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Exploration of Materials Used in 3-Dimensional Printing for the Dental Industry

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Exploration of Materials Used in 3-Dimensional Printing for the Dental Industry

A Thesis Presented
by

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Abstract

A limiting factor in the digitization of dental devices is the availability of materials suitable for use in both dentistry and the new digital technologies. As a rapidly growing industry, three-dimensional printing (3DP) has the potential to disrupt traditional manufacturing and prototyping methods. A review of both restorative materials and the current 3DP materials has lead to a focus on fiber-reinforced composites in the exploration for a new 3DP material. In addition, another area worth exploring and investing in would be 3D bioprinting as it opens up the possibility of regenerative dentistry.

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First and foremost, I would like to thank Dr. Babak Sanii for his invaluable guidance and insight through the entirety of my thesis research. I would also like to thank Dr. Cameron Iverson for agreeing to be my second thesis reader.

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Chapter 1

Introduction

With major changes occurring the dental laboratories, a 2011 article by Richard van Noort concluded that with the digitization of dental devices, the dental materials community will face issues in providing materials suitable for use in both dentistry and the new technologies - potentially steering materials research in a new direction[1]. As a rapidly growing industry with an expanding opportunity set, three-dimensional printing (3DP) has applications in numerous markets, ranging from aerospace to medicine/dentistry[2]. Goldman Sachs and independent research company Canalys have both concluded that the sector is forecasted to grow from the 2013 market value of approximately USD$2.2 billion by at least 400% to a minimum of $11 billion in less than 10 years[2,3]. The combination of the limitless potential the technology offers and the decreasing cost of the machines support the increasing popularity of 3DP in the dental industry. Current 3DP companies that cater to the dental industry (3D Systems, EnvisionTec, Stratasys and its subsidiary Solidscape) offer their own set of machines and respective materials, all mainly geared towards the production of dental prosthetics/indirect restorations and models. A review of the general properties (physical and mechanical) of the three main material types (metals, ceramics and polymers) has lead to a focus on fiber-reinforced composites in the exploration for a new 3DP material. On the other hand, with consideration to advancements in tissue engineering, another area worth exploring and investing in would be 3D bioprinting[4,5,6] as it opens up the possibility of regenerative dentistry. Ultimately, the proposed material must fulfill both dental requirements (biocompatibility tests and standards) as well as 3DP requirements[7].

Chapter 2

Current Situation in Dentistry

Like any other branch of medicine, dentistry's overriding goal is to maintain or improve the patient's quality of life. A goal that can be satisfied by the preventive, corrective, and restorative types of practice. Though restorative dentistry occupies 50-60% of dentists in practice, procedures in all types of practice still involve the replacement or alteration of tooth structure for either aesthetic or functional reasons. However, the ability to produce desired results is limited by the dental material and the technical procedures available[8].

2.1 CAD/CAM Dentistry

Computer-aided design and computer-aided manufacturing (CAD/CAM) was introduced to the field with the goals of improving the design & creation of dental restorations, increasing production speed & convenience of the production processes, as well as reducing unit cost[9]. However, early efforts to incorporate CAD/CAM technology into clinical dentistry failed as the technology was found to be more complicated and harder to efficiently & practically utilize[10]. One of the major improvements that aided the development of current systems includes the commercialization of the Chairside Economical Restoration of Esthetic Ceramics (CEREC) system by the dental company Sirona in 1987[11]. By simplifying the entire process, CEREC was able to make CAD/CAM technology accessible to chairside clinical usage and it comes to no surprise that it is now the most utilized CAD/CAM system available[12].

Based on a combination of subtractive and additive processes, the system generally consists of 3 major components:

1. An acquisition device would scan the desired area, creating a digital impression with intraoral imaging.
2. This is then modified using the 3D CAD software to give a virtual restoration.
3. Using a selected material (commonly solid blocks of ceramic or composite resin), the restoration is produced by the milling machine.

Unlike the conventional method that requires traditional impressions, a temporary restoration, a second appointment and a 1-2 week period of communication between the clinic and dental laboratory - this entire procedure only takes around an hour[13].

Chapter 3

Introduction to 3D Printing

3.1 A Brief History

One of the earliest forms of additive manufacturing (AM) was rapid prototyping (RP) in the 1980s[14]. This is a group of techniques with the ability to quickly manufacture a scale model (prototype) from a digital scheme produced via CAD software. These prototypes allowed earlier product testing and evaluation before producing a finished product. Production of parts is usually accomplished via 3-dimensional printing (3DP) technology or additive layering manufacturing - the method of producing 3D solid objects from a digital file by the successive layering of material onto the printbed.

In the early days, the cost of printing was expensive and so the consumer market & interested industries were limited. With developments in technology, the cost has drastically decreased and has become increasingly available for the general market. Printers that used to cost more than $20,000 USD in 2010 can now be found for less than $1,000[15,16]. Aside from the ability to produce rapid prototypes, 3DP enables the production of products on demand and hyper-

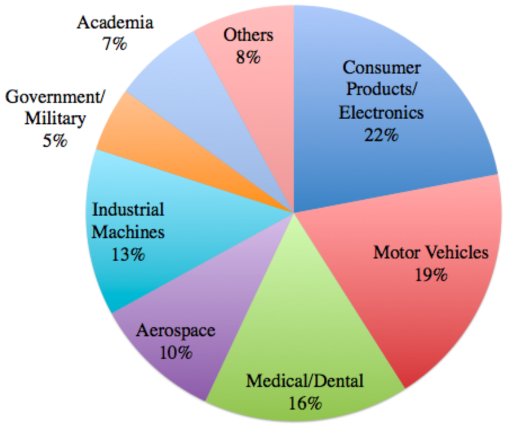


Figure 3.1: 2012 3D Printing revenues by end-market, reported as % of industry revenues. Adapted from Goldman Sachs report on *Creative Destruction*[2].

customization. It also has the potential to reduce costs for complex designs, and lower overhead costs for short-run parts and products[17].

