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## Green Materials for 3D Printing in Dentistry



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### Synonyms

3D printing; Additive manufacturing; Biodegradable dental material; Bone grafts; Bone regeneration; Rapid prototyping

### Definition

The use of green material in 3D printing in dentistry aims to integrate new technology, waste,

pollution, and increase productivity. Ultimately the goal would be a quality treatment for the patient with the least toxicity and pollution for the environment.

### What Is 3D Printing?

Also known as additive manufacturing (AD) and rapid prototyping (RP), 3D printing is manufacturing objects by adding multiple layers of the object, one layer at a time (Andonović and Vrtanoski 2010).

### 3D Printing in Dentistry?

Dentistry and oral and maxillofacial surgery widely use 3D printers. One of these applications is computer-aided design and manufacturing (CAD/CAM) for dental prostheses, which is used in digital dentistry (Dawood et al. 2015). In dentistry and maxillofacial surgery, computed tomography (CT) and cone-beam computed tomography (CBCT), laboratory and intraoral surface scans provide volumetric data to the CAD software, which can later be used in additive manufacturing of objects (Adepu et al. 2017). A recognizable example would be the use of CAD/CAM as a substitute for traditional precious metal alloy casting (Bammani et al. 2013), implant placement surgical guides, and bone defect grafts. Each restoration and reconstruction

used in dentistry is individualized to the patient, requiring a high level of precision in reproducing the jaw, tooth, and implant's complicated geometry (Worthington et al. 2010). 3D printing can provide this level of accuracy while using materials with desirable properties required in dentistry and maxillofacial surgery (Andonović and Vrtanoski 2010). Conventional AM techniques include stereolithography (SLA), fused deposition modeling (FDM), selective laser sintering (SLS), and bioprinting (BP) (Adepu et al. 2017).

Congenital abnormalities, cancers, and trauma lead to the loss of tissue, which needs to be replaced. 3D bioprinting revolves around using suitable biomaterial while providing mechanical and functional properties to maintain tissue (provision of 3D structures for regeneration of natural tissue, ability to degrade to be replaced by natural tissue), and it produces devices that can replace human tissue and organs (Zopf et al. 2013). The 3D model created by CAD software is turned into slices and used in AM devices by depositing each object layer. 3D printing, in comparison to conventional methods, uses raw material more efficiently and reduces the amount of time and energy used for the production of desired objects (Murphy and Atala 2014). Reconstructive maxillofacial surgery uses allografts and autografts to treat anomalies and abnormalities. Autografting is an invasive procedure and causes donor site morbidity as well as longer hospital stays. In both processes, the graft must be shaped precisely to fit the defect, a step that leads to errors. 3D bioprinting allows graft production superior to allografts and autografts in adaptation, safety, and invasiveness (Hallman and Thor 2000). The desired characteristics in bioprinting are biocompatibility, osteoconductivity, porosity to provide tissue ingrowth, vascularization, nutrition conveyance, customizability of shape, size, orientation, and pore conductivity (Wang et al. 2015). Activating the cellular response required for bone regeneration, bone scaffolds must supply ECM with linked porosity and appropriate surface characteristics such as nano-rough topography (Costa-Pinto et al. 2011). Figure 1 shows the process of bone 3D printing.

## Green Material Used in 3D Printing in Dentistry

3D printed scaffolds used in tissue engineering and regenerative medicine can be used in pre-prosthetic surgeries in handling maxillofacial defects. Such scaffolds use polymers, ceramics, natural and synthetic bioplastics, proteins, biomolecules, living cells, and growth factors. It could be said that cells and biomolecules are all green material, making 3D printing in maxillofacial green by itself. Here we concentrate on green material used in the production of scaffolds.

