Review

Current Progress in the Development of Resin Materials with Nanofillers for 3D Printing of Denture Base

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Abstract: Background: Advanced manufacturing techniques, such as three-dimensional (3D) printing, use digital models from computer-aided design to produce 3D objects. They are frequently employed in different areas of dentistry, such as orthodontics, oral implantology, and prosthodontics. Purpose: The aim of this review was to provide a comprehensive overview of 3D-printing technology for denture bases and explore the influence of incorporating different fillers into 3D-printed denture base resins on their physical, mechanical, and biological characteristics. Methods: Relevant studies were identified by searching papers published between 2010 and 2023 in several online databases, such as Scopus, PubMed, Cochrane library, and Google Scholar. The main inclusion criteria used during the search was identifying the papers which added nanoparticles in the resin as an agent to bring different functional characteristics within the 3D-printed denture base resin. Furthermore, even though the search criteria were set for finding papers from the past 10 years, development in this field has accelerated in the past 4–5 years. Findings: Various fillers have exhibited promising results in terms of their ability to improve the functional properties of the 3D-printed denture base resins. However, such improvements come at a higher cost with careful resin preparation when considering the filler particles, the fabrication complexities and the extensive post-processing that is required. Conclusions: The use of 3D-printing approaches and fillers to fabricate dentures is associated with significant benefits in terms of imparting functional properties, consistency in fabrication and opportunities for innovation. However, further research is required to acquire a better understanding of the holistic, long-term performance of various filler materials, concentrations, their clinical relevance and particularly the potential health risks from the fillers.

Keywords: 3D printing; CAD/CAM; polymer resin; nanocomposite; nanoparticles; denture base; physical properties; mechanical properties; biological properties

1. Introduction

1.1. Denture Base Fabrication: Conventional vs. CAD/CAM Techniques

1.1.1. Conventional Fabrication Technique

Conventional denture bases remain the most popular prostheses for treating complete or partial edentulosity [1,2] and their fabrication technique is presented in Figure 1. The most common methods for fabricating denture base resins are: Ref. [1] compression moulding technique, Ref. [2] injection moulding technique, and Ref. [3] computer-aided design/computer-aided manufacturing (CAD/CAM) technology. The first two techniques are employed for manufacturing heat-cured resins in laboratories based on dental technicians’ preferences or equipment availability. The injection moulding technique is faster than...
compression moulding and helps reduce polymerisation shrinkage and material porosity. However, it is a complex procedure that requires specialized flasks and equipment. Consequently, many dental technicians prefer the compression moulding technique [3].

![Diagram of the steps needed for conventional fabrication of denture base.](image)

**Figure 1.** Steps needed for conventional fabrication of denture base.

1.1.2. CAD/CAM Technology

CAD/CAM, a relatively recent approach to denture fabrication, is becoming increasingly prevalent in dentistry [1,2,4,5]. CAD/CAM dentures provide several advantages for both patients and clinicians [6–9]. These dentures can be created in just two appointments, significantly reducing clinical and patient time [7,9]. Manufacturing companies digitally scan and store patient records [1,4]. Consequently, there is no need for recasts or new clinical records if a patient loses or breaks their denture, enabling a quick production of an exact replacement prosthesis [1,4]. Dentures can be fabricated using a subtractive (milling) or additive (3D printing) method [1,4,6,8]. The subtractive technique is currently the most frequently utilized method [6,8].

Any CAD/CAM system comprises three essential components [2,6,10,11]:

1. Data acquisition: this initial phase involves scanning the treatment site or stone model using a digitisation tool or scanner, capturing digital data that are then processed by a computer.
2. Data processing: CAD/CAM software generates the data set required for the intended prosthesis.
3. Manufacturing: The digital data are converted into the desired prosthetic. Once the prosthesis design is completed by the CAD, the information is sent to the production unit, which is controlled by the CAM software.

The subtractive manufacturing (SM) method involves mechanically milling unwanted portions from a pre-polymerised resin block to create a complete denture. This process is controlled by a computer that directs the milling machine according to the desired design [11,12], and it is typically used for producing simple restorations and crowns. Complete denture manufacturing using SM can proceed along two routes.

The first route involves taking a conventional impression of the edentulous area to create a stone model. A wax-up with the teeth arranged is then made, which is later digitised using a digital scanner and sent to the CAM machine. Finally, the CAM machine shapes the complete denture by cutting the resin material block.

The second route begins by taking a digital impression of the edentulous area, which is sent directly to the CAD software. The CAD software then designs the complete denture according to the clinician’s or technician’s specifications, serving as an alternative to the conventional impression combined with the wax-up and teeth-setting steps. The complete
denture design is then sent to the CAM machine as the final step in the denture manufacturing process [13,14]. Figure 2 illustrates the SM steps for creating a complete denture.

Additive manufacturing (AM), as opposed to SM, is typically used for creating complex restorations or prostheses. AM involves joining materials according to three-dimensional (3D) model data designed by CAD software to produce the desired shape. The CAD design is segmented into layers, which are then forwarded to the rapid prototyping machine. The final object is constructed layer by layer [15]. Liquid polymer resin is commonly employed as the material for AM of dental objects, and curing is often necessary to achieve the required strength in the final product [15,16]. AM presents a significant advantage by eliminating material waste associated with SM due to the precise layering following the shape provided by the CAD software [17]. AM includes various techniques tailored to suit different materials and applications [18]. Figure 3 illustrates the AM steps for fabricating a denture.
1.1.3. Comparative Analysis of Fabrication Methods

Comparing the CAD/CAM technique with the traditional method, the CAD/CAM approach generally offers advantages including user-friendliness, speed, time efficiency, and enhanced denture quality [19]. It diminishes the clinician’s chair time needed for the denture fabrication and placement by up to three appointments, facilitates the provision of replacements using saved digital data, and lessens the workload for the technician [20]. However, it is worth noting that many steps in the process, such as functional impression taking, occlusal plane orientation, anterior teeth guidance recording, and jaw registration, are still carried out manually. Furthermore, it shows higher or similar overall precision in the dentures produced as compared to the traditional method [21,22]. Similar in vitro trueness and tissue surface adaptation were observed for CAD/CAM mandibular denture bases made using both AM and SM techniques [23]. Nonetheless, SM shows superior dimensional stability and mechanical properties as compared to AM, owing to the different polymerisation environments associated with each method [24]. The resin blocks in SM are pre-polymerised under high temperature and pressure, while in AM, the liquid resin is light-cured. This discrepancy can lead to the shrinkage of the final denture due to the presence of unreacted monomers in the AM process [25,26]. The average adaptation discrepancy for the AM was reported to be slightly higher (0.08 mm) compared to the subtractive manufacturing (0.06 mm) [23]. These unreacted monomers may also cause allergic reactions in patients or dental technicians who have a sensitivity to polymer resin products [27]. Generally, SM is preferred for small intraoral restorations as it yields a homogeneous end product with satisfactory accuracy. However, for larger, more complex prostheses such as denture bases or facial prostheses, AM is more suitable due to its relatively superior accuracy [28,29]. Table 1 provides a comparison between CAD/CAM techniques and the conventional method across various aspects.

Table 1. A relative comparison between conventional and CAD/CAM methods for denture base manufacturing.

<table>
<thead>
<tr>
<th>Related Factors</th>
<th>Conventional Method</th>
<th>Subtractive Manufacturing</th>
<th>Additive Manufacturing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human errors</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Clinical chair time</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
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<tr>
<td>Number of visits</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Digital archiving</td>
<td>N/A</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Patient-centred outcomes</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>Physical properties</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>Accuracy of the fitted surface</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
</tbody>
</table>
1.2. Three-Dimensional-Printing Technology in Dentistry

The accuracy and reliability of 3D printing have significantly improved in recent years, making it increasingly suitable for dental applications [30,31]. Various dental products, including surgical guides, temporary crowns, denture bases, and dental splints, were produced using 3D-printing technology. Tables 2 and 3 display some of the commercially available 3D printers with their post-cure devices and technical parameters.

