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INNOVATIVE COMPOSITES FOR BIOMEDICAL APPLICATIONS: FDM 3D PRINTING OF FINGER SPLINT USING PLA COMPOSITE

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Abstract:
Choosing the correct biomaterial for an implant can make or break its effectiveness. It's ideal if an implant's substance is biocompatible, inert, long-lasting, and easy to shape. The capacity of 3D printing to create patient-specific implants with bioactive drugs, cells, and proteins has revolutionized the medical and pharmaceutical industries. Metals, ceramics, polymers, and even composites are now used in medical 3D printing. Due to advancements in the biomaterials used in 3D printing technology, an increasing number of companies are leveraging this technology to make custom implants, prostheses, medication delivery devices, and tissue engineering and regenerative medicine scaffolds. This work focuses on 3D printing biomaterials that can be used in healthcare contexts. Researchers are now utilizing a wide variety of biomaterials, and their clinical applications are discussed in length in this article. Finally, this work presents manufacturing of composite PLA filament of 1.75 mm diameter containing Cobalt (Co) and Chromium (Cr) particles followed by 3D printing of finger splint using low-cost 3D printer.

Keywords: FDM, 3D Printing, PLA Composite, Implants

1. Introduction

Three-dimensional printing enables the creation of three-dimensional objects from digital information. This procedure generates a three-dimensional digital object using computer-aided design (CAD) software. SolidWorks is one of the most widely used commercial 3D modeling and rendering programs. Blender, FreeCAD, Meshmixer, and SketchUp are just a few of the numerous online open-source 3D modeling programs. Each of these 3D models is saved in a format that a 3D printing machine can read. STL (stereolithography) and VRML are the most frequently used file formats for 3D printing (virtual reality modeling language). Along with GCode and 3g, 3D printers can read the AMF, GCODE, and 3g file formats. As illustrated in Figure 1, a CAD model is utilized to build a 3D printed object.

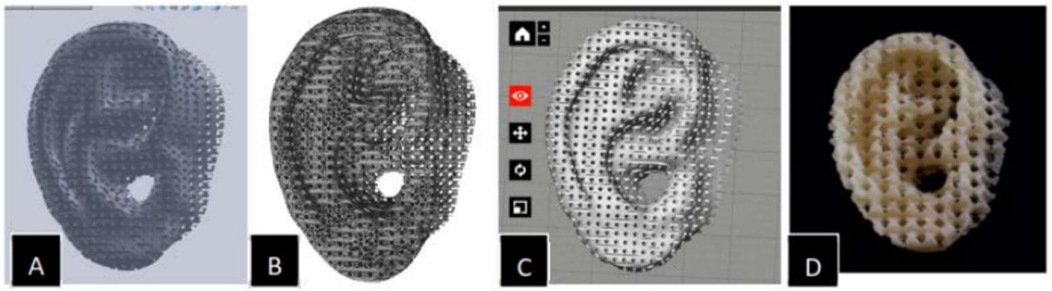


Figure 1: A 3D printing process flow. A - CAD model designed in 3D. B - STL file of the model in stereolithography (STL format). C - Slicing or 3D printing software. D - 3D printed object.

Additive manufacturing constructs the desired thing layer by layer until it is complete. Although the term "3D printing" is frequently used interchangeably with this approach, additive manufacturing spans a broad range of fabrication techniques. Extrusion printing, material sintering, material binding, and object lamination are the four additive manufacturing technologies. To better grasp, the 3D printing process and how it works, consult Table 1 [1-5]. This technology has been around for over 30 years in the automotive and aerospace industries. There was no medical use of this technology other than educational training in medicine. The medical and pharmaceutical industries have recently adopted 3D printing because of recent developments in biodegradable materials. There are numerous clinical uses for modern additive manufacturing processes, and they're emerging at a rapid pace. Biomedical models, surgical tools, bio-printed tissues, and live scaffolds for regenerative medicine have significantly altered healthcare. 3D printing is being employed in various industries, as seen in Table 2.

