

Fostering Novel Materials and Subsisting Technologies for 3D Printing



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Abstract The COVID-19 pandemic made a drastic impact on the human health and overall economy of the world. Other than health-related issues, the global healthcare structure was deeply affected due to an alarming imbalance in the demand-supply chain of critical medical equipment such as ventilators, quarantine closets, oxygen valves, protective equipment, etc., that support patients' life during their battle against COVID-19. The field of 3D printing, or now commonly known as additive manufacturing (AM) has benefitted extremely by capitalizing on the increasing demand for manufacturing medical equipment. As a result, a vast number of start-ups have mushroomed up that are experimenting with various novel materials, techniques, and applications to build 3D printed products in quick turnaround time. Through this paper, we would highlight the propitious application of 3D printing in the biomedical engineering area. The chapter begins by addressing the fundamentals of 3D printing technologies and materials that shall be used to illustrate their whole system environmental impacts in later sections. This is followed by discussion over prominent countless initiatives that are being taken by multiple R&D centers, academic institutes, and various other corporations for the implementation of new technologies and materials to combat this pandemic. Further, the need for novel materials and the use of agricultural waste as compostable biomaterials for a circular economy has been discussed in detail. Aside to this, among the multiple 3D printing processes, a major focus has been on material extrusion, powder bed fusion, and material jetting techniques that are used for the medical sector based on current medical requirement, i.e., automatic door handle openers, face shields/masks, quarantine closets, ventilators, valves, etc. In the end, the conclusion will prove to be a stepping-stone for future research in this direction.

Keywords Biomedical · 3D printing · Three-dimensional printing · Additive manufacturing · 3D materials · Additive manufacturing · COVID

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1 Introduction

3D printing is an additive manufacturing (AM) process of joining materials together to produce a product or part that takes the form of a 3D model. In today's time, 3D printing technology plays a major role in various industries—be it, aerospace engineering, biomedical engineering, automobiles, agriculture, food industry, or medical fraternity, etc. The year 2020 acted as an eye-opener when the COVID-19 pandemic encompassed the whole wide world, and we witnessed a steep increase in the demand for medical equipment—that too at a time when the entire supply chain had been drastically disrupted due to worldwide lockdowns imposed due to the onset of COVID-19 pandemic! This resulted in making the healthcare industry one of the major adopters of 3D printing technology. In the recent past, many new ventures came into existence that are constantly experimenting with various novel technologies, materials, and applications related to 3D printing or additive manufacturing within the healthcare industry. Such start-ups play a crucial role in driving the additive manufacturing industry—not only have they increased the rate at which biomedical equipment is manufactured, but also helped increase the sustainability and durability of the 3D printed products that are being used by the medical fraternity in our fight against the COVID pandemic. The novel 3D printing materials such as ceramic materials, biomaterials, electronic materials, smart materials, and composites are being considered to manufacture biomedical equipment nowadays. The properties of these novel materials should be analyzed in such a way that they meet the new requirements imposed on the products they are being used in, i.e., low energy printing, stable chemical/functional properties, etc. The novel 3D printing technologies aim at improving the existing state of the art technologies to minimize the requirement of the support structures, as well as to produce multiple layers in a single pass process to reduce the manufacturing time and increase the required stability. The two main factors that aid in efficient mass production of 3D printed goods by providing minimal risk for virus transmission through zero-contact process in quick turnaround time are:

- type of materials used
- type of 3D printing technology used.

The new start-ups are frequently experimenting with building new materials, such as smart materials, nanomaterial's, composite materials, or biomaterials, etc., that are capable of being used in 3D printing. However, with the onset of a pandemic, it has been observed that there is a need for advancement in 3D printing material type and technology type that can radically improve the whole system environment and help in further improving the mass production of bio-equipment that are used for providing protection and for testing of COVID-19.

2 Background

Many different types of AM methods are already known to mankind and are currently in use as well. These methods include, for instance, stereolithography (SLA), selective laser sintering (SLS), and digital light processing (DLP), fused deposition modeling (FDM), electronic beam melting (EBM), selective laser melting (SLM), droplet deposition/layering, and direct metal laser sintering (DMLS) (<https://www.sculpteo.com/en/3d-printing/3d-printing-technologies/>). These methods are selected and preferred keeping in mind the industry and type of devices that need to be manufactured. It is crucial to select the right set of materials and technology that must be used to produce the end output. The different technologies corresponding to different end-product requirement can be:

- SLA technique is used to develop the medical/dental products and electronics casings,
- SLS produces electronics housing mounts, custom consumer products, and aerospace hardware,
- The FDM technique builds the custom consumer products and electronics housing, aerospace ducting, automotive components, and food production tools, and
- DMLS is used in turbine engine components, instrumentation parts, medical equipment, and in automotive industries.

