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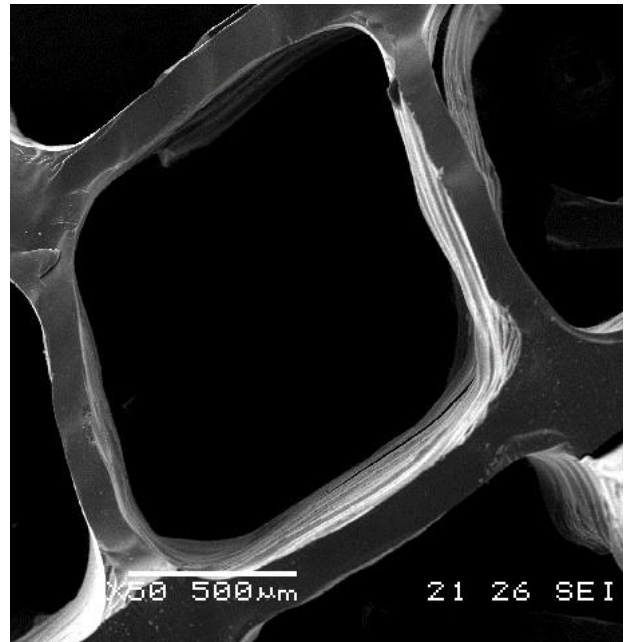
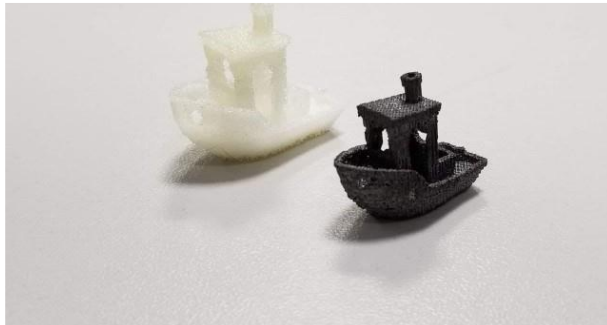
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Ceramic Si-C-N-O cellular structures by integrating Fused Filament Fabrication 3-D printing with Polymer Derived Ceramics

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June 2022

CERAMIC Si-C-N-O CELLULAR STRUCTURES BY INTEGRATING FUSED FILAMENT FABRICATION 3-D PRINTING WITH POLYMER DERIVED CERAMICS

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Abstract

Ceramic additive manufacturing is gaining popularity with methods like selective laser sintering (SLS), binder jetting, direct ink writing and stereolithography, despite their disadvantages. Laser sintering and binder jetting are too expensive, while direct ink writing lacks resolution and stereolithography lacks scalability.

The project aims to combine one of the most versatile, affordable, and readily available 3D printing methods: fused filament fabrication (FFF) with polymer derived ceramics to produce cellular ceramics to overcome the disadvantages posed by the other methods. The process uses a two-step approach. The first step is to 3D print the part using a polymer FFF 3D printer with a thermoplastic polyurethane filament and the second step is to impregnate the part in a polysilazane preceramic polymer and then pyrolyze it in an inert environment up to 1200°C. The resulting product is a high-resolution cellular ceramic of the composition SiOC(N).

This type of cellular ceramic can find an application in several fields such as scaffolds for bone tissue regeneration, liquid metal filtering, chemical and gas filtering, catalytic converters and electric applications. The process can provide an affordable alternative to the products used in these fields currently.

Research motivation

Ceramic materials have been in use for 20,000 years to make statues and utensils. Ceramics possess excellent properties such as high temperature resistance, chemical resistance, high mechanical strength, and many more. These can be used for many applications from ceramic pots to resistors in an electric circuit. Ceramics can find use in almost all applications.

With the advent of 3D printing, components that were extremely difficult to manufacture with the traditional methods, can be manufactured very easily. The time from designing a product to having a finished product is exponentially cut down. With this approach, ceramics can also be 3D printed with exceptional accuracy using wide variety of materials. But 3D printing of ceramics remains expensive and out of reach.

Meanwhile, 3D printing of polymers using filaments has reached to a household level, where you can purchase a 3D printer for a couple of hundred dollars. This can be attributed to the open-source hardware movement. Hobbyists, scientists, engineers, doctors, and teachers are able to produce polymer parts quickly at minimal costs.

The goal of this research is to combine the advantages of open-source 3D printing with ceramic materials, to make the fabrication of ceramic components more accessible and affordable. The research uses a special class of polymers which have a silicon backbone called as “preceramic polymers” as a starting material. These polymers when thermally treated convert into a ceramic material. Combining this with the open-source 3D printing, substantially brings down the cost of manufacturing complex ceramic components.

The aim of the research is to produce high quality ceramic components at an affordable price using 3D printing and preceramic polymers. These ceramics can find applications in fields such as scaffolds for bone regeneration, metal filtration, catalytic converters and many more.

Organization of the Thesis

The thesis is divided into four chapters.

The first one offers an introduction to polymer derived ceramics, additive manufacturing of ceramics, RepRap and open-source 3D printing, and implants for bone regeneration.

The second chapter describes the novel approach to fabricate multi-level porous structures by coating 3D printed polymer structures with polysiloxane preceramic polymer. This approach was used to test the effect of different 3D printing polymers on the final ceramic.

The third chapter utilized the replica method to impregnate 3D printed thermoplastic polyurethane cellular structures with polysilazane preceramic polymer to obtain a ceramic cellular structure with defect free, fully dense struts. The ceramic components produced with this method are also tested for their mechanical and thermal resistance.

The fourth chapter tests the produced ceramic scaffolds for the use of bone tissue regeneration. The scaffolds are subjected to multiple tests which analyze the viability of the material and the structure as an implant material. The tests include cytotoxicity of the material, adhesion of the cells on the scaffolds, proliferation of the cell on the scaffolds and differentiation of the stem cells to the bone cells on the scaffolds with the material and pore stimuli.

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Chapter 1

Introduction

1.1 Polymer Derived Ceramics (PDCs)

The first use of silicon-based polymer derived ceramics was reported in the 70s to produce ceramic fibres for high temperature applications made from polysilazane, polysiloxanes and polycarbosilanes [1]–[3]. Subsequently researchers were able to develop more techniques and make progress in the production of ceramics by the PDC route [4]–[6]. Since then, the technology has come a long way and is now used to produce complex ceramic components, such as SiC fibres [6], which cannot be produced otherwise by traditional manufacturing methods [7].

Preceramic polymers are inorganic polymers which when processed with an appropriate thermal treatment; curing and pyrolysis under inert atmosphere, produce ceramics with a suitable chemical composition. Preceramic polymers are predominantly organosilicon polymers, meaning they possess Si-Si/X- backbone chain.

Polymer derived ceramics exhibit excellent thermal and mechanical properties. The ceramics are resistant to creep and high temperature oxidation as well as crystallization and phase separation up to temperatures as high as 1900°C [8], [9]. Moreover, the processing temperature of such ceramics is substantially low (800- 1000°C). Since the ceramics are obtained from the polymers and not powders, fully dense materials can be obtained at lower temperatures. For examples, fully dense amorphous SiCN via PDC route can be produced at 1200°C, whereas

with the traditional sintering route a ternary ceramic such as SiCN cannot be produced and to have a fully dense Si₃N₄/SiC composites the maximum temperature must be raised above 1700°C. Even to produce Si₃N₄ or SiC, the sintering temperatures reach as high as 1700-2000°C [10].

Because of these advantages, polymer derived ceramics are considered for various applications ranging from high temperature structural applications to advance ceramics such as biomedical, anodes in lithium-ion batteries, electronic micro/nano devices.

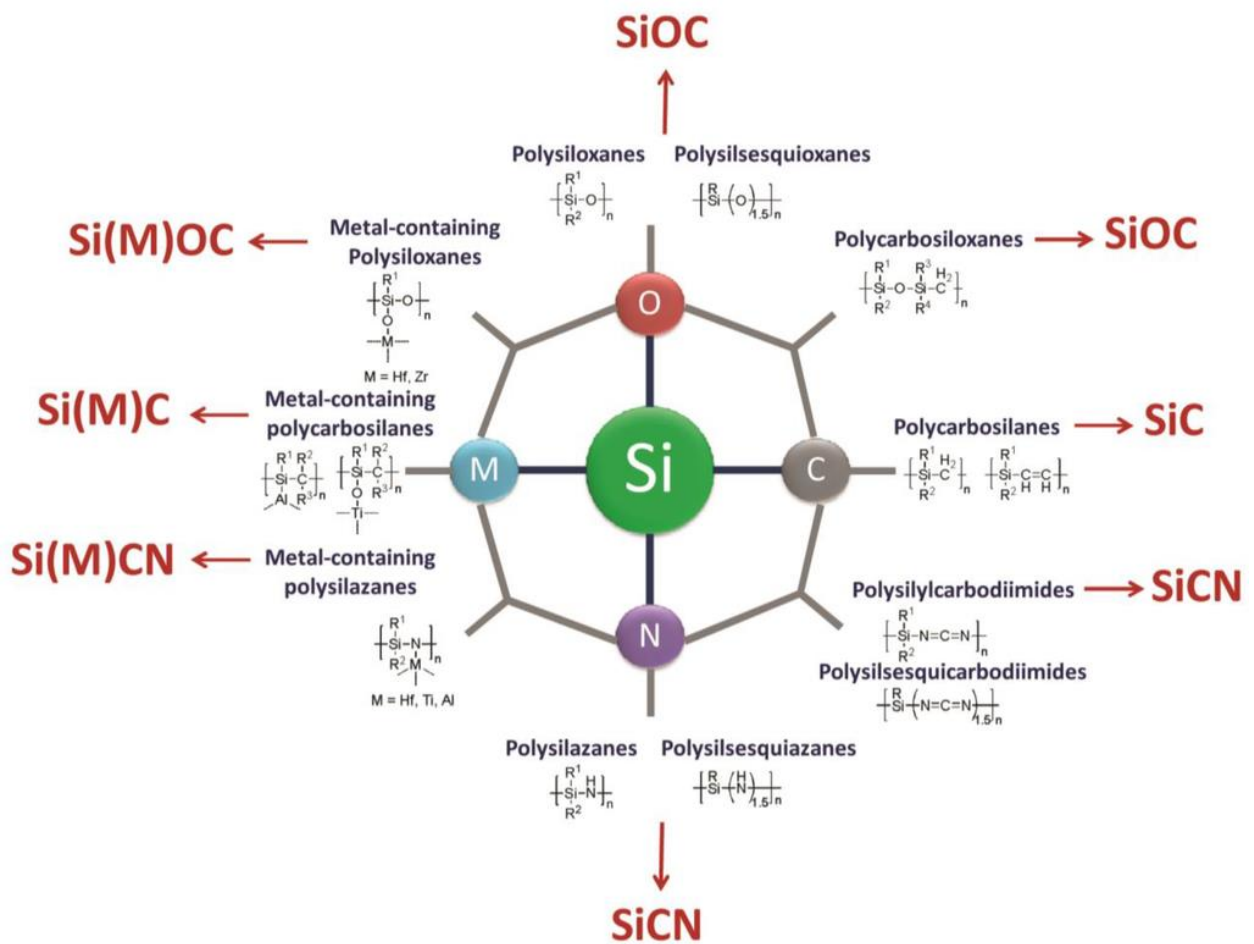


Figure 1: Preceramic polymer precursors [11]

Poly(organo)silanes and poly(organo)carbosilanes

Polysilanes and polycarbosilanes are the primary precursors to obtain silicon carbide. Polysilanes have Si-Si backbone chain with organic functional groups attached to the silicon [12]. Different methods of producing polysilanes have been around for quite a while, first one being a century old Wurtz-coupling reaction producing poly(diphenylsilane) by Kipping [13], [14]. For a while the process by Kipping was the main process to produce polysilanes until a new process was discovered by Chang and Corey which used dehydro-coupling of silanes [15]. Polysilanes are finding more and more applications since they display properties such as photoconductivity and luminescence. Polycarbosilanes are manufactured by a reaction called Kumada rearrangement [16]. The polycarbosilanes is obtained starting from polydimethylsilane where after heating the Si-Si bond is cleaved to form silicon free radical. This is followed by the rearrangement of bonds where the methylene group is inserted into an Si-Si bond and results in formation of Si-CH₂-Si and Si-H groups [16]–[19]. These preceramic polymers result in β-SiC ceramic. Polycarbosilane ceramics can also be manufactured by other reactions such as coupling, cyclopolymerization [20], [21], ring-opening polymerization [22], [23], and thermolytic and catalytic co-ordination techniques [24].

Poly(organo)siloxane

Polysiloxanes, more widely known as silicones are usually used for sealing purpose and construction materials. They also possess very desirable chemical, physical and electrical properties [25]–[27]. Regarding ceramics, they are the primary precursors for SiOC or silicon oxycarbide type ceramics. The general production method of polysiloxanes is a reaction of

chloro(organo)silanes with water [28]. (Figure). Another synthesis method for a type of polysiloxanes called polysilaethers is polycondensation of α - ω functionalized linear silanes [28]. They can also be synthesized by ring opening polymerization of cyclic silaethers [29].

Studies have shown that SiOC ceramics derived from polysiloxanes which are rich in carbon (more than 20% carbon), have greater high temperature resistance to oxidation and are stable without crystalizing compared to those with less carbon content [30]–[33].

Poly(organo)silazanes

Even though polysilazanes were first characterized in 1885 [34]–[37], their use as precursors for silicon carbonitrides, a potential equivalent to polysiloxanes was discovered in 1950s and 60s [38]–[40]. The main use of polysilazanes today is as precursors for ceramic materials and as silylating agents [41]. Polysilazanes are mainly synthesized by ammonolysis reaction of organosilicon chlorides, a method developed by Kruger and Rochkow in 1964 [42]. The first instance of ceramic production from polysilazanes was reported in 1974 when Verbeek et al. produced ceramic fibres [1]–[3], which gave the boost to the reach of polysilazanes as precursors for ceramic products.

The ceramic yield from their polymeric precursors is usually correlated to their molecular weight. Since the molecular weight of polysilazanes is low compared to the other precursors, the ceramic yield is also lower. Many methods have been employed to increase the molecular weight of the polyorganosilazane precursors as well as to improve the degree of crosslinking which would result in higher ceramic yield [43]–[47].

Crosslinking and shaping

One of the main benefit of preceramic polymers in processing of ceramics is that they are polymeric at the processing stage. They can be subjected to all the processing and shaping techniques of polymeric components. This makes them desirable for manufacturing engineering ceramics compared to powders and slurries/pastes. The machining before (and not after) conversion into ceramic avoids issues related to the brittle fracture and tool wear [48]. Another advantage of using preceramic polymers is that polymers are processed at lower temperatures compared to the ceramic powders (sintering). Along with the regular plastic forming processes, some specialized manufacturing processes such as foaming, fiber spinning, supercritical drying can be used to create ceramic foams, fibers and nanofibers, and aerogels, respectively [49].

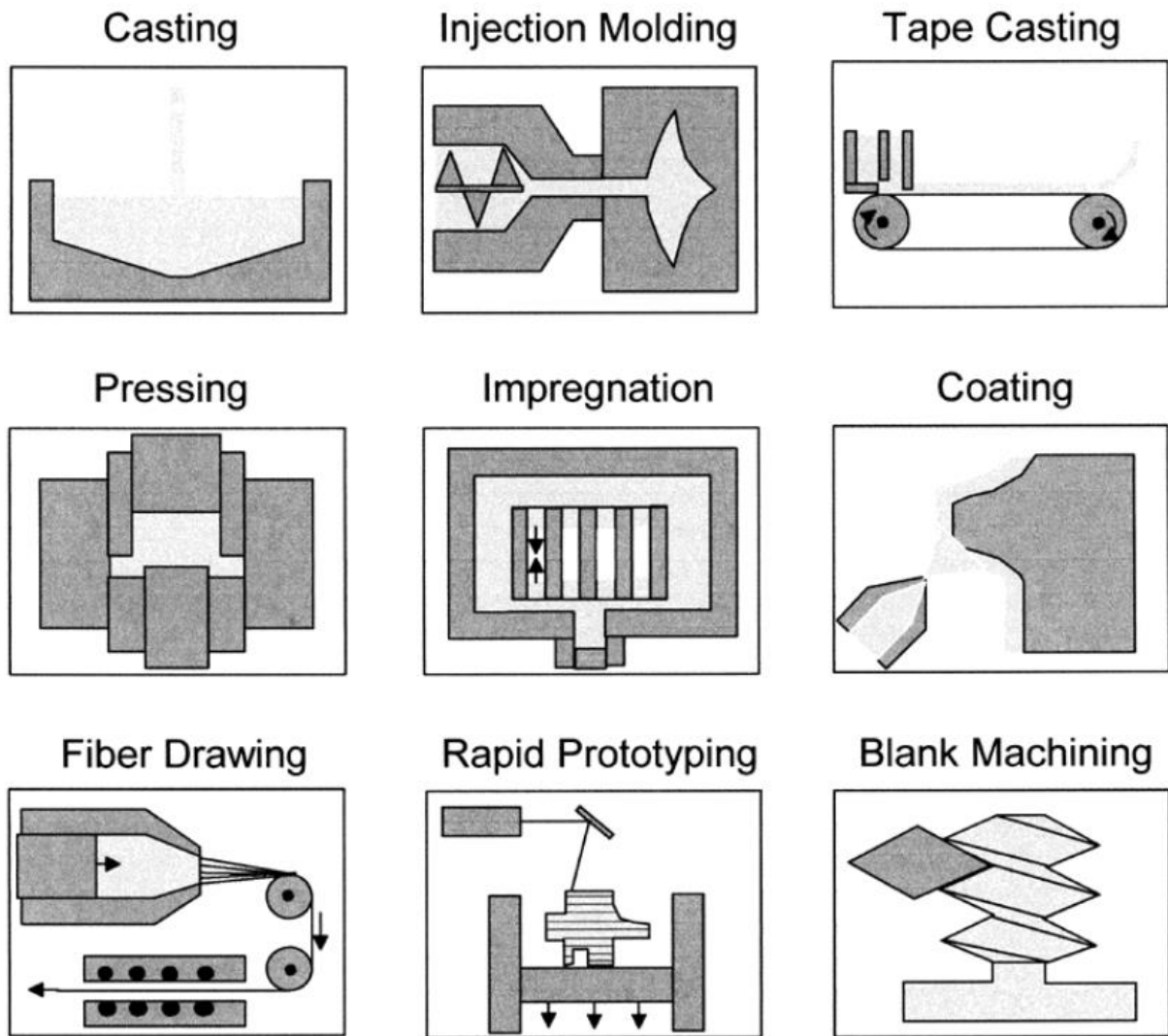


Figure 2: Shaping processes used with preceramic polymers [50]

The preceramic polymers come in the form of a liquid which can be cured or solid powders that can be melted/dissolved and cured. The crosslinking or curing of preceramic polymers can either be done with the polymer shaping or after the polymer shaping. Oxidative curing is primary method for crosslinking, although the ceramic is contaminated with oxygen during the process which can go as high as 15wt% of the ceramic [51], [52]. This in turn lowers the high temperature stability. UV curing can be utilized by grafting photo-sensitive functional groups on the backbone chain of the preceramic polymer [53]–[55]. Low temperature curing can be

achieved by performing the heat treatment in reactive gases such as ammonia, thionyl carbide, nitrogen dioxide, nitric oxide, halogenated or unsaturated hydrocarbon etc [56]–[58]. For silicones having Si-OH groups, they can be cured by dipping into strong alkaline solution [59].

