



Selective laser sintering of in-situ copper-modified polyamide

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DECLARATION OF INDEPENDENT WORK

I, Winston Kagisho Curtis Wolf, _____ and student number _____, do hereby declare that this research project submitted to Central University of Technology, Free State (CUT, FS) for the Master of Engineering in Mechanical Engineering degree is my own independent work; and complies with the Code of Academic integrity, as well as other relevant policies, procedures, rules and regulations of Central University of Technology, Free State; and has not been submitted previously to any institution by myself or any other person in fulfilment of the requirements for the attainment of any qualification.

Signature of student



28 April 2023

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ABSTRACT

Metals, ceramics, glass, and polymers are materials utilized in the design and manufacture of medical devices. Due to the wide variety of features they offer, such as biocompatibility, cost-effectiveness, design freedom, and balanced mechanical properties, polymer materials are increasingly used to fabricate medical device components. Selective Laser Sintering (SLS) or Laser Powder Bed Fusion (LPBF) of plastic materials is an Additive Manufacturing (AM) technique where a bed of powder polymer or elastomer is sintered by laser with the subsequent solidification of the powder layer. Polyamide-based plastic materials are utilized to produce workable AM prototypes and end-use parts. Polyamide 12 (PA12), or Nylon 12, has 12 carbon atoms with a formula $[-(\text{CH}_2)_{11}\text{C}(\text{O})\text{NH}-]_n$ and is a thermoplastic polymer that has excellent impact strength. PA12 is less sensitive to stress cracking than other nylon polymers and has quite low moisture absorption. Copolymerisation or different fillers can modify the physical, mechanical and other properties of polyamide (PA). Microorganisms may quickly colonize various polymer surfaces, especially in-house devices. The surfaces of these devices provide the opportunity to form biofilms that can facilitate the growth of infection and fever-causing microorganisms. The growth of microorganisms can also cause staining, discolouration, odour, and reduction of performance and material properties. As the public becomes more aware of hospital-acquired antibiotic-resistant diseases, alternative antimicrobials are often used in medical devices, equipment housings, and hygienic surface coatings. Copper (Cu) is proven to be an antibacterial agent in medical devices and is nontoxic to humans in low concentrations (Cervantes and Gutierrez-Corona, 1994). The antibacterial characteristics of Cu have made it a popular choice for food and medical device surfaces that are regularly handled. One advantage of SLS is the possibility of producing in-situ sintered materials from powder mixtures. This work evaluates the characteristics of in-situ SLS copper-modified black polyamide 12 (PA12/B) samples with the addition of 10 wt.% and 20 wt.% Cu as antibacterial agent. Roughness and morphological features of manufactured SLS surfaces, porosity, conductivity, mechanical properties and antibacterial characteristics of polymer-metal composite test samples are described in detail. It was shown that polyamide-copper antibacterial composites can improve the functionality of AM parts avoiding infections in users since pure Cu possesses antibacterial capabilities.

Keywords: laser powder bed fusion, selective laser sintering, polymers, medical devices, antibacterial properties, tensile properties, surface roughness, porosity

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Glossary

AM	Additive Manufacturing
ASTM	American Society for Testing and Materials
ABS	Acrylonitrile butadiene styrene
BFRP	Basalt fibre reinforced polymer
BJT	Binder jetting
BM	Ball milling
CB	Carbon black
CFU	Colony-forming units
CPC	Conductive polymer composites
CRPM	Centre for Rapid Prototyping and Manufacturing
CNT	Carbon nanotube
DCM	Dichloromethane
DED	Directed energy deposition
DMLS	Direct metal laser sintering
EC	Electrical conductivity
EMI	Magnetic interference shielding
EOS	Electron Optical Systems
FR	Flame retardant
FRP	Fibre-reinforced composites
FDM	Fused deposition modelling
GNP	Graphene nanoplatelets
GS	Gentamicin sulphate
GO	Graphene oxide
HAI	Healthcare-associated infections
HA	Hydroxyapatite
HDT	Heat distortion temperature
HIPS	High-impact polystyrene
ISO	International Organization for Standardization
LDPE	Low-density polyethylene
L-PBF	Laser power bed fusion
LS	Laser sintering
MEX	Material extrusion
Micro-CT	Micro-computed tomography

MJT	Material jetting
MRSA	<i>Staphylococcus aureus</i>
MWCNT	Multi-wall carbon nanotube
PA	Polyamide
PA12/B	Polyamide 12 black
PBF	Powder bed fusion
PCL	Polycaprolactone
PEEK	Polyether ether ketone
PE	Polyethylene
PLA	Polylactic Acid
PMMA	Poly-methyl methacrylate
PP	Polypropylene
PPE	Personal protective equipment
PSD	Particle size distribution
SHL	Sheet lamination
SLA	Stereolithography
SLS	Selective laser sintering
SLM	Selective laser melting
SEM	Scanning electron microscope
TPU	Thermoplastic polyurethane
UDLD	Ultrasonic dispersion liquid phase deposition
VPP	Vat photopolymerization
VRE	<i>Vancomycin Enterococcus spp.</i>
WPC	Wood plastic composite
2D	Two-dimensional
3D	Three-dimensional

CHAPTER 1: INTRODUCTION

1.1. Background

Additive manufacturing (AM) is a cutting-edge technology that allows the production of a three-dimensional (3D) physical object directly from digital files. Laser Powder Bed Fusion (LPBF) is an AM technology that uses a layer-by-layer system to create complex 3D parts using a laser beam. Historically, the term “Selective laser sintering” (SLS) is used concerning polymer LPBF, and “Selective laser melting” (SLM) is applied to metal laser powder bed fusion. In fact, it is the same process in which the layer-by-layer melting of the powder occurs using a laser beam (Beaman, 2021). A schematic of the SLS process is shown in Figure 1.

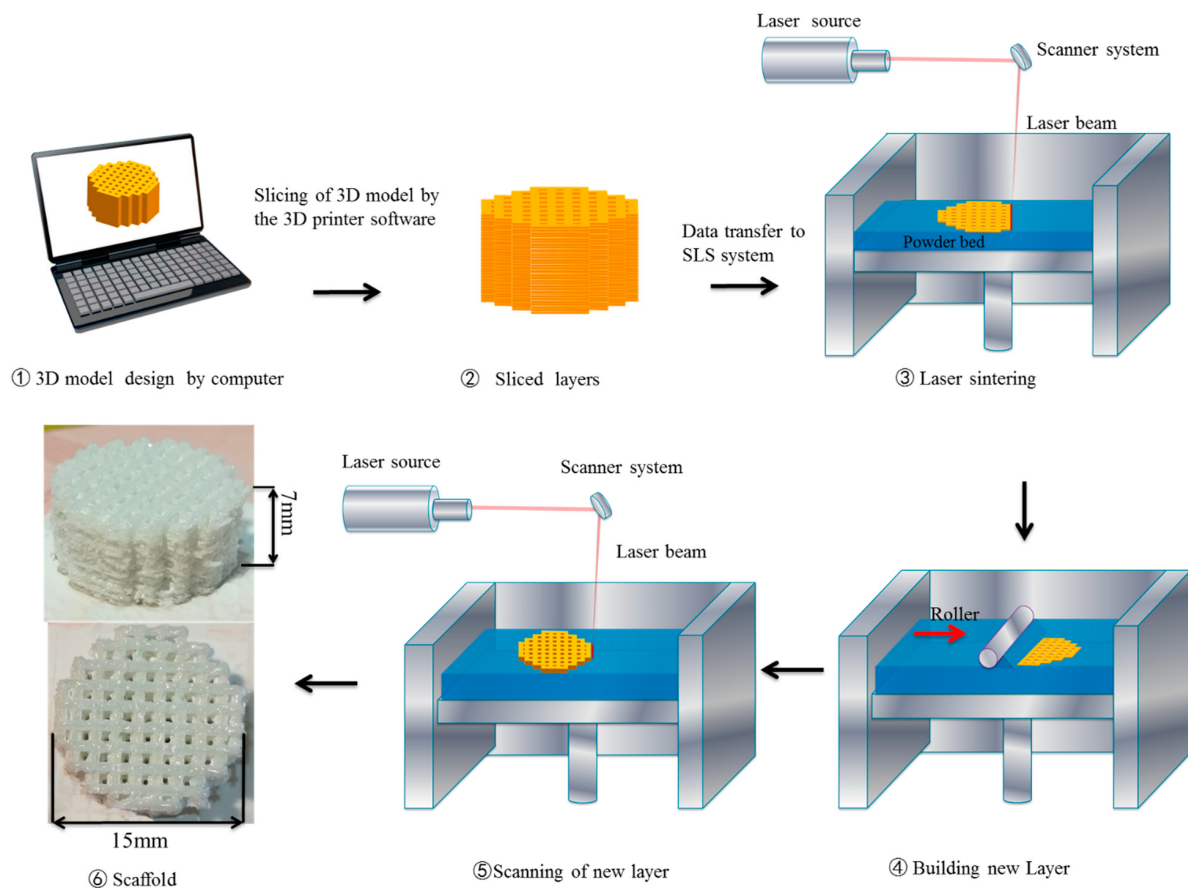


Figure 1. Schematic of the SLS process (Qin et al., 2020)

A laser beam selectively fuses a polymer powder; thus, a component is built up layer by layer in the powder bed. In the first step, the polymer powder is deposited into the building chamber, which is preheated to a temperature between the melting and crystallization point of the semi-crystalline polymer. After the powder material is spread, the cross-section of the part is fused using a laser beam controlled by a scanning system. The surrounding powder acts as a support

structure for the component. After scanning, the building substrate is lowered by the thickness of one layer, and the scanning process is repeated. Hence, a component is manufactured layer by layer.

Commercially available materials for SLS are thermoplastic polymers like polyamide 12 (PA12), polyetheretherketone (PEEK), acrylonitrile butadiene styrene (ABS), polyetherimide (ULTEM), thermoplastic urethane (TPU), polycarbonate (PC) and polypropylene (PP) and some non-commercial materials like polybutylene terephthalate (PBT) (Picard *et al.*, 2020). Due to its large supercooling window, small crystallization shrinkage, and robust processing, polyamide-12 (PA12) dominates the market (Dadbakhsh *et al.*, 2017, Rouholamin *et al.*, 2014, Ziegelmeier *et al.*, 2015). PA2200 from Electron Optical Systems (EOS GmbH) is the PA12-based commercialized polymer characterized by higher crystallinity and melting point, which is considered biocompatible and has stable processing along with repeatable properties of manufactured parts. Several filled commercial materials from EOS are available, such as Alumide (aluminium filled with PA12) and PA12 with glass filler, and carbon and glass filler (ALM PA 640-GSL). Applications include the aerospace, shipping, sports, model making, and motorsport sectors – all areas where EOS also offers ALM HP 11-30, a carbon fibre-reinforced PA11 that shows high strength, impact resistance, and an increased elongation at failure. This material is suitable for the automotive industry, where reduced weight and high strength are required. EOS also produces a flame-retardant PA11 suitable for the aerospace industry.

Nylon is a widely used material in biomedical applications for healthcare devices and implants. As they are in contact with tissues for prolonged periods, the development of antimicrobial strategies is required (Shakiba *et al.*, 2021).

Healthcare-associated infections (HAIs) are the most prevalent complication affecting hospitalized patients worldwide (Allegranzi *et al.*, 2011). HAIs have a major impact on public health, according to Barriga *et al.* (2014), due to the increased average duration of hospital stays, morbidity, death, and the source of high healthcare expenses (Scott, 2009, Brenner *et al.*, 2003). HAIs are caused by several factors, including underlying medical problems (such as complicated diseases) and hospital-related risk factors. Both sporadic cases and outbreaks of HAIs can be traced back to medical equipment and hospital surfaces contaminated with pathogenic microorganisms (Attaway *et al.*, 2012, Kramer *et al.*, 2006). Pathogens can colonize hospital surfaces, and both the spores and vegetative form can survive for long periods (Kramer *et al.*, 2006). Hand hygiene and terminal washing of patient touch surfaces are two critical strategies for limiting the spread of infectious agents inside the hospital (Pittet and Donaldson,

2005). According to Lewis *et al.* (2008) and Salgado *et al.* (2013), 250-500 aerobic colony-forming units (CFUs) per 100 cm² is the microbiological criterion for assessing and monitoring the final cleaning of hospital surfaces. While rigorous cleaning can eliminate most bacteria from hospital surfaces, they are vulnerable to re-contamination, which can happen quickly in some situations (Schmidt *et al.*, 2013).

3D printed polymer components for bone tissue treatment, specific biomedical devices, wound dressings, different kinds of scaffolds have been extensively explored in recent years (Tardajos *et al.*, 2018).

In 2008, the United States Environmental Protection Agency (US EPA) proved copper (Cu) as the first antimicrobial metal. Hard Cu surfaces killed 99% of microorganisms in in-vitro assays within two hours of contact (Prado *et al.*, 2012). The release of ions that disrupt membrane integrity and/or bacterial integrity is principally responsible for Cu's bactericidal effect. The cell wall produces intracellular oxidative stress, which is genotoxic and causes microorganisms to die (Grass *et al.*, 2011, Vincent *et al.*, 2018). One of the benefits of Cu as a bactericidal agent is its low degree of resistance among clinically relevant pathogens. Cu-resistant mechanisms are more common in microorganisms that live in copper-rich niche environments, such as lake habitats and caves (Vincent *et al.*, 2018, Besaury *et al.*, 2013). As a result, research into Cu as a technique for lowering microbial strain in healthcare facilities and minimizing HAIs has risen in recent years (Salgado *et al.*, Schmidt *et al.*, 2013b, Hinsaleasure *et al.*, 2016, Von Dessauer *et al.*, 2016). According to these experiments, solid Cu-coated hospital surfaces have a consistently lower microbial load than control surfaces. Some studies indicated that using Cu-coated surfaces decreases these infections (Salgado *et al.*, 2013, Sifri *et al.*, 2016), but other researchers indicated that the reduction has not been statistically significant (Rivero *et al.*, 2014). Furthermore, the wide range of existing design and data analysis research makes it impossible to evaluate their results and draw definite conclusions (Webber *et al.*, 2017, Chyderiotis *et al.*, 2018). Thus, more research is needed to see how using Cu-coated surfaces affects the occurrence of HAIs.

Cu is now used as an antibacterial, antifouling, algacide, bactericide, molluscicide, nematocide agent, and water purifier. Cu-containing surfaces are particularly effective in lowering *E. Coli* survival, according to Borkow *et al.* (2005, 2004) and Wilks *et al.* (2005). This knowledge also paves the way for developing more sophisticated Cu-based antimicrobial materials like nanoparticles or contemporary multifunctional biomaterials (Muoz-Bonilla *et al.*, 2013, Palza *et al.*, 2013, Ren *et al.*, 2009). In recent years, Cu alloys, salts, and oxides have

been reported as effective biocidal materials against many bacteria (Borkow *et al.*, 2005; Muoz-Bonilla *et al.*, 2013).

Since Cu is an antibacterial material and nylon is more frequently used material in 3D printing, combining these materials in one product can lead to the creation of advanced SLS components for biomedical applications. In 3D printing, antimicrobial properties for components can be realized by i) surface coating or modification of components by specific agents, i.e., surface modification of 3D-printed products; ii) by blending of the initial powder material with antimicrobial agents; iii) doping of initial powder by antibacterial agents. Various methods may be used to prepare powder materials for SLS processing: composite grains, coated grains, and separate grains. Composite grain comprises structural and filler materials processed by melt mixing, followed by milling or grinding (Hao *et al.*, 2009). Coated grains are formed by coating the composite materials with the filler material, such as through dissolution-precipitation (Yan *et al.*, 2011). Due to the ease of preparing the mix of the composite and filler materials and the capacity of the mixture to preserve homogeneity during storage, handling and shipping, the separate grain approach is beneficial. Homogeneity is important to avoid phase separation during handling and to generate consistency in particle size and density after SLS processing.

On the one hand, an increase in the copper content in the SLS composite can enhance its antibacterial properties, and on the other hand, a high filler content can change the specific heat capacity and thermal conductivity of the powder material, change its optical properties, which in turn will lead to a change in the optimal process parameters for SLS. An increase in the proportion of copper in the composite will lead to a change in the rheological properties of the powder to the segregation of materials during application. Therefore, it was decided to investigate the proportion of copper in the composite of 10–20% and try to synthesize this composite material using the process parameters recommended by the manufacturer for a pure material (polyamide 12 black) that does not contain the filler.

This study investigates the properties of in-situ-sintered SLS Cu-modified polyamide 12 black at 10 wt.% and 20 wt.% Cu for biomedical applications. Careful analysis of mechanical and antibacterial properties of composite SLS parts was done.

1.2. Main objectives of the study

The main objectives are as follows:

- Examination of the SLS PA12/B+ Cu composite samples to determine surface roughness in as-built samples.
- Analysis of porosity SLS PA12/B+ Cu composites and Cu distribution on the surface and inside samples.
- Evaluation of the PA12/B+ Cu composite tensile properties and fracture behaviour.
- Evaluation of PA12/B+ Cu composite microstructure and antimicrobial characteristics.
- Draw a conclusion on the suitability of the indicated materials for biomedical applications.

1.3. Research methodology

The methodology is as follows:

- A thorough literature study of the SLS process, together with materials used.
- Study of SLS machines from Sintratec (Swiss) and EOS GmbH (Germany & Swiss), scanning electron microscopy (SEM) and computerized tomography (CT) scanner.
- A comprehensive experimental investigation of polymer composites and their characteristics by SEM and CT scans.
- Analysis of the microstructure of PA 2200, PA12/B and PA12/B with 10 and 20 wt.% Cu powder.
- Mechanical testing of SLS samples and fracture analysis.

The layout of the research methodology is shown in Figure 2.

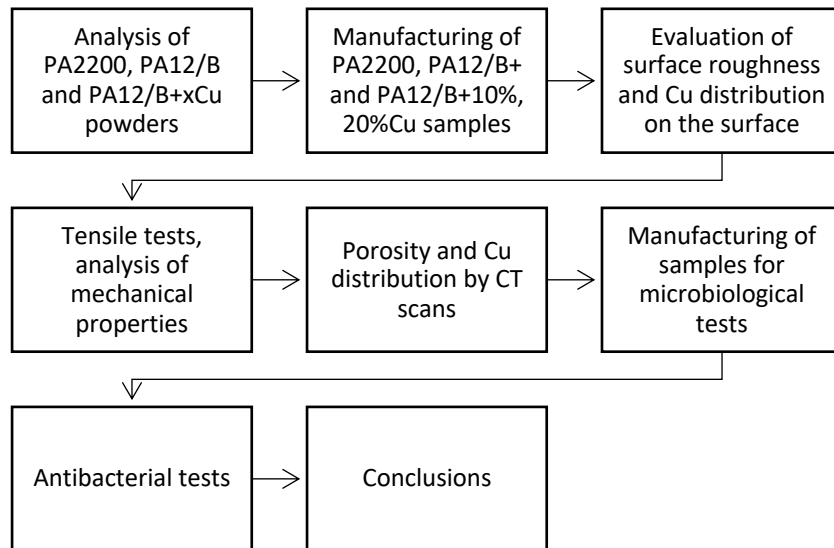


Figure 2. Layout of the research methodology

1.4. Overview of the dissertation

The following outline defines the dissertation structure:

- Chapter 1 presents the study's introduction and context. The study's aims and research methods are discussed in this chapter.
- Chapter 2 presents the literature review relating to the study. AM technology principles and techniques are investigated. The topics covered are AM polymer modifications, the selective laser sintering process, properties of SLS parts and composite powders.
- Chapter 3 describes the materials utilized, as well as the experimental approaches. The tools used to characterize materials and develop and prepare samples are discussed. Microbiological testing is also described.
- Chapter 4 highlights the results obtained and a discussion on the analysis of the microstructure, surface roughness, porosity and mechanical properties of PA12/Cu composite specimens from the blended PA12/B and 10 and 20 wt.% Cu powder. The results of antibacterial tests are presented.
- Chapter 5 summarizes the results, and conclusions are drawn. This chapter also includes suggestions for further research.

1.5. Expected outcomes

- The results will demonstrate the potential of SLS technology for producing parts made of PA12/B + copper with antimicrobial properties that can be used in the future for medical purposes that improve patients' lives.

1.6. Publications and presentations

- W. K. C. Wolf, I. Yadroitsava, I. Yadroitsev. Surface roughness and tensile properties of copper-carbon-polyamide composite by selective laser sintering. In Proc. 21st RAPDASA Annual International Conference, 4–6 November 2020, Stellenbosch University - Central University of Technology, Free State (Bloemfontein) Aerosud (Gauteng), South Africa, pp.107-118, ISBN: 9780639839004.
- W. K. C. Wolf, A. M. Vilardell, A. du Plessis, I. Yadroitsava and I. Yadroitsev. Tensile properties of polyamide 12/black with 10 wt.% copper samples manufactured by laser powder bed fusion. Transactions on Additive Manufacturing Meets Medicine, Vol 3 No 1 (2021): Trans. AMMM, Material Properties, Structural Designs, and Printing Technologies, ID 525, <https://doi.org/10.18416/AMMM.2021.2109525>
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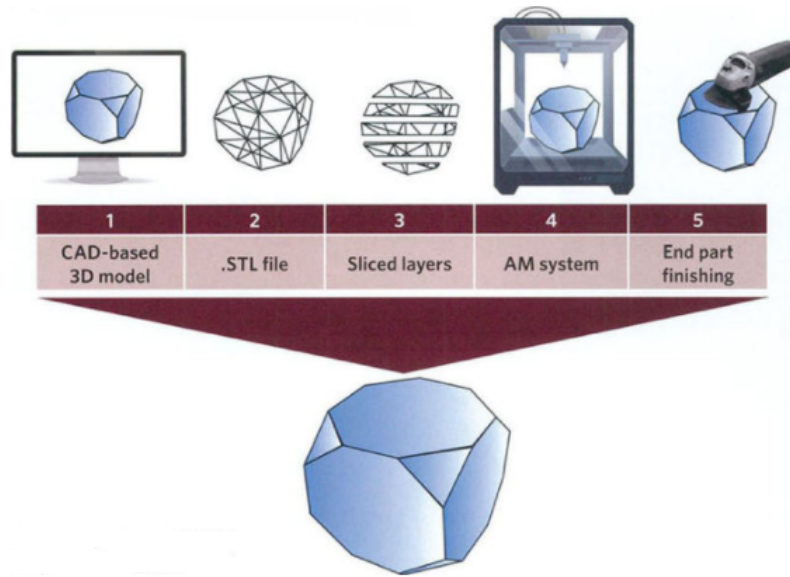
CHAPTER 2. LITERATURE REVIEW

2.1. Additive Manufacturing

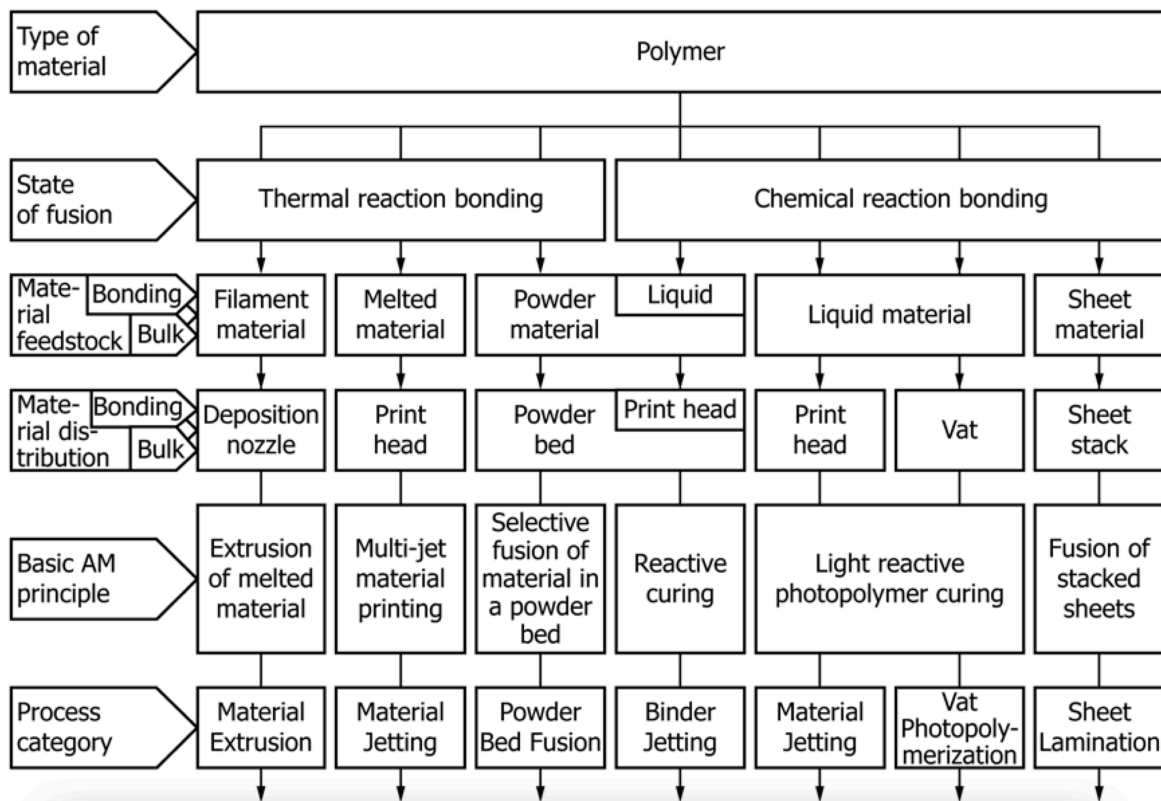
Since the stereolithography (SLA) patent was filed in 1986 (Hull, 1986), new techniques have been developed, such as material extrusion (MEX), material jetting (MJT), binder jetting (BJT), digital light processing, directed energy deposition (DED) and powder bed fusion (PBF) and some others. These and conventional production technologies, such as CNC machining and injection moulding, have advantages and disadvantages. The interaction of some of these innovations with the growth of so many technologies has been a source of ambiguity. As a result, the ASTM International Organization with the International Organization for Standardization (ISO) released the ISO/ASTM 52900:2021 standard, which defines terminology for AM. There are commonalities that all AM processes share, such as the common architecture, as shown in Figure 3, despite the use of different processes and materials (Berman, 2012).

Cutting the digital 3D model to the appropriate number of layers for the component creates the 2D layers (Wendel *et al.*, 2008). This slicing method simulates the physical printing process, in which these sequential layers are printed to create the physical component. The number of layers required depends on several factors, including the component, its orientation, the degree of precision needed, the AM method used, and the file format (Jamieson *et al.*, 1995). In order to produce a component, additional removable support material is required (Wendel *et al.*, 2008, Bikas *et al.*, 2016, Stansbury *et al.*, 2016). The patterns of these printed materials have also been extended. Important expansion into MEX-based machines and many PBF processes have arisen since the initial production using vat photopolymerization (VPP) processes (Gardan, 2016, Stansbury *et al.*, 2016, Kruth *et al.*, 2005; Core-Baillais *et al.*, 2017).

Techniques such as SLA use liquid resin in a vat to solidify layers using ultraviolet light to solidify one layer at a time to form a solid part in the resin vat (Hull, 1986). One of the most widely used AM methods is fused deposition modelling (FDM). Initially, FDM machines were only available for the patenting of pioneering machines. Following the expiration of the main FDM patents, the number of machines available has increased, not only for commercial use but also for domestic hobbyists and customers (Wohlers, 2014, 2020, Stansbury *et al.*, 2016). PBF technology incorporates a range of printing techniques.



(a)



(b)

Figure 3. Additive Manufacturing processes (Dizon et al., 2018a) (a) and overview of single-step AM processing principles for polymer materials (ISO/ASTM 52900:2015) (b)

Selective laser sintering (SLS) and selective laser melting (SLM) technologies are similar as both spread powder over the printing bed to produce the layer and assist with printing the material. Generally, SLS processes manufacture thermoplastic-based products and take

advantage of thermoplastics' glass transition phase (Kruth *et al.*, 2005). SLS machines use a laser beam to rapidly heat the polymer into the glass transition phase, by heating the entire printing chamber to just a few degrees below the material's glass transition temperature (T_g). This is important because it enables the machines to create a slice without bringing all material into the melting process (Wendel *et al.*, 2008).

As described earlier, AM is a layer-by-layer paradigm in the production process, which involves using a 3D computer-generated model, a 3D printer and a printing process to produce the physical model based on the initial model design. Properties of AM material are determined by 1) the nature of the material, 2) the nature of the process for bonding this material, 3) feedstock, and 4) the system that produced this AM material (Figure 4).

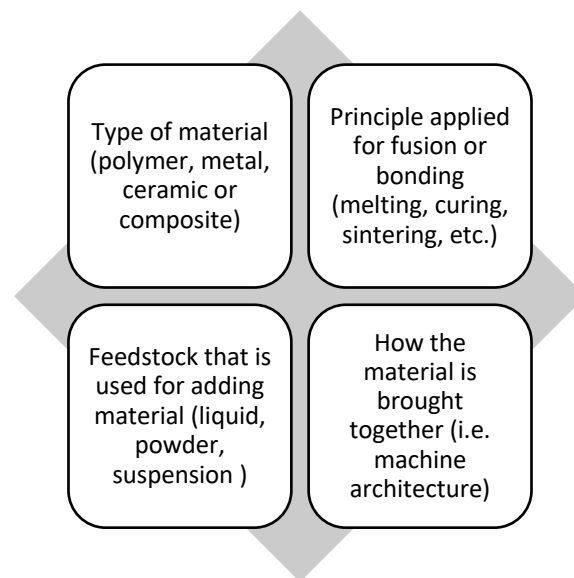


Figure 4. Factors that determine properties of AM material

2.1.1. AM processes

There are seven primary kinds of AM/3DP procedures available, according to the International Standards Organization/American Society for Testing and Materials standards (ASTM F2792:2012a, ISO/ASTM 52900:2021):

- Material extrusion (MEX). MEX is a method of AM in which a heated material is delivered to form a 3D component through a nozzle. This category includes direct ink writing (DIW), fused deposition modelling (FDM), and fused filament fabrication (FFF).

- Material jetting (MJT). MJT is an AM technology that employs a photopolymer and initiator as a build material (in the form of droplets) to construct thin layers that are subsequently cured to make a 3D component. These systems utilize inkjet-head computers, such as the well-known Polyjet machine.
- Binder jetting (BJT). BJT is an AM method that binds powder components together to build a 3D component using a liquid bonding agent. The liquid bonding agent is applied selectively to start a fusion process.
- Sheet lamination (SHL). SHL is an AM technology that combines material sheets or foils to create a finished product. Two of the most well-known SHL technologies are laminated object manufacturing (LOM) and ultrasound additive manufacturing (UAM).
- Vat photopolymerization (VPP). VPP is a method of AM that involves pouring a liquid photopolymer into a motorized vat and curing it selectively with an ultraviolet light-activated polymerization process. The lithography-based AM techniques of digital light stereolithography (SLA) and processing (DLP) can be categorized as follows:
- Directed energy deposition (DED). DED is an AM technique that uses a focused beam of heat radiation to fuse metal and metal-hybrid materials as they are deposited (e.g., in laser or plasma arc technologies). Some of the most frequent innovations in this area include laser deposition (LD), laser-engineered net forming (LENS), and plasma arc melting.
- Powder bed fusion (PBF). PBF is an AM process that uses heat energy to fuse powder bed areas. AM technologies include selective laser sintering (SLS), electron beam melting (EBM), and selective laser melting (SLM).

The key benefits of these AM techniques include design flexibility (for mass product modification), waste reduction (reduced costs), production for faster time to market, and a more competitive manufacturing and supply chain.

2.1.2. Laser powder bed fusion of plastics or selective laser sintering

PBF is a “process used to produce objects from powder materials using one or more lasers to selectively fuse or melt particles at the surface, layer upon layer, in an enclosed chamber”, producing 3D parts from powder materials (ISO/ASTM 5900:2021). Laser powder bed fusion (L-PBF) is an AM technology that uses a laser beam to fuse powder particles. A laser selectively scans a powder bed to fuse the particles. A powder-spreading recoater creates the

powder bed by distributing a homogeneous powder layer on top of the build platform or the top of a previously produced layer known as the build surface. Repeating this procedure and scanning along the specified shape on each build surface yields the additively produced component. The flexibility to build geometries that would be hard to produce with traditional technologies are two of L-PBF's biggest benefits.

L-PBF has revolutionized manufacturing by allowing 3D structures to be made directly from feedstock powders without further processing. L-PBF was invented by Deckard (1989), and the method was first used on metals, then polymers, ceramics, and, most recently, semiconductors (Beaman, 2021). The optimization of laser process parameters, such as laser power, scan speed, and scan spacing is an essential criterion for L-PBF. SLS requires polymer materials with low agglomeration tendencies, reduced shrinkage and warping, and good absorption of laser radiation at laser wavelength (Gibson *et al.*, 2015). Special processes were introduced to produce powders with properties needed for laser powder bed fusion of polymers.