Table 1 Three-dimensional printing methods come in a variety of flavors [1-5].

Process	Principle
Extrusion Printing	
Fused Deposition Modeling (FDM) [1]	A thermoplastic material is melted and laid on to the build platform in layer-by-layer fashion, until the object is formed.
	Materials: acrylonitrile butadiene styrene (ABS), poly lactic acid (PLA), nylon.
Bioprinting [2]	Biological materials are extruded through a nozzle under pressure to lay down materials in sequential layers till the scaffold is built.
	Materials: alginate, chitosan, gelatin, collagen, fibrin.
Material Sintering	
Selective Laser Sintering (SLS) [3]	A high-power laser beam fuses the powdered materials in layer by layer pattern to form an object.
	Materials: nylon, polyamide.
Electron Beam Manufacturing (EBM)	EBM is similar to SLS, except for high power electron beam is used to fuse the powdered particles.
	Materials: titanium, cobalt–chrome alloy.
Stereolithography (SLA) [4]	A UV laser beam selectively hardens the photo polymer resin in layers.
	Each layer is solidified and built on top of next until the object is formed.
	Materials: photopolymers.
Continuous Liquid Interface Production (CLIP) [5]	CLIP is similar to SLA, except for UV beam is passed through a transparent window at the bottom of the resin and build platform raises upwards holding the 3D printed object.
	Materials: photopolymers.
Material Binding	
Binder Jetting/Inkjet [6]	A liquid binding material is selectively dropped into the powder bed in alternative layers of powder–binding liquid–powder, until the final object is formed.
	Materials: starch or gypsum (powder bed) and water (binding agent)
Polyjet	Polyjet printing is similar to inkjet, but instead of binding agents, photopolymer liquid is sprayed in layers onto the build platform and is instantaneously cured using UV light.
	Materials: polypropylene, polystyrene, polycarbonate
Lamination	
Laminated Object Manufacturing (LOM)	Layers of adhesive coated material are successively glued together and cut in required shapes using a laser.
	Materials: thin sheets of paper, polyvinyl caprolactam (PVC) plastic, or metal laminates

Table 2 3D printing has a variety of applications.

Sector	Applications
Industry	Jigs, fixtures, and end-use parts for aeronautical industry Prototypes and spare parts for automotive industry
Medical	Surgical models for perioperative surgical preparations Dental fixtures, bridges, and crowns Customized patient specific implants and prostheses Living tissue scaffolds for tissue engineering and regenerative medicine
Pharmaceutical	Customized implants for drug delivery Tablets, capsules, and other patient specific dosages
Food	Designing and 3D printing complex shaped cakes, cookies, candies, pizzas, and other desserts
Fashion	Jewelry, clothes, shoes, and other accessories
Household	Plates, cups, spoons, holders, and other common household objects
Miscellaneous	Space: building prototypes and parts in space Chemical industry: fabricating complex molecules and compounds Construction: scale models with intricate architectures

2. Literature Review

As long as the biomaterial is in direct contact with biological processes, any tissue or organ can be healed, replaced, or increased. Four biomaterials can be categorized for 3D printing purposes, as illustrated in Table 3. To be suitable for 3D printing, the biomaterial must be biocompatible, printable, and capable of degrading at a rate that the user specifies. For a 3D printing process to work, the final product's intended usage must be considered. It is also important to note that the biomaterials used for dental and orthopaedic implants must be highly long-lasting and biodegradable. Skin and visceral organ applications, on the other hand, require biomaterials that are more malleable and degrade more rapidly. Many biomaterials currently being used in medical 3D printing technologies are suitable for orthodontic purposes. Hydrogels and other soft polymers are utilized in bioprinting cells to create tissue and organs. There is no problem for cells to adapt to their extracellular matrix-like hydrogel microenvironment. Because of their rigidity, complex polymers and composites are commonly used in orthodontics. Soft polymers, such as hydrogels, are often used in the bioprinting of tissues and organs. Cells are easily accommodated in this hydrogel milieu, which resembles an extracellular matrix.