Crosslinking reactions

Inclusion of functional groups such as vinyl, -H, -NH facilitates the crosslinking of the preceramic polymers. Most of the reactions occur around 200-300°C. The temperature of the crosslinking can be lowered by using catalysts.

Polysiloxanes

The reactions which can initiate and promote crosslinking in polysiloxanes are condensation, free radical initiation, transition metal catalyzed addition [60]. Polysiloxanes containing methyl and vinyl groups can be crosslinked using peroxides [61]. The other crosslinking reactions can initiate with silicon hydride units reacting with Si-vinyl groups when subjected to high temperatures [62], [63]. The reactions continue with hydrolysis of hydroxyl and alkoxyl accompanied with the condensation of Si-OH groups and ends with formation of -Si-O-Si- groups.

Polysilazanes

The first of these reactions – hydrosilylation occurs around 100-120°C in oligosilazanes containing vinyl groups and Si-H linkage. This reaction results in the formation of Si-C-Si and Si-C-C-Si linkages. These linkages are not affected by any further reactions such as transamination and Si-N exchange [64]. With higher yield of the hydrosilylation reaction, higher ceramic yield can be obtained. The rate of the reaction can be increased with the addition of the catalysts [65]. Around 300°C dehydrogenation of Si-H and N-H bonds or Si-H and Si-H bonds where the hydrogen is evolved, and Si-N and Si-Si bonds are formed. The next is transamination which occurs around 200 to 400°C when the oligosilazanes are heated. The reaction results in evolution of amines, ammonia or silazanes of the oligomers. This is related to the mass loss during the ceramization process. The vinyl polymerization reaction as suggested by the name polymerizes the silicon with vinyl groups. The reaction occurs at higher temperatures and is not related to any mass loss [66], [67].

The reactions involved in the cross-linking process of polysiloxanes and polysilazanes are shown in Figure 3.

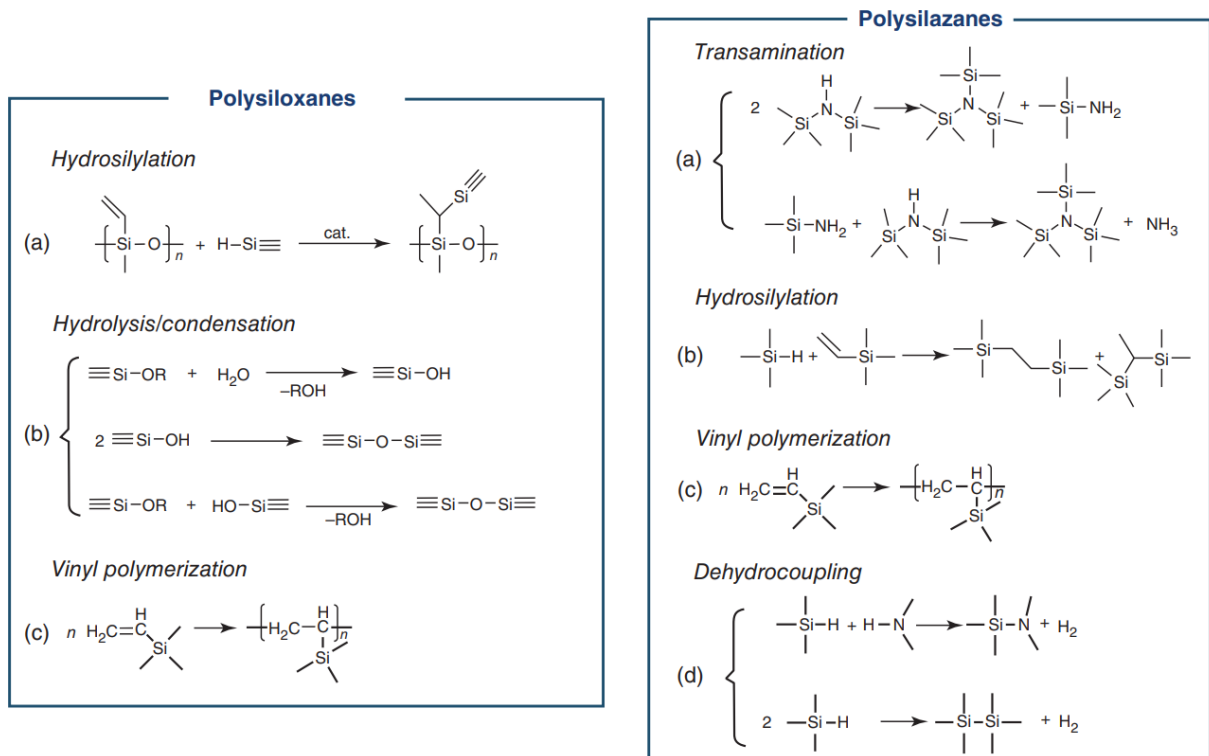


Figure 3: Crosslinking reactions in Polysiloxanes and Polysilazanes [48].

Polycarbosilanes

The crosslinking of polysilanes can either be done with oxygen or without oxygen [6]. The first reaction in both the cases is the formation of silyl radicals as a result of the cleavage of Si-Si bonds and Si-H bonds. Oxidation of the radicals results in formation of Si-OH, -Si-O-Si- and C=O [17], [68]. This yields in SiC ceramics with 10-12% oxygen content [51].

In absence of oxygen Si-H and Si-CH₃ groups react to form -Si-CH₂-Si- with no bond formation occurring between Si-Si. Because of this the oxygen content of the produced SiC material is very low (0.2-0.3%)[69].

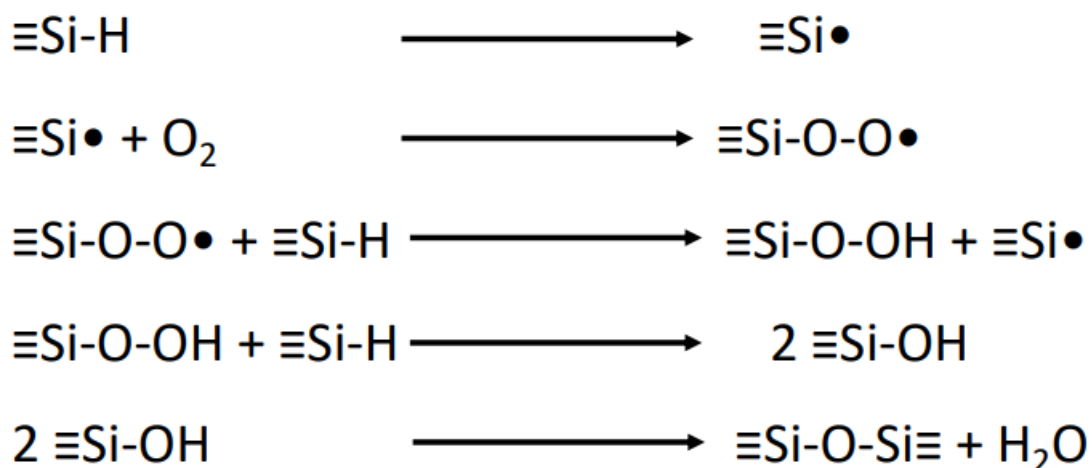


Figure 4: Reactions involved in crosslinking of polycarbosilanes in presence of oxygen [9].

Polymer to ceramic conversion

After the polymeric precursors have been shaped and crosslinked, they have to be converted into ceramic with a thermal or nonthermal radiation procedures such as hot pressing [70]–[72], spark plasma sintering, ion radiation, laser pyrolysis etc. Most common of the heat treatment procedures is oven pyrolysis in a controlled atmosphere [73].

All the organic components are decomposed during the polymer to ceramic transformation. The polymer to ceramic conversion occurs in a wide temperature range, 300 to 800°C. The system undergoes various changes in the microstructure during this transformation. Initially the ceramics are in the amorphous state which can range from 1000-1800°C depending on the composition and the molecular structure. As the temperature is increased the ceramics are devitrified and start to crystallize locally with different phases. During these processes the phase separation is the result of redistribution of the chemical bonds, which further leads to nucleation and growth of the nanocrystals. The phase transition goes from amorphous phase to

separation of the free carbon to forming the nanocrystalline domains. The stoichiometry of the ceramic composition defines the remanent free carbon which is not bonded to silicon.

The final ceramic products which are obtained from each of their corresponding polymeric precursors are shown in figure 5. Depending on the preceramic polymers the behaviour during the polymer to ceramic transformation is different.

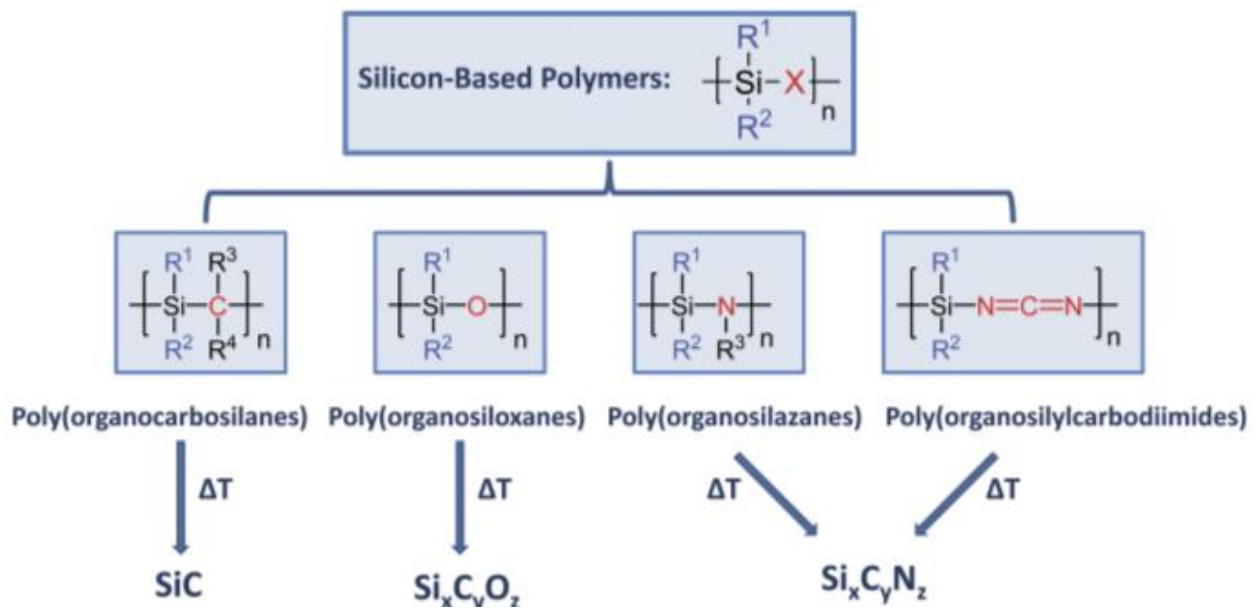


Figure 5: Representation of preceramic polymers and their ceramic products after pyrolysis [10].

Polycarbosilanes

For polycarbosilanes, the transformation usually occurs in the temperature range from 550 to 800 C and the mass loss continues till ~850°C. During the transformation the Si-H, Si-CH₃ and Si-CH₂-Si bonds react releasing methane and H₂ gas where the free carbon is formed. After the

ceramization is completed an amorphous SiC/C ceramic is obtained. When the pyrolysis is continued further the SiC starts to crystallize around 1100°C. Above 1400°C, in presence of oxygen due to the carbothermal reactions the SiC phase shifts to silica due to oxygen contamination.

Polysiloxane

Polysiloxanes when ceramized result in amorphous SiOC ceramics with a free carbon phase [74]. Evolution of gases, as a result of the mineralization reactions, occur in the temperature range 700-900°C. The cleavage of the Si-C and C-H bonds release H₂ and CH₄. This cleavage process is continued till ca. 1000°C until the SiOC/C phase is formed [75], [76]. By changing the pyrolysis environment, the nature of the bonds of the SiOC/C phase changes. With inert pyrolysis environment (N₂, He, Ar) silicon atoms share bonds with oxygen and carbon atoms forming what is known as “mixed bonds unit”. When pyrolyzed in the H₂ environment the SiOC phase comes out to be hydrogen rich and eventually all the free carbon can be eliminated as CH₄. A “pure” silicon oxycarbide network can be obtained [77]. With CO₂ as the pyrolysis environment the SiOC phase contains non mixed bonds because of the cleavage of the Si-C bonds [78]. As the temperature of the pyrolysis is increased above 1200°C the SiOC phase starts to crystallize. The crystallization is the result of SiOC phase being separated into amorphous SiO₂ and beta SiC along with free carbon around 1300°C [79], [80]. This is either accompanied or proceeded, around temperature 1350 to 1400°C, by the carbothermal reduction of the SiO₂ by the free carbon and formation of beta SiC. The amount of free carbon decides the onset temperature of the thermal decomposition of the SiOC phase [81].

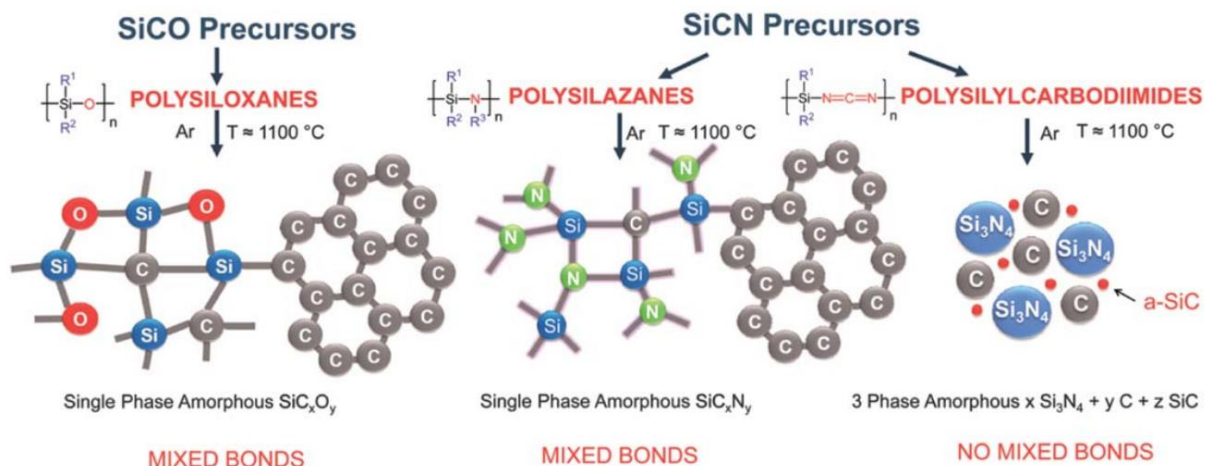


Figure 6: Microstructure of ceramics derived from their precursors in inert atmosphere [82].

Polysilazane

Polysilazanes exhibit different pyrolytic behaviors depending on the type of functional groups present in the polymer chain. During pyrolysis of polyhydrosilazanes, above 550°C, the Si-H and Si-CH₃ groups react and give rise to the Si-CH₂-Si linkages [83]. SiN₄ groups are formed as a result of the reactions involving N-H groups. Significant amount of methane is released due to the replacement of the methyl groups attached to the silicon [84].