### Natural Polymers

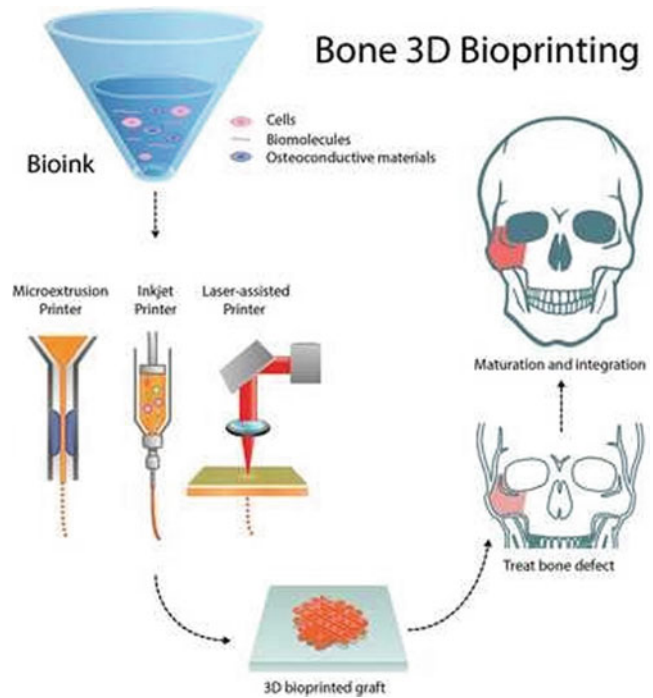
Organic scaffolds in bone regeneration are used in cell and/or drug and/or growth factor delivery due to their cytocompatibility, appropriate cell response, porosity, and controlled degradability (Stoppel et al. 2015). Collagen, gelatin, chitosan, silk, etc., are natural biopolymers used in bone regeneration to mimic natural bone's properties. Collagen is the most abundant polymer in ECM, has poor mechanical properties, can cause infection and/or allergic reaction risks when isolated from animal tissue, and cannot be mass produced (Thrivikraman et al. 2017). Therefore, recombinant collagens and combining collagen with other materials to form composite are necessary for scaffolds. Natural polysaccharides such as chitosan, alginate, and agarose have the desirable natural polymer properties in addition to positively charged surfaces, which allow them to interact with DNA, lipids, proteins, and cell membranes (Costa-Pinto et al. 2011). Silk fibroin can support cell proliferation (Uebersax et al. 2013), induce osteogenesis and bone formation in calvarial bone defects (Uebersax et al. 2013). However, silk-based scaffolds are limited to non-load-bearing areas (Stoppel et al. 2015).

### Dimineralized Bone Matrix (DBM)

DBM, another natural polymer, is an allograft produced by removing the mineral component of bone (Sawkins et al. 2013), which results in a polymer mainly composed of type I collagen along with various growth factors and residue of calcium and phosphate-based particles (Gruskin et al. 2012). It promotes osteoconductivity and

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**Fig. 1** Bone 3D printing  
(Ashammakhi et al. 2019)



osteoinductivity. It has limited mechanical ability and therefore is limited to non-load-bearing areas.

#### Chitosan

Chitosan (CS) is a natural polymer procured from marine sources and is polyelectrolyte and semi-crystalline in nature (Costa-Pinto et al. 2011). Cs biopolymers can be used alone or as composites with bioceramics or polymers. 3D printed scaffolds using CS enable controlled delivery of bioactive molecules via osteogenic functionalization properties. It can promote bone regeneration and prevent infection in recipient defect sites (Yadav et al. 2021). Chitosan's cationic nature allows for its interaction with glycosaminoglycans and proteoglycans, which stimulate cytokines and growth factors in bone tissue regeneration (Costa-Pinto et al. 2011; Yadav et al. 2021).

#### Alginate

As a water-soluble polysaccharide is similar to the extracellular matrix, it is compatible with cartilaginous tissue, supports surrounding chondrocytes (Gharravi et al. 2012), induces chondrocyte proliferation, and has desirable mechanical properties.

3D printed alginate constructs have been used in mesenchymal stem cell differentiation in fibrocartilage repair. When combined with other materials such as chitosan and polylactide, alginate becomes more effective. It can be used in temporomandibular joint cartilage engineering (Gharravi et al. 2012). Its hydrophilicity makes it more biocompatible, and it works synergistically with growth factors to repair bone defects (Drury and Mooney 2003). If not combined with other material, it lacks interaction with cells and proteins (Park and Lee 2014). It is not suitable for load-bearing areas due to its low stiffness, which can be remedied by combining it with other materials like ceramics to form composites (Xavier et al. 2015). Alginate degrades rapidly but can be combined with chitosan and polylactide to form composites with more desirable characteristics.

#### Synthetic Biopolymers

Synthetic biopolymers such as poly( $\epsilon$ -caprolactone) (PCL), polylactic acid (PLA), polyglycolide (PGA), poly(lactide-co-glycolide) (PLGA), poly(propylene fumarate) (PPF), and polyhydroxyalkanoates (PHA) have been used in

scaffold printing (Gunatillake et al. 2003). Recently, natural and synthetic polymers have been combined to get the desired properties from both polymers in scaffold printing (Fu et al. 2012). PCL or PCL-PEG-PCL copolymer nanofibers in collagen or chitosan have both biomimicry and stimulation effects of natural polymers with the desired mechanical properties of synthetic polymers (Thrivikraman et al. 2017).