Table 3 Classification of biomaterials, including their advantages, limitations, and applications.

Type	Advantages	Disadvantages	Applications
Metals and metal alloys	* High material strength	* Corrosive	* Orthopedic implants, screws, pins, and plates
E.g.,: gold, platinum, titanium, steel, chromium, cobalt	* Easy to fabricate and sterilize	* Aseptic loosening * Excessive elastic modulus	
Ceramics and carbon compounds	* High material strength	* Difficult to mold	* Bioactive orthopedic implants
E.g.,: calcium phosphate salts (HA), glass, oxides of aluminum and titanium	* Biocompatibility * Corrosion resistance	* Excessive elastic modulus	* Dental implants * Artificial hearing aids
Polymers	* Biodegradable	* Leachable in body fluids	* Orthopedic and dental implants
	* Biocompatible	* Hard to sterilize	* Prostheses
	* Easily moldable and readily available		* Tissue engineering scaffolds
E.g.,: PMMA*, Polycaprolactone(PCL), PLA, polycarbonates, polyurethanes	* Suitable mechanical strength		* Drug delivery systems
Composites	* Excellent mechanical properties	* Expensive	* Porous orthopedic implants
E.g.,: Dental filling composites, carbon fiber reinforced methyl methacrylate bone cement + ultra-high molecular weight polyethylene	* Corrosive resistant	* Laborious manufacturing methods	* Dental fillings * Rubber catheters and gloves

* PMMA—poly (methyl methacrylate).

In terms of additive manufacturing, FDM is the most used process. The filament can be fed into the build platform and layered to make a finished object after being heated in the print head. Low-cost desktop 3D printers such as Ender-3, MakerBot, Ultimaker, Flashforge, and Prusa are commercially available. These printers can only print on a restricted number of materials, limiting their ability to manufacture high-quality goods. Stratasys printers are high-end FDM machines that can print at greater resolutions and with a broader selection of materials, giving you an indication of the pricing range. Due to their numerous print heads, FDM printers can print various materials at once. As an alternative, the print heads in most multi-head printers are kept clean by using a water-soluble filament. An FDM 3D printer's many parts are shown in Figure 2. Filament extruded from the heated print head is fed into the build platform, where it is applied layer by layer to make the desired object. Consumers can choose from various low-cost desktop 3D printers on the market today. For the FDM technique, ABS is the most often utilized thermoplastic polymer. Some of the most regularly used printed filaments include PLA, nylon, polycarbonate (PC) and polyvinyl alcohol (PVA). Polylactic acid-based polymers like PLA and PCL, both biocompatible and biodegradable, are commonly employed in the medical and pharmaceutical industries.