Vinyl containing polysilazanes show a completely different ceramization behavior. In this case cross-linking reactions such as vinyl polymerization and hydrosilylation occur at lower temperatures. Transamination reactions give rise to ammonia up to 600°C [85]. At temperatures above 600°C hydrogen is evolved because of Si-H/N-H dehydrocoupling reactions along with methane due to Si-CH₃/N-H reactions. As a result, there is a decrease of Si-H, Si-CH₃ and N-H bonds in the temperature range 600 to 800°C. As the end product a ternary ceramic SiCN is produced with the composition $\text{Si}_3\text{N}_4 + \text{SiC}$ and free carbon [86].

1.2 3D printing/ Additive manufacturing of ceramics

In the initial days additive manufacturing was known as rapid prototyping as it was prominently used to help create prototypes and realize the ideas of the engineers. The main advantage of rapid prototyping is that it reduces the total time and cost spent in the product development cycle by reducing the cost and time required to produce prototypes [87]. Another main advantage of the process is that it allows to create very complex shapes that are difficult to produce by other type of manufacturing methods such as casting or machining [88]. As the technology is spread across all the disciplines, not only engineers but also scientists, artists, educators, medical professionals have been able to use it for prototyping [89].

With advances in the technology, it is no longer limited to prototyping. Many of the processes have been developed where the manufactured parts can directly be used as products. This has been also facilitated by the development of CAD (computer aided design). Combined with the computer aided manufacturing (CAM) and computer numeric control (CNC) designing and printing of 3D objects has become easier [90]–[92].

The figure shows revenue generated by the sales of the 3D printed parts in millions for the past 25 years.

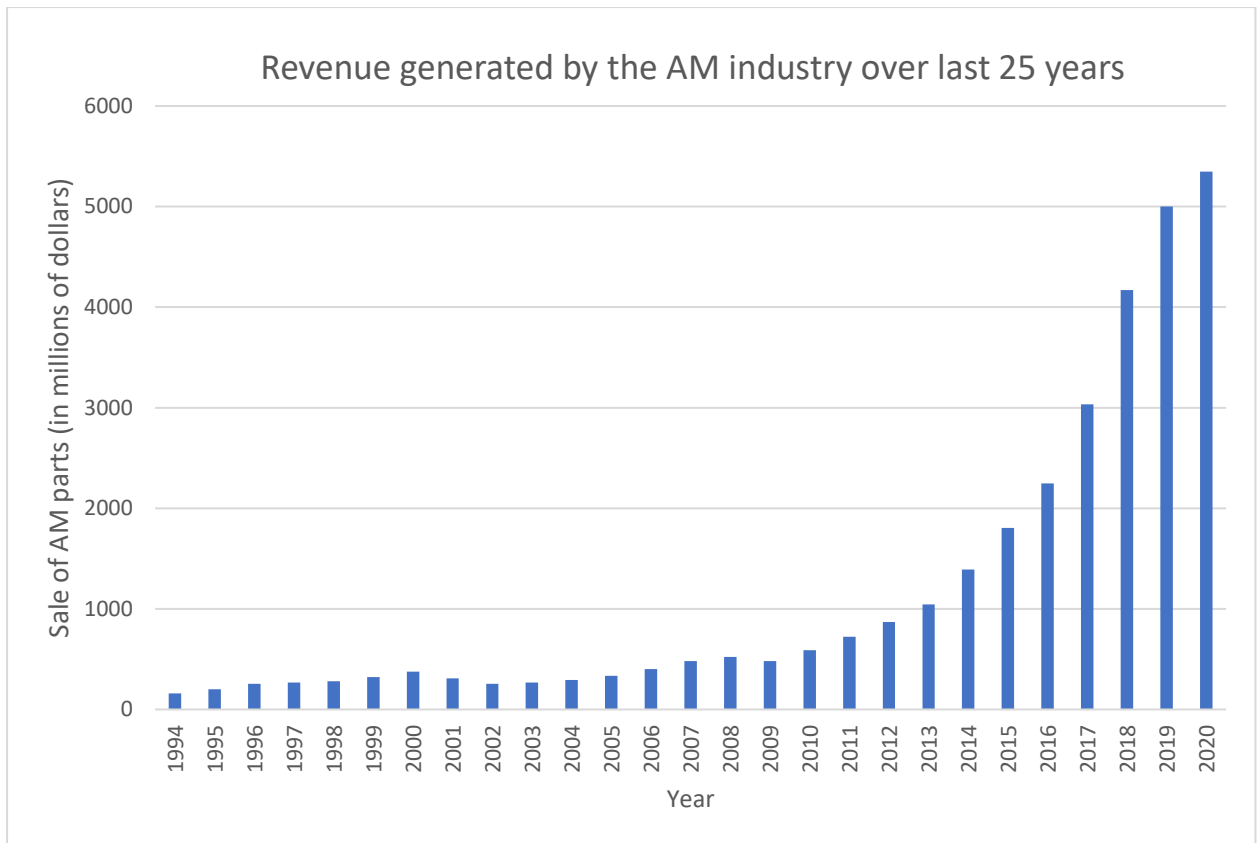


Figure 7: Revenue generated by the AM industry [93]

The adaptation of additive manufacturing into mainstream process is evident by the numbers as reported in Figure 7. This is due to the advantages provided by the manufacturing method [94], [95].

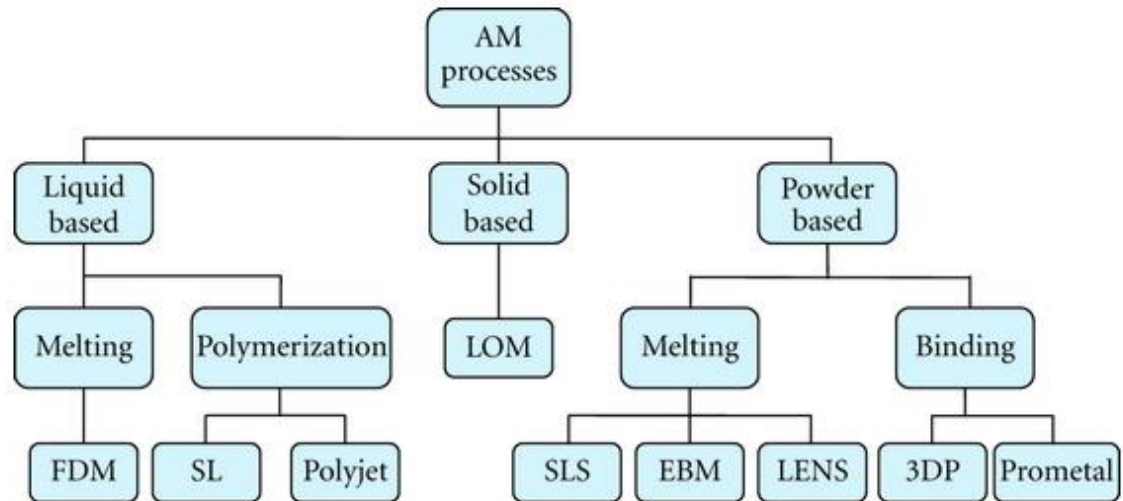
- Production of components which are difficult to manufacture or cannot be manufactured by subtractive manufacturing methods (such as cellular structures and complex geometries)
- Reduced material waste.
- Ability to produce the final product in one step (minimizing number of processes required for manufacturing).
- Flexible development pathway and freedom of design.

- Less logistics to be involved and less parts need to be managed.

Additive manufacturing processes are divided into 7 types of according to the techniques used. There are a number of different techniques that have been developed, some of which are proprietary. But to consolidate the ASTM has recognized seven major types [96].

1. Material Extrusion
2. Vat-photopolymerization
3. Material Jetting
4. Binder Jetting
5. Powder Bed Fusion
6. Directed Energy Deposition
7. Sheet Lamination

These techniques can be further divided according to the feedstock used. The feedstock can be liquid based, solid based or powder based as described in the figure 8. The other is depending on the part produced needs any kind of post processing or not. If the part can be used directly without any further processing, it is called a direct method, if the part needs post processing like binder removal, sintering/ heat treatment, it is categorized as indirect [97].



- FDM – Fused Deposition Modelling
- SL – Stereolithography
- SLS – Selective Laser Sintering
- EBM – Electronic Beam Melting
- LENS – Laser Engineered Net Shaping
- 3DP – 3D printing

Figure 8: Classification of additive manufacturing process based on the feedstock [98].

Ceramic additive manufacturing

Additive manufacturing started with polymeric materials and has reached to a point where final components can be manufactured [99], [100]. The material extrusion additive manufacturing has been hugely widespread due to the RepRap movement, which pushed to open source the manufacturing method [101]. Metal additive manufacturing has also been on the rise because of its utility in producing aerospace/ lightweight topologically optimized parts [102], [103]. Ceramics inherently are difficult to process, the research to develop additively manufactured ceramic parts is ongoing.

- **Material Extrusion**

Material extrusion for ceramics is generally referred as Robocasting. A variant of this method was developed in later years called Direct Ink Writing. Robocasting was originally developed and patented in the Sandia National Laboratories [104]. The method uses a ceramic paste or slurry which is pushed through a nozzle using a piston/screw mechanism to deposit layers of the material. With direct ink writing, a viscous paste with ceramic fillers is pushed through a syringe in similar fashion. These methods produce a green part which later needs to be debinded and sintered as the green part contains organic components from the slurry or the ink which need to be removed which leave porosities. The part then needs to be sintered to obtain a dense ceramic component [105].

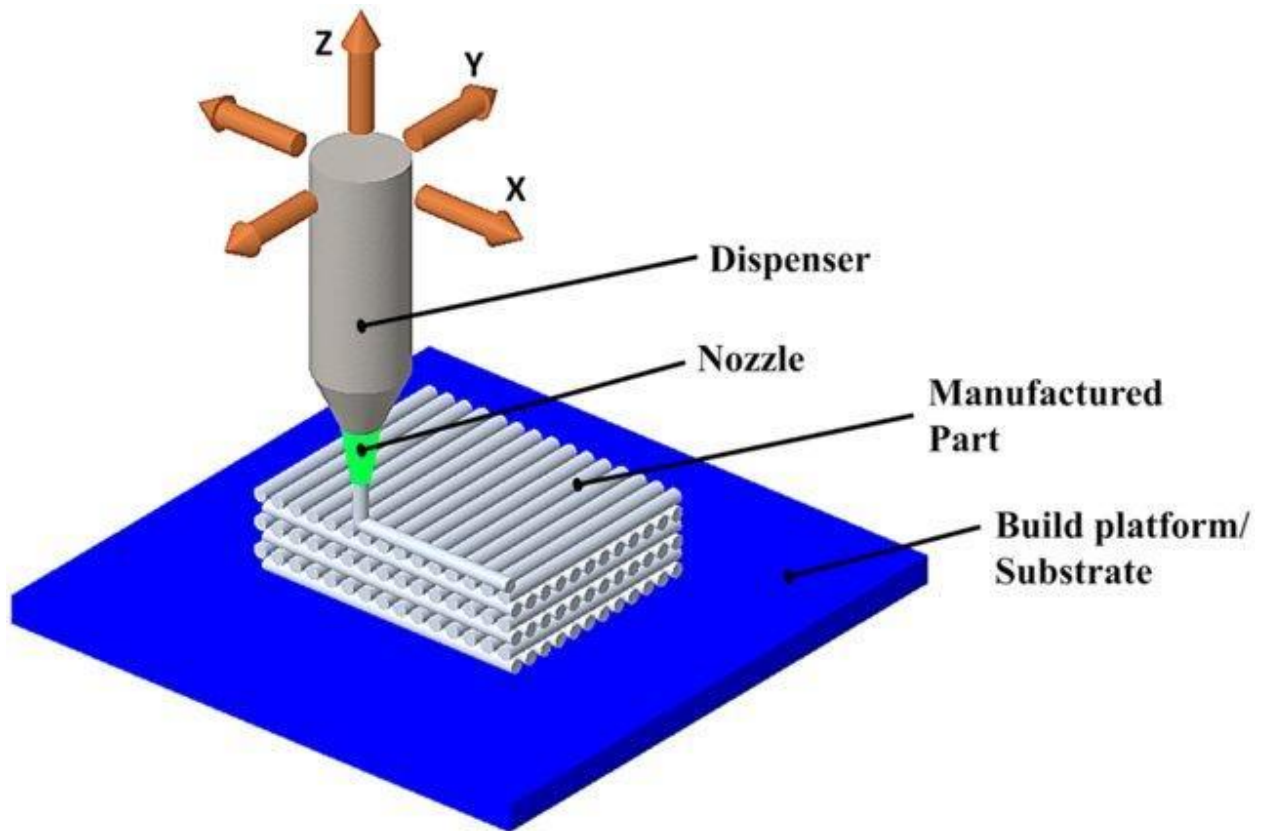


Figure 9: Schematic of Direct ink writing technique [106]

The main advantage of the technique is that a variety of materials can be used with this such as zirconia, alumina etc. Another advantage is that the process is comparatively cheaper than all the other methods. The main challenge of this technique is to maintain the rheology of the slurry or the ink that is used for the manufacturing. Various materials and structures have already been showcased with the robocasting and direct ink writing method [107]–[109].

- **Photopolymerization**

Vat photopolymerization also referred to as stereolithography uses a liquid photopolymer which can be cured/ crosslinked with exposure to specific light frequencies, usually ultraviolet. Stereolithography was patented by 3D systems[110]. It

started as an extension of the 2D printing lithography technology into the third dimension. Stereolithography initially used a laser with a guided mirror system to selectively cure the liquid photopolymer [111]. With the advances in the technology there have been some revisions of the process with Digital light processing and Masked lithography [112]. Both methods use a screen with a light source beneath it, which illuminates the whole layer that is to be cured at one time making the new processes significantly faster than the original stereolithography process [113], [114]. As the newer methods use a liquid crystal display screen to filter the light source beneath, the resolution of the print is dependent on the resolution of the screen [115]. Whereas, in the traditional stereolithography using the laser and mirror system, the resolution depends on the laser spot size [116]. Figure 10 shows the schematic of the process.

Main resin 3D printing technologies

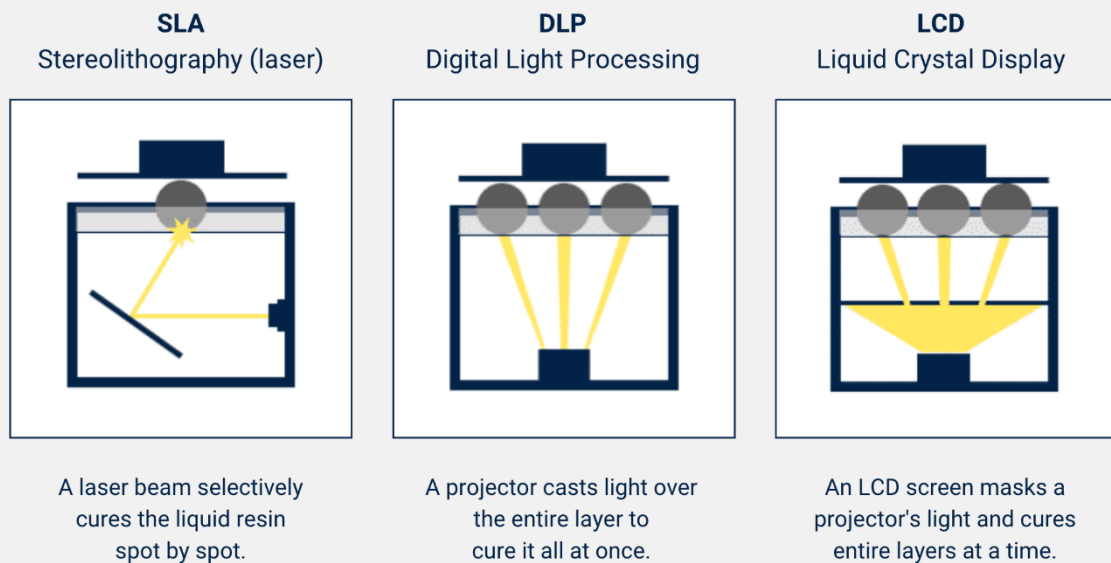


Figure 10: Schematic of Stereolithography, DLP and LCD [117]

- **Material Jetting**

Material Jetting type 3D printing started as an extension of the two-dimensional ink jet printing which has been developed since the 1960s. The initial iterations of the method were depositing particles of a material onto an article [118]. Later wax-based printers were developed where the wax was heated to liquid form and then deposited with a series of nozzles and the allowed to cool down [119]. The current version of the technology includes depositing acrylate-based polymers through the nozzles and the subsequently curing them after each layer with exposure to UV light. Similarly, another method of thermally curing the layers instead of UV exposure can be utilized [119].