Table 1 illustrates the clear description of various conventional 3D printing technologies along with the widely used utilized materials.

The above mentioned techniques have various advantages; however, one advantage common to all the techniques is the formation of strong complex parts. FDM,

Table 1 Overview of 3D printing technologies

| AM method | Technique implied | Preferred materials |
|-------------------------------------|-------------------------|---|
| Stereolithography (SRA) | UV light | Liquid, photopolymer |
| Fused deposition modeling (FDM) | Extrusion | Filament, polymers |
| Selective laser sintering (SLS) | UV light | Powder, polymers, metallic, ceramic |
| Electronic beam melting (EBM) | Electron beam | Powder, metallic |
| Direct metal laser sintering (DMLS) | Laser beam | Powder, metallic |
| Selective laser melting (SLM) | Laser | Powder, metallic |
| Digital light processing (DLP) | Light/energy Deposition | Photopolymers resin |
| Droplet deposition/layering | Inkjet | Powder along with liquid binder, polymer, ceramic, metallic |

for instance, gives low cost and high strength parts whereas DLP is another low-cost technology with good accuracy with relatively quick turnaround time. SLA is another rapid fabrication technology that has the ability to create complex shapes with high resolution. However, with these advantages come certain disadvantages such as production of weak parts that are susceptible to sunlight and heat; grainy and rough surface finish which should also be considered while the selection of efficient technology and materials.

3 Novel Materials

Novel materials are the new advanced materials that have become critical components for new applications of various emerging technologies such as, but not limited to, 3D printing (Lee et al. 2017). We have clustered five types of novel materials further elaborated them in detail in detail below.

3.1 *Composite Materials*

Composite materials are the new materials in the field of 3D printing] (<https://markforged.com/resources/learn/design-for-additive-manufacturing-plastics-composites/understanding-3d-printing-strength/3d-printing-carbon-fiber-and-other-composites>; Blanco 2020; How composite materials are changing the world of additive manufacturing (again) 2017; Kalsoom et al. 2016). Composites typically comprise a core polymer material and a reinforcing material, like chopped or continuous fiber. The composite material offers higher strength and stiffness compared to non-reinforced polymers. In some cases, it can even replace metals like aluminum. The composite 3D printing has the ability to streamline and cut the cost of traditional composite manufacturing. There are numerous methods for fabricating composite components, in addition to 3D printing (Composite 3D Printing: an emerging technology with a bright future 2020). Few examples of these materials are present within AM process. Electronic sensors such as capacitance sensors and piezoresistive sensors are printed using the thermoplastic composite materials that enable the sensing of capacitance changes and mechanical flexing. These new composite materials can be used in additive manufacturing with FDM low-cost technology without any complex circuit requirement and high-cost resources of sensor production.

3.2 Biomaterials

Various types of implants are manufactured today that use biomaterials (Bandyopadhyay et al. 2015; Tappa and Jammalamadaka 2018; Jang et al. 2018). The implant fabricated using biomaterial is considered a success if it is biocompatible, inert, mechanically durable, and easily moldable which has made 3D printing technology revolutionary in medical and pharmaceutical fields. Mostly the biocompatible synthetic polymers, natural polymers, and acrylates-based polymers are preferred which are the recent developments in biocompatible materials that are being used to print the functional living tissues using AM process. These bio-printed tissues are used in organ transplantation that brings a revolution in the biomedical industry by addressing the challenge of organ transplantation.

3.3 Electronic Materials

Conventional AM technologies can fabricate the electronics components, such as resistors, capacitors, antenna, and inductors. The fabrication of flexible thin-film transistors has been reported on plastic substrates with self-synthesized ink and to achieve high resistance value using conducting polymer, resistors are printed on a plastic substrate. There are five materials that can be 3D printed with active properties and integrated into device components:

- (1) An Elastomeric Matrix;
- (2) Conducting Polymers;
- (3) Quantum Dot Nanoparticles;
- (4) A Uv-Adhesive Transparent Substrate Layer;
- (5) Metal Leads;

Therefore, 3D printing is a flexible process to fabricate or manufacture electronic devices.