Carl Deckard invented selective laser sintering (SLS) at the University of Texas in 1986. (Deckard, 1989). Soon after, the Nova Automation and DTM Corporation companies were formed by Deckard and other university members to commercialize their technology. In 2001, DTM was purchased, and since then, 3D Systems Inc. has been selling SLS technology. EOS GmbH (Electron Optical Systems, Germany), formerly a manufacturer of stereolithography and 3D scanning systems, has expanded its product portfolio to include AM laser sintering systems in tandem with the activities of DTM in the United States. The basic schematic design of SLS and some parameters influencing on the process are illustrated in Figure 5.

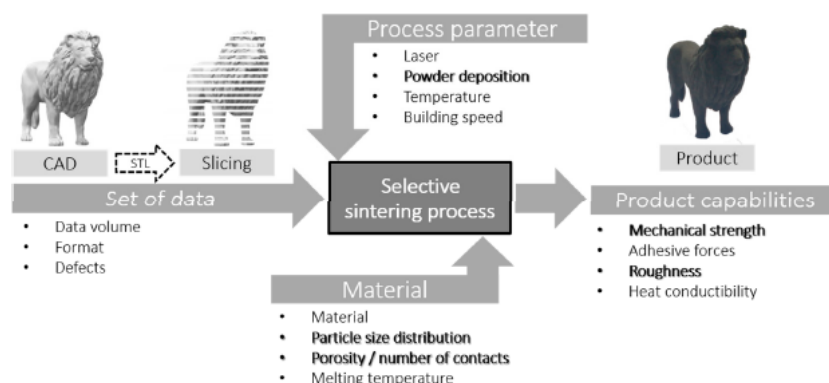


Figure 5. Selective laser sintering process (Beitz *et al.*, 2018)

SLS is an AM technique in which the powder polymer or elastomer bed is used for laser sintering, followed by a solidifying powder layer. A laser beam (usually 10.6 μm CO₂-type

laser for SLS) scans the model contours and layers according to the CAD data. Laser radiation is absorbed and affects the local heating of the powder particles. The powder deposition between the sintering of the adjacent layers is carried out using a re-coater blade to distribute the powder particles supplied by the extraction chamber supplying the powder feed. The printing chamber is kept constant at an elevated temperature, a few degrees below the point of softening of the processed materials, throughout the procedure. The aim is to reduce manufacturing time and decrease the stress concentration and curl distortions formed during layered solidification that is thermally induced.

Generally, the SLS machine consists of the powder supply chamber, the printing chamber, and an extraction chamber. Initially, the chamber is heated to a certain temperature just beneath the material's melting point. In SLS, the base plate moves downwards after the first layer has solidified, allowing a new layer to be placed on top, and the process is repeated until a 3D component is obtained. This procedure usually necessitates a lengthy processing period and the preheating of powders. SLS allows for component fabrication with a resolution of a few tens of microns. The properties of parts rely on various inputs of SLS machine process parameters. The key contributors to the process are the preheating temperature of the powder bed, laser power, scanning speed, scanning spacing, and layer thickness. The deformation of the parts needs to be kept in mind, which can occur at various stages during the build phase (in-built) or after the build phase (post-build). It is generally referred to as “curling” when the first sintered layers of the component are directly affected by distortion, and the rest of the layers are geometrically correct. In the case of “warpage”, the parts were properly built and twisted after finishing (e.g., incorrect cooldown). The differences are shown schematically below in Figure 6.

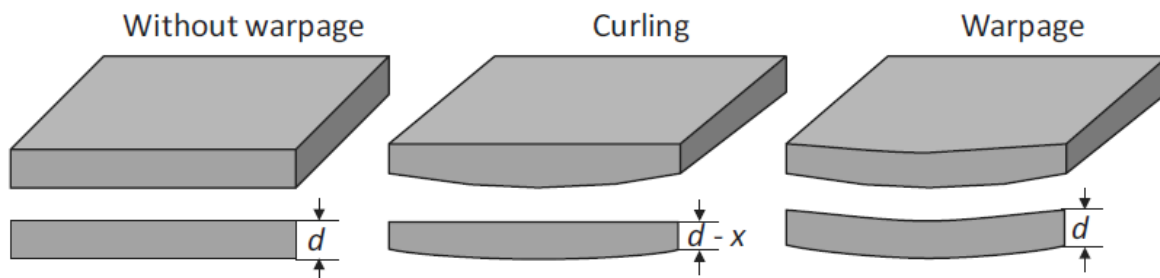


Figure 6. Distortion differences between curling and warpage (Schmid, 2018)

Throughout the process, loose powder particles remain on the build platform to serve as support material. Loose powder can be extracted rapidly and re-used at the end of the production process in calculated repeated cycles.

SLS is applicable for materials with dramatically varying physicochemical characteristics. In addition, in their morphology, sintering and melt behaviour, SLS powders having similar batch content can also differ. The characteristics of the powder strongly influence the properties of the components, such as precision, internal stresses, distortion, and mechanical load response. Figure 7 shows the parameters of material that influence the SLS process.

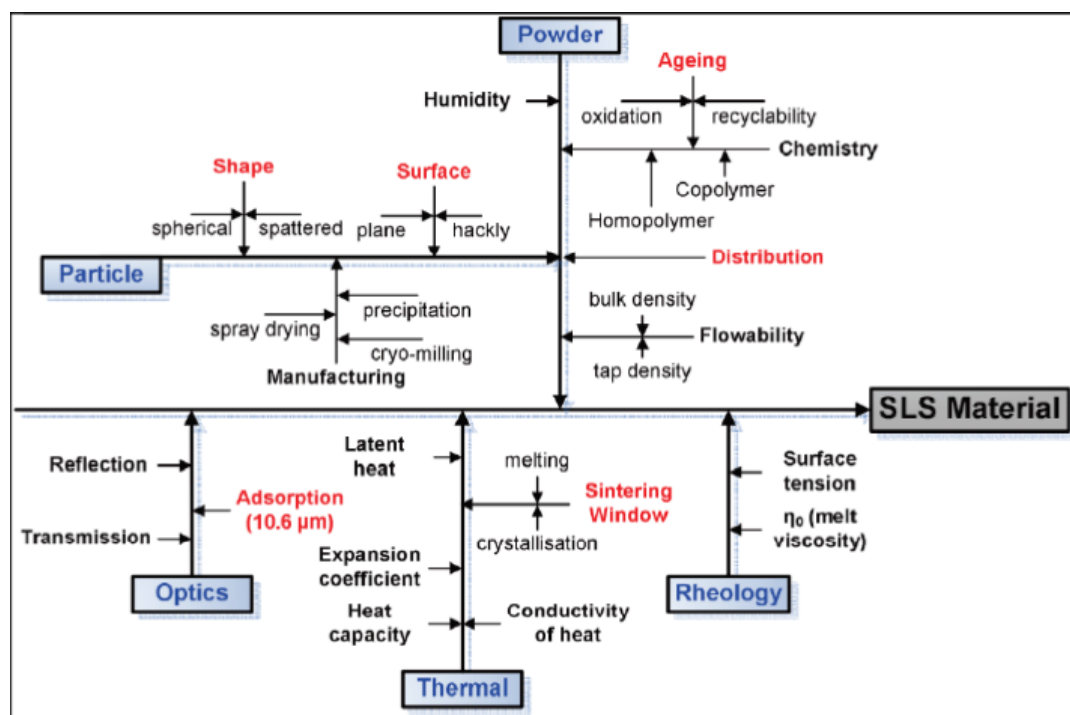


Figure 7. Powder and process parameters on SLS application (Deshmukh *et al.*, 2020)

2.1.3. SLS powders

For SLS, a laser beam fuses consecutive cross-sections of sliced components in a layer-by-layer manner. Polymer properties such as chemical composition and thermo-physical properties, powder morphology and particle sizes, material characteristics, and process parameters influence on final properties of manufactured object. Material properties and process parameters with scanning strategy determine the product's density, microstructure, and mechanical characteristics (Goodridge *et al.*, 2012; Bourell *et al.*, 2014; Verbelen *et al.*, 2016, 2017). One key advantage of using SLS is the availability of a broad range of materials,

including thermoplastics, ceramics, and composites, amongst other AM methods. Composites can be made from polymer-metal, polymer-polymer, polymer-ceramic, and pure ceramic materials (Bourell and Beaman, 2005, Kruth *et al.*, 2007, Hao *et al.*, 2009). Polymers are the most popular and widely used material for SLS today. Other polymers, apart from polyamide-based materials such as polystyrene, polycarbonate, and polyether ether ketone (PEEK), a high-performance polymer, have had moderate success. (Yusheng *et al.*, 2008, Ho *et al.*, 1999, Schmidt *et al.*, 2007, De Leon *et al.*, 2016). Composites such as polystyrene-nano- Al_2O_3 or pure aluminium powder, nylon-11 filled with glass beads or silica nanoparticles, silicon carbide (SiC) polymers, and hydroxyapatite (HA) have been successfully developed for various SLS applications (Haizhong *et al.*, 2006, Mazzoli *et al.*, 2007, Chung *et al.*, 2006, 2008, Dizon *et al.*, 2018b, Hon and Gill, 2003, Zhang *et al.*, 2008). As mentioned, PA12 is the most commonly used polymer in the SLS process, but polyethylene (PE), PEEK, PCL, and TPU are also used (Parandoush and Lin, 2017, Dermanaki Farahani and Dubé, 2017).

There is a significant relationship in SLS printing between powder flowability and the consistency of the resulting product. Powders that flow easily are better distributed during printing, resulting in denser components (Ziegelmeier *et al.*, 2015, Dadbakhsh *et al.*, 2016, Schmid *et al.*, 2013). There have been several attempts to classify how powder spreads, using a powder-spreading unit (rake with variable, known gap size) and a load cell connected to a measurement plate with a predetermined area, Van der Eynde *et al.* (2015) proposed a device that can determine the bulk density of a spread powder in relation to gap height or spreader speed. The modified Hausner Ratio (HR) may be determined with this instrument under powder-spreading conditions at ambient temperature.

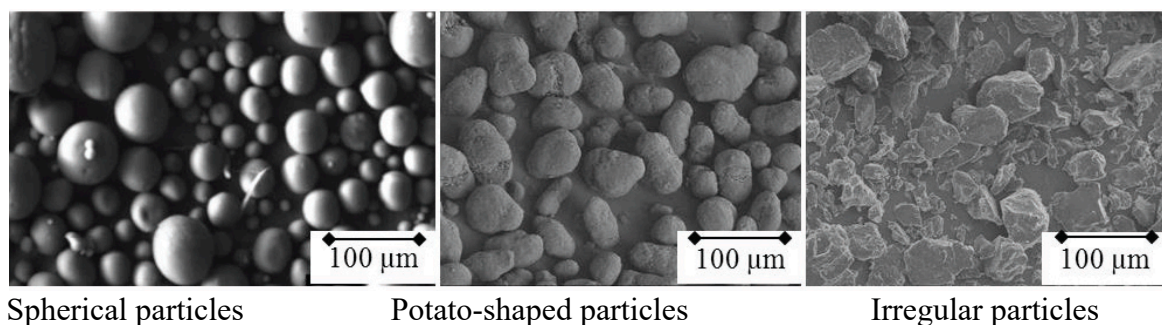
To evaluate the spread capabilities of differentially treated powders, powder-spreading tests on model substrates (usually black) with subsequent image analysis of the area covered have been done. It was found a strong link between the flow function of powder and quality of laser-sintered single layers of polyethylene (Blümel *et al.*, 2015) and polybutylene terephthalate (PBT) powders (Schmid and Wegener, 2016).

One of the most important powder properties in terms of powder-spreading is particle size distribution (PSD). The effect of PSD and morphology on the process potential of powdered material was studied by Kruth *et al.* (2008), Liu *et al.* (2011) and others. It was shown that for effectively used thermoplastics such as PA12, the particle size (MPS) varies from as low as 20 μm to 100 μm : since SLS 3D printers can have layer thickness as thin as 100 μm , it will not be possible to pack bigger particles uniformly. Similarly, if PSD is too uniform, particles cannot

interlock, resulting in pore density, which can contribute to porosity and weakness in finished components. Additionally, due effect of Van der Waals forces, an accumulation of smaller particles will cause flowability reductions if the PSD is too large.

Another important factor in powder is the morphology of the powder particles. The friction particles experience when moving away from each other and when dispersed through a small substrate, as well as their ability to interlock tightly, are strongly influenced by morphology. A scanning electron microscope (SEM) is used to examine the morphology of the powder (Kruth *et al.*, 2008, Goodridge *et al.*, 2012, Verbelen *et al.*, 2016, Ziegelmeier *et al.*, 2013, 2015, Berretta *et al.*, 2014).

Co-extrusion processes can generate spherical particles, precipitation manufacturing processes lead to powder particles with potato-like shapes, and cryogenic milling produces irregular particles similar to chips. Freezer milling may also be used to mix different polymers and produce polymer powders (Figure 8). This procedure has been effectively utilized to mix PA-12 and PEEK (Schultz *et al.*, 2000).



Spherical particles

Potato-shaped particles

Irregular particles

Figure 8. Particle shapes attainable by different production technologies (Schmid and Wegener, 2016)

In contrast to spherical particles, potato-shaped and cryogenic particles are less likely to flow and form defect-free layers (Schmid *et al.*, Van den Eynde *et al.*, 2015). Guo *et al.* (2011) introduced irregular and coarse particles of wood-based fillers and resulted powder had poor flowability, which may cause porous parts, or failed build jobs. On the other hand, spherical powder-filled composites like Alumide have good flow characteristics, similar to other raw polymers with similar morphologies, as reported (Amado *et al.* (2011).

Thermal properties of powder material have a critical role to manufacture SLS defect-free components. Thermoplastics can change their chain into rubbery (flexible) or glassy (rigid) states when heated. The temperature at which polymer changes from a glassy state to a rubbery state is called the “glass transition” temperature (T_g , Table 1). The SLS machine building

chamber temperature is held above the crystallization material temperature during the sintering process to allow the layers to coalesce properly and link together during the glass transformation step (Vasquez *et al.*, 2013). If the chamber temperature is too high, the particles, especially the smaller ones, will begin to undergo a glass transition. If this happens, the powder will start to cake, making it sticky and difficult to spread, causing unintentional melting of particles and resulting in a loss of detail (Schmid *et al.*, 2016). If the chamber temperature is too low, premature crystallization can occur, resulting in distortion or curling (Schmid *et al.*, 2016, 2017).

Table 1. Glass transition (T_g) and melting temperatures (T_m) of common plastics (Greene, 2021)

Polymer	T_g (°C)	T_m (°C)
Low-density polyethylene (LDPE)	– 100	110
High-density polyethylene (HDPE)	– 100	130
Polypropylene (PP)	– 25	170
Acrylonitrile butadiene styrene (ABS)	100	125
Polycarbonate (PC)	149	149
Nylon 6,6	49	250
Polyethylene Terephthalate (PET)	70	240
Polyphenylene oxide (PPO)	200	300
Polystyrene (PS)	95	240

It is critical to ensure that the polymer powder particles are fully bonded within and between layers to achieve complete coalescence. When the polymer material reaches the T_g temperature, it begins to soften, allowing for necking between particles. Particles formed into a slice melt when they are sintered, but if large quantities of the substance exceed the melting T_m at once, it can lead to unintended bonding. This, in turn, can lead to a loss of dimensional precision and feature definition, as stated by Bourell *et al.* (2014), as the melting can occur in a much wider region than the focus point of the laser.

SLS machines use a heated chamber to maintain sintered material above their crystallization temperature. This is useful for adhering successive layers together. It allows the sintered material in the next layer to bond to the sintered material in the previous layer by keeping the material in the T_g step after each layer has been sintered. This layer bonding is important in the

SLS process because it adds strength and results in a smooth, uniform finish, which is desirable in many applications (Wendel *et al.*, 2008; Drummer *et al.*, 2014; Khalil *et al.*, 2016).

This delicate balance between crystallization and melting in SLS ensures that the process employs a consistent, precise application of energy and mass. Heating rate during exposure of laser molten parts the precise and regulated application of light energy from the laser beam, as well as the uniform spread of powdered material from the recoater system onto the printing bed affect on SLS quality (Ziegelmier *et al.*, 2015, Schmid, 2018, Berretta *et al.*, 2016, Caulfield *et al.*, 2007, Sharma *et al.*, 2015; Drummer *et al.*, 2014, Khalil *et al.*, 2016).

The ability of a material to absorb laser energy is crucial to its ability to be sintered. It must convert light energy to heat with the least amount of light reflectivity, transmission, or re-emission. Some of the reflected or absorbed energy is simply lost back into the machine, but if it is large enough, it can cause damage to the machine. The powder-transmitted laser energy can cause unnecessary bonding with lower powder layers (Laumer *et al.*, 2016).

Absorption varies depending on the material and laser wavelength (Figure 9), and powder material is more absorbent than bulk material (Tolochko *et al.*, 2000). Subsequent work has developed a relationship between particle size, subsequent packing fraction, and laser energy absorption (Fan *et al.*, 2007). A graphite powder, titanium dioxide and other additives were used to increase laser absorption (Ho *et al.*, 2002, Goodridge *et al.*, 2011, Kim *et al.*, 2013, Jing *et al.*, 2017).

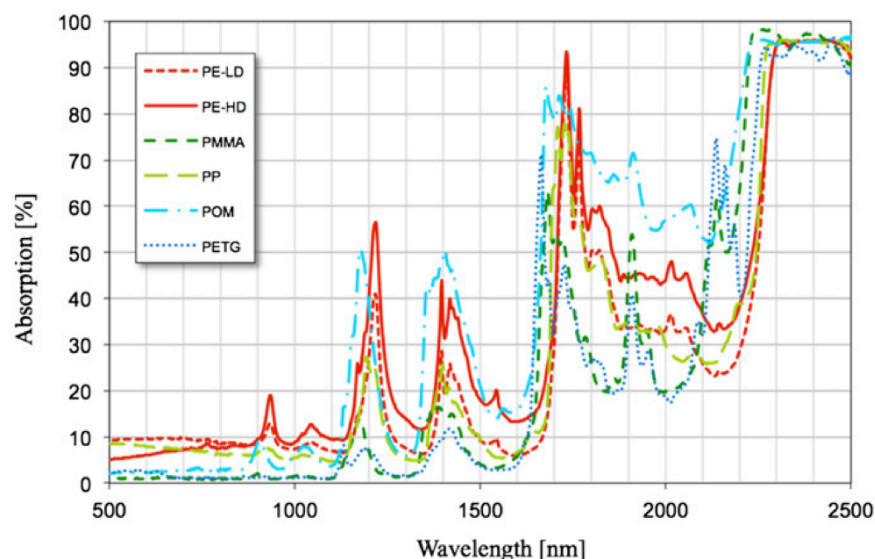


Figure 9. Absorption spectra of different polymer samples with the thickness $d=1.6$ mm (Mingareev *et al.*, 2012). PE-LD, PE-HD is a low- and high-density polyethylene, PMMA is polymethylmethacrylate, PP is polypropylene, POM is polyoxymethylene, and PETG is glycol-modified polyethyleneter-ephthalate

2.1.4. Features and capabilities of SLS

SLS provides performance characteristics of functional parts that are impossible to achieve using other technologies. First, it permits the production of complex structures, lattices, and integrated components, allowing multiple parts to be integrated into a single part, reducing manufacturing time and allowing for significant cost savings by eliminating assembly work.

In SLS, laser beam selectively melts a powder bed that has been heated slightly below the melting point of the polymer to support material fusion and avoid thermal distortion. The newly added powder is fused layer by layer by the moving laser beam in a predefined pattern, forming the desired geometry. High thermal gradients are created during the printing process due to the high energy density laser spot. The material's continuous heating and cooling cause material expansion and shrinkage, which causes residual stresses, which may lead to distortion of the final form, among other defects. Even during the manufacturing phase, failure may occur (Kruth *et al.*, 2003, 2008, Kumar, 2003, Ibraheem *et al.*, 2003).

Control of the process and component efficiency, as well as meeting the needs of high-performance industrial applications, are all requirements that must be met to ensure the competitiveness of the AM process. Simulation tools are needed to predict and mitigate component warpage and to understand the effect of design decisions on the manufacturing process before the part is printed to realize the full value of AM.

The creation of this process simulation faces several challenges:

- The complex thermo-mechanical loadings that occur during the material's layer-by-layer deposition and subsequent cooling.
- The location of bead deposition produces complex microstructures based on the printing toolpath pattern, which drives the macroscopic mechanical behaviour, typically causing anisotropy in AM.
- Differential shrinkage between neighbouring beads or layers is caused by the thermal background of the material deposition, which influences the part's end tolerances.

The need for numerical modelling and prediction of the thermal and mechanical fields produced in SLS appears to be important in understanding the underlying mechanisms that lead to unsatisfactory printed parts, as several process weaknesses, such as part shrinkage, pores, microcracks, delamination, and stress-induced defects such as warping, and distortion remain partially unsolved (Ibraheem *et al.*, 2003, Bikas *et al.*, 2016).

Parts produced utilizing SLS processes have certain qualities that separate them from those that use other AM procedures or conventional technologies. SLS components' accuracy and surface

roughness are highly dependent on the PSD of the powder used, where larger molecules typically cause lower temporal resolution and increased surface roughness (Karapatis *et al.*, 1998). Furthermore, manual finishing processes, such as polishing or finishing, are commonly used to improve surface properties (Schmid, 2018, Senthilkumaran *et al.*, 2009, Liu *et al.*, 2005, 2009). Other differences from the CAD data input arise from the layered processing of the components, similar to the parts made using other AM systems. In the interface between the solidifying layers and the ready-made portions of the manufactured component, temperature radiation and deformation due to sintering causes residual stress. In warping or deformation, relaxation of these stresses may result. Not only are powder properties influenced by the amount of stress, but the amount of stress is often affected by the machine process parameters such as the preheating temperature of the powder bed, laser power, scan speed, scan spacing, and layer thickness. Several different research activities using theoretical and experimental methods in the AM phase (Senthilkumaran *et al.*, 2009, Bourell *et al.*, 2000, Liu *et al.*, 2005, 2009, Ibraheem *et al.*, 2003) were aimed at monitoring and learning, as well as predicting and improving accuracy and surface finishing. Generally, the parts formed by SLS will display a certain degree of porosity, regardless of the material used (Gibson *et al.*, 1997). The free volume sum depends on the PSD, the choice of material and the machine process parameters.

Ajoku *et al.* (2006) investigated the impact of build orientation on the tensile, flexural, and compression properties of SLS-printed PA12 specimens. The tests showed distinct anisotropy in specimens printed in three orientations caused by the varying thermal distributions during the SLS.

Dadbakhsh *et al.* (2017) studied the fundamental mechanisms of PA12 powder on the coalescence fusing behaviour, crystallinity, microstructure, and mechanical properties of SLS-printed specimens. The SLS specimens printed from used powders had poorer tensile strength than those printed from virgin powder particles due to their lower crystallinity and coarse spherulitic microstructure.

2.2. Functionalization of polymers

In recent decades, polymers and plastics have advanced, replacing traditional materials such as glass, metal, and wood. One of the reason is that some artificial materials provide lower material costs than the material they replace. Different fillers have been introduced and widely accepted because they offer numerous opportunities for enhancement and variation of properties of polymers. Fillers are a broad category of materials with a wide range of

applications. Minerals, metals, ceramics, bio-based materials, and other polymers can be used as fillers. In some cases, fillers can have a major effect on the heat transfer and chemical and mechanical stability of the polymer material (Allen *et al.*, 1998, Bai *et al.*, 2015). Some polymers have low mechanical strength for load-bearing applications in their pure state. Adding fillers, such as silica and carbon fibres, generates materials with high mechanical strength (Alsubari *et al.*, 2021, Bai *et al.*, 2013, 2014, Balzereit *et al.*, 2018). Fillers also improve scratch resistance, hardness and wear resistance, electrical and thermal conductivity (Athreya *et al.*, 2010), to change the colour of the material and can act as flame retardants. (Xanthos, 2010, Bourbigot and Duquesne, 2007, Dasari *et al.*, 2013). Marine raw materials showed effective flame-retardancy and antimicrobial properties with polypropylene (Echeverria, 2020). Since the inclusion of a filler alters other features like physical and mechanical properties, good formulation necessitates a grasp of the structure-property relationship.

Heat conduction, static electricity discharge, mechanical signal conversion to an electrical signal, and electromagnetic interference shielding signals are all advantages of metal-filled composites (Nurazreena *et al.*, 2006). Certain metallic elements, such as copper, nickel, magnesium, zinc, stainless steel, silver and gold are added to polymers to improve their thermal, electrical and heat properties (Ye *et al.*, 2019, Mamunya *et al.*, 2002, Suriani *et al.*, 2021, Rusu *et al.*, 2001, Kalyan *et al.*, 2002, Ning and Guo, 2000, Lanzl *et al.*, 2019). Incorporating metal components into polymer-based composites has resulted in developing new promising materials in various technical fields.

2.2.1. Reinforcement

Particle reinforced composites are particles of one material dispersed across a matrix of another. The form, size, and morphology of these particles can all be different. They can be spherical shaped, oval, polyhedron, or irregular. Adding particles to a liquid matrix, which freezes later, growing them in place using methods such as age hardening, pressing together, and then inter-diffusing using a powder process, for example, are all part of the particle composite formation process. Cryogenic ball milling, emulsion precipitation, wet grinding-rounding, spray drying, and dissolution precipitation are some methods used to make composite powders (Yuan *et al.*, 2019, Schultz *et al.*, 2000). The preparation procedure determines the shape, size distribution, components, and particle dispersion within the matrix.

Based on the strengthening process, particle-reinforced polymer composites are divided into dispersion-strengthened and particulate-reinforced composites (Ahmed *et al.*, 1990). The particles in dispersion-strengthened composites are tiny, ranging in size from 0.01 to 0.1 μm . The strengthening takes place at the atomic or molecular level in this case. Another particle-reinforced composite is a particulate composite with coarse particles scattered throughout the matrix material. The interfacial contact between the dispersed and matrix phases is crucial in determining the ultimate characteristics of such composites (Chen *et al.*, 2017, 2018).

The main features of traditional reinforced-composite materials are fibres and matrixes. The main source of strength and reinforcement is fibres, while the matrix connects all the fibres in the form and transfers stresses between the reinforcement materials. Across the spatial paths, the fibres carry loads.

Fibre reinforcement, in particular, appears to be a popular filler for improving polymer characteristics. Pre-blended materials containing discontinuous fibres as an addition have received much attention as viable alternatives to multi-head printers with complicated and expensive designs. Depending on the addition utilized, these additive-based materials have distinct features and capabilities and may achieve suitable mechanical, electrical, or thermal qualities at a low cost. Fibre reinforcing might benefit one of the currently available 3D printing processes.

In the field of AM, rigidity and strength are critical mechanical characteristics to meet operational requirements for some applications (Caulfield *et al.*, 2007, Dizon *et al.*, 2018a). It is common practice to enhance mechanical properties when mechanical strength is required for a specific application. Reinforced thermoplastics are a way to get around these restrictions. To achieve specific characteristics and capabilities, new materials have been created with fillers, such as nanoparticles, carbon nanotubes, fibres, and graphene (Kalsoom *et al.*, 2016). Fibre reinforcements, for example, have received more attention for strengthening the printed polymer properties and are now available for various processes, including FDM, SLA, and SLS (Parandoush and Lin, 2017).

2.2.2. Improvement of tribological properties

In their pure condition, most polymers do not have adequate wear resistance or a perfect friction coefficient (Olea-Mejia *et al.*, 2010). The original answer to this problem was to place a metal coating layer on the surface of a polymer; however, the downside of this method is that the “elastic strain” zones between the polymer substrate and the coating layer are vastly different

(metal). In the second generation, substantial scratch resistance was achieved by enhancing the hardness of the coating by introducing polysiloxane and acrylic materials, both of which have an elastic strain zone in the same range as the substrate. Nanomaterial has recently been used as a filler in anti-friction coatings (Demirci *et al.*, 2005, Al-Kawaz *et al.*, 2017). Fillers or slippage agents can improve the tribological properties of polymeric coatings used in surface applications by lowering the friction coefficient and, thus, the wear rate. They can also improve mechanical properties such as elastic modulus by increasing the elastic response component in an elastoplastic behaviour (Al-Kawaz *et al.*, 2016, Dasari *et al.*, 2009, Gauthier *et al.*, 2006). Various procedures, including indentation and scratch tests, can be employed to investigate the material's surface qualities (Pelletier *et al.*, 2009). Scratching to characterize tribological performance for polymers is the best replacement test for traditional wear, in which a hard indenter is squeezed onto the material under normal load and moves towards the material, and the material's ability to resist mechanically induced surface damage under those conditions is called scratch resistance. The ratio of friction force that is the applied normal load on the tip that travelled over the surface can be used to indicate perceived friction. The normal load may be described as scratch hardness and “tangential hardness” based on “frictional force”, and scratch hardness can be derived from these two forces (Briscoe *et al.*, 2003). Most polymers have viscoelastic and viscoplastic properties, and determining their scratch resistance is difficult because their behaviour is strongly influenced by test conditions such as contact geometry, normal load, loading rate, sliding velocity, and topography (Pelletier *et al.*, 2008). In the frictional process, the polymer's included surface layer may be divided into two regions: the interfacial region, which has a depth of approximately 100 nm, and the cohesive zone. As a result of the “actual contact area” of the interfacial region and the “shear stress” of the subsurface zone, a frictional force is created. Many variables influence interfacial frictional work, including polymer hardness, glass transition temperature, crystallinity, and counterface roughness, and friction is caused by adhesive contacts between polymer surfaces and hard asperities (Friedrich *et al.*, 2011). Nanoparticles have a significant role in influencing the friction and wear resistance of polymers, depending on their composition, volume fraction, size and shape, matrix, and test circumstances (Demirci *et al.*, 2005).

To improve scratch performance for the polymer, coating films as an anti-friction layer are used. Also strain-hardening effect in the bulk material is used to improve elastic properties of the composites. For example, Bai *et al.* (2019) used as 1.5 μm in size solid lubricant Molybdenum disulfide (MoS_2) particles to enhance the tribological performance of the laser

sintered PA12. It was found that incorporating of 1.0 wt% MoS₂ into the PA12 matrix, enhanced impact strength about 11% and reduced coefficient of friction from 0.30 to 0.13.

2.2.3. Colouration

Inorganic and organic pigments are used primarily to give colour to the polymer. A few important factors can affect the stability of a coloured polymeric matrix. The first is the chemical and physical characteristics of the polymer itself, and the second is the environmental conditions in which the process is being used, such as moisture, heat, and environment. The third is the chemical and physical structure and concentration of the pigment, while the fourth is the presence of antioxidants, light stabilizers and other additives (Allen and McKellar, 1980). In certain instances, the mechanical and thermal decomposition processes in polymers are dominated by the polymer form used with a filler or pigment. This is typical of many other pigments, with carbon black being notorious. Pigments with high specific surface area and varying molecular structures may cause many complications in terms of various degradation properties. Review literature indicates that this field of additive chemistry has received limited attention, although the process output and end-use characteristics can be regulated and affected by such processes. The pigments' capacity to catalyze the photooxidation of polymer systems has also earned considerable interest in their mechanical interactions (Allen *et al.*, 1998).

2.2.4. Flame retardants

Polymer materials are made up of hydrocarbon chains, which burn rapidly when subjected to high temperatures and may also smoulder or release smoke when exposed to light (Ilyas *et al.*, 2021, Camino *et al.*, 1988, 1991). Several occurrences involving aeroplanes have happened in the past; however, in recent years, a significant rise in the fire tolerance of polymer composite materials has been recorded following crashes (Woodrow, 2012). The use of halogenated materials in preparing flame retardants (FRs) is cost-effective. However, because of the increased focus on environmental and health hazards regarding FRs, there has been a progressive drop in the acceptance of these goods (De Wit, 2002). Due to their excellent properties, metal-filled polymer composites have become increasingly popular in recent years, notably as flame retardants. EOS developed halogen-free fire retardant Nylon 12 powder that meets the FAR 25.853 60 second burn specification and AIRBUS directive for AM manufactured plastic parts (EOS, 2021).

2.2.5. Conductive polymer composites

Composites are becoming more widespread in applications where electrical conductivity (EC) is a significant material design feature, such as aeroplanes, buildings, and electronic equipment. The addition of highly conductive fillers to the polymer matrix is one of several strategies for improving the EC of composites that have been researched (e.g., metal particles, carbon nanotubes, nanofibres, graphene) (Ladani *et al.*, 2015; 2004; Wei *et al.*, 2011). One problem with EC composites is the difficulty of identifying flaws and damage using electrical-based non-destructive inspection techniques like electrical resistance and eddy current methods.

Conductive polymer composites can combine substantial advantages of plastics and metals, such as lower cost with a high manufacturing rate, design flexibility, non-corrosive qualities, and lightweight features. These compounds can be made using a variety of processes, including an internal mixer, extrusion, and injection moulding (Asyraf *et al.*, 2020, Gonzalez-Gutierrez *et al.*, 2018). To increase the EC of polymer materials, direct addition of carbon fibres and other conductive additives such as copper or silver as well as doping the polymer matrix with highly conductive carbon-based nanoparticles (e.g., carbon nanofibres, carbon nanotubes, graphene), metal particles (copper), polyaniline, or milled carbon nano/micro-sized carbon particles and other conductive materials are used (Zhang *et al.*, 2012, Li *et al.*, 2017).