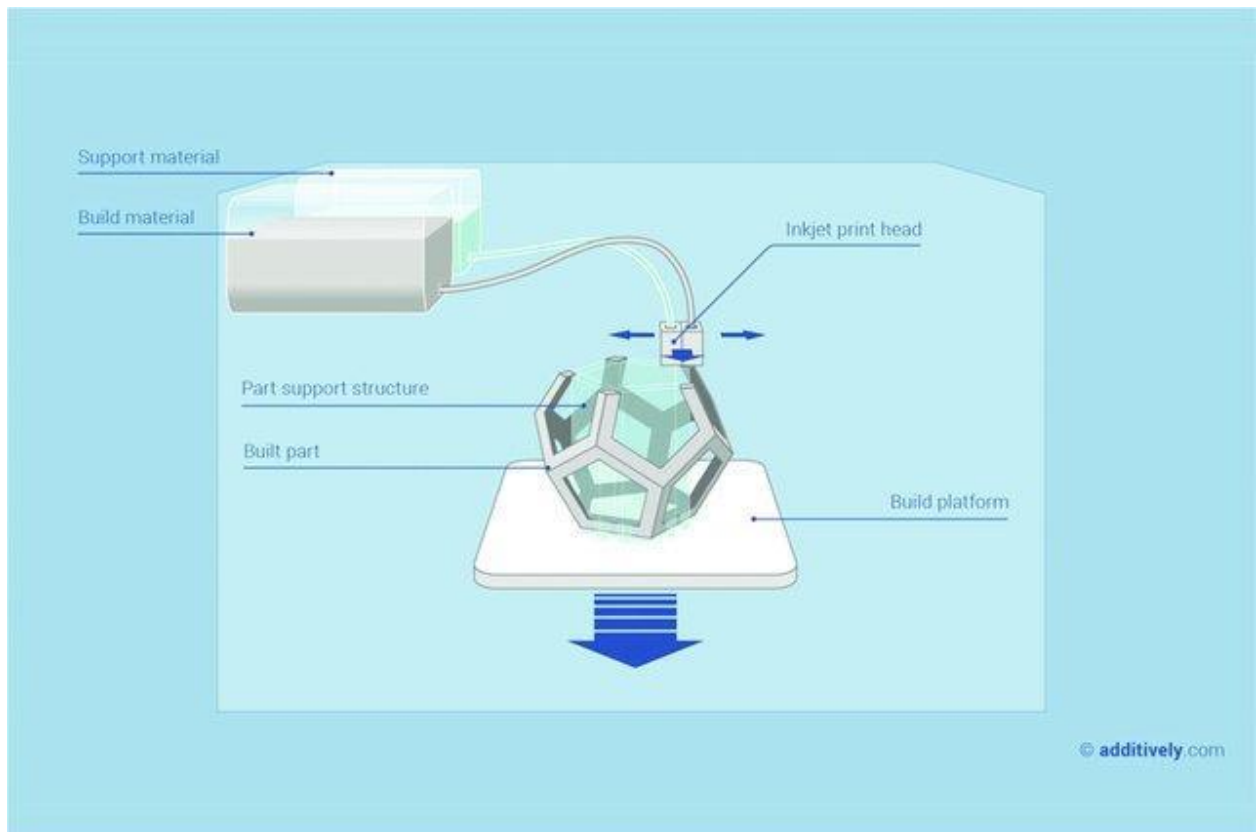


Figure 11: Schematic of material jetting procedure (additively.com)

For ceramic materials instead of liquid polymers a suspension of ceramic powders with some type of solvents is used. Studies have been conducted for zirconia powder mixed with solvents and other additives and alumina powder mixed with wax carriers [120]. Dental implants and restoration parts from zirconia and silicon carbide components have been successfully manufactured using material jetting technique [121]–[123].

The main advantage of this method is that wide variety of materials can be used, and the resolution of the final part is high. But it also comes with the disadvantages that the components need de-binding and postprocessing steps to get a dense ceramic part. The density of the final ceramic part might not be as high. Increasing ceramic loading into the solution increases the viscosity of the solution and might result in clogging of the nozzle.

- **Binder Jetting**

Binder jetting is the original process for which the 3D printing name was coined. The process was developed at Massachusetts Institute of Technology which was then licensed to commercial companies [124]. The process is similar to the material jetting process. But instead of the material being deposited, it is the binder getting deposited on the powder bed. The binder is deposited on by a series of small nozzles (less than 100 microns) on to the bed of powdered material, which bind the layer to the previous one. Then the powder bed is lowered, and the binder is sprayed again. The final part comprises mostly of the powder material and the binder is only used for adhesion. The advantage of this method is that a wide range of materials can be used. The main disadvantage being that the part produced is not entirely dense and need de-binding and sintering and the resolution of the printed part is dependent on the resolution of the ceramic powders [125]

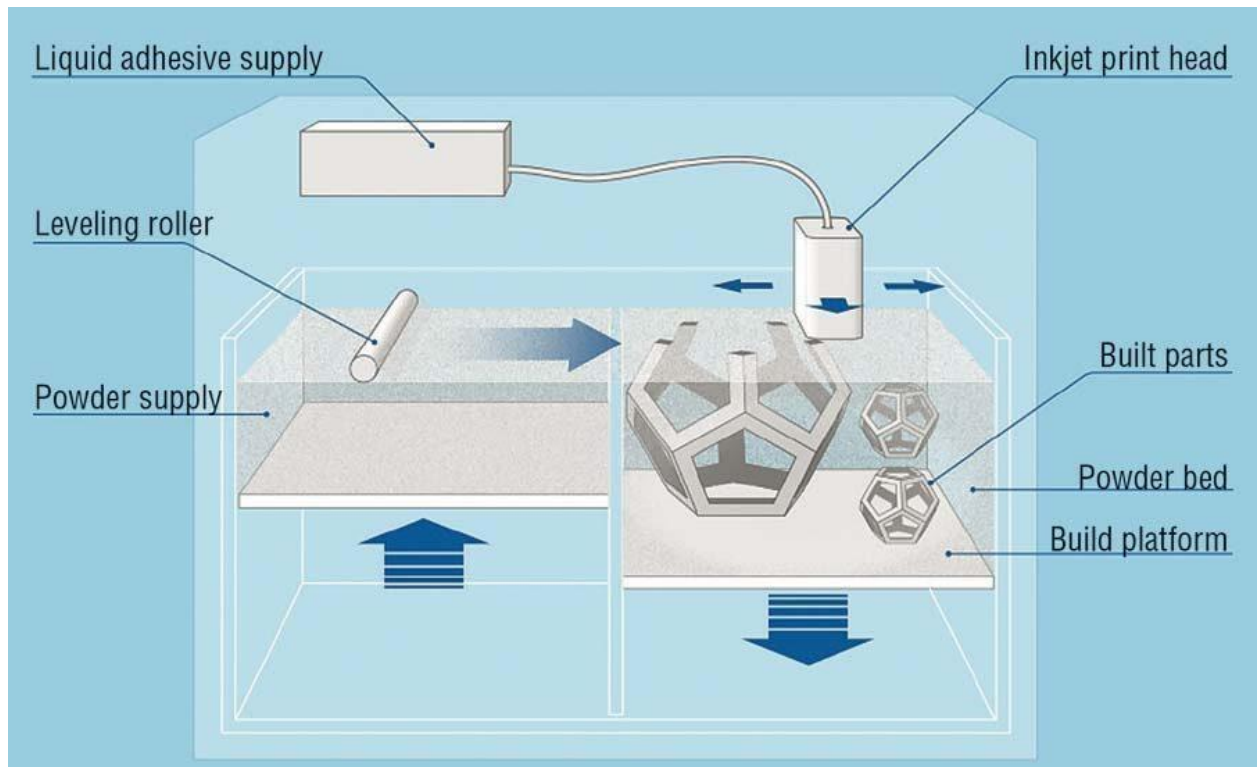


Figure 12: Schematic of Binder Jetting process (additively.com)

- **Powder bed fusion**

Powder bed fusion (PBF) process permits the use of any material that can be melted with an energy source and then solidified again. For ceramic materials selective laser sintering technique is the one that is most used. With PBF, a thin layer of the powdered material is sintered to the previous layer using a laser. After that a new layer of powdered material is deposited and the sintering process is repeated [126], [127].

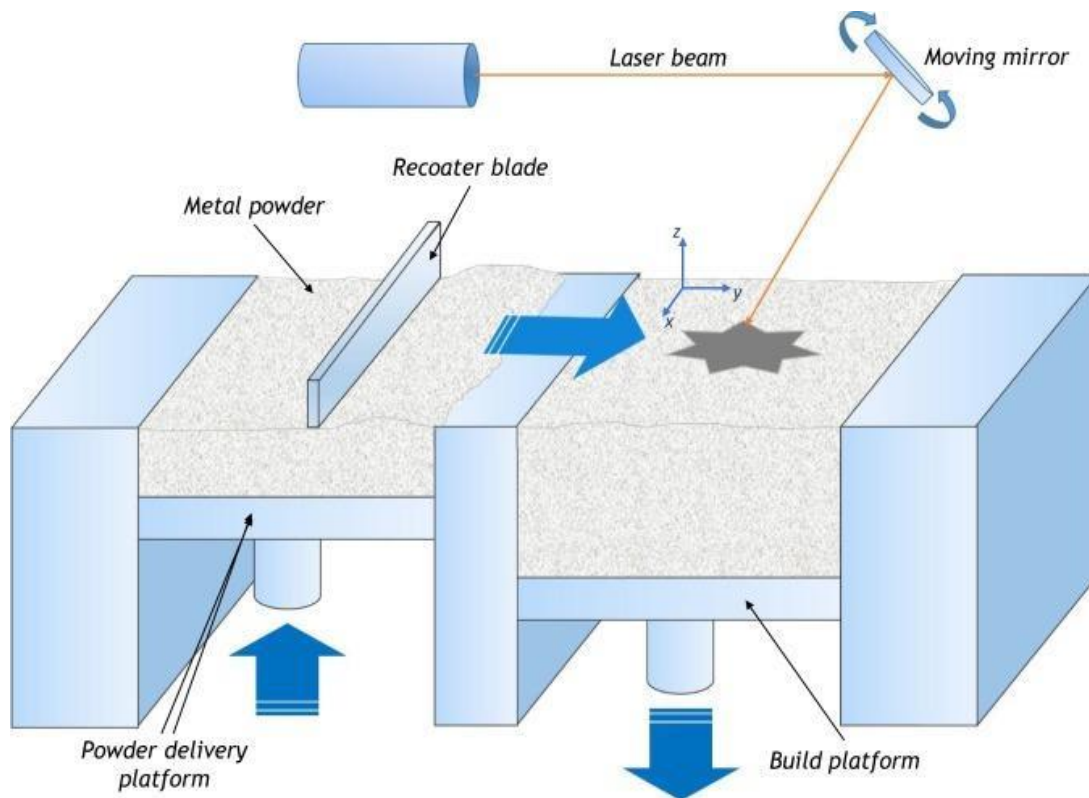


Figure 13: Schematic of Powder Bed Fusion [128]

There are two ways SLS can be utilized with ceramics, direct and indirect. With the direct SLS the ceramic powder itself is sintered using high intensity laser [129]. With the indirect SLS the feedstock is a mixture of an organic binder and a ceramic powder, where during the sintering part only the binder is melted and fused together with the previous layer [130]. With this the debinding of the sacrificial organic binder is required, and the density of the final part is limited due to the starting density of the feedstock which is a mixture of polymer and ceramic[131]. On the other hand, the benefit of the indirect SLS is that the intensity of the laser required in the indirect SLS is much lower compared to the direct SLS [132]. Subsequent infiltration steps can be used to increase the density of the parts in this case.

- **Directed Energy Deposition**

With directed energy deposition method, the ceramic powder is deposited through a nozzle and simultaneously melted and fused with the previous layer using a high intensity laser. Since the method relies on melting of the feedstock, the materials that can be used with this method are limited to those with lower melting points (e.g., oxides). Manufacturing of Al_2O_3 [133] and $\text{Al}_2\text{O}_3\text{-ZrO}_2$ [134] components have been showcased with the DED method. Since there is no use of powder bed the material used, and the wastage of the material is very less with DED. As the final component is manufactured directly, there is no post processing necessary with this method. The main downside of DED in ceramics is the limitation of materials used and the expensive equipment needed.

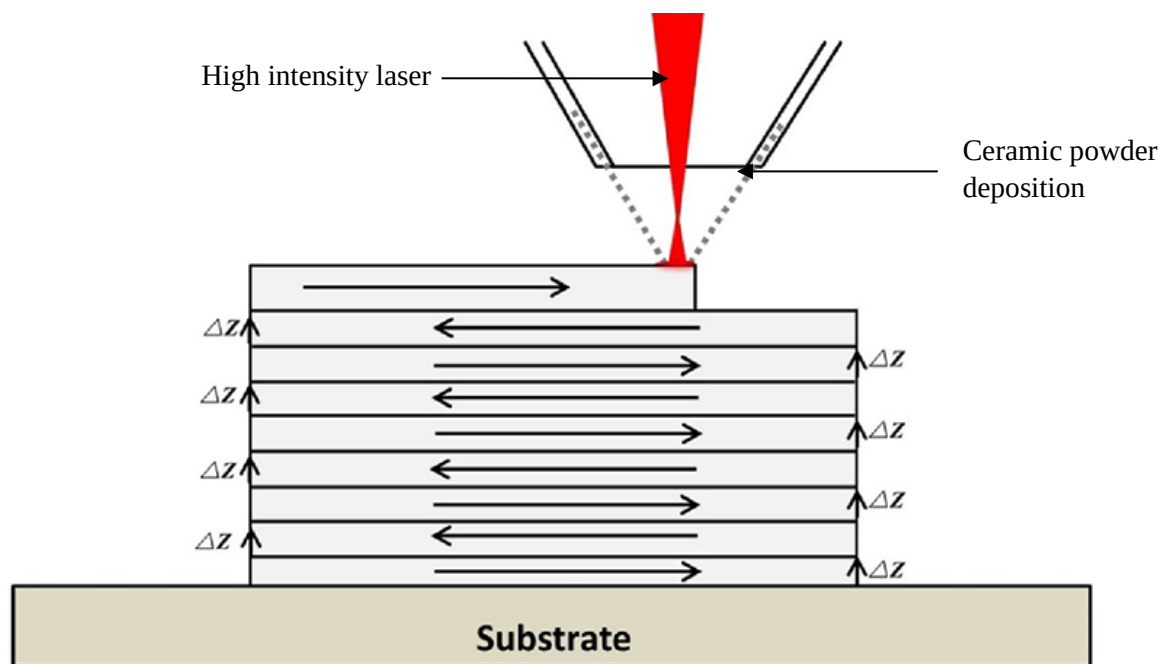


Figure 14: Schematic of ceramic DED process [135].

- **Sheet lamination/ Laminated object manufacturing**

With this method, sheets of material are stacked to make a pile. After each layer a cross section of the 3D component to be manufactured is cut in each of the sheets. The sheets usually have some kind of adhesive to be able to stick to each other. The cross section is cut using a high intensity laser.

For ceramics the sheets are produced by tape casting and then the sheets are used for LOM. Adhesion and delamination are big problems for ceramics as the final parts contain porosities. Parts from zirconia, alumina and Si-SiC have been previously manufactured using the LOM technique[136]–[138].

Further infiltration and sintering is performed on the produced parts to increase their porosity [139].

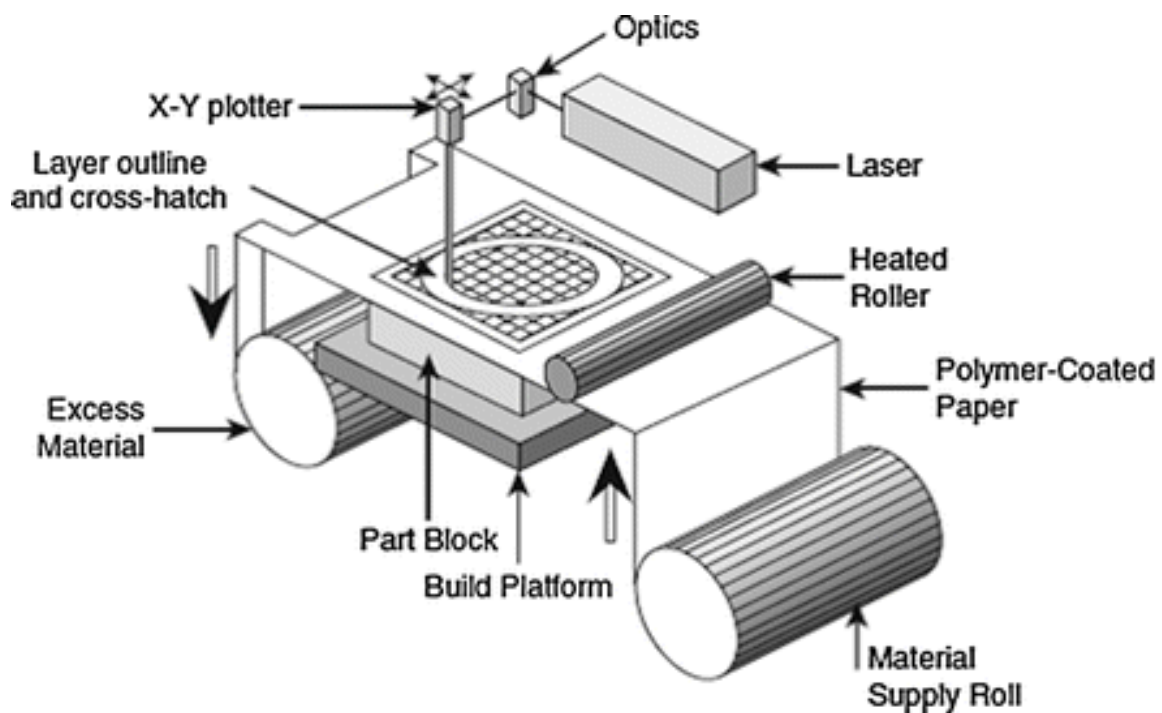


Figure 15: Schematic of LOM process [140]

Table 1: Comparison of Ceramic Additive manufacturing processes [141]–[143]

Ceramic AM process	Process	Feedstock	Advantages	Limitations
Material extrusion	Extrusion of material filled with ceramic particles through nozzle and fusing to previous layer	Ceramic filled paste /Ceramic filled ink Ceramic filled Polymer	Inexpensive Build volume can be scaled	Low resolution Support Structures are needed
Stereolithography	Photocurable liquid resin mixed with ceramics is selectively cured by UV light	UV curable photopolymer resins with Ceramic fillers	High resolution and ability to produce complex parts Smooth surface	High cost (Equipment as well as materials) Limited materials Increased post processing time
Sheet lamination/ Laminated Object Manufacturing (LOM)	Ceramic sheets are bounded together and selectively cut	Preceramic polymer papers Ceramic Tape	High volume capability	Post processing is critical and time consuming Adhesive material has to be selected properly
Binder jetting	Liquid polymer binder is jetted on ceramic powders	Powdered Ceramics and liquid adhesive	Wide range of ceramic powders available	Binder removal and post processing (sintering) is needed Getting high density parts is difficult Costly process Binder selection is critical

Directed energy Deposition	Laser is used to fuse ceramic powder which is simultaneously deposited	Powdered ceramics	Not restricted by part geometry Advantageous for repairs	Powders are detrimental Materials are limited due to operating temperatures Equipment is expensive Powders are expensive Very slow build time
Powder bed fusion / Selective laser sintering	Laser is used to fuse thin layers of powder on a powder bed	Powdered ceramics	No support needed High resolution	Low density parts Expensive equipment Powder production is expensive Powders are harmful Post processing is required
Direct Ink writing	Gel is deposited layer by layer similar to material extrusion	Colloidal ink with mixed ceramic particles	Binder removal is easy	Ink delivery is very critical Controlling rheology is difficult

1.3 Review: 3D printing with polymer derived ceramics

As seen, additive manufacturing of ceramics has its own advantages and disadvantages. Another method to 3D print ceramics is using preceramic polymers. As the process starts from polymeric phase the shaping techniques available are simpler compared to shaping of ceramics. Stereolithography/DLP and DIW are the most common methods used to additively manufacture polymer derived ceramics.

