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REVIEW ARTICLE

A review on chemical composition, mechanical properties, and manufacturing work flow of additively manufactured current polymers for interim dental restorations

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Abstract

Objectives: Additive manufacturing (AM) technologies can be used to fabricate 3D-printed interim dental restorations. The aim of this review is to report the manufacturing workflow, its chemical composition, and the mechanical properties that may support their clinical application.

Overview: These new 3D-printing provisional materials are typically composed of monomers based on acrylic esters or filled hybrid material. The most commonly used AM methods to manufacture dental provisional restorations are stereolithography (SLA) and material jetting (MJ) technologies. To the knowledge of the authors, there is no published article that analyzes the chemical composition of these new 3D-printing materials. Because of protocol disparities, technology selected, and parameters of the printers and material used, it is notably difficult to compare mechanical properties results obtained in different studies.

Conclusions: Although there is a growing demand for these high-tech restorations, additional information regarding the chemical composition and mechanical properties of these new provisional printed materials is required.

Clinical Significance: Additive manufacturing technologies are a current option to fabricate provisional dental restorations; however, there is very limited information regarding its chemical composition and mechanical properties that may support their clinical application.

KEYWORDS

3D printing, additive manufacturing technologies, interim restorations, material jetting, stereolithography

1 | OBJECTIVES

Additive manufacturing (AM) technologies can be used to fabricate 3D-printed interim dental restorations. The aim of this review is to report the manufacturing workflow, its chemical composition, and the mechanical properties that may support their clinical application.

2 | OVERVIEW

AM technologies refer to the fabrication of an object layer-by-layer.[1] Advancements in AM technologies have allowed for its integration into the digital workflow of prosthodontic applications. The American Section of the International Association for Testing Materials (ASTM) international standard organization establishes technical standards for a wide range of materials, products, systems, and services. The ASTM committee F42 on AM technologies determined 7 AM categories: stereolithography (SLA), material jetting (MJ), material extrusion or fused deposition modeling (FDM), binder jetting, powder bed fusion, sheet lamination, and direct energy deposition.[1–4] In dentistry, the most commonly used AM methods are SLA and MJ technologies.

For SLA manufacturing, a building platform is immersed in liquid resin which is then polymerized by an ultraviolet laser.[5–7] The laser traces a cross section of each layer. After the layer is polymerized, the building platform descends by a distance equal to the layer thickness, allowing uncured resin to cover the previous layer. This process is repeated several times until the printed object is built.[5–8] A scanning mirror directs a precise laser beam at a reservoir of ultraviolet (UV) sensitive resin to cure the layer (Figure 1). The depth of cure, which ultimately determines the z-axis resolution, is controlled by the photoinitiator and the irradiant exposure conditions (wavelength, power, and exposure time/velocity) as well as any dyes, pigments, or other added UV absorbers.[9–13]

Digital light processing (DLP) is considered to be within the same AM category as SLA technology by the ASTM because the technologies share many similarities.[1,14] The primary distinction between the SLA and DLP is light source; the cross-sectional image is created by either an arc lamp or semiconductor chip containing a matrix of microscopic mirrors, the latter of which is referred to as a digital micromirror device. Each mirror represents one or more pixels in the projected image. The number of mirrors corresponds to the resolution of the projected image.[15] In safelight conditions, light from the DLP projector passes through a UV transparent window, and the image is projected onto a vat of liquid photopolymer.[15] In this system, the physical object is pulled up from the liquid resin, rather than down and further into the liquid photopolymer. The process is repeated until the 3D object is built.[14,15]

MJ technology is also referred to as polyjet printing, in which a liquid resin is selectively jetted out of hundreds of nozzles and polymerized with ultraviolet light.[9] The UV-curable polymers are applied only where desired for the virtual design and, because multiple print nozzles can be used, the supporting material is co-deposited. In addition, different variations in color or building material can be designated, including spatially graded structures (Figure 2).[16,17]

3 | MANUFACTURING WORKFLOW

The digital workflow to manufacture a provisional restoration (Figure 3) with a 3D printer consists of the following sequence: data acquisition, data processing, and manufacturing procedures.[18]

- Data acquisition involves digitization procedures normally performed by an extraoral or intraoral scanning device, in which the patient's mouth or the working casts are converted into a standard tessellation language (STL) file.
- Data processing involves the virtual design of the provisional restoration using specific CAD software. Because of the limitations of the AM manufacturing process, specific parameters must be controlled during the digital design. Minimum thickness is one such parameter that must be taken into consideration, and this value varies depending on the building material and AM technology used for the fabrication process. CAD software has tools that allow complete control over the thickness of the digital design. It is very important to consider this parameter when processing digital model data for the sake of the printed object's structural integrity.

