



# Three-Dimensional Printing Materials for Maxillofacial Structure Development: A Review

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## ABSTRACT

A 3D printing is an additive manufacturing technique that has wide applications in various fields, including healthcare, especially in producing complex and entangled geometries like maxillofacial structures. Various 3D printing techniques are available; however, the range of biomaterials satisfying the printability criteria is limited. Generally, 3D printing biomaterials fall under classes as such a metals, ceramics, polymers, composites and hydrogels. In maxillofacial structure development, 3D printing is used for manufacturing surgical guides, models, splints, patient-specific implants and facial prostheses. This review describes various 3D printable materials and a brief overview of 3D printing techniques, specifically explored in maxillofacial structure-related applications. 3D bioprinting materials are beyond the scope of this review.

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## INTRODUCTION

This is an era witnessing the evolution of manufacturing paradigms from mass-produced to custom-made products; from subtractive to additive manufacturing approaches and from static to dynamic shape morphing materials. In three-dimensional printing (3DP), an object is typically created by layer-by-layer addition of materials in a predetermined form or shape with digital data sets and computer-aided designing using a 3D printer. 3D printing has a wide range of applications in various industries, from aerospace to healthcare. This technology has synonyms like 'Rapid Prototyping' (RP), or 'Solid Free Form Technology' (SFF).<sup>1</sup> ASTM F2792-12a has classified additive manufacturing technologies into 7 main categories: binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination and vat photopolymerization.<sup>2</sup>

Maxillofacial region is an intricate network of various complex anatomical structures. This region has a rich supply of blood vessels and nerves, and its proximity and connection to structures like brain cause treatment of any serious injury of the maxillofacial region risky, and complete recovery is often challenging. Interindividual variability in this region

with respect to contour and dimensions makes it difficult to standardize the products manufactured for treatment, which may lead to profound differences in a person's appearance. Defects in maxillofacial region can have a physical and psychological impact on patients. Etiologies of such defects can be congenital, due to genetic abnormalities, developmental disturbances or acquired due to trauma or surgery.<sup>3</sup> The pioneering usage of Stereolithography (SL) in an oral and maxillofacial surgery was reported by Brix and Lambercht in 1985. In 1990, Mankovich *et al.* used SL for treating patients with craniofacial deformities.<sup>4</sup>

Integration of 3D printing or rapid prototyping techniques in various subfields of maxillofacial surgery like trauma surgery, orthognathic surgery, implant surgery, and reconstructive surgery helped develop evidence-based treatment planning, educate students and patients, and reduce overall treatment time, more predictable and precise outcomes and cost-effective treatments.<sup>5</sup> Development of 3D bioprinting made it possible to develop functional tissues for maxillofacial tissue regeneration. Advancement in 3D printable smart materials, which can alter and transform shapes and functions with dynamic changes in internal milieu led to the emergence of four-dimensional printing.<sup>6</sup>

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The term 4D printing was first coined by Skylar Tibbitts in 2012.<sup>7</sup> Materials like metals and alloys, polymers, ceramics, composites, bioprintable ink with or without cells and cellular components are commonly used for additive manufacturing.<sup>2</sup>

**STEPS IN FABRICATION OF A 3D PRINTED MODEL (FIGURE 1)**

Image acquisition of patient using modalities like computed tomography (CT), 3D surface scanning like photogrammetry, CT Angiography, ultrasound (US) or any other volumetric imaging to obtain data in Digital Imaging and Communications in Medicine (DICOM) file.<sup>8</sup>

- Segmentation of DICOM into a 3D CAD file format like STL (Standard Tessellation Language or STereoLithography), as required by the 3D printer.
- Primary processing and redundancy of STL data.
- Creation of virtual 3D model (3D Biomodelling) for proper