3.4 Ceramics Materials

This type of 3D printing uses materials such as clay or other fluid-dense materials for additive manufacturing processes. Compared with metal and polymers, ceramic materials have an extremely high melting point which is one of the biggest challenges in additive manufacturing. There is a new way to fabricate ceramics parts using 3D printing with particular pre-ceramics monomers fusing with ultraviolet (UV) photo-initiator. Therefore, these 3D printed ceramics parts give excellent thermal stability without shrinkage (Chen et al. 2019; Ceramic 3D printer: all about ceramic 3D printing 2020; 3D printing with technical 2020). These ceramics materials are of

great interest in porous burners, protection systems, electronic device packaging, propulsion components, and micro-electromechanical systems.

3.5 Smart Materials

Materials that have the capability to transform their shape or geometry under the impact of external parameters are known as smart materials (<https://www.sculpteo.com/en/3d-learning-hub/best-articles-about-3d-printing/smart-materials/>; Smart materials: 3D printing self-healing capsules for concrete 2019). 3D printing of these smart materials gives rise to 4D printing applications. 4D printing is a fledgling topic in the field of 3D printing where the fourth dimension is time. The basic principle of 4D printing is the use of programmable smart materials for 3D printing that can moderately change the shape over time based on external parameters, such as heat and water. One such example of this type of material is cellulose fibrils (nanocellulose).

All these various types of new materials explained above play a major role in 3D printing's long term future. Table 2 represents a summary of the novel materials and their utilization in the 3D printing field.

Table 2 Novel materials in 3D printing (Lee et al. 2017)

| Novel materials category | Materials | AM process | Application |
|--------------------------|---|-------------------------|---|
| Smart materials | Shape memory polymers | Vat photopolymerization | Actuator, sensor, jewelry, gripper |
| Ceramic materials | UV curable monomers | Vat photopolymerization | Thermal protection |
| Electronic materials | Silver nanoparticle ink, conductive polymer, quantum dot | Material jetting | Thin-film transistor, antenna emitter, resistors, LEDs |
| Composite materials | CB/PCL | Material extrusion | Sensors |
| | Verowhite Plus and Tangoblack Plus | Material jetting | Fracture resistant composites |
| | Barium Titanate Nanoparticle/Polyethylene Glycol Diacrylate | Vat photopolymerization | 3D piezoelectric polymers |
| Biomaterials | Hydrogels, functional inks | Material extrusion | Tissue engineering, cardiac micro-physiological devices |

4 Novel Technologies

In today's time, the most widely used technique for the production of 3D printing devices is Fused Deposition Modeling (FDM). It is a type of low-cost material extrusion process. A wide range of materials can be used in this technique. However, there is a need for new 3D printing technologies as FDM suffers from slow speed and sometimes also leads to the problem of warping.

Recently, new 3D printing techniques are being researched upon that would eradicate the existing disadvantages of conventional 3D printing techniques. These are listed herein and further explained in detail below: (1) computed axial lithography (CAL) (Davide 2019) (Tetsuka and Shin 2020), (2) continuous liquid interface production (CLIP) (Service RF 2019), (3) rotational 3D printing (Novel 3D printing technique yields high-performance composites Arranging fibers just like nature does 2018), (4) inverted multi-material laser sintering (Hanaphy 2020).

4.1 Computed Axial Lithography (CAL)

The 3D printing technique that is inspired by computed tomography (CT) is called computed axial lithography (CAL). This technique is based on photopolymerization and utilizes photo-responsive material placed in a liquid made from polymer and is subjected to CT scans to obtain a flexible and complex 3D object which later is crafted to the desired shape by projecting light to a rotating cylinder. Through the utilization of CAL, the support structure that is a major requirement of conventions 3D printing techniques can be circumvented. This technique also eliminates the requirement for supports and one can build complex and nested structures that were previously challenging or nearly impossible to print. The process is almost layer-less without involving any relative motion between resin and printed part—thereby providing immense strength to the structures produced via this technique (Bhattacharya et al. 2018).