  When the design of the object is completed, the STL file is exported to the printer, where build variables and parameters for slicing and adding support structures are specified. This procedure is similar to a Computer numerical control (CNC) machine that calculates a unique milling protocol for every job it receives. Printer parameters are dependent of the AM technology and the 3D printer.

  Other printing parameters that are controlled by the operator include building material, color, and the size of the object. Printing a resilient material may require a different printing angulation, or it may require different ratios and positioning of either supportive

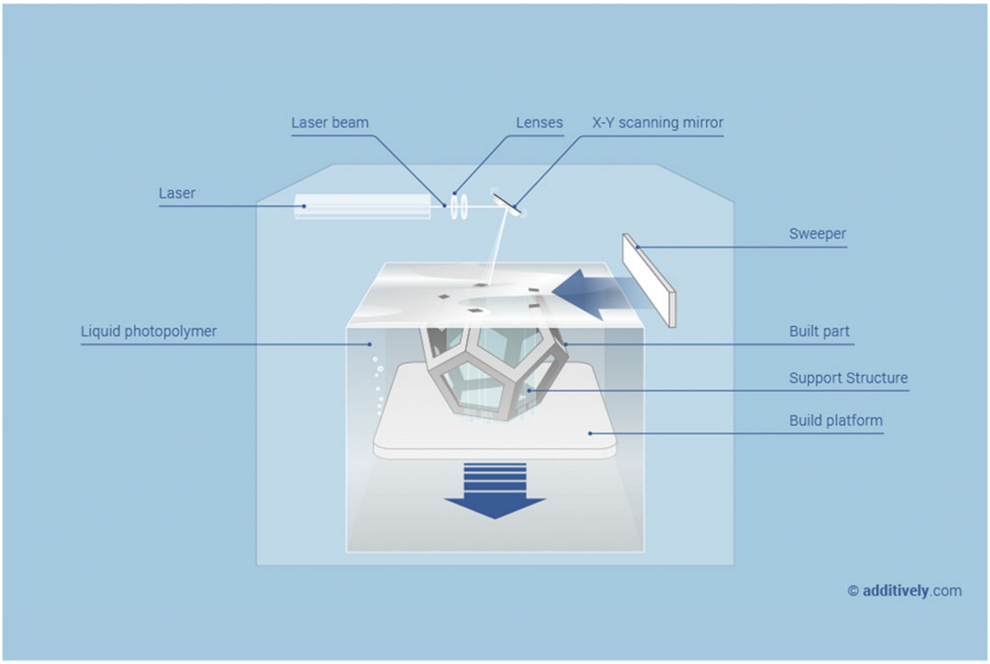

FIGURE 1 Stereolithography additive manufacturing technology scheme. Illustration courtesy of Additively.com

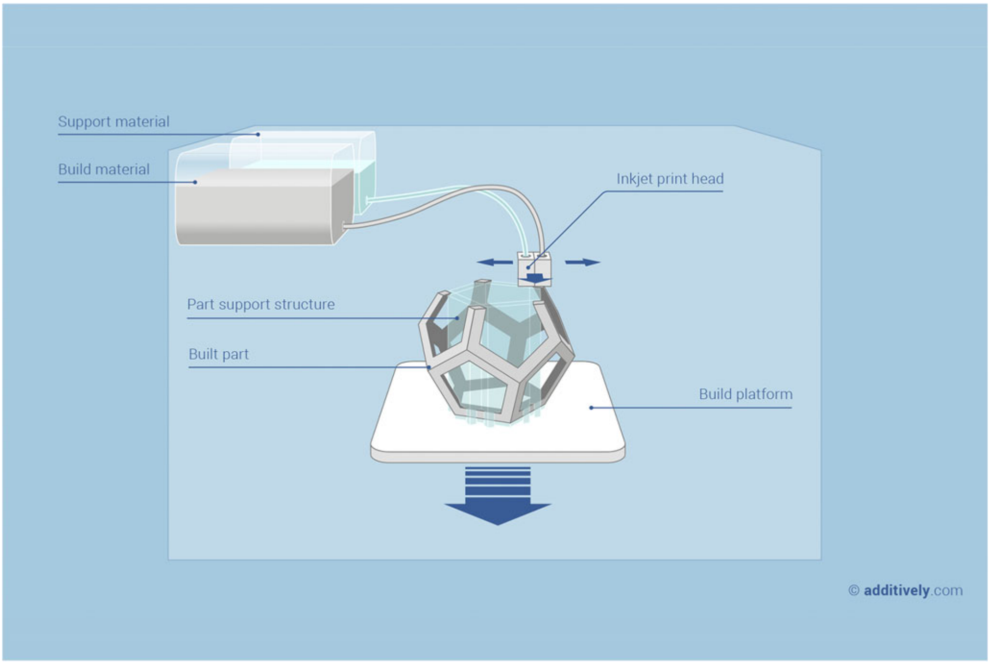

FIGURE 2 Material jetting 3D-printing technology scheme. Illustration courtesy of Additively.com