Conducting polymers is a new form of material with good application potential in the field of microsystems. Figure 10 shows an overview of conducting polymers and conductive polymeric composites (CPCs) with a wide range of conductivity.

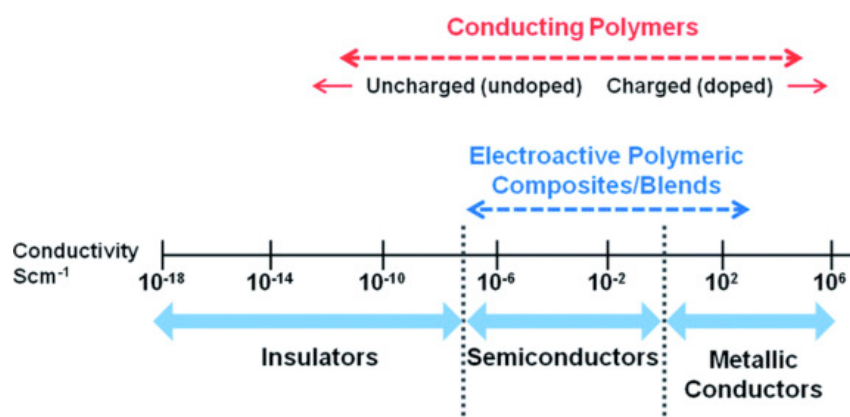


Figure 10. Conductivity range of polymers and polymeric composites (Kaur *et al.*, 2015)

By incorporating conductive fillers into insulating polymers, EC can be added while preserving the polymeric properties. Nano-sized conductive fillers, including CNTs, graphene, and metal nanoparticles, have recently received much interest and have been thoroughly researched to manufacture polymer-based conductive composites. The conductivity of these composites is due to the conductive pathways of filler particles within the polymer matrix. Many variables, including dispersion, geometry, abundance, and the intrinsic properties of the nanofillers, affect the creation of conductive pathways. Furthermore, the filler–matrix interactions are critical in determining the electrical properties of the nanocomposite. It is important to use a composite preparation process that offers the optimum filler distribution. EC is determined by the concentration of conducting filler in a composite. At a critical loading known as the percolation threshold, as seen in Figure 11, the conductivity increases by many orders of magnitude with minor changes in the filler loading. A conductivity rises to the filler material level after passing the percolation threshold. At the percolation threshold, the filler concentration is necessary to form a continuous conductive network across the composite. As the aspect ratio (length to diameter) of the filler increases, the value of the percolation threshold decreases (Brigandi *et al.*, 2014). The ECs of the various conductive fillers are summarized in Table 2.

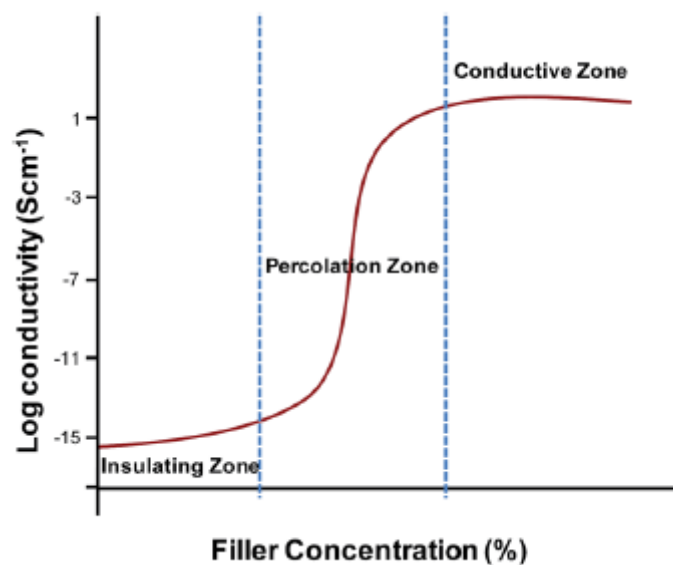


Figure 11. Polymer composite conductivity due to filler concentration (Ruschau *et al.*, 1992)

Table 2. EC of different conductive fillers (Gulrez *et al.*, 2014)

Fillers	Conductivity of bulk material, S/cm
Pt nanoparticles	$\sim 10^5$
Ni powder	$\sim 10^5$
Carbon nanotubes	$\sim 10^3$
Graphene	$\sim 10^4$

2.2.6. Antibacterial properties

Biomedical engineering focuses on the production and improved flexibility, strength and patient compatibility of biopolymeric materials for tissue generation to prevent implant refusal and toxicity. Various alternative methods, including antimicrobial polymeric materials, the insertion and release of antimicrobial agents or the application of antibacterial functionality through the surface modification of the component, may be used to provide antibacterial activity to the 3D-printed part.

Polymer composites have been investigated to make antimicrobial 3D-printed components. These composites were made with graphene and metals such as zinc, copper, and silver, among others (Thokata *et al.*, 2017, Hortigüela *et al.*, 2016, Shen *et al.*, 2008, Vargas-Alfredo *et al.*, 2017, Radheshkumar and Münstedt, 2006). The antimicrobial behaviour of polymer/metal nanocomposites based on thermoplastic matrices in Figure 12 shows bacterial adsorption on the polymer surface. Water with dissolved oxygen reaches the surface of embedded metal nanoparticles, allowing dissolution or corrosion processes; metal ions penetrate the composite surface, damaging the bacterial membrane, which is then diffused into the bacteria. As far as polymers are concerned, although various types of particles may be embedded in these matrices, nanometric fillers are good candidates due to their outstanding properties (Palza, 2015).

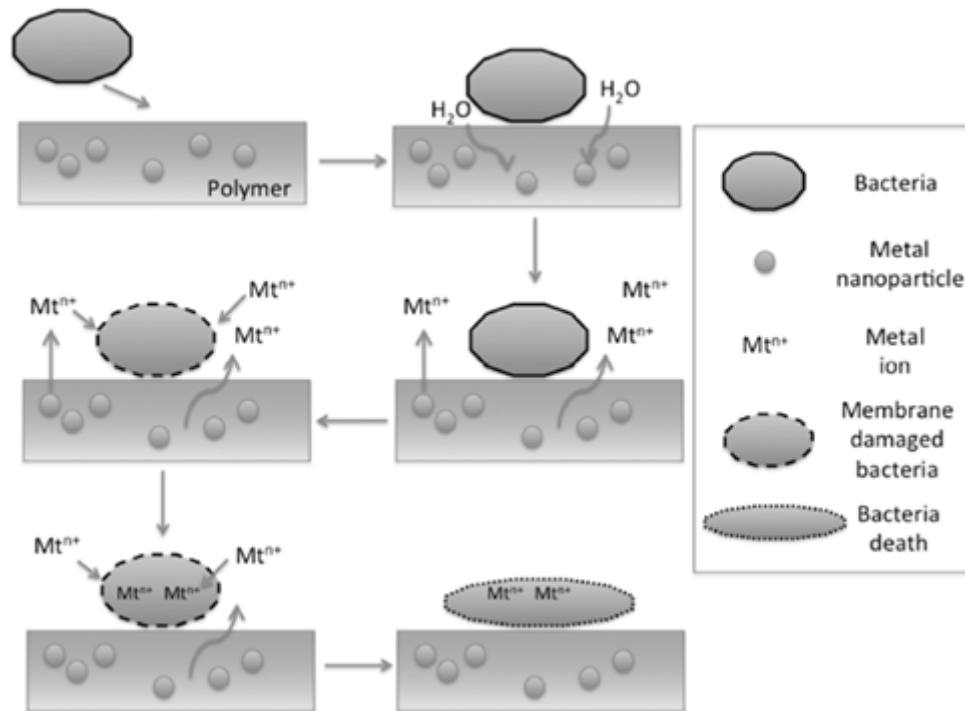


Figure 12. Schematic representation of the antimicrobial behaviour of polymer/metal nanocomposites (Palza, 2015)

Zuniga (2018) used antibacterial PLACTIVE™ to create 3D-printed prosthetics and verified their properties to destroy some bacteria. The author suggested that this knowledge was important in implementing a post-operative or transitional prosthesis of the 3D-printed prostheses. The prosthesis was made with PLACTIVE™ (1% of antibacterial nanoparticle additive, Copper 3D), a high-quality polylactic acid polymer. The study's main finding was that the 3D-oriented antibacterial filament can be used effectively for prostheses and that its antibacterial properties were not compromised. This study found that polylactic acid with additives of 1% Cu nanoparticles had up to 99.99% efficacy against *S. Aureus* after an incubation period of 24 hours.

Although Cu^+ contributes to the toxicity of highly reactive hydroxyl radicals causing Fenton-like reactions, Cu^{2+} can be regarded as an important bacterial agent (Teitzel *et al.*, 2006, Summers *et al.*, 1978). The mechanism of Cu toxicity can be clarified by several methods, such as displacement of essential metals from their natural functional groups or facilitating activities and relationships. Cu^{2+} can form organic complexes with microorganism ligands, resulting in either polymeric acid and protein conformational structure defects or enhancements in oxidative cytosolic and oxidative equilibrium reactions. Cu ions are the major ingredients that destroy or hinder the development (static effect) of micro-organisms (Borkow *et al.*, 2005).

This metal is more affected by gram-positive bacteria than gram-negative bacteria since the latter has a double membrane and the periplasmic space decreases the transport of ions concerning the impact of the microorganism on Cu's biocidal behaviour (Muñoz-Bonilla *et al.*, 2013, Kunz *et al.*, 2010, Rice *et al.*, 2007). It is noteworthy that Cu can achieve a powerful antimicrobial effect by adding its ions or particles to different matrices, such as polymers or ceramic materials (Palza *et al.*, 2010-2018, Cioffi *et al.*, 2005, Delgado *et al.*, 2011).

The inclusion of Cu nanoparticles in traditional polymers used in SLS 3D printing might have interesting clinical applications in the production of antiviral consumables (Palza *et al.*, 2015, 2018). Polymers can be mixed with Cu nanoparticles to increase the adsorption of microorganisms, even though they are not naturally antibacterial. Cu ions and accompanying hydroxyl radicals destroy DNA and RNA, rendering the virus inactive (Palza *et al.*, 2015).

Palza (2015) noted that incorporation of metal-based particles into polymers is a versatile route to take advantage of their strong antimicrobial properties producing novel biocide materials and allowing a further extension of the range of applications. In this context, metal nanoparticles produce a broad range of polymer nanocomposites with a high release of metal ions and, therefore, antimicrobial behaviours.

The Cu 3D-printed face mask Nanohack 2.0 (Figure 13 and Figure 14) aims to include Cu's antibacterial and antiviral capabilities (Copper 3D, 2020). Three layers of non-woven polypropylene (PP) embedded with nano-copper make up the filtration system.



Figure 13. Stopgap face mask (Copper 3D, 2020)

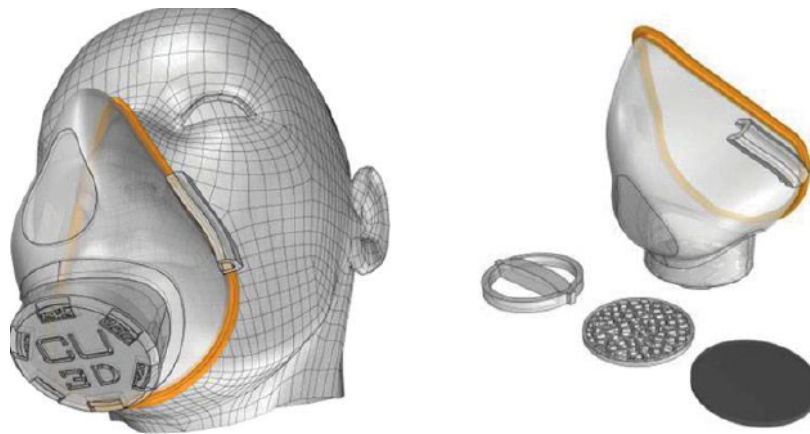


Figure 14. Nanohack 2.0 mask, PP with nano-copper incorporated in it, and 3-part filtration (Copper 3D, 2020)

Although there are several examples related to copper and silver nanoparticles embedded into different polymer matrices, as discussed in the literature, further research is needed to support the development of novel bioactive polymeric materials for hospital equipment.

2.3. SLS composites

Nylon, polypropylene (PP), polyethylene (PE), thermoplastic polyurethane (TPU), polyetheretherketone (PEEK), and polystyrene (PS) are some of the polymeric SLS materials that have been intensively studied. Glass beads, silica, graphene, carbon nanotube (CNT), carbon black (CB), aluminium (Al), and copper (Cu) are examples of micron and nano-level fillers that may be added to polymers to improve their thermal, electrical, and mechanical characteristics (Yuan *et al.*, 2019, Goh *et al.*, 2019, Salmoria *et al.*, 2011).

Polyamide 12 (PA12), Polyamide 11 (PA11), and Polyamide 6 (PA6) are intriguing materials for AM as they are engineering polymers with high mechanical characteristics, minimal water absorption, and a low melting temperature compared to other polyamides. PA12 is the most widely used polymer in PBF processes, with a market share of over 90%, due to these characteristics and its favourable behaviour in the L-PBF process (Goodridge *et al.*, 2012, Stichel *et al.*, 2017).

Due to the extreme significant benefits of mechanical and electrical properties, CNT has become a common nanofiller in the SLS process. SLS parts made with PA12 containing 0.1 wt.% CNT showed a 123.9% increase in impact strength, a 54.0% increase in Young's modulus, and a 6.2% increase in tensile strength without losing elongation at break (Bai *et al.*, 2013). CNT also increased the crystallization temperature of nanocomposites, hampered

polymer chain mobility through interfacial forces between CNT and polymers, and increased porosity in SLS components. Salmoria *et al.* (2011) used fatigue tests to show that adding 0.5 wt.% multi-wall carbon nanotube (MWCNTs) to PA12 improved composite strength while slowing the creep failure process.

Zhang *et al.* (2017) suggested a new form of wood-plastic composites (WPCs) specifically designed for the SLS process. WPCs with CNT concentrations ranging from 0.05 to 0.15 w.t%, 14 wt.% wood fibre, and 86 wt.% PE. The mechanical properties of the PES/wood composite material were significantly improved when 0.1 wt.% CNT was added (i.e., + 76.3% tensile strength, + 227.9% bending strength, and + 128.7% elasticity modulus).

CNTs were also used to coat PA12 powders to increase heat conduction and absorption compared to smooth PA12 (Yuan *et al.*, 2016). Regarding SLS, it was found that CNTs stay at powder boundaries, creating a network that improves mechanical properties.

The CNT-coated composites had a higher electrical conductivity and a larger sintering window than sections without a separated structure (ternary composites). The piezoelectric strain coefficient also increased from 1.7 to 2.1 pC/N. The inclusion of CNT could promote the conduction of laser-generated heat during the SLS operation, as Bai *et al.* (2018) demonstrated via numerical simulation. The conductivity of SLS-manufactured TPU/CNT composites unexpectedly improved when CNT content was higher than 0.2 wt.%, with a value of 10^{-1} S/m at 1 wt.% CNT. After 1000 stretching cycles, the electrical resistance of 3D-printed composites containing 0.5 wt.% increased by 40%, remaining stable after 1000 bending cycles (Li *et al.*, 2017).

The incorporation of CNT into PA and TPU powders at a low loading fraction (1% wt.%) resulted in improved thermal conductivity of parts provided by the SLS process (Yuan *et al.*, 2018). In addition, the addition of carbon 45anofibers (CNFs) improved the mechanical properties of PA12. Compared to unfilled PA12 SLS components, adding 3 wt.% of CNF increased the storage modulus by 22% (Goodridge *et al.*, 2011).

Athreya *et al.* (2010) produced PA12 powders with carbon black (CB) content of 4 wt.%. Although the modulus of SLS nanocomposite parts decreased slightly, the conductivity increased to 1×10^{-4} S/cm.

Saleh *et al.* (2021) used the SLS process to fabricate polymeric composites containing multi-walled CNTs. Heat conduction and heat absorption were found to have improved in the composites created. It was also discovered that adding CNTs increased tensile strength,

toughness, and elongation at break without lowering tensile modulus. The crystallinity and microstructure formed by the polymer molecules are strongly related to the part properties (e.g., mechanical and tribological properties) (Toda *et al.*, 2016). As a result, altering crystallization behaviour with nanoadditives directly impacts the SLS powder processability and the final part properties. Several techniques for incorporating nanoparticles as additives have been published in the literature, including melt compounding, milling, and ex situ dispersion into polymer solution (Zheng *et al.*, 2004, Goodridge and Wei *et al.*, 2011). Most of these techniques have an issue with the filler clumping together throughout the AM process. In order to achieve a large surface area of nanoparticles accessible by the polymer chains and prevent processability problems, a high degree of agglomeration necessarily leads to a higher requirement for filler (by light scattering and inhomogeneous particle quality). It is clear that enhancing nanoparticle dispersion, lowering filler mass fractions, and improving the interfacial interaction between polymer and filler are critical (Kim *et al.*, 2013, Athreya *et al.*, 2010).

The properties of SLS composites are influenced by the dispersion morphology of fillers, which is linked to the composite powder preparation methods. SLS's main technology is powder design and preparation. In general, four types of composite powders are used in SLS processing:

- (1) melt extrusion and pulverization provide a well-dispersed inorganic/polymer powder.
- (2) inorganic polymer-coated powder made by solution coating and spray drying.
- (3) a plain mechanically mixed mixture of polymer and inorganic powder.
- (4) liquid phase absorption and deposition of inorganic particles-wrapped polymer powder.

Different preparation methods result in different powder structures, resulting in differences in SLS component efficiency. For example, the conductive filler can be uniformly dispersed within the polymer using both melt and solution mixing, while the conductive fillers are coated on the particle's surface using mechanical mixing and the liquid phase absorption and deposition method. Because of the uniform filler dispersion in the polymer matrix, using powders prepared by melt mixing and solution mixing will improve the mechanical properties of the materials to some extent. However, the improvement in conductivity is low because conductive networks are difficult to shape. Since conductive filler-coated polymer particles are more likely to form an isolated conductive network between them and only a small amount of filler is needed to form a conductive path and network, SLS parts made by mechanical mixing and liquid phase absorption have better electrical properties (De Leon *et al.*, 2016).

Mechanical mixing is the focus procedure, which refers to directly mixing conductive filler and polymer powder content by ball milling, high-speed mixer, grinding, and other methods to produce a composite powder. The method is simple and suitable for commercial mass manufacturing, and it is commonly used to improve the mechanical and thermal properties of SLS composite powders.

A nano-composite powder can be obtained through electrostatic interaction, in which nanoconductive fillers are adsorbed on the surface of the polymer micro powder. These nanofillers then form 3D conductive networks between the fused polymer particles during printing. Direct ball milling was used by Athreya *et al.* (2010) to produce PA12 powder with 4% CB (Figure 15). It was shown that the flexural modulus of the SLS PA12/B composites was lower than that of pure PA12 because CB agglomeration prevents mutual fusion between the particles.

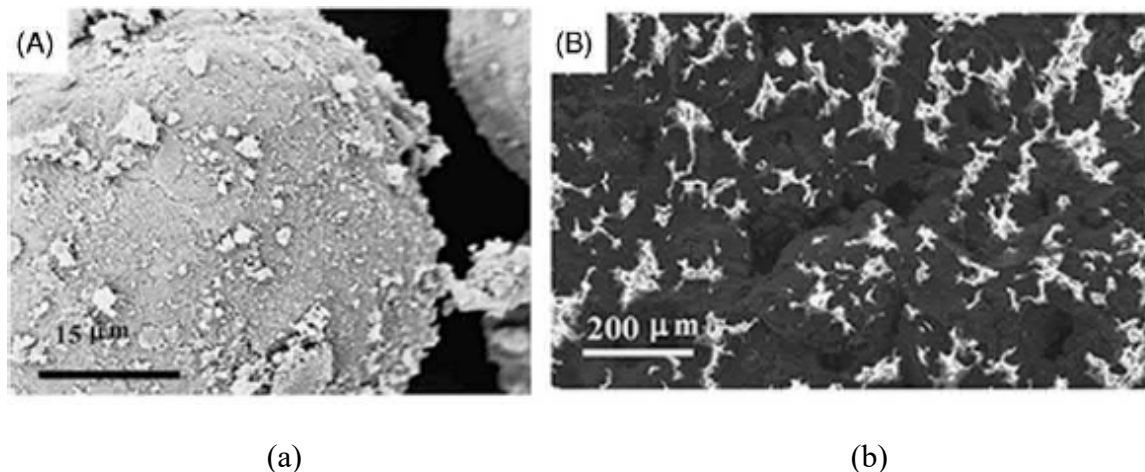


Figure 15. SEM images of (a) CB-coated PA12 particle and (b) PA12/B composite (Athreya *et al.*, 2010)

A large amount of fillers can degrade the materials' mechanical and processing properties (Table 3). The sintering properties of powders and the final conductive properties of SLS-printed products are influenced by powder processing methods, conductive fillers, and matrix materials. Table 3 lists the relevant works to compare the influencing factors of SLS-processed conductive composites and their mechanical properties.

Table 3. Mechanical and conductive properties of SLS-printed composites (Gan et al., 2020)

Polymer	Filler	Powder preparation method	Mechanical properties		Electrical properties		
			Tensile strength (MPa)	Strain at break (%)	Modulus (MPa)	Percolation (wt%)	Conductivity (S/m)
PA12	Carbon black	Mechanical mixing	–	–	1450 (4 wt% CB)	4 wt%	1×10^{-2} (4 wt% CB)
PA12	GNP	Liquid phase absorption and deposition	44 (3 wt% GNP)	–	2200 (3 wt% GNP)	3–5 wt%	1×10^{-5} (5 wt% GNP)
PA11	GNP	Melt mixing	42 (1 wt% GNP)	–	2120 (7 wt% GNP)	7 wt%	10^{-9} (7 wt% GNP)
PA12	GNP	Liquid phase absorption and deposition	44.3 (3 wt% GNP)	–	2100 (3 wt% GNP)	3–5 wt%	6.4×10^{-6} (5 wt% GNP)
PA11	MWCNT	Melt mixing	37 (3 wt% MWCNT)	–	1050 (3 wt% MWCNT)	>3 wt%	10^{-3} (7 wt% GNP)
PA	rGO	Liquid phase absorption and deposition	–	–	221 (4 vol.% rGO)	0.05 vol.%	10^{-1} (8 vol.% rGO)
PA12	MWCNT	Liquid phase absorption and deposition	–	–	–	0.5 wt%	10^{-2} (1 wt% MWCNT)
PA12	CB	Mechanical mixing	22 (1.5 wt% CB)	16 (1.5 wt% CB)	243.85 (1.5 wt% CB)	1.5–3 wt%	5×10^{-1} (10 wt% CB)
TPU	MWCNT	Liquid phase absorption and deposition	17.5 (0.2 wt% MWCNT)	465 (0.2 wt% MWCNT)	–	0.2 wt%	0.38 (1 wt% MWCNT)
TPU	MWCNT	Liquid phase absorption and deposition	–	–	–	0.5 wt%	10^0 (1 wt% MWCNT)
TPU	GE	Liquid phase absorption and deposition	6.54 (0.5 wt% GE)	380 (0.5 wt% GE)	–	0.5–1 wt%	5×10^{-4} (1 wt% GE)
TPU	SWCNT	Liquid phase absorption and deposition	10.2 (0.5 wt% SWCNT)	415 (0.5 wt% SWCNT)	–	0.05 wt%	0.14 (0.5 wt% SWCNT)
Phenolic/epoxy	Nature graphite (NG)	Mechanical mixing (carbonization and infiltration)	33.4 (flexural strength), 40 vol.% NG)	–	–	–	38,000 (65 vol.% NG)
Phenol formaldehyde/epoxy	GF	Solution mixing (infiltration and curing)	96.2 MPa (80 vol.% GF)	–	–	–	5×10^{-6} (80 vol.% GF)

The impact of Cu particles on the characteristics of flame-resistant, halogen-free polyamide PA2210FR was investigated by Balzereit *et al.* (2018). It was shown that porosity of the PA2210FR was raised when the Cu concentration increased up to 5 wt.% however, greater Cu values of 10 and 20 wt.% dramatically reduced the porosity of the material. Overall, the Cu concentration stabilized the SLS process in terms of ultimate tensile strength (UTS) and tensile strain at UTS. A polyamide-copper-compound with 20% Cu powder (CuCHUF) 10 μm also was successful. It shows process's potential for use in electronic devices such as moulded interconnect devices (MID), antennas, and housings that use Cu as a conductive material with unique electrical characteristics.

Thokala *et al.* (2017) used SLS to produce a PA11-Cu composite for medical device applications. Cu added to the polymer at 2%, 5%, and 10% resulted in rapid crystallisation due to its ability to function as a nucleating agent. Furthermore, the mechanical test revealed that composites containing 5% and 10% Cu had a beneficial reinforcing impact on the final structure. Long-term antibacterial action was also observed in the corresponding ion release for these composites. As a function of Cu additive loading levels, antimicrobial efficacy, ion release rates, morphology, and mechanical properties of PA11/Cu composites were investigated. All PA 11/Cu composites tested were active against E. Coli (ATCC 8739) within 24 hours, with bacterial reduction rates of >99.9%. Preliminary ion release experiments showed that composites with 5% and 10% Cu additive loading values were particularly effective at releasing ions for lengthy periods.

2.4. Properties of SLS PA12-based parts

As it was mentioned above, PA12 dominates the market among the polymeric materials utilized in SLS. This arises from the thermoplastic polymer's unique thermal properties. PA12 is a semicrystalline polymer with a considerable temperature difference between the start of melting (during heating) and the start of crystallisation (via cooling). This wide temperature range allows the polymer powder to be melted with a laser beam while the material remains heated (and molten at usually 160 °C–180 °C until the cooling down step, which consolidates the component all at once. This maximizes consolidation while reducing warpage (Choy *et al.*, 1977, Goodridge *et al.*, 2012, Dadbakhsh *et al.*, 2017, Wang *et al.*, 2015).

In recent years, much research has been conducted on the chemical, electrical, and mechanical properties of PA12 pieces printed using PBF. Caulfield *et al.* (2007) used SLS to investigate the density and mechanical properties of printed PA12 specimens as a function of laser power,

hatch spacing and scanning speed. In order to predict the tensile properties of SLS-printed PA12 materials, a nonlinear equation was constructed based on the results of the experiments to explain the relationship between energy density and tensile properties. As mentioned above, many efforts have been made to improve the qualities of polymer SLS components by developing nylon composites. In order to further enhance their mechanical and thermal properties, PA powders can reasonably be reinforced with other materials: fibres, particles and nanoparticles (Dickson *et al.*, 2017, Sofian *et al.*, 2001).

Goodridge *et al.* (2011) found that adding CNT (3 wt.%) to PA12 improved mechanical properties by 22%. PA12 was modified using CNTs to increase mechanical properties (Bai *et al.*, 2015). The flexural modulus of the laser-sintered components was 13% higher, the flexural strength was 10.9% higher, and the Young's modulus was 54% higher. When compared to pure PA12, the crystallization temperature of PA12-CNT powder was raised, which was responsible for the interfacial force between CNTs and PA12, impeding the mobility of PA12 chains. The porosity of the CNT composites, on the other hand, increased. The effect of MWNTs combined with PA12 on mechanical characteristics was also investigated by Salmoria *et al.* (2011). Simulated studies on PA12-CNT showed that adding CNT to the powder bed assists in carrying the laser heat broader and deeper into the powder bed. In comparison to pure PA12, CNT-coated PA12 enhanced heat conduction and heat absorption (Yuan *et al.*, 2016).

Many attempts have been made to improve the mechanical response of polymeric SLS powders by adding graphene. Kim *et al.* (2013) used a nitric acid solution to oxidize the graphene nanoplatelets (GNP) and boost interfacial bonding. The tensile strength of laser-sintered pieces containing 0.1 wt.% usable GNP was 15% higher than that of unfilled PA12. Simultaneously, 3D-printed SLS parts containing usable GNP showed 9.2% and 11.3% increases in Young's modulus and tensile strength, respectively.

Xiong *et al.* (2022) concentrated on creating PA12 powders coated with CNTs and using the sintering method to build networks in the PA12/CNTs composites. A combination of ultrasonic dispersion and liquid phase deposition (UDLD) and ball milling (BM) methods were used to prepare PA12/CNT powders. For comparison, composite powders with a uniform dispersion of CNTs in the PA12 matrix were made using a combination of melt compounding and the cryogenic pulverization process (MP), and these powders were utilized to build products using SLS. PA12/CNT nanocomposite components were made simultaneously using the standard melt compounding compression moulding method. The findings reveal that the PSD and flowability of composite powders made by both the BM and UDLD procedures meet the

requirements for the SLS 3D printing process and that the coating of CNTs on the surface of PA12 powder particles was achieved as expected. The optical microscope and SEM observations show that in the 3D-printed parts printed using the BM (bPA12-CNTs) and UDLD (uPA12-CNTs) methods, complete conductive segregated networks were successfully generated from the coated CNTs at the interfaces, but not in the MP 3D-printed parts (mPA12-CNTs). The electrical conductive percolation threshold for the bPA12-CNTs system could be as low as 0.347 wt.%.

Advances in composite 3D printer development have not stopped researchers from developing materials containing fillers, including nanoparticles, CNTs and graphene, from attaining unique properties and capabilities. For example, PA12 was made with a high-volume ratio of carbon fibre (maximum 50%) (Yan *et al.*, 2011). Pre-modification of carbon fibres by oxidation resulted in uniform distribution of carbon fibres and excellent interfacial adhesion between fibres and matrix. Flexural strength and modulus were increased by 114% and 243.4%, respectively, by adding the maximum of 50 wt.% of carbon fibres.

Commercial PA12 powder is unable to absorb sufficient Yb-fibre wavelength. However, polymer particles can be changed with appropriate additions to improve absorption. This can be accomplished using inorganic nanoparticles based on caesium tungsten oxides, antimony tin oxides, organic laser dyes, or carbonaceous materials. CNT stands out among carbonaceous additives with several more beneficial qualities, including strong mechanical strength, stiffness, good electrical conductivity, thermal conductivity, and high laser light absorption over a broad-spectrum range (Gan *et al.*, 2020). Yuan *et al.* (2016) investigated the effect of depositing multi-walled carbon nanotubes (MWCNT) on the surface of PA12 on polymeric composites' thermal and mechanical properties. Due to the characterisations, composite powders had superior heat conductivity and heat absorption than pure polymers. Furthermore, the stable sintering range of composite powders was expanded, making the sintering method more appropriate. Another study by Yuan *et al.* (2018) examined the electrical and thermal conductivity characteristics of single-walled carbon nanotube (SWCNT)-doped PA12 and polyurethane polymer composites produced by SLS. When the thermal and electrical conductivities of SLS parts were compared to those of hot press components, it was discovered that CNT improves thermal conductivity, allowing laser heat to surround a larger area while penetrating deeper into the polymer bed (Bai *et al.*, 2015).

The EC and bending behaviour of SLS PA12 nanocomposite structures filled with CB in SLS were studied by Athreya *et al.* (2011). The findings revealed that nanocomposite structures,

including additives, had five times the EC of pure PA12 polymer but a lower flexural modulus, owing to a weak matrix-filler interface. Despite this, there has been relatively little study into the effects of Cu on SLS-produced materials, particularly their thermal and antibacterial properties. Much study has not been done on integrating the thermal, electrical, and mechanical properties of metal-added SLS-produced polymer composite structures. Özbay *et al.* (2021) studied the effect of energy density and filler types on PA12 by comparing pure PA12 to two distinct Cu fillers (dendritic and spherical forms) at 15 wt.%. Particle size distribution and heat analyses were used to identify components and mixes. They found that spherical particles have a larger and wider PSD than dendritic particles. Cu-filled samples crystallized faster and showed greater crystallisation than pure PA12. Cu-filled sample processing also necessitated greater chamber temperature and energy density requirements. Surface roughness decreased slightly as the energy density increased, especially in spherical Cu-filled samples. According to dynamic mechanical tests, both filler types showed higher transition temperatures and modulus values. PA12's flexural properties were improved by both filler types, with spherical-filled samples having much higher values. Both strength and modulus results shifted somewhat as energy density increased. The inclusion of both Cu types increased EC, as predicted. In spherical Cu-filled regions, conductivity values improved considerably.

2.5. Medical product development using polymer AM

2.5.1. AM to make pharmaceuticals

FabRx is the first firm in the world to use SLS to make pharmaceuticals (Sintratec, 2022) (Figure 16). The SLS Sintratec Kit was used to create oral printlets that contained a combination of pharmaceutical polymers, a medication (paracetamol), and a colourant typically used in the pharmaceutical sector for tablet coating. SLS produced the first printlets using only pharmaceutical-grade components, demonstrating that the inserted medicine did not deteriorate throughout the sintering process. After printing, the printlets were immediately depowdered (Figure 16b). The medication was completely intact after the SLS process. The disintegration of a fast-dissolving printlet from contact with water to the stage on the right (Figure 16c, d) took less than three seconds.

