max.

LCD 3D printing is almost identical to DLP technology; however, the light source is a liquid crystal display screen instead of a projector. The LCD screen can have very high resolution, however, due to poor light output, the precision of LCD printing technology is inferior to DLP (Quan et al. 2020). Generally, 3D printers that use LCD screens as the light source are less expensive than DLP 3D printers but share the quality of faster print times due to the ability of the screen to cure a layer all at once, as opposed to SLA technology.

One of the most interesting 3D printing techniques developed to utilize photo-polymerizing resin is the Continuous Liquid Interface Production (CLIP). Basic tenants of CLIP are similar to DLP but the difference is that CLIP uses an oxygen-permeable membrane below the UV image projection plane, which inhibits photopolymerization and creates a persistent liquid interface that allows the print speed to increase drastically from hours to minutes (Tumbleston et al. 2015). Commercially available printers that utilize CLIP technology are only produced by a company known as Carbon and their printer the M1 and more recently M2. The oxygen-permeable membrane technology is especially expensive which makes these printers substantially more cost-prohibitive for the average dentist looking to get exposed to 3D printing and therefore are generally seen in a commercial lab environment.

Resolution, Accuracy, and Precision

Resolution can be defined in the context of 3D printing as the smallest detail that can be replicated in the printed object (Revilla-León and Özcan 2019). Precision is a measure of the machine’s ability to produce objects with the same 3D dimension repeatedly and trueness is the measure of how close the dimensions of the printed object are to the true value of the object (Revilla-León and Özcan 2019). In general, resolution can be broken down into two components: the x-y dimension, which is based on the size of the laser beam for SLA and pixel size in DLP/LCD/CLIP, and in the z dimension which is determined by the height of each layer (Nestler et al. 2020).

SLA technology has been known to have lower resolution than other techniques and but one study showed that it may be more accurate but less precise than the DLP technique for printing orthodontic patient models (S. Y. Kim et al. 2018). Comparing DLP and CLIP one study has shown that there was a statistically significant difference in trueness between full-arch maxillary casts printed with CLIP and DLP where CLIP technology produced higher trueness, although DLP did meet the clinically acceptable threshold (Rungrojwittayakul et al. 2020).

Overall, it must be noted that due to the high number of contributory factors that can affect the accuracy and precision of the final product of 3D printing, not to mention the varied number of protocols for different printers and materials used, it is nearly impossible to draw general conclusions from the above studies. For example, clinically acceptable thresholds in trueness can vary depending on the study that you read, some studies set the threshold at 200-300 μm for orthodontic purposes (S. Y. Kim et al. 2018; Sohmura et al. 2001). However, when evaluating the clinical acceptability for fabricating definitive dental prostheses on a printed die then the threshold can be as low as 50 μm based on the standard set from Type IV dental stone expansion (Park and Shin 2020).

Another factor that must be considered is how the object is positioned on the build plate as well as the support structure. Alharbi et al. 2016 investigated the effect of different build angles ranging from 90-270 degrees for single crowns using SLA 3D printing and found all the crowns were dimensionally accurate (range of 27-42 μm). However, the author's recommended a build angle of 120 degrees to limit the position and amount of supports that were close to the margin to avoid damage during finishing and polishing of the crown (Alharbi, Osman, and Wismeijer 2016b).

Mechanical Properties

Mechanical properties of 3D printed resins have been a concern when compared to subtractive milling and even traditional fabrication techniques. Berli et al. investigated these comparisons between occlusal splints by testing 3 different materials in each category of pressed, milled, and 3D printed material (total of 9 materials). The study found that mean flexural strength values of milled (95.1-122.0 MPa) and pressed (92.8-99.5 MPa) were similar but drastically decreased with all 3D printed materials tested (13.0-63.3 MPa) (Berli et al. 2020). Build orientation/layer orientation has been shown to also influence the mechanical properties of 3D printed resins. Alharbi et al. showed that when objects were printed vertically (layers oriented perpendicular to the load) there was an improvement in compressive strength compared to objects printed horizontally (layers oriented parallel to load) (Alharbi, Osman, and Wismeijer 2016a). In addition, when comparing flexural strength and build orientation, one study found that a 0-degree orientation (layers oriented perpendicular to load) had the highest flexural strength followed by 45-degree orientation, and the worst-performing was 90-degree orientation (layer orientation parallel to load) (Shim et al. 2019). However, in a contradictory study, the highest mean values for flexural strength were observed with the 90-degree orientation (layer orientation parallel to load) and the lowest mean flexural strength with the 0-degree group (layer orientation perpendicular to load), which was not expected by the investigators (Unkovskiy et al. 2018).

Influence of Post-processing

Post-processing of 3D printing photo-polymerized resins can be a very important step and can differ from manufacturer to manufacturer. Most manufacturers recommend rinsing the freshly printed object in an alcohol bath (70-99% isopropyl alcohol) and then curing residual unreacted monomer with a specific light source (generally 405 nm wavelength) (Msallem et al. 2020). One study compared four different post-curing units and assessed the degree of conversion/degree of polymerization of one specific temporary crown and bridge 3D printing resin and found that the highest degree of conversion was achieved by a different post-curing unit that was not the manufacturer's recommendation for the resin (Reymus, Lümkemann, and Stawarczyk 2019). The authors hypothesized that the reason the non-manufacturers recommended unit achieved the highest degree of conversion was due to the curing process occurring under a nitrogen-rich atmosphere that prevents an oxygen inhibited layer and allows complete polymerization on the surface of the resin (Reymus, Lümkemann, and Stawarczyk 2019). Another study investigating the effects of post-processing highlighted the possibility of "UV-induced bending" where distortion from non-uniform volume shrinkage of the resin prepared by a DLP printer occurred during the post-curing process (Wu et al. 2019). The influence of post-curing on mechanical properties was investigated by Reymus et al. This study fabricated three-unit fixed dental prostheses using 4 different 3D printing temporary crown and bridge resins that were post-cured by three different commercially available units and subjected to fracture load testing (Reymus et al. 2020). The author's found that the most influential factor affecting fracture load tolerances of each of these different resins was the type of post-curing unit (Reymus et al. 2020).

Prior to post-curing of 3D printed resins fabricated by vat-polymerization, rinsing the freshly printed object in a solvent is required to remove uncured liquid resin (Taormina et al. 2018). However, there are no universally accepted guidelines to follow for what solvent to use, what percentage/strength of solvent (i.e., 70-99% isopropyl alcohol), or for how long the object should be rinsed for. One study evaluated the influence of two different solvents, 99% isopropyl alcohol (IPA) and tripropylene glycol monomethyl ether (TPM) as well as rinsing times (5, 7, 9, 11 minutes) on the accuracy of additively manufactured dental model resin (Mostafavi et al. 2020). The study concluded that TPM solvent yielded higher trueness values compared to IPA, and the optimal length of time for rinsing with TPM would be 3-4 minutes in an ultrasonic bath followed by 2-3 minutes in a second ultrasonic bath (Mostafavi et al. 2020). However, if one decides to use 99% IPA as the solvent then the rinsing protocol that yielded the highest manufacturing accuracy was 3 minutes in a first ultrasonic wash followed by 2 minutes in a second ultrasonic wash (Mostafavi et al. 2020).

