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Tese

Caracterização de resinas restauradoras impressas em 3D: Influência do tipo de solvente, pós-cura UV e tecnologias de impressão

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“A mente que se abre a uma nova ideia
jamais voltará ao seu tamanho original.”
(ALBERT EINSTEIN)

Resumo

FINCK, Nathalia Silveira. **Caracterização de resinas restauradoras impressas em 3D: Influência do tipo de solvente, pós-cura UV e tecnologias de impressão** Orientador: Rafael Ratto de Moraes. 2024. 54f. Tese (Doutorado em Odontologia) – Programa de Pós-Graduação em Odontologia, Universidade Federal de Pelotas, Pelotas, 2024.

Com o rápido avanço da impressão 3D na odontologia, as restaurações dentárias têm se beneficiado de novos materiais e processos. No entanto, devido à novidade da tecnologia e à complexidade dos fatores envolvidos, como materiais, impressoras, lavagem em solvente e tempos de pós-processamento UV, ainda há um conhecimento limitado sobre o desempenho completo dessas abordagens. Esta tese investigou as propriedades mecânicas, térmicas e de superfície de resinas utilizadas na impressão 3D de restaurações dentárias, avaliando como diferentes fatores influenciam o desempenho desses materiais. Inicialmente, foram analisadas três resinas provisórias (Resilab 3D Temp, Printax Temp e Prizma Bioprov), impressas utilizando uma tecnologia SLA/LCD. A lavagem dos espécimes foi realizada com álcool isopropílico ou etanol, e os tempos de pós-cura testados foram de 5, 10 e 30 min. As variáveis-resposta estudadas incluíram tenacidade à fratura (K_{IC}, MPa$\sqrt{m}$), microdureza Knoop (kgf/mm²), rugosidade (Ra, µm), brilho (unidades de brilho) e grau de conversão C=C (%GC). Os resultados desta etapa revelaram que a Resilab apresentou maior microdureza com álcool isopropílico e 30 min de pós-cura UV, enquanto a Printax se destacou em microdureza com etanol absoluto. K_{IC}, rugosidade e brilho foram significativamente influenciados tanto pelo tipo de solvente utilizado na pré-lavagem quanto pelo tempo de pós-cura, evidenciando variações importantes entre as diferentes resinas estudadas. Em uma segunda etapa, o foco foi na comparação das propriedades entre uma resina provisória (Prizma 3D Bioprov) e uma resina permanente (Prizma Bio Crown), impressas utilizando duas tecnologias distintas (DLP e LCD) e submetidas a tempos de pós-cura de 5 ou 30 min. Nesta fase, observou-se que a resina permanente, de maneira geral, apresentou um GC superior ao material provisório, sendo esse grau mais elevado após 30 min de pós-cura, especialmente quando a impressão foi realizada com a tecnologia DLP. A análise térmica, conduzida por calorimetria exploratória diferencial, revelou um pico exotérmico proeminente entre 160 e 170°C nos espécimes pós-curados por 5 min, que se tornou menos intenso após 30 min de pós-cura, sugerindo um processo de cura mais completo e eficaz com o tempo prolongado. Como conclusão geral desta tese, os resultados demonstram que a escolha do tipo de resina e o ajuste preciso dos parâmetros de pós-processamento, como o solvente utilizado na pré-lavagem e o tempo de pós-cura, são essenciais para otimizar suas propriedades mecânicas, térmicas e estéticas das restaurações dentárias impressas em 3D. A combinação adequada desses fatores pode potencializar a durabilidade e a eficácia clínica das restaurações impressas.

Palavras-chave: Impressão tridimensional. Polímeros. Propriedades de superfície. Fenômenos físicos.

Abstract

FINCK, Nathalia Silveira. **Characterization of 3D printed restored resins: Influence of solvent type, UV post-curing and printing technologies**. Advisor: Rafael Ratto de Moraes. 2024. 54f. Thesis (PhD in Dentistry) – Graduate Program in Dentistry, Universidade Federal de Pelotas, Pelotas, 2024.

With the rapid advancement of 3D printing technology in dentistry, dental restorations have benefited from new materials and processes. However, due to the novelty of the technology and the complexity of the factors involved, such as materials, printers, solvent washing, and UV post-processing times, there is still limited knowledge about the full performance of these approaches. This thesis investigated the mechanical, thermal, and surface properties of resins used in 3D printing for dental restorations, assessing how different factors influence the performance of these materials. Initially, three provisional resins (Resilab 3D Temp, Printax Temp, and Prizma Bioprov) were analyzed, printed using SLA/LCD technology. The washing of specimens was performed with isopropyl alcohol or ethanol, and the post-curing times tested were 5, 10, and 30 min. The response variables studied included fracture toughness (K_{IC}, MPa$\sqrt{m}$), Knoop microhardness (kgf/mm²), roughness (Ra, µm), gloss (gloss units), and degree of C=C conversion (%DC). The results of this stage revealed that Resilab showed higher microhardness with isopropyl alcohol and 30 min of UV post-curing, while Printax excelled in microhardness with absolute ethanol. K_{IC}, roughness, and gloss were significantly influenced by both the type of solvent used in pre-washing and the post-curing time, highlighting important variations among the different resins studied. In a second stage, the focus was on comparing the properties between a provisional resin (Prizma 3D Bioprov) and a permanent resin (Prizma Bio Crown), printed using two distinct technologies (DLP and LCD) and subjected to post-curing times of 5 or 30 min. In this phase, it was observed that the permanent resin generally presented a higher DC compared to the provisional material, with this degree being higher after 30 min of post-curing, especially when the printing was done with DLP technology. Thermal analysis, conducted via differential scanning calorimetry, revealed a prominent exothermic peak between 160 and 170°C in the specimens post-cured for 5 min, which became less intense after 30 min of post-curing, suggesting a more complete and effective curing process with prolonged time. As a general conclusion of this thesis, the results demonstrate that the choice of resin type and the precise adjustment of post-processing parameters, such as the solvent used in washing and post-curing time, are essential for optimizing the mechanical, thermal, and esthetic properties of 3D-printed dental restorations. The proper combination of these factors can enhance the durability and clinical efficacy of printed restorations.

Keywords: Printing, Three-dimensional. Polymers. Surface properties. Physical phenomena.

Sumário

1 Introdução

A odontologia digital tem permitido um melhor planejamento, modificação e simulação de tratamentos. Normalmente, segue um fluxo de trabalho que consiste nas seguintes etapas: aquisição de dados por digitalização, projeto do objeto no software de desenho assistido por computador (CAD) e, por fim, sua fabricação pelo sistema de manufatura assistida por computador (CAM) que poderá ser pelo método aditivo ou subtrativo. Ou seja, apenas a impressora não será suficiente para a construção do objeto. É necessário um software CAD para a projeção virtual e, posteriormente, impressão (DAWOOD *et al.*, 2015; TAHAYERI *et al*., 2018; KESSLER *et al*., 2019; MOON *et al*., 2021).

A impressão 3D, também conhecida como prototipagem rápida ou manufatura aditiva, teve seu início na década de 80, ou seja, há mais de 25 anos, o que permitiu que patentes expirassem e essa técnica se tornasse cada vez mais popular, por isso as impressoras estão cada vez mais baratas, mais leves e menores (TAHAYERI *et al*., 2018). Além disso tem sido utilizada em diversas áreas, como na indústria de automóveis, aviação e tem avançado no mercado da medicina e odontologia. Na odontologia, tem se destacado na confecção de guias cirúrgicos, guias endodônticos, modelos de diagnóstico, materiais calcináveis, reconstrução maxilofacial, aparelhos ortodônticos, regeneração tecidual guiada, próteses parciais removíveis, dispositivos oclusais, restaurações provisórias e permanentes (PARK *et al*., 2020; TASAKA *et al*., 2020; MOON *et al*., 2021).

O processo de fabricação de um objeto por impressão 3D acontece através da adição de camadas de material ao material e por esse motivo, essa técnica é chamada de manufatura aditiva, uma vez que vai adicionando uma camada após a outra (DAWOOD *et al.*, 2015).

A impressão pode ser realizada por métodos como: Modelagem por deposição fundida (FDM), processamento de luz digital (DLP), estereolitografia (SLA) e display de cristal líquido (LCD) (BALLETTI *et al*., 2017; TAHAYERI *et al*., 2018; KESSLER *et al*., 2019; CHATURVEDI *et al*., 2020; RYU *et al*., 2020; MOON *et al*., 2021).

Em 1984, Chuck Hull patenteou a primeira máquina de estereolitografia. Esta técnica de impressão utiliza um laser de varredura que é direcionado por um espelho

para rastrear a superfície da cuba preenchida por resina fotopolimerizável para a construção de cada camada. O laser traça a camada na superfície da resina líquida e, em seguida, a plataforma de construção desce para que outra camada seja construída e assim de forma sucessiva. Como vantagens, está a fabricação rápida e a capacidade de criar formas de alta complexidade com materiais de menor custo. Entretanto, está disponível apenas para polímeros líquidos fotopolimerizáveis e o prazo de validade e vida útil da cuba são limitados (DAWOOD *et al*, 2015; BALLETTI *et al*., 2017; TAHAYERI *et al*., 2018).

As impressoras que utilizam DLP utiliza um projetor de fonte de luz ultravioleta (UV) para a polimerização de cada camada da resina líquida através da elevação da plataforma. Toda a camada é polimerizada de uma vez e isso permite maior rapidez. Como vantagens, pode-se citar a boa precisão, método rápido e produção de superfícies lisas. Já entre as desvantagens das impressoras DLP, está o fato de não poder ser esterilizado por calor e estar limitado a modelos de pequeno porte (DAWOOD *et al*, 2015; RYU *et al*., 2020; MOON *et al*., 2021). As impressoras DLP e SLA permitem maior resolução dos produtos, quando comparado a FDM, o que permite produzir materiais delicados como os dispositivos odontológicos. Além disso, são fáceis de manusear e possuem tamanhos satisfatórios (REYMUS *et al*., 2019; PARK *et al*., 2020). As impressoras LCD também são baseadas na técnica de fotopolimerização, porém utilizam cristais líquidos em vez de um projetor de luz como acontece nas impressoras DLP. A técnica que utiliza impressoras LCD é barata quando comparada às outras e apresenta uma boa resolução. Entretanto, apresenta uma vida útil mais curta (MOON *et al*., 2021).

Ao comparar o método da manufatura aditiva e subtrativa, a literatura aponta que a manufatura subtrativa apresenta maior desperdício de material (até 90%), já que envolve cortes na estrutura dos materiais produzindo calor e uma força desfavorável e apresenta algumas limitações como geometrias de alta complexidade que não podem ser reproduzidas com sucesso, além da necessidade de troca das fresas (TAHAYERI *et al*., 2018; REYMUS *et al*., 2019). A literatura aponta que o melhor ajuste foi obtido com ângulos de construção de 150° e 180° e que há influência da direção de construção do objeto sobre as propriedades mecânicas. Além disso, o ajuste marginal e interno de provisórios impressos pode variar dependendo do ângulo de construção (REYMUS *et al*., 2019; RYU *et al*., 2020).