Today, the field of 3DP continues to develop and its potential to revolutionize manufacturing is quickly becoming a reality as the applications of 3DP continue to spread to new industries such as cosmetics (Mink) and food (Foodini). The 2013 3DP market had an estimated value of \$2.2 billion within a \$30 billion design-to-manufacture value chain. According to Goldman Sachs, the market has a forecasted compound annual growth rate of 23% and 2021 revenues of at least \$11 billion[17].

In 2013, Goldman Sachs published a report that named 3D printing as one of the eight disruptive themes, whereby creative destruction was defined as "an open, free and capitalistic society innovation [with the ability to] disrupt certain industries, forcing established companies and business models to either adapt or die."[17] The classification of 3DP as a creative disruption to traditional manufacturing and prototyping methods is supported by the decreasing cost and increasing consumer use availability, improving materials and processes (increased

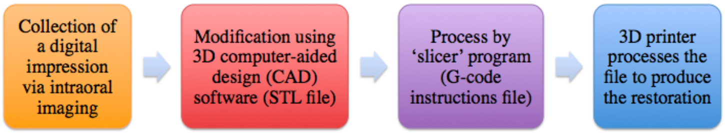


Figure 3.2: The process of manufacturing a 3DP-produced restoration[19].

resolution, faster build time), the feature of adaptability/hyper-customization, and lastly, the expanding opportunity set (Fig. 3.1). The key verticals of the 3DP market are shown to include aerospace, automotive, health care, and consumer industries. Conclusions of a detailed 180-page Credit Suisse report on 3DP indicated that “the four markets alone (which comprise around 50% of the AM market today) represent sufficient opportunity to sustain 20-30% annual revenue growth, bolstered by the technologyś transition from prototyping to end use parts and expansion into metals.”[18] In addition, with more than 14 thousand dental labs in the U.S., dental applications are said to contain the most potential in the health care vertical[18].

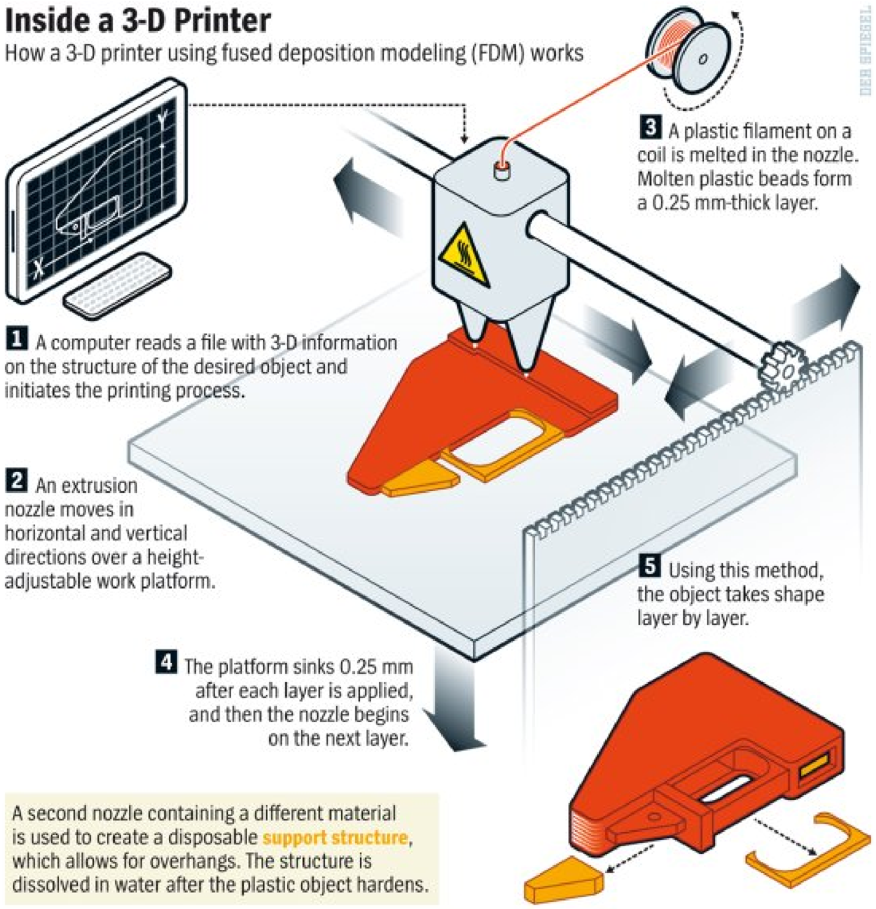
3.2 Methods and Technologies

The 3D model, creating using CAD and saved as an STL file, must be processed by a ’slicer’ program before it can be printed (Fig. 3.2). The ’slicer’ converts the model into virtual horizontal cross sections in the form of a G-code instructions file. Following the G-code instructions, the 3D printer builds the successive layers that are joined or automatically fused to create the final shape[19]. Higher resolution objects can be achieved by printing an oversized version and removing the excess via a subtractive process with resolution greater than the printer resolution (described by layer thickness). For 3DP, there is more than one method to realize the object and the difference between these lies in the way in which layers are deposited, the way in which materials are used and the type of materials that can be used. These can be categorized into 7 main types of: extrusion (fused deposition modeling, FDM), wire, granular (selective laser sintering, SLS), powder bed & inkjet head 3DP, laminated, and light polymerized (stereolithography, SLA)[20]. The 3 widely adopted 3DP technologies are FDM, SLS and SLA - all of which are briefly explained below[14,20,21]:

- FDM involves the direct application of molten plastic in closely packed lines via tiny nozzles (Fig. 3.3). Trademarked by Stratasys Inc., the technique is capable of creating objects with features as small as a fraction of a millimeter. The method has a wide range of materials including thermoplastics, eutectic materials, porcelain, and metal clay.
- Similarly, SLS also involves melting or softening material to produce the successive layers and utilizes comparable materials, though in powder form. Unlike FDM, this technique uses a high powder laser to selectively sinter powdered material, whilst the presence of untouched powder dismisses the need for a support structure.
- SLA employs a vat of liquid ultraviolet-sensitive photopolymer resin and an ultraviolet laser. For each layer, the laser beam traces a pattern, curing and solidifying the photopolymer. The technique is known for its speed, strength of produced objects (strong enough to be machined), and the high cost for both machine and material.