Although the values for degree of conversion in this study were similar to those found in the literature, there have been studies showing an increased level of polymerization when samples were cured in an oxygen-deprived environment. A study comparing different curing units on the degree of conversion of temporary crown and bridge 3D printed resins found that the highest values were produced when samples were cured under a nitrogen-enriched environment (Reymus, Lümkemann, and Stawarczyk 2019). The reasoning behind this phenomenon is likely due to the oxygen inhibited layer that prevents the outermost surface of photo-polymerizable resins from completely curing in an oxygen-rich environment (Sacher and França 2019). Anecdotally, there is a trend among the 3D printing community to post-cure in a medium such as water or glycerin, similar to what is recommended when final curing intra-oral dental composite resins (Bijelic-Donova et al. 2015). However, there appears to be a trade-off demonstrated by a recent article where fracture resistance and flexural strength of a dental provisional 3D printed resin were statistically significantly decreased when comparing specimens cured in water and/or glycerin vs. dry (Scherer et al. 2021). The authors of that study theorized that the decrease in mechanical properties was likely due to the resin absorbing water when submerged/cured in glycerin or water (Scherer et al. 2021).

Biocompatibility is a major factor that must be considered when dealing with photo-polymerizable composite resins in the context of dentistry. The degree of conversion is an important parameter that can affect the biocompatibility of dental resins (Franz et al. 2009). Specifically with regards to 3D printed dental resins, one study compared the degree of conversion of multiple 3D printed crown and bridge provisional resins and cell viability/cytotoxicity (D. Kim et al. 2020). When post-curing was not performed, cell viability was only 12-16% but when post-curing was performed cell viability increased to approximately 49%, which shows that post-curing and a higher degree of conversion are required for a biocompatible resin (D. Kim et al. 2020).

Statement of the problem

Due to the rapid progress of additive manufacturing in the dental field, there appears to be a lack of research examining the impact that post-processing methods have on the chemical properties of 3D printed materials especially those produced by vat photopolymerization.

Purpose of the study

The aim of this study was to investigate the effects of different post-curing units on the chemical properties (degree of polymerization) of 3D printed resins to determine whether less expensive alternative post-curing units can be a viable alternative to the manufacturer's recommended units.

Objectives of the study

- Evaluate the degree of conversion that four available curing units can achieve for a common 3D printed dental model resin
- Provide evidence to support or negate the use of commercially available alternative post-curing units for 3D printed resins

Null Hypotheses

H_{01}: There are no differences in the degree of conversion for the manufacturer's recommended curing unit for the 3D printed resin in question compared to the alternative curing units investigated.

H_{02}: There are no differences in the degree of conversion for different curing time intervals.

Chapter 2

Materials and methods

Sample Preparation

A standardized geometric shape was designed with free CAD software, Meshmixer (Autodesk Research, Mill Valley, CA, USA), with dimensions of 10x4x2.5 mm. The sample design was exported in the standard tessellation language (STL) format and prepared for printing with a free slicing software Chitubox (CBD-Tech, Shenzhen, Guangdong, China). A total of 45 samples were fabricated with an LCD printer (Phrozen Sonic Mini, Phrozen 3D, Hsinchu City, Taiwan) using MSLA Dental Modeling resin (Apply Lab Work, Torrance, CA, USA). The samples were printed directly on the build plate in groups of 5 in a 0° orientation to ensure even exposure to the LCD screen to limit discrepancies when testing the samples. The printing parameters used included: 100 µm layer thickness, six bottom burn-in layers with 30 second exposure time for the burn-in layer, and a 6-second normal layer exposure time as per manufacturer's recommendations (Apply Lab Work, Torrance, CA, USA). The samples were then subjected to a two-step alcohol wash with 85% ethyl alcohol for four minutes in a preliminary rotary alcohol wash unit (Anycubic Wash and Cure, Anycubic 3D, Shenzhen, China) to remove the bulk of uncured resin and for one minute in the second final stationary wash of 85% ethyl alcohol to remove any remaining resin. Post-curing of the samples was performed by four distinct curing units, including the unit recommended by the company that produces the 3D printer that was used to fabricate the samples the Phrozen Cure V2 (Phrozen 3D, Hsinchu City, Taiwan), a commercial acrylic nail UV LED curing unit (SUNUV, Shenzhen, China), a homemade curing oven fabricated from a readily available UV LED light source (FastToBuy, Shenzhen, China) and the Triad® 2000™ tungsten halogen light source (Dentsply Sirona, York, Pennsylvania, USA). A sample size of n = 45 was used based on power calculations for dental material testing which would yield reasonable confidence limits with small bias (Quinn and Quinn 2010). Post-curing was performed in two separate time intervals, 15 minutes and 45 minutes. Five samples were assigned for each of the four curing unit groups for both curing time intervals. In addition, five samples were collected directly from the printer and were not subjected to any post-curing methods were also included in the study as a baseline reference.

3D Printer: Phrozen Sonic Mini

Figure 1. Phrozen Sonic Mini UV Photocuring LCD Resin 3D Printer 5.5" Monochrome LCD Screen, ParaLED Tech, with 2.8'' Smart Touch Screen Offline Printing, Print Volume: 4.7 x 2.6 x 5.1 in. (Phrozen 3D, Hsinchu City, Taiwan)

Wash Unit: Anycubic Wash and Cure

Figure 2. Anycubic all-in-one wash and cure unit with rotary washing times of 2, 4, and 6 minutes (Anycubic 3D, Shenzhen, China)

Specifications of Curing Units

Phrozen Cure V2 (PC)

Figure 3. Phrozen Cure V2 (Phrozen 3D, Hsinchu City, Taiwan)

Constructed with a metal box with a plastic UV protection window in the front of the door. 365 nm, 385 nm, and 405 nm LEDs line the sides and the top of the enclosure rated at 60 watts as per the manufacturer. On the base of the enclosure, a rotating table provides even light distribution during curing of the printed objects.

SUNUV UV Nail Curing Unit (NC)

Figure 4. A commercial acrylic nail UV LED curing unit (SUNUV, Shenzhen, China)

Constructed with a plastic dome enclosure with 39 separate LEDs in the 365 nm and 405 nm on the top and sides of the enclosure rated at 48 watts according to the manufacturer. Unlike other curing units the printed objects remain stationary on the bottom of the enclosure.

Triad® 2000 VLC Curing Unit (TC)

Figure 5. Triad® 2000™ tungsten halogen light source (Dentsply Sirona, York, Pennsylvania, USA)

Constructed with a plastic and metal cylindrical enclosure with a single 200-watt tungsten-halogen bulb as the light source. A rotating table on the base of the enclosure allows exposure of the entire object being cured as the single bulb will not provide even light distribution.

Homemade UV LED Curing Unit (HC)

Figure 6. Homemade curing unit fabricated from UV light source, metal enclosure and solar turntable.

A “homemade” curing unit was constructed with various readily available components including a metal cabinet enclosure (LIXHULT, IKEA, Smaland, Sweden), lined with reflective aluminum tape (Reflectix, Markleville, IN, USA), a UV LED light source consisting of 20 individual 405 nm LEDs with 20 watts total as per the manufacturer (FastToBuy, Shenzhen, China) and a rotating solar turntable (Sovol 3D, Paris, France) activated by the light source to provide even exposure of the printed objects.