material or rigid material. In addition, a risk of overexposure is presented when a clear or transparent object is fabricated, as the light that polymerizes new layers can transfer through newly solidified material to the initial layers of a fabrication. However, this challenge is not present for materials that absorb light more readily. The part's geometry and the chosen print orientation can cause a similar distortion, as light also transfers through the resin tray. Therefore, there should be some strategy when deciding print orientation to minimize potential overexposure when using certain materials and printing certain geometries.

- Manufacturing procedures follow the layer-by-layer buildup of an object using the file on the 3D printer. In addition to calibrating 3D printers periodically, these instruments must be calibrated when room conditions or printer locations change to assure consistency and accuracy. This process of adjustment and fine-tuning compares the readings of an instrument with a standard, thereby check the instrument's accuracy.

  Post-processing, object cleaning, and post-curing are then performed to complete the polymerization process. Each printer has post-processing recommendations provided by the manufacturer.

4 | RESOLUTION, ACCURACY, PRECISION, AND TRUENESS

Different factors define the capabilities of a 3D printer. These factors summarily reflect the quality of the printed object. Different technologies or printers may vary in suitability, depending on the function of the printed object. For example, a printed provisional restoration requires up to a 125-μm marginal and internal fit, which is more specific and restrictive than what is required of a custom tray.[19,20]

Resolution is the smallest feature that the 3D printer can reproduce, and it is specific for each technology and printer. The resolution of a 3D printer should be defined on each x, y, and z-axis in micrometer or dots per inch (dpi), in which the z-axis normally corresponds to the layer thickness. Precision or repeatability refers to a 3D printer's capacity to manufacture the same object with the same 3D dimensions. Trueness refers to the discrepancy between the printed object and actual dimensions of the desired object.[21]

Different factors, such as laser speed, intensity, angle and building direction,[19–25] number of layers,[21,26] software,[27] shrinkage between layers,[24,26] amount of supportive material,[23] and post-processing procedures,[26] can affect the accuracy (precision and trueness) of the printed object. Because of protocol disparities, technology selected,

FIGURE 3 Additively manufactured interim dental restoration before the removal of the supportive structures

TABLE 1 Summary of some additively manufactured polymers, approved for interim dental applications, provided by the manufacturers

Brand	Name	Definition Certification provided	Wavelength (nm)
Detax	FreePrint Temp	Monomer based on acrylic esters for manufacturing of 3D-printed crowns and bridges based on acrylic esters. Class IIa CE-certified Not FDA-approved	LED UV 405 or 378-388
DWS	Temporis	Light curable nanocomposite Class IIa CE-certified Not FDA-approved	405
Envisiontec	E-dent 100	Microfilled hybrid material Class IIa CE-certified	365-405
	E-dent 400	Class IIa CE-certified FDA-approved	
Nextdent (vertex dental)	C&B	Microfilled aterial Class IIa CE-certified FDA-approved	Blue UV-A (315-400) + UV-blue (400-550)
	C&B MFH	Microfilled hybrid material Class IIa CE certified FDA-approved	
Stratasys	VeroGlaze, MED620	Not class IIa CE-certified Not FDA-approved	200-400

and parameters of the printers and material used, it is notably difficult to compare results obtained in different studies.

5 | POLYMERS FOR 3D-PRINTED INTERIM RESTORATIONS

5.1 | Chemical composition

When performing interim restorations, there are a limited number of AM polymers available and approved for intraoral use (Table 1).[9] Conventional provisional materials can be divided into 2 groups according to their chemical composition: those based on monomethacrylates or acrylic resins and those based on dimethacrylates or bis-acryl/composite resins such as bisphenol A-glycidyl dimethacrylate and urethane dimethacrylate (these resins are polymerized by light).[28–30] AM provisional materials seem to follow the same classification, and some information regarding their chemical composition is listed in Table 2. However, the manufactures did not release all the information that was requested by the authors. It remains unclear if the chemical composition differs from conventional provisional dental materials, as the manufacturing process differs from conventional and CNC procedures. To the knowledge of the authors, there is no published article that analyzes the chemical composition of these new 3D-printing materials.