3.3 Dental 3D Printing

3DP companies marketing the dental industry are promoting the usage of 3DP as a method of reducing labor and materials cost while providing a higher clinical quality and consistency throughout the manufacturing process. The applications of such printers are geared towards dental restorations, models and



Inside a 3-D Printer

How a 3-D printer using fused deposition modeling (FDM) works

1 A computer reads a file with 3-D information on the structure of the desired object and initiates the printing process.

2 An extrusion nozzle moves in horizontal and vertical directions over a height-adjustable work platform.

3 A plastic filament on a coil is melted in the nozzle. Molten plastic beads form a 0.25 mm-thick layer.

4 The platform sinks 0.25 mm after each layer is applied, and then the nozzle begins on the next layer.

5 Using this method, the object takes shape layer by layer.

A second nozzle containing a different material is used to create a disposable **support structure**, which allows for overhangs. The structure is dissolved in water after the plastic object hardens.

Figure 3.3: The process of forming an object using FDM[22]

moulds. Companies that currently produce 3D printers for the dental industry include 3D Systems, EnvisionTec, Stratasys and its subsidiary Solidscape - all of which produce printers that manufacture waxups, drill guides, temporaries, partials, orthodontics, and models. Each company produces their own set of machines and materials. The technology employed by these machines can differ based on company. For instance, German manufacturer EnvisionTec uses the Scan, Spin, and Selectively Photocure (3SP$^{\text{TM}}$) Technology[23]. A review of the current dental printers that produce restorations indicate that regardless of company, they all employ the same method of SLA.

Chapter 4

Dental Restorations and their Materials

Dental materials can either be used for purely aesthetic purposes, or used to restore the function, integrity, and morphology of a missing tooth structure. Aside from classifying materials based on its basic composition (metal, ceramic or polymer), they can also be classified based on use, location of fabrication, or longevity of use[24]. As the broadest classification, location of fabrication simply indicates if the material is a direct or an indirect restoration. Direct restorations include amalgams, composites and glass ionomers, and are the malleable fillings that are placed and formed intraorally. Indirect restorations are fabricated on a model or cast of the patient's oral cavity, producing prostheses such as inlays, onlays, veneers, crowns... Based on the products of current dental 3DP systems, I will be focusing on indirect restorative materials.

Restorative materials can be categorized by 3 general types of: metals, ceramics, and polymers. As a wide spectrum of properties are present within each basic material type, generalizations in properties aid in the selection of a used materials. Since no one class of material possess all desired traits, it is not surprising that materials tend to be used in combination, an example of which would be the usage of ceramometals in indirect restorations. In the discussion of materials properties, it must be considered that physical properties of materials may either refer to the umbrella term for all properties, or refer more specifically to the "properties based on the laws of physica that describe mass, energy, force, light, heat, electricity, and other physical phenomena." [24]. For the purposes of this thesis, material properties will be categorized into two broad groups of physical (encompasses optical, thermal and electrical characteristics) and mechanical.

4.1 Physical Properties

There are numerous physical properties by which a material can be described by and no single, individual property can be used as a measure of quality. Thus, for the interests of this paper, only several properties will be explored. By doing so, a more holistic view on the physical requirements of materials can be provided and will also serve as a brief overview on the theory behind the selection of restorative materials.

- **Density** is dependent on the type of atoms present and the structure of the material. It is defined as the mass per volume (gm/cm^3). If prosthetics such as partial dentures are made of metals, the restoration has a tendency to become 'unseated' if ill-fitted to the remaining teeth. This occurs because metals have high atomic numbers and closely packed atoms in solids[24].
- **Boiling and melting points** are respectively defined as the temperature at which a liquid boils and the temperature at which a solid will melt.

These are specific to individual compounds and mixtures, and will help to determine the suitability of a material for the use in 3DP.

- **Vapor pressure** identifies a liquid's tendency to evaporate and become a gas. Materials such as glues and paints have high vapor pressure and are commonly useful as solvents. The evaporation of such materials leaves behind a thin layer of the desired viscous liquid. However, in other circumstances, this value can also help to identify potential issues associated with a used material. If a restoration is composed of a material with a high vapor pressure, such as methyl methacrylate (common component of composites), the resultant porosity and production of a weakened product (such as a denture) can be avoided by utilizing processing techniques that minimize the evaporation of said material[24].
- **Glass-transition temperature** (T_g), a value always lower than the melting temperature, only applies to polymers and represents the transition between the glassy and rubbery state. This value will help to indicate if a polymer is a suitable 3DP thermoplastic - a type of plastic material that is pliable above the T_g and fully crystallized below the value[7]. Thermoplastics are different from thermosets in that the transition is reversible[25].
- **Thermal conductivity** is the rate of heat flow through a material, dependent upon several factors including distance traveled, area through which travelled, and the difference in temperature between source and destination. Materials such as metals with high thermal conductivity are known as conductive materials and may induce pulpal sensitivity if placed in close proximity to the pulp - thus explaining why an insulating base is used beneath the metal restoration in situations when caries are deep. This value is tightly related to thermal diffusivity as both are important factors to consider in the prediction of thermal energy in a material[8,24].

- **Coefficient of thermal expansion** is a measure of the change in some volume with respect to the change in temperature. However, this state quantity α is more complicated than implied by the explanation as it may be a linear (α_L), area (α_L) or volumetric expansion (α_V). The interest in this quantity arises from the relationship between the coefficient of the material in relation to that of enamel and dentin. While today's materials more closely match the coefficient of thermal expansion of teeth, the early restorative materials of the 1950s such as polymethyl methacrylate shrink and expand 7 times more than tooth structures. In such situations where there is a great mismatch between material and teeth, the process of heating & cooling, and accompanying opening & closing of gaps between restoration and tooth, is known as percolation - a phenomenon that results in microleakage, tooth sensitivity, and recurrent decay[7,8].

- **Electrical conductivity** is an important factor during electrosurgery or electronic pulp testing, and is linked to stress corrosion. In terms of dental materials, a new amalgam filling may hurt when touched with a metal fork due to galvanic shock - a result of electricity flowing from the fork to the amalgam and through the pulp, as there is a difference in the potentials of the dissimilar metals[7,24].