Degree of Conversion

Fournier-transform infrared spectroscopy (FTIR) analysis was performed to analyze the difference in functional groups of the resin using a Nicolet 6700 FTIR Spectrometer (ThermoFisher Scientific, Waltham, MA, USA). Infrared spectra in the range of 400-4000 cm^{-1} were generated from 120 scans for each sample beginning with unpolymerized liquid resin as a baseline, then subsequent samples from each test group. These spectra were analyzed in the absorbance mode and the values corresponding to the aliphatic C=C peak (1637 cm^{-1}) and aromatic C-C peak (1525 cm^{-1}) before post-processing and after post-processing were used to determine the degree of conversion (Sacher and França 2019). An example spectrum is portrayed in Figure 8. OMNIC^{TM} Spectra Software was used to add a baseline correction for each spectrum. Degree of conversion was calculated using the formula displayed below in Figure 7.

$$\mathrm{DC\%} = 1 - \left[\frac{\mathrm{C_{aliphatic}}/\mathrm{C_{aromatic}}}{\mathrm{U_{aliphatic}}/\mathrm{U_{aromatic}}}\right] \times 100$$

Figure 7. Degree of the conversion equation

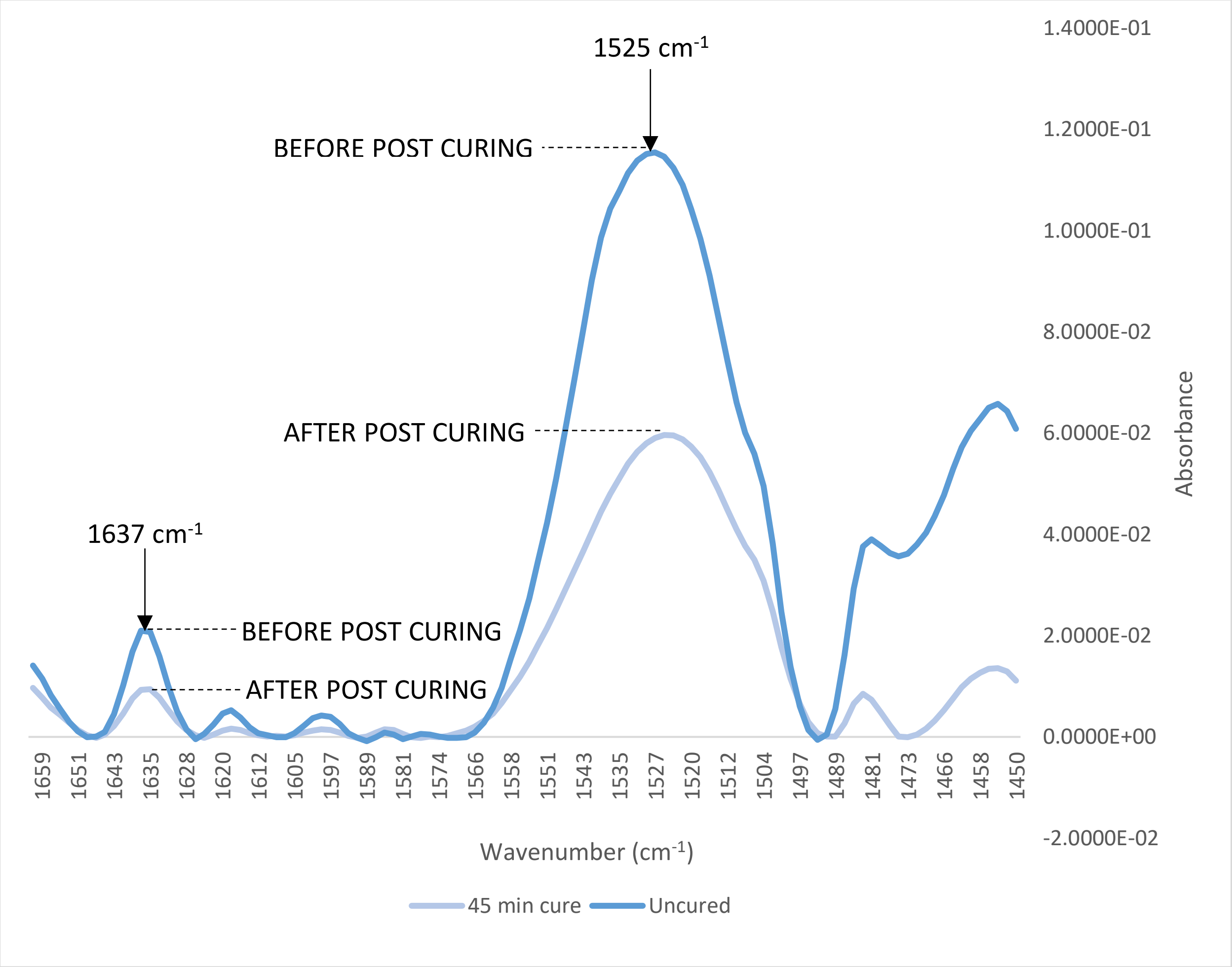

Figure 8. FTIR spectrum for Homemade UV LED Curing Unit (HC)

Statistical Analysis

Statistical analysis was completed with Origin Lab software (Origin Lab Inc., Northampton, Massachusetts, USA). The data were analyzed statistically using a two-way ANOVA followed by Tukey's Post-hoc test. A significance level of $\alpha = 0.05$ was used for all statistical analyses applied.

Chapter 3

Results

The mean values for degree of conversion and their standard deviations are presented in Table 1 and graphically represented in Figure 9. The values for 0 minutes were calculated from measuring the degree of conversion on the samples straight from the printer and did not undergo any post-curing to use as a baseline reference. The Phrozen Cure V2 had the highest overall mean degree of conversion value, 69.6% with a 45-minute curing time. The Triad® 2000 VLC Curing Unit had the lowest mean degree of conversion value at the 15-minute interval with 66.2% and tied the lowest mean degree of conversion at the 45-minute interval with the Homemade Curing Unit, both with 68.2%. Summary tables of FTIR raw spectral data and corresponding DC values for uncured, 15-minute cure and 45-minute cured samples can be found in Tables 2-4.

Table 1. Mean degree of conversion and standard deviation

	Curing Time (Minutes)	**Mean**	**Standard Deviation**
HC	0	63.1	1.7
	15	66.7	1.7
	45	68.2	1.0
NC	0	63.1	1.7
	15	67.4	2.1
	45	69.2	0.6
PC	0	63.1	1.7
	15	66.8	0.6
	45	69.6	0.5
TC	0	63.1	1.7
	15	66.2	2.1