Table 2. Three-dimensional printers with their operating parameters [32–35].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Formlabs Form2</th>
<th>NextDent 5100</th>
<th>EnvisionTEC One</th>
<th>ASIGA Max UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Country</td>
<td>USA</td>
<td>Netherlands</td>
<td>USA</td>
<td>Australia</td>
</tr>
<tr>
<td>Printer technology</td>
<td>SLA</td>
<td>DLP</td>
<td>DLP</td>
<td>DLP</td>
</tr>
<tr>
<td>Light source</td>
<td>UV laser</td>
<td>LED light projector</td>
<td>LED light projector</td>
<td>LED light projector</td>
</tr>
<tr>
<td>Light source wavelength (nm)</td>
<td>405</td>
<td>405</td>
<td>385</td>
<td>385</td>
</tr>
<tr>
<td>Light source resolution (micron)</td>
<td>N/A (laser)</td>
<td>65</td>
<td>93</td>
<td>62</td>
</tr>
<tr>
<td>Laser power (mW)</td>
<td>250</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Layer thickness (micron)</td>
<td>25–300</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 3. Post-cure boxes and their parameters [32–35].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Formlabs</th>
<th>NextDent</th>
<th>EnvisionTEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Country</td>
<td>USA</td>
<td>The Netherlands</td>
<td>USA</td>
</tr>
<tr>
<td>Number of light sources</td>
<td>13</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>LED power per light source (W)</td>
<td>39</td>
<td>18</td>
<td>n/a</td>
</tr>
<tr>
<td>LED wavelength (nm)</td>
<td>405</td>
<td>300–550</td>
<td>390–420</td>
</tr>
<tr>
<td>Maximum temperature (°C)</td>
<td>80</td>
<td>60–80</td>
<td>70</td>
</tr>
</tbody>
</table>

The American division of the International Association for Testing Materials (ASTM) International Standard Organisation created voluntary consensus-based technical standards for a diverse array of materials, products, systems, and services. The ASTM Committee F42
on AM technologies has identified seven AM categories: stereolithography (SLA) or digital light projection (DLP), material jetting (MJ) or polyjet printing (PP), material extrusion (ME) or fused deposition modelling (FDM), selective laser sintering (SLS) or selective laser melting (SLM), binder jetting, and direct energy deposition [36]. The fundamental differences between these technologies concern the materials utilised and how the layers are constructed to generate the 3D object [16]. SLA and DLP are the two primary 3D-printing technologies used in dental applications [14,15,30,31,37,38].

1.2.1. Stereolithography Technique (SLA)

SLA was invented by Chuck W. Hull, and during the same period, Prof. André filed a distinct patent for SLA technology in France [39]. SLA represents an efficient means of creating complex shapes with high accuracy and precision; it is typically used to create resin-based items [16,40]. The SLA comprises a photosensitive liquid resin reservoir, model build platform, and laser, which cures the resin [30,31]. The build platform is immersed in liquid resin during the construction process, and ultra-violet (UV) laser is used to polymerise the resin. After polymerising each layer, the platform elevates by a distance corresponding to the layer’s thickness, allowing the uncured resin to cover the previous layer. The process is repeated until the entire object is printed. In laser-based SLA 3D printing, a UV laser is employed to outline the cross-sections of the object. The laser is focused using a series of lenses, and then it is reflected by a pair of motorized scanning mirrors, known as galvanometers. These scanning mirrors accurately direct the laser beam toward the reservoir of UV-sensitive resin, curing each layer in the process [30,31]. The depth of cure is determined by the photoinitiator and irradiation exposure conditions (such as wavelength, power, and exposure time or speed), as well as any added dyes, pigments, or other UV absorbers, and this ultimately influences the z-axis resolution [16,41]. In general, the layer thickness in the SLA process relies on the standards set by the specific printer model. This thickness can range from 15 to 150 µm, with a surface roughness of approximately 35 to 40 µm Ra. The UV light wavelength required to polymerise the raw material also varies depending on the printer, typically falling within the range of 200 to 500 nm [36]. One of the key benefits of SLA technology is its ability to print complex geometries. However, a primary limitation is the need for support structures during the manufacturing process. These support structures consume additional material and result in increased production and post-processing time [42].

1.2.2. DLP Techniques

Larry Hornbeck, from Texas Instruments, developed the technology for DLP in 1987 [36]. DLP system shares similarities with SLA technology and is classified under the same AM category by the ASTM [36]. In contrast to SLA, DLP employs ultraviolet light (not a laser) to cure the liquid resin layer by layer. The digital micromirror device, a key component of DLP technology, is a rectangular array of mirrors that make up the microsystem [16,40]. The resolution of the projected image is directly related to the number of mirrors, with each mirror representing one pixel or more. The angles of individual micromirrors can be adjusted [30,31]. A single pixel of light from the light source is projected onto the printing surface after being reflected by the micromirror [30,31]. DLP offers several advantages over traditional SLA, including faster layer fabrication, as it can print and cure an entire layer across the build plate within a few seconds. Additionally, DLP uses less material, resulting in lower production costs. The use of DLP printing is anticipated to grow within the dental industry due to its accuracy and efficiency [14,15,30,31,37,38]. Figure 4 is a schematic diagram of the SLA and DLP manufacturing technologies.
1.2.3. Material Jetting (MJ, PP)

MJ technology, also known as polyjet printing (PP), involves selectively jetting liquid resin from numerous nozzles and curing it with UV light [16]. The UV-curable polymers are applied only in areas specified by the virtual design. Since multiple print nozzles can be used, support materials are co-deposited alongside the primary material. Furthermore, this method allows for different colours and building materials with varying properties to be used, including the creation of structures with spatially graded properties [43, 44].

1.2.4. Material Extrusion (ME, FDM)

ME or Fused Deposition Modelling (FDM) was first developed by Scott Crump in the early 1990s and commercialised by Stratasys. The original patents have since expired, leading to numerous FDM brands entering the consumer market [11]. FDM involves extruding thermoplastic material through a nozzle, where it is heated and deposited layer by layer. The nozzle moves horizontally while a platform moves vertically after each new layer is deposited [18, 45]. Although many factors influence the final quality of an FDM-produced model, it has significant potential and viability when these factors are effectively controlled. FDM shares similarities with other 3D-printing processes, such as layer-by-layer construction, but it differs in that material is added through a nozzle under constant pressure and in a continuous stream. To achieve accurate results, this pressure must be maintained steadily and at a consistent speed. Material layers can be bonded using temperature control or chemical agents [46]. The nozzle depositing material always has a radius, as it is impossible to create a perfectly square nozzle, which impacts the final quality of the printed object [47]. Compared to other processes, FDM offers lower accuracy and speed, and the final model’s quality is limited by the material nozzle thickness. In applications requiring high tolerances, factors like gravity and surface tension must be considered. Typical layer thickness in FDM ranges from 0.178 to 0.356 mm [36].

1.2.5. Selective Laser Sintering (SLS, SLM)

Laser-based manufacturing of objects from powder involves two main processes: selective laser sintering and selective laser melting. These methods involve melting and layering powdered material with a laser to create the final product [48, 49]. “Selective Laser Sintering” (SLS) is the term used for processing polymers and ceramics, while “Selective Laser Melting” (SLM) or “Direct Metal Laser Sintering” are applied to the fabrication of metals and alloys [11]. SLS/SLM technology is highly suitable for use in dentistry, particularly in prosthetic dentistry, as it allows for a wide range of dental materials to be deployed in
the fabrication of dental structures. These materials include thermoplastic polymers, waxes, metals and alloys (such as titanium and its alloys, cobalt-chrome alloys, and stainless steel), ceramics, and thermoplastic composites. SLS can be employed to create maxillofacial prostheses, functional skeletons, and individual scaffolds for tissue engineering using polymers and composites. When processing metals and alloys using SLM, various products can be manufactured, including bulk and porous orthopaedic and dental implants, dental crowns, bridges, and frameworks for partial prostheses [11,50,51]. During the manufacturing process, numerous dental constructions can be fabricated on the machine table simultaneously, significantly increasing the productivity of this technology [49,52].