#### Biogenic Polyphosphate

Printed biogenic polyphosphate (bio-polyP) scaffolds have remarkable resolution and can be fabricated without further processing. Bio-polyP increases the release of bone morphogenic protein 2, accelerates bone mineralization, preserves bone integrity, and prevents resorption by inhibiting differentiation into osteoclasts (Wang et al. 2013). It can be used in craniomaxillofacial bone defect repair (Wang et al. 2015). Bio-polyP can stimulate osteocytes to undergo an anabolic process, regulate scaffold porosity, and show osteoconductivity. It can be combined with silicon and calcium to form composites with more desirable characteristics.

#### Biogenic Silica

Biogenic silica (BSi) is very similar to bio-polyP in its properties and biochemical reactions (Müller et al. 2013). It is resistant to unfavorable environmental conditions (Müller et al. 2013). The BSi scaffolds have the required porosity for effective nutrient diffusion in avascular hard tissues present in the craniofacial skeleton (Plazas Bonilla et al. 2014). They can provide effective drug delivery. BSi is biocompatible, bioactive, and can stimulate osteoblast differentiation. BSi can be combined with alginate and collagen to form composites with more desirable characteristics (Vallet-Regí 2010).

#### Bioceramics

Bioceramics can upregulate osteogenesis, allow for space maintenance in defect reconstruction and rapid population of cells onto scaffolds, and promote cell proliferation; however, their brittle nature makes them an unsuitable implantation choice in load-bearing craniofacial sites (Obregon et al. 2015).

#### Hydroxyapatite

It has a stoichiometric similarity to natural bone's mineral phase, and it has been known as a bio-compatible bone replacement. HA implants assembled by techniques other than 3D printing, such as hydrothermal conversion, polymer sponges, and bulk ceramic processing, are limited in their ability to control porosity. HA scaffolds with desired characteristics for bone replacements have been produced using 3D printing methods (Fahmy et al. 2016). Further, these scaffolds can act as templates for primary cell attachment following tissue formation, and the patient's cells can be seeded into these scaffolds (Leukers et al. 2005). Due to their expensiveness and lack of optimal interaction with bonding liquids, HA granules do not meet the requirements for 3D printing and need further development (Lin et al. 2019). HA provides osteoconductivity, biocompatibility, mechanical stability, and non-immunogenicity. HA can be combined with chitosan and polyamides to form composites with more desirable characteristics.

#### Calcium Phosphate

Calcium phosphate compounds can chemically bond to hard tissue. Tricalcium phosphate (TCP) shows more biodegradability than other materials such as hydroxyapatite (HA). Implants produced using TCP release Ca and PO<sub>4</sub> ions, which aid in bone formation (Sun et al. 2001). TCP slowly resorbs in physiological conditions, and calcium phosphate cement (CPC) can be molded freely to the defect. However, it lacks microporosity, which can be resolved by using defined structuring using 3D-printing (Gbureck et al. 2007). TCP provides osteoconductivity and can be molded into defects in granule form; however, it lacks microporosity and must be sintered at a low temperature. It can be combined with collagen and hydroxyapatite to form composites with more desirable characteristics. Medical-grade polycarpic acid-tensioned-tricalcium phosphate used in the production of scaffolds by fused deposition modeling is biocompatible and therefore can be considered as green (Yefang et al. 2007).

### Bioglass

Bioactive glasses (BG) can support osteoblast cells and bond to soft and hard tissue, making them potentially useful in the healing and regeneration of bone defects. It can stimulate angiogenesis in the presence of vascular endothelial growth factor (VEGF). It shows osteoconductivity and osteoinductivity (Rainer et al. 2008), and by its bioactive HA and carbonated hydroxyapatite (CHA), the surface layer allows interfacial bonding to tissue without scar layer formation (Hench 1998). BGs can be cytotoxic to the surrounding tissue. BGs can be combined with polyethylene and poly alpha-hydroxyacid to form composites with more desirable characteristics.

### Composites

No single biopolymer can satisfy all requirements of bone graft material; therefore, composites of collagen and apatites have been developed. Polymer/ceramics composites have the high wear resistance of ceramics and high toughness of polymers, making composites a suitable candidate for manufacturing biphasic porous scaffolds used in regenerating damaged tissue like the TMJ (Inzana et al. 2014). Low-temperature 3D printing allows for the construction of scaffolds without harm to seeded cells or drugs, or growth factors.