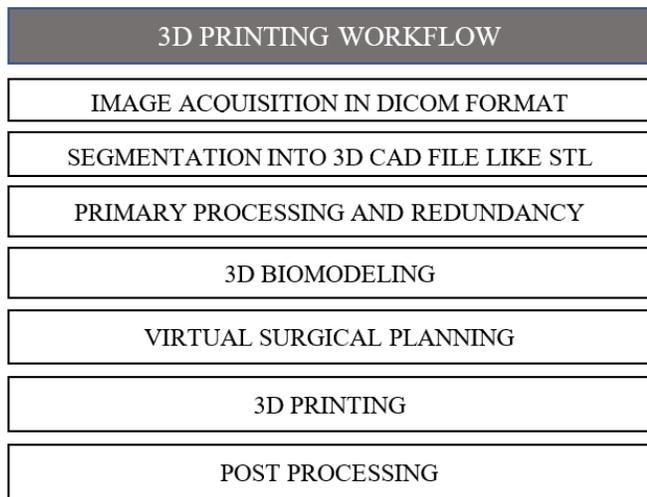


Figure 1: Workflow of 3D printing

visualization and demarcation of region of interest, for necessary modifications and virtual surgical planning by concerned medical experts.

- 3D printing of final model using appropriate technologies.
- Post-processing of the 3D model.<sup>9</sup>

**APPLICATIONS OF 3D PRINTING TECHNOLOGY IN MAXILLOFACIAL SURGERY**

Preoperative treatment planning; maxillofacial reconstruction, facial skin regeneration, maxillofacial fracture treatment, virtual planning and fabrication of surgical guides and templates for guided implant placement, fabrication of custom prosthesis for orthognathic surgery and dentofacial deformities, customized temporomandibular joint reconstruction, maxillofacial tissue-engineered scaffolds, nasal reconstruction, customized medical protective equipment, simulation models for training students, and educational tool for patients. 3D printing technology is specifically based on its application in craniomaxillofacial surgery into four types: I- Contour models, II – Guides, III- Splints and IV- Implants.<sup>4</sup> Additionally, Facial epithesis is fabricated for purposes like auricular reconstruction.<sup>5</sup>

3D printing materials is a rapidly progressing field and is giving tremendous advancements in applying rapid prototyping technologies to other dimensions. 3D printing materials used for maxillofacial structure development are mostly the same as those used in conventional orthopedic applications. Based on the end purpose and desired properties, 3D printable materials are selected; accordingly, suitable fabrication technique is also determined. One material itself can be used in different 3D printing techniques. Some of the general properties required for 3D printable ink materials are mentioned in Figure 2.

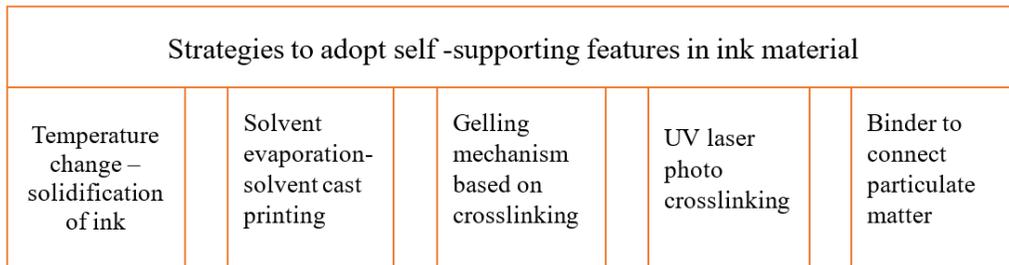


Figure 2: General properties of 3D printable materials

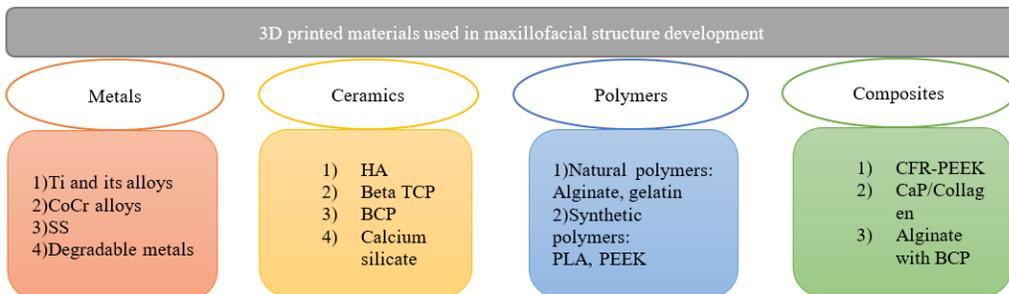


Figure: 3D printed material classification

In general, printable biomaterials can be categorised into four types: (Figure 3)