	45	68.2	0.4

**HC = Homemade curing unit, NC = SUNUV nail curing unit, PC = Phrozen Cure V2, TC = Triad® 2000 VLC Curing Unit*

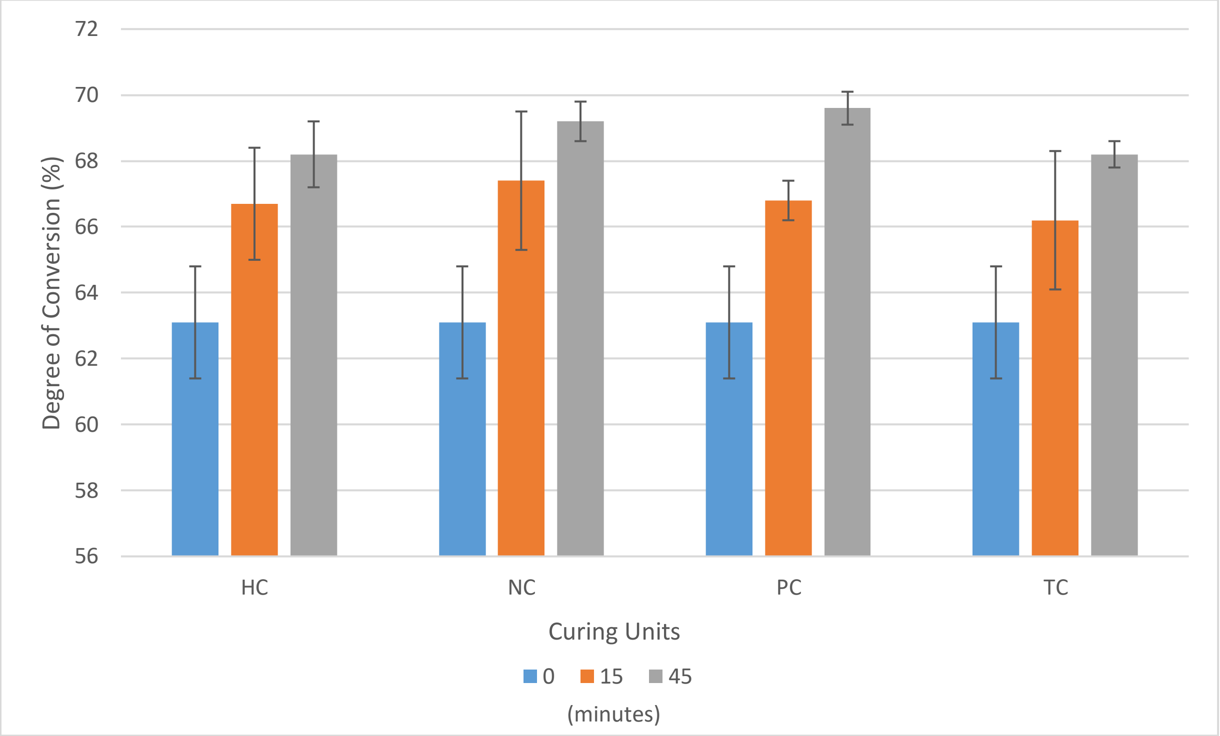

Figure 9. Mean and standard deviation for degree of conversion (%) for HC = Homemade curing unit, NC = SUNUV nail curing unit, PC = Phrozen Cure V2, TC = Triad® 2000 VLC Curing Unit

Based on the two-way ANOVA test the type of light-curing unit did not yield statistically significant differences in the degree of conversion ($p = 0.171$), however, there was a statistically significant difference in the mean degree of conversion between the 15-minute and 45-minute curing time interval ($p = 2.32 \times 10^{-5}$). Tukey's post-hoc test indicated that when comparing individual light-curing units there was a statistically significant difference in the degree of conversion for the Phrozen Cure V2 between the 15-minute and 45-minute curing time ($p = 0.029$).

Table 2. FTIR raw spectral data and corresponding degree of conversion for 15-minute cure time

	Method	**Peak at 1525 cm^{-1}**	**Peak at 1.637 cm^{-1}**	**DC (%)**
HC 1	LED	9.1263E-02	1.4373E-02	67.4
HC 2	LED	8.9915E-02	1.3643E-02	68.6
HC 3	LED	8.4069E-02	1.3351E-02	67.2
HC 4	LED	9.8771E-02	1.6233E-02	66.0
HC 5	LED	9.9544E-02	1.7276E-02	64.1
NC 1	LED	6.4644E-02	9.9856E-03	68.1
NC 2	LED	7.5056E-02	1.2644E-02	65.2
NC 3	LED	6.1123E-02	9.3808E-03	68.3
NC 4	LED	7.5324E-02	1.2562E-02	65.5
NC 5	LED	6.0145E-02	8.7075E-03	70.1
PC 1	LED	8.219E-02	1.318E-02	66.8
PC 2	LED	8.20E-02	1.30E-02	67.2
PC 3	LED	7.39E-02	1.22E-02	65.8
PC 4	LED	7.04E-02	1.12E-02	67.1
PC 5	LED	7.98E-02	1.28E-02	66.9
TC 1	Halogen	1.2023E-01	1.8420E-02	68.3
TC 2	Halogen	1.2271E-01	1.9883E-02	66.5
TC 3	Halogen	1.0493E-01	1.6359E-02	67.8
TC 4	Halogen	1.2263E-01	2.0403E-02	65.6
TC 5	Halogen	3.4669E-02	6.2053E-03	63.0

**HC = Home curing unit, NC = SUNUV nail curing unit, PC = Phrozen Cure V2, TC = Triad® 2000 VLC Curing Unit*

Table 3. FTIR raw spectral data and corresponding degree of conversion for 45-minute cure time

Curing unit	**Method**	**Peak at 1525 cm^{-1}**	**Peak at 1.637 cm^{-1}**	**DC (%)**
HC 1	LED	5.9662E-02	9.3557E-03	67.6
HC 2	LED	5.0517E-02	7.5167E-03	69.2
HC 3	LED	4.8129E-02	7.2416E-03	68.9
HC 4	LED	5.6832E-02	8.6990E-03	68.4
HC 5	LED	6.0455E-02	9.7061E-03	66.8
NC 1	LED	4.6652E-02	7.0032E-03	69.0
NC 2	LED	3.5050E-02	5.2340E-03	69.1
NC 3	LED	3.6530E-02	5.3360E-03	69.8
NC 4	LED	3.5011E-02	5.1169E-03	69.8
NC 5	LED	3.9651E-02	6.0516E-03	68.4
PC 1	LED	4.0350E-02	6.0756E-03	68.9
PC 2	LED	4.0188E-02	5.8128E-03	70.1
PC 3	LED	3.9716E-02	5.8691E-03	69.4
PC 4	LED	4.0083E-02	5.8141E-03	70.0
PC 5	LED	3.8298E-02	5.6081E-03	69.7
TC 1	Halogen	1.1623E-01	1.7741E-02	68.4
TC 2	Halogen	9.2312E-02	1.4456E-02	67.6
TC 3	Halogen	9.1168E-02	1.3956E-02	68.3
TC 4	Halogen	9.5098E-02	1.4479E-02	68.5
TC 5	Halogen	1.1341E-01	1.7477E-02	68.1

**HC = Homemade curing unit, NC = SUNUV nail curing unit, PC = Phrozen Cure V2, TC = Triad® 2000 VLC Curing Unit*

Table 4. FTIR raw spectral data and corresponding degree of conversion for uncured samples direct from printer

Curing Unit	**Method**	**Peak at 1525 cm^{-1}**	**Peak at 1.637 cm^{-1}**	**DC (%)**
UC 1	LED	1.1466E-01	2.1017E-02	62.1
UC 2	LED	1.0966E-01	2.0559E-02	61.2
UC 3	LED	1.1935E-01	2.1689E-02	62.4
UC 4	LED	1.2217E-01	2.0854E-02	64.7
UC 5	LED	1.2099E-01	2.0349E-02	65.2