- **Viscosity**, a handling characteristic, is the ability of a material to flow and is dependent on temperature. Measured as grams/meter•second or as poise (P), the viscosity of water at 20°C of 0.01 P or 1 centipoise (cP) provides a perspective on the values of viscosity. Impression materials have high viscosities of 100,000-1,000,000 cP that reflect its ability to flow poorly[26]. When considering a liquid's ability to wet a surface, a low viscosity is desired. Wetting a surface with an adhesive material (e.g. sealant) allows the formation of chemical and micromechanical bonding.

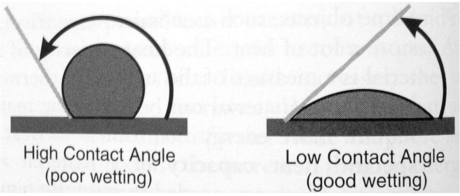


Figure 4.1: Illustration of the relationship between contact angle and ability to wet a surface[24].

It is measured by the determination of the contact angle of a liquid on a solid. An example in dentistry is the production of a plaster cast from an impression. If good wetting occurs, the fine details of the impression will be reproduced. In contrast, the bubbles that commonly result from poor wetting will lead to insufficient detail and an unusable cast (Fig. 4.1)[24]. Other factors that affect the contact angle include surface roughness, surface functional groups, impurities, porosity, and surface energy[27].

- **Abrasion resistance** is simply the wear resistance of dental restorations to food and opposing teeth, as well as that of natural teeth with opposing restorations. With harder materials more resistant to abrasion than softer materials, the hardness of a restorative material in comparison to that of teeth must be considered in the materials selection process. An ideal material is hard enough so that it does not wear away and yet soft enough to prevent excessive wear of opposing teeth - characteristics that have been referred to as the Goldilocks principle. Typically, the properties of a material need to fit within a certain range of values, not the maximum, to be more ideal for usage[24,26].

- **Solubility** is an important factor to consider since restorations are exposed to various aqueous fluids in the mouth. Restorative materials should not appreciably dissolve in the mouth as excessive solubility leads to loss of material and increased risk of recurrent decay. Solubility of a material is found via the immersion of a test sample and is the mass dissolved into the water (mass lost). Some dental cements have noticeable solubilities that are clinically significant[8,24].

- **Water sorption** is measured in a similar manner as solubility, where it is instead the weight gained, and is the degree of water absorption by a material. Analogous to the osmatic swelling of red blood cells, materials will also swell when water is absorbed. Determination of the solubility and water sorption of materials that concurrently dissolve and absorb water is difficult for obvious reasons[8,24].
- **Color**[8,28] is a subjective and complex experience that is a psychological response to a physical stimulus - the light waves detected by the photoreceptor cells of eyes. The color of light is determined by its wavelength (λ) in the visible region of 400-700 nm. According to the Trichromatic theory, color vision results from the ratio of activity among 3 different types of photoreceptor cone cells that are each sensitive to short, medium and long wavelengths. According to one of Grassmann's laws, the eye can distinguish differences in only three parameters of color - the dominant wavelength, luminous reflectance, and excitation purity. These three dimensions of color are otherwise respectively known as hue, brightness and saturation/chroma. The dominant wavelength is the distinctive characteristics that places a particular color in the spectrum. Luminous reflectance is a color's perceived intensity and is determined chiefly by the total amount of light reaching the eye - this value must not be confused with 'lightness', which is determined by the brightness of stimulus relative to its surroundings. A white standard is assigned a luminous reflectance of 100, and a black standard a value of 0. Lastly, the excitation purity is a color's purity or vividness of its hue, and can also be defined as the

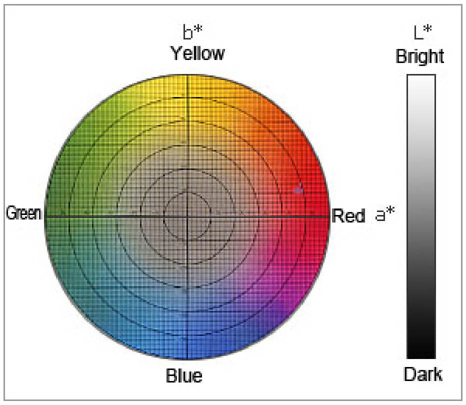


Figure 4.2: CIE1976L*a*b* color chart[29]

degree of difference from the achromatic color perception most resembling it, values of which range from 0 to 1.

Color is commonly measured as reflected light by instrumental or visual technics, both of which use 3 numbers to describe a color. Instrumental technique involves the measurement of color with a spectrophotometer or a colorimeter, whereby reflectance values and tabulated color-matching functions allow for the calculation of the tristimulus values (X, Y, Z) - that indicate the amount of the 3 primary colors required to additively produce the color in consideration - and the $L^*a^*b^*$ color space (Fig. 4.2).

The popular system for the visual determination of color is known as the Munsell Color system and involves matching the test object to color tabs, otherwise known as a shade guide (Fig. 4.3). Each tab has hue, chroma, and value (light or darkness of color) numbers assigned. Some manufacturers use a standard set.

In addition, the fluorescence of restorative materials must also be considered as the appearance of restorations is affected by resultant fluorescence caused by the interaction of teeth and dental materials with ultraviolet

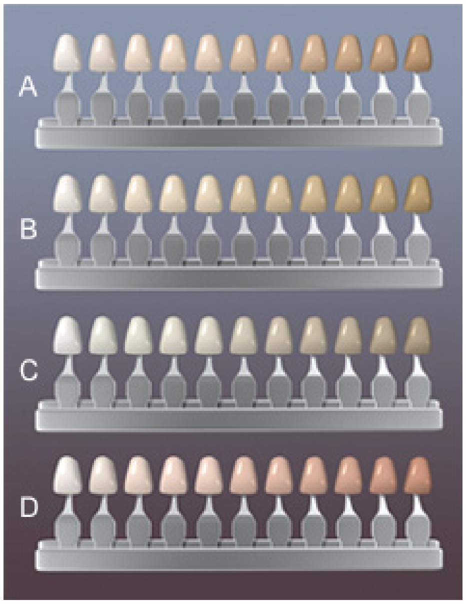


Figure 4.3: An example of a common shade guide with the four basic shade ranges of (A) reddish brown, (B) reddish yellow, (C) gray, and (D) reddish gray[30].

light (365 nm). If the fluorescence of a restorative material is inadequate, it will appear dark in certain lighting. Conversely, excessive fluorescence will make the material 'glow' in the same lighting. Thus, fluorescing agents such as rare earths (excluding toxic and weakly radioactive uranium) are added to some restorative materials and dental porcelains to mimic the natural appearance of teeth.