The first attempt of producing 3D structures using inorganic preceramic polymers was reported by Pham and colleagues [144] on a nano level. In this research, polyvinylsilazane was functionalized with 2-isocyanatoethyl methacrylate which was activated by ultraviolet wavelength between 350 nm to 450 nm. The structures created were on the scale of micrometres with the line width of up to 210 nm.

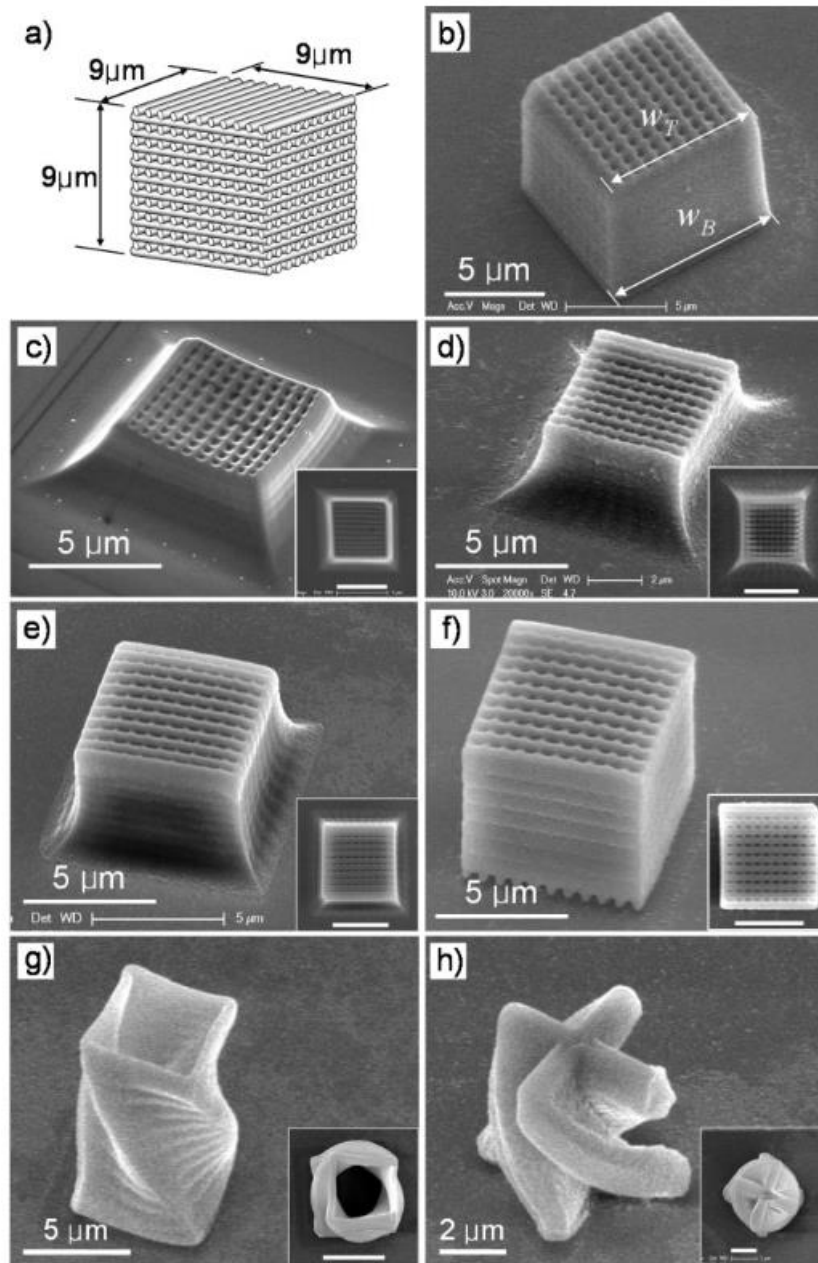


Figure 16: Ceramic microstructures created by the nanolithography process. (a) Schematic of the structure (b) polymeric structure without filler (c) corresponding ceramic structure (d-f) Ceramic structures obtained from mixing 20, % 30% and 40% silica with the resin (g) ceramic twisted tube (h) micro cruciform with the twisting angle of 90.

During the late 2000s, most of the research in additive manufacturing of polymer derived ceramics focused on micro and nano structures. Park and colleagues [145] showcased a process

for fabrication of SiC microstructures with near zero shrinkage. The process uses a system of inorganic polymeric precursors, allylhydridopolycarbosilane (AHPCS – a precursor for stoichiometric SiC) mixed with organometallic additive (η^5 -cyclopentadienyl-methyl)-trimethylplatinum (CpPtMe₃). Where (CpPtMe₃) acts as a photo-initiator for the stereolithography technique when exposed to the UV wavelength of 365nm.

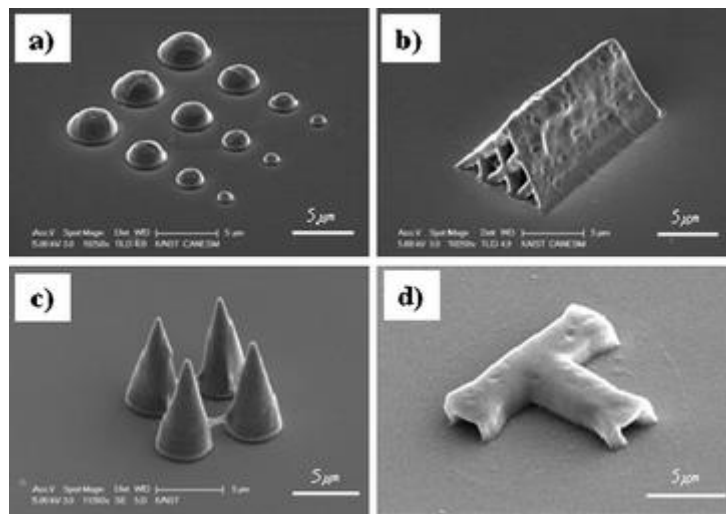


Figure 17: SiC mictristructures manufactured by stereolithography technique (a) multiscale hemispheres (b) microchannels (c) cones (d) multichannel [145].

Martinez-Crespiera and colleagues [146] demonstrated the fabrication of SiOC microcomponents using photolithography for micro-electromechanical systems (MEMS). Polysiloxane preceramic mixed with a photoinitiator was coated on a silicon wafer and was subsequently crosslinked using UV irradiation masks. The Si wafer was then pyrolyzed in argon atmosphere at 1100°C to obtain the final microstructures.

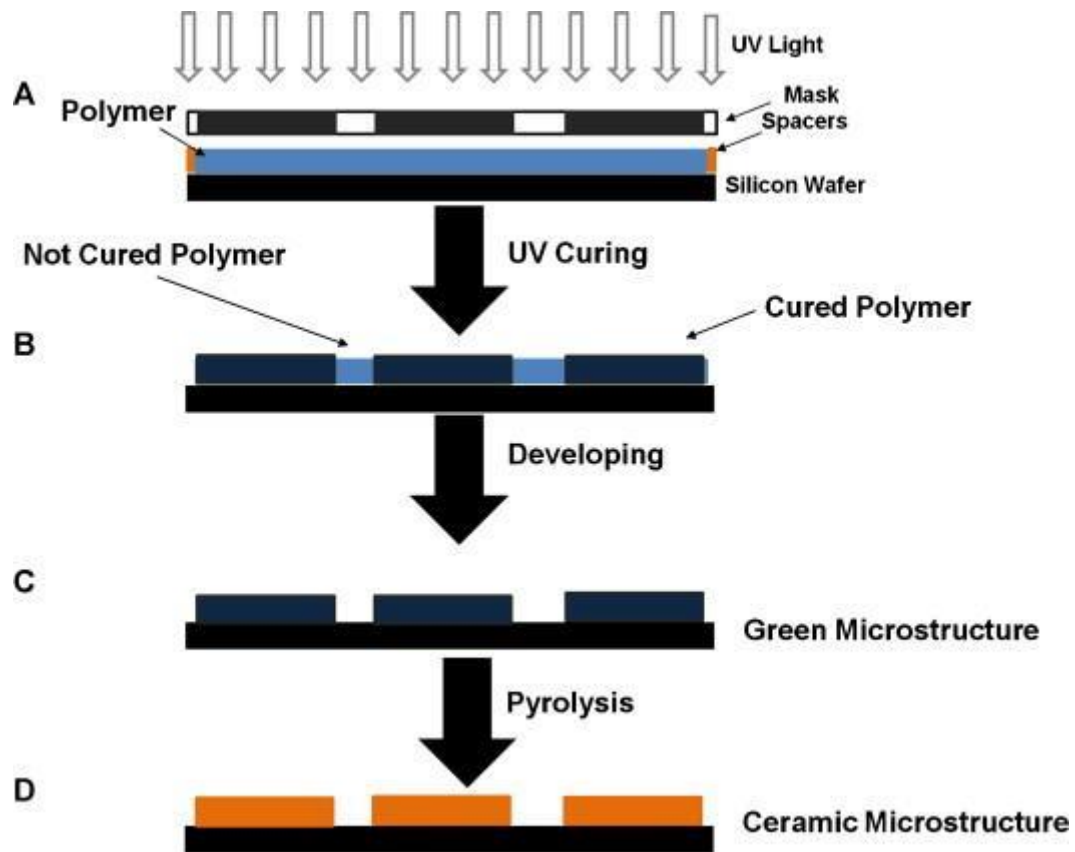


Figure 18: Schematic of the process of obtaining SiOC ceramic microstructures on silicon wafers using photolithography approach [146].

One of first three dimensional representation of stereolithography of polymer derived ceramics was given by Zanchetta and colleagues [147]. The research shows usage of a preceramic polymer engineered for photo-absorption for 3D stereolithography. The preceramic polymer is produced from mixing silicon, organically modified silicon alkoxide and 3-(trimethoxysilyl)propyl methacrylate. The manufactured resin is then used to produce 3D structures with CeraFab 7500 (a commercially available lithography-based printer developed by LITHOZ). The method allowed the fabrication of features of the size up to 200 microns.

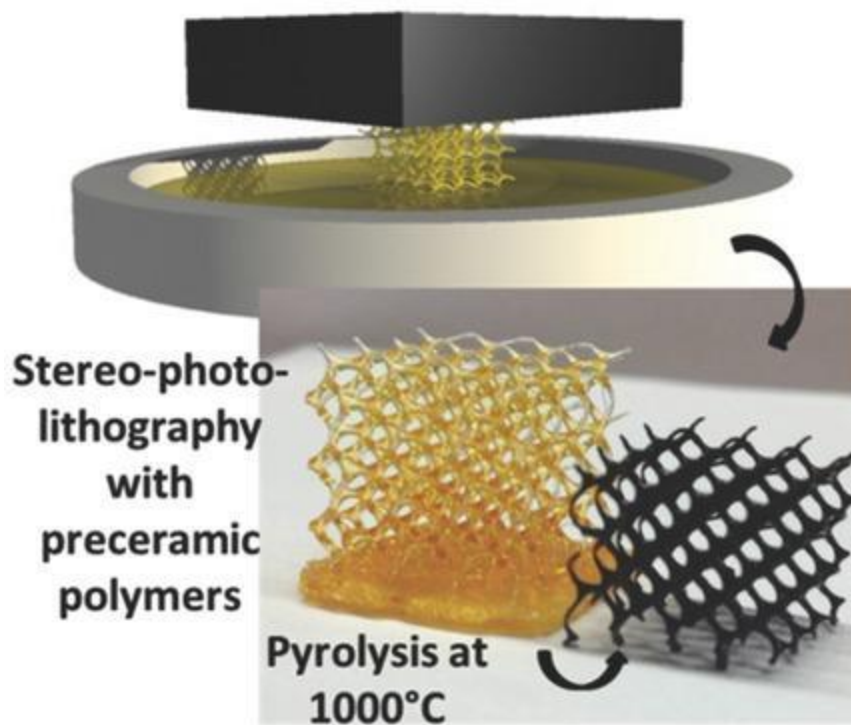


Figure 19: Schematic of stereolithography process and the final ceramic product [147]

De Hazan et al [148], in their work used allylhydriopolycarbosilanes (SMP-10, Starfire systems) and allylmethylhydridopolycarbosilanes (SMP-877, Starfire systems) mixed with multifunctional acrylate monomers 1,4 Butanediol diacrylate (BDDA) and 1,6 Hexanediol diacrylate (HDDA) and liquid photoinitiators (TPOL, Rahn) for aiding the crosslinking with the UV exposure. The SMP-877 was mixed with BDDA in ratio 1:1 and 1:2 with 2% TPOL and 0.25% polymerization inhibitor Genorad 16 to increase the shelf life.

The mixture was then additively manufactured using commercially available stereolithography 3D printer Freeform Pico plus (Asiga) with the UV wavelength 405nm having resolution 39 microns. The layer height was set to 50 microns with the exposure time of 4 seconds for each layer.

The printed parts were then pyrolyzed in argon atmosphere till 1300°C and held for 2 hours to obtain the final ceramic structures.



Figure 20: Ceramic parts produced from the SMP-877/BDDA mixture with stereolithography [148].

Wang and colleagues [149] demonstrated the fabrication of ceramic components using stereolithography technique for three preceramic polymers, methylvinylhydrogenpolysiloxane (polyamic SPR-212), allylhydridopolycarbosilane (SMP-10) and methylvinylhydrogen polycarbosilazane (Durazane 1800). 1,6-hexanedithiol, phenylbis(2,4,6-trimethylbenzoyl) phosphineoxide (BAPOs) was used as the photoinitiator, Sudan Orange G as a photoabsorber and hydroquinon, a radical scavenger to terminate the reactions.

The process uses thiolene click reaction for crosslinking of the preceramic polymers where thiol groups from the 1,6-hexanedithiol react with alkene functional groups from the preceramic polymers. The UV exposure initiates the cleavage process producing free radicals, which further gives way to the click reaction. Thiolene click reaction is described in the figure below.

