A literature review of current 3D printing materials in dentistry

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Introduction

The current generation of 3D printers are lighter, cheaper, and smaller, making them more accessible to the chairside digital dentist than ever before. 3D printers in general in the industrial and chairside setting can work with various types of materials including ceramics, polymers as well as metals.

Evidence presented in many studies show that an ideal material used for dental restorations is characterised by several properties related to durability, cost-effectiveness, and high performance (Rayyan et al, 2015). The range of materials used for provisional dental restorations should be non-toxic, biocompatible, inert, reasonably inexpensive, and aesthetic with change in colour or appearance after fabrication and complete resin polymerisation through curing (Balkenhol et al, 2009).

Furthermore, the material for dental restoration should be easy to manipulate, dimensionally stable under all conditions through sufficient strength and resilience, and easy to polish and repair. The material also needs to be chemically stable in the oral cavity by being insensitive to water sorption and dehydration; hence lead to a lack of expansion, shrinkage, or cracking (Vaidyanathan, Vaidyanathan and Arghavani, 2016).

Current materials

There is currently a wide range of materials used in the dental sector of 3D printing. These are summarised in Table 1, with a more in-depth description below of the most widely used materials specifically used in dentistry.

Current long-term 3D printed ceramics and current restorative resins

Considering the requirements for a non-toxic, biocompatible, and inert material, the range of materials available for use in 3D printed dental restorations are limited. On the other hand, the fabrication process of CAM milling manufacture requires high temperatures to convert ceramic materials into restorations suitable for placement in the mouth.

Ceramic 3D object is currently extremely limited in dentistry as it is manufactured by binding fine ceramic powder to a binder where a traditional process of ceramic restorations such as lithium dislocate is ground from ceramic blocks in chairside setting (Elizabeth, 2014).

Ceramic materials have several ideal properties for use in long term dental restorations such as lead-free, non-toxic and watertight; however, ceramic is a complex material to design a 3D object as it requires a number of considerations in design due to the

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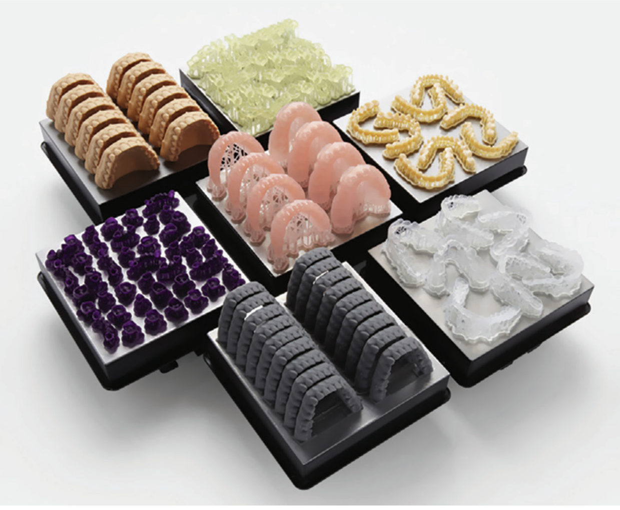

Figure 1: A variety of dental resin materials

Figure 2: Surgical guides are an example of the use of biocompatible resins used in dentistry

different structural changes the object may undergo during the finishing process.

The current 3D printers developed for dental applications are limited in their use of metals and ceramic materials to produce provisional dental restorations and are variable in the effect of print direction and accuracy (Brenes et al, 2020).

Most of the 3D printing materials used in dental restorations are polymers. Unlike the ceramics and metals, the chemical and physical properties of polymers are characterised by elasticity and tensile strength, which potentially provide high-performance and durability features required for use as a dental restorative material (Vaidyanathan, Vaidyanathan and Arghavani, 2016).

In orthodontic practice, 3D printing technologies have produced a wide array of prosthetics for dental restorations using polymer materials such as denture bases, artificial teeth, temporary crowns, bridge and crown facings, and implants (Oberoi et al, 2018; Stewart and Bagby, 2018).

Studies have reported the use of polymers in 3D printing technologies for dental applications, including implant fixture construction and intervention, maxillofacial reconstruction (Fernandes et al, 2016), metal bridges (Gebhardt et al, 2010). Other studies have reported the application of 3D printing in manufacturing dental prosthetics used in dentistry as orthodontic appliances (Al Mortadi et al, 2015) as well as the fitting surfaces and the frameworks of removable partial dentures (Carter et al, 2016).

The majority of polymers used as dental restorative materials such as resins are prepared using the methods of addition polymerisation, and in particular SLA and DLP technologies.