1.3. Effect of Printing Parameters

Accuracy is an important factor when assessing an object produced by AM. Three-dimensionally-printed surgical guides were reported to have superior accuracy when placing the implant compared to conventional surgical guides [53]. Other studies reported a 13% deviation of the 3D-printed object from the original design [54], which was related to numerous factors, including the operator manipulation of the data, the printable material, and the printing process [55,56]. Some parameters in the printing process cannot be manipulated by the operator, such as the printing velocity and cure depth, while others can be adjusted, such as the printing orientation, printing wavelength, and the object’s position on the build platform. Moreover, the after-printing process, including washing, cleaning, and final curing time and temperature, can also be manipulated. These pre- and post-processes affect not only the accuracy of the printed objects but also their mechanical properties [57,58]. Table 4 shows the parameters and their effect on the printed material. Figure 5 illustrates different printing orientations with respect to the direction of force.

<table>
<thead>
<tr>
<th>Printing Parameters</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printing orientations</td>
<td>Horizontal orientation improves the flexural strength [58,59] and the compressive strength [58]. Vertical orientation improves the flexural strength [57,60] and the flexural modulus [57]. Horizontal orientation improves the accuracy of the print [61].</td>
</tr>
<tr>
<td>Position on the build platform</td>
<td>Printing in the middle of the build platform improves the accuracy of the print [60].</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>Thinner layering improves the tensile and the impact strength [62].</td>
</tr>
</tbody>
</table>

Figure 5. Direction of the force applied to the specimen surface during the flexural strength test in relation to the layer orientations: (a) horizontal (0°), (b) angled (45°), and (c) vertical (90°).

1.4. Aim

Most of the published reviews have discussed heat-cured, microwave-cured, or self-cured PMMA, but not 3D-printed resin. To date, there is little evidence to show any improvement in the mechanical properties of 3D-printed acrylic materials over conventional PMMA. The present review aimed to provide a comprehensive overview of 3D-printing technology for denture bases, exploring the influence of incorporating different fillers into
3D-printed denture base resins on their physical, mechanical, and biological characteristics. Additionally, this review seeks to highlight the evolution and advancements made to improve 3D-printed denture base resins for complete denture manufacturing, contrasting these with conventional PMMA and discussing the properties of the resultant acrylic composite materials. Figure 6 presents some examples of 3D-printing applications from the general medical field to specific denture bases.

Figure 6. Scope for the applications of 3D printing.

2. Methodology

A comprehensive search was conducted across multiple databases, including PubMed, Scopus, Google Scholar, and the Cochrane Library, using the keywords ‘3D printing’, ‘Nanocomposite’, and ‘denture base’. Emphasis was placed on articles published in English from 2010 to 2023 that employed 3D-printing technology and had nanoparticles integrated into 3D-printed denture base resin materials for the assessment of physical, mechanical, and biological properties of the resulting composite materials. Articles published before 2010, those not in English, studies employing subtractive or conventional methods, research not involving 3D-printed materials or not related to denture bases, as well as studies exclusively on pure 3D-printed resins without nanoparticle incorporation were excluded. A total of 86 non-duplicate articles were found and only 14 of them were relevant. Six articles were related to pure 3D-printed resins, 6 articles were related to tissue engineering, 35 articles were not related to 3D-printing materials, and 23 articles were not related to denture base material. Two articles were excluded after reading the full study. The selected 14 articles were reviewed to obtain all relevant data related to 3D-printed resin and any additions or enhancements to the available material. Full texts of the selected articles were thoroughly reviewed, and the following information were extracted: resin materials and filler particles used, the fabrication techniques employed, properties of the new composite materials and any possible clinical significance. The literature screening procedure is presented in Figure 7.
Figure 7. Article selection methodology for the review.

3. Three-Dimensional Printing of Denture Base Nanocomposites

Figure 8 outlines the areas considered in this review based on the research carried out on 3D printing of denture base nanocomposites. Table 5 also summarises information based on the same areas from the selected articles. The following sections will provide detailed information based on these areas.
### Table 5. Summary of information extracted from selected studies.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Added Particles/Weight Percentage</th>
<th>3D-Printing Technology</th>
<th>Characterisation</th>
<th>Specimen Shape and Size</th>
<th>Clinical Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Totu et al. [63,64]</td>
<td>TiO$_2$ (0.1–2.5 wt%)</td>
<td>DLP</td>
<td>Biological/Antimicrobial: Candida species: <em>C. scotti</em>; Bacterial species: <em>Staphylococcus aureus</em>; Cytotoxicity: fibroblasts</td>
<td>N/A</td>
<td>The denture made with this material can resist fungal growth.</td>
</tr>
<tr>
<td></td>
<td>Particle size: 56–170 nm</td>
<td></td>
<td>Microscopy: SEM, EDX</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chemical: FTIR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chen et al. [65,66]</td>
<td>TiO$_2$/PEEK (1–4 wt%)</td>
<td>SLA/DLP</td>
<td>Biological/Antimicrobial: Candida species: <em>C. scotti</em>; Bacterial species: <em>E. coli</em>, <em>Staph aureus</em>; Cytocompatibility/Cytotoxicity</td>
<td>N/A</td>
<td>The denture made with this material has better mechanical properties and can resist bacterial and fungal growth.</td>
</tr>
<tr>
<td></td>
<td>Particle size: 30–40 nm</td>
<td></td>
<td>Microscopy: SEM; TEM</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chemical: FTIR; XRD</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: Flexural strength and modulus; Impact strength</td>
<td>−64 × 10 × 3.3 mm</td>
<td></td>
</tr>
<tr>
<td>Mangal et al. [67,68]</td>
<td>Nanodiamonds (0.1 wt%)</td>
<td>DLP</td>
<td>Biological/Antimicrobial: Bacterial species: <em>Streptococcus mutans</em></td>
<td>−20 × 20 × 3.5 mm</td>
<td>3D-printed objects made with composite materials have better mechanical and physical quality compared to the original material. Resistance to <em>S. mutans</em> is proven.</td>
</tr>
<tr>
<td></td>
<td>Particles size: 4–255 nm</td>
<td></td>
<td>Physical: Surface roughness; Accuracy; Water sorption and solubility, Hydrophilicity</td>
<td>−15 × 1 mm disc</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Microscopy: SEM; TEM</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chemical: FTIR</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: Flexural strength and modulus; Impact strength; Hydrothermal fatigue; Surface microhardness</td>
<td>−64 × 10 × 3.3 mm, −64 × 12.7 × 3.2 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tribological: Wear resistance</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>Added Particles/Weight Percentage</td>
<td>3D-Printing Technology</td>
<td>Characterisation</td>
<td>Specimen Shape and Size</td>
<td>Clinical Significance</td>
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<td>----------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Chen et al. [69]</td>
<td>Cellulose nanocrystals (CNCs)-silver nanoparticles (AgNPs) (0.05, 0.1, 0.15, 0.2 and 0.25 wt%)</td>
<td>DLP</td>
<td>Biological / Antimicrobial: Bacterial species: <em>Staphylococcus aureus</em>, <em>E. coli</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cytocompatibility / Cytotoxicity: fibroblasts</td>
<td>64 x 10 x 3.3 mm</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chemical: FTIR</td>
<td></td>
<td>Composite resin (CNCs-AgNPs 0.10-0.25 wt%) exhibits strong antibacterial activity with no discernible cytotoxic impact. Due to the uniform distribution of AgNPs throughout the resin matrix, the group with CNCs-AgNPs of 0.10 wt% exhibited the best mechanical qualities.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Microscopy: TEM</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Radiation: XPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: Flexural strength, elastic modulus and impact strength</td>
<td>64 x 10 x 3.3 mm</td>
<td></td>
</tr>
<tr>
<td>Liao et al. [70]</td>
<td>P-6S-NP3 (1–3 wt%)</td>
<td>DLP</td>
<td>Biological / Antimicrobial: Bacterial species: <em>Staphylococcus aureus</em>, <em>E. coli</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particle size: 3100–3500 nm</td>
<td></td>
<td></td>
<td>64 mm x 10 mm x 3.3 mm</td>
<td>3D-printed objects made with composite material have better mechanical and physical quality compared to the original resin. Resistance to <em>S. aureus</em> and <em>E. coli</em> is proven.</td>
</tr>
<tr>
<td></td>
<td>6S-NP3 (3 wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particle size: up to 4100 nm</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Physical: Water contact angle</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chemical: FTIR; XRD</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Microscopy: SEM</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: Flexural strength and modulus; Impact strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duan et al. [71]</td>
<td>Thermochromic pigments (0.3–1.0 wt%)</td>
<td>SLA</td>
<td>Physical: Conversion rate; Colour change behaviour</td>
<td>−13 x 5 mm cylinder Eiffel tower structure sample</td>
<td>Objects or appliances printed with this composite material have better mechanical properties and provide a thermosensor function to them</td>
</tr>
<tr>
<td></td>
<td>Particle size: 3–4 µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chemical: FTIR</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Microscopy: SEM</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: Tensile strength; Young’s modulus; Elongation at break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alshaikh et al. [2]</td>
<td>ZrO₂ nanoparticles (0.5–5.0 wt%)</td>
<td>DLP</td>
<td>Flexure strength and elastic modulus</td>
<td>64 x 10 x 3.3 mm</td>
<td>The ZrO₂NPs supplement enhanced the 3D-printed resins’ mechanical properties.</td>
</tr>
<tr>
<td></td>
<td>Particle size = 40 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Impact strength</td>
<td>50 x 6 x 4 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Surface roughness and hardness</td>
<td>15 x 2 mm</td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>Added Particles/Weight Percentage</td>
<td>3D-Printing Technology</td>
<td>Characterisation</td>
<td>Specimen Shape and Size</td>
<td>Clinical Significance</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------------------</td>
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<td>---------------------------------------------------------------------------------</td>
<td>-------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Gad et al. [72]</td>
<td>SiO$_2$ Nanoparticles (0.25 wt% and 0.50 wt%)</td>
<td>DLP</td>
<td>Physical: Surface roughness and hardness</td>
<td>64 × 10 × 3.3 mm</td>
<td>While the inclusion of Silicon dioxide nanoparticles did not result in any significant changes in the surface roughness, the result revealed an overall increase in the mechanical properties of the modified 3D-printed resin.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: Flexural strength, Impact strength</td>
<td>10 × 2 mm</td>
<td></td>
</tr>
<tr>
<td>Aati et al. [73]</td>
<td>Ag/MSN (0.0–2.0 wt%) Size = 3 nm</td>
<td>DLP</td>
<td>Biological/Antifungal: Fungal species: C. albicans</td>
<td>N/A</td>
<td>The addition of Ag/MSN significantly enhanced the mechanical and antimicrobial properties without showing adverse effect on human fibroblasts.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cytotoxicity: human oral fibroblasts</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Physical: Surface hardness, surface roughness, water sorption and solubility, FTIR</td>
<td>−15 × 1 mm disc</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Microscopy: TEM, AFM</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: Flexural strength, fracture toughness</td>
<td>−65 × 10 × 3.3 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>−39 × 8.0 × 4.0 mm</td>
<td></td>
</tr>
<tr>
<td>Khattar et al. [74]</td>
<td>ZrO$_2$ nanoparticles (0.5–5.0 wt%) Size = 40 nm</td>
<td>DLP</td>
<td>Biological/Antifungal: Fungal species: C. albicans</td>
<td>−15 × 2 mm</td>
<td>Incorporating ZrO$_2$ nanoparticles into 3D-printed resin at a low concentration (0.5 wt%) leads to a significant reduction in the adhesion of C. albicans without affecting the surface roughness of the printed material.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Physical: surface roughness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Douri et al. [75]</td>
<td>ZnO nanoparticles (2.0, 3.0, and 4.0 wt%)</td>
<td>DLP</td>
<td>Physical: Surface hardness, surface roughness</td>
<td>N/A</td>
<td>The addition of ZnO improved the flexural strength and decreased the surface roughness, while the surface hardness was not affected.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mechanical: flexural strength</td>
<td>−64 × 10 × 3.3 mm</td>
<td></td>
</tr>
</tbody>
</table>
3.1. Denture Base Polymers for 3D Printing