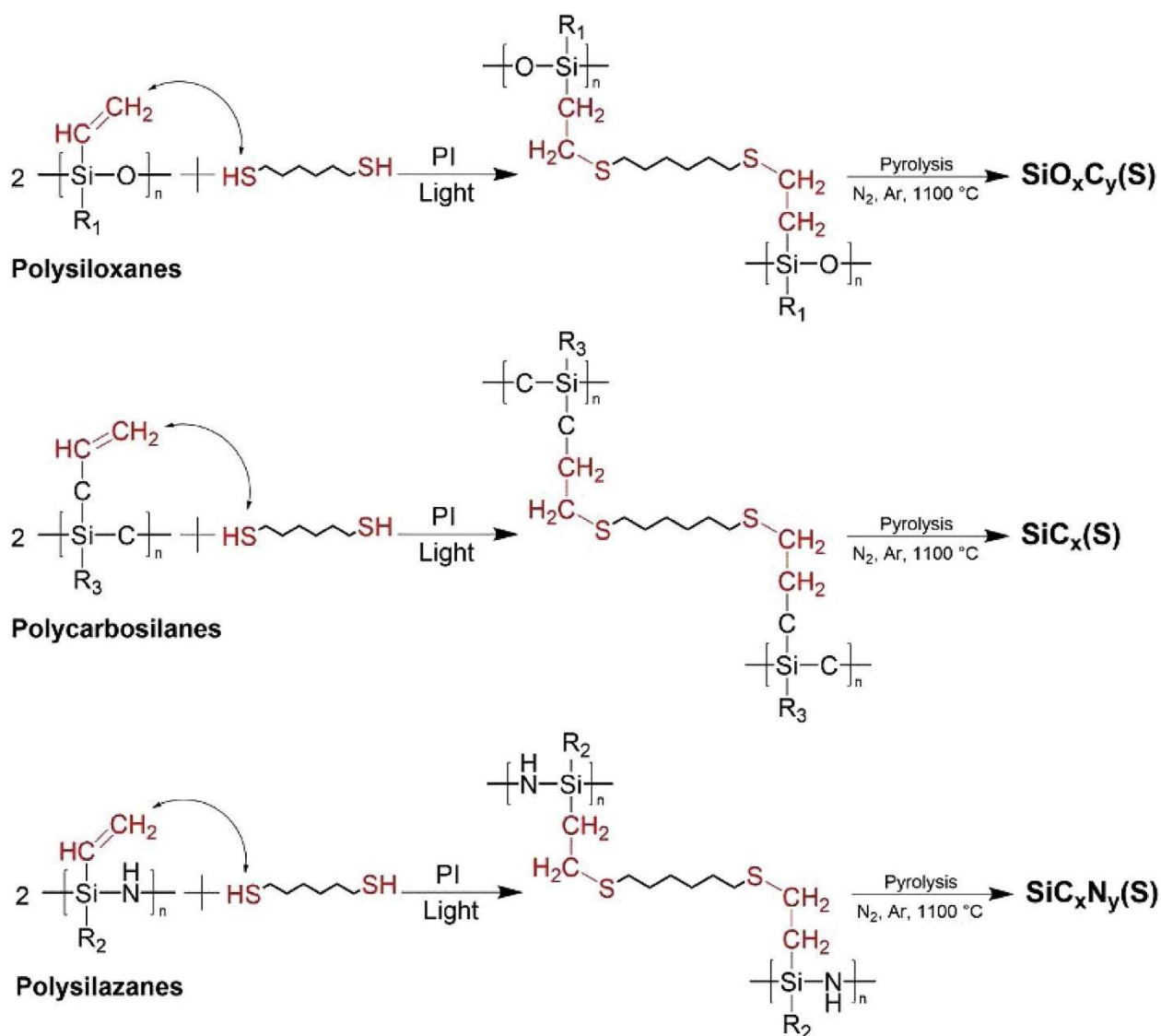


Figure 21: Thiolene click reactions involved in crosslinking of preceramic polymers [149]

The produced resin was then used to fabricate 3D parts using stereolithography based Open-Source 3D printer (LittleRP, USA), followed by the pyrolysis procedure to obtain the ceramic parts.

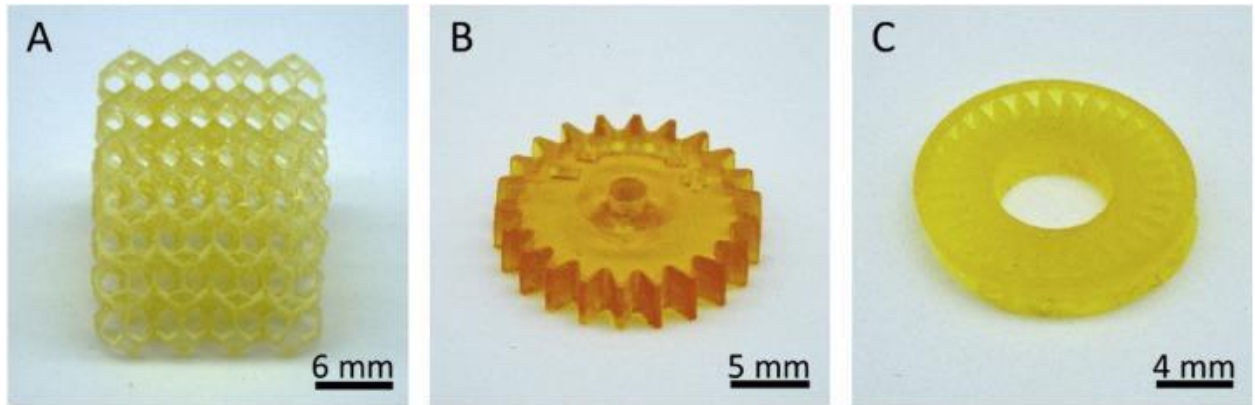


Figure 22: additively manufactured parts with DLP technique [149].

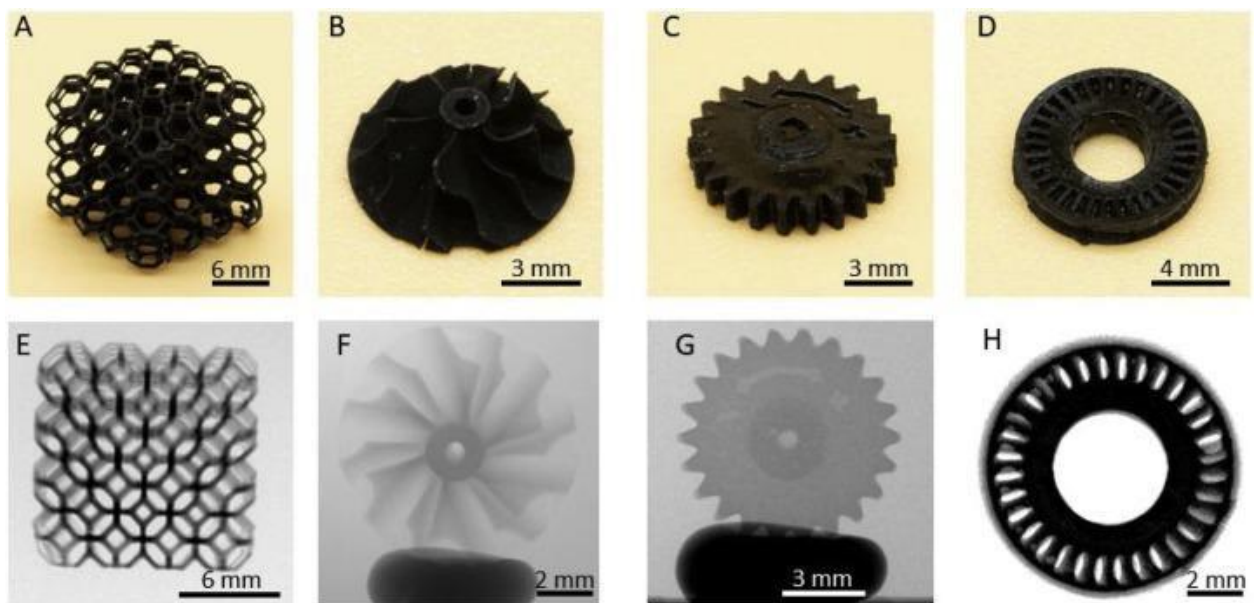


Figure 23: Converted ceramic parts after pyrolysis [149].

With the development of stereolithography technology, 3D printing with DLP, and LCD methods has become faster and more accessible. Researchers have shown that the

photosensitive resin mixtures can also be used with DLP technique. Schmidt et al. demonstrated the use of polysiloxane preceramic mixtures with added photoinitiators and photoabsorbers [150][104].

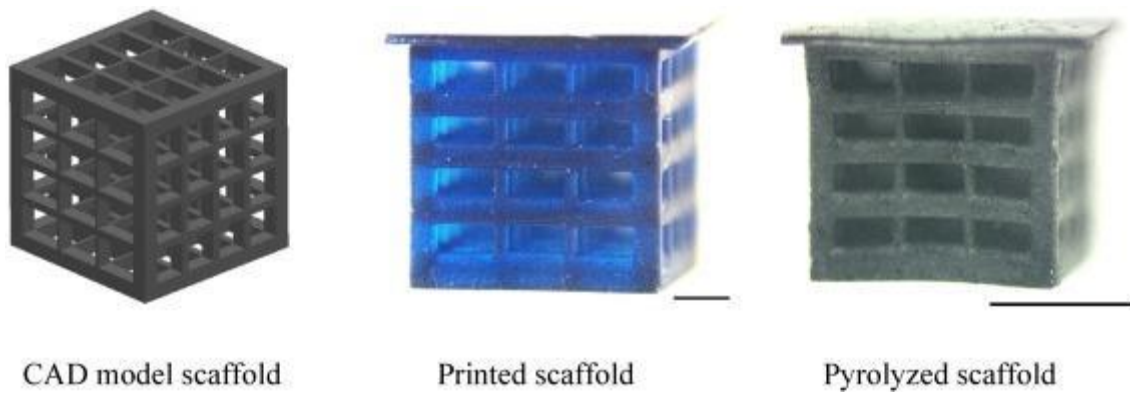


Figure 24: CAD model, printed part and pyrolyzed ceramic part using polysiloxane preceramic polymer [150].

Wang and colleagues manufactured silicon nitride ceramics using DLP with liquid polysilazane preceramic mixed with the commercial resin [151].

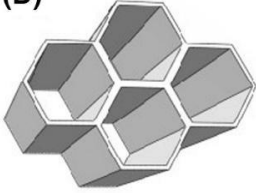
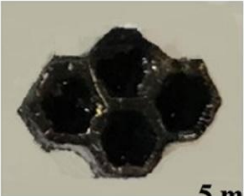
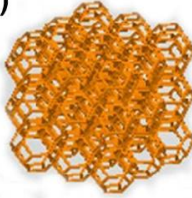
Shape	CAD model	Green body	Pyrolyzed body
Cuboid	(A) 	(B) 	(C)  10 mm
Honeycomb	(D) 	(E) 	(F)  5 mm
Lattices	(G) 	(H) 	(I)  5 mm

Figure 25: CAD models, printed parts and pyrolyzed ceramic components using DLP technique with polysilazane preceramic polymer [151].

Manufacturing of quaternary silicon ceramics such as SiBCN is also possible with DLP based 3D printing as shown by Li and colleagues, where they used polyborosilazane liquid preceramic polymer mixed with photocurable acrylic resin [152].

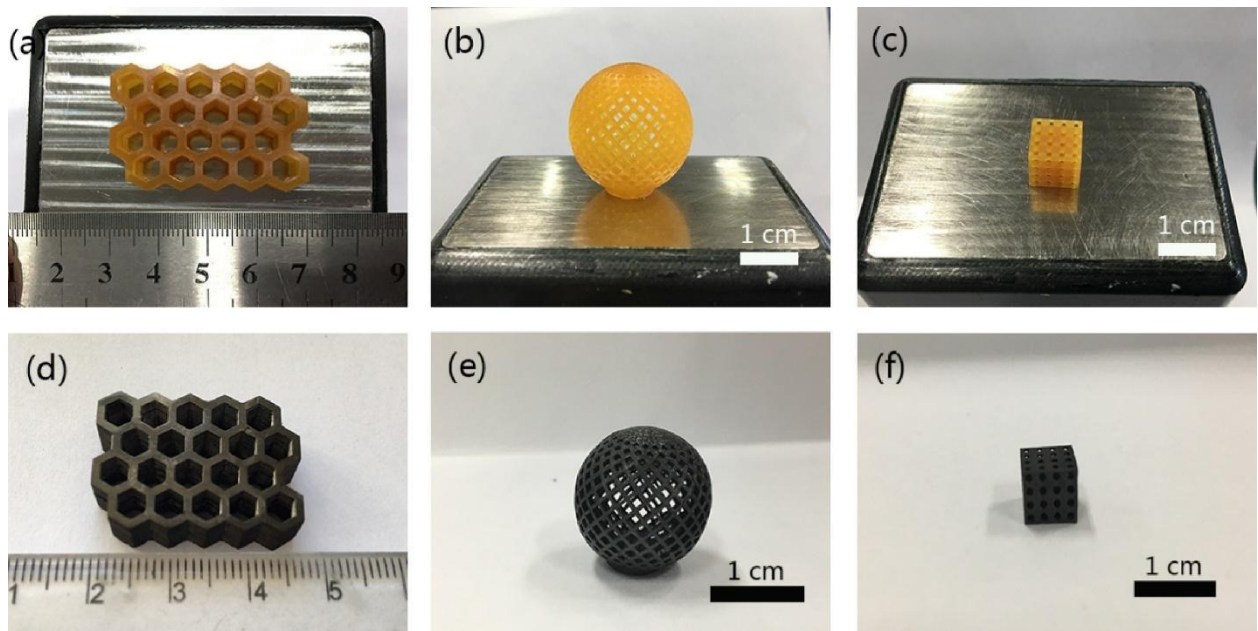


Figure 26: 3D printed and pyrolyzed ceramic components manufactured using DLP technique with polyborosilazane preceramic polymer [152].

The other popular method of additive manufacturing ceramics using preceramic polymers is direct ink writing or DIW. The fundamental concept of DIW with preceramic polymers is, a liquid preceramic polymer is used as a base for the ink and is mixed with a solvent and solid ceramic or preceramic polymer particles used as fillers. The primary requirement of the process is that the ink must have optimum rheology and viscoelastic properties. Various methods can be applied to maintain the ink rheology such as polymer bridging [153]. Once the part is 3D printed, it is followed by the thermal treatment in the inert atmosphere.

Larson et al. [153] reported production of colloidal inks comprising boro-polycarbosiloxane mixed with silicone made into a colloidal dispersion with SiC particles. Toluene is used as a solvent for the preceramic polymers and 2-propanol for the colloidal particles. The excess solvents are then evaporated, and the ink is transformed into a Newtonian fluid. The inks were

then extruded with a syringe 3D printer made from a modified CNC machine with the needles of diameter 330 μm and 250 μm with the layer height of 150 μm .

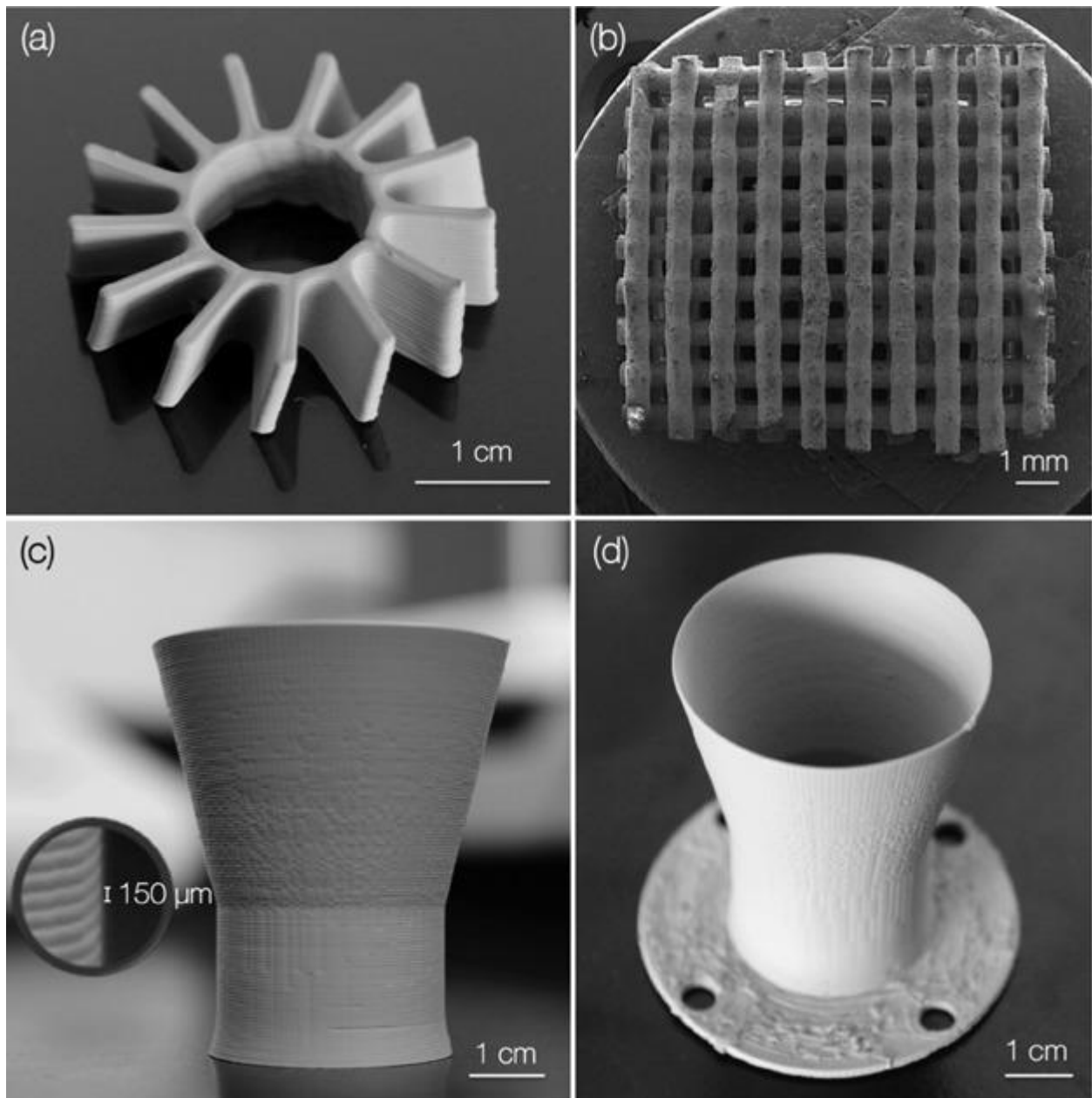


Figure 27: SiC ceramic structures manufactured with direct ink writing. (a) printed turbine fan (b) SEM of sintered lattice structure (c) as printed microwave feedhorn (d) sintered feedhorn [153].