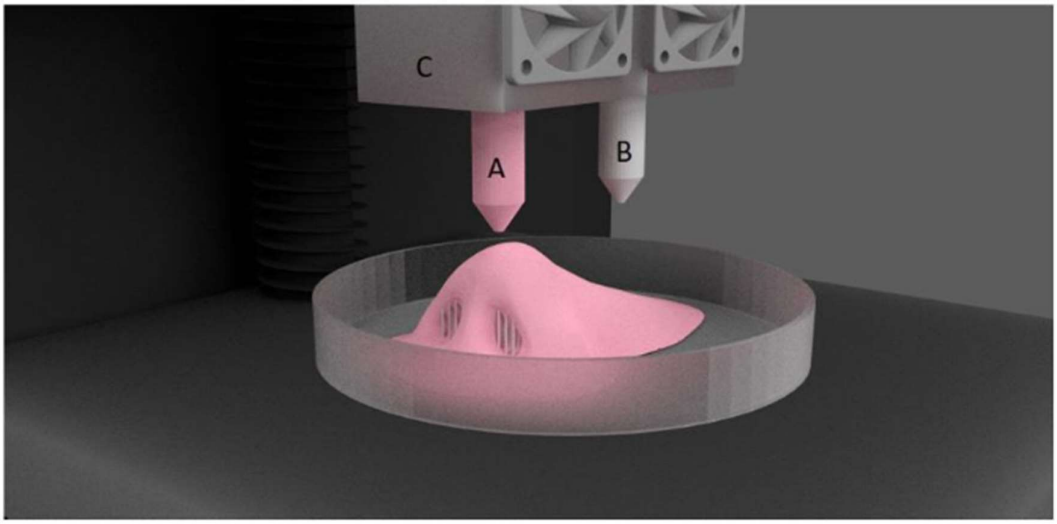


Figure 2 FDM 3D printer with two heads.

There are many factors to consider while printing biocompatible scaffolds. Raster angle, layer height, and raster thick are examples of these variables. As a biopolymer in FDM, PCL can improve bioactive scaffolds like PCL/chitosan or PCL/-TCP (tricalcium phosphate) [6-9]. FDM-based construction provides higher mechanical qualities and is more exact in dimensions. Consequently, 3D printing is widely employed in industrial prototyping. Using the FDM method, implants, prostheses, anatomical models, and surgical guidance can all be made. Antibiotics [10], chemotherapy [11], hormonal medicines [12] and nanoparticles [13,14] have all been combined in injections using thermoplastic polymers [15,16]. Various plastics, including ABS and TPU, are employed to create surgical planning and simulation models [17, 18]. These simulations can also be used to help patients understand what to expect during surgery. The clinical biomaterials utilized in the FDM technique are shown in Table 4.

Table 4 A summary of the biomaterials that are utilized in FDM-based 3D printing.

Materials	Fabrication Process	In Vivo/In Vitro Model	Key Findings	Ref.
		Scaffolds for tissue engineering and regeneration		
PCL + Chitosan	Porous PCL scaffolds were 3D printed at 130 °C, print head speed of 1–3 mm/s and 1.5–3.0 bar pressure. Thermosensitive chitosan hydrogel was filled inside the pores of PCL scaffold.	Rabbit bone marrow mesenchymal stem cells (BMMSCs)	3D printed scaffolds showed greater cell retention and proliferation of BMMSCs. Stronger osteogenesis and higher bone matrix formation shows their applications in bone tissue engineering.	[8]
PCL + β-TCP	PCL melted at 110 °C and β-TCP powder is added. Membranes were 3D printed at 110 °C and at 900 kPa.	Alveolar bone defects on beagles	The 3D printed PCL/β-TCP membranes showed enhanced bone regeneration capabilities than PCL or collagen membranes alone.	[9]
PLA + biodegradable calcium phosphate glass	Printing pressure 10–80 psi, 3 mm/s nozzle speed, print head temperature 40 ± 5 °C. Cross-linked with 8% (w/v) NaOH in 70% ethanol.	Human monocytes	PLA based scaffolds increased the production of IL-6, IL-12/23 and IL-10.	[9]
		Drug Delivery		
PCL	Extruded PCL filaments with female sex hormones (E1, E2, E3 and progesterone) at 90 °C and 3D printed at 110 °C in the shape of commonly used implants including discs, pessaries, subdermal rods, intrauterine devices (IUD) and surgical mesh.	Estrogen receptor luciferase reporter cells (14/10)	FDM can be used to fabricate patient specific personalized medicine for drug delivery. The 3D printed hormonal constructs showed biocompatibility and bioactive retention.	[12]
PLA	PLA pellets coated with gentamicin and methotrexate were extruded as filaments at 170 °C and 3D printed as beads and catheters using Makerbot 3D printer (FDM based) at 220 °C.	Osteosarcoma cells (for chemotherapeutics) and *E. coli* (for antibiotics)	3D printed PLA constructs successfully retained the bioactivity. Clear demarcating zones of inhibition was seen for gentamicin constructs and decrease in cell viability of osteosarcoma cells proved the cytostatic effect of methotrexate constructs.	[11]
Olea gum resins (benzoin, myrrha and olibanum) doped with metal oxide nanoparticles (TiO_2, P25, CuO, and MoO$_3$)	Natural gum resins added with 10% metal oxides were extruded as filaments at 70–85 °C and 3D printed into discs (18 mm × 5 mm) at 80 °C while maintaining the build platform temperature at 60 °C and at a print head speed of 10 mm/min.	*Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, and *Candida albicans*.	Naturally occurring polymers can be successfully 3D printed. Discs with just the resins prevented only surface associated microbial growth. Additionally, metal oxide nanoparticles increased the bacteriostatic effects of the natural polymers.	[13]
PVA	PVA filament was milled and powdered. Paracetamol and caffeine were added and extruded as filaments at 180 °C. These filaments were 3D printing into tablets and capsules at 200 °C with print head speed of 150 mm/s		Novel oral dosage forms were successfully fabricated. Capsules with alternating layers of caffeine and paracetamol were 3D printed.	[16]
		Surgical guides and implants		
ABS	CAD models were developed using CT files of patient and 3D printed. FDM fabricated models were scanned again for comparison	Perioperative surgical simulation of conjoined twin separation surgery	The 3D printed models resembled the CT data of the patients and had an overall mean deviation of less than 2 mm.	[17]
TPU *	Pharmaceutical grade TPU powder was extruded into filaments and 3D printed into fistula stents, which were modelled from patient's 3D reconstructed fistulography and CT scan images	A 45-year-old man was implanted with this tailor-made fistula implant	The 3D printed implant was effective in treating the enterocutaneous fistula	[18]