In dentistry, most dental resins are based on methacryrates due to relatively easy processing, costs, and aesthetics. Denture base materials are often supplied in either gel or powder-liquid form (Vaidyanathan, Vaidyanathan and Arghavani, 2016). The powder consists of acrylic or copolymer heads, an initiator like benzoyl peroxide, pigments (mercuric sulphide, cadmium sulphide, or dyes), and opacifiers where one the most effective being titanium dioxide. They also contain dyed synthetic fibres to stimulate the blood vessels underlying the oral mucosa, plasticisers, and inorganic particles such as glass fibres and beads or zirconium silicate (Abdulmohsen et al, 2016). Conversely, the liquid is composed of a monomer particularly methyl methacrylate, an accelerator, inhibitor, plasticiser, and a cross-linking agent.

For the gel form of denture base materials, it basically contains all the components of particle-liquid form but lacks chemical accelerators. The dental materials in gel form are commonly stored in the refrigerators since the material's shelf life is significantly affected by the amount of inhibitor present and its storage temperature (Hayden, 2015).

The current dental restorative materials applied in dentistry encompass photosensitive resins, as a polymer or particle-reinforced composite. Biocompatible polymers are widely used in dentistry for general restorative procedures and the most common 3D printers available to use chair side accommodate similar polymer-based 3D printing resins.

3D printed indirect dental restorations may involve either

Table 1: A list of materials used with 3D printing in dentistry grouped by manufacturing technology

Printing technology	Materials available
Polyjet printing	Photopolymers
Multi-jet printing	Plastics, ceramics and metals
Fused deposition modelling (FDM)	ABS, polypropylene, polycarbonates, polyesters
Selective laser sintering (SLS)	Plastics, ceramics and metals
Selective laser melting (SLM)	Metals
SLA / DLP	Photopolymers, plastics and ceramics

particle-reinforced composites, which are similar to the direct restorative composites, or fibre-reinforced composites (Hayden, 2015). The particle-reinforced composites are typically produced in the dental laboratories to improve the materials physical and mechanical properties such as density, elasticity, and strength using polymerisation process through heat and pressure.

For the fibre-reinforced fibreglass composites, they are produced using the same technology of making fibreglass sports equipment where fibre mesh is embedded in polymers (Peñate et al, 2015).

Dental resin-based composites are structures comprising a highly cross-linked matrix reinforced by a dispersion of glass ceramics and resin filter particles and/or short fibres (Vaidyanathan, Vaidyanathan, and Arghavani, 2016; Hayden, 2015). Many of these resin-based composites are now highly aesthetic with excellent translucency; hence, becoming the most popular of the aesthetic or tooth-coloured filling materials for use in dental clinics (Nayar, Bhuminathan and Bhat, 2015).

The resin materials can also be made in various consistencies by altering the glass particle size and consistency as well as the filler content, which allows easily manipulation and moulding to a tooth shape that is long lasting and durable once polymerised and full cured (Anusavice et al, 2013).

Polymeric resins are increasingly being used in dentistry for dental restorations, replacing tooth structure and missing tooth. One advantage of these polymeric resins is their ability to bond with other resins, directly to the tooth structure or to other restorative materials such as amalgam. For example, a denture base with attached denture could be used to restore chewing ability when all teeth are missing. Most of these restorative and prosthetic applications are based on photo-polymerisable methacrylate resins (Balkenhol et al, 2009; Peñate et al, 2015).

Several manufacturers are working on 3D printed resin versions of these same polymers for use in orthodontic clear aligners, denture bases, artificial teeth, surgical guides etc. As one of the largest vendors of 3D printing materials, Stratasys has been reported to have developed various types of dental 3D printing materials such as wax deposition modelling (WDM) and polyjet materials (Hayden, 2015).

The WDM are used to manufacture extremely accurate diagnostic wax-ups, paired with a removable wax-blend materials, referred as Truesupport, which can be removed at relatively low temperatures. It has been reported that Stratasys 3D printers using WDM produce the most accurate wax-ups in the dental industry.

Additionally, other 3D printing benefits of WDM include the ability to directly produce from digital files, no waste disposal issues, high-quality casting with minimal post-processing procedures, and TSCA-registered for safety.

Metals

A material commonly used in dentistry is metal which is popular for the use in strengthening restorations or incorporation into frameworks. This has led to these materials to be researched and developed for additive manufacture, mainly via selective laser sintering (SLS). Due to favourable levels of strength, cobalt-chromium and titanium metals have seen the most developments (Khaing, Fuh and Lu, 2001).