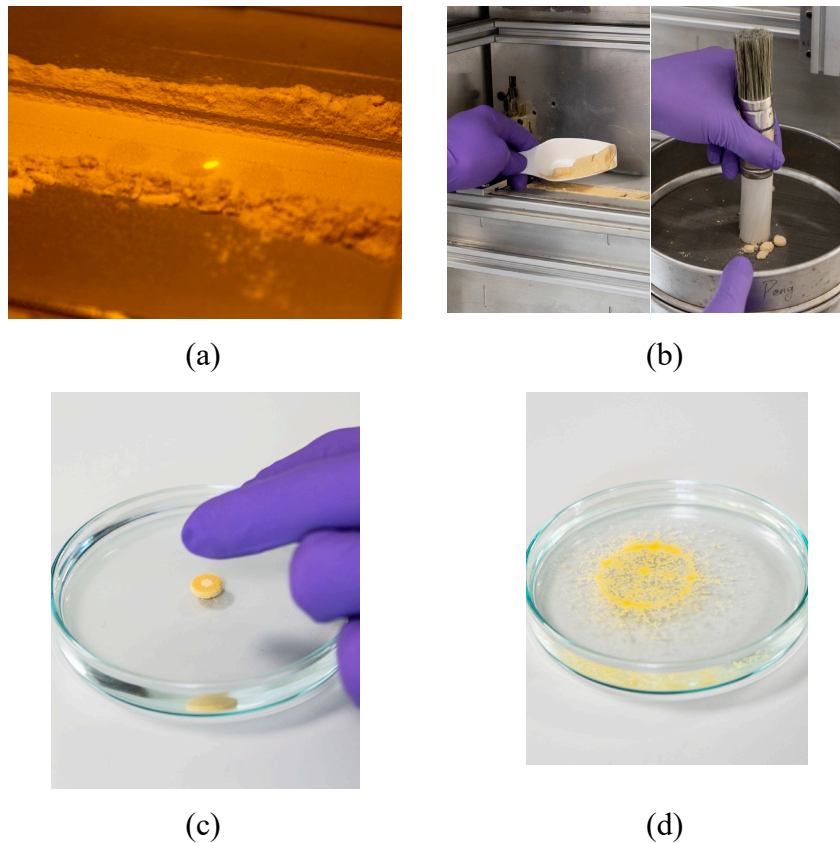


Figure 16. SLS process (a) and printlets depowdered (b); view of the tablet (c) and tablet placed in water resulting in the tablet dissolving (d) (Sintratec, 2022)

2.5.2. Pre-operative models

AM has a critical role to play in medical product development. Customized models for surgical planning, pre-operative models, patient-specific guides for cutting, and specific guided surgery devices produced by AM are used more and more by surgeons, clearly illustrating that AM has been adopted by medical professionals and has shown great progress over the past decade Tan *et al.*, 2020. The utilization of high-definition computed tomography (CT) images to create personalized implants is one of the most common uses of AM technology (Tran *et al.*, 2020).development Pre-operative models in PA12 of a patient's skull help surgeons plan intricate surgery to the last detail. This significantly decreases the operating time by lowering the risk of consequences from protracted surgeries, such as infections or severe blood loss. Employing medical models created in PA12 material and using 3D printing technology for surgical planning and simulation is a novel method. Pre-operative models are ideally adapted for skeletal modifying intervention diagnostics and accurate pre-operative planning. These methods allow surgeons to recreate anatomical components as 3D physical models, giving

them a realistic image of complicated structures before surgery. Depending on the surgical model's application, these models can represent the physical geometry of patients' anatomical features, the mechanical characteristics of the tissue, or both.

Over the past decade, the Centre for Rapid Prototyping and Manufacturing (CRPM), located at the Central University of Technology, Free State (CUT), produced several pre-operative models. The first case study, shown in Figure 17, describes the successful percutaneous aspiration of an orbital hydatid cyst in a paediatric patient with a 3D-printed positioning guide as an alternative to conventional surgery. The device was 3D printed in an EOSINT P385 SLS machine in PA2200 at the CRPM. The 3D-printed guide was used to accurately guide the insertion of a spinal needle through the skin into the cyst to aspirate the cyst with a hypertonic saline solution, as indicated in Figure 17d-e. A three-month post-operative follow-up showed that the cyst had substantially shrunk, and the diplopia resolved. The results of the procedure are shown in Figure 18.

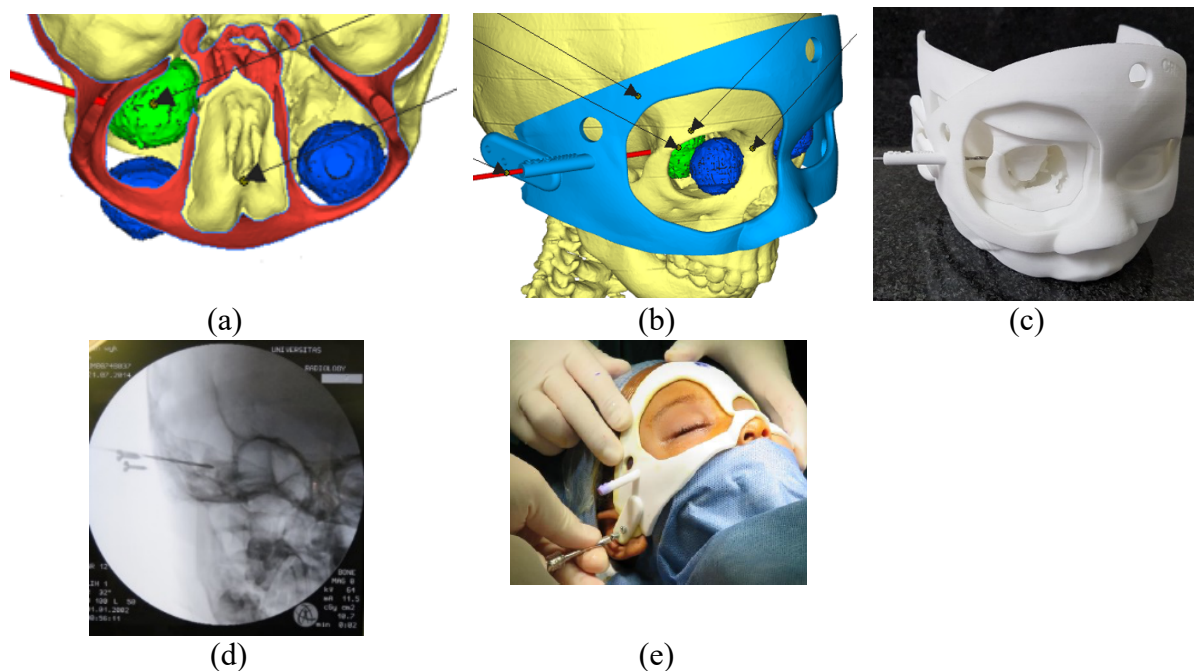


Figure 17. Location of cyst, coloured green, indicated in (a) and 3D-printed positioning guide illustrated in (b), model surgery performed on planning model with the 3D-printed guide (c), X-ray image verifying the correct position of the spinal needle (d); 3D positioning guide during operation (e)

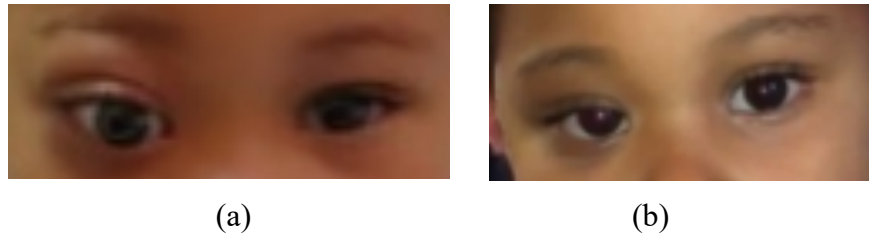


Figure 18. The abnormal protrusion (proptosis) of the right eye prior to treatment and (a) and the result three months post-operatively (b)

In another case, the CRPM assisted a young woman 32 years of age who suffered from an ossifying fibroma tumour in her lower jaw. A team of surgeons removed the resected tumour with the help of 3D printing technology (Figure 19). The surgeons used SLS technology to print an accurate size in PA12 to be used on the patient to hold both sections of the lower jaw in place after the removal of the actual tumour.

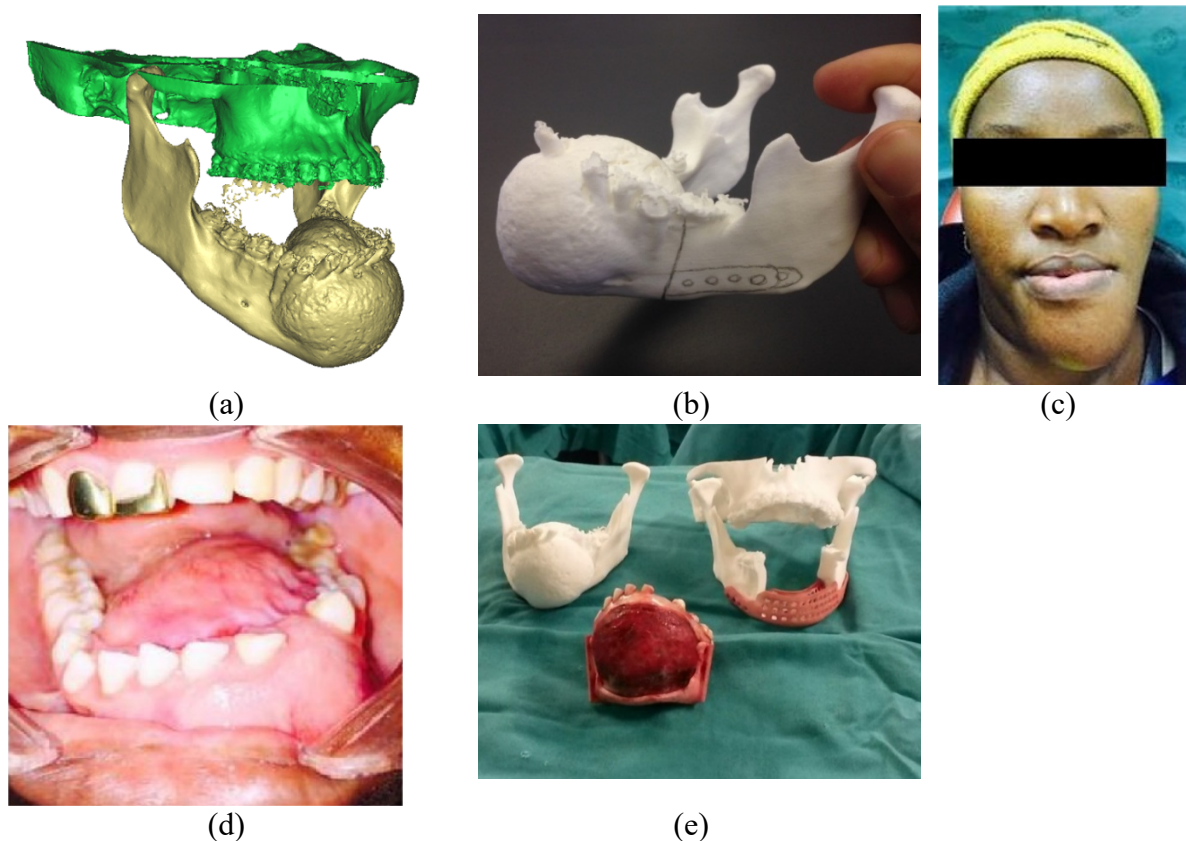


Figure 19. Model surgery performed on planning model (b) Mandible with the fibroma of a 32-year-old female patient with an ossifying fibroma tumour of the lower jaw (c,d) and the actual resected tumour removed from the patient (e)

The surgery was carried out successfully. Using the cutting guides, the titanium implant fitted perfectly after the tumour had been resected Figure 20. Just 24 hours post-surgery, the patient was already able to move her jaw normally again.



(a)



(b)

Figure 20. Patient after surgery (a) and 24 hours later (b)

2.5.3. Health-promoting goods

AM is used to design and manufacture health-promoting goods that improve well-being and performance at home and in treatment. Back discomfort is one of the most common reasons for being unable to work. Lower back pain is the second most common cause of disability in US adults, and in Germany, for example, approximately one in every three persons suffers from back pain on a regular or ongoing basis (Freburger *et al.*, 2015). One treatment option is extension therapy, performed in specially designed and mechanically adjusting relief chairs (Figure 21) by Sintratec AG.



(a)



(b)



(c)



(d)

Figure 21. The spinal discs between vertebrae (a) grow chair (b, c, d) (Sintratec, 2022)

Respiratory equipment using 3D-printed adapters also was developed in cooperation with Sintratec (Figure 22).



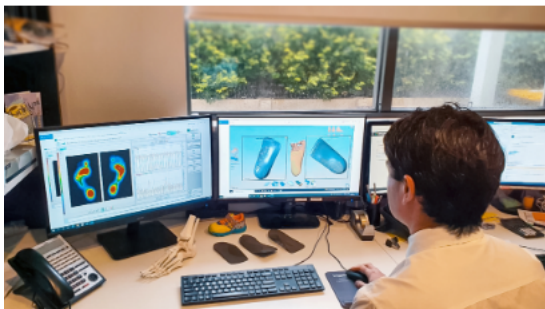
(a)



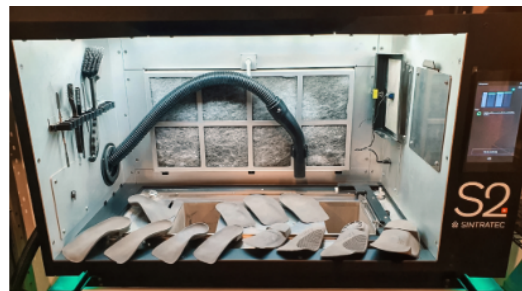
(b)

Figure 22. AM mask adapters (a) and the modification of the diving masks (b) (Sintratec, 2022)

Doctors use the 3D printer's manufacturing capabilities to help patients to enhance their lower limb, foot, and ankle health. Advanced Family & Sports Podiatry (AFSP), an Australian firm, creates personalized foot orthoses using the Sintratec S2 technology (Figure 23). 3D parts must be extremely accurate, flexible and have intricate structures to mould and aid foot and ankle function. ASFP podiatrists create personalized and semi-customized foot orthoses utilizing Sintratec PA12 material. Patients may have a tailored product within 24 hours instead of two weeks when orthoses were manufactured by conventional technology (Sintratec, 2022).



(a)



(b)



(c)



(d)

Figure 23. The podiatrists at AFSP use modern 3D technologies to create personalized foot orthoses (a), 3D-manufactured orthoses (b) and fitting orthosis (c, d) (Sintratec, 2022)

2.5.4. COVID-19 challenges

In response to the COVID-19 outbreak, designers developed plastic door handles, anti-touch keychain tools, face masks, shields and adjusters, nasal swabs, respirator parts and many other devices (Rapid3D, 2022, Callahan *et al.*, 2020, Williams *et al.*, 2020).

An anti-touch keychain is a tool small enough to carry in a pocket to minimize COVID-19 infections in public. A snap mechanism allows the tool's tip to be extended and retracted, safely closing it off even after it has made contact with potentially contaminated surfaces (Figure 24). It was 3D-printed using the Sintratec S2 technology and is used to access public doors and input credit card pins.

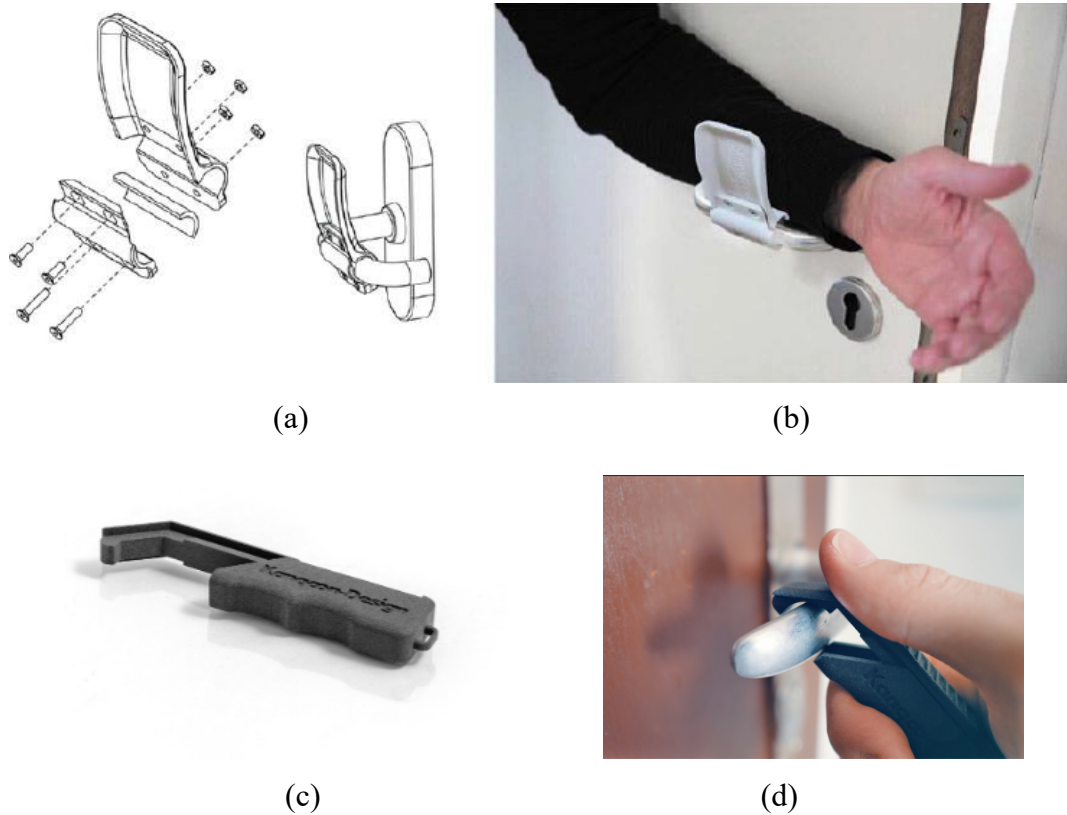


Figure 24: Door handles to reduce hand contact (a, b) (Materialise, 2020) and door opener retractable (c, d) (Sintratec, 2022)

One major disadvantage of using AM polymers in applications such as masks, valves, and no-contact devices, according to Van Doremalen *et al.* (2020), is that SARS-CoV-2 has high durability on plastic (up to 72 hours) on touchable surfaces. Virus stability on Cu touchable surfaces is reduced to four hours. Borkow *et al.* (2010) showed that masks coated with copper oxide (CuO_2) could lower the danger of influenza virus infection in the environment without compromising the masks' filtering capabilities. A thought arose that these masks also provide protection from other infections due to CuO_2 's robust antiviral and antibacterial characteristics

and hence constitute an essential supplementary arsenal in the fight against the spread of infections by harmful diseases. The use of CuO_2 in the mask layers and the fabrication of the masks with these materials do not add major expenditure to the masks' pricing. CuO_2 should be integrated into other PPE to further protect the wearer and the environment.

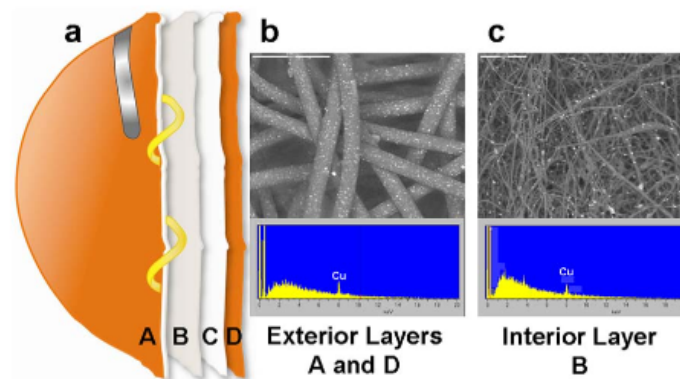


Figure 25. CuO_2 impregnated test mask composition (Borkow et al., 2010)

2.6. Summary

This chapter covered a wide variety of subjects, including state-of-the-art L-PBF technology, strengths and limitations, and essential SLS process parameters. Historical background information on AM methods was given, including understanding the physical phenomena in the SLS process and the materials employed, which have been demonstrated to be critical, as the final qualities of the SLS components are heavily reliant on them.

Commercialized polymer materials have stable processing and repeatable properties for manufacturing components. Nonetheless, current materials fail to meet the needs of many practical applications. That is why composite materials were introduced to overcome this lack of properties available in sintered parts.

A review of materials for SLS was done. PA12 is a well-known SLS plastic material for biomedical applications utilized to make functional prototypes and end-use parts. Antibacterial composites were presented since pure Cu exhibits antibacterial characteristics.

Customized models for surgical planning, pre-operative models, touchable surface devices, patient-specific guides for cutting, and specific guided surgery devices produced by L-PBF are increasingly used by surgeons, clinicians, researchers, and pharmacists. This clearly illustrates that AM has been adopted by medical professionals and has shown great progress over the past decades, with much progress expected in the future.

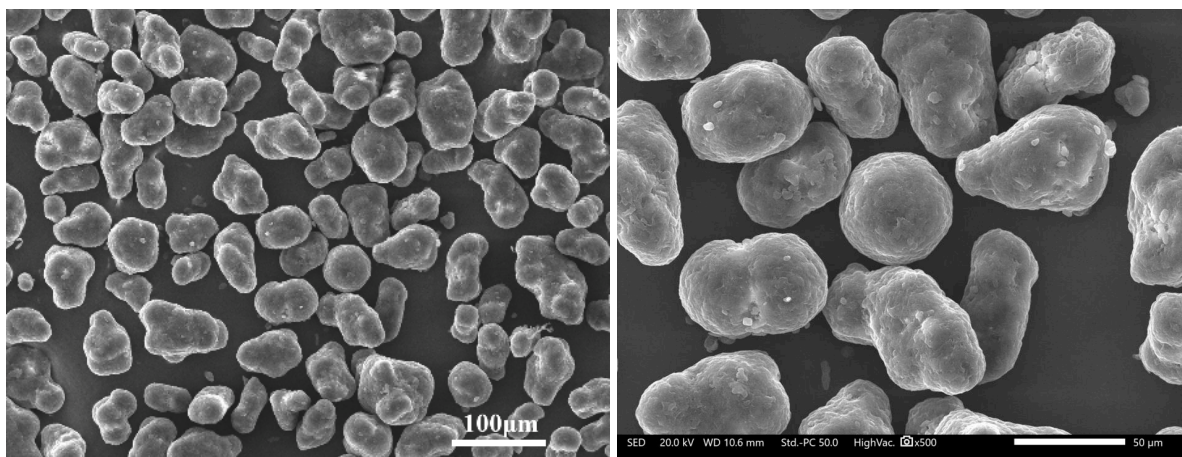
CHAPTER 3: MATERIAL AND METHODS

This chapter describes powder materials, L-PBF systems and procedures for manufacturing samples, measuring equipment used during the experimental work and the design of experiments.

3.1. Materials

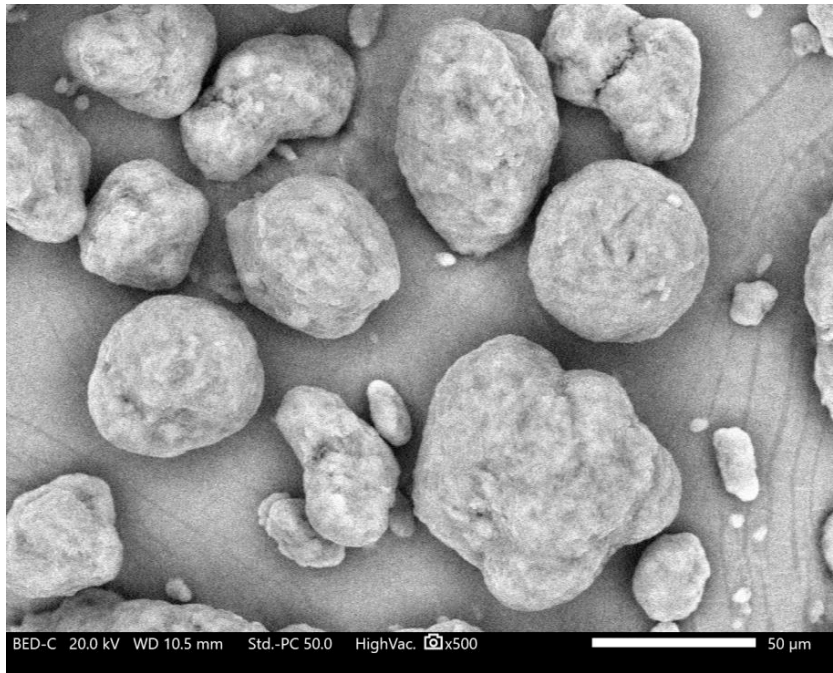
3.1.1. PA2200 powder

Polyamide 2200 (PA2200) powder was used as reference material in this study. PA2200 from EOS GmbH (Krailling, Germany) is a robust, durable, and strong plastic based on nylon PA12 material. Since PA2200 has good chemical resistance for cleaning and sterilization, it is used for personal protective equipment (PPE) and in biomedical applications (EOS, 2020). Particle size specified for a batch of used PA2200 powder was $d_{10}=34.9\ \mu\text{m}$, $d_{50}=55.6\ \mu\text{m}$ and $d_{90}=83.5\ \mu\text{m}$. PA2200 powder particles have inclusions of several micrometres that can be seen on the particle surface in SEM (Figure 26). The size and morphology of inclusions are similar to the findings of Verbelen *et al.* (2016), showing that they are titanium dioxide (TiO_2) particles. TiO_2 enhances the flowability and absorption of nylon material and acts as a nucleating agent for SLS (Schmid, 2018). The melting point for virgin material indicated by the supplier is 186.3°C .



(a)

(b)



(c)

Figure 26. SEM photo of PA2200 powder: SE (a, b) and BSE mode images (c)

3.1.2. PA12/B powder

PA12/B powder from Sintratec was used in this study as the main material (70% virgin and 30% used). Pure nylon is transparent for the Sintratec diode laser wavelength (445 nm), so Sintratec added black colourant (carbon) to improve the absorption of laser beam energy in the diode laser wavelength. PA12/B powder has an anthracite (black) colour. The 10th, 50th and 90th percentiles of the powder's equivalent diameter (weighted by volume) are $d_{10}=33\text{ }\mu\text{m}$, $d_{50}=60\text{ }\mu\text{m}$ and $d_{90}=85\text{ }\mu\text{m}$, respectively (Figure 27). PA12/B solid material has a density of $1000\text{--}1150\text{ kg/m}^3$ and a melting temperature of $177\text{ }^{\circ}\text{C}\text{--}185\text{ }^{\circ}\text{C}$, as indicated by Sintratec.

PA2200 and PA12/B have very close powder size distribution and similar potato-like shapes of particularities. Virgin powders have an insignificant amount of particles with size less than $15\text{--}20\text{ }\mu\text{m}$ (Figure 26a, c and Figure 27a, c,d). This corresponds to results obtained by Olejarczyk et al. (2020) that also tested these materials supplied by EOS and Sintratec and found that tested powders have an insignificant share of particles with size of $20\text{ }\mu\text{m}$.

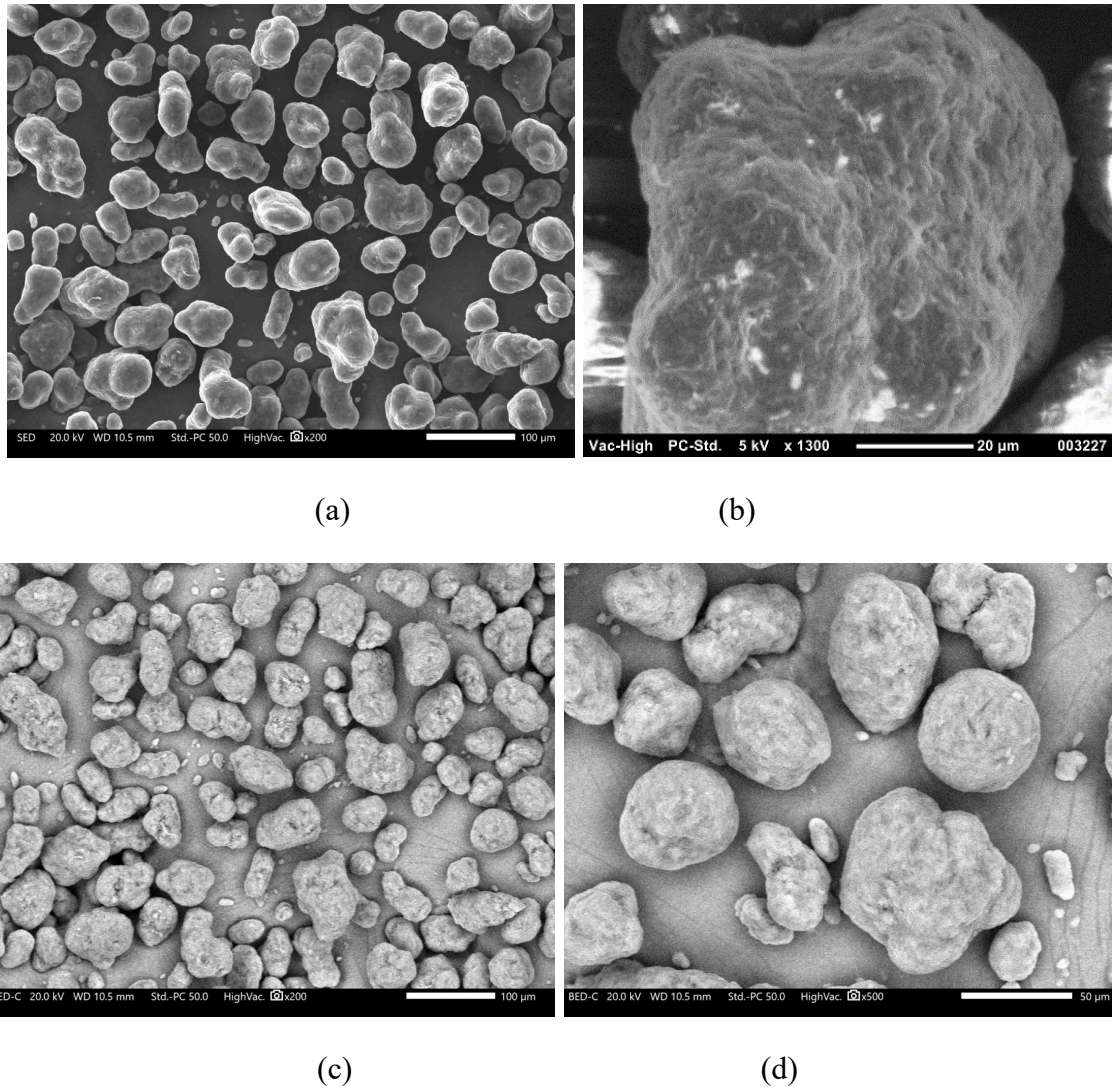


Figure 27. SEM photos of PA12/B powder: SE mode (a, b) and BSE mode (c, d)

3.1.3. Copper powder

The Cu (–45 μm) (TLS Technik GmbH & Co. Spezialpulver KG) powder was 99.9% pure. The 10th, 50th and 90th percentiles of the powder's equivalent diameter (weighted by volume) are $d_{10}=9\text{ }\mu\text{m}$, $d_{50}=22\text{ }\mu\text{m}$ and $d_{90}=38\text{ }\mu\text{m}$, respectively. The Cu powder was gas atomized and spherical (Figure 28). As a result, the maximum size of the Cu powder and the average size of the PA12/B powder were compatible.

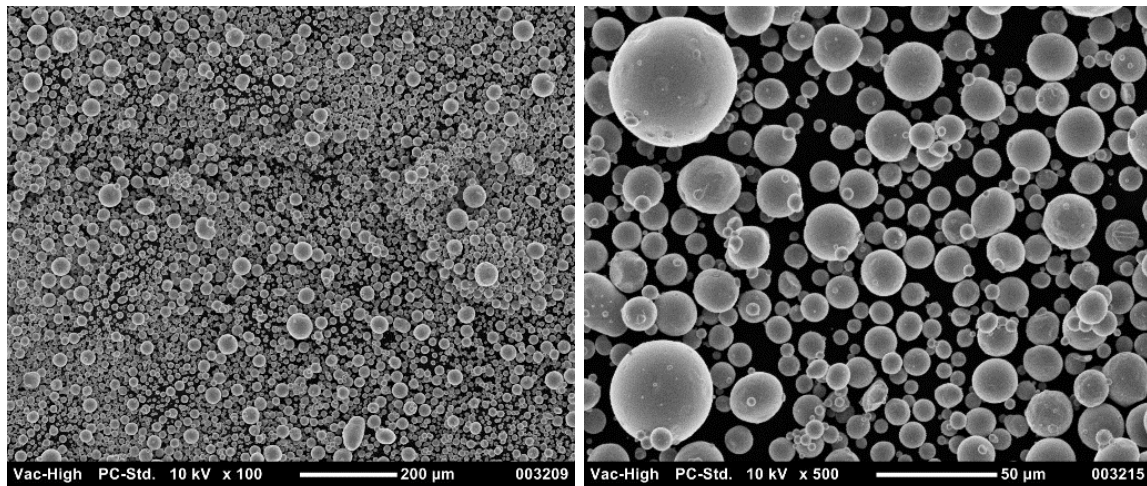


Figure 28. SEM photo of Cu powder

3.1.4. Powder preparation and mixing

The matrix material, PA12/B and the pure Cu powder were sieved manually using a 150 µm sieving tool, as shown in Figure 29a. The powder preparation of new and old PA12/B was mixed using a mixing ratio of 70 virgin:30 used, which was provided.