As propriedades mecânicas das resinas impressas e convencionais podem diferir (Park *et al*., 2020). Como exemplo, coroas provisórias feitas por impressão 3D podem apresentar maior microdureza do que aquelas feitas por métodos convencionais, além de o envelhecimento poder afetar as propriedades mecânicas desse material impresso. Após cair a patente das impressoras que utilizam polímeros como as, já citadas, DLP, LCD e SLA, a manufatura aditiva se tornou mais acessível a todos e a odontologia. Entretanto, não há uma padronização referente ao tratamento destes materiais após as impressões e durante a definição dos parâmetros para cada tipo de impressora. Outro fator considerado é a variação do valor de cada tipo de impressora no mercado, já que há impressoras com baixo custo e outras com alto custo. O ponto a ser questionado é a real diferença prática que cada uma delas faz na rotina clínica e na eficiência da reabilitação dos pacientes (DIGHOLKAR *et al*., 2016; REYMUS *et al*., 2019; ZIMMERMANN *et al*., 2019).

Após o processo de impressão, há necessidade de o material passar por uma pré-lavagem e um processo de pós-cura. Tais etapas não estão, na maior parte dos materiais, padronizadas. Entretanto, esses processos serão determinantes no comportamento mecânico e físico que possam apresentar. Por isso, o solvente utilizado no processo de pré-lavagem deveria ser mais bem elucidado, apresentando o comportamento dos materiais quando utilizado o etanol ou o álcool isopropílico, uma vez que podem influenciar nas propriedades. O mesmo ocorre com o tempo de exposição à pós-cura que, de acordo com a literatura, pode ser mais eficiente otimizando a intensidade da luz e o tempo (KANG *et al*., 2022; KIM *et al*., 2022; SOTO-MONTERO *et al*., 2022). Porém, observa-se a falta de informações de pós-processamento providas pelo fabricantes, o que dificulta o uso clínico.

1.1 Objetivo geral

O objetivo desta tese é avaliar o desempenho laboratorial de resinas odontológicas utilizadas em impressão 3D com foco no pós-processamento, nas propriedades mecânicas, além de análises de superfície e térmica.

1.2 Objetivos específicos

- Avaliar o efeito de diferentes protocolos de pós-processamento em propriedades selecionadas de três resinas restauradoras comerciais de impressão 3D para restaurações provisórias;
- Avaliar o uso de etanol como uma alternativa ao álcool isopropílico para pré-lavagem da resina não curada;
- Investigar a possibilidade de otimizar o processo de pós-cura usando tempos de UV mais curtos (5 ou 10 min) em comparação com uma polimerização de luz UV de 30 min.
- Investigar os efeitos combinados de dois tipos de impressoras 3D (uma DLP e uma LCD) e dois diferentes tempos de pós-cura (5 e 30 minutos) nas propriedades mecânicas e térmicas de duas resinas de impressão 3D para restaurações dentárias (uma provisória e uma permanente).

2 Capítulo 1[1]

Effects of solvent type and UV post-cure time on 3D-printed restorative polymers

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Abstract

Objectives: This study evaluated the impact of different solvents and UV post-curing times on properties of 3D printing resins for provisional restorations. Methods: The post-processing methods were tested using two solvents (isopropyl alcohol or absolute ethanol) and three UV times (5, 10, or 30 min). The resins tested were Resilab 3D Temp, Printax Temp, and Prizma Bioprov. Microhardness (kgf/mm2), fracture toughness (KIC, MPa√m), surface roughness (Ra, μm), gloss (gloss units), and degree of C=C conversion (%DC) were measured (n=8). All response variables were collected from the same specimen. The specimens were 3D printed using an SLA/LCD printer (150◦ angulation, 50 μm layer thickness). Light exposure times were adjusted for each material, and the post-processing methods were applied using an all-in-one machine immediately after printing. Data were analyzed using Three-Way ANOVA (α =0.05). Results: Microhardness was affected by UV post-cure time and 3D resin. Resilab showed higher microhardness with isopropyl alcohol and 30-min UV time, while Printax had higher microhardness with absolute ethanol. KIC was influenced by solvent type, UV time, and 3D resin, with varying effects on different resins. Roughness was affected

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by 3D resin and UV time, but no significant differences were seen for Resilab or Prizma. Gloss was influenced by 3D resin, and for Prizma, it was lower with specific solvent/UV time combinations. DC was influenced by 3D resin, with each resin behaving differently. Significance: Tailoring the combination of 3D resin, solvent washing type, and UV post-curing time is important to achieve optimal mechanical and aesthetic outcomes for restorations.

Keywords: Isopropyl alcohol**,** Ethanol**,** Post-processing methods**,** Additive manufacturing**,** Dental restoration.

Introduction

The digital workflow has gained popularity in dentistry, and numerous acrylic-based photosensitive resins are now available for additive manufacturing of crowns and bridges. However, there are still many aspects to be investigated concerning the 3D printing process of restorative polymers. A review study on 3D-printed provisional materials revealed that their fracture strength tends to be higher than that of conventional acrylic restorations and comparable to their milled provisional counterparts [1]. However, regarding other physical properties, varying results were reported [1], which can be attributed to several factors including differences in printing layer thickness [2], printing orientation [3-5], equipment used [6], resin composition [2], and post-processing procedures [7-10].

After 3D printing, the conversion of monomers to polymers is not complete, necessitating post-processing steps. The initial step involves washing the printed restorations in a solvent to remove residual monomers. This step is crucial to improve surface properties and also because residual monomers can have cytotoxic or allergic effects on human cells [11-13]. Isopropyl alcohol is commonly used for washing, although other solvents have been tested [8,14,15]. Isopropyl alcohol was shown not to affect the flexural strength of temporary resins [16], whereas tripropylene glycol monomethyl ether has been suggested to enhance accuracy and precision of polymers [8]. A study showed that an ultrasonic bath is more effective than a rotary washer or simple immersion in the solvent for eluting residual monomers [14]. Additionally, a 3-min ultrasonic or rotary washer bath with isopropyl alcohol has been found to improve cell viability compared to soaking the resin [14]. However, the effects of routinely used

solvents, such as absolute ethanol, on the characteristics of 3D-printed resins are still uncertain.

Subsequent to washing, the degree of C=C conversion (DC) in 3D-printed polymers is enhanced through UV light-polymerization chambers. UV polymerization time and intensity may improve DC and influence the mechanical and optical properties of the polymers [4,9,10,17]. A previous study showed that increasing UV time beyond 60 min does not significantly increase the DC or affect the flexural strength with different polymerization temperatures [17]. Another study observed that the surface accuracy of an acrylic-based resin was similar when UV exposures for 15 min or 30 min were used at the same temperature [18]. However, the impact of post-curing on different 3D printing resins may vary due to their unique compositions, including initiators and monomers. Despite studies evaluating the effect of post-processing steps on surface and optical properties of 3D-printed resins [4,8-10,14-18], limited information exists on fracture toughness and gloss [19] and particularly when all tests are conducted using the same specimen across different methodologies. In addition, a comparison between short vs. longer UV exposure times could provide valuable insights for clinicians and laboratories during post-processing of additive-manufactured restorative polymers.

This study aimed to evaluate the effect of different post-processing protocols on selected properties of three commercial 3D printing restorative resins for provisional restorations. We assessed the use of absolute ethanol as an alternative to the commonly used isopropyl alcohol for washing the uncured resin. Furthermore, we investigated the possibility of optimizing the post-curing process by using shorter UV times (5 or 10 min) compared to a 30-min UV light-polymerization. The tested hypotheses were as follows: (i) the type of solvent would not influence the selected properties, and (ii) increased UV post-curing times would improve the performance of the 3D-printed polymers.

Materials and methods

Study design and tested materials

This *in vitro* study investigated the effects of two washing solvents (isopropyl alcohol or absolute ethanol) and three different UV light post-cure times (5, 10, or 30 min) on selected properties of three 3D printing resins used for provisional restorations.

The tested resins were Resilab 3D Temp (Wilcos, Petropolis, RJ, Brazil), Printax Temp (Odontomega, Ribeirao Preto, SP, Brazil), and Prizma Bioprov (Maquira, Maringa, PR, Brazil), all in shade A3. Table 1 provides detailed information about the 3D printing resins used in this study. The following response variables were evaluated: Knoop microhardness (kgf/mm^2), fracture toughness (K_{IC}., MPa$\sqrt{m}$), surface roughness (Ra, μm), surface gloss (gloss units - GU), and DC (%). A minimum sample size of 8 specimens per group was determined, as the pilot study with microhardness tests yielded a minimum sample size of 7. The sample size calculation considered an experimental design with 6 independent groups, a minimum detectable difference in hardness means of 11.6, an expected standard deviation of residuals of 5.4, and α=0.05 and β=0.2 as the significance and power levels, respectively.

3D printing and post-processing methods

All response variables were collected from the same specimen specifically designed for the fracture toughness test using Autodesk Meshmixer (San Francisco, CA, USA) and 3D Builder (Microsoft, Redmond, WA, USA). The bar-shaped specimens measured 24 mm in length, 5 mm in height, and 2.5 mm in width. They featured a V-shaped notch at the center, with dimensions of 2.5 mm in height and 0.4 mm in bottom width. The specimen design was exported as an STL file and printed using a desktop stereolithography/liquid crystal diode (SLA/LCD) display printer (Photon Mono 4K; Anycubic, Shenzhen, China) with a 4K LCD resolution, 35 μm XY resolution, and 10 μm Z-axis accuracy. The printing platform was adjusted to a 150° angulation [20], with lift and retract speeds set at 1 and 3 mm/s, respectively. For all 3D resins, six burn-in layers were included, and the normal layers had a thickness of 50 μm. The light exposure times for burn-in and normal layers were adjusted for each material based on the pilot study results (Table 1).

Immediately after printing, the various post-processing methods were applied using an all-in-one machine (UW-01; Creality, Shenzhen, China). Washing was performed using either isopropyl alcohol (>99%, Togmax, Curitiba, PR, Brazil) or absolute ethanol (Perfyl Tech, Sao Bernardo do Campo, SP, Brazil) for 3 min. The machine was a rotary washer that used an electromagnetic propeller to agitate the solvent during the washing process of the uncured resin. Following the washing step, the specimens underwent UV post-curing for 5, 10, or 30 min. The specimens were positioned at the periphery of the platform, and the UV post-cure time was evenly

divided between the top and bottom sides of each specimen. Specifically, after half of the designated time had elapsed, the specimens were rotated inside the chamber to expose the other side to UV light. Subsequently, the supports were removed using a double-faced diamond disc (Duraflex; American Burrs, Palhoca, SC, Brazil), and all specimens were wet-polished using 1200- and 2000-grit SiC abrasive papers (Norton Abrasivos, Guarulhos, SP, Brazil) to achieve improved finishing and polishing.