* TPU—thermoplastic urethane.

Aside from FDM, the most utilized additive manufacturing techniques in medicine are extrusion-based bioprinting, inkjet, and polyjet (see Table 1). In this work, discussion is limited to FDM 3D printing. This work showcases manufacturing of composite PLA filament of 1.75 mm diameter containing Cobalt (Co) and Chromium (Cr) particles followed by 3D printing of finger splint using low-cost 3D printer.

3D printing using PLA is revolutionizing biomedical industry as PLA is biocompatible [19]. PLA is one of the most widely used and approved by the Food and Drug Administration (FDA) of the United States for biomedical applications. Ramot et al. [20] and Middleton and Tipton [21] concluded PLA is safe to use in implants. 3D printing enables customization of medical products, drugs, and devices. 3D printing using PLA filament is cost effective and increases productivity [22]. According to Mertz [23], the customized implants, fixtures, and surgical tools have a positive impact on clinical success rate. Despite biocompatibility and safety of PLA in medical industry, insufficient mechanical strength, as well as inappropriate degradation rate, necessitate further research in this field for improvement [24]. Composite PLA is viewed as one of the viable options to overcome some of the drawbacks of pure PLA filament in biomedical applications [25].

A composite PLA filament is a combination of two or more constituents or phases, resulting in unique properties that cannot be achieved from either component alone. In particulate matrix PLA composite filament, PLA is matrix and particles of polymers, metals, ceramics, etc. are dispersed across filament. Recently, numerous attempts have been made to enhance the bio-performance and other properties of PLA using particulate composites of PLA. The incorporation of metal particles and producing particulate PLA composite is a promising approach to improve the properties, bioactivity and biocompatibility of 3D Printed PLA parts in biomedical applications. Literature review indicates that several metallic particles such as steel, copper, magnesium, nickel, titanium, etc. are added to the PLA filament to fabricate particulate composite PLA filament [26]. This particulate PLA composite filament is used for 3D printing parts. Different metallic particles have shown different enhancements for biomedical applications. However, the use of particulate composite PLA filament is challenging in 3D printers, as filament breakage and nozzle clogging may occur during 3D printing by the FDM process [27-28]. It is observed that none of the previous work used two different metallic particles simultaneously. Besides none of the previous work reported use of Cobalt (Co) and Chromium (Cr) particles in PLA. Cobalt and Chrome alloys are often used for medical implants due to biocompatibility. Therefore, the objective of this work is to manufacture composite PLA filament containing Co and Cr particles followed by 3D printing of finger splint.