- **Interaction of material with x-rays** is an important factor in the clinical interpretation of radiographs. Radiolucent materials are not seen on radiographs and include some ceramic materials & denture acrylic resin. Radiopaque materials do appear on radiographs and examples include metal restorations. To facilitate the diagnosis of recurrent decay, manufacturers have formulated dental restorative materials that have the same radiopacity as enamel[24].

4.2 Mechanical Properties

Mechanical properties are the measured responses (plastic and elastic) of materials under pressure. These properties can give information on elastic deformation (proportional limit, resilience, elastic modulus, dynamic Young's modulus, shear modulus, flexibility, Poisson's ratio), plastic deformation (percent elongation, hardness), or a combination of the two types of deformation (toughness, yield strength). For full understanding of these properties, the concepts of stress and strain must first be considered.

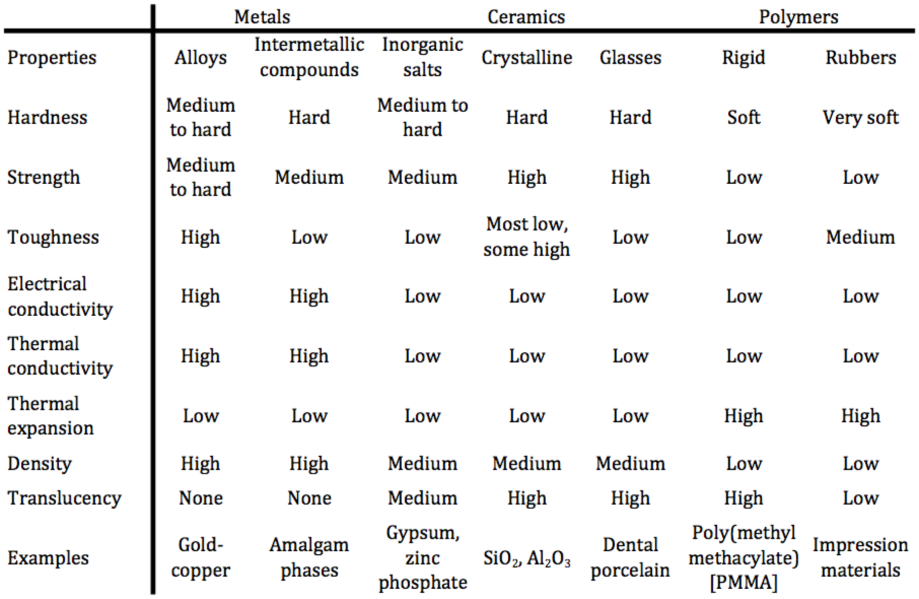
Stress is the force applied over an area of an object whilst strain is the distortion of an object in response to stress. There are 3 main types of stress present in dental structures under a force - tensile, compressive and shear. In situations where the total stress exceeds the strength of the material, the structure will collapse. In the oral environment, as the tensile strength of typically brittle restorative materials is commonly less than the shear strength values, tensile failure is more likely to occur than shear failure. In addition, shear failure would require the application of a force adjacent to the interface - a requirement that is difficult to fulfill even under experimental conditions.

The strength of a material can be defined in two ways: the ability to resist deformation (yield strength), and the stress required to cause a fracture (ultimate strength). For dental materials, when referring to the strength of a material, we typically refer to the ultimate strength. In describing material strength, the properties of proportional limit, elastic limit, yield strength, ultimate tensile strength, shear strength, compressive strength, and flexural strength are all used to provide a complete view.

Another important mechanical property is hardness - the resistance of a material to indentation or penetration. This can be determined by various methods, most of which consist of making a dent in the surface of a material with a specified amount of force in a controlled and reproducible manner, and then measuring the size of this indentation. The most frequently used tests for hardness are known by the names Barcol, Brinell, Rockwell, Shore, Vickers, and Knoop. For 'spongy' materials, such as impression materials and other elastic polymers, that do not form permanent indentations when tested for hardness using the above mentioned techniques, durometer measurements must instead be used as an indication of hardness. In this instance, a durometer measures how deep into the material a steel ball will sink as a representation of hardness[7,8,24,26].

4.3 Properties of an Ideal Dental Material

- Non-toxic and not biohazardous for obvious reason. The material will need to be registered by the USA Toxic Substances Control Act (TSCA)
- Lack of disposal concerns - if there were disposal concerns, the material would most likely be toxic or biohazardous.
- No shrinking, expanding or cracking. The material needs to be insensitive to dehydration and insoluble - essentially, chemically stable in the oral cavity.
- Nonirritating
- Biocompatible - must pass all biocompatibility tests, which are later described.
- Aesthetic - there needs to be sufficient translucency or transparency. Material needs to be capable of being tinted or pigmented without any change in color or appearance after fabrication.



	Metals		Ceramics			Polymers	
Properties	Alloys	Intermetallic compounds	Inorganic salts	Crystalline	Glasses	Rigid	Rubbers
Hardness	Medium to hard	Hard	Medium to hard	Hard	Hard	Soft	Very soft
Strength	Medium to hard	Medium	Medium	High	High	Low	Low
Toughness	High	Low	Low	Most low, some high	Low	Low	Medium
Electrical conductivity	High	High	Low	Low	Low	Low	Low
Thermal conductivity	High	High	Low	Low	Low	Low	Low
Thermal expansion	Low	Low	Low	Low	Low	High	High
Density	High	High	Medium	Medium	Medium	Low	Low
Translucency	None	None	Medium	High	High	High	Low
Examples	Gold-copper	Amalgam phases	Gypsum, zinc phosphate	SiO_2, Al_2O_3	Dental porcelain	Poly(methyl methacylate) [PMMA]	Impression materials

Figure 4.4: Comparison of the properties of the three basic material types[26]

- Easy to manipulate, and no production of toxic fumes or dust during the handling and manipulation steps.
- Reasonably inexpensive in terms of minimum materials cost and the processing method, which should not be complex.
- Photosensitive
- Tasteless, odorless
- Physical properties include sufficient strength and resilience, resistance to applied forces, and dimensional stability under all conditions.
- Easy to polish and easy to repair.