Surface roughness and gloss measurements

The measurements were conducted immediately after polishing the surface of the specimens. Surface roughness was assessed using a profilometer (Surfcorder SE1700; Kosaka Laboratory, Tokyo, Japan) with 0.01 mm resolution, equipped with a diamond stylus (tip diameter 2 mm) positioned perpendicular to the long axis of the specimen. The specimens were fixed to plastic stubs using wax, and the measurements utilized a screening length of 8 mm, a cut-off point of 0.25 mm, and a speed of 1 mm/s. The recorded average roughness (Ra, μm) was calculated as the mean of three readings taken on each specimen. Then, surface gloss was measured using a glossmeter (ZGM 1120; Zehntner, Zurich, Switzerland) with a 60° incident light angle and reflection angles relative to the vertical axis. Three readings were taken on each specimen, and the average values were recorded as the surface gloss (GU).

Fracture toughness (K_{IC}) and microhardness analyses

K_{IC} was determined using the single-edge notched beam method [21]. The specimens were positioned in supports with a 20 mm span, and the notch was positioned opposite to the load application. Three-point bending tests were conducted at a constant speed of 0.5 mm/min until failure using a testing machine (Instron model 5569A; Instron, Norwood, MA, USA). The calculation of K_{IC} (MPa$\sqrt{m}$) followed a previously described method [21]. For the microhardness measurements, the same bars retrieved from the fracture toughness tests were used. The specimens were fixed using wax, and five Knoop indentations were made on the surface of each specimen, with a minimum distance of 500 μm between each indentation. A digital microhardness tester (HMV-2000; Shimadzu, Tokyo, Japan) was used, applying a load of 50 gf for 10 s. The Knoop microhardness (kgf/mm^2) was determined as the average of three readings for each specimen.

Degree of C=C conversion

The DC was determined using Fourier-transform mid-infrared spectroscopy (Carry 630; Agilent, Santa Clara, CA, USA) equipped with a single attenuated total reflectance device consisting of a diamond crystal. The measurements were conducted 2 to 3 weeks after obtaining the specimens. During this period, the specimens were kept in lightproof containers for dry storage. Initially, a preliminary reading was taken in the absorbance mode with 128 scans and a resolution of 4 cm^{-1} to measure the unpolymerized resins (monomer). Spectra were taken from 1500 to 1800 cm^{-1} wavelengths. For the DC measurements, the 3D-printed bar-shaped specimens were pressed against the diamond crystal to obtain additional readings after polymerization. The DC was calculated using a baseline technique [22] and measuring the intensity (peak height) of the C=C stretching vibration at 1635 cm^{-1} (aliphatic), while using the symmetric aromatic stretching vibration at 1608 cm^{-1} as an internal standard. The formula used for calculating the DC was as follows:

$$DC\ (\%) = \{1 - [Abs_{(aromatic)} / Abs_{(aliphatic)}]_{polymer} / [Abs_{(aromatic)} / Abs_{(aliphatic)}]_{monomer}\} \times 100.$$

Data analysis

Data for each response variable were subjected to statistical analysis using Three-Way Analysis of Variance - ANOVA (3D resin × solvent type × UV post-cure time). The inclusion of the 3D resins as an independent variable in the analysis aimed to explore the relationship among all three variables, although direct comparisons across the materials were not the primary focus of the study. Pairwise multiple comparison procedures were conducted using the Student-Newman-Keuls method. The significance level was set at $\alpha=0.05$. Prior to the analyses, the microhardness data underwent log transformation to meet the assumptions of normality and equal variance tests. Additionally, surface roughness, surface gloss, DC, and fracture toughness data were transformed to ranks before the analyses were performed. All statistical analyses were carried out using SigmaPlot 12.0 software (Systat Software Inc., Chicago, IL, USA).

Table 1. Formulation of tested resins for 3D printing of provisional restorations

3D resin	Manufacturer	Lot	Composition [a]	Exposure time (burn-in; normal layers) [b]
Resilab Temp	Wilcos	1421	Not available	40 s; 4 s
Printax Temp	Odontomega	PDR-22022101	Methacrylate and acrylate monomers, aromatic methacrylic oligomer, aliphatic methacrylic oligomer, phosphine oxide, pigments, stabilizers	30 s; 3 s
Prizma Bioprov	Maquira	165821	Methacrylate ester monomers, methacrylate oligomers, acrylic monomers, pigments, photoinitiator	30 s; 2.5 s

[a] Information provided by the manufacturers. [b] Parameters adjusted in a pilot study.

Results

Microhardness

Results are summarized in Table 2. The microhardness was significantly influenced by the UV post-cure time ($p=0.018$) and 3D resin ($p <0.001$). The interactions of 3D resin ×solvent ($p<0.001$) and 3D resin ×UV time ($p=0.023$) also showed significant influence. However, the factor solvent type ($p=0.066$) and the interaction solvent type ×UV post-cure time ($p=0.076$) were not significant. Specifically, for Resilab resin, the microhardness was higher when isopropyl alcohol was used, and it was also higher with a UV post-cure time of 30 min. For Printax resin, the microhardness was higher when washed with absolute ethanol, and no significant differences were observed across different UV times. Regarding Prizma resin, no significant differences were observed when using different solvents or UV times. Comparing the effects of different solvents on microhardness, the highest changes ranged from 11% to 26% depending on the specific resin used. Similarly, the highest variations in microhardness resulting from different UV post- cure times ranged between 10% and 20%.

Table 2. Means (95% confidence intervals) for Knoop microhardness, kgf/mm^2 (n=8)

3D resin	Solvent type	UV post-cure time			
		5 min	10 min	30 min	
Resilab	Isopropyl alcohol	15.4 (1.0)	14.5 (0.9)	15.6 (1.3)	a
	Absolute ethanol	12.0 (1.0)	13.1 (0.8)	14.7 (0.7)	b
		B	B	A	
Printax	Isopropyl alcohol	18.3 (0.7)	17.4 (1.9)	18.7 (2.0)	b
	Absolute ethanol	20.4 (1.5)	18.5 (1.4)	19.0 (1.3)	a
		A	A	A	
Prizma	Isopropyl alcohol	13.8 (1.1)	13.8 (0.6)	13.8 (0.9)	a
	Absolute ethanol	12.2 (0.7)	13.8 (0.9)	14.3 (1.0)	a
		A	A	A	

For each 3D resin, capital letters indicate differences between UV post-cure times, lowercase letters indicate differences between solvent types ($p<0.05$). The factor solvent type and the interaction solvent type × UV post-cure time were not significant.

Fracture toughness

Results are presented in Table 3. The factors solvent type ($p=0.004$) and UV post-cure time ($p<0.001$) were found to be significant, while their interaction was not significant ($p=0.737$). Other significant sources of variation for fracture toughness included the 3D resin ($p=0.007$), as well as the interactions 3D resin ×solvent ($p<0.001$) and 3D resin ×solvent ×UV time ($p<0.001$). For Resilab resin, no significant differences were observed across different UV times when the solvent used was isopropyl alcohol. However, when absolute ethanol was used, the fracture toughness was lower for 5- and 10-min UV post-cure times compared to the 30-min UV time. For Printax, the opposite trend was observed. When the solvent used was absolute ethanol, no significant differences were observed across different UV times. However, when isopropyl alcohol was used, the fracture toughness was significantly higher for the 30-min UV time compared to the 5- and 10- min UV times. Regarding Prizma, no significant differences were observed across different solvents. However, higher KIC was generally observed for the 30-min post-cure time compared to the shorter UV times. Comparing the effects of different solvents, the highest changes in KIC ranged

from 7% to 74% depending on the resin, whereas the highest variations resulting from different UV times ranged between 34% and 113%.

Table 3. Means (95% confidence intervals) for fracture toughness (K_{IC}), MPa√m (n=8)

3D resin	Solvent type	UV post-cure time		
		5 min	10 min	30 min
Resilab	Isopropyl alcohol	6.6 (1.0) A,a	6.5 (1.0) A,a	7.2 (1.0) A,a
	Absolute ethanol	3.8 (0.5) B,b	4.5 (0.8) B,b	6.8 (1.1) A,a
Printax	Isopropyl alcohol	3.7 (0.7) B,b	5.1 (0.7) B,a	7.9 (1.8) A,a
	Absolute ethanol	5.0 (0.5) A,a	6.0 (0.4) A,a	6.4 (1.5) A,a
Prizma	Isopropyl alcohol	4.7 (0.3) B,a	4.9 (0.2) B,a	5.9 (0.3) A,a
	Absolute ethanol	4.4 (0.3) B,a	4.9 (0.6) AB,a	5.9 (0.6) A,a

For each 3D resin, capital letters indicate differences between UV post-cure times, lowercase letters indicate differences between solvent types ($p<0.05$).

Surface roughness and gloss

Figure 1 presents a summary of the results for surface roughness and gloss. For roughness, the factor solvent type did not show statistical significance ($p=0.704$), while UV post-cure time ($p=0.021$) and the interaction solvent type × UV time ($p=0.005$) were found to be significant. Other significant sources of variation for roughness were the 3D resin used ($p<0.001$) and the interaction 3D resin × UV time ($p=0.042$). Notably, no significant differences in surface roughness were observed for Resilab or Prizma when different solvent types or UV post-cure times were applied. However, for Printax, the roughness was significantly lower when absolute ethanol was used and the specimens underwent UV post-curing for 5 and 10 min. Comparing the effects of different solvents on surface roughness, the highest variations ranged from 56% to 80% depending on the resin, whereas the highest changes resulting from different UV times ranged between 40% and 92%.