**UC = uncured samples directly taken from printer*

Chapter 4

Discussion

This study evaluated the effects of alternative light-curing units on the degree of conversion of a 3D printed dental model resin at two common curing time intervals. The results of this study yielded a statistically significant difference in the degree of conversion values between the 15 and 45-minute curing time intervals and therefore reject the second null hypothesis ($p = 2.32 \times 10^{-5}$). However, there was no statistically significant difference in the degree of conversion values between light-curing units, which led to the acceptance of the first null hypothesis. ($p = 0.171$)

The degree of conversion values found in this study fell within the normal range of 3D printed resins available currently in the scientific literature, however, to the author's knowledge most of the studies available on the degree of conversion have investigated prosthodontic provisional 3D printed resins, not dental model resin (D. Kim et al. 2020). When compared to other photo-polymerized resins used in dentistry including dental adhesives and orthodontic bonding resin, even though the object size and shape were different, the degree of conversion values in this study were also comparable (de Araujo et al. 2015; Robertson et al. 2016). The logical explanation of this result can be explained due to the inherent nature by which the degree of conversion values are measured through infrared spectroscopy. The sampling depth of a specimen with FTIR is generally approximately 5 µm from the outside of the specimen (Sacher and França 2019). 3D printed resins are cured in layers generally between 25-100 µm initially and during post-processing the outer layer receives the highest amount of light energy, which would explain the similar values in degree of conversion across multiple different resins, including dental adhesives, orthodontic bonding resin and multiple types of 3D printed dental resins.

Another parameter that can affect the properties of 3D printed resins is layer thickness. A study that investigated layer thickness and degree of conversion found that for objects tested directly from the printer without post-curing that a layer thickness of 25 µm had the highest values of degree of conversion, followed by 50 µm and 100 µm (Reymus, Lümkemann, and Stawarczyk 2019). However, once these objects were post-cured the highest values for degree of conversion were found in the samples printed with 100 µm and 50 µm layer thickness with 25 µm samples having the lowest degree of conversion (Reymus, Lümkemann, and Stawarczyk 2019). This phenomenon may be explained by "over-curing" that potentially can happen when the light source penetrates deeper than the layer thickness, which can, in turn, lead to inaccuracies as well as excess heat generation that has the potential to negatively impact polymerization at the single-layer level (O'Neill, Kent, and Brabazon 2017; Choi et al. 2009). The layer thickness used in the printing of the samples used in this study was 100 µm, which appears to be optimal layer thickness from a degree of conversion standpoint but also from a practicality standpoint as decreased layer thickness leads to longer print times and sometimes unnecessary accuracy depending on the dental application.

Overall, the differences in the degree of conversion values among the four different light-curing units tested were minimal and statistically insignificant. Based on the results of this study curing samples for 45 minutes with the Phrozen Cure V2 will yield the highest overall mean degree of conversion value (69.6%). The Triad® 2000 VLC Curing Unit and the Homemade Curing Unit will yield the lowest mean degree of conversion values at the 15-minute interval with 66.2% and 45-minute interval with 68.2% respectively. However, in common practice, any of these curing units will give a similar degree of conversion percentage. Alternatively, when investigating the length of curing time there was a statistically significant difference in the degree of conversion values when comparing 15-minute to 45-minute curing intervals (p = 0.029). This finding is in accordance with other studies that show a gradual increase in the degree of conversion values coinciding with increased post-curing time (D. Kim et al. 2020).

Study Limitations

One of the limitations of this study would be that it was performed during the global pandemic of COVID-19 where supply chains of isopropyl alcohol were extremely compromised for 70% IPA let alone 99%. The solvent that was used in this study was 85% ethyl alcohol, which is a common solvent for rinsing 3D printed objects in countries where isopropyl alcohol is not readily available due to safety concerns regarding the flammable nature of the solvent. However, to the author's knowledge there are no scientific studies comparing ethyl alcohol as a solvent in the post-processing of 3D printed resins and therefore could have affected the results of this study regarding the degree of conversion values.

Another limitation of this study could have been not including one of the light-curing units that cure under an oxygen-deprived-nitrogen-rich atmosphere. All the curing units investigated in this study did not control for the environment that they cure under. As previously mentioned, curing under a nitrogen-rich environment may result in a higher degree of conversion values and may have been beneficial to investigate these types of units and compare them to the alternative curing units investigated in this study (Reymus, Lümkemann, and Stawarczyk 2019).

Most 3D printed resins available currently have special formulations and secret patented compositions that make analysis quite difficult. In this study, the dental model resin from ApplyLabWork that was used did not disclose exact chemical composition, which proved to be challenging when analyzing the specific functional peaks for FTIR spectroscopy. In the current study, the 1525 cm^{-1} wavenumber was used for the analysis of the aromatic C-C functional group as opposed to other 3D printed resins that use 1608 cm^{-1} peak, which could be a source of discrepancy when comparing the literature.

Future Recommendations

In the future it would be beneficial to investigate the effects of these alternative curing units with regards to the physical characteristics of this dental model resin, perhaps correlating the degree of conversion values with flexural strength or hardness of the material. Another future consideration would be to investigate the effect of these alternative curing units on the degree of conversion values found within the internal aspects of the sample specimens, not just the superficial layers of 3D printed objects. Although manufacturer’s recommendations are considered the gold standard for 3D printing protocols, there need to be further studies investigating how different variables affect the outcomes of 3D printing in the dental field.

Chapter 5

Conclusions

The results from this study highlight that while there were slight differences between the investigated curing units the overall degree of conversion values were comparable. Within the limitations of this study, the following conclusions can be drawn.

- The type of light-curing unit did not yield statistically significant differences in the degree of conversion values.
- There was a statistically significant difference in the degree of conversion values between the 15-minute and 45-minute curing interval.
- When comparing individual light-curing units there was a statistically significant difference in the degree of conversion for the Phrozen Cure V2 between the 15-minute and 45-minute curing time ($p = 0.029$).

Both the dental-specific light-curing units investigated: Phrozen Cure V2 and Triad® 2000 VLC Curing Unit were comparable in the context of the degree of conversion and level of post-curing efficacy to the off-label SUNUV Nail curing unit and even a Homemade Light Curing unit easily fabricated from readily available components. In addition, curing time intervals have a positive effect on the degree of conversion values and should be carefully determined depending on the specific resin and application within the context of dentistry.

Hypotheses Revisited

H_{01}: There are no differences in the degree of conversion for the manufacturer’s recommended curing unit for the 3D printed resin in question compared to the alternative curing units investigated.

- No statistically significant differences in the degree of conversion values between curing units investigated – **Null hypothesis accepted**

H_{02}: There are no differences in the degree of conversion for different curing time intervals.

- Statistically significant differences in the degree of conversion values were found between 15-minute and 45-minute curing time intervals – **Null hypothesis rejected**

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Appendices

Appendix 1. Journal Article Manuscript for Journal of Prosthodontics

Title: The Effect of Different Post-Curing Methods on Chemical Properties of 3D Printed Resin

Running Title: Post-curing Methods of 3D Printed Resin

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The Effect of Different Post-Curing Methods on Chemical Properties of 3D Printed Resin

Abstract

Purpose: To investigate the effects of different post-curing units on chemical properties (degree of polymerization) of 3D printed resins to determine whether less expensive alternative post-curing units can be a viable alternative to manufacturer’s recommended units.