With the requirements for a non-toxic, biocompatible and inert material, the range of metals available for use as dental restorations is limited. Whilst ceramics require high firing temperatures, ceramic objects can be manufactured using

3DP to produce greenware (unfired pieces). For ceramic 3DP, the object is produced by binding fine ceramic powder to a binder, and then finished through the traditional process of pottery making (twice fired)[31]. Whilst ceramic restorations are lead-free, non-toxic, watertight...with numerous ideal properties[8], ceramics is a trickier material to design as the structural changes the object may undergo during the finishing process must be considered. Lastly, the 3D printers that have been developed for the dental industry do not currently use ceramic and thus, polymers will be the only general material type that will be considered in the exploration of new dental 3DP materials. By doing so, the conclusions of this thesis will be more applicable and practical.

In addition, the requirements of a restorative material depend on the specific restoration and its location within the oral cavity. For instance, the physical and mechanical requirements of a veneer are different from that of a dental crown. Thus, it would not be possible to determine a set of fixed properties that would apply to all restorations.

As for the general properties of materials, a comparison indicates that no one class possesses all desired traits (Fig. 4.4). Focusing on metals, although they do have the ideal mechanical properties (high hardness, strength and toughness), its high electrical conductivity and thermal conductivity are unideal. High electrical conductivity would lead to greater occurrences of galvanic shock, and high thermal conductivity increases the likelihood of discomfort from hot and cold conditions. Because of the difference in ideal properties across these materials, a new basic materials category of ‘composites’ was introduced in the late 1950s and early 1960s[32]. In materials science, the term refers to a physical mixture of any phases. As indicated, rigid polymers do not have ideal mechanical properties and so the proposed material will instead be a composite - however, in order to do so, the basics of polymers must first be understood.

4.4 Polymers

The behavior of polymers is fundamentally different from both ceramics and metals, this arises from the modulus of elasticity and the strength of polymers at a molecular level (Fig. 4.4). Since the introduction of acrylic polymers in 1937, this group of materials now includes vinyl acrylics, polystyrene, epoxies, silicones, polyethers, polycarbonates, polyvinylacetate-polyethylene[8]. Whilst the primary usage of polymers has been in prosthetics such as denture bases, their application has expanded to include artificial teeth, direct tooth restorations, crown and bridge facings, implants, impressions, and temporary crowns[24]. The general method of preparing polymers involves a series of chemical reactions by which the macromolecules (polymer) is formed from a large number of individual units (monomers), the two main methods of preparation are addition polymerization (free-radical, ring-opening, and ionic) and condensation polymerization[8]. Most resins are based on methacrylates due to relatively easy processing, the aesthetics, and cost. The characteristic biological, physical, aesthetic, and handling properties of polymers are the reason why the material has the potential to provide the balance of performance features and properties required for use as a dental restorative material[7].

Acrylic dental resins are derivatives of ethylene and contain a vinyl group. Two acrylic resin series that are of particular interest in dentistry are derived from acrylic acid and methacrylic acid, both of which undergo addition polymerization. Most resins are based on methacrylates, particularly methyl methacrylate which is a transparent liquid at room temperature and is a good organic solvent. Polymerization of this monomer can be completed via visible light, ultraviolet light, heat or use of a chemical initiator. Denture base materials are typically supplied in a powder-liquid or a gel form. The powder contains:

- Acrylic polymer or copolymer beads

- An initiator such as benzoyl peroxide
- Pigments (mercuric sulfide, cadmium sulfide...) and/or dyes
- Opacifiers, most effective one being titanium dioxide
- Dyed synthetic fibers to stimulate the blood vessels underlying the oral mucosa
- Plasticizers
- Inorganic particles such as glass fibers and beads or zirconium silicate

On the other hand, the liquid is composed of the monomer (typically methyl methacrylate), inhibitor, accelerator, plasticizer, and a cross-linking agent. The gel form of denture base materials essentially contains all the same components as the powder-liquid form, but lacks chemical accelerators. For this form, the storage temperature and amount of inhibitor present greatly affects the shelf life of the material - thus, these are commonly stored in the refrigerator[8].

Fixed indirect restorations can be made from either particle-reinforced composites, which are very similar to the direct restorative composites, or fiber-reinforced composites. Whilst particle-reinforced composites are processed in the dental labs to improve density and polymerization via heat and pressure, the latter is produced via the same technology used to make fiberglass sports equipment (embedding of fiber mesh in polymers)[24]. As fiber-reinforced composites are relatively new, the material type still requires more long-term clinical data. As shown by the direction of dental research of polymers, these types of reinforced composites is an area of particular interest due to the improved physical and mechanical properties.

Chapter 5

Biocompatibility & Standards for Dental Materials

The selection of restorative materials is not only based on the physical and mechanical properties, but is also based on its survival performance. Typically, selected materials have known long-term survival performances that are supported by clinical experience. For materials without clinical survival data over a minimum period of 3-years, reliable short-term (less than 3-years) clinical data must first be evaluated. If such data is absent, the material has to be evaluated based on its fulfillment of the requirements stated by dental materials specifications and standards. In the circumstance that these are all met, then it can be said that the material will perform satisfactorily if properly utilized. In the process of proposing new materials, the biocompatibility of the material must first be determined before investigating if the material complies with the regulations and standards.

Cellular responses to a restorative material are dependent upon the interactions that arise from the biological interface created when the material is placed in the body. With numerous potential reactions, these have classically been divided into the categories of toxic, inflammatory, allergic, and mutagenic reactions. These adverse effects can be determined by the two key properties of the rate of degradation and the material's surface characteristics.