The food and drug administration (FDA) from the United States Department of Health and Human Services controls and supervises medical devices to determine if they are appropriate for commercial use. Similarly, the European Union (EU) uses CE marking on medical devices that comply with EU regulations, enabling the commercialization of the product in the European countries (ISO 13485). 3D-printed provisional materials available on the market are CE-

TABLE 2 Summary of chemical composition of the additively manufactured polymers, approved for interim dental applications, provided by the manufacturers

Brand	Name	Chemical composition	Inorganic filler (wt%)
Detax	Freeprint Temp	NP[a]	NP[a]
DWS	Temporis	Mixture of multi-functional acrylic monomers, esters of acrylic acid	NP[a]
Envisiontec	E-Dent 100	Tetrahydrofurfuryl methacrylate, urethane dimethacrilate, phosphinoxide, and multifunctional acrylic resins	49.8 (0.04-0.7 μm particle size of inorganic fillers)
	E-Dent 400	Monomer based on acrylic esters	NP[a]
Nextdent	C&B	NP[a]	NP[a]
	C&B MFH	NP[a]	NP[a]
Stratasys	VeroGlaze MED620	2-Hydroxy-3-phenoxypropyl acrylate 4-(1-oxo-2propenyl) morpholine Exo-1, 7 7-trimethylbicyclo[2.2.1]hept-2-yl acrylate Tricyclodecane dimethanol diacrylate Bisphenol-A epoxy acrylate oligomer, 2, 4, 6 Trimethylbenzoyldiphenylphosphine oxide	NP[a]

[a] Abbreviation: NP, not provided.

TABLE 3 Summary of the mechanical properties of additive manufacturing polymers available on the market for interim dental applications, provided by the manufacturers

Mechanical property	Freeprint Temp, DETAX	Temporis, DWS	E-Dent 100, Envisiontec	E-Dent 400, Envisiontec	C&B, Nextdent	C&B MFH, Nextdent	VeroGlaze, MED620, Stratasys
Colors	A1, A2, A3	N, A1, A2, A3, A3.5, B1	A1, A2, A3	A3.5	A2, A3.5	A2, A3.5	A2
Tensile strength (MPa)	NP[a]	35-50	30 N/mm^2	NP[a]	NP[a]	NP[a]	54-65
Elongation at break (%)	NP[a]	2-3	NP[a]	NP[a]	NP[a]	NP[a]	15-25
Flexural strength (MPa)	NP[a]	85-135	>100	85	85-100	100-130	80-110
Modulus of elasticity (MPa)	NP[a]	2900-4200	>4500	2100	2300-2500	2400-2600	2200-3200
Water sorption	NP[a]	<40 (mg/μm^3)	18.1 (μg/mm^3)	30 (μg/mm^3)	<30	<30	1.2-1.5
Water solubility	NP[a]	<1.4 (mg/μm^3)	5 (μg/mm^3)	5 (μg/mm^3)	<5	<5	NP[a]
Hardness shore (*D*)	NP[a]	91-93	NP[a]	89-90	80-90	NP[a]	83-86
Vickers hardness (HV)	NP[a]	NP[a]	25	NP[a]	NP[a]	NP[a]	NP[a]
Maximum recommended time in the intraoral environment	NP[a]	6 mo	1 y	1 y	NP[a]	NP[a]	Up to 24 h
Minimum area recommended for connector, anterior bridges (mm^2)	NP[a]	NP[a]	12	12	NP[a]	NP[a]	NP[a]
Minimum area recommended for connector, posterior bridges (mm^2)	NP[a]	NP[a]	14	14	NP[a]	NP[a]	NP[a]
Minimum wall thickness, occlusal (mm)	NP[a]	NP[a]	2	2	NP[a]	NP[a]	NP[a]
Minimum wall thickness, circumferential (mm)	NP[a]	NP[a]	1.5	1.5	NP[a]	NP[a]	NP[a]

[a] Abbreviation: NP, not provided.

certified and/or FDA-approved. Moreover, a class IIa CE certification generally constitutes low to medium risk, and these devices are certified to be installed within the body between 60 minutes and 30 days.

5.2 | Mechanical properties

Understanding the mechanical properties of provisional dental materials is necessary to evaluate newer 3D-printing provisional materials, verify the manufacturers' claims, and further compare it with conventional materials to discern an optimal material and a suitable technique for long-term provisional FDPs.[19,30,31] Thus, various mechanical properties such as flexural strength, hardness, impact strength, and color stability become critical. Marginal discrepancy, flexural strength, and microhardness of provisional materials are important parameters, particularly when the patient must use the provisional restoration for an extended period, when the patient exhibits parafunctional habits, or when long-term prostheses are planned.