Methods: Forty-five samples were fabricated with an LCD printer (Phrozen Sonic Mini, Phrozen 3D, Hsinchu City, Taiwan) using MSLA Dental Modeling resin (Apply Lab Work, Torrance, CA, USA). These samples were divided randomly into four different groups for post-curing by four distinct curing units, the Phrozen Cure V2 (Phrozen 3D, Hsinchu City, Taiwan), a commercial acrylic nail UV LED curing unit (SUNUV, Shenzhen, China), a homemade curing oven fabricated from a readily available UV LED light source (FastToBuy, Shenzhen, China) and the Triad® 2000™ tungsten halogen light source (Dentsply Sirona, York, Pennsylvania, USA). Degree of conversion was measured by FTIR spectroscopy using a Nicolet 6700 FTIR Spectrometer (ThermoFisher Scientific, Waltham, MA, USA).

Results: The Phrozen Cure V2 had the highest overall mean degree of conversion value, 69.6% with a 45-minute curing time. The Triad® 2000 VLC Curing Unit had the lowest mean degree of conversion value at the 15-minute interval with 66.2% and tied the lowest mean degree of conversion at the 45-minute interval with the Homemade Curing Unit, both with 68.2%.

Conclusion: The type of light curing unit did not yield statistically significant differences in degree of conversion values. There was a statistically significant difference in degree of conversion values between the 15-minute and 45-minute curing interval. When comparing individual light curing units there was a statistically significant difference in degree of

conversion for the Phrozen Cure V2 between the 15-minute and 45-minute curing time ($p = 0.029$).

KEYWORDS: Additive manufacturing, post-curing 3D printing, degree of conversion

Introduction

Digital dentistry has become ever increasingly popular in recent years among private practitioners, researchers, and educational institutions alike. At the heart of digital dentistry, a significant amount of attention has been focused on computer-aided design and computer-aided manufacturing, commonly referred to as CAD/CAM. The computer-aided design (CAD) side of the workflow in dentistry initially involves a method of digitizing data, such as a desktop or intraoral scanner to capture a digital impression, and software to manipulate that data and design a myriad of different restorations or appliances.[1] The computer-aided manufacturing (CAM) portion of the workflow can be broken down into two basic processes including subtractive manufacturing and additive manufacturing.[2]

Additive manufacturing, commonly known as 3D printing, has become an extremely popular topic of interest in recent years especially within the dental community. There are currently seven main categories of additive manufacturing techniques which include: vat photopolymerization, material jetting, material extrusion or fused deposition modeling, binder jetting, powder bed fusion, sheet lamination and direct energy deposition.[3] Within dentistry, the most commonly used methods of additive manufacturing are vat photopolymerization and material jetting.[2] Many of the same materials used in a subtractive manufacturing process can also be used in an additive manufacturing fashion but the nature of 3D printing lends itself to be less wasteful due to the fact that the only material used is the material needed to produce the object.[4]

One of the main differences between a subtractive and an additive approach is the rigorous post-processing step that is necessary for 3D printed objects but is generally not required in the subtractive method.[5] Specifically with polymers, each type of 3D printing technology and individual printer may have their own manufacturer's recommendations for post-processing and post-curing.[6] There appears to be a lack of research examining the impact that corrects or incorrect post-processing methods have on properties of 3D printed materials especially those produced by vat photopolymerization. Given the high expense for dental specific post-processing units, there is a trend among dentists to approach the post-processing stage with a "DIY" mentality, which includes using less expensive alternative curing units. This off-label use of alternative curing units may not meet the same criteria set by the manufacturer's recommendations for the specific materials used. The degree of polymerization/degree of conversion can be an important factor in achieving sufficient mechanical properties and biocompatibility of photo-polymerized resins.[7] Therefore, the degree of conversion is an ideal parameter to measure the effectiveness of different post-curing units. The aim of this study will be to investigate the effects of different post-curing units on the degree of polymerization of 3D printed resins to determine whether less expensive alternative post-curing units can be a viable alternative to the manufacturer's recommended units.

Materials and methods

A standardized geometric shape was designed with free CAD software, Meshmixer (Autodesk Research, Mill Valley, CA, USA), with dimensions of 10x4x2.5 mm. The sample design was exported in the standard tessellation language (STL) format and prepared for printing with a free slicing software Chitubox (CBD-Tech, Shenzhen, Guangdong, China). A total of 45 samples were fabricated with an LCD printer (Phrozen Sonic Mini, Phrozen 3D, Hsinchu City, Taiwan) using MSLA Dental Modeling resin (Apply Lab Work, Torrance, CA, USA). The samples were printed directly on the build plate in groups of 5 in a 0° orientation to ensure even exposure to the LCD screen to limit discrepancies when testing the samples. The printing parameters used included: 100 µm layer thickness, six bottom burn-in layers with 30 second exposure time for the burn-in layer, and a 6-second normal layer exposure time as per manufacturer's recommendations (Apply Lab Work, Torrance, CA, USA). The samples were then subjected to a two-step alcohol wash with 85% ethyl alcohol for four minutes in a preliminary rotary alcohol wash unit (Anycubic Wash and Cure, Anycubic 3D, Shenzhen, China) to remove the bulk of uncured resin and for one minute in the second final stationary wash of 85% ethyl alcohol to remove any remaining resin. Post-curing of the samples was performed by four distinct curing units, including the unit recommended by the company that produces the 3D printer that was used to fabricate the samples the Phrozen Cure V2 (Phrozen 3D, Hsinchu City, Taiwan), a commercial acrylic nail UV LED curing unit (SUNUV, Shenzhen, China), a homemade curing oven fabricated from a readily available UV LED light source (FastToBuy, Shenzhen, China) and the Triad® 2000™ tungsten halogen light source (Dentsply Sirona, York, Pennsylvania, USA). A sample size of n = 45 was used based on power calculations for dental material testing which would yield reasonable confidence limits with small bias [8]. Post-curing was performed in two separate time intervals, 15 minutes and 45 minutes. Five samples were assigned for each of the four curing unit groups for both curing time intervals. In addition, five samples were collected directly from the printer and were not subjected to any post-curing methods were also included in the study as a baseline reference.

Fournier-transform infrared spectroscopy (FTIR) analysis was performed to analyze the difference in functional groups of the resin using a Nicolet 6700 FTIR Spectrometer (ThermoFisher Scientific, Waltham, MA, USA). Infrared spectra in the range of 400-4000 cm^{-1}

were generated from 120 scans for each sample beginning with unpolymerized liquid resin as a baseline, then subsequent samples from each test group. These spectra were analyzed in the absorbance mode and the values corresponding to the aliphatic C=C peak (1637 cm^{-1}) and aromatic C-C peak (1525 cm^{-1}) before post-processing and after post-processing were used to determine the degree of conversion.[9] An example spectrum is portrayed in Figure 2. OMNIC™ Spectra Software was used to add a baseline correction for each spectrum. The degree of conversion was calculated using the formula displayed below in Figure 1. The data were analyzed statistically using a two-way ANOVA followed by Tukey's *post-hoc* test. A significance level of $\alpha = 0.05$ was used for all statistical analyses applied.