Cu powder was mixed with the matrix material, PA12/B, in a weight ratio of 10 and 20 wt.%. The Cu and PA12/B powders were mixed in the horizontal rotating drum mixing station shown in Figure 29b for five hours at 60 rpm to ensure homogenous distribution. After mixing the material, it was left for 12 hours for drying at room temperature. The mixture was then sieved once through a 150 µm sieving tool and loaded into the SLS machine for building the mechanical specimens. The material preparation was performed at room temperature.

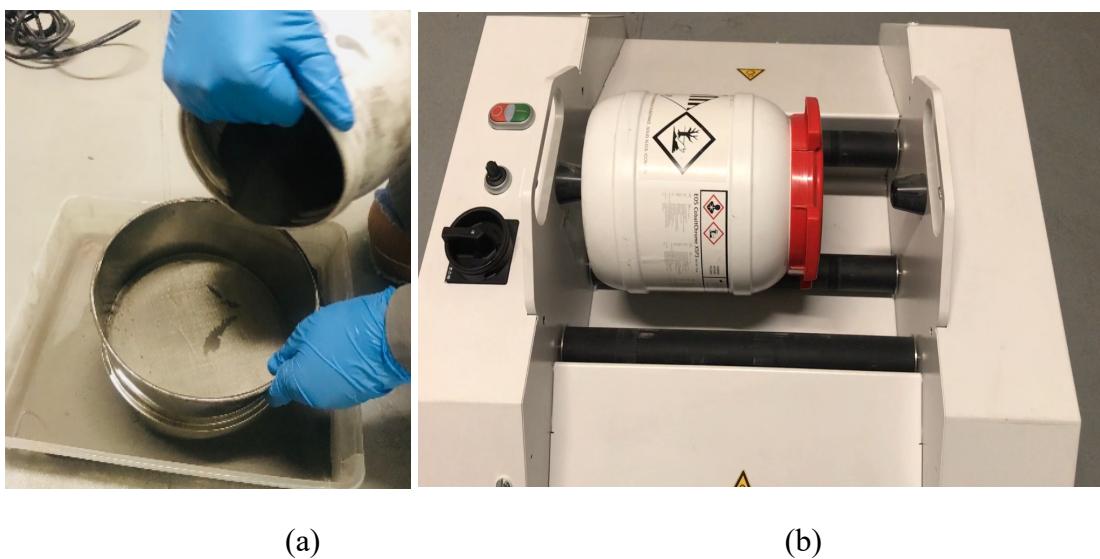


Figure 29. Manual sieving procedure (a) and horizontal mixing station (b)

3.2. Systems used for manufacturing samples

3.2.1 EOSINT P396 system

Printing of samples with PA2200 supplied by EOS was done on the EOSINT P 396 SLS printer (Figure 30). The printer has a CO₂ laser with a maximum power of 70 W.

The PSW version 3.8. control software was used. The layer thickness was 120 μm , with a hatch distance of 300 μm , and scanning speed of 4 m/s. Laser power was 45 W with a scanning speed of 4 m/s during manufacturing. The machine has a build volume that can produce parts of up to 340 x 340 x 600 mm.



Figure 30. EOSINT P396 SLS 3D printer machine installed at CRPM, CUT

Six specimens were printed in the XY and YZ axes using the EOSINT P396 SLS printer with an automated multi-box feedstock powder with a virgin/used mixture ratio of 50:50 and the printing settings specified by the EOS. The laser beam fused the contours of all parts before hatching their inside sections throughout each build exposure layer. The specimens were cooled to room temperature in the building chamber and removed from the build platform once the sintering process was completed. The entire SLS process was carried out in a nitrogen-rich

build chamber. The build processing procedures were conducted with build parameters, as shown in Table 4.

Table 4. Standard EOSINT P396 PA2200 process parameters (EOS GmbH, 2020)

Parameter	Value	EOS parameters recommended for PA2200 powder
Layer thickness	µm	120
Hatch spacing	µm	300
Laser speed	mm/s	4000
Printing surface target heating temperature	°C	156.2
Printing surface target printing temperature	°C	168
Chamber target heating temperature	°C	130
Chamber target printing temperature	°C	130
Preheating time	hour	2

3.2.2 Sintratec S1 System

PA12/B and composite samples were manufactured with a Desktop Sintratec S1 3D printer (Figure 31). The system consists of a process chamber with a recoating system, a platform heating module and elevating system, a fibre laser optical system, a process computer with process control software, and a collection of regular maintenance accessories.

In the class of desktop 3D printers, the Sintratec S1 system is one of the “low budget” sinter laser printers used by Sintratec AG (Brugg, Switzerland) as a specialist SLS printer for AM and research production activities. PA12 black (PA12/B) as printing material and thermoplastic elastomer (TPE), also black, can be processed. The printer needs an external PC with Sintratec Central (SC) operating software. The machine has a built-in volume that can produce parts of up to 130 x 130 x 180 mm, but the manufacturer recommends staying within 110 x 110 x 160 mm.

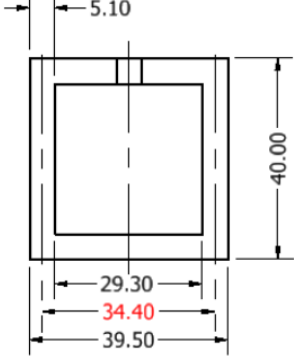
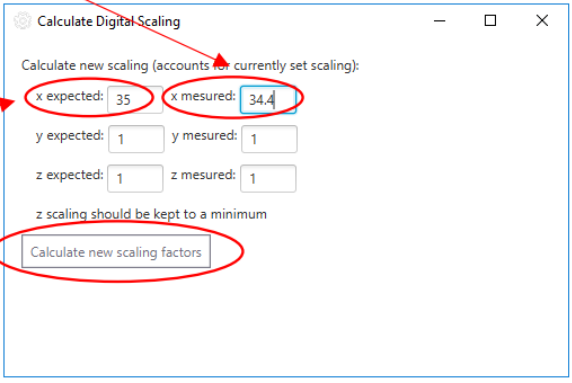
The printer works with a fast-moving 2.3 W diode laser in the visible blue wavelength range of 445 nm. Sintratec S1 recommends using 50–100 µm powder layer thickness. Dimensional and shape deviations of approximately 100–200 µm and a tolerance gap of less than 300 µm are expected.



Figure 31. SINTRATEC S1 Desktop 3D printer installed at CRPM, CUT

The laser speed was kept constant at 0.65 m/s in all experiments since it is the ideal printing speed, according to the manufacturer. When printing, a choice can be made between the two quality modes, “strength” and “speed”. The speed mode allows parts to be produced faster but with lower quality. Strength is highly recommended for good mechanical properties.

Before printing, the machine must be calibrated as the manufacturer prescribes in Figure 32 below. Calibration aims to obtain a print result in which the external and internal dimensions correspond to the dimensions of a component.

In order to fine-tune the dimensional accuracy of the print result, two steps must now be carried out. First the component should be scaled and then the custom print parameters adjusted. The scaling is done as follows and is identical for the x and y axis: The inner and outer dimensions are measured, added and divided by two to obtain the mean dimension. $\frac{29.3 + 39.5}{2} = 34.4mm$	
At a dimensionally accurate print, the expected average mass in this example would be 35mm. $\frac{30 + 40}{2} = 35mm$ Now the expected and the measured measurement are entered into the calibration window. This procedure is now repeated for the y-axis. The z-axis is not affected and can be measured and entered without further calculations.	

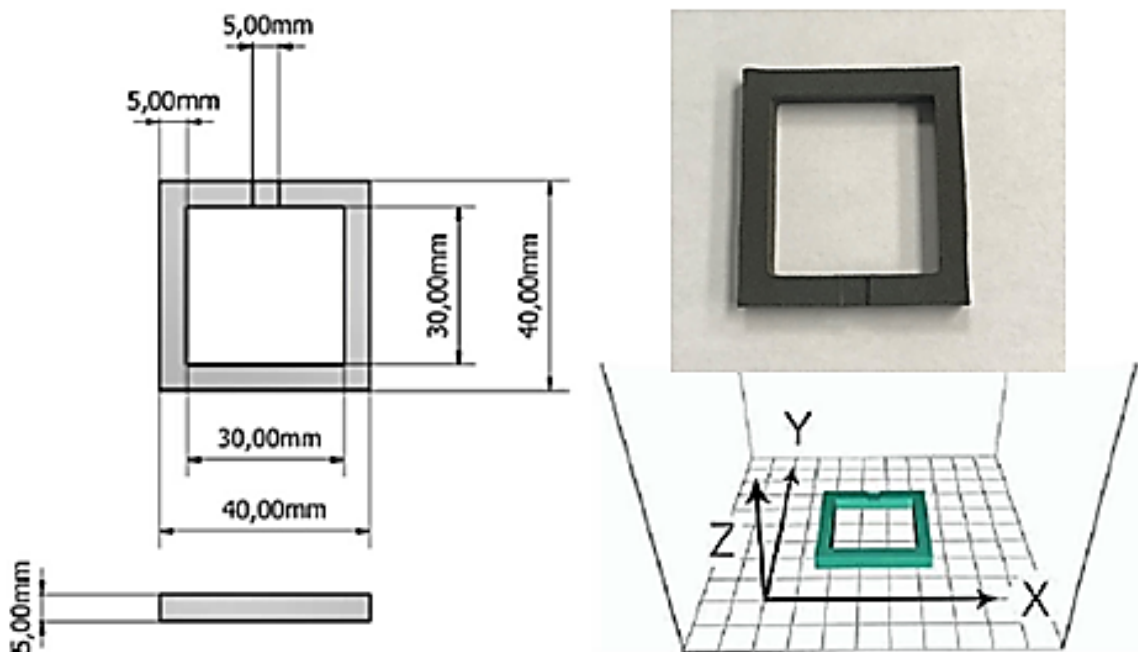


Figure 32. Orientation of the calibration job (a) and target measurements (b)
(User_manual_BA_SI_EN, Sintratec AG, 2018)

Preparing the S1 System for manufacturing:

- Empty excess/overflow powder container.
- Empty the collecting powder tray.
- Clean the glass cover of the laser with ethanol.
- Move the two platforms to the required position in a small or large step.
- Fill the powder container platform until it has been evenly and adequately filled to the top.
- Compaction of powder.
- Fill the print container platform with powder until it has been evenly filled to the top.
- Smooth the top surfaces as much as possible with a spatula on the print platform side.
- With the recoater, the powder is moved from the powder container across the print container, and that powder surface is smoothed out.
- The excess powder will drop into the excess powder container.
- The whole SLS process starts automatically with no interventions by the operator.

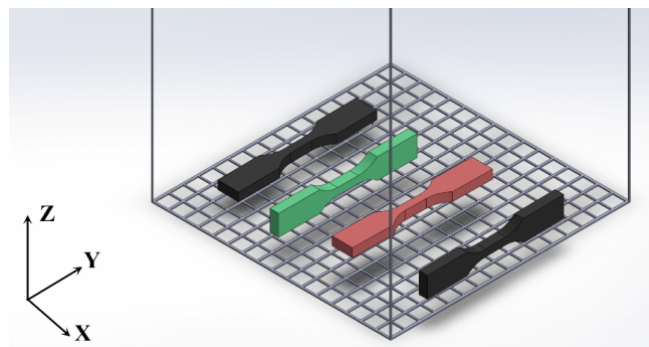
For experiments, standard process parameters recommended by Sintratec AG for PA12/B powder were used, as shown in Figure 32. Six specimens were produced in the XY and YZ directions in the S1 system. Lastly, the PA12/B powder was also prepared for the cubical test specimens. Specimens were produced with 1-time recycled powder using a recommended virgin/used powder mix ratio of 70:30.

Table 5. Standard Sintratec S1 PA12/B process parameters (Sintratec AG, 2018)

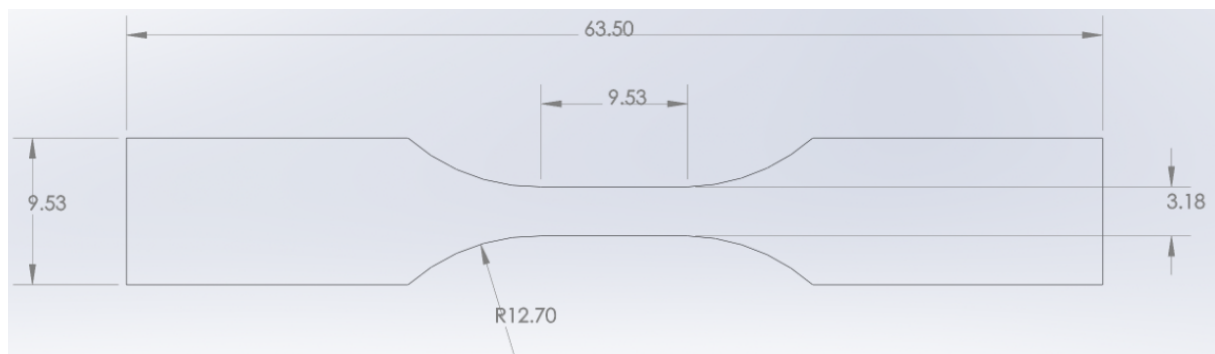
Parameter	Value	PA12/B
Layer thickness	μm	100
Hatch spacing	μm	150
Laser speed	mm/s	650
Printing surface target heating temperature	°C	150
Printing surface target printing temperature	°C	170
Chamber target heating temperature	°C	140
Chamber target printing temperature	°C	140
Preheating time	hour	1.75

3.3. Design of experiments

Samples using PA2200, PA12/B, and PA12/B with 10, 20 wt.% of copper mixtures were manufactured in the XY and YZ directions (Figure 33). For each set, surface roughness measurements (3–6 samples per set) and CT scans (one sample per set) were conducted and analyzed. Samples in the XY and YZ orientations using PA12/B powder, a powder mixture of PA12/B + 10 wt.% Cu as well as + 20 wt.% Cu were manufactured by the Sintratec S1 machine. A scanning speed of 650 mm/s and hatch distance of 150 μm with a layer thickness of 100 μm was used. The surface roughness and porosity of the 3D samples were studied. The mechanical properties, fractography, and surface morphology were analyzed. For each material and orientation, 3–10 micrographs and a minimum of six surface roughness measurements were done. Specimen dimensions for tensile tests corresponded with ASTM D638-14 standard (Type V), as is shown in Figure 33, and have a rectangular shape with a 9.5 mm gauge length, 3.2 mm width and 4 mm thickness.



(a)



(b)

Figure 33. Schematic diagram of specimens' position and orientations (a) and geometry of tensile specimens (b)

Antibacterial studies were done for SLS samples made from PA12 powder, PA12/B that contains PA12 and carbon as well as composites PA12/B with 10 and 20 wt% of Cu. Since addition of carbon can change antibacterial properties of PA12, PA12 powder from EOS was considered as a control material. PA12 from EOS (PA2200) is one of the medical device material that is used to produce patient-specific guides and prosthesis, pre-operative planning models, and a plastic cranial mould.

Rectangular samples of 7 x 7 x 3 mm size were produced and analyzed for antibacterial tests from mixtures of PA12/B, and 10 and 20 wt.% of Cu (100 samples per set) as well as PA2200 powder.

3.4. Analytical equipment

3.4.1. Microscopes

The microstructural investigation was performed using

- ZEISS Axio Scope.A1 optical microscope (Figure 34). The micro-images were captured using AxioVision SE64 software.
- JEOL JSM-IT500 operated at 20 kV scanning electron microscope (SEM), and Jeol JCM-5000 NeoScope operated at 10–15 kV were used to study powders and fracture surfaces to gain more comprehensive information about the materials.



(a)



(b)

Figure 34. ZEISS optical microscope (a) and JEOL Neoscope SEM (b)

For JEOL IT500 SEM observations, samples were coated with a conductive Os nanolayer to inhibit charging, reduce damage and improve the secondary electron signal required for topographic examination during SEM. SEM by JEOL IT500 was performed at Nagoya

University (Japan) by Dr A.M. Vilardell from the Department of Materials Process Engineering.

3.4.2. Surface roughness measurements

Surface roughness measurement is a method of calculating the small imperfections on an object's surface. The height and depth (R_z) of the fine abnormalities and their interval (R_a) were used to categorize them. Mitutoyo Corporation's Surftest SJ-210 portable surface roughness tester was used to measure the samples' surface roughness (Figure 35). The set parameters on the Surftest SJ-210 used to conduct the measurements are documented ISO 1997 standards for roughness measurements. The parameters used for the measurements were as follows: six randomly selected sampling were tested along the long side of tensile specimens; a transition length of 15 mm. A Gaussian filter was selected with a cut-off length $\lambda_c=2.5$ mm. Student's t -test ($p<0.05$) was used to find statistically significant difference in averages from different sets and orientations.



Figure 35. Surftest SJ-210 portable surface roughness tester

3.4.3. Tensile testing

Specimens were manufactured in different directions, as indicated in Figure 33. Specimen dimensions corresponded with ASTM D638-14 standard (Type V), and tensile tests were done at a speed of 1.5 mm/min by an MTS Criterion universal testing machine (Figure 36) with an extensometer of 12.5 mm in size.



Figure 36. MTS criterion model 43 electromechanical universal test systems machine

3.4.5. Micro-computed tomography

X-ray micro-computed tomography (Micro-CT) was utilized to assess porosity in 3D samples and metal particle distribution in a PA12/B polymer matrix. CT scans were performed at the Stellenbosch CT facility (Stellenbosch University, South Africa) using the General Electric Nanotom S system and data visualization and analytic system from Volume Graphics VGSTUDIO MAX 3.1. Tensile samples were scanned at 200 kV and 70 μ A, with a voxel size of 15 μ m and 2400 images recorded in a full rotation of the sample. The data was processed according to guidelines in Du Plessis *et al.* (2018, 2018a). Smaller samples (cubes of 7 mm x 7 mm x 7 mm) were scanned with a higher resolution of 6 μ m with similar scanning parameters.

3.4.6. Four-probe method testing of electrical conductivity

In the four-probe method, a battery serves as a DC power source, a voltmeter measures the potential difference across the samples, and an ammeter measures the current in the circuit. Using this method, a small current in the milliamperere range (mA) passed through the sample, and the voltage across the sample was monitored as a function of temperature at a constant supply voltage. The resistance (R) of pure PA2200, PA12/B, PA12/B + 10 wt.% Cu and PA12/B + 20 wt.% Cu was measured, as shown in Figure 37. The resistivity (ρ) and the conductivity (σ) of the samples were calculated using their dimensions.

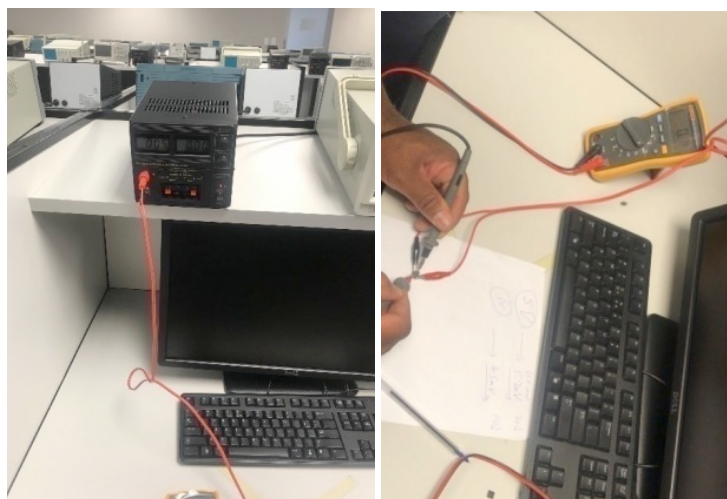


Figure 37. Resistance measurements at Electronics Lab, CUT

3.5. Microbiological testing

3.5.1. Inhibition of planktonic bacterial growth

Bacterial pure cultures of *E. Coli* (CECT405) were used for biomaterial testing. The medium used for bacteria culture was Luria Bertani (LB) (10g NaCl, 10g Tryptone, 5g yeast extract in 1L of distilled water). For agar plates, 15 g of agar was added to the LB medium. All experiments were performed with two replicates per sample (Figures 4 and 5) and repeated at least three times. Bacterial suspensions at a concentration of approximately 10⁵ colony forming units (CFU)/mL were used for biomaterial testing. Several steps were required to obtain this bacterial suspension. First, an overnight culture was incubated in a shaker (INFORS HT) at 37 °C and 200 r.p.m. from a colony in a Petri dish stored at 4 °C or from bacterial cultures in cryo-preservation. The next day a subculture was carried out for 1.5–2 hours until the optical density (OD) of the culture reached approximately 0.4 at 600 nm; it was measured with Infinite M Nano (TECAN). Once achieved, a dilution of 1:1000 was performed, and then 1 mL of culture was plated in each well, as shown in Figure 38. Before placing the materials, the OD was registered.

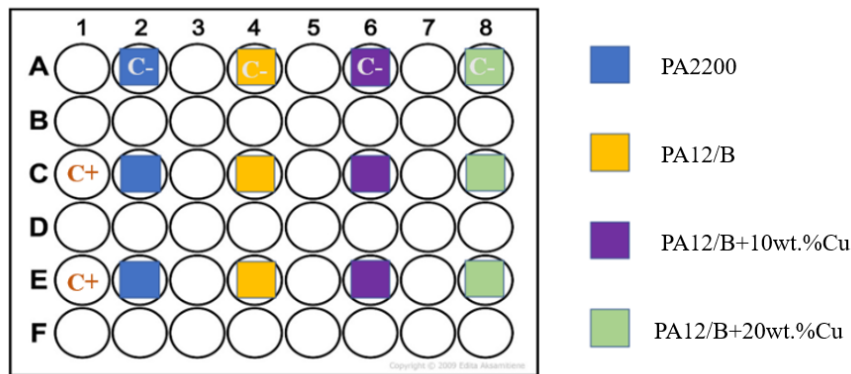


Figure 38. Schematic overview of sample distribution for performing the experiments with PA and PA composite samples. Negative controls (C-) consisted of a sample and LB without bacteria inoculation, while positive controls (C+) were bacterial suspension without materials.

Once the plates were ready, they were placed in a shaker and incubated at 37 °C and 100 r.p.m for 24 hours. After the incubation, an aliquot of each well per duplicate was extracted to perform the CFU enumeration; serial dilutions were performed until 1:106. Eventually, 50 µL of this final dilution was plated in Petri dishes. Then the biomaterials were removed, and the optical density (OD) was recorded again. Experiments were repeated at least three times to ensure reproducibility and were normalized for comparison.

Data were analyzed with IBM SPSS statistics using nonparametric tests such as U-Mann Whitney, Kruskal Wallis, Wilcoxon, and sign tests. The data were normalized by subtracting the negative control from OD data obtained, and the result was divided by the positive control value. The p-value <0.05 was considered significant. These investigations were done in Institut Hospital del Mar d'Investigacions Mèdiques (Spain) by Dr. N. Garsia-Giralt.

3.5.2. Antibacterial effect by ion diffusion in plates

The growth inhibition by diffusion of ions was tested from bacterial cultures in the 48-well plates using a dilution of 1:2. Diluted suspensions of 100 µL were plated in agar Petri dishes. The Petri dishes were split into four quarters; 2 samples of each material were placed in one of the quarters (Figure 39). After incubation at 37 °C for 24 hours, pictures were obtained.



Figure 39. Schematic overview of sample distribution for performing the experiments on the antibacterial effect of ion diffusion in Petri dishes

Summary

The materials and framework defining the procedures used in the study were given in this chapter. TLS Technik GmbH & Co. Spezialpulver KG supplied the powder materials PA12/B, neat PA2200, and pure copper. Powder particles exhibited good sphericity, as demonstrated by SEM images, and comparable sizes: The 10th, 50th, and 90th percentiles of equivalent diameter (weighted by volume) for PA2200 powder were 34.9 μm , 55.6 μm , and 83.5 μm , respectively, and 9.45 μm , 21.9 μm , and 37.5 μm for Cu powder.

The Sintratec S1 system used to conduct the experiments was briefly described. An optical microscope was used to show topography, composition, and dimension measurements, while a roughness meter was used to assess surface roughness. In addition, conductivity was measured using four-point probes, and the rate reduction of the bacterium was determined using an antibacterial test. All the experiments were also reported in detail.

CHAPTER 4: RESULTS AND DISCUSSION

4.1. Surface roughness of samples

Table 6 shows the average values and the standard deviations for surface roughness measured by the touch probe tester in different places on the tensile samples. In PA 2200 samples built in the XY direction, the average surface roughness R_a was $9.7\text{ }\mu\text{m}$, and in YZ samples, it was about $11\text{ }\mu\text{m}$. Slightly lower surface roughness values in samples built in the XY direction compared to the YZ samples indicate a smoother and flatter surface, which is typical for SLS objects (Schmid *et al.*, 2017) since surface roughness was measured on the top surface for XY samples and the side surface in YZ samples, see Figure 33. Root-mean-square (R_q) roughness was $12\text{--}14\text{ }\mu\text{m}$; R_z was about $50\text{--}59\text{ }\mu\text{m}$. Maximum peak height R_p and maximum depth (R_v) were near $28\text{--}33\text{ }\mu\text{m}$, and maximum roughness of samples R_t and $R_{z1\text{max}}$ were close to the average value of powder particles ($60\text{--}75\text{ }\mu\text{m}$). The degree of asymmetry R_{sk} was near 0, so amplitude distribution curves were symmetrical (Table 6 and Figure 40).

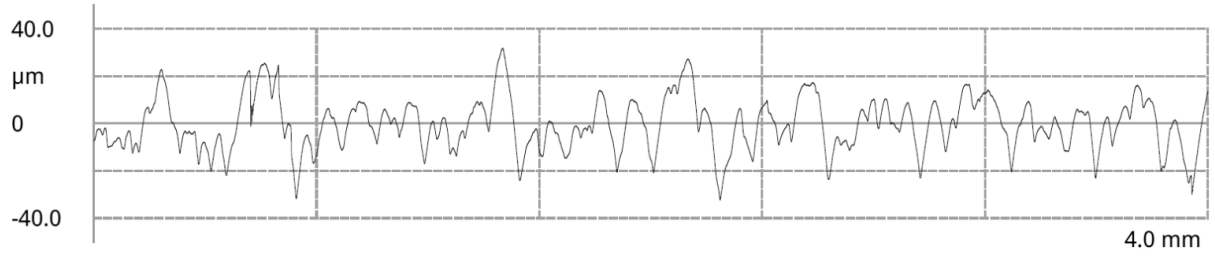
All PA12/B samples built in the YZ direction had slightly higher roughness than XY samples, but from the statistical *t-test*, this difference was insignificant ($p < 0.05$). Compared with PA2200 YZ samples, the roughness was lower in PA12/B YZ samples. No statistically significant difference in average values was found in XY and YZ samples made from PA12/B (*p*-values were about 0.1). The arithmetic mean of the absolute values of roughness profile from the mean line R_a was $9\text{--}10\text{ }\mu\text{m}$. Root-mean-square (R_q) roughness was $11\text{--}12\text{ }\mu\text{m}$; maximum height was about $50\text{ }\mu\text{m}$, corresponding to shrinkage of powder material during the sintering process. Maximum peak height R_p and maximum depth (R_v) were near $25\text{--}27\text{ }\mu\text{m}$, and maximum roughness of samples R_t and $R_{z1\text{max}}$ were close to the average value of powder particles ($70\text{--}75\text{ }\mu\text{m}$). The degree of asymmetry R_{sk} was near 0, so amplitude distribution curves were symmetrical as for PA2200 samples.

Table 6. Surface roughness of evaluated samples (Mean $\pm$ S.D.)

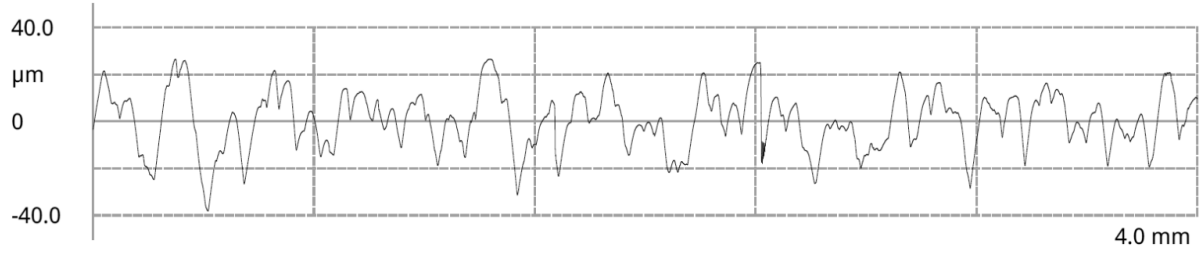
Parameter	PA2200		PA12/B		PA12/B + 10 wt.% Cu		PA12/B + 20 wt.% Cu	
	XY	YZ	XY	YZ	XY	YZ	XY	YZ
Ra, μm	9.7 $\pm$ 0.82	11.0 $\pm$ 0.44*	9.2 $\pm$ 0.51	9.96 $\pm$ 0.84#	8.6 $\pm$ 0.94	9.3 $\pm$ 0.80	10.4 $\pm$ 1.28	11.4 $\pm$ 1.37
Rq, μm	12.2 $\pm$ 0.83	13.9 $\pm$ 0.36*	11.3 $\pm$ 0.60	12.1 $\pm$ 0.93#	10.7 $\pm$ 1.02	11.6 $\pm$ 1.06	13.0 $\pm$ 1.48	14.1 $\pm$ 1.54
Rz, μm	52.4 $\pm$ 4.15	58.6 $\pm$ 2.44*	50.5 $\pm$ 3.3	54 $\pm$ 3.34#	49 $\pm$ 2.9	52 $\pm$ 5.8	53.0 $\pm$ 5.58	59.1 $\pm$ 4.45
Rp, μm	23.7 $\pm$ 1.43	25.9 $\pm$ 1.36*	25.1 $\pm$ 2.22	26.4 $\pm$ 2.86	23.6 $\pm$ 2.75	26.6 $\pm$ 4.83	25.2 $\pm$ 1.77	29.4 $\pm$ 2.17
Rv, μm	28.5 $\pm$ 3.33	32.7 $\pm$ 2.24*	25 $\pm$ 3.3	28 $\pm$ 1.5#	25 $\pm$ 2.5	25.5 $\pm$ 2.7	27.8 $\pm$ 4.06	29.7 $\pm$ 2.66
Rt, μm	64.2 $\pm$ 9.8	64.6 $\pm$ 8.8	69 $\pm$ 10.8	75 $\pm$ 10.4	66 $\pm$ 8.9	69 $\pm$ 9.2	67.7 $\pm$ 9.3	75.6 $\pm$ 10.1
Rsk	-0.01 $\pm$ 0.19	-0.14 $\pm$ 0.11	0.01 $\pm$ 0.23	0.01 $\pm$ 0.12	-0.06 $\pm$ 0.28	0.05 $\pm$ 0.44	-0.03 $\pm$ 0.33	0.16 $\pm$ 0.35
Rz1max	60.6 $\pm$ 5.17	72.3 $\pm$ 5.22*	65 $\pm$ 11.1	72 $\pm$ 11.4	62 $\pm$ 9.1	64 $\pm$ 8.8	62.0 $\pm$ 0.80	75.6 $\pm$ 4.86

* - statistically significant difference in means (*t-test*, $p < 0.05$): comparison with correspondent values from XY set,

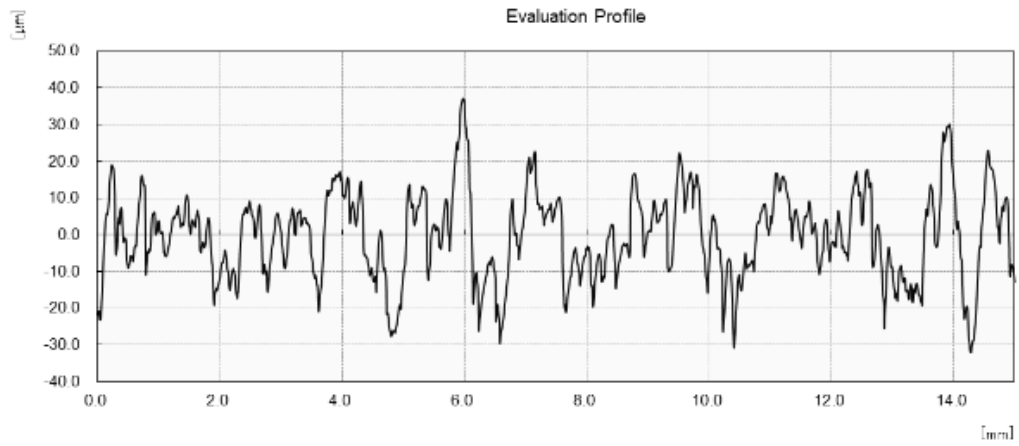
- comparison with PA2200 samples from the correspondent set (XY or YZ)