1. Metals
  - Non-biodegradable Metals -Titanium (Ti) and its alloys, Cobalt-Chromium alloys, Stainless Steel (SS)
  - Biodegradable metals- Magnesium (Mg) -based, Zinc (Zn)- based, Iron (Fe)-based
  - *Ceramics*<sup>4,27,28,34</sup>: Tricalcium phosphate (TCP), Calcium phosphate (CaP), Hydroxyapatite (HAP), bioglass, Farringtonite powder ( $Mg_3((PO)_4)_2$ )
2. Polymers<sup>4,27,28,34</sup>
  - *Natural*: Gelatin, Matrigel, Alginate, Fibrin, Biogenic polyphosphate, biogenic silica, Hydrogels like Starch and Dextran
  - *Synthetic*: Polycaprolactone (PCL), Poly-L-lactide (PLLA), poly-lactic-co-glycolic acid (PLGA), PEG, Perfluorodecalin (PFD), PEGDA, Polyetherketoneketone (PEEK), Ultra High Molecular Weight Polyethylene (UHMWPE), Poly Methyl Methacrylate (PMMA), Silicon elastomer
3. *Composites*<sup>4,34</sup>: D, L-PLGA/L-PLA, Alginate with BCP, Nanohydroxyapatite/polyamide (n-HA/PA), Calcium Phosphate with Collagen

## OVERVIEW OF RAPID PROTOTYPING TECHNIQUES WITH MATERIALS USED

### Stereolithography (SLA)

Ultraviolet (UV) laser beam is projected onto a bath of liquid photopolymer resin followed by decremental movement of the first formed layer and then the next layer is formed. This is a type of vat polymerisation technique. Process continues till the required configuration is met. Technique is relatively less time consuming and has high product resolution. This technique can be effectively used in the reconstruction of internal frameworks, and creation of larger objects. Lack of surface smoothness, limited shelf life and vat life, removal of support material, overcuring and compromised mechanical strength, and only applicable to costly light-curable resin are some of its limitations. Materials used in this technique must be to some degree brittle and light like acrylic and epoxies.<sup>6</sup> Beta-TCP, PEGDA, methacrylate monomers, epoxy resin can be printed using this technique.<sup>12</sup> Application includes fabrication of surgical guides like implant drill guides and templates.

### Extrusion-based Bioprinting

Or direct writing. In this technique, bioink which is a thermoplastic material, is extruded through a nozzle by mechanical (piston or screw) or pneumatic force to form continuous microfilaments deposited and solidified on a substrate.<sup>9</sup> Basic principle of this technique is loading and liquefaction of printed material. Fabrication process is safe and simple because no powder, laser or solvent is used. The path of nozzle is pre-programmed to the desired configuration by a scanner system. This is the most commonly used approach and includes mainly 2 techniques: Fused deposition modelling (FDM) and Fused filament fabrication (FFF). Equipment is relatively inexpensive and highly versatile. High porosity

and good mechanical strength are some of the advantages. Suitable for surgical guide, scaffold and implant fabrication. Multiple printheads are also available, which can be employed for printing different materials simultaneously. Materials like thermoplastic polymers, composites, and metal alloys with low melting point can be successfully printed using this technique. PLA, PLGA, PEEK, Bioglass, BCP, Wallastonite, magnesium is some of the materials printed using extrusion-based techniques.<sup>13</sup>

### Laser Sintering

Comes under powder bed fusion of RP technologies. ‘Selective laser sintering (SLS)’, ‘selective laser melting (SLM)’ and ‘direct metal laser sintering (DMLS)’ are the various techniques with relatively same principles coming under this category. This process is also based on layer-by-layer addition of substrate and fusing them with high energy laser like Argon, CO<sub>2</sub>, Nd: YAG and others, which is selected based on the absorptivity of material to be printed. Mechanical properties are maintained in this technique which helps in functional prototyping. Metal, ceramic and polymer powders can be printed using this technique.<sup>6</sup> Some of the limitations of this technique are polymer is to be in powder form and not suitable for the fabrication of larger parts. Some of its applications include the fabrication of surgical osteotomy guides, titanium orbital floors, sub-periosteal dental implants, and custom-made cranial plates.