### Calcium Phosphate/Collagen

3D bioprinting in low temperatures allows the addition of natural polymers such as collagen to provide both mechanical and bioactive properties (Inzana et al. 2014).

### Hydroxyapatite/Polyamide

Polyamides improve the mechanical properties of HA scaffolds and enable them to mimic the composition, structure, and properties of natural bone (Li et al. 2011).

### Cell/Hydrogel

Organ or tissue bioprinting uses tissue engineering utilizing AM techniques, wherein layered hybrid structures are formed with organized architecture and cellular placement using hydrogel matrices and cells at the same time (Fedorovich et al. 2008). This material allows for printing

vascularized bone grafts already seeded with cells that would have needed to migrate into the scaffold in bone grafts produced by other material.

### Titanium

Its high corrosion resistance, high strength/weight ratio, and biocompatibility have made it a favorable biomaterial to be used in medical 3D printing. It has already been used in implant production, such as dental implants, screws, and membranes. Titanium porous scaffolds have been 3D printed and show high potential for 3D printing due to their good mechanical properties and biocompatibility (Wiria et al. 2010).

### Bioplastics

It is worth mentioning that bioplastics produced from renewable biomass such as corn starch, vegetable oils, and fats, or straw may be used in 3D printed high precision dental instruments such as implant placement surgical guides, wedges, etc. The bioplastic family includes, but is not limited to, starch-based plastics, cellulose-based plastics, protein-based plastics, aliphatic polyesters (polylactic acid or PLA), polyamide 11, or bio-derived polyethylene. Bioplastics can be a substitute for petroleum, derived plastics.

## Cross-References

- ▶ [Antimicrobial and Antiviral Properties of Herbal Green Materials](#)
- ▶ [Biopolymer Scaffolds, Biomedical Applications](#)
- ▶ [Chitosan Green Materials In Dentistry, Applications](#)
- ▶ [Green Materials for Wound Healing](#)

## References

- Adepu S et al (2017) Three-dimensional bioprinting for bone tissue regeneration. *Curr Opin Biomed Eng* 2: 22–28
- Andonović V, Vrtanoski G (2010) Growing rapid prototyping as a technology in dental medicine. *Mech Eng Sci J* 29(1):31–39