PEEK and nylon

A 3D printing material of recent development for use in dentistry has been the polyether materials such as polyether ether ketone (PEEK) and nylons for use in frameworks, to strengthen other materials and in 3D printed flexible dentures. These materials have a higher melting point and as such require a fused deposition modelling (FDM) printer with a high temperature, high precision nozzle tip (Dizon et al, 2018).

Like most 3D printing applications, the benefits of using 3D printed metals, peeks and nylons are many, including faster processing, less wasteful additive rather than subtractive manufacture as well as less manual labour and labour intensive processes.

However, there are limitations to the fabrication of restorations and frameworks using additive manufacturing. Rather than a homogenous structure, fabrication of these materials with 3D printing may result in porous structures that are inherently susceptible to staining, fracture and cracking (Dizon et al, 2018; Turner, Strong and Gold, 2014).

Proposed materials for exploration

Reinforced composites

The most popular and commonly used polymeric denture base material within dentistry is known as polymethylmethacrylate (PMMA). It is an extremely stable, transparent thermoplastic that does not decolour in the presence of UV light, and exhibits remarkable ageing properties (Anusavice et al, 2013).

PMMA is a resin-based material that has been used in 3D printing technologies to fabricate dental provisional restorations to protect oral structures such as pulpal tissue from thermal sensitivity, physio-mechanical pain, and bacterial contamination (Balkenhol et al, 2009). For the purposes of implant treatment, larger framework restorations and dentures, these PMMA 3D printed prostheses require high tensile and flexural strengths to be adequate for long term use. This underscores the importance of using materials with sufficient wear resistance and mechanical strength in orthodontic clinical practice (Abdulmohsen et al, 2016).

Conventional self-polymerising PMMA-based resin materials have been shown with a number of limitations, including high polymerisation shrinkage, water sorption and heat generation, and thus there are concerns that these limitations may pass over to 3D printed PMMA restorations (Patras et al, 2012).

Conventional fabrication using PMMA with a mixture of self-polymerising powder and liquid requires longer cure times than would be practical for a chairside setting (Patras et al, 2012). Considering one of the advantages of digital manufacturing is speed and efficiency, the use of 3D printed resin materials need to be both a viable alternative to conventional resin materials to support long-term dental applications in orthodontic practice (Peñate et al, 2015).

In particular, the recent advancements in routine dental practices with chairside CAD/CAM dentistry – such as 3D printed prosthodontic treatments – have been driven by the introduction of new processing technologies and dental materials.

A number of dental laboratory processes can be used to fabricate either fixed or removable dental prostheses such as crowns using a variety of dental materials (Chen et al, 2018). The advancement of both casting gold alloys and the associated accuracy in dental casting technologies has contributed to the persisting use of these prostheses (Bajraktarova-Valjakova et al, 2018).

New dental ceramic materials, such as glass ceramics as well as lithium silicates/disilicates and zirconia-based ceramics, have been successfully used by CAD/CAM enabled dental clinics, with several studies showing excellent long term success rates over 10 years (Miyazaki et al, 2013). Therefore, any new 3D printing material must be equal to or show alternate benefits to these well studied materials as well as biosafety and excellent aesthetics (Guess et al, 2011).

Zirconia-based materials

Among all dental ceramics, zirconia is the most popular biomaterial of choice in contemporary dental restorations in dentistry, particularly as a structural material for crowns, bridges, inserts, and implants (Miyazaki et al, 2013).

Zirconia (zirconium dioxide) provides optimum properties of a material for dental use, including tensile strength, fatigue resistance, and outstanding wear properties and biocompatibility (Della Bona, Pecho and Alessandretti, 2015).

Zirconium (Zr) has similar biochemical properties to titanium (Ti) metal, in which both are commonly used in implant dentistry as they lack the capacity to hinder the bone forming cells (osteoblasts) to facilitate osseointegration (Grandin, Berner and Dard, 2012).

Although zircornia is characterised as useful dental biomaterial, zirconia-based materials present several challenges in its dental practice applications as they are difficult to adhere to compared to other glass ceramics and composite materials (Della Bona, Pecho and Alessandretti, 2015).

The adhesive bond between ceramics and resin-based materials comes is through a combined micro mechanical and chemical interaction across the contact interface.

The overall bond strength is highly dependent on the surface treatment and surface energy through silination of the glass ceramic to increase its wettability (Della Bona, Pecho and Alessandretti, 2015; Della Bona et al, 2014).