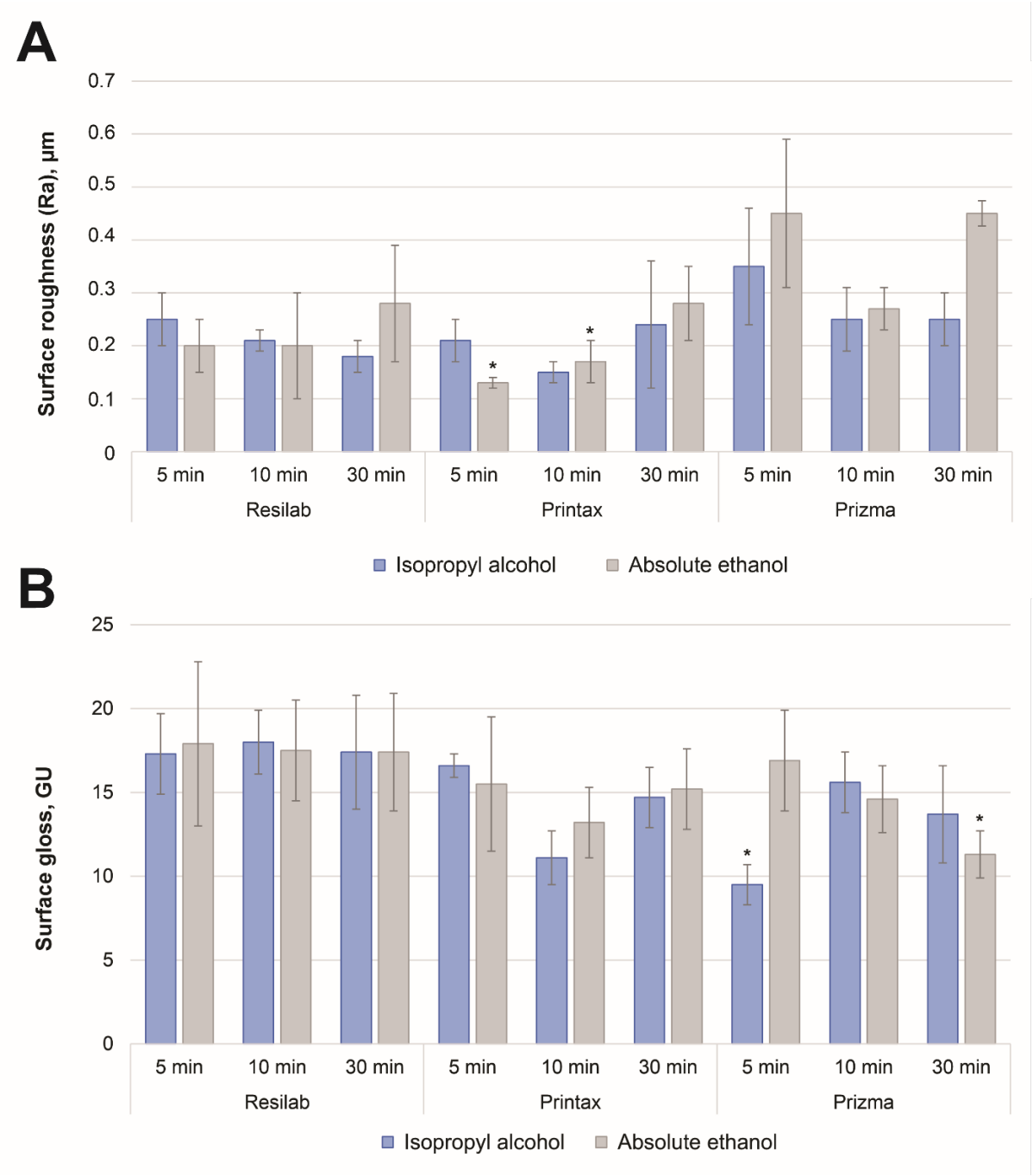

Figure 1. Surface roughness (A) and gloss (B) results (means ± 95% confidence intervals). The effects of solvent types and UV post-curing times were generally not significant, except for the differences indicated by asterisks for each 3D resin ($p<0.05$).

Surface gloss results showed that the factors solvent type ($p=0.612$) and UV post-cure time ($p=0.618$), as well as the interaction solvent type × UV time ($p=0.342$), did not exhibit statistical significance. However, significant sources of variation for surface gloss were found in the 3D resin used ($p<0.001$), and the interactions 3D resin × UV time ($p<0.001$) and 3D resin × solvent × UV time ($p<0.001$). Specifically, no

significant differences in surface gloss were observed for Resilab or Printax when different solvent types and UV post-cure times were applied. Nevertheless, for Prizma, the surface gloss was significantly lower in the combinations of isopropyl alcohol/5 min UV time or absolute ethanol/30 min UV time. Comparing the effects of different solvents on gloss, the highest changes ranged from 4% to 78% depending on the specific resin used. Similarly, the highest variations in gloss resulting from different UV post-cure times ranged between 4% and 64%.

Surface topography and elemental composition

SEM images depicting the surface topography of specimens from different 3D resins are presented in Fig. 2. Visible surface scratches resulting from the polishing procedures were observed. The variations in topography between surfaces washed with isopropyl alcohol and Absolute ethanol were minimal; at ×2000 magnification, surfaces washed with isopropyl alcohol appeared slightly more irregular, especially for Printax. Complementary EDS analysis indicated that Resilab and Prizma specimens exhibited between 8 wt% and 10 wt% of the combined elements Si, Ti, and Al, suggesting that this could represent the inorganic content of these two resins. In contrast, Printax specimens showed less than 5 wt% of these inorganic elements, with no Si content, indicating a very low inorganic filler loading for this resin. The EDS analysis further revealed that the carbon content on the specimens varied between 64.5 wt% and 72.3 wt% across the resins. On average, specimens treated with isopropyl alcohol exhibited a higher carbon contente compared to those treated with absolute ethanol, with increases of 1.6 wt% (Prizma), 3.0 wt% (Resilab), and 7.4 wt% (Printax). This difference suggests a higher polymeric content on the surface when treated with isopropyl alcohol.

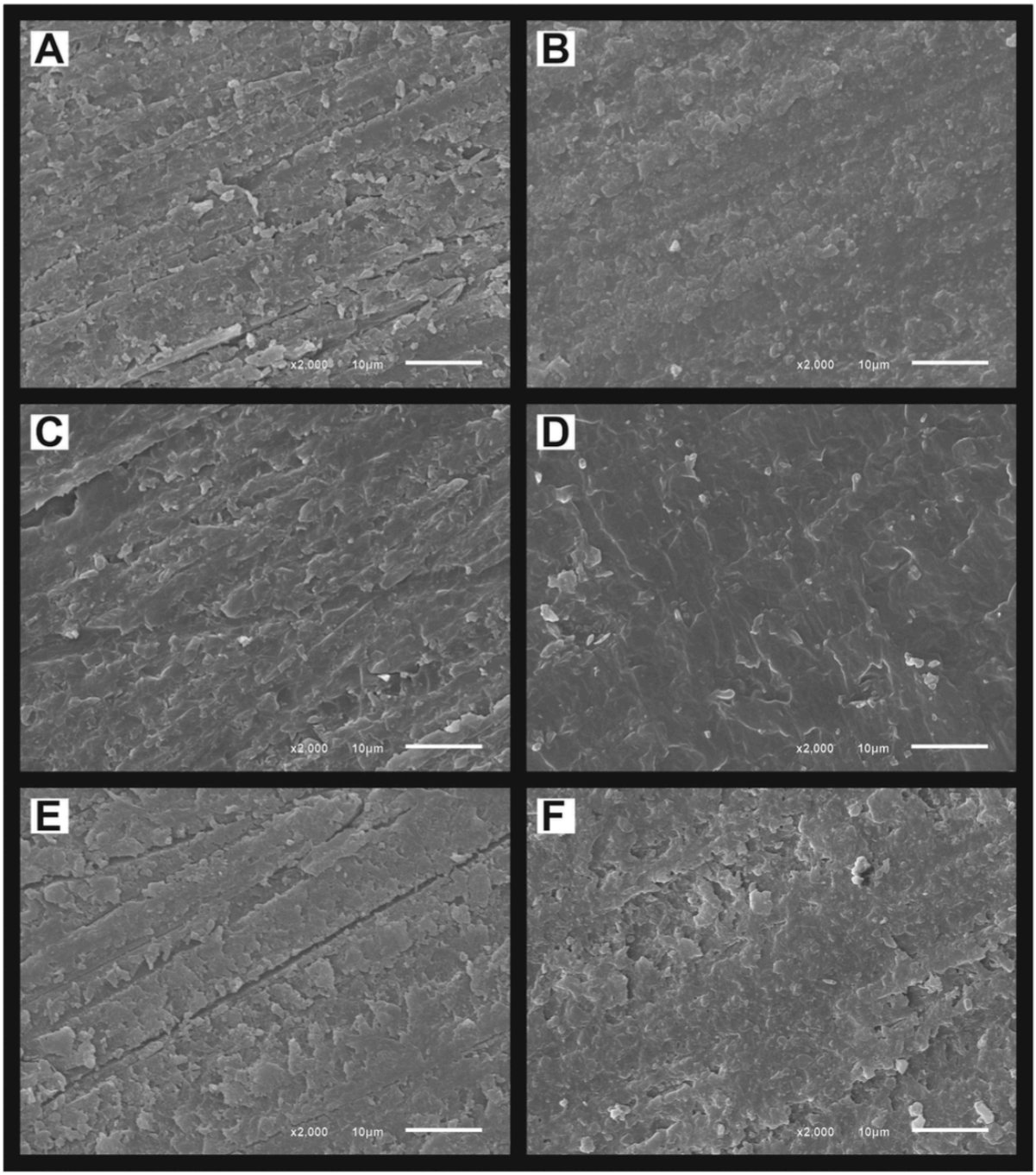

Figure 2. SEM images illustrating the surface topography of the distinct 3D resins subjected to different post-processing protocols (×2000 magnification). A: Resilab resin, isopropyl alcohol, 30 min UV time; B: A: Resilab resin, absolute ethanol, 30 min UV time; C: Printax resin, isopropyl alcohol, 30 min UV time; D: Printax resin, absolute ethanol, 30 min UV time; E: Prizma resin, isopropyl alcohol, 5 min UV time; F: Prizma resin, absolute ethanol, 5 min UV time. Visible surface scratches resulting from the polishing procedures were observed. The variations in topography between surfaces washed with isopropyl alcohol and absolute ethanol were minimal. Surfaces washed with isopropyl alcohol appeared slightly more irregular, especially for Printax.

Degree of C=C conversion

Data for DC are summarized in Table 4. The factor 3D resin was. significant (p=0.001) whereas solvent type (p=0.061) and UV post-cure time (p=0.4) were not. The only significant interaction was 3D resin x UV time (p <0.001), while all other associations were not significant (p ≥0.107). Each resin showed a distinct behavior. For Resilab, higher DC was observed for the 30-min UV time compared with shorter times. For Printax, the only difference was the better result for DC for the 5-min UV time compared with 30 min. For Prizma, the best results were observed for the 10-min UV time compared with the other times. Comparing the effects of different solvents, the highest changes in DC ranged from 14% to 48% depending on the resin, whereas the highest variations resulting from different UV times ranged between 20% and 61%.