Pierin and colleagues [154] demonstrated fabrication of SiOC ceramic structures using DIW. The research used liquid silicone preceramic polymer doped with already crosslinked particles of the silicone resin. The preceramic polymers mixed with propanol solvent and a catalyst. The ink was then printed using a custom 3 axis 3D printer with 200 μm needle. The printed parts were then heat treated in two stages, first to 200°C to complete the crosslinking of the preceramic polymers in air atmosphere. The heat treatment was then completed to 1000°C, in argon atmosphere [154].

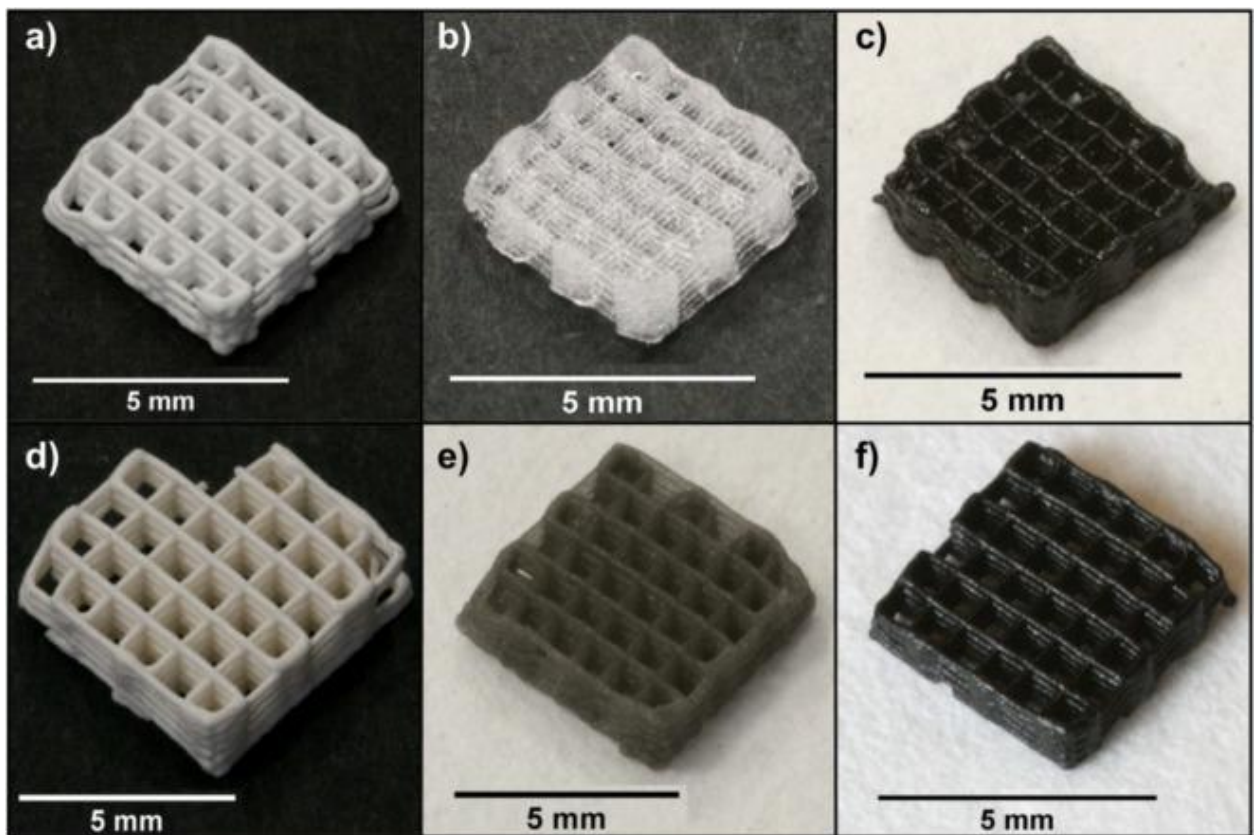


Figure 28: Printed, crosslinked and pyrolyzed ceramic cellular samples with DIW technique [154].

Researchers have also investigated manufacturing of mineral based DIW using inorganic mineral fillers. Zocca and colleagues [155] produced ceramic scaffolds for biomedical applications. The ink for the DIW was produced with isopropyl alcohol as the base solvent.

Powders of polymethylsilsesquioxane preceramic polymer (precursor for SiO_2), ZnO and CaCO_3 were mixed to obtain the $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ (hardystonite) as the final composition of the ceramic. The mixing of the powders was done using ball milling. Fumed silica was also added to control the thickness of the ink produced. The printed scaffolds were then heat treated up to 1200°C in nitrogen flow or static air, for removal of the organic binders and completion of the sintering process.

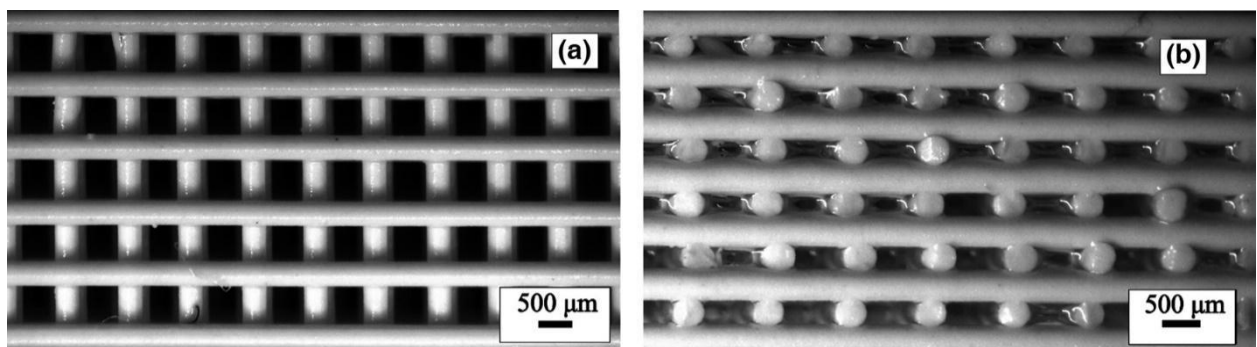


Figure 29: Ceramic cellular structures produced with DIW (a) top view, and (b) side view [155].

Elsayed et al. [156] demonstrated the production of wollastonite-diopside glass ceramic scaffolds. The ink was prepared using isopropyl alcohol mixed with the silicone resin powder and fumed silica for the SiO_2 yield, then mixed with the active oxide fillers CaCO_3 and $\text{Mg}(\text{OH})_2$ in their respective amounts to obtain the wollastonite ($\text{CaO} \cdot \text{SiO}_2$) and diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) composition. Anhydrous sodium pyrophosphate was added as an extra filler. The ink was then extruded using a commercial 3D printer (Powerwasp Evo, Wasp, Massa Lombarda, Italy) modified with a syringe extruder with the nozzle size of 410 microns. The printed structures were then pyrolyzed at 1400°C giving rise to a homogeneous glass structure. The pyrolysis atmosphere can be changed in order to obtain different compositions from the

preceramic polymer. Pyrolysis in non-oxidative atmosphere resulted in SiOC instead of SiO₂ (as in oxidative atmosphere).

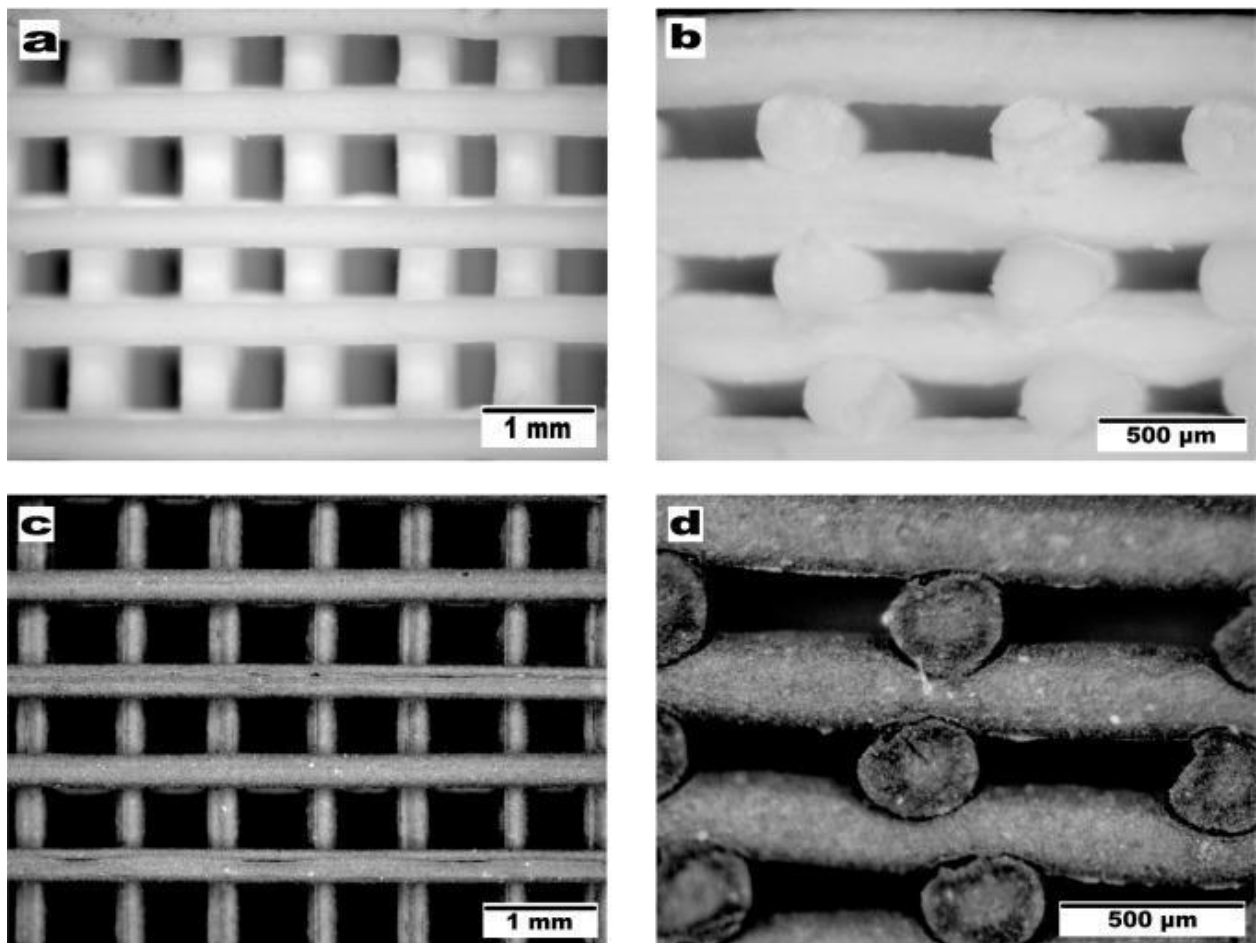


Figure 30: Micrographs of wollastonite-diopside scaffolds (a, b) in air; (c, d) nitrogen (the dark color is due to the presence of residual carbon from the decomposition of the silicone resin [156]).

Binder Jetting

There can be multiple approaches used with binder jetting type of additive manufacturing. One is using solid preceramic powder blends as the base and using organic solvents to fabricate the

structures. The other is using preceramic polymer solutions as binders for the preceramic polymer powder bases.

Zocca and colleagues [157] in their research used polymethylsilsesquioxane preceramic polymer powder as the base with organic solvents. As some sort of binding/ crosslinking is needed while printing, two approaches were discussed. First mixing the crosslinking catalyst with the powder along with the solvent (zirconium acetylacetonate and isopropanol). The solution is then dried and milled again to make the feedstock powder and isopropanol was used as the printing binder. The second easier approach is mixing a liquid catalyst with the binder liquid, which avoids the powder mixing and milling steps. In this case the tin-octoate is directly mixed with 1-hexanol and hexylacetate.

The ceramic components were printed with Voxeljet Teststand VTS 16 (Voxeljet Technologies GmbH, Germany) with 128 jets and blade recoater. The printed parts were left overnight on the printing bed to let the excess solvent evaporate. The green components were then heat treated in two steps. First till 150°C in air to complete the crosslinking process, then to 1000 or 1200°C in nitrogen atmosphere to complete the ceramization.

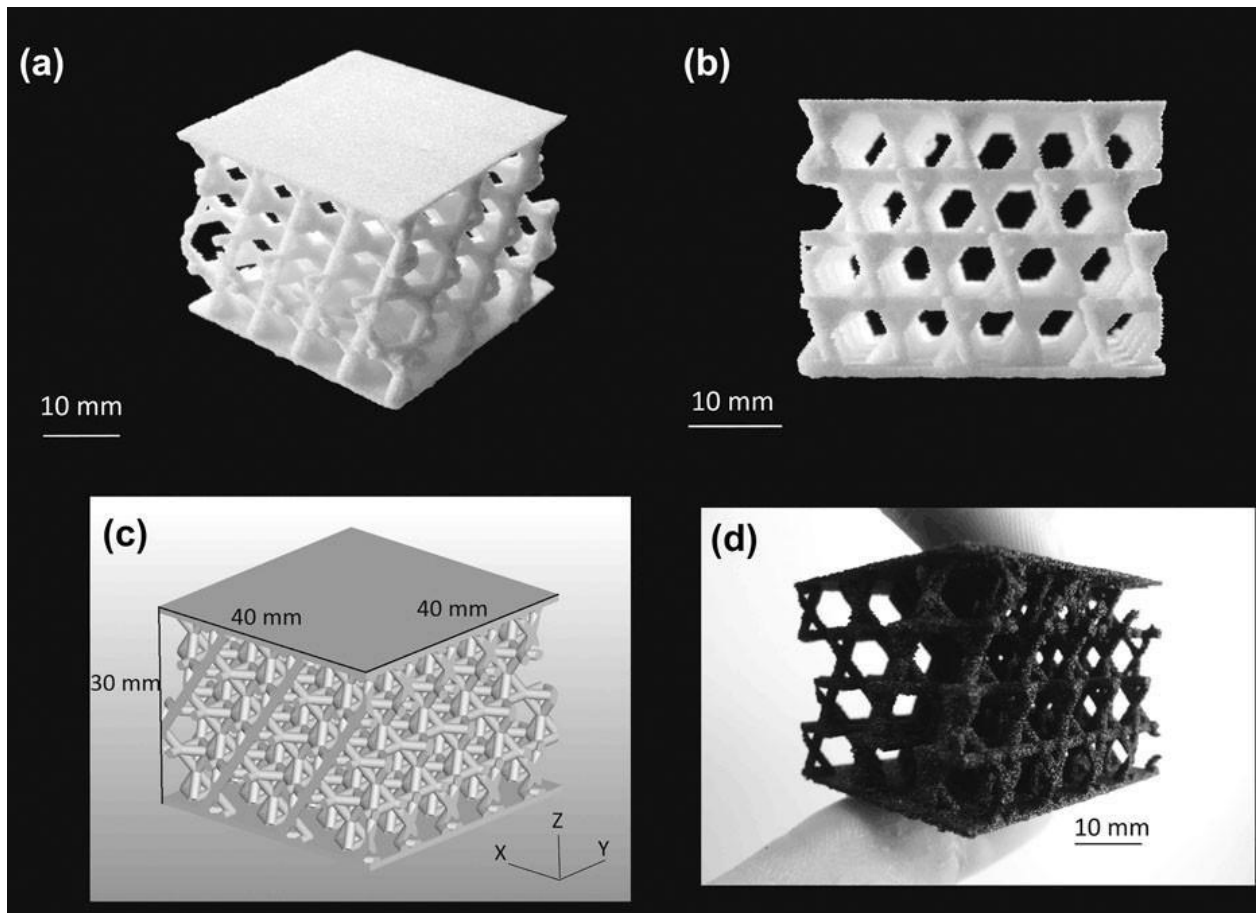


Figure 31: (a) polymer 3D printed printed Kagome structure, (b) front view (c) CAD-model (d) SiOC ceramic structure ceramized at 1200 °C [157].

Zocca and colleagues also demonstrated fabrication of silicate porous ceramics with the same method. Where, along with the preceramic polymer, calcium carbonate powder and a commercial glass powder which results in apatite-wollastonite glass ceramic system was used [158].