The mechanical properties of conventional provisional dental materials are better described in the literature.[29,32–34] However, authors of the present review attempted to collect a complete description of the mechanical properties of 3D-printing provisional materials directly from the manufacturers (Tables 3 and 4), but not all of the requested information was released.

Digholkar et al.[35] analyzed and compared the flexural strength and microhardness of printed microfilled hybrid composite (E-Dent 100; Nexdent; Soesterberg, Netherlands) (AM group), milled polymethyl methacrylate (PMMA), and conventional PMMA provisional dental materials. There were significant differences in flexural strength values among the AM group (79.54 Mpa), the milled group (104.20 MPa), and the conventional group (95.58 MPa). In addition, significant differences were also found between the mean

TABLE 4 Summary of the hazards identification of the additive manufacturing polymers available on the market for interim dental applications

Hazard identification	Freeprint Temp, DETAX	Temporaris, DWS	E-Dent 100, Envisiontec	E-Dent 400, Envisiontec	C&B, Nextdent	C&B MFH, Nextdent	VeroGlaze, MED620, Stratasys
Acute toxicity	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	Category 4
Skin corrosion/irritation	NP[a]	Category 2	NP[a]	NP[a]	NP[a]	NP[a]	Category 2
Serious eyes damage/irritation	NP[a]	Category 2	NP[a]	NP[a]	NP[a]	NP[a]	Category 1
Skin sensitization	NP[a]	Category 1	NP[a]	Category 1	NP[a]	NP[a]	Category 1B
Specific target organ toxicity (single exposure)	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	Category 3
Specific target organ toxicity (repeated exposure)	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	Category 2
Acute aquatic toxicity	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	NP[a]	Category 1
Chronic aquatic toxicity	NP[a]	NP[a]	NP[a]	Category 4	NP[a]	NP[a]	Category 1

[a] Abbreviation: NP, not provided.

microhardness values (Knoop hardness number) of the AM (32.77), milled (25.33), and conventional (27.36) groups. Based on this study, AM provisional material analyzed (E-dent 100; Nexdent) presented significantly lower flexural strength but higher microhardness when compared with our current provisional dental materials.

Alharbi et al.[23] evaluated the effect of printing orientation on the mechanical properties of cylinder-shaped hybrid composite resin printed specimens (Temporis shade A1; DWS; Thiene, Italy). Vertically printed specimens with layers oriented perpendicular to the load direction presented significantly higher compressive strength than horizontally printed specimens with layers parallel to load direction.

Brain et al.[24] studied the manufacturing tolerance of 4 polymer AM printers following the manufacturers' parameters. Two geometries were analyzed. The AM material was selected based on the print resolution, specification of the production unit, software, and manufacturing time. Only 2 of the 4 printers used the same AM material. Differences in production tolerance were found between the different printers and technologies. The results showed an accuracy from −61 to 92 μm.

Ide et al.[25] analyzed the capacity of 3D printers to reproduce acute angles (60°, 45°, 30°, 20°, 10°, and 5°) considering the building printing direction on 6 triangular prism-shaped specimens using 1 polyjet and 2 FDM AM printers. Each printer used a different AM material. They concluded that the dimension production tolerance of the printers of geometry analyzed was less than 1.00 mm in all the x-, y-, and z-axes, but the acute angles could not be reproduced precisely.

Unlike conventional and CNC manufacturing procedures, AM technologies enable the production of geometries that are otherwise expensive and time consuming to produce or simply not possible to fabricate.[36] In the case of subtractive technologies, access to small spaces is limited and the bur size imposes limitations on the dimensions of a manufactured object.[2–4] AM technologies also enable the printing of multiple patterns at a time, although the number of patterns will depend on the size of the patterns and the building platform.

Because of the lack of information available, the maximum number of pontics and the minimum size of connectors recommended for 3D-printed provisional restorations remain unclear. It is also uncertain whether these materials can be repaired, or if relining printed objects with conventional materials is a viable option for repair. Furthermore, the behavior of this material over time in a patient's mouth is not well described.

6 | CONCLUSIONS

The rapid development and expansion of applied AM technologies will likely continue as the list of printable dental materials grows. Although there is a growing demand for these high-tech restorations, additional information regarding the chemical composition and mechanical properties of these new materials is required. Understanding how these materials compare with conventional provisional materials will allow for dental professionals to create more robust treatment plans, thereby improving quality of care.

DISCLOSURE OF INTERESTS

The authors did not have any financial interest in any of the companies or products used in this study.

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