Table 4. Means (95% confidence intervals) for degree of C=C conversion, % (n=8)

3D resin	Solvent type	UV post-cure time		
		5 min	10 min	30 min
Resilab	Isopropyl alcohol	34.2 (12.6)	49.6 (12.2)	55.2 (10.6)
	Absolute ethanol	46.5 (13.9)	36.5 (15.9)	56.9 (8.2)
		B	B	A
Printax	Isopropyl alcohol	76.0 (3.7)	67.4 (6.5)	63.3 (8.5)
	Absolute ethanol	66.3 (10.6)	65.1 (7.1)	57.2 (12.3)
		A	AB	B
Prizma	Isopropyl alcohol	36.8 (15.5)	59.1 (26.1)	45.0 (20.6)
	Absolute ethanol	43.7 (18.9)	41.9 (22.9)	30.3 (12.5)
		B	A	B

For each 3D resin, capital letters indicate differences between UV post-cure times (p<0.05). The factors solvent type and UV post-cure time were not significant.

Discussion

This study is the first to evaluate the combined effect of different washing solvents and UV light post-cure times on 3D printed resins for dental restorations. The results demonstrated that both the choice of solvent and UV post-cure time can

significantly influence the microhardness, fracture toughness, roughness, and gloss of the 3D-printed polymers, and their effects can vary depending on the specific resin used. These findings emphasize the impact of solvent selection and UV exposure time on the characteristics of the 3D-printed restorative polymers, suggesting potential optimization strategies for improved surface quality and mechanical behavior.

The type of washing solvent significantly influenced KIC and demonstrated significant interactions with other factors in various analyses, supporting the idea that the first hypothesis could not be rejected. The composition of the 3D resin appears to play an important role in the solvent's effect. Printax exhibited the highest microhardness and the lowest roughness when using absolute ethanol, while isopropyl alcohol in combination with 30-min UV post-curing yielded the highest microhardness for Resilab. This discrepancy can be attributed to the differential interactions of the solvents with compounds presented in the formulation of the resins. Absolute ethanol interacts better with aliphatic compounds, whereas isopropyl alcohol interacts better with aromatic compounds [23,24]. When there is a better match between the solvent and resin formulation, the solvent may diffuse and react more effectively within the uncured material and the polymerized structure. This interaction may influence the production and remnants of porosity after the solvent is evaporated, ultimately affecting surface qualities. The roughness and microhardness of the other resin tested, Prizma, were not affected by either the solvent type or UV time. However, its gloss was reduced when post-cured for 5 min after isopropyl alcohol washing or post-cured for 30 min after absolute ethanol washing. Despite this, none of the differences in gloss (ΔGU) observed exceeded the acceptability threshold (ΔGU<36) [25], suggesting that these differences may not be clinically significant.

Microhardness and KIC data were consistent indicating that different materials reacted differently to washing with different solvents. When analyzing the KIC results, it was observed that Prizma was not affected by either the solvent type or UV post-curing time. However, for Resilab washed in absolute ethanol and Printax washed in isopropyl alcohol, their KIC results were influenced. Interestingly, each solvent had contrasting effects on the microhardness and toughness of these two materials. Absolute ethanol improved KIC of Resilab and microhardness of Printax, whereas isopropyl alcohol improved the microhardness of Resilab and KIC of Printax. This difference in the results may be attributed to the nature of the tests conducted. The fracture toughness test assesses the ability of pre-notched specimens to resist crack

propagation during a bending test, which is a bulk property evaluation. On the other hand, microhardness primarily reflects the surface conditions of the resins. Thus, besides the composition, the KIC of the 3D printing resins may have been influenced by internal porosities that allowed varying degrees of solvent absorption. A previous study [16] observed that isopropyl alcohol washing resulted in higher flexural strength compared to bio-ethyl alcohol, indicating the influence of solvents on bulk material properties. However, the study only tested one 3D printing resin, highlighting the need for further investigation.

UV post-curing time had a significant impact on the majority of the tested properties, and as a result, the second hypothesis could not be rejected. However, the effect of UV post-curing on most properties was influenced by the specific 3D resin and/or solvent used. These findings highlight the consequential role of 3D resin composition and its interactions with different solvents and post-processing methods. For Printax, the smoothest surface was achieved when washed with absolute ethanol and post-cured for 5 or 10 min. It appears that absolute ethanol left fewer surface porosity after evaporation, consistent with the SEM images, but the longer curing time resulted in increased roughness. Surprisingly, the UV post-curing time did not independently affect the DC. This finding suggests that even short UV post-curing times can increase the C=C conversion at the surface of the specimens, while their influence on the bulk of the polymer is likely minor. For DC, a significant interaction with the 3D resin type was observed. Resilab benefited the most from a 30-min post-curing time, as it increased its DC and also improved K_{IC} when washed with absolute ethanol. Previous studies have indicated that increasing post-curing time leads to higher DC and improved mechanical properties [9,17]. However, our findings suggest that a 10-min post-curing time resulted in similar or even higher DC compared to a 30-min time for Printax and Prizma, respectively. Interestingly, another study observed that UV post curing times did not significantly influence the initial DC [9]. However, when the specimens were aged, those subjected to less than 10 min of UV time exhibited increased roughness [9].

Currently, most dental 3D resins available are formulated for provisional or temporary restorations, such as the ones tested herein, which are not intended for long-term clinical durability. Consequently, a key question arises as to whether the observed laboratory differences hold clinical significance. While a definitive answer to this question remains uncertain, if the goal is to create longer-lasting restorations,

individualizing the choice of solvent and UV post-cure time for each resin might be essential to optimize both esthetic and mechanical outcomes. One limitation of testing commercial materials is the lack of detailed information about their specific formulations, including the composition of monomers and filler particles. This complexity becomes particularly challenging when various factors influence the behavior of the tested materials. To partially overcome this limitation, we conducted elemental chemical analysis on the surface of the specimens. One finding of this analysis was that the 3D resins had a low filler loading, consistent with materials for provisional restorations. Future studies should investigate the effects of post-processing protocols on 3D resins intended for longer-lasting, perhaps "definitive" restorations. Even newer materials labeled for "permanent" restorations still lack established clinical validation for extended durability. The definitions of terms such as durable, permanent, and definitive when applied to 3D-printed materials for dental restorations are topics that require exploration relying on clinical studies rather than solely on laboratory analyses or indications from manufacturers.

It is important to acknowledge limitations in our methodology. While we tested three different 3D resins, only one printing angulation (150◦) was examined, and the specimens were not subjected to aging, factors known to influence the surface and mechanical properties of 3D resins [3,4,9]. Another noteworthy aspect is the resin selection and its compatibility with the 3D printer. In this study, a budget printer was used, and the printing parameters were adjusted in pilot studies—an essential step in achieving an optimal combination between any 3D resin and a printer, even when using more expensive ones. Although differences in 3D printers can impact the final printed structures, the literature is relatively limited in comparing low and high-cost printers for restorative polymers. A recent article comparing the trueness and precision of 12 printers concluded that the current range of 3D printers can achieve clinically acceptable levels of accuracy [26]. The study found no discernible differences between budget and more expensive printers in producing dental models. Nevertheless, a strength of this study is that all response variables were collected from the same polymer specimen, allowing for a more controlled scenario to compare results obtained from different tests, which encompassed both surface and bulk polymer properties of clinical relevance. Future studies should consider subjecting 3D-printed restorative polymers to aging and exploring more in-depth analyses of polymer properties, such as dynamic mechanical analysis, for a comprehensive understanding of their behavior.

Conclusions

This study highlights the importance of tailoring the combination of 3D resin, solvent washing type, and UV post-curing time to achieve optimal physical and chemical results for dental restorative polymers. Specific findings from our study include:

- The choice of 3D resin had the most significant impact on the mechanical and aesthetic outcomes of 3D-printed restorative polymers;
- Isopropyl alcohol or absolute ethanol could improve the polymer properties or surface qualities depending on the specific 3D printing resin used. However, the solvent tended to have a lesser effect on these properties with increasing UV post-curing time;
- The UV post-curing time of 30 min was found to be generally effective in achieving the best results for most cases. However, it is essential to consider the solvent used, as it influenced the optimal post-curing time. In certain instances, the 30-min UV time was not necessary.

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3 Capítulo 2[2]

Mechanical and thermal properties of restorative polymers: Comparing provisional and long-term resins, 3D printers, and post-curing times

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Abstract

Objectives: This study examined the effects of two 3D printers (DLP vs. LCD) and two post-curing times (5 min vs. 30 min) on the mechanical and thermal properties of provisional and long-term resins for restorations. Methods: Bar-shaped specimens were printed using Flashforge Hunter (DLP) and Anycubic Photon Mono M5s (LCD), and resins Prizma 3D Bioprov (provisional) and Prizma Bio Crown (long-term). Two post-curing times were tested: 5- and 30-min. Response variables (n=10) included fracture toughness (K_{IC}, MPa$\sqrt{m}$), Knoop microhardness (kgf/mm²), and degree of C=C conversion (%DC). Thermal analysis was conducted using differential scanning calorimetry (DSC). Data were analyzed using three-way ANOVA (α=0.05). Results: The provisional resin generally exhibited superior K_{IC} compared to the long-term resin. Increasing the post-curing time enhanced K_{IC} in most conditions. No microhardness differences across any group were detected. The long-term resin generally had higher DC than the provisional material, and DC was higher for the 30-min post-curing time compared to the 5-min time for the provisional resin printed by the DLP printer. In the

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DSC analysis, an exothermic peak around 160 to 170°C was observed prominently in the 5-min post-cured specimens and was less intense in the 30-min specimens. This indicated that longer post-curing times resulted in more complete curing of the resins. The printer type had a minor effect on the performance of restorative polymers.
Significance: Resin type is crucial for 3D-printed dental restoratives, and longer post-curing times improve mechanical and thermal properties. There is potential for enhancing materials for longer-lasting 3D-printed restorations.

Keywords: Ultraviolet Rays, Mechanical Tests, Differential scanning calorimetry, Printing, Three-Dimensional.

Introduction

The interest and research in 3D printing with resin-based materials in dentistry have experienced rapid growth. This increase is due to the method's versatility and significant advancements in equipment, including enhanced resolution and precision, improved photopolymerization processes, more efficient and controlled construction techniques, and the continuous development and refinement of new materials [1-6]. The literature is increasingly abundant with information on the printing process of polymers for varied clinical uses [7-12]. However, considerable uncertainty remains regarding the additive manufacturing of dental restorations that can be considered definitive or long-lasting.

Formulations of resins for dental restorations exhibit significant variability, with numerous provisional materials available and a growing number of products now claiming to offer durable restorations. Additionally, the types, brands, and qualities of printers, as well as the most effective post-processing methods for printed structures, remain areas of active exploration. One of the ongoing uncertainties in the process of printing restorations is the impact of different printer technologies [8-10,13]. Printers employing digital light processing (DLP) and liquid crystal display (LCD) technologies are among the most commonly used. Both operate on similar principles of vat photopolymerization. DLP printers use a light projector to display an image onto the resin, solidifying it layer by layer and exposing the entire resin layer to light simultaneously, which results in faster print speeds [1,5,14]. In contrast, LCD printers

create a mask that selectively blocks light from the LED back panel and generally have lower light transmission efficiency [3,7].