4.2 Continuous Liquid Interface Production (CLIP)

The 3D printing technique is 100X faster! This technique is also based on photopolymerization, where ultraviolet light is projected inside a space filled with liquid resin which is circulated with a liquid coolant from beneath to reduce the effect of warping and cracking of the final 3D printing product (Januszewicz et al. 2016; Johnson et al. 2016). A continuous liquid interface production (CLIP) is achieved with an oxygen-permeable window below the ultraviolet image projection plane. The CLIP creates a “dead zone” (persistent liquid interface) where photopolymerization is inhibited

between the window and the polymerizing part. We delineate critical control parameters and show that complex solid parts can be drawn out of the resin at rates of hundreds of millimeters per hour. These print speeds allow parts to be produced in minutes instead of hours (Tumbleston et al. 2015).

4.3 Rotational 3D Printing

Rotational 3D printing is a new technology that aids in making stronger parts! This additive manufacturing programs the fiber orientation within epoxy composites in specified locations to generate structures with characteristics of high strength and stiffness (A new spin on 3D printing can produce an object in seconds 2020; Rotational 3D printing: a new technology for stronger parts 2018; Raney et al. 2018). This is done with the help of a spinning nozzle—hence the name rotational printing. Since the process allows us to modify the complex microstructures of the material, therefore, the parts produced have higher strength and stiffness, thereby increasing damage tolerance.

4.4 Inverted Multi-material Laser Sintering

Selective laser sintering (SLS) is a traditional process for 3D printing a metal that uses a laser beam to focus upon a print bed filled with metal powder. When the laser beam moves back and forth in a pre-defined pattern, it melts and fuses the powder into a solid at selected areas. The product is built up gradually, one layer at a time, with the addition of more powder. However, the switching of two metals back and forth is a difficult process, especially when both the metals have different melting points (Upside-down 3D printing tech creates multi-material 2020).

Inverted multi-material laser sintering technique is a new and improved version of SLS that reduces the steps for printing by sintering multiple powders materials of thermoplastic and metal in a single run. This is achieved through inverting the laser inside the 3D printer and replacing the powder bed box with multiple glass plates. Through this new technique, embedded circuit boards and robotic components could be easily printed.

5 Conclusion and Future Scope

We believe the world is forever changing and medicine is always going to be one area where research is bound to always continue. The scope of additive manufacturing in the medical industry is limitless. With the advancement in medical technology, people have been living longer. The medical fraternity is benefiting hugely through

the use of 3D printing, where the outcome is truly astonishing and remarkable. We can now think of creating 3D printed organs and other medical equipment in a quick turnaround time. To conclude, we believe that this pandemic has really helped us identify 3D printing as the most viable option that comes with many advantages as it can provide quicker and better alternative solutions to most of the traditional processes. With the ability to apply 3D printing into almost any industry very amicably, the evolution of this technology will always remain an ongoing task as we constantly strive for developing better materials and new and improvised methods to yield unimaginable outcomes in the shortest time-span. With the advent of all these novel materials and technologies in 3D printing, every industry can take benefits in their object manufacturing process, especially the biomedical industry as 3D printing technology can address the major issues they are facing during this COVID-19 pandemic time. For example, in Italian hospitals, as the number of Coronavirus patients increased, they required breathing machines and on the other side, the original suppliers were unable to fulfill this sudden high demand for oxygen valves. So, in response to this situation, an engineering firm of Brescia started implementing 3D printing to meet the requirements of hospitals and this step has saved many patients lives (Petch 2020).

In the current scenario of COVID, a major need of every person may be a healthcare worker or patient or any other person who wants to stay protected from the virus is personal protective equipment (PPE). Out of the long list of PPE's such as face shield, masks, respirators gloves, goggles or glasses, gowns and head cover, masks or respirators remains a top priority requirement for all. As COVID-19 is carried mainly through the association with an infected person, the major issue faced while using these products is virus transmission when an infected person touches the final end-product, and the virus stays over the surface for a certain time. Table 3 highlights