It has been reported that of all types of acid-resistant bonding for ceramic dental restorations like glass ionomer (GI) and hydrophobic phosphate monomers containing 10-methacryloyloxydecyl-dihydrogen-phosphate(MDP) monomer, resin-based composite systems are the most popular and effective for high bond strength between a wide range of materials (Della Bona et al, 2014; Matinlinna, 2014).

Several studies have shown that quality and the durability of the micro-mechanical and/or chemical bond between glass ceramic and resin-based materials has a high impact on the long-term success rates of the prosthesis placed (Della

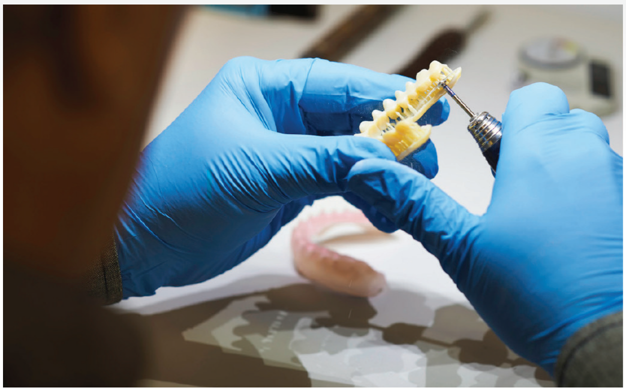

Figure 3: Temporary 3D printed teeth for use in a 3D printed denture

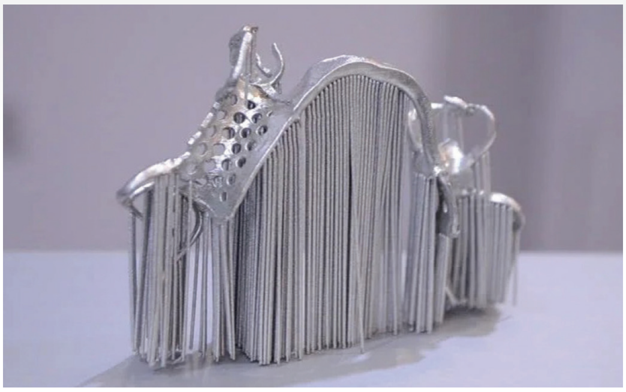

Figure 4: SLS 3D printed metal partial denture framework in CoCr

Bona and Kelly, 2008; Della Bona et al, 2007).

The non-reactive or acid-resistant surface of zirconia often poses a major concern related to poor adhesion or reduction of bond strength to other substrates (Della Bona et al, 2007).

Furthermore, chemically polymerised materials available for provisional dental restorations using either PMMA or resin-based composites have unique properties, which depend on the composition of the chemical monomer (Oba et al, 2014).

It has been demonstrated that different monomers vary in their chemical effects such as polymerisation shrinkage, exothermic reactions, marginal fit, colour stability, periodontal responses and fracture strength (Della Bona, Pecho and Alessandretti, 2015). The fracture strength of the provisional restorative materials relates to the mechanical properties (Kim and Watts, 2007).

In terms of mechanical strength and physical properties, the superiority of zirconia has largely been utilised for aesthetic dental restoratives, including crowns and bridges (Karaokutan, Sayin and Kara, 2015). Zirconia is typically veneered with feldspathic porcelain due to its insufficient translucency; nevertheless, the strength of the veneering porcelain has been indicated as inadequate in its function as a dental restorative (Miyazaki et al, 2013). The main clinical feature of failed zirconia-based restorations has been reported to be due to the wear and fracture of the laminated porcelain layer (Alp, Murat and Yilmaz, 2019). However, 'full contour' zirconia-based restorations without a porcelain layer have been shown to be problematic in some cases with wear of the opposing teeth causing gross fracture and ultimate total failure of the prosthesis (Della Bona, Pecho and Alessandretti, 2015; Cha et al, 2017).

In a study by Park and colleagues (2018), wear resistance of the 3D printed resin material was compared to the milled and the conventional self-cured resin materials opposing zirconia and metal antagonists (CoCr alloy). The basic component of all the three resin materials was similar but the study found differences in wear patterns between the materials and the casted cobalt-chromium (CoCr) alloy denture abraders.

This study suggested that the properties of PMMA-based resin materials could vary according to the fabrication methods used. When CoCr alloy metal abrader was applied in the 3D printed resins, cracks occurred as well as separation of the inter-layer bonds between layers of resin. This occurs as the bond that occurs between layers is weaker than the bond formed between each consecutive 3D printed layer (Park et al, 2018).

The results of the study by Park and colleagues (2018) indicated that the clinical use of 3D printing technologies presents a more convenient and promising technique fabricating provisional dental restorations and increase productivity in dentistry.