A study has shown that DLP technology surpasses LCD in producing smaller, more precise features due to its intense light source, while LCD provides better visual quality and performs slightly better for larger parts [7]. Specifically, 3D printing of temporary dental restorations was more accurate with DLP, especially for larger restorations [14]. DLP printers also demonstrate higher accuracy in printing dental models compared to LCD [15]. However, different printer types did not influence surface roughness and produced similar cellular responses in human gingival fibroblasts [8]. The focus is now on developing new polymers suitable for long-term restorations, which must have higher filler content and improved mechanical properties [4,12] to last longer in the oral environment, such as crowns and possibly bridges. Questions about the impact of printing technologies and UV post-curing times remain relevant. Recent studies indicate that post-curing times affect the mechanical performance of 3D-printed polymers [10,13], with generic instructions potentially insufficient for full curing [16]. Additionally, investigating the thermal properties of 3D-printed polymers could provide a more comprehensive understanding of material performance under different printing technologies and post-curing durations.

The aim of this study was to investigate the effects of two types of 3D printers (one DLP and one LCD) and two different post-curing times (short vs. long) on the mechanical and thermal properties of two 3D printing resins for dental restorations (one provisional and one long-term). The null hypothesis was that no significant differences would be observed for any of the factors investigated.

Materials and methods

Study design and tested materials

This in vitro study with a 2 × 2 × 2 factorial design investigated the effects of two types of 3D printers (one DLP and one LCD) and two different post-curing times (5 and 30 min) on selected properties of two 3D printing resins for dental restorations. The resins tested, both in shade A2, were intended for provisional and long-term restorations, with detailed information provided in Table 1. The DLP printer used was Flashforge Hunter (Hangzhou, Zhejiang, China) with full HD 1080p light engine resolution from LED light source, 62.5 μm XY resolution, and 25 μm Z axis accuracy.

The other printer was a masked stereolithography LCD printer (Anycubic Photon Mono M5s; Shenzhen, Guangdong, China) with a 12K resolution from mono LED matrix UV light source, 19 μm XY resolution, and 10 μm Z axis accuracy.

The following response variables were evaluated: fracture toughness (K_{IC}, MPa√m), Knoop microhardness (kgf/mm²), and degree of C=C conversion (%DC). The minimum sample size required for the mechanical tests was calculated based on the results of a pilot study with microhardness tests, which yielded a minimum sample size of 7. The calculation considered an experimental design with 6 independent groups, a minimum detectable difference in hardness means of 11.6, an expected standard deviation of residuals of 5.4, and α=0.05 and β=0.2 as the significance and power levels, respectively. The number of specimens printed per group was increased to 10 to compensate for any potential loss of specimens during testing. Additionally, a thermal analysis of printed specimens was conducted using differential scanning calorimetry (DSC).

Table 1. Composition of the provisional and long-term 3D resins for dental restorations tested

3D resin (type)	Manufacturer	Lot	Composition [a]
Prizma 3D Bio Prov (provisional)	Makertech Labs, Tatui, SP, Brazil	092523	Methacrylate ester monomers, methacrylate oligomers, acrylic monomers, pigments, photoinitiator
Prizma 3D Bio Crown (long-term)	Makertech Labs	235923	Methacrylate monomers, amorphous silica, urethane dimethacrylate, titanium dioxide, silanized zirconia, ceramic fillers, diphenyl (2,4,6,trimethylbenzoy)-phosphine oxide

[a] Information provided by the manufacturer.

3D printing and post-processing parameters

Geometric bar-shaped specimens were designed for the K_{IC} test using Autodesk Meshmixer (San Francisco, CA, USA) and 3D Builder (Microsoft, Redmond, WA, USA), with dimensions of 24 mm in length, 5 mm in height, and 2.5 mm in width. The specimens had a V-shaped notch at the center measuring 0.4 mm in bottom width and 2.5 mm in height. The specimens were exported as STL files and printed using the different printers, with the printing platform adjusted to a 150° angulation. The

printing parameters for each resin-printer combination are presented in Table 2 and were adjusted in a pilot study.

After printing, the specimens were washed twice for 5 min each in a glass container using a brush and fresh isopropyl alcohol. Post-curing was performed for either 5 min or 30 min in a curing machine with 40 W power and 405 nm + 365 nm UV lights (Anycubic Wash and Cure). The bars were placed on the periphery of the machine, and the post-curing time was evenly divided between the top and bottom sides of each specimen. After post-processing, the printing supports were removed with a double-sided diamond disc (Duraflex; American Burrs, Palhoca, SC, Brazil), and all specimens were wet-polished with 1200- and 2000-grit SiC abrasive papers (Norton Abrasivos, Guarulhos, SP, Brazil).

Table 2. Parameters used for 3D printing different resins with different printers [a]

3D printer	Provisional resin	Long-term resin
DLP	Layer height: 50 μm	Layer height: 50 μm
	Curing time: 3.6 s	Curing time: 3.0 s
	Adhesion layers curing time: 15 s	Adhesion layers curing time: 20 s
	Transition layers: 8	Transition layers: 8
	Light intensity: 90%	Light intensity: 80 %
MSLA/LCD	Layer height: 50 μm	Layer height: 50 μm
	Curing time: 6.5 s	Curing time: 6 s
	Adhesion layers curing time: 25 s	Adhesion layers curing time: 25 s
	Transition layers: 8	Transition layers: 8
	Light intensity: 100%	Light intensity: 100%

[a] Parameters adjusted in a pilot study.

Fracture toughness and microhardness measurements

K_{IC} was determined using the single-edge notched beam method [17] in three-point bending mode with supports spanning 20 mm, where the bar-shaped specimens were positioned with the notch opposite to the load application (n=10). The tests were conducted at a speed of 0.5 mm/min until failure using a mechanical testing machine (EMIC DL-500; Instron Brasil, Sao Jose dos Pinhais, PR, Brazil). The calculation of K_{IC} (MPa$\sqrt{m}$) followed a previously described method [17]. After the test, the fragments were used for microhardness analysis with a digital microhardness tester (model FM-

700; Future-Tech Corp., Tokyo, Japan), applying a load of 50 gf for 10 s. The specimens were fixed using wax, and five Knoop indentations were made on the surface, with a minimum distance of 500 μm between each indentation. The Knoop microhardness number (kgf/mm²) was determined as the average of five readings for each specimen (n=10).

Degree of C=C conversion

Additional specimens were obtained for each group (n=5) and the DC was determined using Fourier transform mid-infrared spectroscopy (Cary 630; Agilent, Santa Clara, CA, USA) equipped with a single reflection zinc selenide attenuated total reflectance (ATR) accessory. The printed specimens were kept in light-tight containers in dry conditions for 2 days after post-processing. A preliminary reading of each resin was taken in absorbance mode with 128 scans and a resolution of 4 cm^{-1} . Spectra were obtained from wavelengths of 1500 to 1800 cm^{-1}. The 3D-printed specimens were pressed against the ATR crystal for spectral acquisition. The %DC was calculated by using the peak absorbance area of the C=C stretching vibration at 1635 cm^{-1} (aliphatic) and the symmetric aromatic stretching vibration at 1608 cm^{-1} as an internal standard. The formula used to calculate the DC was as follows:

$$DC\ (\%) = \{1 - [Abs_{(aromatic)} / Abs_{(aliphatic)}]_{polymer} / [Abs_{(aromatic)} / Abs_{(aliphatic)}]_{monomer}\} \times 100.$$

Differential scanning calorimetry

A thermal analysis was conducted with a calorimeter (model Q200; TA Instruments, New Castle, DE, USA) using the same specimens used in the DC analysis (n=2). The specimens were obtained from bars that were cut into parallelepiped shapes using a diamond disc. Each specimen, weighing approximately 4 mg, was placed in a partially closed aluminum crucible for analysis. DSC curves were obtained under an argon flow rate of 50 mL/min and a heating rate of 10 K/min, performing two heating and cooling cycles for each specimen. The procedure started at room temperature, cooling down to -10°C, where the specimen was maintained under isothermal conditions for 5 min. It was then heated up to 200°C and again maintained under isothermal conditions for 5 min. Subsequently, a cooling cycle was performed, from 200°C to -10°C, with the specimen maintained under isothermal conditions for 5

min at each extreme of the cycle. This constituted the first heating-cooling cycle. A second cycle was then performed.

Data analysis

Data normality was analyzed using the Shapiro-Wilk test. Levene's test was used to verify the homoscedasticity of variances. K_{IC}, microhardness, and DC data was statistically analyzed using Three-Way Analysis of Variance (3D resin × printer type × post-curing time) and Tukey's post hoc test with GraphPad Prism 10.2.3 (GraphPad Software; Boston, MA, USA). The significance level adopted was $\alpha=0.05$. DSC curves were charted and qualitatively analyzed.

Results

Results for K_{IC} are presented in Figure 1. All three factors were significant: 3D resin ($p<0.001$), printer type ($p=0.005$), and post-curing time ($p<0.001$), as well as all interactions among factors ($p\leq0.041$) except for the triple interaction ($p=0.2$). The type of resin accounted for 35% of the total variation in K_{IC}. The provisional resin generally exhibited superior K_{IC} compared to the long-term resin. The printer type had a less pronounced effect, with only one group showing a significant difference (lower K_{IC}) – the provisional resin printed by LCD and post-cured for 5 min. Increasing the post-curing time from 5 min to 30 min enhanced K_{IC} in all conditions except for the long-term resin printed by the DLP printer.

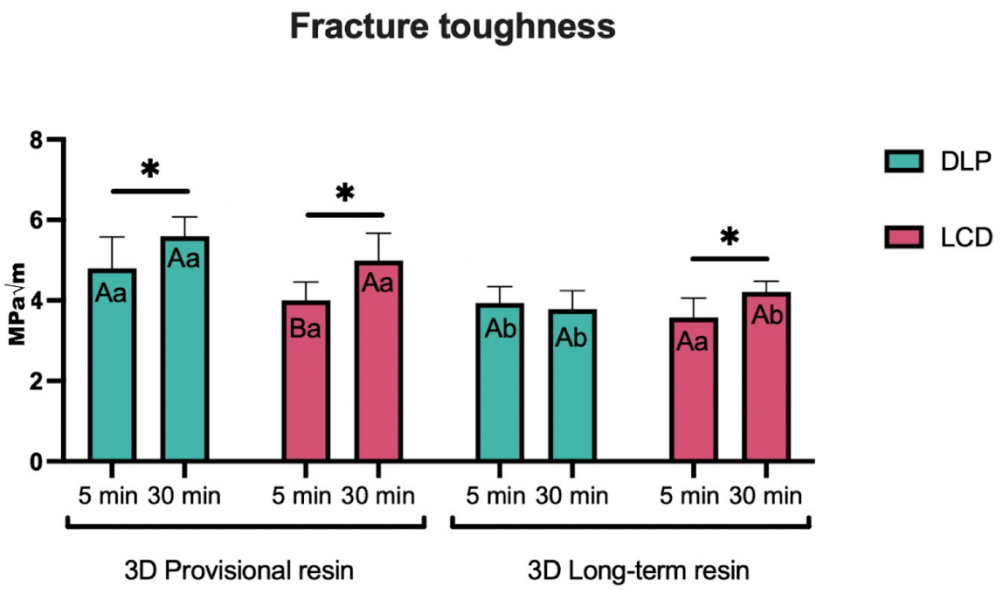

Figure 1. Means + standard deviations for fracture toughness (KIC, MPa√m), n=10. Uppercase letters compare different printers (DLP vs. LCD) for the same resin and post-curing time, while lowercase letters compare the two resins (provisional vs. long-term) for the same printer and post-curing time. Asterisks above the bars indicate significant differences between the 5 and 30-min post-curing times for the same printer/resin combination.