Table 3 Lifetime on different surfaces

| Type of surface | Virus stay time |
|--------------------------|-----------------|
| Plastic | 3–4 days |
| Polypropylene plastic | 3 days |
| Metal | 5 days |
| Paper | 3 h |
| Cardboard | 24 h |
| Ceramic | 5 days |
| Aluminum | 2–8 h |
| Stainless steel | 2–3 days |
| Copper | 4 h |
| Glass | 4 days |
| Outside of surgical mask | 7 days |
| Surgical glove | 8 h |

different stay time of the COVID virus on different surfaces used (<https://www.bigstockphoto.com/image-368913025/stock-vector-coronavirus-infographic-lifetime-of-covid-19-virus-infection-on-different-surfaces-and-materials%2C-d>; <https://www.webmd.com/lung/how-long-covid-19-lives-on-surfaces>; <https://scroll.in/article/957211/dirty-money-can-coronavirus-spread-through-bank-notes>). As can be referred from Table 3, for the basic surgical mask, the lifetime stay of the virus is 7 days; therefore, these cannot be used again and again and hence require optimization in the supply of these. Also, these surgical masks do not provide complete protection from bacteria or viruses due to inherent loose fit. N95 masks, which are the reusable form of masks with tight-fitting, use steel for staples and aluminum for nose clip, which also inherent virus lifetime for a minimum of 2–3 days. These issues can be resolved by using 3D printed products, but for that certain improvements are also required in the materials and the technologies.

For the optimization of supply, 3D printed face masks are in production, however, the major guidelines issued by FDA for surgical masks and respirators such as filtration and infection control are not effectively provided by these 3D printed face masks. Many individuals are working in this direction so as to maximize filtration support and reusability of these 3D printing masks by including special additive materials during 3D printing such as biocompatible polymer containing a copper nanocomposite (<https://copper3d.com/hackthepandemic/>) or silver ions (<https://3dprint.com/273171/3dfils-introduces-line-of-silver-ion-antibacterial-3d-printing-filaments/>) or NaCl filter as a middle filter (Sachan 2020). Although the role of these materials is not yet known for COVID, yet these materials provide additional antimicrobial properties to the mask which should also be well investigated for efficient results (Table 4).

Also, to solve the loose fit issue for masks, research is being focused on customizing mask seal design (Mang et al. 2018). To fix this 3D laser scanning for scanning facial parameters such as face and nose length and structure to generate N95 template can be utilized which can further be used with Fused Deposition Modeling 3D printer utilizing Acrylonitrile Butadiene Styrene plastic.

Apart from the PPE kits, the other area where most of the research is being focused on is 3D printed quarantine booths, which have also witnessed a shortfall due to the rise in cases of COVID around the world. The solid urban construction where waste material as a raw material is used could provide rigid support to the structure of quarantine booth (Petch 2020), however, the limitation faced here is higher expenses faced and size issue. Therefore, it is impertinent to investigate more on the type of materials that can be further utilized in this scope to eradicate the abovesaid disadvantages. Aside to this, another structure, i.e., 3D printed testing booths in parallel to the utilization of Fiberglass composites as raw material for building a lighter and sturdier structure can be a hot topic of future research.

As mentioned previously, FDM is a priority choice for producing 3D printing products and COVID products are no exception here (Mang et al. 2018).

Apart from the FDM technique, research should also be aligned towards the possibility of finding new techniques which utilize object formation inside a liquid

Table 4 3D printed examples, reported in the news, in the fight against COVID-19 (Mang et al. 2018)

| AM technology | AM product for supporting healthcare professional |
|---------------|---|
| FDM | Hand sanitizer holder |
| FDM | Door handle attachment |
| FDM | Screw less hand-free door handle openers |
| FDM | Vision/face shield |
| FDM | Face masks (E.G. surgical & N95 respirator) |
| FDM | Non-invasive positive end expiratory pressure (PEEP) masks |
| FDM | 3D printed quarantine booths |
| FDM | Ventilators |
| FDM | Parts to convert existing manual ventilator systems into automatic ones |
| FDM | Adaptors for a variety of medical devices |
| SLS & FDM | Oxygen valves |
| SLA | Venturi type valves for respirators (Needs Regulatory Approval) |
| SLA | COVID-19 test swabs |
| SLA | 3DP lung models for use in surgical planning & understand COVID-19 |

which would result in a germ-free end-product—a high priority requirement during the COVID pandemic.

One of the other techniques is computed axial lithography (CAL). The computed axial lithography can build a full 3D structure in a single step using liquid resin as it works on sequential illumination from many different angles using series of 2D images. It has an added advantage that it can build the objects very quickly—a quality that is much sought after, given the current situation. And there is another technique, continuous liquid interface production (CLIP) that utilizes liquid resins beneath which liquid coolant is placed and can print a huge structure in a limited time.

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