### Selective Electron Beam Melting

Highly energetic fast moving electron beams are used to selectively bombard powder material loaded in a build tank. Powder is then allowed to melt layer-by-layer following the cross-sectional profile of the material to be printed. Compared to lasers, electron beam has the advantages of high material absorption rate, high focusing and printing resolution in the order of nanometers.<sup>11</sup>

### Inkjet Printing

Droplets are ejected from jets by either piezoelectric, electrostatic or thermal actuation. This droplet falls on a substrate, spreads, fuses and solvent evaporate, and then a dried film is formed. Inkjet printers have high droplet size, deposition rate control, accuracy and resolution. This technique is highly used in bioprinting due to its compatibility with living materials.<sup>12</sup> Use of high viscosity materials, blocking of printhead nozzle due to higher cell density, inability to produce continuous flow are some of the limitations of this process.<sup>11</sup>

### Poly-jet and Multi-jet Printing

Both techniques use photopolymers; and is cured by UV light. Layers are built one over the other. Same material or different materials can be printed simultaneously by loading them into the multiple jetting heads. Therefore, complex anatomical details can be easily printed using this technique.<sup>11</sup>

### Digital Light Processing

This is a technique similar to SLA printing, except that a light projection system is used instead of UV laser beam.<sup>6,11</sup>

## MATERIALS USED IN 3D PRINTING

### Metals

RP technologies like SLM, SLS and EBM, atomic diffusion additive manufacturing (ADAM), nanoparticle Jetting (NPJ), and Inkjet3D printing were used for metal 3D printing.<sup>14</sup> Advent of direct metal laser sintering (DMLS)/Laser Engineered Net Shaping (LENS)/Laser Rapid Forming (LRF) technique escalated the application of metals in 3D printing. Metals with mechanic properties such as higher yield strength, toughness, hardness, wear resistance, biocompatibility is mainly used. Metallic biomaterials are generally 3D printed in powder form or by using a binder polymer. Main applications of metallic biomaterials are related to bone tissues.

Conventional metallic biomaterials applied in maxillofacial structures are mainly Ti, Co-Cr, SS, owing to their excellent biocompatibility and mechanical strength. However, the elastic modulus of these materials varies greatly from natural bone, resulting in stress shielding. Porous metallic implants were then developed to overcome this limitation. 3D printing technologies were greatly explored to achieve porous architecture. All these metals are non-biodegradable, necessitating more than one surgical intervention for their corrections and removal after implantation; led to the advent of using biodegradable biometals like Mg, Zn, and Fe. This shift is summarised in Figure 4.

### Titanium and its Alloys

Due to low electrical conductivity and passive oxide layer formation these materials exhibit excellent biocompatibility and high corrosion resistance. Along with these properties and its osseointegrative nature, this is a material of choice for cranioplasty. Titanium implants are mainly fabricated from CP-Ti (commercially pure Ti) and Ti-64 (Ti6Al4V) alloy. ASTM classified Ti alloys into 5 grades, of which Grade 1–4 comes under CP-Ti and Grade 5 comes under Ti6Al4V. Surgical grade 5 Ti is most biocompatible with elastic modulus of 114-120GPa, which is extremely high concerning that of 0.5GPa in cancellous and 17GPa in cortical bone. As a result of which, stress shielding occurs, leading to bone resorption. Another problem with Ti6Al4V is the release of Al and V ions into systemic circulation, causing cytotoxicity. Corrosion product of this alloy- ‘rutile’ composed mainly of TiO<sub>2</sub> can potentially affect heart, lungs and liver.<sup>15</sup> To avoid such unforeseen effects on using long-term Ti implants more stable titania coating is

given. Ti6Al4V has poor wear resistance. So surface treatment is mandatory. Ti provides greater mechanical strength and can be used to immobilize fracture parts. To overcome stress-shielding effect porous Ti implants were created using AM techniques and were found to promote stability and long-term effectiveness than conventional Ti implants. Porous Ti can support vascularisation and improves bone integration.