In terms of microhardness analysis (Figure 2), there were no statistically differences across any of the factors or interactions among factors, irrespective of the 3D resin, printer, or post-curing time ($p \geq 0.0805$). For DC (Figure 3), all three factors were significant: 3D resin ($p < 0.0001$), printer type ($p = 0.0016$), and post-curing time ($p = 0.0027$), as well as the interaction between 3D resin and post-curing time ($p < 0.0001$). The type of resin accounted for 62% of the total variation in DC. The long-term resin generally had higher DC than the provisional material. Additionally, DC was higher for the 30-min post-curing time compared to the 5-min time for the provisional resin printed by the DLP printer.

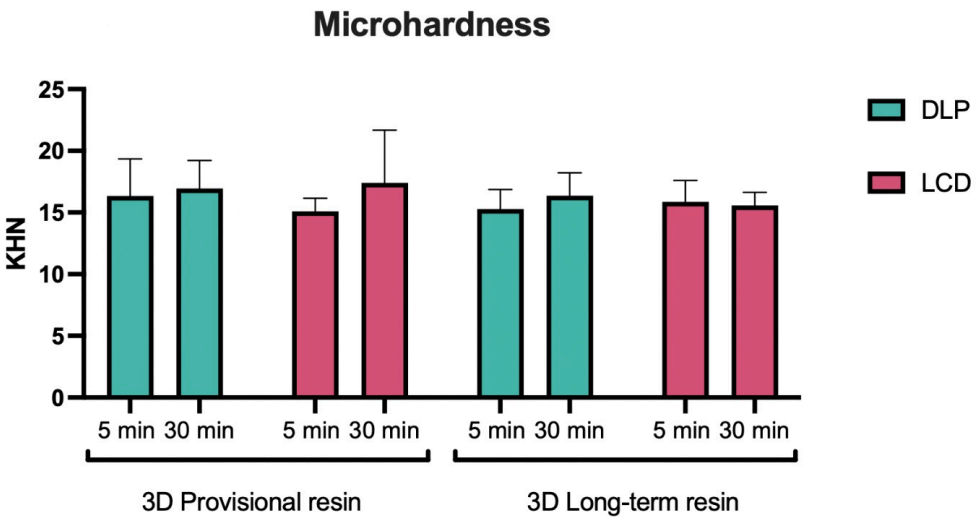

Figure 2. Means + standard deviations for Knoop microhardness number (KHN, kgf/mm²), n=10. No significant differences were observed across the experimental groups, irrespective of the type of resin (provisional vs. long-term), 3D printer (DLP vs. LCD), or post-curing time (5 min vs. 30 min).

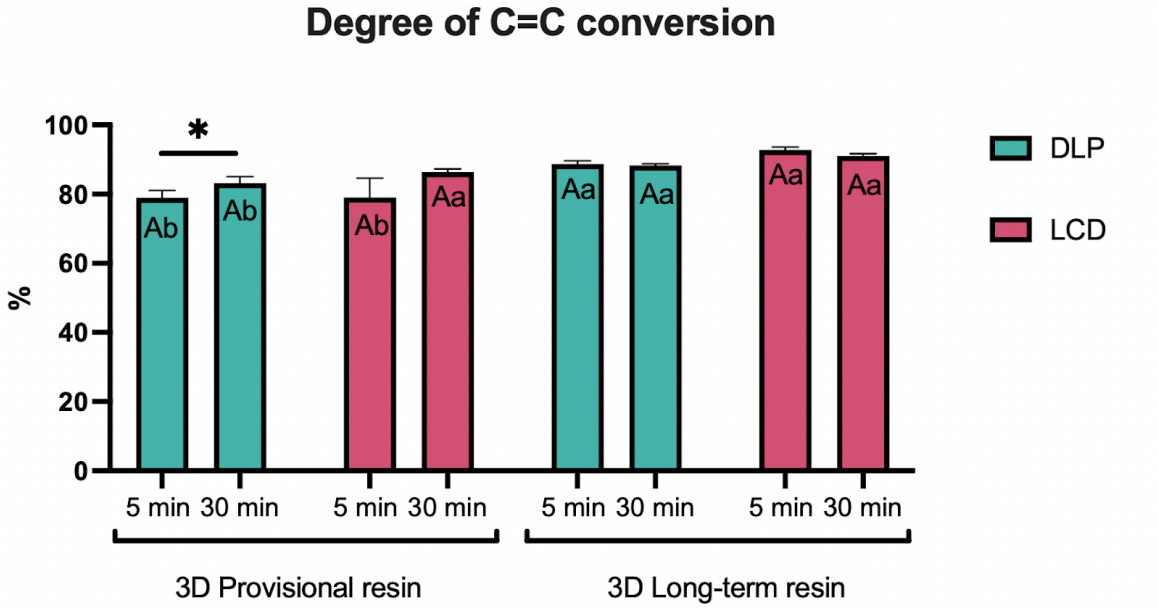

Figure 3. Means + standard deviations for the degree of C=C conversion (%), n=10. Uppercase letters compare different printers (DLP vs. LCD) for the same resin and post-curing time, while lowercase letters compare the two resins (provisional vs. long-term) for the same printer and post-curing time. Asterisks above the bars indicate significant differences between the 5 and 30-min post-curing times for the same printer/resin combination.

Results for the thermal analysis are presented in Figures 4 and 5. In general, the DSC analysis revealed a transition, somewhat complex, around 65 to 75°C, where the material shifted from a rigid structure to a rubbery state. A significant difference between the analyzed specimens is a characteristic peak with a maximum around 160 to 170°C, observed prominently in the 5-min post-cured specimens and less intense in the 30-min specimens. This exothermic peak is seemingly associated with a crystallization process that occurs more prominently in the 5-min groups and only during the first heating cycle; it is not observed during cooling or in the second heating cycle.

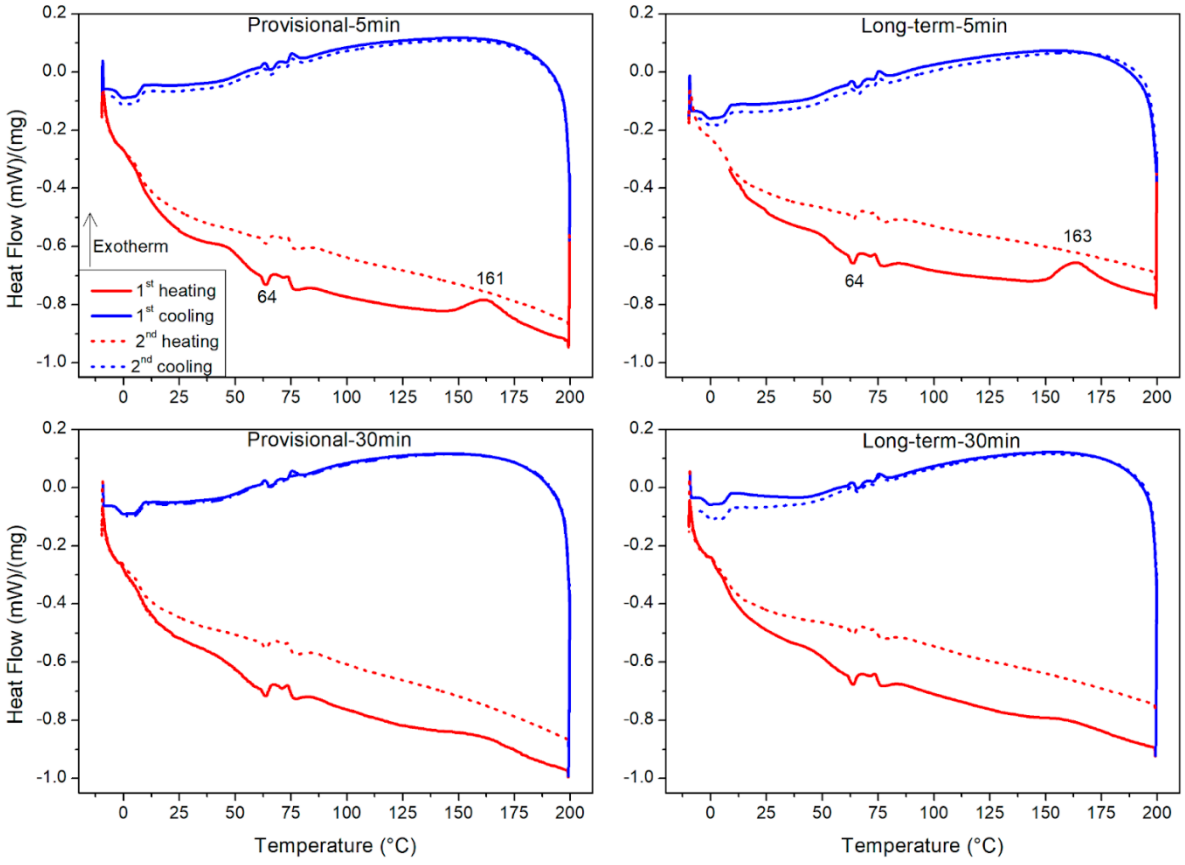

Figure 4. DSC curves for the provisional and long-term resins printed using the LCD printer. Each subplot compares the effects of two different post-curing times (5 min vs. 30 min). The curves illustrate the heat flow as a function of temperature for two heating and cooling cycles. The exothermic peak around 160°C is more pronounced in the 5-min post-cured specimens during the first heating cycle, whereas the 30-min post-cured specimens exhibit more stable thermal properties, with reduced exothermic peaks.