- Ashammakhi N et al (2019) Advancing Frontiers in bone bioprinting. *Adv Healthc Mater* 8(7):1801048
- Bammani SS, Birajdar PR, Metan SS (2013) Application of CAD and SLA method in dental prosthesis. *AMAE Int J Manuf Mater Sci* 3(1):14–18
- Costa-Pinto AR, Reis RL, Neves NM (2011) Scaffolds based bone tissue engineering: the role of chitosan. *Tissue Eng Part B Rev* 17(5):331–347
- Dawood A et al (2015) 3D printing in dentistry. *Br Dent J* 219(11):521–529
- Drury JL, Mooney DJ (2003) Hydrogels for tissue engineering: scaffold design variables and applications. *Biomaterials* 24(24):4337–4351
- Fahmy MD et al (2016) Three-dimensional bioprinting materials with potential application in preprosthetic surgery. *J Prosthodont* 25(4):310–318
- Fedorovich NE et al (2008) Three-dimensional fiber deposition of cell-laden, viable, patterned constructs for bone tissue printing. *Tissue Eng Part A* 14(1):127–133
- Fu S et al (2012) Injectable and thermo-sensitive PEG-PCL-PEG copolymer/collagen/n-HA hydrogel composite for guided bone regeneration. *Biomaterials* 33(19):4801–4809
- Gbureck U et al (2007) Resorbable dicalcium phosphate bone substitutes prepared by 3D powder printing. *Adv Funct Mater* 17(18):3940–3945
- Gharravi AM et al (2012) Design and fabrication of anatomical bioreactor systems containing alginate scaffolds for cartilage tissue engineering. *Avicenna J Med Biotechnol* 4(2):65–74
- Gruskin E et al (2012) Demineralized bone matrix in bone repair: history and use. *Adv Drug Deliv Rev* 64(12):1063–1077
- Gunatillake PA, Adhikari R, Gadegaard N (2003) Biodegradable synthetic polymers for tissue engineering. *Eur Cell Mater* 5(1):1–16
- Hallman M, Thor A (2000) Bone substitutes and growth factors as an alternative/complement to autogenous bone for grafting in implant dentistry. *Periodontol* 2008(47):172–192
- Hench LL (1998) Biomaterials: a forecast for the future. *Biomaterials* 19(16):1419–1423
- Inzana JA et al (2014) 3D printing of composite calcium phosphate and collagen scaffolds for bone regeneration. *Biomaterials* 35(13):4026–4034
- Leukers B et al (2005) Hydroxyapatite scaffolds for bone tissue engineering made by 3D printing. *J Mater Sci Mater Med* 16(12):1121–1124
- Li J et al (2011) Computer-aided design and manufacturing and rapid prototyped nanoscale hydroxyapatite/polyamide (n-HA/PA) construction for condylar defect caused by mandibular angle ostectomy. *Aesthet Plast Surg* 35(4):636–640
- Lin K et al (2019) 3D printing of bioceramic scaffolds—barriers to the clinical translation: from promise to reality, and future perspectives. *Materials* 12(17):2660
- Müller WE et al (2013) Inorganic polymers: morphogenic inorganic biopolymers for rapid prototyping chain. *Prog Mol Subcell Biol* 54:235–259
- Murphy SV, Atala A (2014) 3D bioprinting of tissues and organs. *Nat Biotechnol* 32(8):773–785
- Obregon F et al (2015) Three-dimensional bioprinting for regenerative dentistry and craniofacial tissue engineering. *J Dent Res* 94(9 Suppl):143s–152s
- Park H, Lee KY (2014) Cartilage regeneration using biodegradable oxidized alginate/hyaluronate hydrogels. *J Biomed Mater Res A* 102(12):4519–4525
- Plazas Bonilla CE et al (2014) New porous polycaprolactone-silica composites for bone regeneration. *Mater Sci Eng C Mater Biol Appl* 40:418–426
- Rainer A et al (2008) Fabrication of bioactive glass-ceramic foams mimicking human bone portions for regenerative medicine. *Acta Biomater* 4(2):362–369
- Sawkins MJ et al (2013) Hydrogels derived from demineralized and decellularized bone extracellular matrix. *Acta Biomater* 9(8):7865–7873
- Stoppel WL et al (2015) Clinical applications of naturally derived biopolymer-based scaffolds for regenerative medicine. *Ann Biomed Eng* 43(3):657–680
- Sun L et al (2001) Material fundamentals and clinical performance of plasma-sprayed hydroxyapatite coatings: a review. *J Biomed Mater Res* 58(5):570–592
- Thrivikraman G et al (2017) Biomaterials for craniofacial bone regeneration. *Dent Clin N Am* 61(4):835–856
- Uebersax L et al (2013) Biocompatibility and osteoconduction of macroporous silk fibroin implants in cortical defects in sheep. *Eur J Pharm Biopharm* 85(1):107–118
- Vallet-Regí M (2010) Nanostructured mesoporous silica matrices in nanomedicine. *J Intern Med* 267(1):22–43
- Wang X et al (2013) The deep-sea natural products, biogenic polyphosphate (bio-PolyP) and biogenic silica (bio-silica), as biomimetic scaffolds for bone tissue engineering: fabrication of a morphogenetically-active polymer. *Mar Drugs* 11(3):718–746
- Wang MO et al (2015) Evaluating 3D-printed biomaterials as scaffolds for vascularized bone tissue engineering. *Adv Mater* 27(1):138–144
- Wiria FE, Shyan JY, Lim PN, Wen FG, Yeo JF, Cao T (2010) Printing of titanium implant prototype. *Materials & Design* 31:S101–5
- Worthington P, Rubenstein J, Hatcher DC (2010) The role of cone-beam computed tomography in the planning and placement of implants. *J Am Dent Assoc* 141:19S–24S
- Xavier JR et al (2015) Bioactive nanoengineered hydrogels for bone tissue engineering: a growth-factor-free approach. *ACS Nano* 9(3):3109–3118
- Yadav LR et al (2021) Chitosan-based 3D-printed scaffolds for bone tissue engineering. *Int J Biol Macromol* 183:1925–1938
- Yefang Z et al (2007) Comparison of human alveolar osteoblasts cultured on polymer-ceramic composite scaffolds and tissue culture plates. *Int J Oral Maxillofac Surg* 36(2):137–145
- Zopf DA et al (2013) Bioresorbable airway splint created with a three-dimensional printer. *N Engl J Med* 368(21):2043–2045