Bioinertness of Ti-based bone implants can be reduced by adding bioactive molecules like BMP, PPF, Magnesium ions etc. or by surface modification. Both can improve surrounding tissue response towards implant and minimise implant failure. Patient-specific implants made from Ti are used to reconstruct the mandibular body, ramus, condyle, floor of orbit, nasal bone, temporal bone and frontal bone.<sup>21</sup> Ti can also be used in the manufacture of surgical guide stents. Customized pre bent Ti plate with the help of RP reconstructive models significantly reduced the treatment time and helped surgeons to predict the cosmetic effects of surgery.<sup>10</sup> Using EBM technique, patient-specific porous Ti cranial implants were made, and is intended to overcome stress shielding effect along with its precise fit offered by 3D printing.<sup>3</sup> A novel fully customized distraction assembly system for maxillofacial distraction osteogenesis made with 3D printed Ti was found more accurate than a conventional distraction device.<sup>18</sup> Combination of expansion flap along with 3D printed Ti mesh to repair a child’s craniofacial defect. Covering of Ti mesh with flap prevented exposure-related complications like loss of body temperature, swelling of brain tissue and wound bleeding.<sup>19</sup> Ackland *et al.* developed 3D printed ‘Melbourne’ prosthetic TMJ for a patient with end-stage osteoarthritis in which condylar component and screws were made from Ti-64.<sup>20</sup> Patient-specific Porous NiTi fixation plate made with SLM was compared to dense and porous Ti6Al4V for a mandibular reconstruction surgery using ‘finite element analysis (FEA)’ to evaluate the effect of porosity on mechanical features like compression, strength and elastic modulus and found Ni-rich NiTi a proper choice for PSI.<sup>21</sup>

### Stainless Steel (Iron-Chromium-Nickel based alloy)

SS materials are biocompatible and possess high strength with an elastic modulus of 200GPa. Austenitic 316L SS is the most commonly used type of implant material. They are corrosion-resistant. Due to its poor wear resistance, their use is restricted to fixation devices mainly. Kanubaddy *et al.* compared single

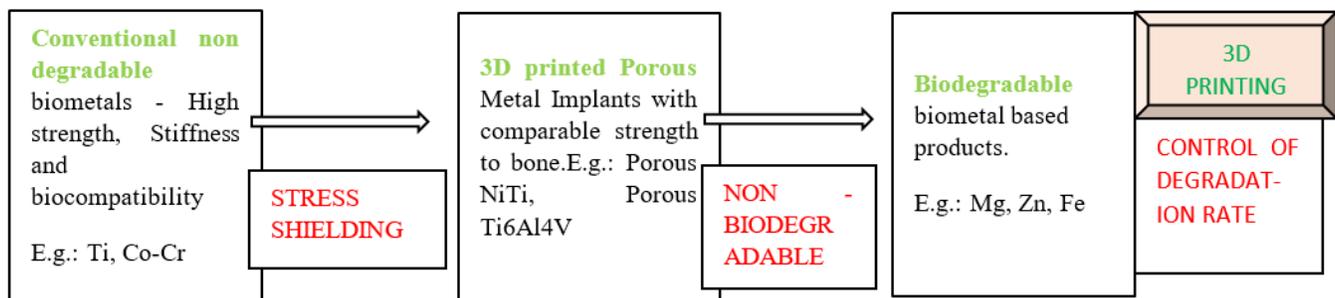


Figure 4: Paradigm shift from conventional to biodegradable metallic biomaterials

SS linear miniplate and 3D printed SS rectangular grid plate for internal fixation of mandibular angle fractures. 3D printed rectangular grid plate showed better inter-fragment stability mainly due to its configuration and 3-dimensional adaptability to the fracture line.<sup>22</sup>

#### *Cobalt-Chromium Alloys*

Co-Cr alloys are biocompatible, corrosion and wear-resistant and have adequate mechanical strength compared to SS alloys.<sup>23</sup> Vitallium, a CoCrMo alloy, was used in midface reconstruction. Hitzler *et al.* evaluated microstructure and physio-mechanical properties of 3D printed Co-Cr-Mo and Co-Cr-W alloys commonly used in fixed and removable dental prosthesis. The study confirmed that SLM systems can fabricate these alloys but need further research on the alterations that can happen in those materials with heat treatments. Zheng *et al.* used Co-Cr-Mo alloy to fabricate the mandibular handle component of a 3D printed TMJ prosthesis.<sup>24</sup>

#### **Biodegradable Metals**

Biodegradable metals are suitable for fabricating temporary implants and fixation devices, thereby avoiding a surgical reintervention. Incorporating 3D printing in biodegradable metal fabrication can help adjust their degradation rate according to the purpose. 3D printing of biodegradable metals is still in the bud stage and their clinical application in maxillofacial region needs further studies and trials, but it has a promising potential once dealt with the existing constraints.<sup>25</sup>