In response to the demand for denture base materials suitable for 3D printing that offer superior physical, mechanical, thermal, and aesthetic properties, acrylic materials dominate the dental market. The 3D-printable acrylic materials are light-cured; some examples now available include 3D resins from Formlabs (Somerville, MA, USA), NextDent (Soesterberg, The Netherlands), ASIGA (Alexandria, Australia), and EnvisionTEC (Dearborn, MI, USA). Other 3D-printable denture base materials are available that use LED light flashes and a specific type of gas for the post-curing process, rather than the combination of constant LED light and heat. These materials include FotoDent denture (Dreve), LC Denture (IMPRIMO), and Optiprint denture (dentona). Table 6 shows some commercially available 3D-printed acrylic materials with their properties for denture base manufacturing. However, 3D-printed materials generally have disadvantages that need addressing, such as reduced mechanical properties, including flexural and impact strength, and polymerisation shrinkage [76]. Therefore, acrylic materials should evolve using different technologies to improve the aforementioned properties. The literature indicates that the incorporation of reinforcing agents can yield new composite materials with improved mechanical, physical, or biological properties. In the dental field, many attempts were made to improve 3D-printed resins by adding different types of fillers [65,76–81], and the properties of the resulting composite material depend on the nature, shape, size, and distribution of the inorganic fillers.

<table>
<thead>
<tr>
<th>Commercial Name</th>
<th>Digital Denture</th>
<th>Denture 3D+</th>
<th>Denture Base II</th>
<th>DentureTEC</th>
<th>Denture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Company</td>
<td>Formlabs</td>
<td>NextDent</td>
<td>DENTCA</td>
<td>Saremco</td>
<td>Detax</td>
</tr>
<tr>
<td>Printing wavelength (nm)</td>
<td>405</td>
<td>405</td>
<td>385/405</td>
<td>385</td>
<td>385</td>
</tr>
<tr>
<td>Printing temperature (°C)</td>
<td>31</td>
<td>18–28</td>
<td>18–30</td>
<td>35</td>
<td>23–25</td>
</tr>
<tr>
<td>Post-cure time (minutes)</td>
<td>30</td>
<td>30</td>
<td>20–60</td>
<td>4000 flashes (N* gas)</td>
<td>2000 flashes (N* gas)</td>
</tr>
<tr>
<td>Post-cure temperature (°C)</td>
<td>80</td>
<td>60</td>
<td>&gt;60</td>
<td>Not needed</td>
<td>Not needed</td>
</tr>
<tr>
<td>Post-cure wavelength (nm)</td>
<td>405</td>
<td>300–550</td>
<td>320–405</td>
<td>320–500</td>
<td>320–500</td>
</tr>
</tbody>
</table>

N*: nitrogen gas.

3.2. Denture Base Filler Particles Used for 3D Printing

As previously mentioned, nanotechnology has effectively improved the dental industry. The need to improve the material’s properties on a wider scale is supported by the variety of nanomaterials with different properties that can be used to improve the current acrylic system. Modification of the acrylic resin by incorporating different nanofillers can enhance the mechanical, physical, and biological properties of the nanocomposite material [63,65,67].

3.2.1. Titanium Dioxide Nanoparticles and PEEK Microparticles

Nanotechnology has recently been introduced into the dental field. As a result, researchers have focused on how to improve dental materials and applications using this technology. The literature shows that reinforcing some of the current materials with nanoscale agents, such as metal oxides, noble metals, and carbon atoms, can contribute to improving the physical and mechanical properties of the polymeric materials [82]. TiO2 is one of the biocompatible materials suggested for addition to 3D-printed resin due to its superior properties such as low-cost, chemically stable, non-corrosion, strength and proven antimicrobial properties against gram-positive/negative bacteria, fungi, and viruses [76,83]. Therefore, TiO2 nanoparticles were recommended in particular for use as a filler for denture base materials.
On the other hand, polyetheretherketone (PEEK) comes as semi-crystalline plastic particles with very good mechanical properties that could be used as fillers for polymeric materials. PEEK is a non-toxic, lightweight, non-corrosive material, with a low elastic modulus close to human bones, which makes it an excellent material to be used as a filler [84–87]. The literature shows that small additions of TiO$_2$ nanoparticles or a combination of TiO$_2$ nanoparticles/PEEK microparticles to the 3D-printed resin could positively affect the mechanical, physical, and biological properties of the resultant composite material [63,65,76].