3. Research Methodology

The objective of this work is to manufacture particulate composite of PLA filament of 1.75 mm diameter containing Co and Cr particles followed 3D printing of finger splint using low cost FDM 3D printer. Therefore, this section presents methodology of manufacturing particulate composite PLA filament, 3D printing of finger splint and associated challenges of using Co-Cr PLA filament.

3.1 Manufacturing of particulate composite PLA filament

PLA granules (pallets) and metal (Cobalt and Chromium) particles are used for manufacturing of particulate composite PLA filament. PLA granules are purchased from Rivika Bio Industries

Pvt. Ltd. India [29]. Cobalt (Co) and Chromium (Cr) metallic particles are purchased from Laxmi Narayan & Sons, India [30]. Average size of Co and Cr powder particle is 325 mesh and 200 mesh respectively. Particulate composite PLA manufacturing is three step process as shown in Table 3. Initially, PLA granules are heated to 80 °C for about 1 hour to remove moisture. This step is called de-moisturization. After de-moisturization second step is melting and mixing. During this step PLA granules are poured in a hopper to pass through a three-temperature melting process. Granules are melted gradually at 180, 190 and 200 degrees. Molten PLA is maintained for about 1 hour at each stage for achieving uniformity in the melting furnace. 2.0% Co and 2.0% Cr metallic particles by weight are mixed with molten PLA by stirring continuously for uniform mixing of metallic particles. Mixed molten PLA is extruded through a mold to obtain particulate composite PLA filament of 1.75 mm diameter. This final stage is called extrusion of filament. After solidification, the filament is removed from the die and cleaned. The diameter is measured at various locations and diameter accuracy is within ±0.1 mm.

Table 5 Fabrication of particulate composite PLA filament

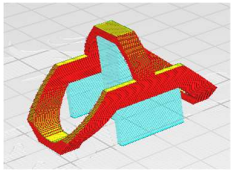
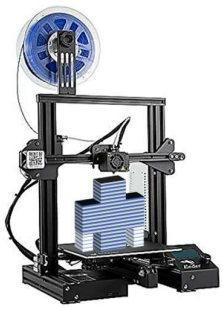
Filament Fabrication Machine	Filament Fabrication Process	Filament Fabrication Process – Pictorial Representation
	*Step 1 - De-Moisturisation*	 Co Particles  PLA Granules  Cr Particles
	Step 2 - Melting & Mixing	
	Step 3 - Extrusion of filament	

3.2 3D Printing of finger splint using particulate composite PLA

In this work particulate composite PLA filament is used for 3D Printing. This work uses Ender-3 open-source low-cost 3D printer [31]. Ender-3 works on FDM technology. Table 6 shows Ender-3 with its specification, stages of 3D printing and slicer parameters configured for 3D

printing. Ender-3 has a build volume of 220 x 220 x 250 mm and precision of ±0.1 mm. Computer Aided Design (CAD) modeling of finger splint is carried out in SolidWorks software [32] followed by slicing in Cura software [33].

Table 6 FDM 3D printing of finger splint specifications and parameters

3D Printing Process	Specifications of Ender-3	
CAD Modelling 	**Machine Parameter**	**Value**
	Machine Weight	*6.62 Kg*
	Machine Size	*440 x 440 x 465 mm*
	Printing Size	*220 x 220 x 250 mm*
	Printing Speed	*≤ 180 mm/s*
	Printing Precision	*± 0.1 mm*
Slicing 	*Nozzle Diameter*	*0.4 mm*
	Bed Temperature	*≤ 100 °C*
	Nozzle Temperature	*≤ 270 °C*
	Power Supply	*Input AC 115V/230V Output DC 24V 270W*
3D Printing 	**Cura Slicer Settings**	
	Slicer Parameter	**Value**
	Layer Height	*0.2 mm*
	Line Width	*0.2 mm*
	Support	*Enabled*
	Support Line Width	*0.12 mm*
	Wall Thickness	*0.4 mm*
	Top Thickness	*0.4 mm*
	Bottom Thickness	*0.4 mm*
3D Printed Finger Splint 	*Infill*	*100 %*
	Infill Pattern	*Concentric*
	Nozzle Temperature	*200 °C*
	Bed Temperature	*60 °C*
	Print Speed	*50 mm/s*