#### *Mg-based Biodegradable Metals*

Biocompatible and has elastic modulus similar to cortical bone, hence minimal discomfort compared to Ti and SS alloys. Mg ions produced as a degradation product of magnesium biometal is an essential macronutrient and can promote bone mineralization. Increase in pH can increase the rate of degradation of Mg biometals and hydrogen gas released as a by-product can lead to the formation of localized gas cavities, interferes with osseointegration of implant. Due to their flammability Mg alloys 3D printing using Laser powder bed fusion is considered challenging. Mg-based fracture fixation systems are used in mandibular, midface and frontal fractures.<sup>25</sup> Mg-doped Wollastonite with TCP scaffolds accelerates bone regeneration capacity in calvarial defects compared to pure Wollastonite and TCP scaffolds.<sup>13</sup>

#### *Zn-based Biodegradable Metals*

Has an important role in cellular-signal transduction, hard tissue regeneration and wound healing. Compared to Pure Zn, Zn alloys have better mechanical properties and can retain the biocompatibility as in its pure form. Zn-based alloys have degradation rate between Mg and Fe, and is a potential candidate for fracture fixation systems.<sup>25</sup> Zn-4Cu alloy implant, Zn-2Mg alloy implants was found to have potency to be used in maxillofacial surgery, but is currently limited to in-vitro studies.<sup>23</sup>

#### *Fe-based Biodegradable Metals*

Iron is an essential trace element and has excellent mechanical strength similar to 316L SS. Fe shows slow corrosion rate

and insoluble degradation products compared to Zn and Mg. Fe-based scaffolds were one of the first 3d printed scaffolds. Porous Fe-based scaffolds were found to reduce stress shielding. However, its application in the maxillofacial region needs further research.<sup>23,25</sup>

Limitation of metallic biomaterials includes hypersensitivity reactions, MRI incompatibility, stress shielding and prosthetic loosening.

#### **Bioceramics**

These are inorganic biomaterials used in repair, augmentation and reconstruction of hard tissues. They can be natural or synthetic in origin. These materials are biocompatible, brittle, low heat and electrical conductance and have a high melting point.

Bioceramics materials are mainly categorized into Bioinert ceramics- alumina (Al<sub>2</sub>O<sub>3</sub>), zirconia (ZrO<sub>2</sub>), Bioactive ceramics- bioglass, tricalcium phosphate (TCP), biodegradable ceramics – Hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>)- HA, calcium phosphate (CaP)-CPC

Alumina and zirconia are bioinert, highly compatible, great corrosion and wear resistance. Along with these physiomechanical and chemical properties, they can withstand high stress without fracture. These properties make them suitable implant materials for hard tissues and have long time survival predictions. Bioactive materials can induce a positive response in the body by forming a chemical bond between implant surface and body, which can accelerate repair and reconstruction of hard tissues. Bioactive materials are used in maxillofacial hard tissue engineering. Bioglass can induce bone regeneration by forming an appetite layer in presence of body fluid. Bioglass cannot be reshaped and is hence restricted to use as coating and reinforcing materials.<sup>26</sup> TCP is used as injectable bone cement.

Biodegradable ceramic materials can be degraded by body itself and can avoid surgical reintervention to remove such implants. 3D printed porous CPC scaffolds enhance cell attachment and proliferation. They are used as bone grafts, bioactive implant coatings, in dentistry and bone tissue regeneration. HA can show osteoconductive effect due to their interconnecting pore structure like that of natural bone.

#### **Polymers**

Vinyl, styrene and polyester polymers are the most common type of 3D printable materials in maxillofacial surgery due to their tunable mechanical properties, biocompatibility, and controllable degradation rates. Polymers can be natural, semisynthetic or synthetic based on their source. Polymers mostly used in 3D printing are ABS, PLA, PCL, PC, PEEK, PP, Polyamides, Thermoplastic PU.<sup>27</sup> Natural polymers like starch, dextran, gelatin, and synthetic polymers like PCL, PLA, PLGA are used in direct 3D printing. Materials like gelatin, chitosan and PCL are used in indirect 3D printing. PEEK, PEKK and ULTEM are high-performance polymers with good mechanical properties and thermal resistance and are stronger and lighter than metals.<sup>27</sup>