3.2.2. Nanodiamonds

Nanodiamonds are a carbon-based material that are scientifically proven to improve the thermal and mechanical properties of acrylic resin [77]. Nanodiamonds are preferred over metal and metal oxide nanoparticles as a filler for resin materials as they are more chemically stable, biocompatible, and do not have a cytotoxic effect. Nanodiamonds were proven to enhance the antimicrobial and mechanical properties (e.g., flexural strength, surface hardness, and wear resistance) of acrylic material [79,88,89].

3.2.3. Silver Nanoparticles (AgNPs)

Silver nanoparticles are one of the most commonly used nanofillers added to different products due to their antimicrobial properties and lower toxicity compared to ionic silver [90]. However, one major problem associated with silver nanoparticles is the aggregation and the lack of proper dispersion of the nanoparticles within the composite material. Surface grafting modification and silane coupling agent treatment are among the suggested solutions to overcome this issue [91].

3.2.4. Thermochromic Pigments

Thermochromic pigments are additive materials that affect the colour of the resultant composite reversibly and repeatedly in response to the change in temperature. It is a colour-changing microcapsule material that includes electron transfer equilibrium within the molecule, and proton gain–loss among particles. It becomes colourless when the temperature rises over 31 °C, and goes back to its original colour when the temperature is below 31 °C. It was successfully added to the 3D-printed resin, and improved the mechanical aspects of the hybrid material in addition to the ability to change colour [71].

3.2.5. Zirconium Oxide

Zirconium oxide (ZrO$_2$), also known as zirconia, is a common bioceramic material that has gained popularity over time due to its high biocompatibility and bioactivity [2,5,11,92]. Zirconia exists in three main crystallographic forms: tetragonal, cubic, and monoclinic. Along with excellent aesthetics, zirconia also exhibits a remarkably high fracture toughness, flexural strength, and durability [2,92]. The distribution and size of the zirconia filler particles and the extent to which the filler adheres to the matrix are two criteria that significantly impact the mechanical performance of zirconia-reinforced 3D-printed denture bases [12,93].

3.2.6. Silicon Dioxide

The incorporation of silicon dioxide nanoparticles into 3D-printed denture base resins is previously known, as they enhance the thermal and physical properties of the resultant composite material due to their high surface energy, large surface area, and strong interaction with the polymer [72]. Furthermore, favourable outcomes were observed when silicon dioxide nanoparticles were introduced at lower concentrations (0.25 wt%) [94] compared to higher concentrations (1.0 wt% and 5.0 wt%) [95].

3.2.7. Zinc Oxide

In recent times, ZnO nanoparticles have attracted increased attention as versatile inorganic nanoparticles because of their distinct optical, biochemical, electrical, biological,
biocompatible, cost-effective, non-hazardous, and environmentally stable properties [96]. Some researchers have documented that incorporating ZnO nanoparticles at different concentrations resulted in improved flexural strength of 3D-printed acrylic resin and also enhanced certain physical and mechanical characteristics of a heat-cured denture base resin [97,98].

3.3. Fabrication Techniques

3.3.1. Functionalisation

The composite material’s properties depend mainly on the interaction between the polymer matrix and the inorganic fillers [76]. The term composite material here refers to a material that has two or more distinct constituents, which are not bonded chemically to each other. However, some types of fillers do not have this bond with the polymer matrix, which hinders the final properties of the composite material. Hence, coupling agents were introduced to solve this issue. A coupling agent is a chemical agent that chemically bonds two phases to each other in a composite material [99].

In most of the studies, authors used different coupling agents to promote the chemical interaction between the filler particles and the 3D-printed resin material and to facilitate their homogenous dispersion. Different methods were used to promote this reaction. Chen et al. [65] used the hydrothermal method, where 34 mL of tetrabutyl titanate was added to 100 mL of HCl solution and stirred for 2 h. Two layers were produced, and the lower layer was heated at 180 °C for 12 h. The reaction was left to cool at room temperature before adjusting the pH to 7.4 using 1 M NaOH. The resultant solution was centrifuged and the precipitates were then washed twice using ionized water and alcohol. Lastly, the TiO$_2$ nanoparticles were obtained by vacuum drying. After that, 10 g of TiO$_2$ nanoparticles were mixed with 300 mL of ethanol and sonicated for 5 min before mixing with the coupling agent (KH570). This mixture was heated to 80 °C for 5 h, centrifuged, washed, and vacuum dried to obtain silanated TiO$_2$.

Chen et al. used TiO$_2$ nanoparticles mixed with carboxylic acid (acrylic acid). They mixed 0.5 g of TiO$_2$ nanoparticles with 14.4 g of carboxylic acid and 16 g of hexane in an ultrasonic mixer for 20 min under 0 °C. The mixture was left at room temperature for 2 days. The mixture was then centrifuged for 1 h at 12,000 rpm to remove the carboxylic acid residues from the TiO$_2$ nanoparticles. Finally, the TiO$_2$ nanoparticles were dried in an oven under vacuum conditions.

Totu et al. [63] used the modified sol–gel procedure using 1.11 mmol titanium tetra-butoxide (Ti(OBu)$_4$) with 2.4 mmol dimdone (5,5-Dimethylcyclohexane-1,3-dione) to be mixed with 100 mL of alcohol. This mixture was left to react in a colloid mill (with 25 g of quartz grinding balls of 1 mm diameter) at 250 rpm to synthesize silanated TiO$_2$.

Liao et al. [70] simultaneously silanised and grafted the surface of nano silver-loaded zirconium phosphate 6S-NP3 at two stages. Silanisation at the first stage was performed using MPS (γ-Methacryloxypropyltrimethoxysilane) under an acidic condition. A total of 4 g of 6S-NP3 and 150 g of deionized water were ultrasonically dispersed in a 500 mL container for 1 h. Meanwhile, 50 g of deionized water and 1 g of acetic acid were dropped together. Following that, the suspension was transferred into a 500 mL flask with a machine stirring at 200 rpm and heated to 30 °C. Next, MPS and cyclohexane were added to the mixture and the temperature was increased up to 80 °C and maintained for 1.5 h. Lastly, the M-6S-NP3 was extracted using a vacuum oven at 80 °C for 12 h. The second stage was about grafting M-6S-NP3 with 3D-printed resin using free radical polymerisation. Then, 1 g of M-6S-NP3 was ultrasonically mixed with xylene for 0.5 h. Then, 0.1 g BPO initiator and 10 g MMA were mixed with the suspension and heated at 80 °C in a water bath for 8 h. P-6S-NP3 was obtained through centrifugal separation and dried in a vacuum oven at 80 °C for 12 h.

Utkarsh et al. [68] used purified unfunctionalized nanodiamond (ND) powder and anhydrous aminated nanodiamond (A-ND) powder. Nanodiamond particles were reported to have the tendency to agglomerate [100,101]. Hence, the authors used chloroform as a
solvent with probe sonication and magnetic stirring to achieve a homogenous distribution of the particles. The composite solution was degassed in a vacuum for 2 h and then used with the 3D printer without any further modifications. The authors also suggested the surface functionalisation of the nanoparticles to overcome this issue, in addition to the use of an organic solvent base technique to achieve homogenous dispersion which they used in their study.

Duan et al. [71] used the coupling agent (MPTMS/KH70) to functionalise thermochromic pigments. The coupling agent was mixed with ethanol under mechanical stirring for 4 h at 50 °C, and the mixture’s pH was adjusted to 5 by adding droplets of acetic acid. After that, thermochromic pigments (pink and blue) were added to the previous mixture and dispersed using an ultrasound mixer for 15 min at a temperature of 50 °C. The silanated thermochromic pigments were washed with water and ethanol, and dried for 4 h at 50 °C.

Alshaikh et al. [2] used the silane-coupling agent 3-(trimethoxysilyl)propyl methacrylate (TMSPM) with the ZrO₂ nanoparticles to prevent the agglomeration of the nanoparticles. On the other hand, Gad et al. [72] treated the surface of SiO₂ nanoparticles with silane binding agent, 3-trimethoxysilyl propyl methacrylate, 97% (γ-MPS) to enhance the distribution of the nanoparticles within the 3D-printed denture base resin.