Limitations

Another limitation of 3D printed materials occurs as the surface of these materials are vulnerable to oxygen inhibition. As these prostheses could then be subject to immediate exposure to saliva through direct patient contact, the long-term mechanical strength and long-term colour stability could be reduced (Balkenhol et al, 2009). Conversely, blocks used in CAD/CAM systems are constructed with the optimum polymerisation conditions in place for complete and uniform polymerisation without inhibition.

Studies have shown that provisional dental restorations fabricated from materials in CAD blocks (monomethacrylate or dimethacrylate) have superior mechanical properties compared to those fabricated by both conventional and

3D printing technologies (Rayyan et al, 2014; Peñate et al, 2015).

A meta-analysis study by Astudillo-Rubio and colleagues (2018) found no significant difference between monomethacrylates (PMMA) and dimethacrylates (PEMA) in regard to their fracture strength, the ability to prevent the propagation of cracks. However, both groups vary according to the way they interrupt the cracks propagation where dimethacrylate materials are less susceptible to crack propagation in the presence of water (Abdulmohsen et al, 2016; Astudillo-Rubio et al, 2018).

PEMA may therefore be a potential avenue for increased strength in future 3D printing materials, which are less brittle than PMMA based materials (Rayyan et al, 2014; Peñate et al, 2015).

Over time, water absorption by non-cross-linked polymers subsequently weakens the material, which gradually diminishes the plasticising effect and the associated fracture toughness (Balkenhol et al, 2009).

Polymethylmethacylate (PMMA) resin remains one of the most commonly used materials for provisional dental restorations within dentistry due to greater flexural strength compared to PEMA. It has been reported that provisional dental restorations based on PMMA have many advantages, including:

- Colour stability
- Aesthetics
- Marginal fit
- Tensile
- Strength.

Furthermore, a number of PMMA dental models can be easily fabricated, polished, and repaired using the 3D printers, which not only reduces the production time but also allows multiple 3D copies to be produced without altering the dental anatomy (Alp, Murat and Yilmaz, 2019; Cha et al, 2017; Park et al, 2018).

However, as the studies above have shown, the flexural strength of PMMA decreases gradually over time, meaning current formulations may be inadequate for use as long-term restorations.

Studies have reported that the use of PMMA resin materials in dental restoration cause irritation of oral tissues, have low wear resistance, and high volume shrinkage due to leaching of the free monomer (Patras et al, 2012; Park et al, 2018).

Future developments with graphene and fibreglass reinforcement

Based on evidence presented in meta-analysis by Astudillo-Rubio and colleagues (2018), several studies reported that the structure of the provisional dental restorations could be reinforced with fibreglass or graphene to improve their flexural strength and fracture toughness, and this could be a possible route for 3D printer materials to provide more suitable long term restorations (Kim and Watts, 2004; Hamza, Johnston and Schricker, 2014).

These strengtheners may not make the material completely immune to fracture, but may simply change the fracture path to allow easy repair of chips rather than a full catastrophic fracture leading to ultimate failure of the prosthesis (Astudillo-Rubio et al, 2018). Therefore, if 3D printing resin can incorporate graphene or polyethylene fibres into the polymer matrix, this should result in a stronger restoration (Nayar, Ganesh and Santhosh, 2015; Gopichander, Halini Kumarai and Vasanthakumar, 2015).

Hamza, Johnston and Schricker (2014) assessed this reinforcement effect following the addition of 1% of the polyhedral oligomeric silsesquioxane (POSS). The results indicated that 'the reinforcement effect of POSS on flexural strength depended on the brand', suggesting that particular chemical composition of the provisional materials determines the ability of POSS to improve their mechanical properties, which may mean that some 3D printer resin brands may perform better than others even if based on similar material technology.

Conclusion

Current materials in 3D printing provide a wide range of possibilities for providing more predictable workflows as well as improving efficiency through less wasteful additive manufacturing in CAD/CAM procedures.

Incorporating a 3D printer and a digital workflow into a dental practice is challenging but the wide range of manufacturing options and materials available mean that the dentist should be well prepared to treat patients with a more predictable and cost effective treatment pathway.

As 3D printing continues to become a commonplace addition to chairside dental clinics, the evolution of these materials, in particular reinforced PMMA, resin incorporating zirconia and glass reinforced polymers offer increased speed and improved aesthetics that will likely replace subtractive manufacturing milling machines for most procedures (Nayar, Ganesh and Santhosh, 2015; Gopichander, Halini Kumarai and Vasanthakumar, 2015).

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