**Polyethyletherketone (PEEK)**

Is a semi crystalline linear polycyclic aromatic polymer, widely used in fabrication of craniofacial patient-specific implants, in reconstructive surgeries and is a potential alternative to overcome limitations with metallic and ceramic biomaterials.<sup>28</sup> PEEK has elastic modulus of 3.6GPa.<sup>27</sup> Due to its strength, toughness, stiffness, tolerance to gamma radiation, stability against hydrolysis, and sterilisable nature PEEK filaments are suitable to make load-bearing implants. Its bioinertness and hydrophobicity reduce its binding ability with surrounding soft tissues.<sup>26</sup> PEEK PSI are used in nasal bone, floor of orbit, temporal and frontal bone reconstruction.<sup>29</sup> Osseous integration of PEEK depends on its surface topography. FFF technique can enhance its surface properties. Shifting from conventional to 3D printed PEEK devices reduces cost and treatment period, making it possible to fabricate complex geometries. Sustained maintenance of high temperature while extrusion is one of the critical factors to be considered while 3D printing of PEEK to avoid black specs.<sup>28</sup>

**Ultra-High Molecular Weight Polyethylene – UHMWPE**

Was used in the manufacture of glenoid fossa component of 3D printed TMJ prosthesis.<sup>[24]</sup> Porous PE have been used for facial bone augmentation.<sup>26</sup> Acrylonitrile Butadiene Styrene (ABS) is available in wide range of colours and is a strong filament plastic material.<sup>16</sup> PGA, PLGA and PLA are the most widely used degradable polymers for maxillofacial defect repair. PLGA has in vivo osteoconductive properties. However large PLGA prosthesis can undergo bulk degradation causing release of lactic and glycolic acids in high levels resulting in pH drop and tissue loss.<sup>30</sup> In a study by Mehra *et al.*, a portion of autogenous bone cells was incorporated into 3D printed PLGA scaffold for the treatment of osteoporotic mandibular fracture. PCL is a commonly investigated polymer due to its optimal mechanical properties, stiffness, slow degradation, biodegradability, excellent rheologic and viscoelastic properties upon heating.<sup>30</sup> In SLS systems, PCL in the form of beads in size range of 10–100 micrometer is used. PCL scaffolds printed using SLS shows good porosity with interconnectivity and elastic modulus like bone.<sup>31</sup> Usage of 3D printed PCL scaffold for TMJ disc regeneration showed risk of articular disc damage due to stress shielding. Visser *et al.* used 3D printed PCL scaffold with cell carrier as alginate for hybrid cartilage ear reconstruction; to avoid slow degradation of PCL scaffold by increasing its porosities using melt electro writing technique which can otherwise become a barrier in tissue formation. PCL with 93–98% porosity was comparable to original cartilage.<sup>32</sup> Custom face masks made up of PCL have been used in facial skin regeneration.<sup>33</sup> Polypropylene Fumarate (PPF) is a biodegradable and photocrosslinkable polymers used in SLA. PPF combined with diethyl fumarate DEF is the printing solution for SLA. PPF/DEF ratio plays a significant part in enhancing the mechanical strength of final scaffold. PPF polymer is also used in bone cement to repair maxillofacial fractures and mandibular reconstruction.<sup>30,31</sup> Poly (butylene terephthalate)-PBT is a thermoplastic polymer

used in FDM to fabricate bone scaffolds that can match trabecular bone in porosity. PBT PEO (polyethylene oxide) coatings in Ti implants can enhance its osseointegrative property.<sup>31</sup>

**Hydrogels**

Hydrogels are hydrophilic polymeric networks that can absorb and retain water. These materials can mimic extracellular matrix (ECM).<sup>27</sup> These are smart biomaterials that allow for distribution and adhesion of cells and molecules. Hydrogels can be 3D printed. Their gelation process can affect cell life and resolution of 3D printing (Figure 5).

Highly stable and mechanically tunable hydrogels can be obtained through chemical and photo crosslinking. It is the most accepted bioink material.<sup>35</sup> 3D plotting or Direct ink writing is mainly applicable for hydrogel printing. 3D printed hydrogels with 19.7–87.2% porosities and high interconnectivity are used in making scaffolds for treating cleft defects.<sup>32</sup> Adding HA to hydrogel can enhance its mechanical properties and can improve its use in hard tissue reconstruction (Figure 6).<sup>35</sup>

Modification in AM technology to print programmable, shape memory, self-healing hydrogels can escalate this technology to a new dimension.