Aati et al. [73] used MCM-48 amine-functionalized mesoporous silica nanoparticles with silver nanoparticles to facilitate particle distribution within the 3D-printed resin. The mesoporous silica powder was mixed with the material in a 3:2 ratio (weight to weight). This blend was vigorously stirred under dark conditions at 80 °C for a duration of 96 h. Following this, the resulting yellow solution was subjected to centrifugation at 4000 rpm. The resulting supernatant was discarded, and the remaining material was thoroughly washed three times, alternating between ethanol and distilled water. Subsequently, the slurry was placed in an oven at 60 °C overnight. The dried powder was then collected and incrementally added into the liquid resin while subjecting them to continuous magnetic stirring for 1 h. Subsequently, the mixture underwent 10 min of sonication using an ultra-homogeniser powered at 250 watts.

Khattar et al. [74] used a silane coupling agent 3-(trimethoxysilyl)propyl methacrylate (TMSPM) to initiate the connection between the ZrO₂ nanoparticles and the resin matrix. This agent was employed to modify the surface of the ZrO₂ nanoparticles by introducing reactive groups via a silanisation process. To achieve this, the silane coupling agent was initially dissolved in acetone. Subsequently, the ZrO₂ nanoparticles were introduced to this solution, and the mixture was stirred for a duration of 60 min. Afterward, the acetone was removed through a rotary evaporator, followed by a cooling step to acquire the silanised ZrO₂ nanoparticles. These silanised ZrO₂ nanoparticles were weighed using an electronic scale and then incorporated into the 3D-printing resin. The resulting mixture of resin containing ZrO₂ nanoparticles was thoroughly blended and stirred using a magnetic stirrer for a period of 30 min.

3.3.2. Mixing

Mechanical mixing is an important step to achieve a homogenous distribution of the filler particles within the polymer matrix. It constitutes the rotation of the different materials within one vial at a certain speed for a given amount of time until a homogenous mixture is achieved. The filler particles with or without functionalisation were gradually added to the 3D-printed resin with the recommended weight percent under continuous mechanical stirring for a specific amount of time, based on the amount of liquid resin and filler particles. Once the mixing is finished, the material becomes ready for printing without any further modifications. The resulting material exhibited a better performance in terms of mechanical and physical properties compared to the pure 3D-printed resin. The end product was successfully printed as 3D objects using the aforementioned printing methods [63,65,67–71,102].
3.3.3. 3D-Printing Techniques

SLA and DLP are the most commonly used technologies for dental applications due to their capability in faster manufacturing at high-resolutions [36]. This process involves curing liquid resin into hardened plastic with a controlled light source, forming covalent bonds. Initially, the material remains in a semi-cured “green state”, where surface molecules can bond with new layers. As layers cure, covalent bonds form uniformly in the X-, Y-, and Z-axes. After printing, the product is still in the green state and requires post-curing to complete polymerisation and set mechanical properties. Tables 2 and 3 show some of the commercially available 3D printers with their post cure devices and their technical parameters.

3.4. Characterisation of the Composite 3D-Printed Denture Base Materials

3.4.1. Physical Characteristics

The round nano-sized diamond particles were considered as one of the ideal fillers when considering the development of a composite material [100]. Modifying the 3D-printed resin with nanodiamonds demonstrated a significant improvement in the physical properties of the material. Mangal et al. [68] studied the effect of adding nanodiamond particles to 3D-printed resin, and they observed a significant improvement in the physical properties of the resultant nanocomposite material compared to the control group. Surface hardness and surface roughness were significantly improved when small quantities of nanodiamond particles were added. Previous studies also demonstrated significant improvements in the physical properties of polymeric materials after the addition of nanodiamond particles in different percentages [68]. However, in order to achieve this, a uniform dispersion of the nanoparticles within the polymer matrix is required. In addition to that, Mangal et al. studied the effect of adding nanodiamond particles to the wettability of the resultant material, and they found a significant decrease in the contact angle between the water and the nanocomposite material. Water sorption and solubility were also reported to decrease after the addition of nanodiamond particles. Furthermore, a significant improvement in the surface wear resistance was reported after adding a small quantity of nanodiamond particles within an environment that simulated cleansing with a toothbrush, but with minimal changes in the surface roughness. Another test was performed by the authors in regard with the wear rate [68], and the nanodiamond particle groups exhibited a significant increase in the wear resistance against stainless steel and titanium counter surfaces compared to the control group.

Also, Mangal et al. [67] assessed the accuracy of the plain 3D-printed resin samples and the nanocomposite-printed samples with a CAD file used for printing these samples. They scanned the samples using a digital scanner to evaluate all the printed groups to the reference CAD file, and they determined the root-mean-square (RMS) values of the samples by a superimposition method to determine the trueness values of the samples. The results showed the absence of any significant morphological changes between the three groups based on the RMS statistical values, and the results of the superimposed images compared to the CAD file showed deviation in a ±200 µm range.

Duan et al. added silanated thermochromic pigments to 3D-printed resin to examine the resultant composite material [71]. They used two types of pigments: blue and pink, and it was noticed that the colour of the resultant material started to fade after the material was exposed to a temperature higher than 31 °C. It was also noticed that the pigments did not affect any of the printing parameters of the printed material.

Aati et al. [73] investigated the impact of incorporating Ag/MSN nanoparticles on surface hardness, surface roughness, degree of polymerisation, and water sorption and solubility. Surface hardness displayed a linear improvement trend up to a 1.0 wt% addition, beyond which the surface hardness value started to decline significantly. This decrease was attributed to particle agglomeration at higher concentration levels. The assessment of composite material surface roughness revealed that, despite an increase in surface roughness, the results remained below the recommended threshold for surface roughness.
The degree of polymerisation was also examined, and although there was a declining trend in the value, it did not reach a significant level with an addition of 1.0 wt%. However, with a 2.0 wt% addition, the measurement exhibited a significant decrease. This decrease was attributed to the dark coloration of the specimens due to nanoparticle aggregation, which could hinder the curing light from penetrating deeper layers. Water sorption and solubility were analysed, and the addition of Ag/MSN nanoparticles did not result in a significant difference in water sorption values. Conversely, a significant effect was observed in water solubility values, where the values decreased due to the entrapment of water molecules within the samples, resulting in some negative readings. Both water sorption and solubility values adhered to the standards outlined in ISO 10477 [103].

The impacts of silicon dioxide (SiO$_2$) and zirconia oxide (ZrO$_2$) additives on the surface roughness of 3D-printed denture base resin were investigated by Gad et al. and Alshaikh et al. [2,72] Their findings suggested no significant alterations in surface roughness for nanocomposite materials compared to the unmodified variants, and the printing parameters could have a more prominent effect after the addition of the nanoparticles. Contrary to their findings, Khattar et al. [74] reported a significant increase in surface roughness after the addition of ZnO nanoparticles compared to the unmodified material. On the other hand, the surface hardness was significantly increased with the addition of SiO$_2$ nanoparticles, while the addition of ZrO$_2$ nanoparticles showed an insignificant increase in the value.

Finally, Al-Douri et al. [75] examined the impact of incorporating ZnO nanoparticles on the surface hardness and surface roughness of a 3D-printed resin. They observed no significant effect of adding the nanoparticles on the surface hardness, although the values experienced a slight decrease. In contrast, the effect on the surface roughness was quite different, with the values being significantly reduced upon the addition of ZnO nanoparticles. The authors explained this phenomenon as the inclusion of nanoparticles filling the micro gaps between the particles and the resin matrix. Consequently, this minimizes the irregularities on the surface and voids that might occur during the processing of the denture base material.

3.4.2. Mechanical Characteristics

Chen et al. reviewed some of the mechanical properties of 3D-printed resin combined with TiO$_2$ and with the combination of TiO$_2$/PEEK [65]. They concluded that the addition of 1.0 wt% of TiO$_2$ increased the flexural strength (75.3 MPa) and flexural modulus (2181.8 MPa) compared to the control group (69.2 MPa and 2100 MPa). However, the addition of 2.0 wt% of TiO$_2$ caused some issues during printing. They had some issues with printing such as shedding and over-solidification, which caused the printing process to fail. The possible reason for this failure was the aggregation of the TiO$_2$ nanoparticles within the polymer matrix. Furthermore, the increased amount of TiO$_2$ nanoparticles over a critical value led to the over-absorption of ultraviolet light, which could have affected the curing process. This may have decreased the mechanical properties of the nanocomposite material and failure to complete the curing process. For the sake of further improvements, the authors added PEEK microparticles to improve the TiO$_2$ nanoparticles dispersion and to further improve the mechanical properties of the resultant composite material. The results showed that the TiO$_2$/PEEK composite material improved flexural strength (>80 MPa), flexural modulus (>2250 MPa), and rupture work (>1500–2000 J/m$^2$), compared to the control group (69.2 MPa, 2100 MPa, and <1100 J/m$^2$, respectively).