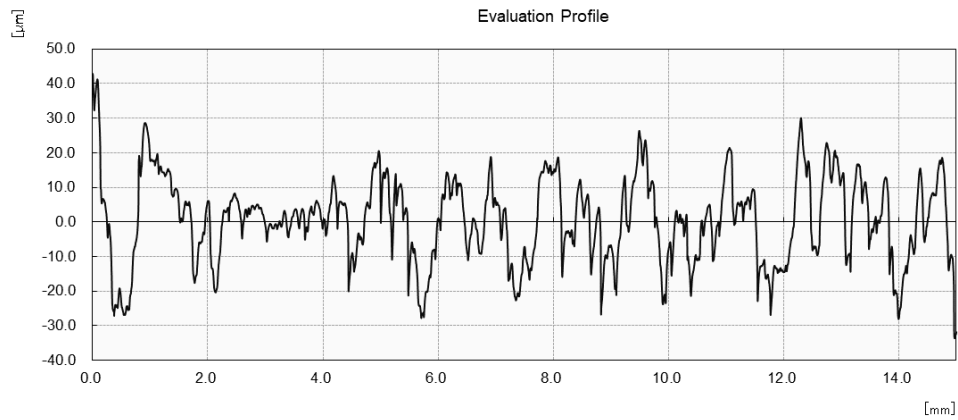
(a)



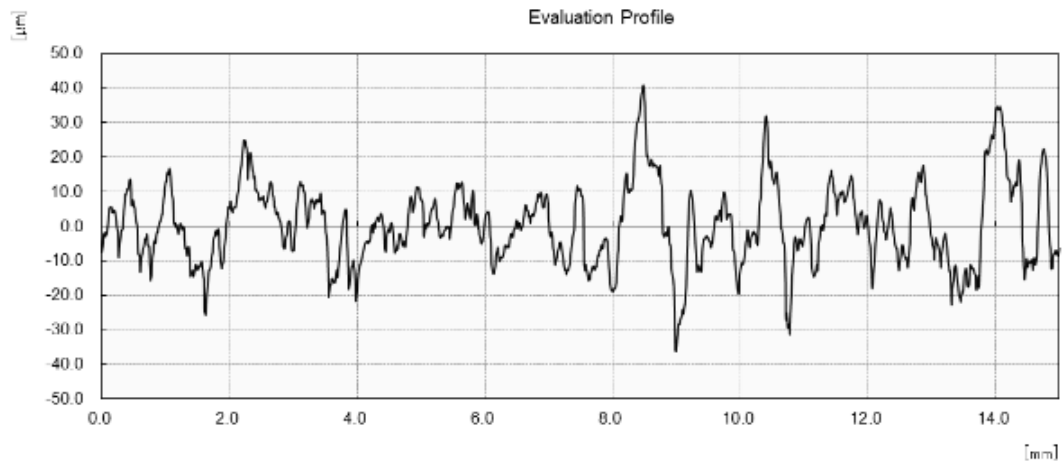
(b)



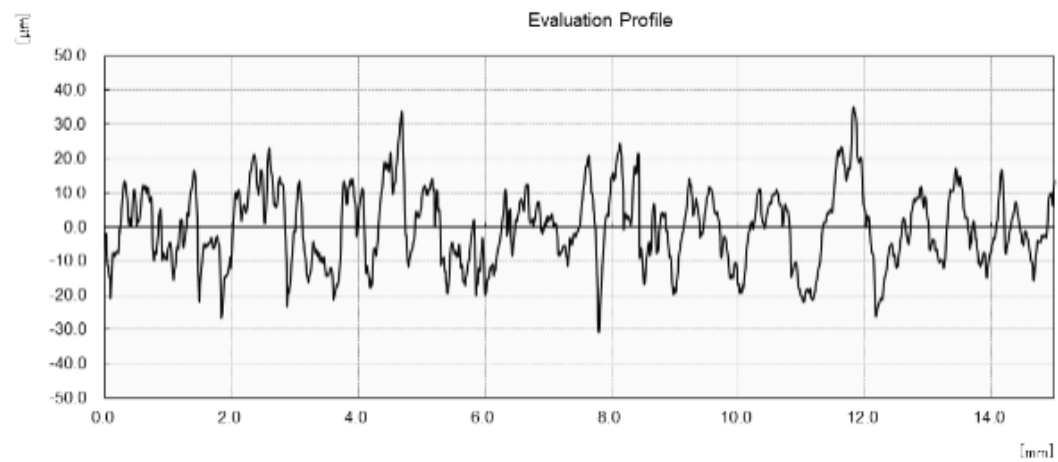
(c)



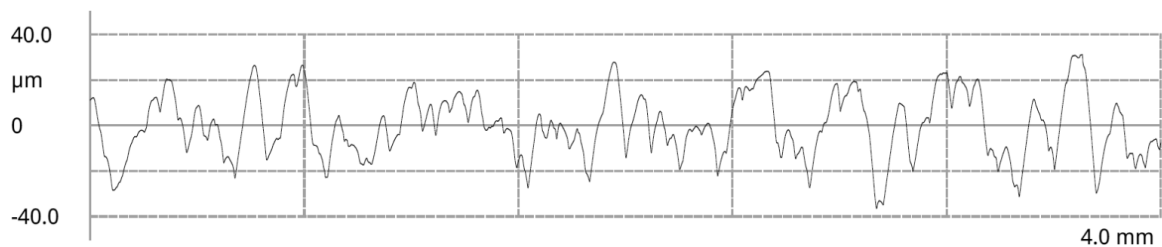
(d)



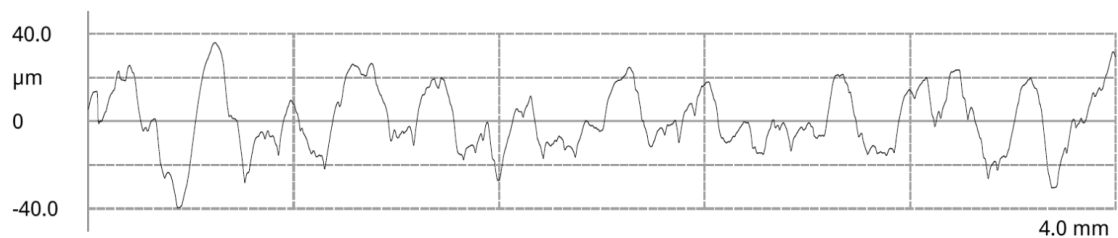
(e)



(f)



(g)



(h)

Figure 40. Roughness profiles of PA200 samples (a,b), PA12/B (c,d) and PA12/B + 10 wt.% Cu (e,f) and PA12/B + 20 wt.% Cu samples (g,h): XY (a,c,e,g) and YZ (b,d,f,h) samples

No statistically significant differences were found when t -test ($p < 0.05$) was done to compare average values of the roughness of PA12/B with and without 10 wt.% s copper addition.

Typical roughness profiles look very similar, as shown in Figure 40. In PA12/B + 20 wt.% Cu specimens, the difference in surface roughness was similar to 10% addition. No statistically significant differences in means roughness values (heteroscedastic *t-test*, $p < 0.01$) were found between samples made from different materials and similar materials made in the XY and YZ directions.

It must be noted that analysis of the top surfaces of rectangular samples showed a homogenous distribution of Cu particles and that they were randomly distributed in the samples (Figure 41).

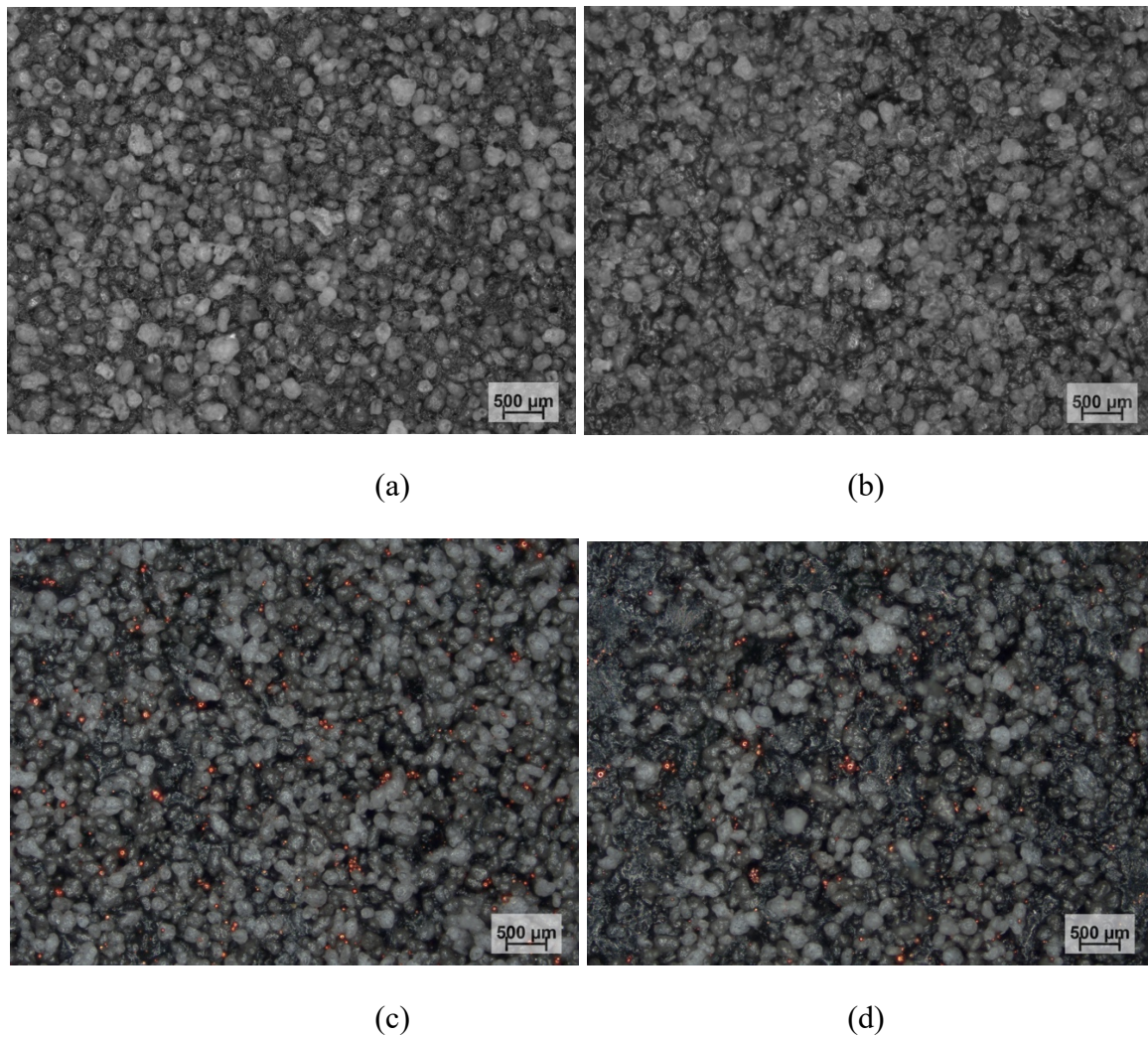


Figure 41. Top surface of samples built in the XY direction (a, c) and YZ direction (b,d) samples from PA12/B + 10 wt.% Cu (c,d) (image received by optical microscope). Cu particles are visible as bright spots in c) and d) photos.

4.2. Porosity

In L-PBF if the laser power and scanning speed are non-optimal for the chosen layer thickness, particles with a big diameter may not melt completely, creating lack of fusion porosity (Yadroitsev *et al.*, 2021, Dizon *et al.*, 2018a). An excess power density can lead to the keyhole mode porosity (Caulfield *et al.*, 2007). CT scans found no pores in PA12/B rectangular samples. From the observation of the micro-CT scan, the bright spots across the bed of the pure PA/B cubes result from small powder contamination (Figure 42a).

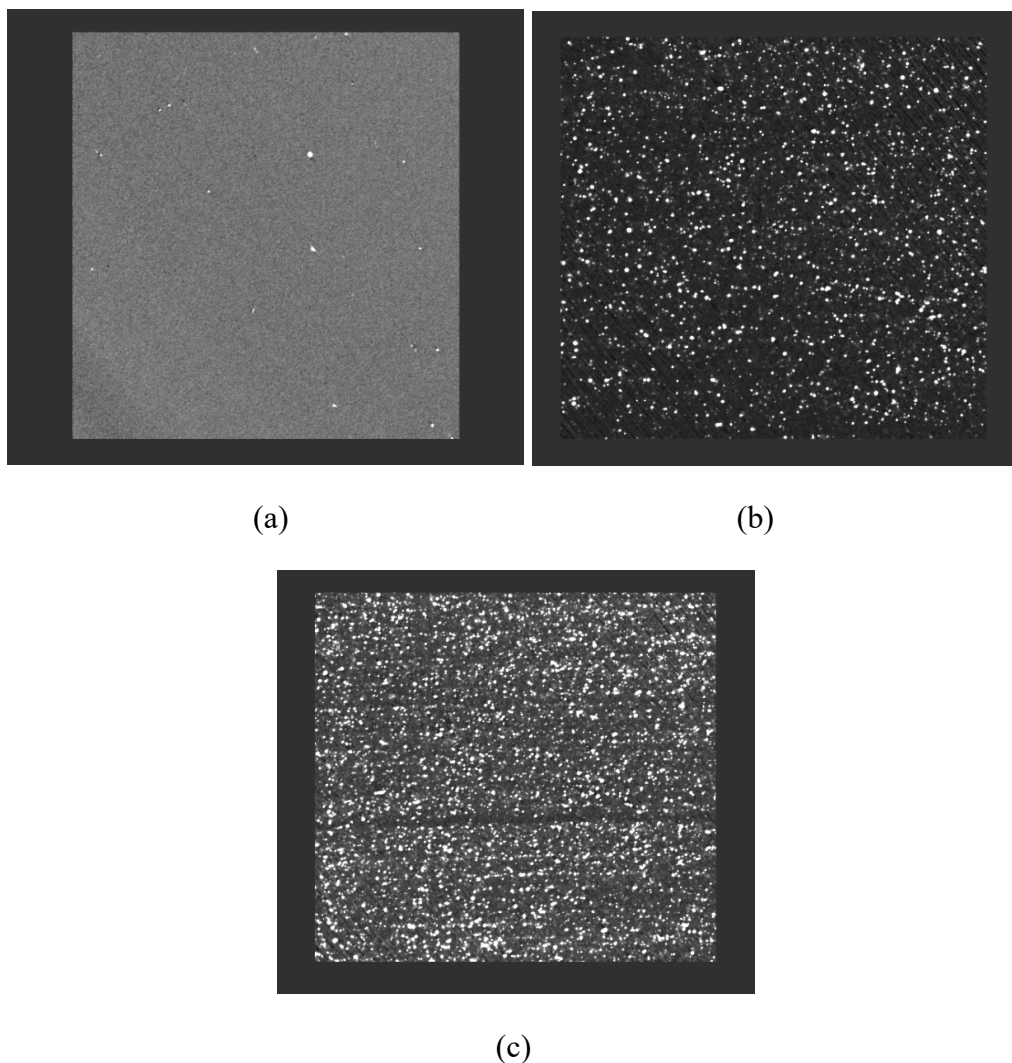


Figure 42. Micro-CT scan images of rectangular samples (a) PA12/B, (b) PA12/B + 10 wt.% Cu and (c) PA12/B + 20 wt. % Cu

A high density of PA12/B samples revealed by MicroCT scans was supported by cross-sectioning and microscopic analysis (Figure 43 c, d). In cross-sections of PA12/B samples, white particles were visible with an average size of about 40 μm , as seen using the digital Smart Zoom microscope. In comparison with the initial average size of particles of 60 μm , it is possible to assume that these residual particles were semi-sintered and were surrounded by melted areas.

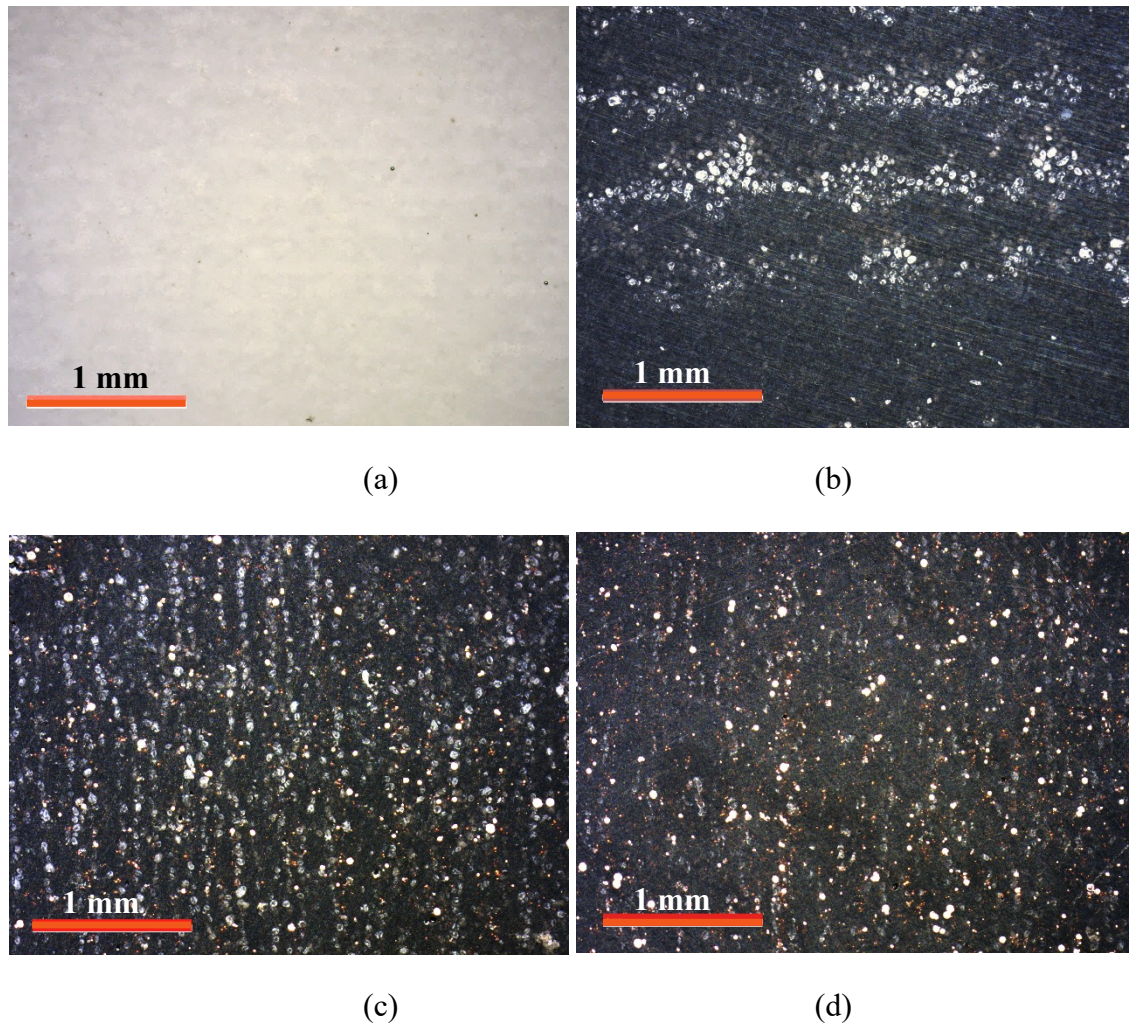
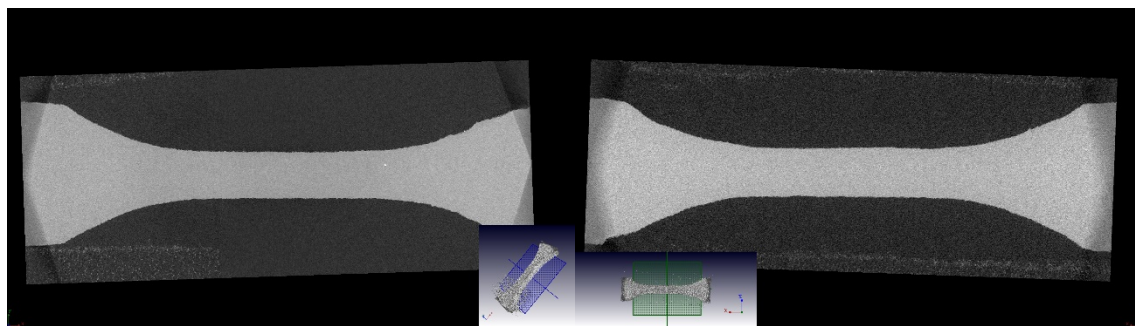
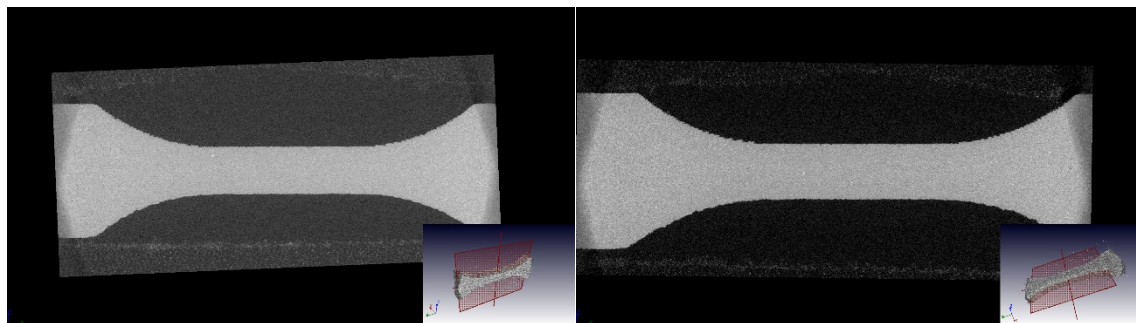


Figure 43. Cross-sections of samples: (a) PA2200, (b) PA12/B, (c) PA12/B + 10 wt.% Cu and (d) PA12/B + 20 wt.% Cu

No porosity was found by CT scans of the tensile samples made from PA12/B in different directions (Figure 44-Figure 45.)

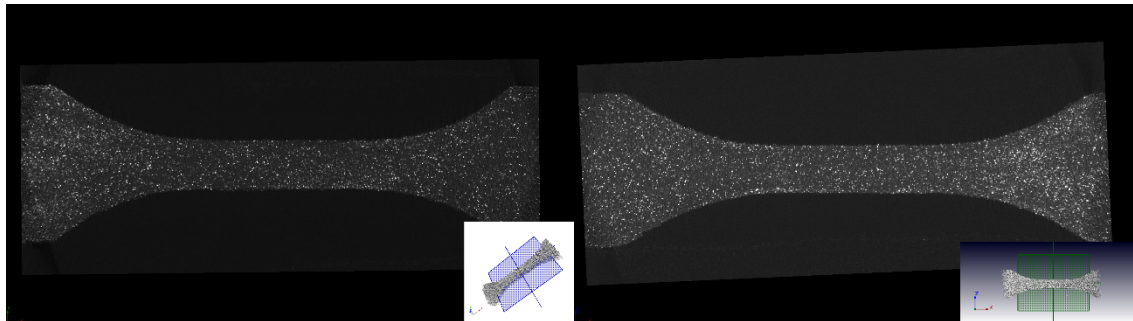


(a)

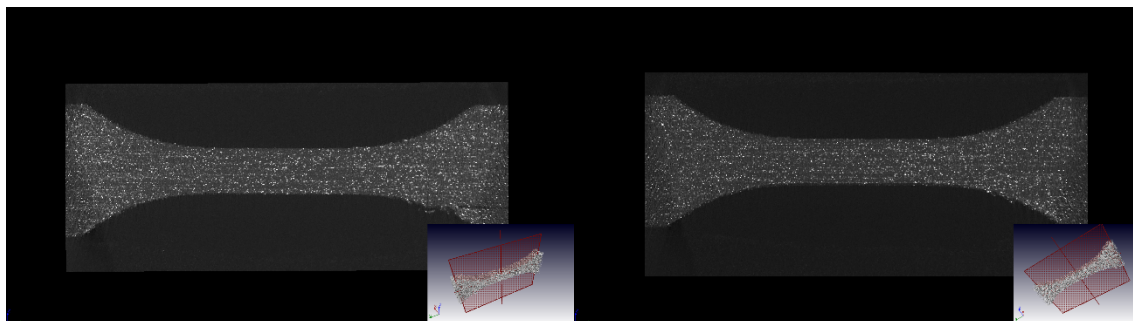


(b)

Figure 44. CT scan cross-sections of PA12/B samples manufactured in XY (a) and YZ directions (b)



(a)



(b)

Figure 45. CT scan cross-sections of PA12/B+10 wt.% Cu samples manufactured in XY (a) and YZ directions (b)

Figure 46 depicts the imperfection in dimensions for PA12/B samples grown in the YZ direction with 20%. Goodridge *et al.* (2012) looked at the inconsistency in dimensions and properties of SLS polymers, highlighting the effect of uneven temperature distribution in the building volume, as well as other process variables such as orientation, energy, layer thickness, and powder condition. The compression exerted by the recoating system on the top layer of the composite powder into the bottom layer may also influence the dimension imperfection in the YZ direction.

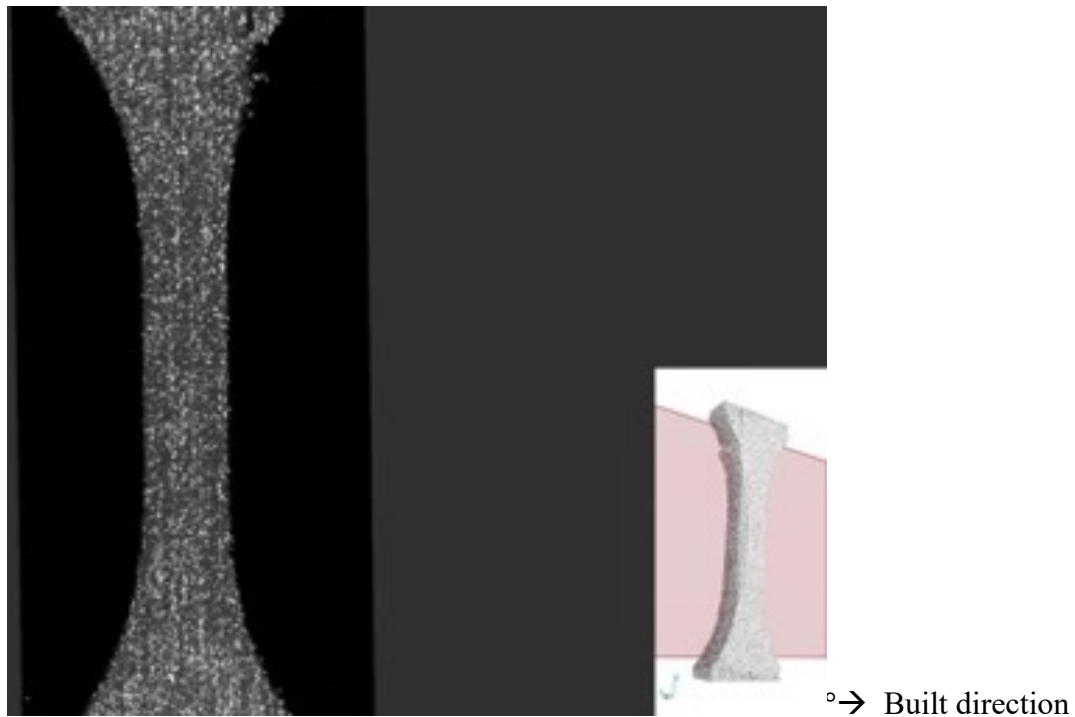
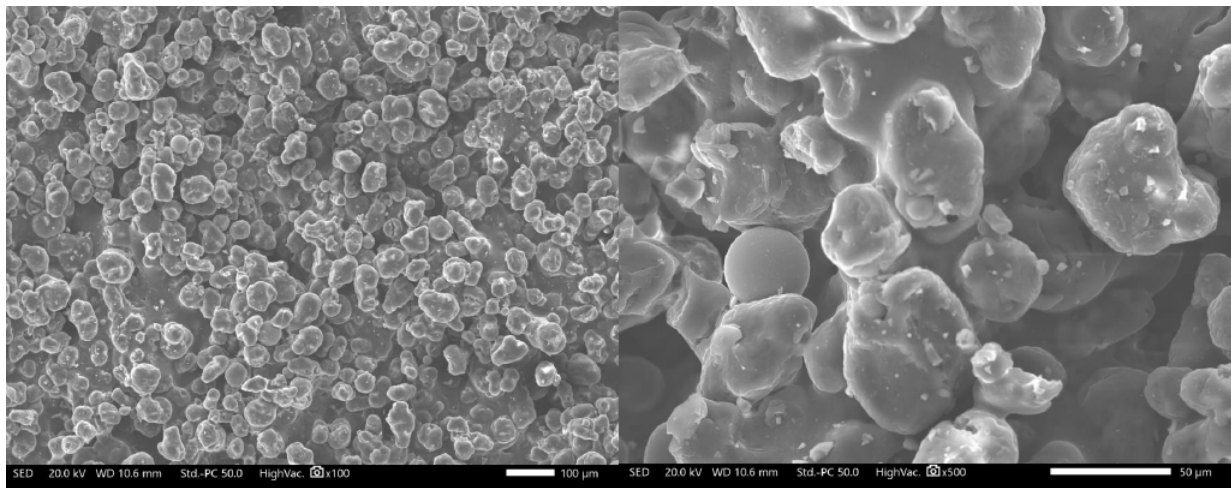


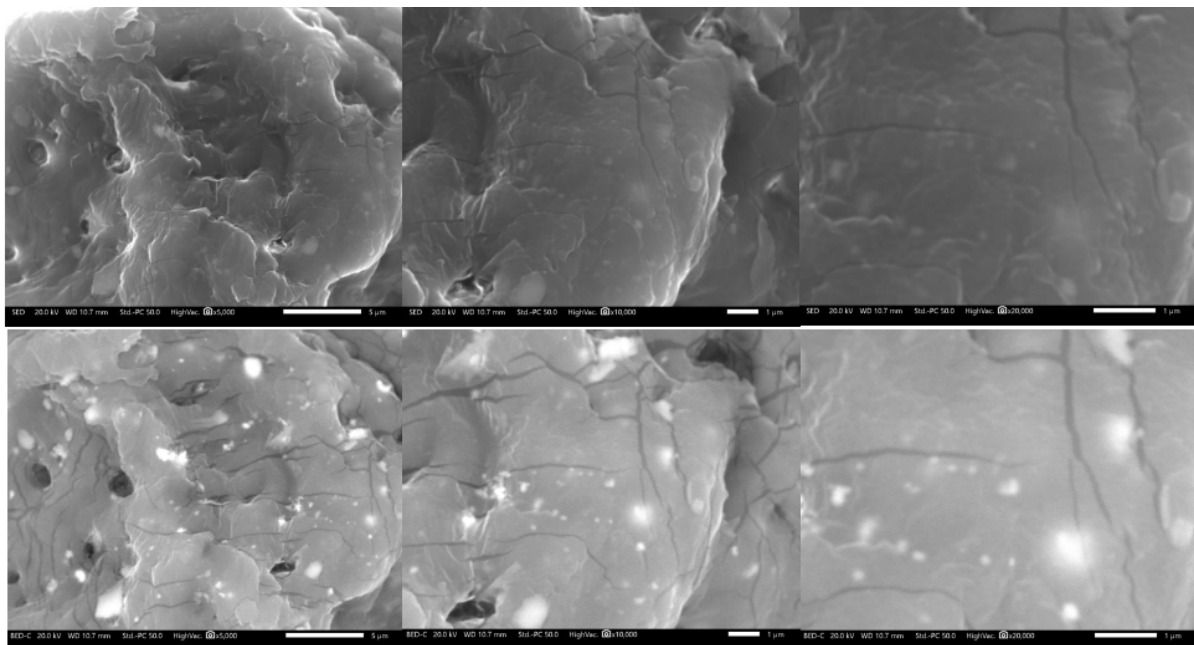
Figure 46. Tensile samples CT cross-sections for PA12/B with 20% in YZ directions.

4.3. Microstructure

Figure 47 shows the surfaces of the PA2200 SLS samples. At high magnifications, inclusions are spread in the interfaces. The morphology of virgin PA12 and used PA12 were compared by Dadbakhsh *et al.* (2017). The virgin PA12 has an aspherical shape and rough surfaces, and it was determined that the size of powders remained virtually unaltered after ageing, ranging from 55–60 μm on average, as illustrated in Figure 47.