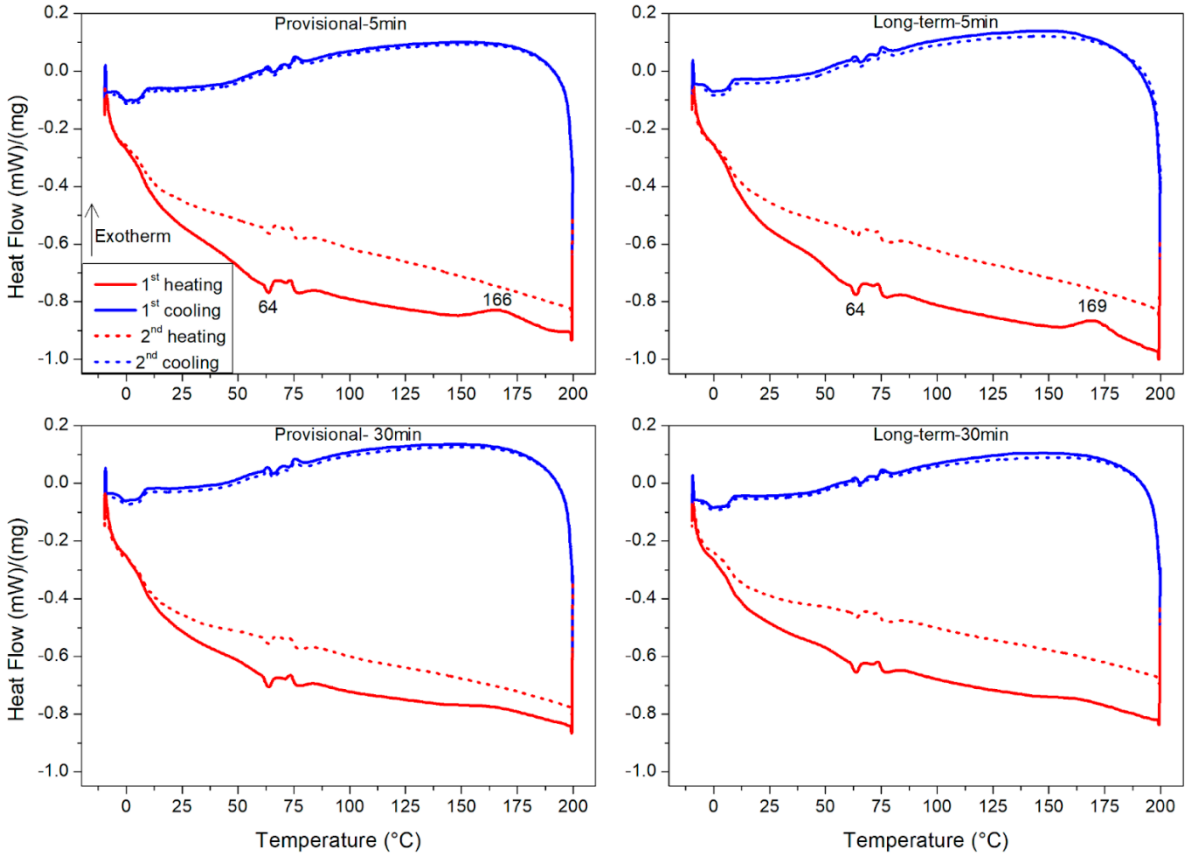

Figure 5. DSC curves for the provisional and long-term resins printed using the DLP printer. Each subplot compares the effects of two different post-curing times (5 min vs. 30 min). The curves illustrate the heat flow as a function of temperature for two heating and cooling cycles. A prominent exothermic peak around 170°C in the 5-min post-cured specimens during the first heating cycle was observed, whereas the 30-min post-cured specimens demonstrated reduced crystallization tendencies, indicating more complete curing.

When comparing the DSC curves for the LCD (Figure 4) and DLP (Figure 5) printers, both provisional and long-term resins exhibited similar thermal behaviors regarding the glass transition temperature (Tg) and crystallization peaks. However, the extent of curing differed based on the post-curing time. Longer post-curing times resulted in more complete curing of the resins, as indicated by the reduced exothermic peaks during the second heating cycles. This suggests that the residual monomer content decreased with longer post-curing times, leading to more stable thermal properties. Both figures demonstrate that the exothermic peak around 160 to 170°C, associated with crystallization, is more pronounced in the 5-min post-cured specimens for both printers and resins. This peak diminishes significantly in the 30-min post-cured

specimens, suggesting that extended post-curing reduces the crystallization tendency, thereby stabilizing the polymer structure.

Discussion

This study indicates that when 3D printing dental restorations, the material remains the primary factor influencing polymer performance. The provisional resin generally exhibited superior KIC compared to the long-term resin, despite having a lower DC. Another important factor influencing the characteristics of 3D-printed polymers was the post-curing time. The longer duration (30 min) generally resulted in polymers with enhanced mechanical performance and more stable thermal properties compared to the shorter duration (5 min). The type of printer (LCD vs. DLP) had a minor effect on the performance of the restoratives. Considering these findings, the null hypothesis was rejected.

The mechanical performance of the resin formulated for long-term restorations did not meet expectations compared to the provisional material. The long-term resin tested here contains zirconia as a filler. It is known that the addition of filler particles is limited because it influences the rheological properties of resins [12] and may exceed the capabilities of current vat photopolymerization 3D printing technologies [6]. To ensure fluidity, monomers are needed in the resin system, but this reduces intermolecular cohesion energy and negatively impacts mechanical performance or introduces defects during production [18,19]. A recent study showed that 3D-printed resins for dental restorations contain less than 35 wt% of filler particles [11]. Another study comparing 3D-printing with conventional layering and subtractive methods for preparing resin composite structures showed that the 3D-printed polymer had a higher elastic modulus but lower fatigue strength [20]. Additionally, extensive variability has been reported across five resins for 3D-printing of restorations, including similar performance between temporary and definitive materials after aging [11]. Thus, there is still progress to be made to improve the mechanical performance of 3D-printed polymers for dental restorations so that they may approach the performance of conventional composite restorations and provide consistently durable results.

Although efforts are being made to develop laboratory procedures for restorations that are simple, automated, and less time-consuming, reducing the post-curing time for 3D-printed restoratives does not appear to be beneficial at the moment.

The longer post-curing time generally resulted in polymers with better properties compared to the shorter time. This aligns with recent findings that a 30-min post-curing time is effective in achieving the best results for most cases [10], noting the influence of solvent use during post-processing. The post-curing process aims to crosslink unreacted monomers after printing, enhancing the elastic modulus and strength [21]. It seems that on the surface of the specimens even the short time was effective, since no differences in microhardness were observed in the study. However, longer post-curing times have been associated with increased DC, improved mechanical properties, and better color stability [13,22-24]. Furthermore, post-curing can significantly alter the DC distribution in the material [25] and potentially affect the anisotropy of the printed structure [19]. The positive effect of longer post-curing times was evident in the DSC thermal analysis, which showed a characteristic exothermic signal near 160 to 170°C during the first heating cycle of the 5-min specimens, indicating pronounced crystallization that became much less intense with 30-min curing. This suggests that longer post-curing times result in more complete curing, reducing residual monomer content and stabilizing the polymer structure.

The minor differences observed for polymers printed using LCD or DLP printers are promising for the overall clinical applicability of 3D printing in dentistry. The printers tested vary not only in printing technology but also in LED resolution, printing resolution, accuracy, and costs. However, significant differences in specimens printed by either printer were rarely observed, with the resin type and post-curing time having a more pronounced effect on mechanical performance and thermal properties of the restoratives. Most current literature on the effect of different 3D printers in dentistry focuses on resins for dental models rather than restorations. One study testing 12 printers indicated that the current range can produce clinically acceptable levels of accuracy, with no major differences between budget and more expensive printers, suggesting all 3D printers can produce reliable, reproducible models [26]. This is in accordance with another study showing that both DLP and LCD printers can accurately print dental models for orthodontic appliances [15]. Additionally, industrial printers used in dental laboratories have been linked with better trueness and precision when printing models compared to in-office dental desktop printers [27]. The present study goes further and suggests the potential applicability of both LCD and DLP printers in preparing restorative polymers.

This study has certain limitations, including the absence of specimen aging, which means the results provide an immediate snapshot of the performance of 3D-printed polymers for dental restorations. Future research that tests the influence of mechanical loading or thermo-hydrolytic aging could offer a better understanding of the long-term performance of these restorative materials. However, by comparing different combinations of printers, materials, and post-curing times, this study advances the knowledge in 3D-printed restorative polymers. Additionally, to our knowledge, this is the first study to investigate the thermal properties of 3D-printed restoratives in dentistry. The results of the thermal analysis can serve as a basis for future comparisons and pave the way for new studies aimed at better understanding the polymer structures obtained via different methods and subjected to various post-processing protocols. Future research comparing more materials and testing dental restorations with more realistic geometries under cyclic loading conditions closer to clinical scenarios is necessary.

Conclusions

The performance of 3D-printed restorative polymers primarily depended on the type of resin and post-curing time used. The long-term resin generally exhibited a higher degree of C=C conversion but lower fracture toughness compared to the provisional resin. Longer post-curing time (30 min) typically resulted in polymers with improved mechanical performance and more stable thermal properties compared to shorter time (5 min). Minor differences were observed between polymers printed with LCD and DLP printers, and structures obtained by both printing technologies exhibited similar thermal behavior. There appears to be potential for improving the performance of materials intended for longer-lasting 3D-printed restorations.

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4 Considerações finais

Esta tese destacou a importância de ajustar cuidadosamente a combinação de resina 3D, tipo de solvente para lavagem e tempo de pós-cura UV para otimizar as propriedades físicas e químicas dos polímeros restauradores dentais. Os principais achados incluíram:

- A escolha da resina 3D teve o impacto mais significativo nos resultados mecânicos dos polímeros restauradores impressos em 3D;
- O uso de álcool isopropílico ou etanol absoluto pode melhorar as propriedades mecânicas ou de superfície dos polímeros, dependendo da resina específica utilizada. No entanto, o efeito do solvente tende a diminuir com o aumento do tempo de pós-cura UV;
- Um tempo de pós-cura UV de 30 min mostrou-se geralmente eficaz para obter os melhores resultados. Porém, é fundamental considerar o solvente utilizado, pois ele influencia o tempo ideal de pós-cura; em alguns casos, 30 min de UV não foram necessários;
- Poucas diferenças foram observadas entre os polímeros impressos com tecnologias LCD e DLP, ambas apresentando comportamento térmico semelhante;
- A resina para restaurações permanentes geralmente apresentou um grau de conversão de C=C mais alto, mas menor tenacidade à fratura em comparação à resina provisória;
- Na análise térmica, as resinas mostraram comportamento semelhante, mas o tempo de pós-cura mais longo resultou em uma polimerização mais completa, proporcionando propriedades térmicas mais estáveis;
- Existe potencial para aprimorar os materiais destinados a restaurações dentárias impressas em 3D, visando a criação de estruturas que possam ser consideradas permanentes.

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