**Composites**

These materials are a combination of two or more biomaterials such that they can overcome the limitations of individual biomaterials and perform intended action effectively. The reinforcement element and matrix are integrated to improve the properties of final product. 3D printed Ti/CaP composite implant for reconstructing complex craniofacial defects have been found to promote osseointegration and bone regeneration without compromising aesthetic outcomes.<sup>36</sup> PEEK/HA porous scaffold created using SLS promoted osseointegration and is a

PRINTABLE HYDROGELS			
FLOW UNDER MODEST PRESSURE	SUFFICIENT INTEGRITY AND VISCOSITY	QUICK SOL-GEL TRANSITION	MECHANICAL PROPERTIES

Figure 5: Properties of printable hydrogels

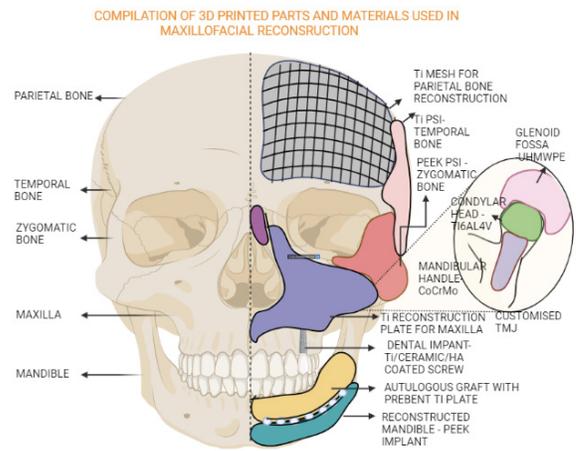


Figure 6: Compilation of various maxillofacial parts can be made using 3D printing

potential composite for craniofacial implants.<sup>26</sup> Mesenchymal stem cells in polyamide/HA composite scaffold showed excellent biocompatibility and cell attachment.<sup>30</sup> HA, TCP and chitosan added to PMMA improved its *in vitro* and *in vivo* osseointegration. PMMA composites with HA and BCG showed apatite layer formation in simulated body fluid. Carbon fiber reinforced PEEK material – CFR PEEK has increased strength and elastic modulus than conventional PEEK implants. Wu *et al.* prepared composite with PEEK and nano titania n-TiO<sub>2</sub> and found improved biological characteristics like cell attachment and osteoblast spreading.<sup>26</sup>

### 3D Bioprinting Technique

Bioink containing ECM-like material with cells and active molecules are added with CAD system to manufacture scaffold. Phases of bioprinting: Pre bioprinting phase – choosing of material and model creation; Bioprinting phase – using bioink and biopaper printing is done as per the digital data; post-processing phase-printed construct is transferred to a bioreactor.<sup>37</sup>

### DISCUSSION

In this review paper, the authors have focussed on the 3D printing materials used in the maxillofacial structure-related applications (Figure 6). The available literature confirms the importance, applications, necessity and future perspectives of 3D printing in this field as extremely wide and promising.

Face is the foremost identity of an individual as it is unique. Hence, any deformities or defects on this require a tailor-made solution. The advent of 3D printing offers precision and ease of availability for such issues. Titanium and its alloys are the most commonly used biomaterials for developing patient-specific implants in maxillofacial region. Currently, to overcome the limitations of high strength metallic biomaterials several modifications are done using 3D printing. Usage of PEEK implants is also gaining significant importance. Research in the field of 4D printable materials and nano-bioprinting is making 3D printing a fruitful and promising field in maxillofacial surgeries. However, the materials available for 3D printing are still limited and demand further research.

### CONCLUSION

Optimisation of biomaterial for a purpose is dependent on its material parameters like chemical composition, mechanical and biologic properties, architecture, degradation kinetics and much more. Intricate architecture, porosity, adaptability, bioactiveness, and strength of biomaterials can be manipulated using 3D printing. Biomaterials used in AM have not changed much overtime. Lack of appropriate printable biomaterials and standardised manufacturing guidelines are some of the limiting factors of AM in biomedical applications. Development of resilient scaffolds and focus on nanoarchitecture will be the future milestone of 3D printing.

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