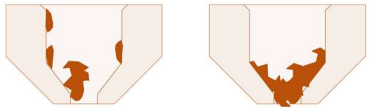
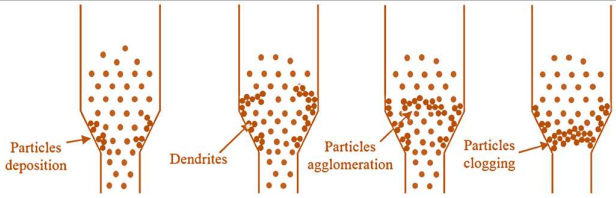
3.3 3D Printing challenges with particulate composite PLA filament

There are several challenges while using particulate composite PLA filament for FDM 3D printing. Following three major problems are observed while using PLA/Co-Cr filament during this work:

- Nozzle clogging: 3D printer nozzle clogging and abrasion is major problem challenge while using particulate composite PLA filament. Nozzles are also subjected to a higher risk of clogging as shown in Table 7. Frequent nozzle cleaning or replacement of nozzle is required. Abrasion of nozzle is another challenge. Upgrading 3D printer nozzle to stainless steel, nickel-plated brass (better heat transfer), or another hardened alloy may be necessary, since brass nozzles wear out much faster from metal abrasion.

- Filament breakage: Filament should be kept dry and in a cool place to reduce moisture exposure. With metal fill, especially at higher percentages, the filament is little more brittle and should be handled with care.
- Cura settings: Print settings can be a challenge. The more metal in the filament, the more difficult it may be to find the correct settings for a good print. Considerations must be made for adjusting temperature, retraction, and first-layer thickness. Higher temperature settings are used in case of PLA/Co-Cr filament.

Table 7 – 3D printing nozzle clogging phenomena

Cause	Hot End	Nozzle Clogging Process
Pure PLA sticks to nozzle leading to clogging.		
Deposition of Co-Cr particles plus sticking of PLA matrix leads to nozzle clogging		

4. Conclusions

The conclusions of this work are as listed below:

- Medicine has significantly benefited from 3D printing, and this technology will only get better. Examples of clinical applications include custom-made implants and prostheses for individual patients, tissue regeneration scaffolds, biosynthetic organ manufacturing, personalized medicine delivery systems, and anatomical modeling for perioperative simulations, among others. Personalized treatment, cost-efficiency, speed, and improved production are just a few of the advantages of 3D printing in the medical field.
- In terms of additive manufacturing, FDM is the most used process. The filament can be fed into the build platform and layered to make a finished object after being heated in the print head. Low-cost desktop 3D printers such as Ender-3, MakerBot, Ultimaker, Flashforge, and Prusa are commercially available.
- PLA is one of the most widely used and approved by the Food and Drug Administration (FDA) of the United States for 3D printing. Despite biocompatibility and safety of PLA in medical industry, insufficient mechanical strength, as well as inappropriate degradation rate, necessitate further research in this field for improvement. Composite PLA is viewed as one of the viable options to overcome some of the drawbacks of pure PLA filament in biomedical applications.
- Successfully fabricated particulate composite PLA filament by adding bioinert metals Cobalt and Chromium for FDM based 3D printing of biomedical device. The percentage of Co and Cr in PLA matrix is limited to 0.5 % each by weight. The particulate composite

PLA filament is three stage process de-moisturization, melting & mixing followed by extrusion of filament.

- Finger splint is successfully 3D printed using particulate composite PLA filament on Ender-3 low-cost 3D printer. Three major problems are observed while using PLA/Co-Cr filament during 3D printing. These problems are nozzle clogging, filament breakage and printing settings.

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