Within the States, materials are governed by the Council on Dental Materials, Instruments, and Equipment (later called the Council on Scientific Affairs) of the American National Standards Institute/American Dental Association (ANSI/ADA), which approved Document No. 41 for Recommended Standard Practices for Biological Evaluation of Dental Materials in 1972. In 1982 the document was improved to include mutagenicity tests and changed to a three tier linear paradigm materials screening of initial/primary, secondary, and usage tests. Initial tests are often *in vitro* in nature and consists of: cytotoxicity assays, mutagenesis assays, detection of immune responses, complement activation assays, hemolysis assays, oral and intraperitoneal LD50 assays. Materials with sufficiently favorable responses from primary tests will then be evaluated by secondary tests, and likewise for usage tests - both of which are *in vivo* in nature.

The international standard for biocompatibility tests is governed by the International Standards Organization (ISO) Standard 10993. Unlike ANSI/ADA Document No. 41 that is limited to dental devices, the ISO 10993 standard covers all biomedical devices and of 2002, the standard consisted of 16 parts that each addressed a different aspect of biological testing.

Aside from passing the three tiers of biocompatibility tests, dental restorative materials must also gain the Seal of Acceptance of the American Dental

Association (ADA) and pass the U.S. Food and Drug Administration (FDA) regulations for usage in the USA. Usage internationally is granted by meeting the ISO standards[7,8,26].

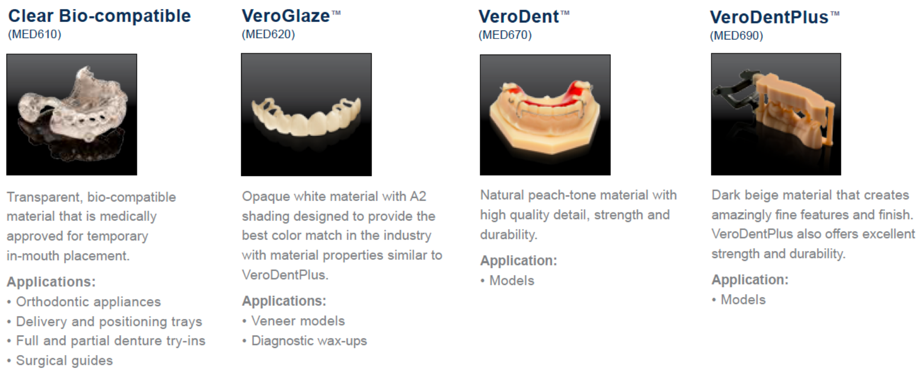
Chapter 6

Dental 3DP Materials

6.1 Current Materials

A review of the materials offered by Stratasys, 3D Systems and EnvisionTec indicate that the all the current materials are photosensitive resins - thus confirming that the focus on polymers and composites would indeed make the conclusions of this thesis more applicable.

Currently the largest vendor of 3DP in terms of unit shipments[17], Stratasys has developed two major types of dental 3DP materials known as wax deposition modeling (WDM) and PolyJet materials[33]. WDM is used to produce extremely precise diagnostic wax-ups, paired with a removable wax-blend material (termed TrueSupport) that can be easily removed at relatively low temperatures. Stratasys printers using WDM are said to produce the most accurate wax-ups in the industry, but other printing benefits of WDM include direct production from digital files, high-quality casting with minimal post-processing, no waste disposal issues, safe and TSCA-registered. As for the PolyJet materials, the technology is a form of stereolithography and involves the application



Clear Bio-compatible
(MED610)

Transparent, bio-compatible material that is medically approved for temporary in-mouth placement.

Applications:
- Orthodontic appliances
- Delivery and positioning trays
- Full and partial denture try-ins
- Surgical guides

VeroGlaze™
(MED620)

Opaque white material with A2 shading designed to provide the best color match in the industry with material properties similar to VeroDentPlus.

Applications:
- Veneer models
- Diagnostic wax-ups

VeroDent™
(MED670)

Natural peach-tone material with high quality detail, strength and durability.

Application:
- Models

VeroDentPlus™
(MED690)

Dark beige material that creates amazingly fine features and finish. VeroDentPlus also offers excellent strength and durability.

Application:
- Models

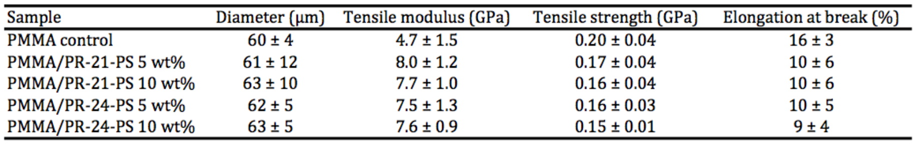
Figure 6.1: A comparison of the four dental 3DP material available from Stratasys[33]

of photopolymer onto a build tray. With a ability to support a wide range of materials, dental PolyJet technology consists of four specifically engineered dental materials (VeroDent, VeroDentplus, VeroGlaze, bio-compatible material MED610). Comparison of the materials (Fig. 6.1) demonstrates that whilst all are photosensitive resins, the applications differ based on the composition of the resin.

6.2 Proposed Materials to be explored

6.2.1 Reinforced Composites

Also known by its commercial names Plexiglas and Acrylite[34], poly(methyl methacrylate) (PMMA) is a transparent thermoplastic that is extremely stable. It doesn't decolorize in the presence of ultraviolet light, and also exhibits remarkable aging properties[7]. Commonly used a denture base material, it remains a popular and commonly used material within dentistry. As stated by Alla et al., the reasons for its popularity included "its ease of processing, low cost, lightweight, excellent aesthetic properties, low water sorption and solu-



Sample	Diameter (μm)	Tensile modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)
PMMA control	60 ± 4	4.7 ± 1.5	0.20 ± 0.04	16 ± 3
PMMA/PR-21-PS 5 wt%	61 ± 12	8.0 ± 1.2	0.17 ± 0.04	10 ± 6
PMMA/PR-21-PS 10 wt%	63 ± 10	7.7 ± 1.0	0.16 ± 0.04	10 ± 6
PMMA/PR-24-PS 5 wt%	62 ± 5	7.5 ± 1.3	0.16 ± 0.03	10 ± 5
PMMA/PR-24-PS 10 wt%	63 ± 5	7.6 ± 0.9	0.15 ± 0.01	9 ± 4

Figure 6.2: Comparison of the mechanical properties of the PMMA/CNF composite fibers[37], whereby PR-21-PS and PR-24-PS are two grades CNFs that were obtained from Applied Sciences Inc., of Cedarville, OH. Out of the two, PR-21-PS has the larger diameter.

bility, and ability to be repaired easily."[35] Like any other material, it is not perfect in every aspect and one of the main drawbacks is its poor mechanical performance that leads to increased likelihood of failure during clinical service (Fig. 4.4). Attempts to address the inferior mechanical properties resulted in the research of reinforced PMMA composites[35].