Following the same approach, Mangal et al. studied the effect of adding ND and A-ND to 3D-printed denture base resin [67,68]. Both nanocomposite materials showed improvements in the flexural strength, flexural modulus, and impact strength, with the A-ND (116.4 MPa, 2989.6 MPa, and 19.3 kJ/m$^2$, respectively) composite material showing a significant difference compared to the control group (88.5 MPa, 2654.3 MPa, and 12.0 kJ/m$^2$, respectively) and the ND nanocomposite group (104.8 MPa, 2766.5 MPa, and 16.0 kJ/m$^2$, respectively). The author explained that the higher values of the A-ND nanocomposite group could be linked to the stronger covalent linkage with the polymer matrix, and the
better mono dispersion state of the nanoparticles (which was confirmed by transmission electron microscope) compared to the pure ND group. 

Along the same line, Duan et al. tested the mechanical performance of thermochromic pigments with 3D-printed resin [71]. The results showed a decline in the mechanical properties including tensile strength (30.3–31.6 MPa), young modulus (574.7–629.3 MPa), and elongation at break (7.4–10.0%) compared to the unmodified material (32.1 MPa, 651.5 MPa, and 11.0%, respectively). The authors interpreted this drop in the mechanical properties as the ineffective bonding between the thermochromic pigments and the resin, which led to the material failure. Therefore, they decided to use a silane coupling agent called methacryloxypropyltrimethoxysilane (MPTMS) to overcome this problem. As a result, some of the mechanical properties such as Young’s modulus (982.2 MPa) and tensile strength (43.0 MPa) were improved significantly compared to the unmodified resin and 3D-printed/thermochromic pigments groups. However, those aspects improved on the account of elongation at break (flexibility) (5.8%). The increased mechanical properties between the filled groups were due to an increase in the conversion rate of the silanated group compared to the unsilanated group by nearly 15%. This led to the formation of chemical bonds between the carbon atoms which needed more energy to break compared to the hydrogen bond in the other group. It was also noticed that with the increased addition of the silanated thermochromic pigments beyond the optimal level, the tensile strength decreased, where the addition of 1 wt% of the silanated thermochromic pigments had almost the same value as the unmodified material. As for the Young’s modulus, an increase in the silanated thermochromic pigments decreased its value, whereas each increase in weight of 0.2 wt% of the fillers caused a drop of 20 MPa in Young’s modulus value.

Liao et al. [70] studied the effect of adding P-6S-NP3 at different concentrations (1.0–3.0 wt%) to 3D-printed denture base resin. They found that the addition of P-6S-NP3 improved the flexural strength (73.5 MPa), flexural modulus (1220.9 MPa), and impact strength (1814.5 J/m$^2$) of the resultant composite material compared to the unmodified material (50.0 MPa, 1061.7 MPa, 1210.7 J/m$^2$ for the flexural strength, flexural modulus, and impact strength, respectively), where the best flexural strength values were achieved with the addition of 2.0 wt% of P-6S-NP3. However, the addition of nano silver-loaded zirconium phosphate (6S-NP3) without surface treatment or grafting showed poor mechanical properties compared to the P-6S-NP3 groups and the control group. This was explained due to aggregation of the nanoparticles within the composite material which were easily peeled under stress. Those data proved the effect of the proper dispersion and compatibility of P-6S-NP3 within the composite material.

Chen et al. [69] evaluated some of the mechanical properties after adding CNC-Ag nanoparticles to 3D-printed denture base resin. They showed that the flexural strength was increased 6% and 12% after adding 0.05 and 0.1 wt%, respectively. The flexural strength was not changed with the addition of 0.15 and 0.20 wt% and decreased when the fillers reached 0.25 wt%. The flexural modulus also showed a slight increase with the filler addition up to 0.20 wt%, and then a slight decrease after further addition. The impact strength of the composite material was increased in all the groups compared to the unmodified material, with a significant increase shown with the addition of 0.05 and 0.1 wt% (48% and 73%, respectively).

To simulate the oral environment, Mangal et al. [67] performed a hydro-thermal fatigue experiment where they immersed their samples in water baths for a number of cycles, which accelerated the physiological ageing of the nanocomposite. Under these circumstances, the ageing effect occurred, which decreased the mechanical properties of the nanocomposite material. However, the flexural strength, elastic modulus, and modulus of resilience were significantly higher in the nanocomposite test groups (111.2 MPa, 2816.3 MPa, 2.2 MPa, respectively) than in the control group (86.4 MPa, 2640.0 MPa, 1.4 MPa, respectively).

Gad et al. [72] explored the effect of incorporating SiO$_2$ NPs on mechanical properties. They reported improvements in flexural strength (89.3 MPa) and impact strength (10.8 KJ/m$^2$) of the nanocomposite material in comparison to the unmodified material.
(69.0 MPa and 9.9 KJ/m² for the flexural and impact strength, respectively) and advised adding less than 0.5 wt% due to the low density of SiO₂ NPs relative to other metal oxides. In addition, they investigated the effect of the thermocycling ageing, noting a negative impact on the tested properties on the nanocomposite material (84.8 MPa and 9.4 KJ/m²) and the unmodified material (64.5 MPa and 8.2 KJ/m²).

In the same vein, the impact of the ZrO₂ NP addition on the mechanical properties was studied [2]. Alshaikh et al. probed the effects of incorporating a range of 0.5–5.0 wt% ZrO₂ NPs into 3D-printed denture base resin. Based on their results, they concluded that the additions improved flexural strength (73.7–88.1 MPa), elastic modulus (1022.9–1244.3 MPa), impact strength (2.4–3.3 KJ/m²), and surface hardness (17.0–21.1 VHN) of the nanocomposite material compared to the unmodified one (60.8 MPa, 751.8 MPa, 1.9 KJ/m², and 17.9 VHN).

Aati et al. [73] incorporated Ag/MSN nanoparticles into the 3D-printed resin, and they studied their effect on flexural strength and fracture toughness. They concluded that the flexural strength was decreased with the addition of the nanoparticles (80.6–96.2 MPa) compared to the control (94.1 MPa), but this decrease was not significant, except for 2.0 wt%, and the resultant nanocomposite was in compliance with the ISO 20795-1, 2013 [104]. The authors interpret this as a limitation in the operation of 3D printers, where the initial curing time and intensity during layer formation are insufficient to activate the monomer and initiate bonding in the initial phase. Consequently, during the later stage of post-curing, the UV light primarily affects the nearest surface layer, enhancing its hardness, but it does not adequately reach the deeper internal structure. In contrast to flexural strength, the introduction of Ag/MSN nanoparticles led to a significant enhancement in the fracture toughness of 3D-printed resin. This increase was found to be significant in all the modified samples (2.18–2.19 MPa) when compared to the control group (1.7 MPa). The existence of the Ag/MSN complex has impeded crack propagation, thus imparting an improved protective attribute to nanocomposites. These nanocomposites are constructed with an advanced capability to resist the spread of formed cracks.

Al-Douri et al. [75] reported a significant increase in the flexural strength of a 3D-printed resin after the addition of ZnO nanoparticles (119.3–126.1 MPa) compared to the control (111.4 MPa). This increase was observed with an up to 3.0 wt% addition of the nanoparticles. The increase observed in the experimental groups can be attributed to the role of nanoparticles as fillers that integrate into the resin matrix. This integration reduces gaps, spaces, and fractures within the resin material. Furthermore, the proper distribution of nanoparticles allows them to interpose between the linear chains of the polymer, resulting in reduced polymer chain mobility and an increase in flexural strength. However, it is worth noting that the addition of 4.0 wt% ZnO nanoparticles led to a decrease in flexural strength (106.3 MPa), in contrast to lower concentrations. This decrease might be explained by a reduction in the load-bearing cross-sectional area of the polymer matrix. It is also possible that an excessive number of filler particles is causing stress concentration. One potential cause of this decrease could be incomplete resin wetting of the fillers. Moreover, ZnO may interfere with the integrity of the polymer matrix.