Results

The mean values for degree of conversion and their standard deviations are presented in Table 1 and graphically represented in Figure 3. The values for 0 minutes were calculated from measuring degree of conversion on the samples straight from the printer and did not undergo any post-curing to use as a baseline reference. The Phrozen Cure V2 had the highest overall mean degree of conversion value, 69.6% with a 45-minute curing time. The Triad® 2000 VLC Curing Unit had the lowest mean degree of conversion value at the 15-minute interval with 66.2% and tied the lowest mean degree of conversion at the 45-minute interval with the Homemade Curing Unit, both with 68.2%.

Based on the two-way ANOVA test the type of light-curing unit did not yield statistically significant differences in the degree of conversion ($p = 0.171$), however, there was a statistically significant difference in the mean degree of conversion between the 15-minute and 45-minute curing time interval ($p < 0.001$). Tukey's *post-hoc* test indicated that when comparing individual light-curing units there was a statistically significant difference in the degree of conversion for the Phrozen Cure V2 between the 15-minute and 45-minute curing time ($p = 0.029$).

Discussion

This study evaluated the effects of alternative light-curing units on the degree of conversion of a 3D printed dental model resin at two common curing time intervals. The results of this study yielded a statistically significant difference in the degree of conversion values between the 15 and 45-minute curing time intervals and therefore reject the second null hypothesis ($p < 0.001$). However, there was no statistically significant difference in the degree of conversion values between light-curing units, which led to the acceptance of the first null hypothesis. ($p = 0.171$)

The degree of conversion values found in this study fell within the normal range of 3D printed resins available currently in the scientific literature, however, to the author's knowledge most of the studies available on the degree of conversion have investigated prosthodontic provisional 3D printed resins, not dental model resin[10]. When compared to other photo-polymerized resins used in dentistry including dental adhesives and orthodontic bonding resin, even though the object size and shape were different, the degree of conversion values in this study was also comparable.[11,12] The logical explanation of this result can be explained due to the inherent nature by which the degree of conversion values are measured through infrared spectroscopy. The sampling depth of a specimen with FTIR is generally approximately 5 μm from the outside of the specimen.[9] 3D printed resins are cured in layers generally between 25-100 μm initially and during post-processing the outer layer receives the highest amount of light energy, which would explain the similar values in the degree of conversion across multiple different resins, including dental adhesives, orthodontic bonding resin and multiple types of 3D printed dental resins.

Another parameter that can affect the properties of 3D printed resins is layer thickness. A study that investigated layer thickness and degree of conversion found that for objects tested directly from the printer without post-curing that a layer thickness of 25 μm had the highest values of degree of conversion, followed by 50 μm and 100 μm.[13] However, once these objects were post-cured the highest values for degree of conversion were found in the samples printed with 100 μm and 50 μm layer thickness with 25 μm samples having the lowest degree of conversion.[13] This phenomenon may be explained by "over-curing" that potentially can happen when the light source penetrates deeper than the layer thickness, which can, in turn, lead to inaccuracies as well as excess heat generation that has the potential to negatively impact polymerization at the single-layer level.[14,15] The layer thickness used in the printing of the samples used in this study was 100 μm, which appears to be optimal layer thickness from a degree of conversion standpoint but also from a practicality standpoint as decreased layer thickness leads to longer print times and sometimes unnecessary accuracy depending on the dental application.

Overall, the differences in the degree of conversion values among the four different light-curing units tested were minimal and statistically insignificant. Based on the results of this study curing samples for 45 minutes with the Phrozen Cure V2 will yield the highest overall mean degree of conversion value (69.6%). The Triad® 2000 VLC Curing Unit and the Homemade Curing Unit will yield the lowest mean degree of conversion values at the 15-minute interval with 66.2% and 45-minute interval with 68.2% respectively. However, in common practice, any of these curing units will give a similar degree of conversion percentage. Alternatively, when investigating the length of curing time there was a statistically significant difference in the degree of conversion values when comparing 15-minute to 45-minute curing intervals ($p = 0.029$). This finding is in accordance with other studies that show a gradual increase in the degree of conversion values coinciding with increased post-curing time.[10]

One of the limitations of this study would be that it was performed during the global pandemic of COVID-19 where supply chains of isopropyl alcohol were extremely compromised for 70% IPA let alone 99%. The solvent that was used in this study was 85% ethyl alcohol, which is a common solvent for rinsing 3D printed objects in countries where isopropyl alcohol is not readily available due to safety concerns regarding the flammable nature of the solvent. However, to the author's knowledge there are no scientific studies comparing ethyl alcohol as a solvent in the post-processing of 3D printed resins and therefore could have affected the results of this study in regard to the degree of conversion values.

Another limitation of this study could have been not including one of the light-curing units that cure under an oxygen deprived-nitrogen rich atmosphere. All the curing units investigated in this study did not control for the environment that they cure under. As previously mentioned, curing under a nitrogen-rich environment may result in a higher degree of conversion values and may have been beneficial to investigate these types of units and compare them to the alternative curing units investigated in this study.[13]

Most 3D printed resins available currently have special formulations and secret patented compositions that make analysis quite difficult. In this study, the dental model resin from ApplyLabWork that was used did not disclose exact chemical composition, which proved to be challenging when analyzing the specific functional peaks for FTIR spectroscopy. In the current study, the 1525 cm^{-1} wavenumber was used for the analysis of the aromatic C-C functional group as opposed to other 3D printed resins that use 1608 cm^{-1} peak, which could be a source of discrepancy when comparing the literature.

In the future it would be beneficial to investigate the effects of these alternative curing units with regards to the physical characteristics of this dental model resin, perhaps correlating the degree of conversion values with flexural strength or hardness of the material. Another future consideration would be to investigate the effect of these alternative curing units on the degree of conversion values found within the internal aspects of the sample specimens, not just the superficial layers of 3D printed objects. Although manufacturer's recommendations are considered the gold standard for 3D printing protocols, there need to be further studies investigating how different variables affect the outcomes of 3D printing in the dental field.

Conclusions

The results from this study highlight that while there were slight differences between the investigated curing units, the overall degree of conversion values were comparable. Both the dental specific light curing units investigated: Phrozen Cure V2 and Triad® 2000 VLC Curing Unit were comparable in the context of degree of conversion and level of post-curing efficacy to the off-label SUNUV Nail curing unit and even a Homemade Light Curing unit easily fabricated from readily available components. In addition, curing time intervals have a positive effect on degree of conversion values and should be carefully determined depending on the specific resin and application within the context of dentistry.