Since 1986 when Ruyter et al. published an article on the development of carbon/graphite fiber reinforced PMMA[36], improvements in technology and techniques have allowed for the development of better composites. In 2004, Zeng and colleagues modified PMMA with single wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT) to produce nanocomposites with enhanced properties (mechanical and electrical, Fig. 6.2). The SWNT/PMMA composites were processed using a combination of solvent casting and melt mixing, whilst the MWNT/PMMA composites were also processed by melt blending. Between the two grades of carbon nano fibers (CNF), the study indicated no difference in the resultant mechanical and thermal reinforcements of the PMMA matrix. As commercial grades of PMMA have T_g values ranging from 85 to 165°C, the produced PMMA/CNF composites have a maximum T_g value of around 200°C - a temperature at which current 3DP machines are capable of operating at[37].

With previous research on similar fiber-reinforced PMMA conducted by Ruyter in 1986, this type of composite may potentially already have the neces-

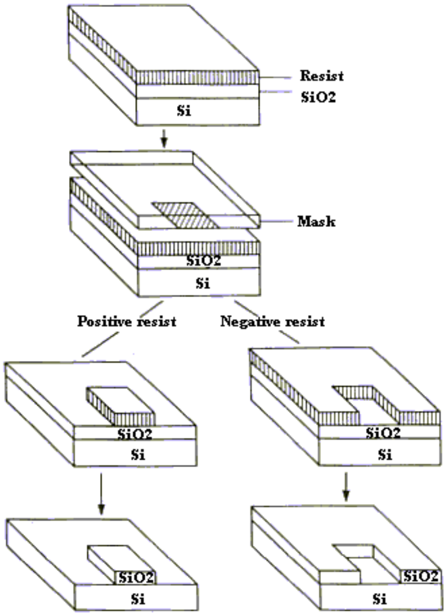
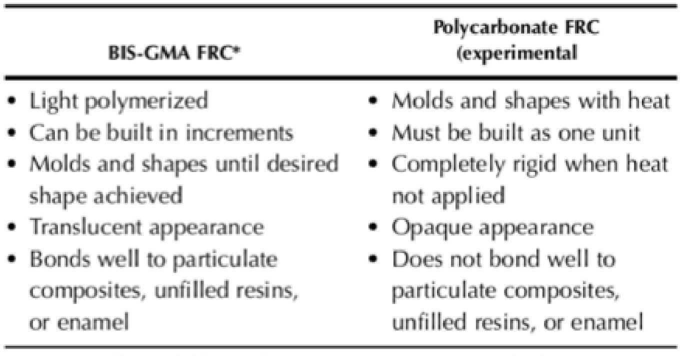


Figure 6.3: Diagram illustrating the difference between a positive (left) and a negative (right) photoresist[38].

sary clinical data that would enable its clinical usage as a restorative material. The only issue would be the conversion of the composite into forms suitable for usage with current SLA dental printers and future printers. For instance, the composite will need to be produced in the form of spools/filaments for use with future FDM printers, or into powder form for use with future SLS printers. As for use with current printers, the main issue with this composite is that as a positive photoresist (Fig. 6.3), PMMA is a light-sensitive material that becomes soluble when exposed to ultraviolet light[39] and is thus incompatible with the current dental 3DP technology. Therefore, PMMA would have be replaced by a photosensitive resin in the PMMA/CNF matrix to enable its usage with the SLA printers. A photopolymer that could be used is methacrylate bis-GMA - a dimethacrylate monomer that is commonly used in composite resins[40].

A comparison of PMMA and Bis-GMA's handling characteristics indicate



BIS-GMA FRC*	Polycarbonate FRC (experimental
• Light polymerized	• Molds and shapes with heat
• Can be built in increments	• Must be built as one unit
• Molds and shapes until desired shape achieved	• Completely rigid when heat not applied
• Translucent appearance	• Opaque appearance
• Bonds well to particulate composites, unfilled resins, or enamel	• Does not bond well to particulate composites, unfilled resins, or enamel

Figure 6.4: Comparison of handling characteristics of fiber-reinforced composites (FRC)[41]. *Commercially available as FibreKor (Jeneric/Pentron) as of February 1997, and as Splint-It (Jeneric/Pentron) as of September, 1997.

that the latter is more suitable for use in both 3DP and composites (Fig. 6.4). However, with concerns on the widespread use of bisphenol A (BPA) and its adverse health effects, it is important to state that the American Dental Association has addressed the issue - materials made with bis-GMA do not degrade into BPA after coming into contact with enzymes in the saliva[42].

In addition, since polymers are easy to manipulate and 3DP offers hyper-customization, it would be worthwhile to look into developing 3DP dental systems that would enable the selection of color, in a manner similar to a digital shade guide, or the matching of color based on the patient's teeth.

6.2.2 Bioprinting

On a different note, if developments in 3D printing for medical science and research are combined with advancements in tissue engineering, regenerative dentistry may be realized through 3DP. This field of 3DP is known as 3D bioprinting and from a medical science perspective, it would allow for the production of replacement human tissues, organs, and blood vessels - ultimately leading to the potential elimination of the need for organ donors and possibility of having on-demand human tissue for use in surgeries.

Tissue engineering of the tooth crown, root, and periodontium was already investigated in 2006 by Hu et al.[43] and researchers have started to look into 3D dental bioprinting technology using human dental pulp cells mixture as a bioink[44].

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