(a)



(b)

Figure 47. SEM image of (a) PA2200 sample with details of surface morphology (b)

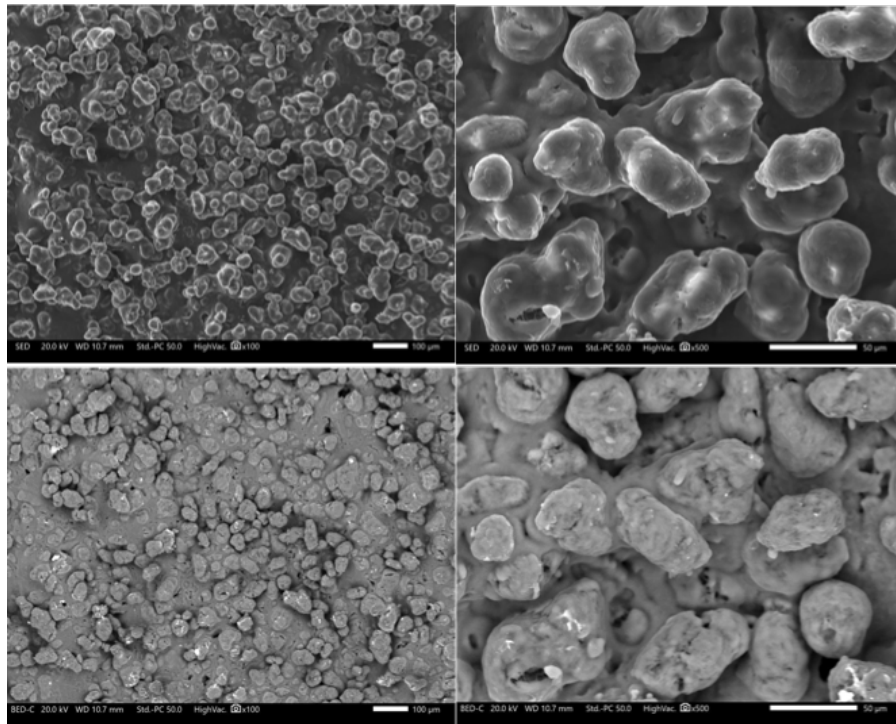
The aged powders, however, appear to have increased cracking after being stored at high temperatures (note that cracking can still exist in the virgin powder but to a much lesser extent). The source of these fractures is unknown. However, they could be caused by the evaporation of residual alcohol and absorbed moisture (originating from precipitation-solution production or external humidity) and/or following process cycle expansion/shrinkage stages. However, these morphological changes may obstruct the flow of the powders, worsening the SLS surface finish and causing an orange peel appearance. It is worth remembering that unmolten particles in the powders can have a big impact on melt flow, consolidation, and crystal formation and, therefore, on the SLS components' characteristics. During the SLS process, the powders are

sintered by laser in a short time, and the powder cools quickly from the melt. As a result, the molten particles harden quickly, leaving insufficient time to fill the gaps between them. Furthermore, Stoia *et al.* (2020) indicated that just a portion of the coalescence occurred, resulting in particle bonding in the form of small bridges in the PA2200 sample. The flowability of powder melts reduces as the recycling time increases, and the viscosity of the solution rises (Wudy *et al.*, 2014). The number of pores in specimens depend on these variables (Bourell *et al.*, 2000, Dupin *et al.*, 2012, Becker, 2016).

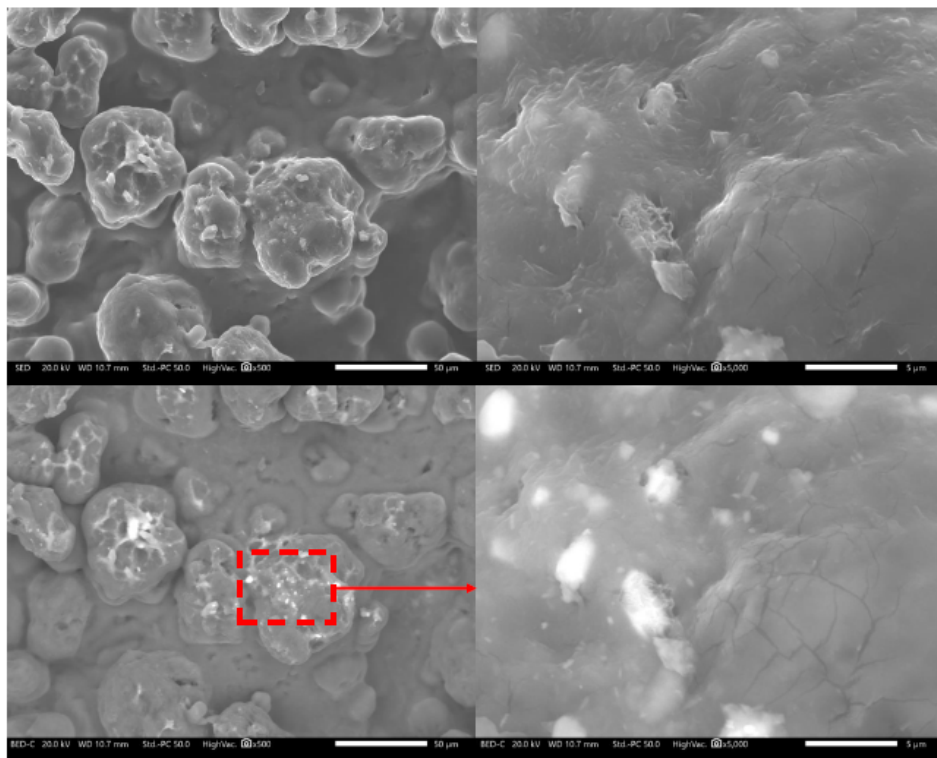
Sintratec PA12/B material appears to have similar geometry to the smaller size of inclusions of PA2200. Figure 47a is taken at 500 x magnification, and the morphologies of individual particles are visible at this magnification. At 10,000 and 20,000 x magnification, the differences in the surfaces of the particles are much more apparent (Figure 47b,c). At this magnification, the surface of the PA12/B appears to have rougher, slightly less uniform surfaces than PA2200. The PA12/B also has more irregular, less spherical particles attached to the SLS surface.

Figure 48 shows SEM images of the surfaces of the PA12/B samples. It shows a highly segregated structure in the PA12/B sample. It has microstructures comparable to those seen in sintered and compression moulded polymer–CB composites (Chan *et al.*, 1997, Yacubowicz *et al.*, 1990). Compared to a system with evenly dispersed CB, a highly segregated structure has less contact area between the polymer and the reinforcing agent. Furthermore, the absence of an external load during the SLS process, such as a shear force or compressive stress, is thought to result in carbon black aggregates with poor load transfer characteristics.

The SEM of the PA12/B + 10, 20 wt.% Cu shows that Cu particles were distributed preferentially on the surfaces of the polymer particles and formed round powder spots, which enhanced the homogeneous melting behaviour of the composite (Figure 49).

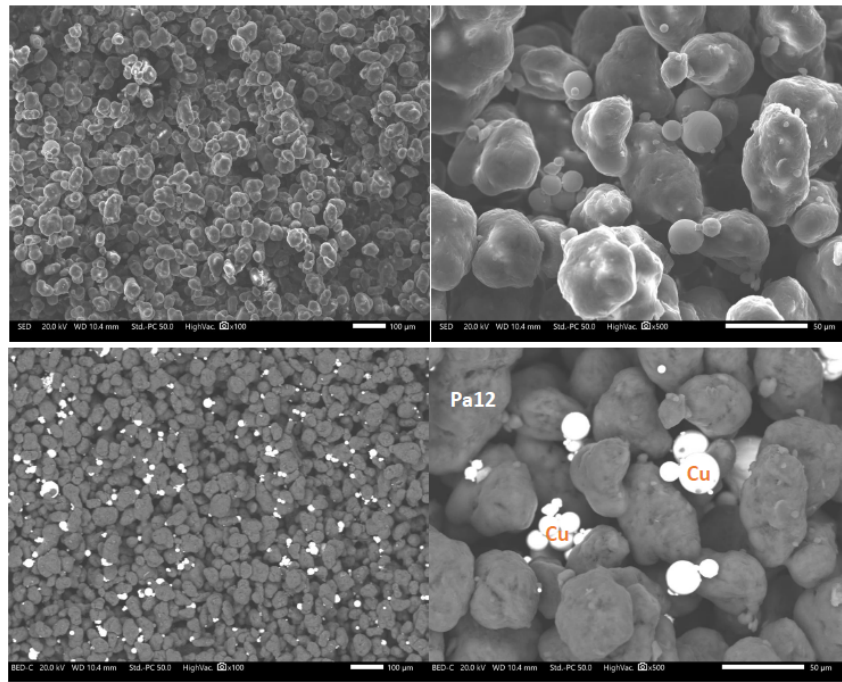


(a)

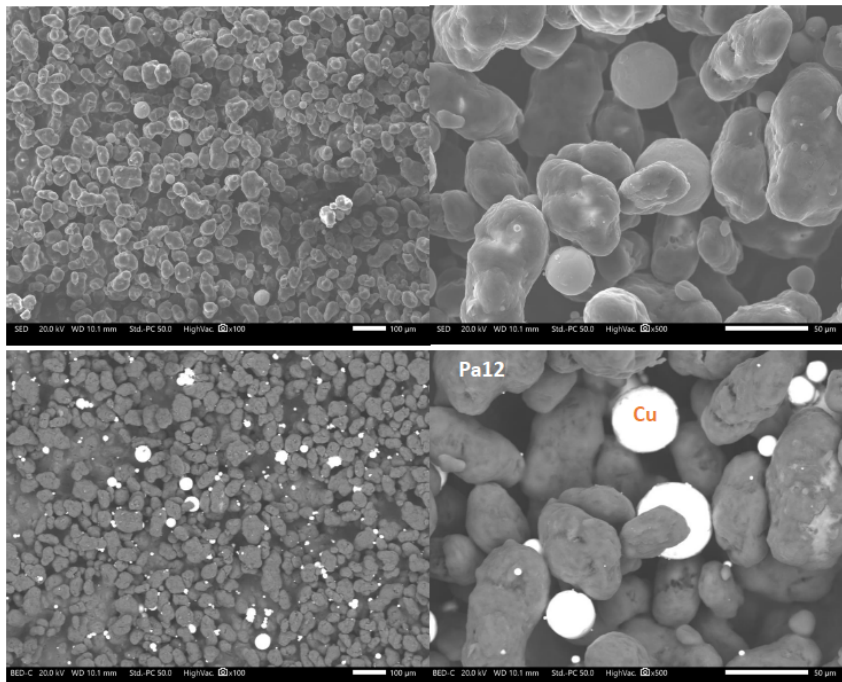


(b)

Figure 48. SEM image of PA12/B sample (a). Inhomogeneity is visible as white spots (b)



(a)



(b)

Figure 49. SEM image of (a) PA12/B + 10 wt.% Cu and (b) PA12/B + 20 wt.% Cu SLS surfaces

Figure 50 shows the XRD patterns of powders and sintered materials. The first peak at 2θ of 21.05° is associated with the γ crystal form, and the second peak at 2θ of 22.1° is associated with α crystal form of PA 12(Figure 50a).

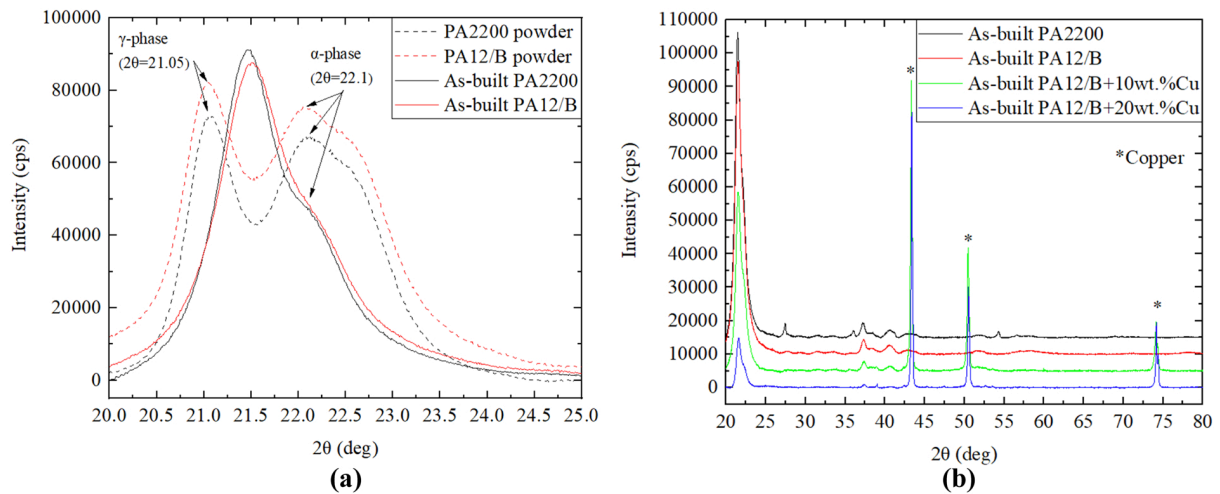
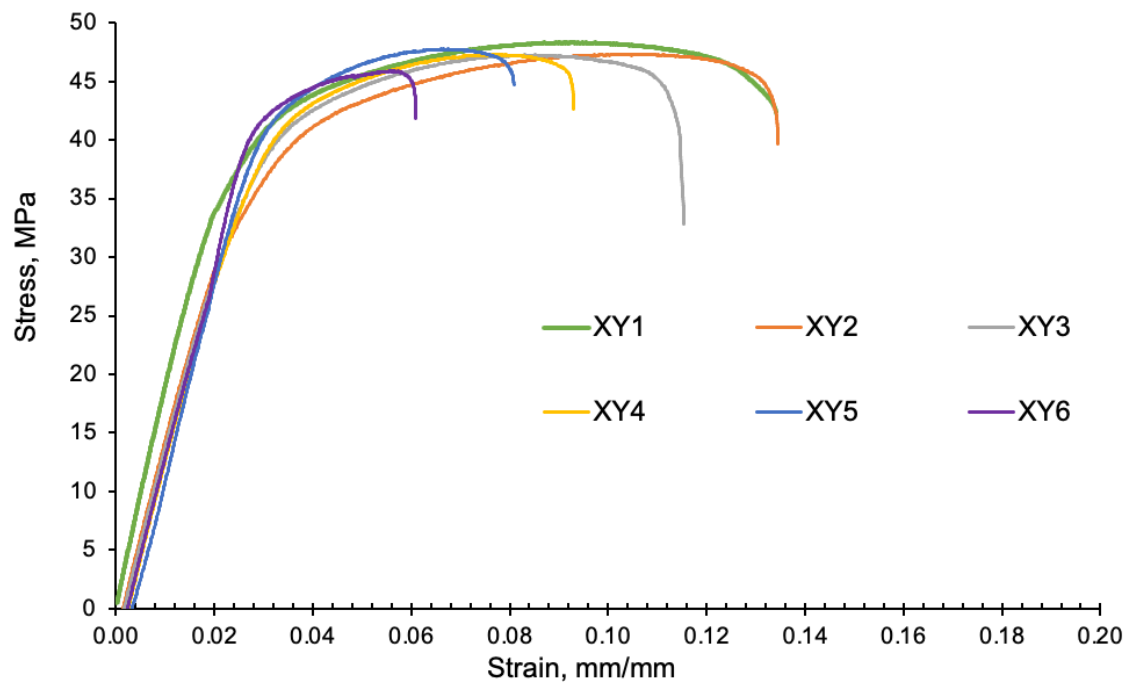


Figure 50. XRD patterns of PA2200, PA12/B powders and as-built SLS samples: high (a) and low magnification (b)

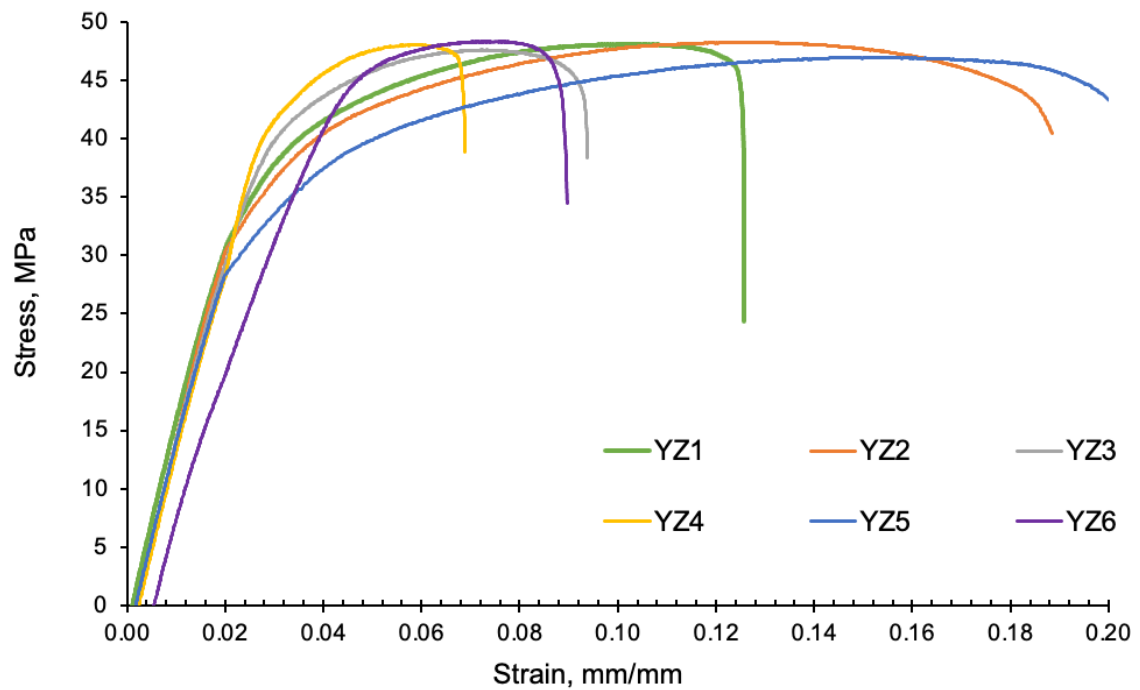
After SLS, the crystal structure of the samples changed due to the transformation of $\alpha \rightarrow \gamma$ when heated to the melting point. However, the α phase still exists in SLS samples. A full XRD pattern showed the presence of Cu, as expected for composite samples (Figure 50b).

4.4. Mechanical properties

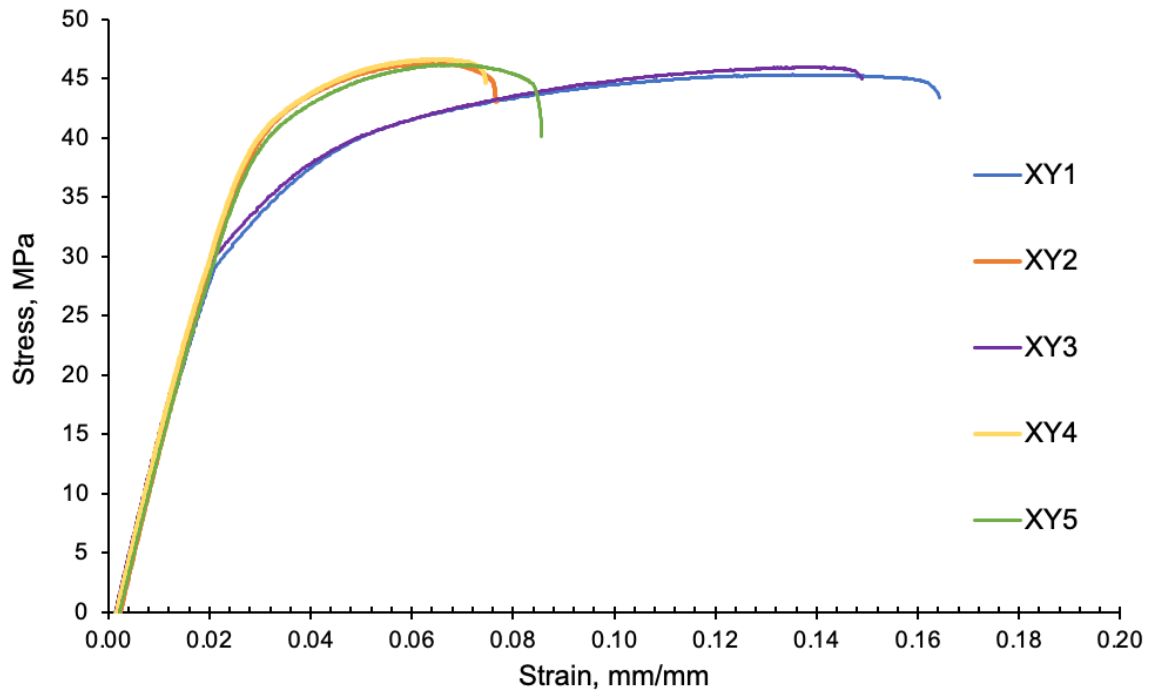
The tensile stress-strain curves of the as-built SLS samples are shown in Figure 51 and are summarized in Table 7. It was found that as-built samples had no statistically significant difference (*t-test*, $p < 0.05$) in yield strength, UTS, modulus of elasticity and elongation at break (Table 7). As shown in Figure 51, differences in mechanical properties of the XY specimens in each series were small; only coefficients of variation were about 30% in elongation. For samples built in the YZ direction, offset yield stress and elongation vary significantly (~30% and ~45%, correspondingly).



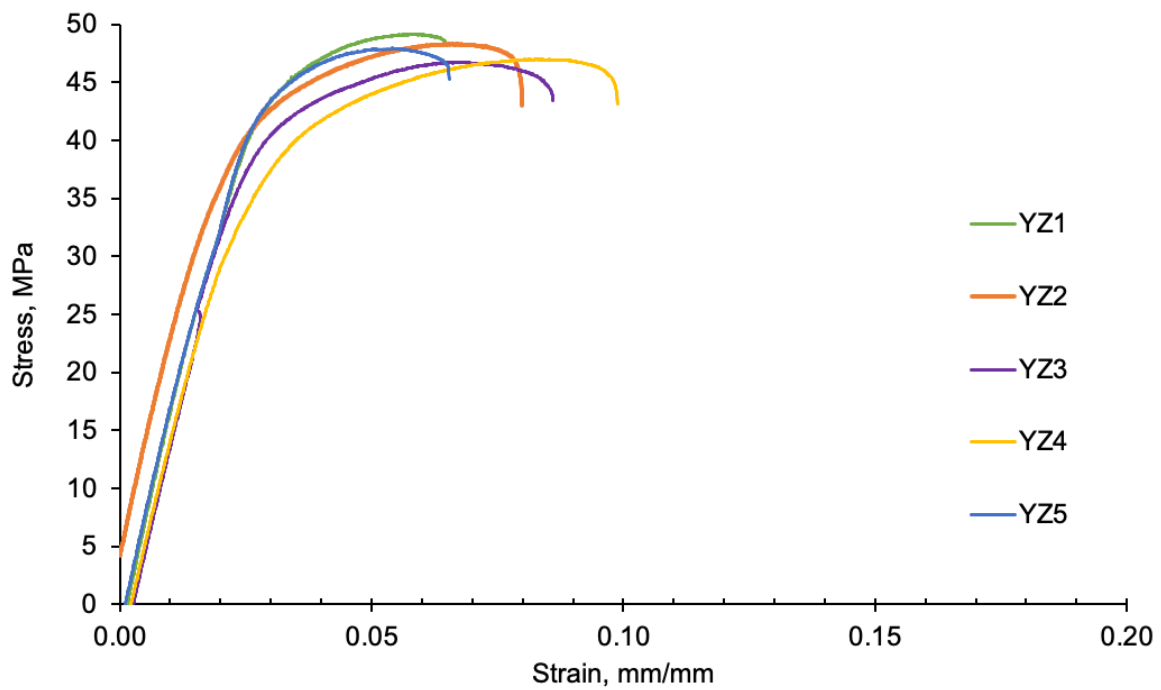
(a)



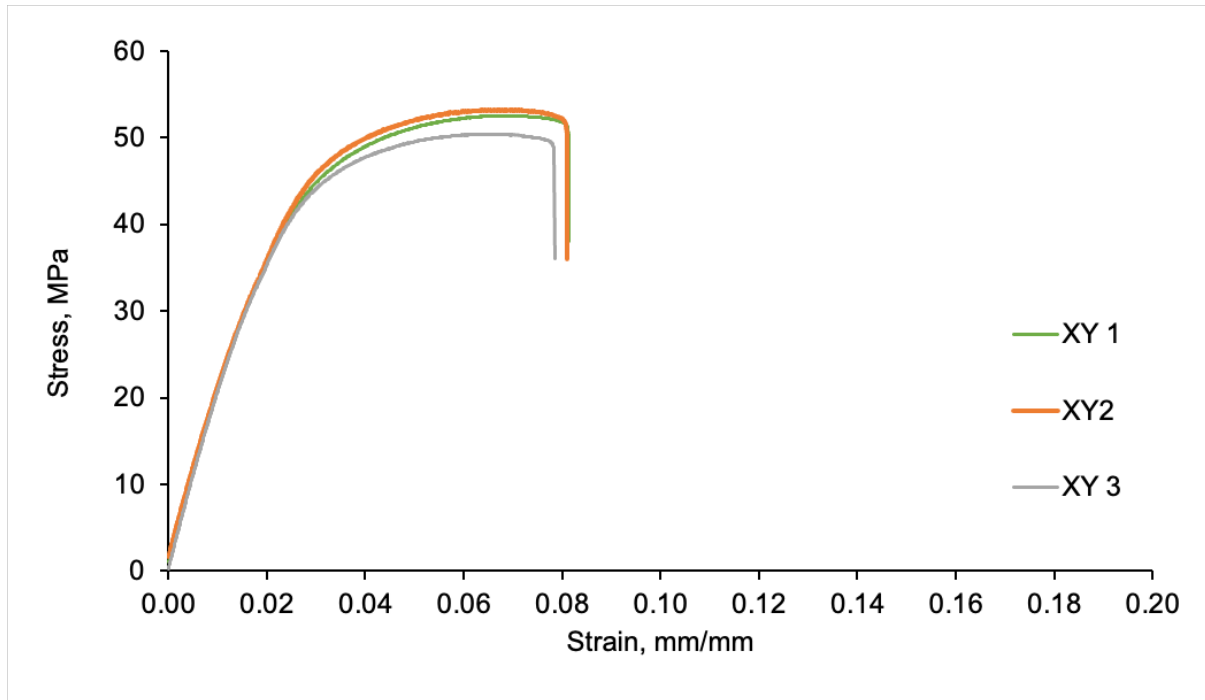
(b)



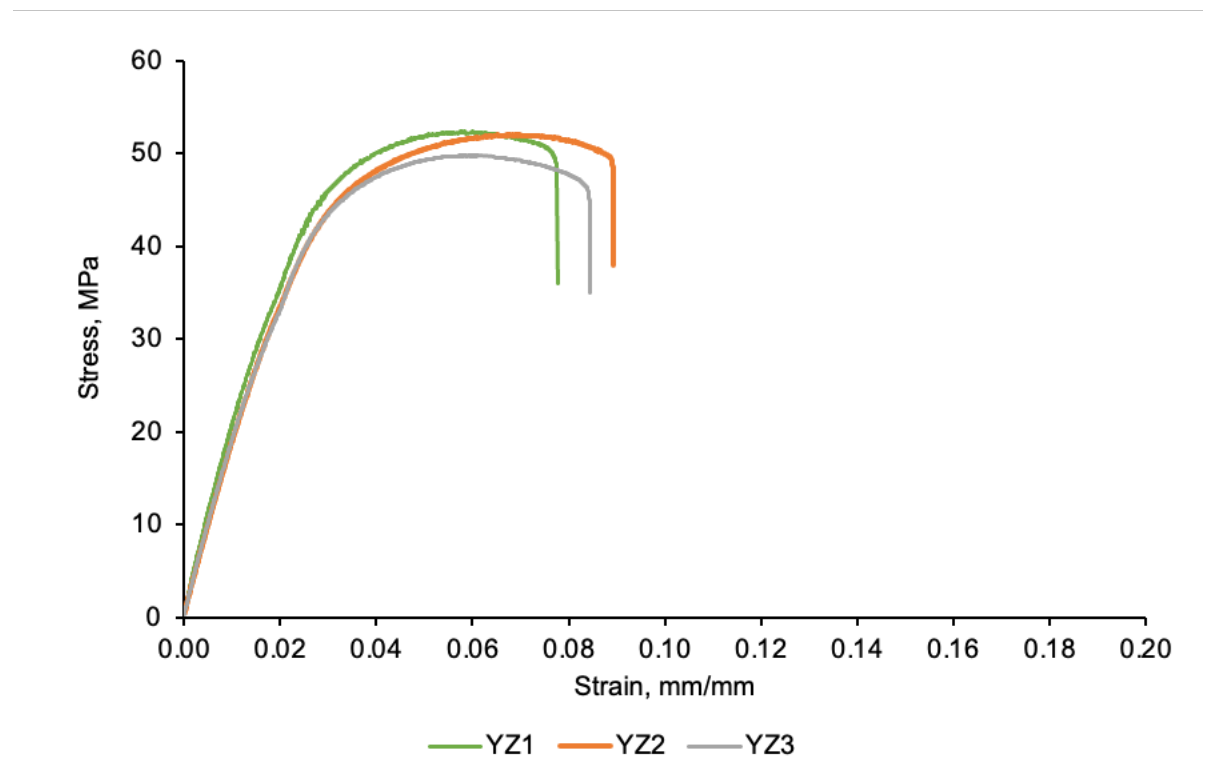
(c)



(d)



(e)



(f)

Figure 51. Stress–strain diagrams of PA12/B samples (a,b), PA12/B + 10 wt. % Cu samples (c,d) and PA12/B + 20 wt. % Cu samples (e,f) manufactured in XY (a,c,e) and YZ (b,d,f) directions

Table 7. Tensile properties of samples manufactured in different directions

Specimens		YTS (Offset 0.2 %), MPa	Elastic modulus, MPa	UTS, MPa	Elongation, %
PA2200	Set 1 (XY direction), N=5 Coefficient of variation	42 ± 2.4	1735 ± 69	48 ± 0.3	16.6 ± 0.9
		5.5%	4.0%	0.6%	5.5%
	Set 2 (YZ direction), N=5 Coefficient of variation	42 ± 1.0	1729 ± 27.8	47 ± 0.4	15.6 ± 2.5
		2.4%	1.6%	0.9%	16.3%
	Set 1 (XY direction), N=6 Coefficient of variation	39 ± 3.7	1772 ± 101	47 ± 1	10 ± 3.1 ^x
		9.4%	5.7%	1.7%	29.8%
PA12/B	Set 2 (YZ direction), N=6 Coefficient of variation	33 ± 4.2 ^x	1821 ± 57 ^x	48 ± 1	13 ± 5.7
		12.6%	1.1%	1.1%	44.9%
	Set 1 (XY direction), N=5 Coefficient of variation	31 ± 3.5 [#]	1795 ± 45	46 ± 0.5	11 ± 4.3
		11.4%	2.5%	1.1%	39.3%
	Set 2 (YZ direction), N=5 Coefficient of variation	33 ± 7.4	1967 ± 68 ^{*,#}	48 ± 1	8 ± 1.4
		22.6%	3.5%	2.0%	17.7%
PA12/B + 10 wt.% Cu	Set 1 (XY direction), N=3 Coefficient of variation	30 ± 0.6 [#]	2125 ± 48 ^{#,10}	52 ± 1.5	8.0 ± 0.2
		1.9%	2.3%	2.9%	2.4%
	Set 2 (YZ direction), N=3 Coefficient of variation	29 ± 1.0	2039 ± 133	51 ± 1.4	8.3 ± 0.6
		3.4%	6.5%	2.7%	6.9%
	Set 1 (XY direction), N=3 Coefficient of variation	30 ± 0.6 [#]	2125 ± 48 ^{#,10}	52 ± 1.5	8.0 ± 0.2
		1.9%	2.3%	2.9%	2.4%

t-test, $p < 0.01$;

^x statistically significant difference with the corresponding set of white PA2200 samples;

^{*} statistically significant difference with set 1 (XY);

[#] statistically significant difference with the corresponding set without Cu;

¹⁰ statistically significant difference with the corresponding set with 10 wt.% Cu

Samples were tested in a parallel direction of the SLS layer in both cases for sets XY and YZ. These results are close to the tensile results of PA12/B specimens with similar dimensions to the present work that Wang et al. (2015) received, where UTS was found at 49–51 MPa with elongation at break of 10–16%. Compared with PA2200 samples manufactured with the EOS

P396, Sintratec PA12/B samples showed a higher difference in elongation at break, lower YTS and higher elastic modulus. A change in the stress–strain response after the incorporation of the copper additive by Thokala *et al.* (2017) was observed where the elastic modulus increased at 1056.71 MPa (5 wt.% Cu) and 1110.98 (10 wt.% Cu), respectively.

The discrepancy in elongation at break is most likely due to the cooling time for SLS components, which might take several hours. According to Goodridge *et al.* (2012) and Zarringhalam *et al.* (2006), rapidly cooled sintered components have a greater elongation at break than slowly cooled sintered parts. Aside from a different elongation at break, it is crucial to understand that slower cooling (greater crystallinity) causes more shrinkage (Shi *et al.*, 2004). The adjacent sintered layers' bonding strength is less than that of other directions, according to Hofland *et al.*, 2017, and the specimen was fractured even before plastic deformation. As a result, the cycle times significantly impact the elongation at break of the SLS samples in the XY and YZ building directions.

For PA12/B +10 wt.% Cu, it was found that as-built samples had no statistically significant difference (*t-test*, $p < 0.05$) in yield strength, UTS, modulus of elasticity and elongation at break. Table 7 shows that differences in mechanical properties of XY specimens (set 1) were small; only coefficients of variation were about 30 % for elongation. For samples built in the YZ direction (set 2), offset yield stress varies significantly (~23%) and elongation of about 18%. A comparison of tensile properties of samples with 10 wt.% and without copper addition shows that only elongation on break was different; all other parameters were very similar. The maximum values obtained with PA12/B + 20 wt.% Cu of the samples built in the XY direction for UTS and modulus of elasticity was 52 MPa and 2129 MPa, respectively, and elongation at break was recorded at 8%, which is within the allowable range of laser-sintered PA12/B.