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Figures

$$DC\% = 1 - \left[\frac{C_{aliphatic}/C_{aromatic}}{U_{aliphatic}/U_{aromatic}}\right] \times 100$$

Figure 1. Degree of conversion equation

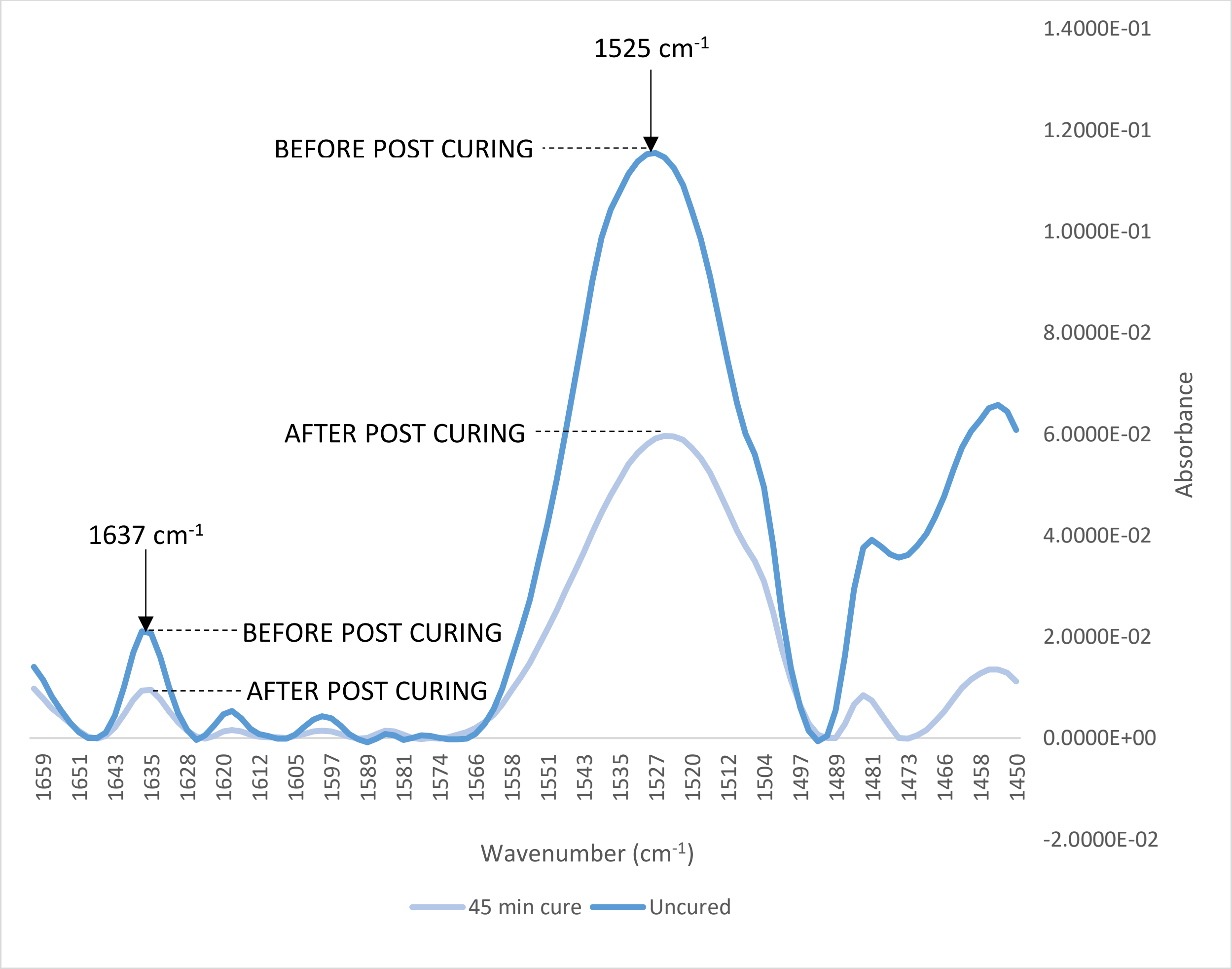

Figure 2. FTIR spectrum for Homemade UV LED Curing Unit (HC)

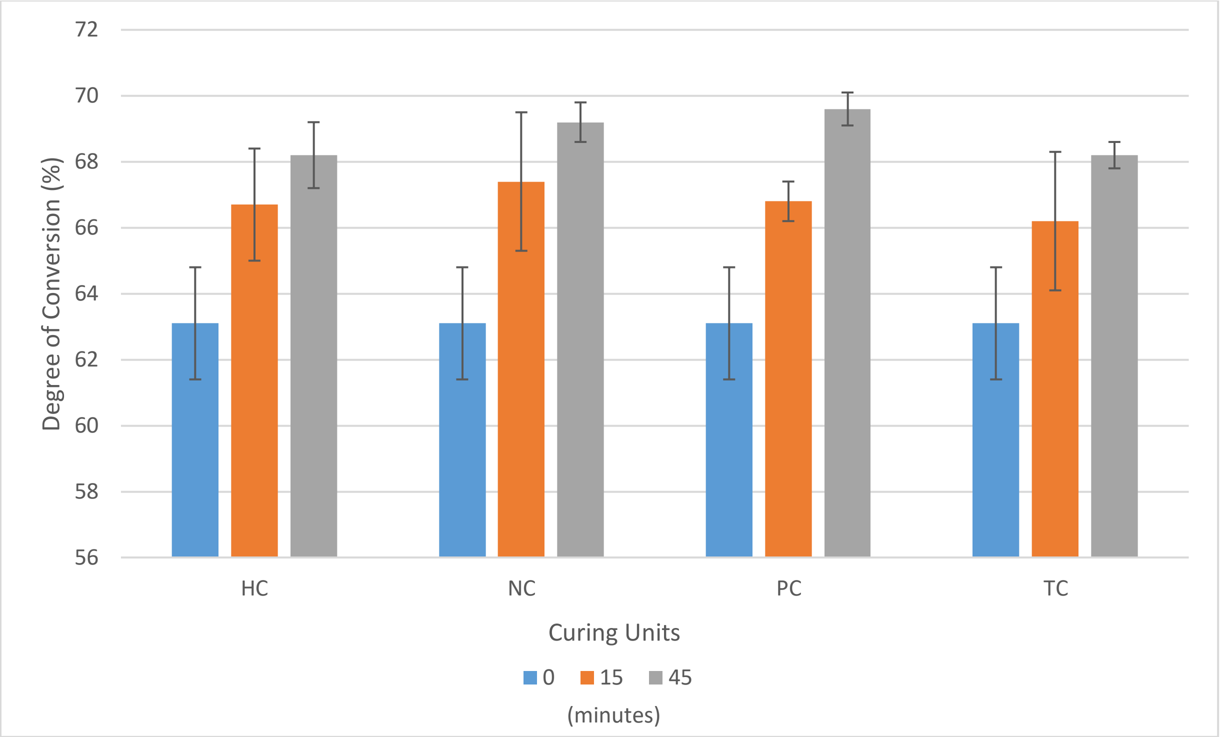

Figure 3. Mean and standard deviation for degree of conversion (%) for HC = Homemade curing unit, NC = SUNUV nail curing unit, PC = Phrozen Cure V2, TC = Triad® 2000 VLC Curing Unit

Tables

Table 5. Mean degree of conversion and standard deviation

	Curing Time (Minutes)	**Mean**	**Standard Deviation**
HC	0	63.1	1.7
	15	66.7	1.7
	45	68.2	1.0
NC	0	63.1	1.7
	15	67.4	2.1
	45	69.2	0.6
PC	0	63.1	1.7
	15	66.8	0.6
	45	69.6	0.5
TC	0	63.1	1.7
	15	66.2	2.1
	45	68.2	0.4

**HC = Homemade curing unit, NC = SUNUV nail curing unit, PC = Phrozen Cure V2, TC = Triad® 2000 VLC Curing Unit*