3.4.3. Biological Characteristics

TiO₂ nanoparticles were proven to have antimicrobial properties due to cytotoxic oxygen radicals [105]. While it is a chemically stable material, under certain conditions it decomposes and oxidizes organic and inorganic compounds. Therefore, it is considered as an antimicrobial additive [106]. Totu et al. [63] discussed the advantages of using TiO₂/3D printed acrylic resin as a denture base, and their study was aimed at improving the antifungal characteristics of the currently available materials. Thus, they developed a 3D-printed-TiO₂ nanocomposite material with enhanced properties for the manufacture of denture prostheses, and to the authors’ knowledge, they were the first to use and investigate this material. They obtained this material by adding different amounts of TiO₂ nanoparticles to 3D-printed resin (0.2%, 0.4%, 0.6%, 1.0%, and 2.5%). Experimental data gained by FTIR
testing proved that the interaction between the nanoparticles and the polymer occurred successfully with the addition of 0.4 wt% TiO$_2$. The newly obtained nanocomposite material proved to have an antifungal effect, specifically for Candida species. It was observed that 3D-printed-TiO$_2$ nanocomposites can completely block the growth of Candida scotti, and this was confirmed by the 2, 3, 5-Triphenyltetrazolium chloride (TTC) test. Furthermore, the nanocomposite material showed an excellent antibacterial effect against Staphylococcus aureus and showed no cytotoxic effect on fibroblast cells.

Chen et al. [65] tested the effect of 3D-printed-TiO$_2$ nanocomposite and 3D-printed-TiO$_2$/PEEK nanocomposite on bacterial growth. They used Staphylococcus aureus and E. coli species on their test. The results were promising as both nanocomposite types showed antibacterial properties against the aforementioned strains compared to the control group. Furthermore, they performed a cytotoxicity test using fibroblast culture, and they noticed that the survival rate at the first day was slightly reduced. Following that, the cells showed a significant proliferative tendency until day 7, where the cell viability was close to the control group. As a result, the nanocomposite showed a good cytocompatibility effect and a potential effect in promoting cell activities. They performed a cytocompatibility test on dental pulp cells of different test groups to demonstrate their effect on the cells. The test groups containing TiO$_2$ showed greater survival percentages compared to the groups without TiO$_2$, and they concluded that TiO$_2$ nanoparticles are cytocompatible.

Utkarsh et al. [68] tested the effect of 3D-printed-nanodiamond nanocomposite on Streptococcus mutans species (S. mutans) for a total of 48 h. The results showed a statistically significant difference in the resistance of 3D-printed nanodiamonds to the S. mutans biofilm formation compared to the control group.

Liao et al. [70] evaluated the antibacterial effect of adding silver nanoparticles. They used two bacterial species in their study (S. aureus and E. coli). The P-6S-NP3 showed good antibacterial properties compared to the control groups (plane PMMA and non-modified silver nanoparticles) which did not show any antibacterial effect. However, the composite material exhibited a better antibacterial efficacy against E. coli compared to S. aureus.

Similar to Liao et al., Chen et al. [69] assessed the antibacterial effect of a CNC-Ag-3D-printed composite material with the same bacterial species for 24 h. The bacterial concentration was reduced to 50% for both species compared to the control group (plane PMMA) with the addition of 0.05 wt% nanoparticles. For the other groups (0.1–0.25 wt%), the bacterial concentration was significantly reduced for both species indicating an excellent antibacterial effect. The nanocomposite material showed almost no toxic effect on fibroblasts L929 after 7 days compared to the negative control group.

Aati. et al. [73] studied the biocompatibility of the addition of Ag/MSN nanoparticles into 3D-printed resin, and they found that the ions released from the resin itself in addition to the silver ion release was a concern. In general, all test samples, including those with a 2.0 wt% content of Ag/MSN, exhibited cell viability exceeding 75%. Therefore, in accordance with ISO standard 10993-5 [107], it can be concluded that the modified 3D-printed resin is biocompatible and does not induce any significant cytotoxic effects. Moreover, they studied the effect of the nanoparticles on the growth and adhesion of Candida albicans, and they revealed that the Ag/MSN-modified 3D-printed resin has demonstrated a significant reduction in biofilm formation and adhesion, even after a 3-month aging period. This suggests that Ag/MSN nanoparticles have potential as an advanced antimicrobial material for long-term drug delivery and release. The system operates through multiple microbicidal mechanisms involving amine-functionalised MSN and the release of Ag nanoparticles/ions. These mechanisms include electrostatic interactions with microbial cell membranes, enhanced surface properties, increased contact with microorganism membranes due to small nanoparticle size, disruption of cell walls, and interactions with cellular components leading to cell damage and death.

Finally, Khattar et al. investigated the effect of incorporating ZrO$_2$ into 3D-printed resin. Their investigations revealed that the introduction of ZrO$_2$ nanoparticles was found to influence Candida albicans adhesion. Notably, the 0.5% ZrO$_2$ nanoparticle-infused 3D-
printed resin group exhibited a significant reduction in *Candida albicans* count when compared to both heat-polymerised PMMA and other 3D-printed resin groups. This decrease is likely attributable to the antibacterial properties of ZrO$_2$ nanoparticles, a characteristic established in prior research. The presence of specific ZrO$_2$ nanoparticles near the *Candida albicans* cell membrane on the resin’s surface may contribute to its antifungal attributes. Also, nanoparticles can engage with fungal cells through various mechanisms, including hydrophobic contact, electrostatic attraction, and van der Waals forces, leading to structural and functional changes in the fungal cell membrane and the inhibition of normal growth processes. Nonetheless, elevated concentrations were associated with greater cell growth, possibly due to the aggregation of ZrO$_2$ nanoparticles and the formation of clusters either within the resin matrix or on its surface. Conversely, the minor addition of the nanoparticles (0.5%) showed a significant decrease in the *Candida albicans* count.

3.5. Clinical Significance

Clinical trials are necessary to validate the performance and long-term patient satisfaction with 3D-printed complete dentures using in a real clinical context. Currently, most studies are concentrated on the fundamental characterisation of 3D-printed specimens with modifications, and there is limited exploration of complete denture trials in actual patient treatments [108]. One study employed digital Light Projection Manufacturing (DLP), using an EnvisionTEC perfactory 3D printer to craft complete dentures from 3D-printed/TiO$_2$ nanocomposite material [20]. A total of 45 complete edentulous arches were treated (31 maxillary and 14 mandibular), and regular clinical assessments were conducted to evaluate denture retention and stability at one week, six months, 12 months, and 18 months. Before inserting the 3D-printed dentures into the patients’ mouths, an initial examination revealed poor fit in both the upper and lower arches. After 18 months of continuous use, the new nanocomposite-based 3D-printed dentures displayed satisfactory clinical performance, with a significant enhancement in retention and stability. Although there were no major complications observed within the 18-month period, a slight reduction in retention and stability was noted. Consequently, further investigations are warranted to establish the clinical viability of 3D-printed denture base materials.

4. Conclusions and Future Challenges

Based on this review, it could be concluded that the addition of different types of fillers to improve the properties of 3D-printed denture base resin for constructing a complete denture base seems promising. The improved mechanical, physical, and biological properties are reported based on small quantities of the added particles, and any further addition could deteriorate the properties of the resultant composite material. However, further investigations are needed to confirm these results since there are only a few published articles evaluating the effect of adding different types of fillers to 3D-printed resins.

The clinical performance and durability of these materials are still questionable. Therefore, it is essential to investigate these composite materials in an environment similar to the oral cavity for more realistic results.

There are still challenges hindering the advancement of 3D printing in dentistry and its broader applications in the creation of fully functional parts, in contrast to temporary restorations, models, and prototypes. Nonetheless, the rapid and dynamic progress in recent digital manufacturing technologies presents a global sprint, posing an additional challenge to keep up with the state-of-the-art [109].

supervision, N.S., H.D. and J.H.; project administration, H.D. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available within the article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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