PA12/B was found to have a tensile strength between 43.1 and 47.8 MPa, a tensile modulus of 1610 MPa and an elongation of 8.9%. A comparison between the XY and YZ samples from PA12/B + 20 wt.% Cu with PA12/B, and PA12/B + 10 wt.% Cu showed that the 20% Cu addition material has a comparable strength, a significantly higher tensile modulus, and much lower but still in range of elongation at break for normal laser-sintered PA12/B.

The rise observed in the modulus is most likely caused by the Cu particles imposing constraints on the polymer matrix's gross deformability under mechanical loading. The amount of these constraints is determined largely by the formation of frictional forces at the polymer particle

interface, which grows as the Cu additive concentration increases. This led to solidified layers and therefore showed a higher UTS (51-52 MPa).

If polymer and a composite material are stretched to the same length, then the matrix itself (without the participation of a solid filler) should provide required deformation, and therefore it deforms more strongly than pure polymer (without filler) and the deformation of polymer matrix increases with the concentration of filler. Increased deformation of the matrix polymer leads to decrease in yield strength of PA12/B +Cu composite material.

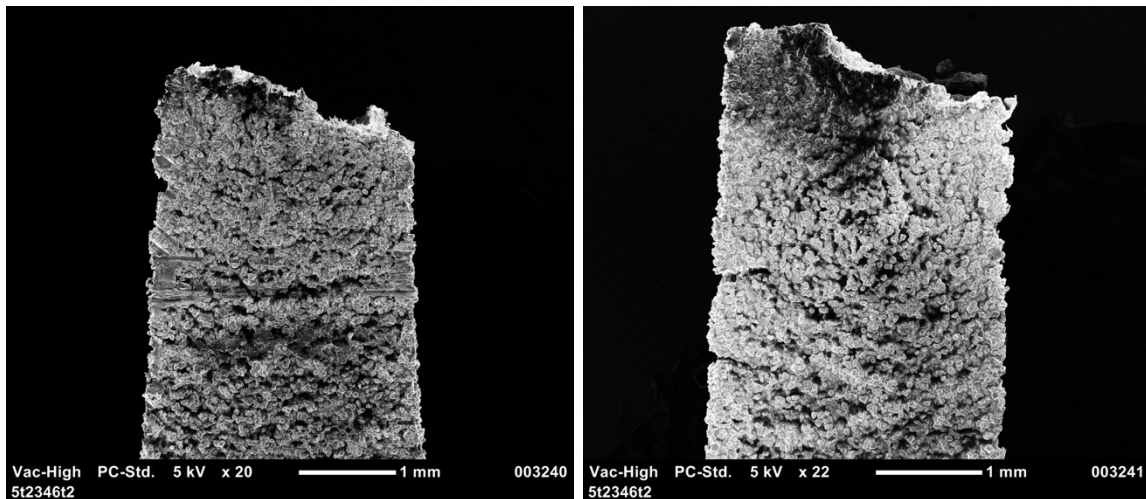
The decrease in elongation seen at break is largely due to the restricting effects on matrix flow produced by the interaction of neighbouring Cu particles. Also Cu addition can change thermal and optical properties of composite powder; the amount of unmolten and completely melted material in SLS samples can vary thus changing in mechanical properties can be more prominent with Cu addition.

4.5. Fracture analysis of PA12/B and PA12/B + 10, 20 wt.% Cu samples

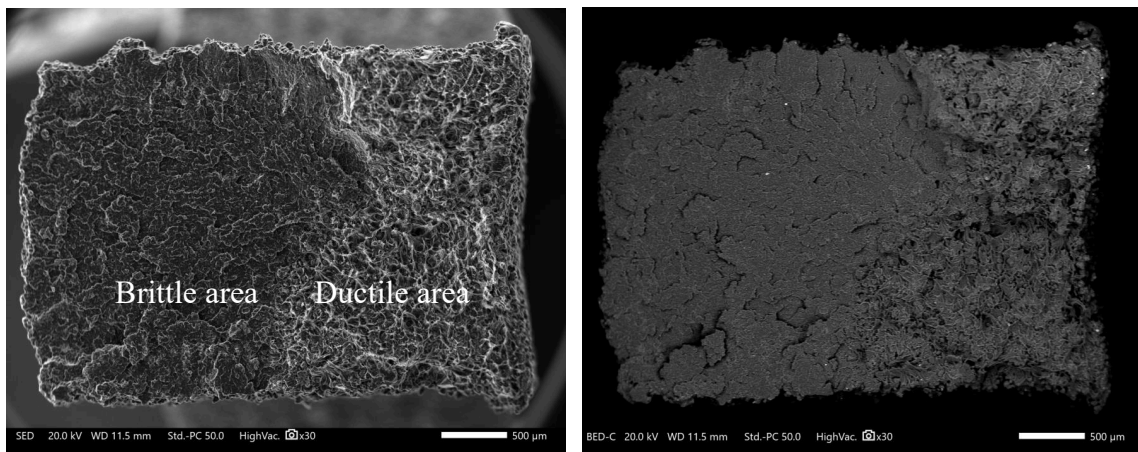
A tensile fracture demonstrated the complex brittle/ductile nature of the PA12/B specimens, as shown in Figure 52. Fairly flat surfaces indicate the brittle fracture mode of samples (see Figure 52a). However, elongated fibres and dimples on the fracture surface in Figure 52b and c in the core show complex ductile behaviour of this SLS material. Semi-sintered particles facilitated crack creation, and their fracture surfaces were flat (Figure 52c).

More layers in set 2 (YZ samples) increase the likelihood of defects, so big cracks were found in different areas of the gauge in Figure 53d, but fractures showed similar complex behaviour to set 1.

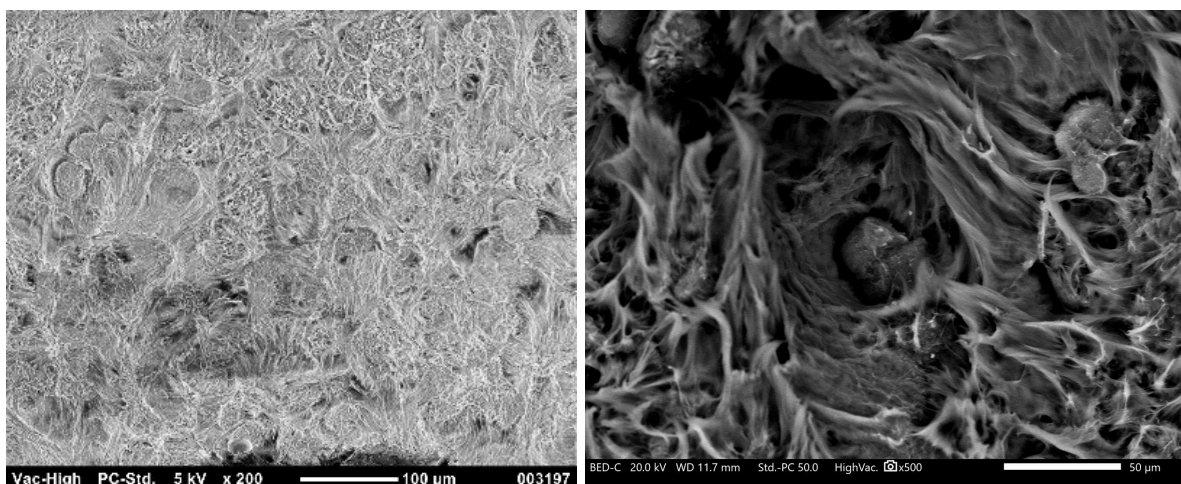
In Figures 54c and e, semi-sintered particles are clearly visible as isolated spheres with a diameter of about 40–50 μm . This can be a reason for the more brittle behaviour of the samples produced from PA12/B compared with PA2200 samples sintered by CO₂ laser that show 18% elongation. These semi-sintered particles act as stress concentrators and promote brittle fracture of PA12/B samples.



(a)



(b)



(c)

Figure 52. Typical fractures of PA12/B samples manufactured in the XY direction: side view of fracture (a), top view in SE (left) and BSE (right) modes of SEM (b); fibres and semi-sintered particles (c)

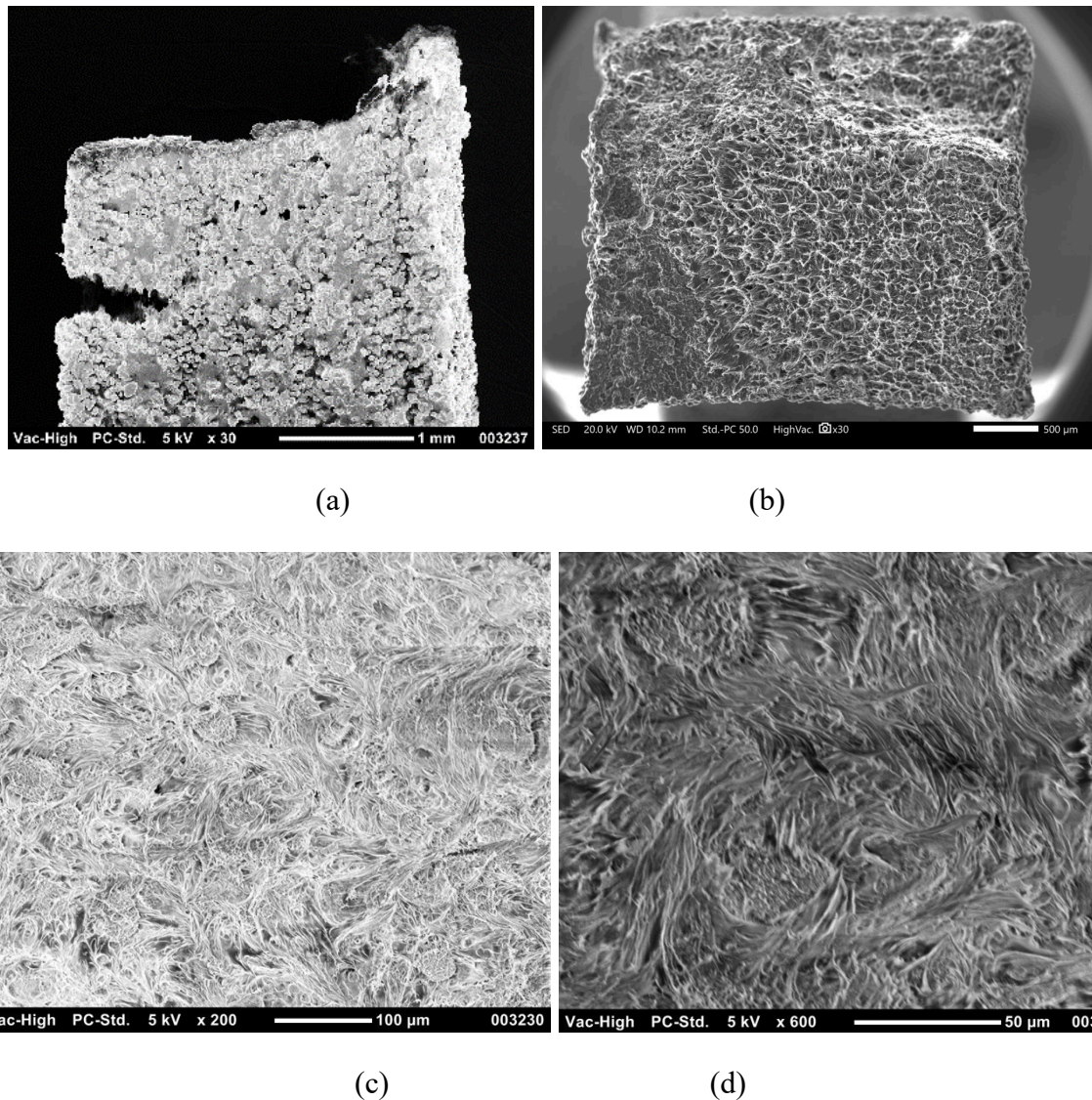
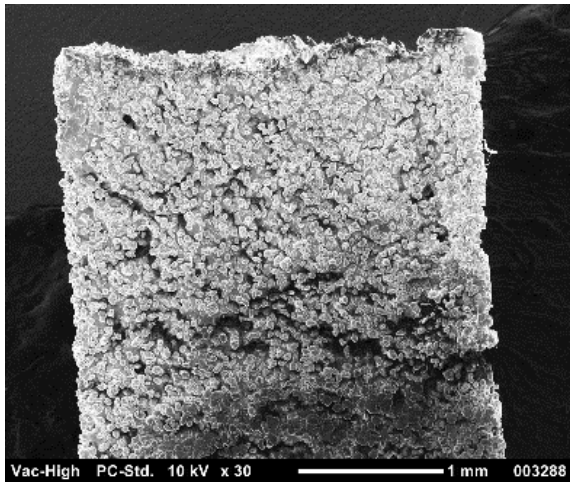
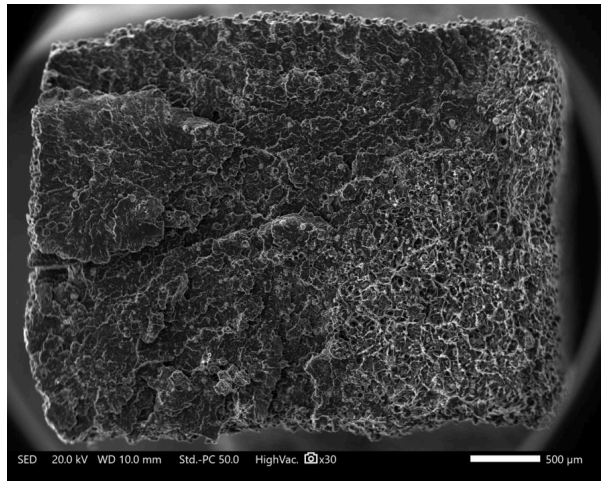


Figure 53. Typical fractures of PA12/B samples manufactured in the YZ direction

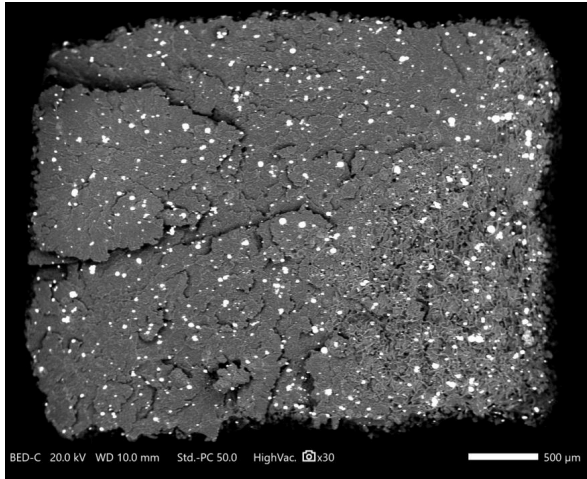
Figure 54 presents typical fractures of composite PA12/B + 10 wt.% Cu samples manufactured in the XY and YZ directions. These specimens had more brittle behaviour than the PA12/B samples, with lower elongation and more smooth areas of the fracture surface. Poor particle-matrix adhesion of big Cu particles can cause lower ductility of these samples. Cano *et al.* (2018) investigated the tensile properties of PA12 and PA12 filled with glass. Fracture tests were performed perpendicular and parallel to the layered structure. The fracture behaviour of the composite was unaffected by the orientation, similar to the present study, but fracture resistance of PA12 was higher than that of the composite due to the poor adhesion of the glass beads to the matrix. In the presented work, 10 wt.% Cu addition was not a decisive factor in the UTS and YS of composite samples.



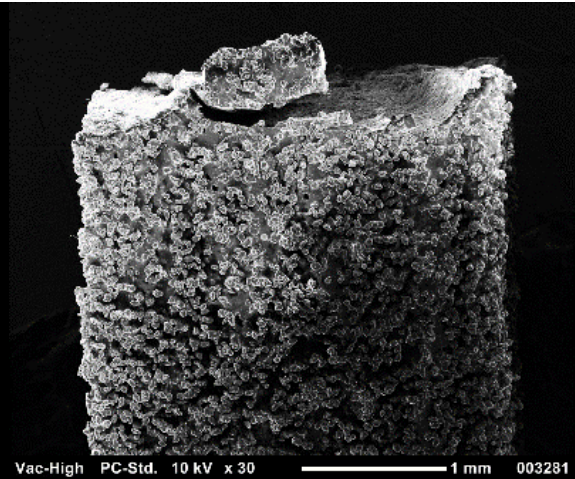
(a)



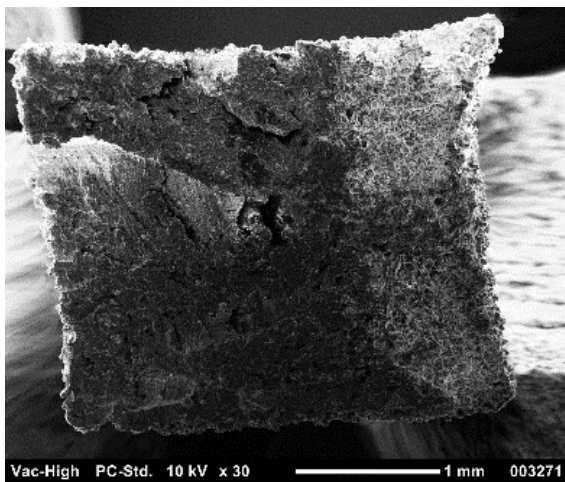
(b)



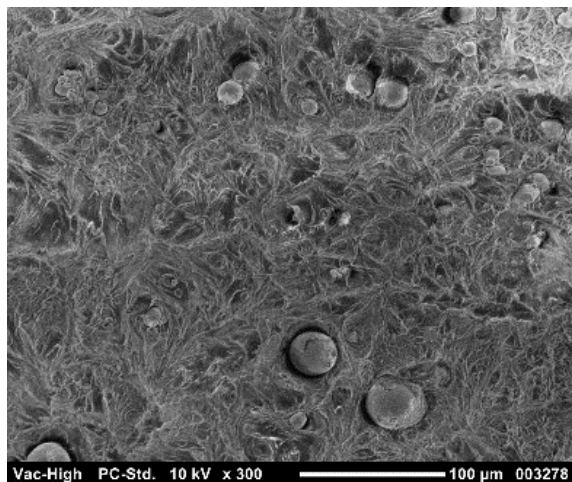
(c)



(d)



(e)



(f)

Figure 54. Typical fractures of PA12/B + 10 wt.% Cu samples manufactured in the XY (a,b,c) and YZ (d,e,f) directions. Round Cu particles are visible at high magnification in (c,f)

The fracture surfaces of the SLS samples produced with PA12/B + 20 wt.% Cu in the XY direction after tests are shown in Figure 55. There are a series of small dimples, but the cleavage fracture with a river pattern in (a), (b), (c) and (d) indicate the occurrence of more brittle behaviour of these samples under loading than in samples without Cu addition.

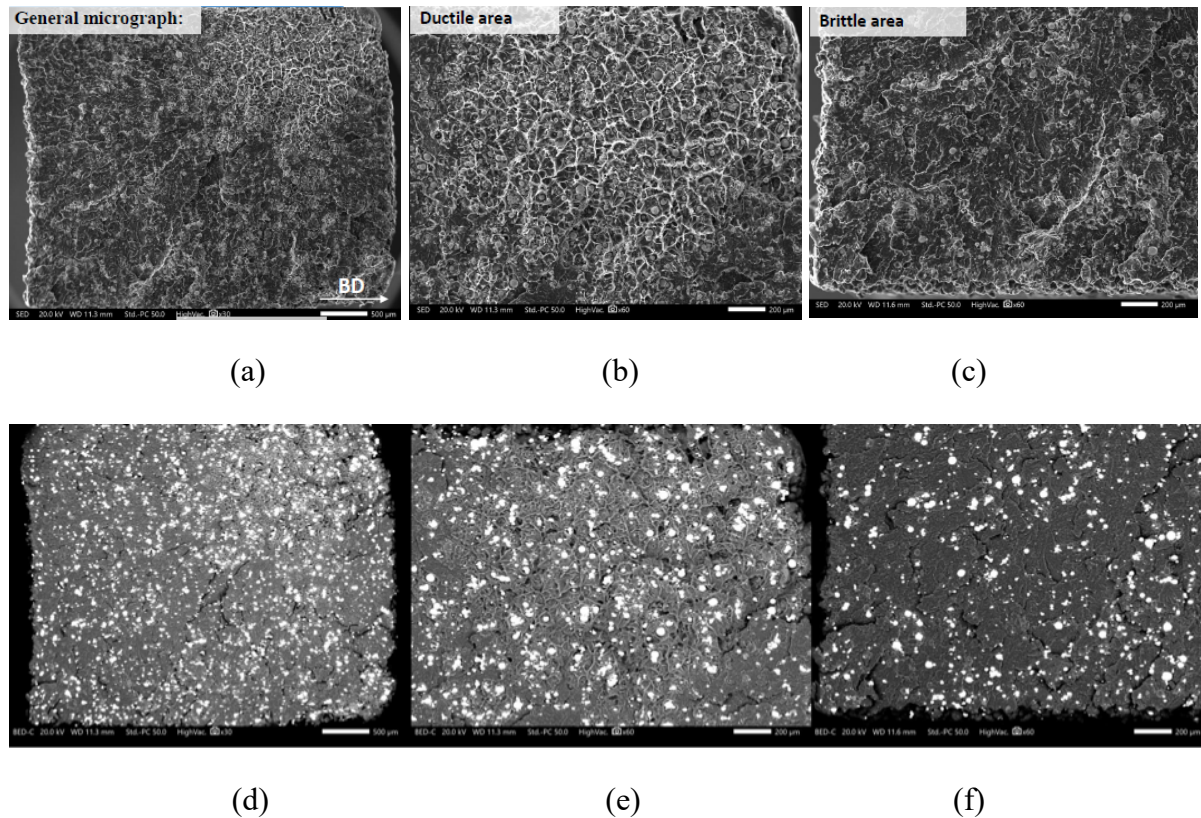


Figure 55. Typical fractures of PA12/B + 20 wt.% Cu samples manufactured in the XY (a,b,c) and YZ (d,e,f) directions. Round Cu particles are visible at high magnification in (c,f)

The fracture surfaces of the SLS samples produced with PA12/B + 20 wt.% Cu in the YZ direction after tests are depicted in Figure 56. The fracture surface characterization of SLS samples in the YZ direction is identical to that in the XY direction. Due to inadequate absorbed radiation energy and less plastic deformation, the fracture surface of the specimen in the YZ building direction contains more unmolten Cu powders and fewer split dimples than in the XY direction. The absorbed laser radiation energy of powders fluctuates in different directions throughout the SLS process. The powders absorb laser energy, causing them to melt and bond together. The upper and lower surfaces of the powder establish interaction with other powders owing to gravity and pressure, while the side surface has the potential to develop pores. It means that in set 2, Figure 56(c) and (e) ductility is observed and (e) and (f) brittleness is shown with a significant number of unmelted particles, and Cu round particles are visible in white.

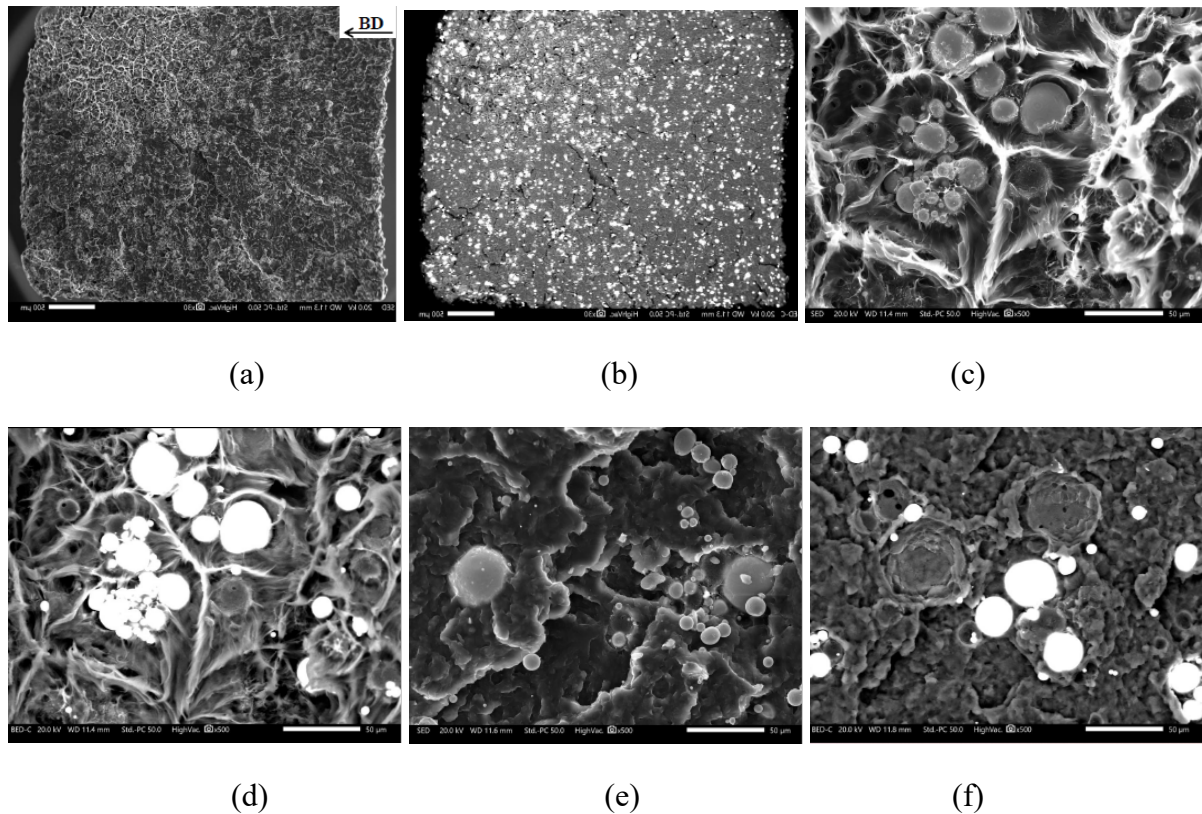


Figure 56. Typical fractures of PA12/B + 20 wt.% Cu samples manufactured in YZ (a,b,c) and (d,e,f) directions. Round Cu particles are visible at high magnification in (c,d,e,f)

The laser energy absorbed by the powder on upper and lower surfaces is smaller than that of the side surface. As a result, the molten powder is thinner, resulting in poor bonding strength along the building direction. Furthermore, when the laser energy declines from the top to the bottom of the powder layer, the bottom powders attached to the sintered layers become thinner. The strength of the powder upper and bottom interfaces is weaker than that of the powder side interface during tension with the load perpendicular to sintered layers (YZ direction), so unmolten powders in the fracture surface are easy to debone but difficult to pull out, resulting in much unmolten powder observed in Figure 56 (f).

4.6. Electrical conductivity analysis

Four probes were placed on each cube sample of the materials listed in Table 8. Connections were made with a constant current passing through the outer probes by connecting it to the constant current source of the set-up. The current was set to 8 mA (Table 8). There was no direct link of conductive material inside the matrix.

Table 8. EC results

Materials	Current, I (mA)	Voltage, V (mV)
PA2200	8 mA	0 mV
PA12/B	8 mA	0 mV
PA12/B+10 wt. %Cu	8 mA	0 mV
PA12/B+20 wt. %Cu	8 mA	0 mV

4.7. Antibacterial tests

PA2200, PA12/B, and composite samples did not show any inhibition haloes, despite Cu percentage by agar well cut diffusion method against *E. Coli* (Figure 57). Figure 58 shows optical density (OD) data from *E. Coli* after an incubation of 24 hours. No significant differences were observed between the two types of polyamides, PA2200 and PA12/B. However, a significant growth reduction was observed with the addition of 10 wt.% Cu compared to PA2200 and P12/B, and by adding 20% Cu when compared to PA2200. Results show that the increase in Cu led to a reduction in *E. Coli*.

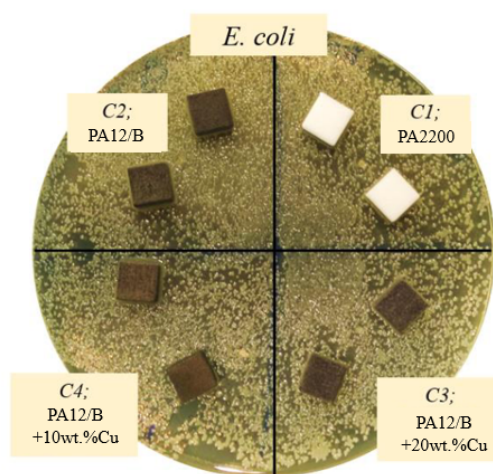


Figure 57. Agar well cut diffusion method against *E. Coli*

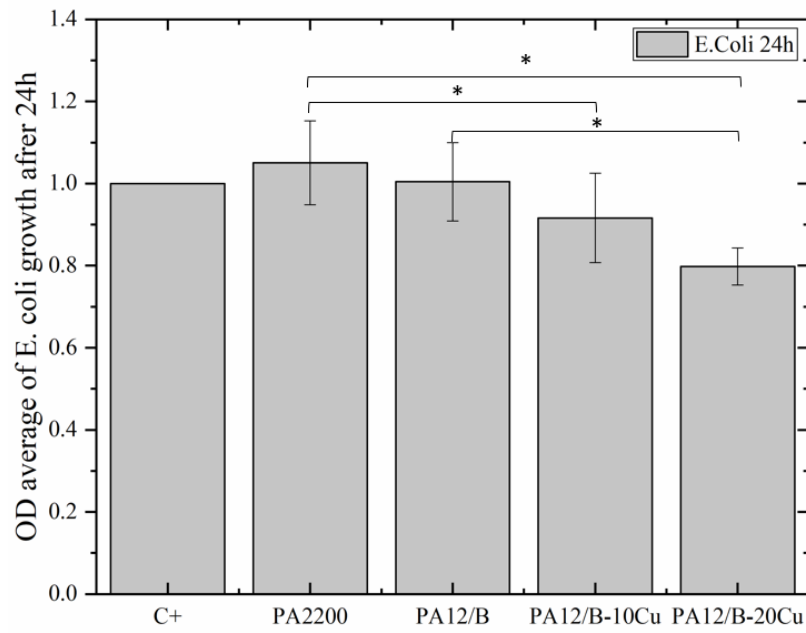


Figure 58. Graphic representation of the normalized absorbance average variation between the different sample conditions after 24 hours of E. Coli incubation (n=6) (p-value <0.05)

CHAPTER 5: CONCLUSIONS AND FUTURE RESEARCH

This work prepared, characterized, and presented PA12/B with Cu addition material for Sintratec S1 3D printing. PA12/B with Cu addition was created as a mixed composite. Mechanical, surface roughness, morphological, and antibacterial properties of samples were studied. It was demonstrated that in-situ modified PA12/B by Cu powder will hopefully be widely used in the future in various applications that requires antibacterial properties: filters, medical devices, hospital/public goods. While any processability difficulties were noted and discussed, the advantages of 3D printing may be used in applications that require these standards. It was found that:

- The in-situ modified samples of PA12/B with 10 and 20 wt.% Cu were pore-free. Cu particles were evenly distributed in the polymer matrix.
- Yield strength, ultimate tensile strength (UTS), elastic modulus, and elongation at break were all comparable between PA2200 and PA12/B. However, larger anisotropy and standard deviations were found in PA12/B samples, likely owing to processing by different systems as well as Sintratec powder inhomogeneity and the modification agent, which causes changes in the material's absorptivity, resulting in semi-sintered areas in solid material.
- An adding Cu particles (10 wt.% and 20 wt.%) to PA12/B resulted in an increase in elastic modulus but a loss in yield strength and elongation at break. The results showed that PA12/B + 20 wt.% Cu samples had the greatest elastic modulus, UTS and the lowest elongation at break.
- Fractography showed a lower ductility in YZ PA12/B composite samples than XY samples, indicating that scaffoldings or fine SLS parts from this material could preferably be manufactured in the XY direction.
- A reason for the appearance of semi-sintered areas that was found by fracture analysis, can be the inhomogeneity of the chemical composition of the initial PA12/B particles.
- Introducing Cu into the polymer matrix might improve antibacterial capabilities of material. First antibacterial assays show a significant reduction of *E. Coli* with the addition of 10% and 20% Cu after the 24-hour incubation compared to pure PA2200 samples. The addition of 20% Cu decreased significantly *E. Coli* growth in comparison with PA12/B. Thus, these materials can be used as a self-sanitizing component as infection control strategies in healthcare facilities. Further assays are recommended to

be performed with gram-positive bacteria (e.g. *S. Aureus*) to see its behaviour with the addition of Cu and at other time intervals, such as 48 hours, to see the trend of bacteria reduction.

From the point of view of non-porosity and mechanical properties, the addition of 10-20% copper seems to be optimal for this polymer. The antibacterial properties of the composite also inspire optimism, but it is possible to continue research with a higher concentration of copper powder. Optimization of copper concentration should be carried out taking into account the use of the final SLS product. Recommended future work includes studies on correlation of surface roughness with mechanical and antibacterial properties as well as investigating whether there are new developments in commercializing antibacterial materials. The results will demonstrate the potential of SLS technology for producing parts made of polyamide/copper with antimicrobial properties that can be used in the future for medical purposes that improve patients' lives.

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