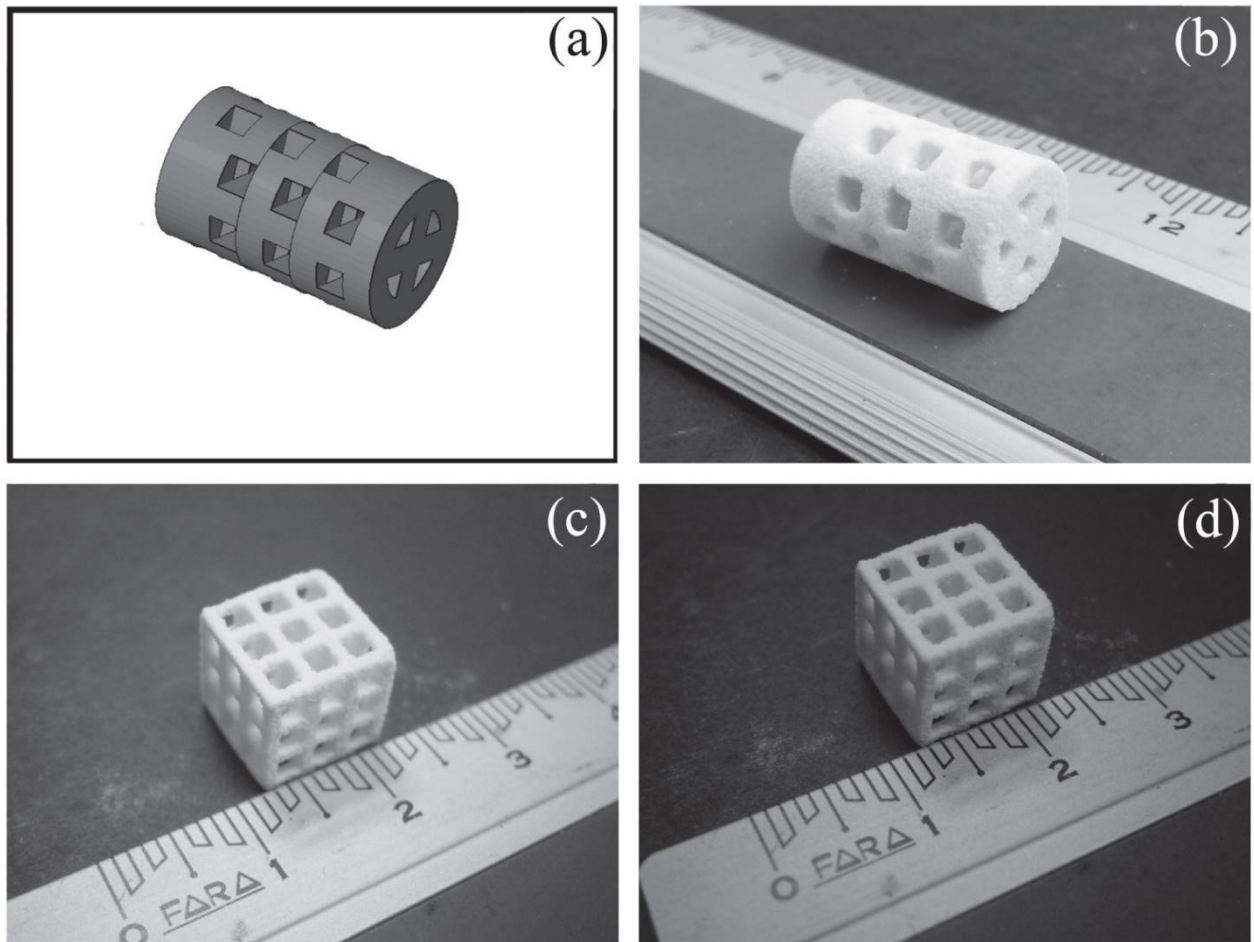


Figure 32: Images of (a) CAD model of a cylindrical porous scaffold, (b) 3D-printed scaffold, (c) HG cubic scaffold after 3D printing and (d) cubic scaffold after heat treatment [158].

Selective Laser Curing

Selective laser curing has been also demonstrated for additive manufacturing of polymer derived ceramics. Friedel and colleagues [159] used polysiloxane precursor powder mixed with SiC as a feedstock with laser curing process to manufacture polymer components. A CO₂ laser was used to cure the polysiloxane preceramic powder at temperatures around 400°C. Then the green part was further treated in inert atmosphere at 1200°C to obtain the final ceramic part of the composition Si-O-C/SiC.

The parts obtained after the sintering/ thermal processing, are porous similar to most of the sintering processes. To reduce the porosity the parts were then infiltrated with liquid silicon at 1500°C. After the infiltration, almost fully dense parts were obtained.

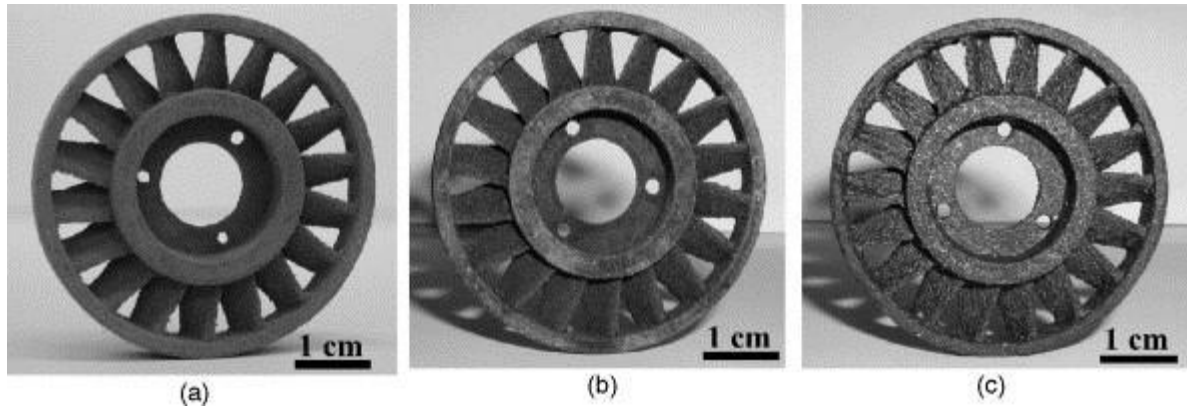


Figure 33: (a) 3D printed part with selective laser curing (b) pyrolyzed part (c) silicon infiltrated part [112].

Sinderlar et al. [160] showcased a similar method using polysiloxane preceramic polymer powder (polymethylsilsesquioxane) loaded with alumina powder as filler. Aluminium-acetylacetonat powder was also added as a catalyst to aid the curing reaction. Polymethylsilsesquioxane has a melting point of 50°C, which is suitable for the laser curing. A 200 W CO₂ laser with 10.6 µm wavelength was used for this step. After this process, the parts were pyrolyzed at 1000°C in nitrogen atmosphere to obtain the final ceramic product. Only 3% shrinkage was observed in the final ceramic part after the pyrolysis step.



Figure 34: A model of a turbine wheel fabricated with selective laser curing and subsequent pyrolysis [160].

1.4 FFF Open-Source 3D printing

‘Open source’ as a concept has been around for more than 30 years. It started with the software community when problems arose from the co-operative development. AT&T wanted to claim UNIX software as their intellectual property, when in reality the software was developed by many researchers coming together[161]. The solution to the problem was to enforce some ground rules for collaborative development. One of the researchers came forward to establish the free software foundation and the GNU project in 1983 [162].

The main thought behind creating the free software foundation was that the people should have more freedom and should appreciate the freedom. Here free does not mean free of cost but the freedom of use, modify and redistribute.

The first open-source license, General Public License (GPL) was also called Copyleft, as a pun on Copyright. Later this led to the formation of Open-Source Initiative and creation of Open-Source Software trademark was created which would let people transfer the work of other people. The open-source definition describes the terms of the open-source license. The main terms state that, with the open-source license, the code/software must be freely redistributable. The source code of the software must be allowed for redistribution. The license must also allow derivatives and modifications and must be redistributed with the same terms [163], [164].

There are several major benefits of open sourcing the licenses. First and foremost is that free distribution leads to innovation development by the communities. As the open-source code is consumed and run completely by and for the users, the feedback loop of deployment and testing is shortened when the users are the developers. This becomes a nonhierarchical process where the conditions always favor the communities who innovate [165], [166].

The success of Open-Source Software was widely appreciated and led to commercial success of many open-source software programs. Similar thought rose in the design and hardware community, and thus began the push for Open-Source Hardware (OSHW)[167]. This led to formation of a similar license/definition of Commons Based Peer Production in 2006. The same methodology of open-source software cannot be imposed on to the OSHW as there are some obvious barriers such as, need for the production of the physical objects. In the case of OSHW a cost is associated with physically producing the product [167], [168].

The main challenges to OSHW were and still are that ~~the~~ it needs a physical product. The designs of the licensed with OSHW need to be validated to close the loop. The community needs a platform to collaborate on physical product innovation to publish a more or less finished design [169].

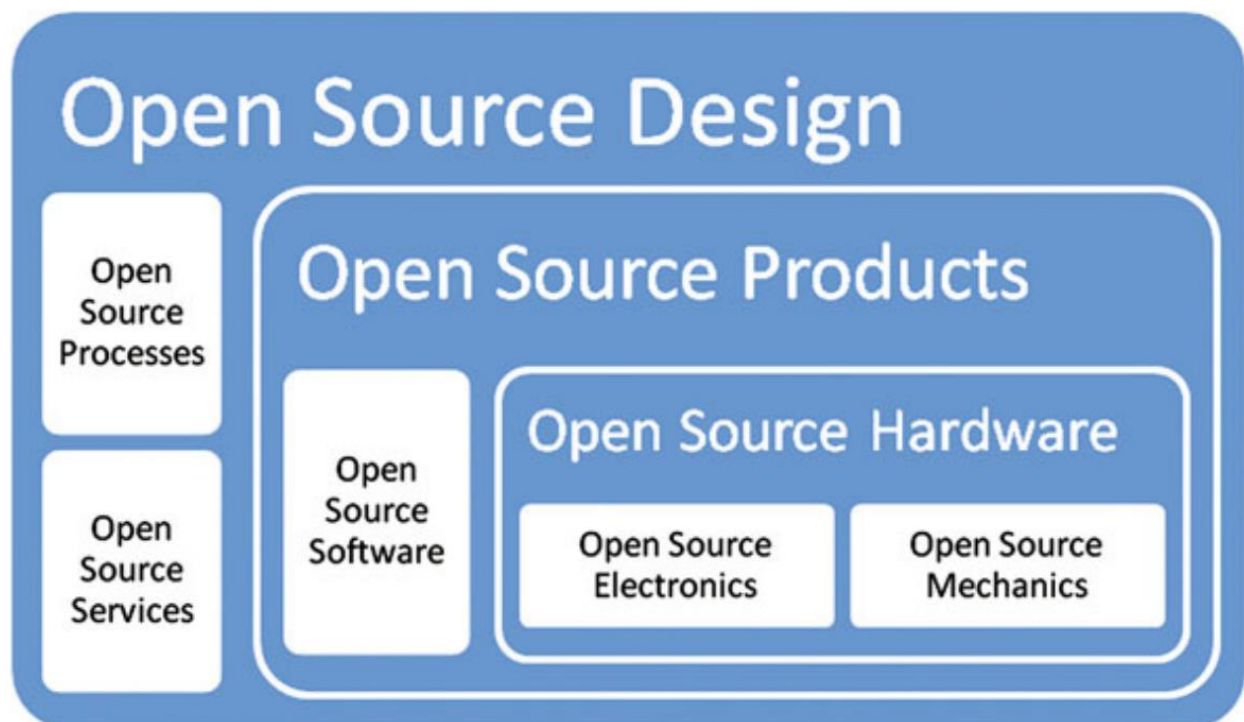


Figure 35: the taxonomy of open-source design [167].

With advances in 3D printing, it became easier to create the designs with a relative ease. But 3D printing itself was a proprietary technology. 3D printing has been around since 1980s. Charles Hull was the first one to try making 3D dimensional objects by curing a liquid resin in a vat with an ultraviolet laser in 1983[170]. He named the process “Stereolithography” and later on founded the first ever 3D printing company – 3D systems[110]. A researcher at the University of Texas at Austin invented a process to sinter metal powder on a bed to create a 3D structure. The method was named “selective laser sintering”[126]. For the filament-based method, S. Scott Crump invented the “fused deposition modelling” method which uses the cartesian system for the movement of the axes and a continuous feed of a polymer filament is dispensed by a heated nozzle. He founded the company Stratasys based on the method and the term FDM was patented and copyrighted [171]. Initially 3D printing was only thought of as ~~only~~ as a supply not a standalone production system. With the revolution in the consumer product design, advancements in the manufacturing technologies were being made rapidly but they were locked by intellectual property. At one point the development ran into a bottleneck where the capitalism pushed every new technology to be made proprietary which made the products expensive as a result. The best 3D printers in 2005 sold for more than 2 million dollars [172].

The innovation in the domain of 3D printing and design was continuing in the background. Research institutes in Belgium were focusing on using 3D printing for biological applications such as medical equipment and prothesis. Netherlands created “Shapeways” a platform for sharing 3D printed designs and to promote the general public to utilize 3D printing [172].

In 2005, Adrian Bowyer a mechanical engineering professor at the University of Bath in England started developing a 3D printer based on a similar technology to FDM and started documenting and blogging the creation. He called it the RepRap, short for “replicating rapid

prototype” where almost 50% of the 3D printer itself was 3D printed. Since the term FDM was patented and copyrighted, he labeled the new method as Fused Filament Fabrication (FFF). The whole project evolved as an Open-Source 3D printing project. He thought of the RepRap as a self-evolving project [101], [173].

Since the design for the RepRap is publicly available, more than 15 companies have started commercially selling 3D printers based on the design. The first one to start was Makerbot in 2009. With the growth of the OSHW platform and expansion of the market 3D printers have become increasingly cheaper. A 3D printer of the size of 30 x 15 x 15 cm printer costed \$2200 in 2014 (MakerBot Replicator 2), and in 2022 you can purchase printer with the print volume 25 x 22 x 22 that costs only \$200 (Creality Ender 3) [174], [175]. This evolution was possible because of the open-source movement, which removed the barriers from the intellectual property and the boost in the innovation sector that came with it.

The RepRap was made with the self-reproduction in mind. It had a design similar to the FDM where the filament of a polymer material was fed through a heated chamber and then extruded through a nozzle to deposit material on a bed. Like a CNC it was based on a 3-axis setup and was controlled easily using computer software. Most of the structural components of the RepRap were designed so that they can be manufactured with the 3D printer itself.

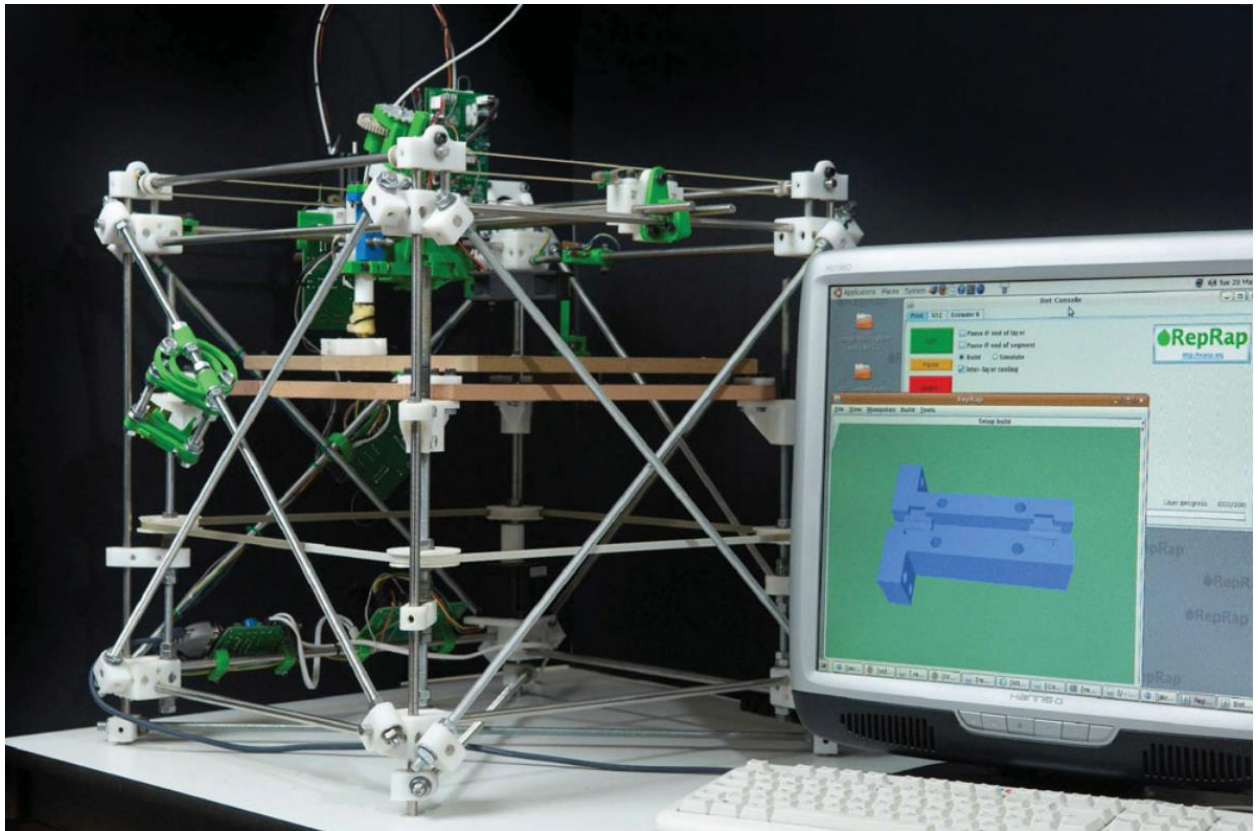


Figure 36: The version I of the RepRap machine [101].

This crude and simple design evolved through stages and now we have 3D printers based on the same concept with sophisticated functions like automatic bed levelling, automatic nozzle cleaning, filament runout sensors, high precision belt drives, hot ends with the ability to print various polymers with melting points up to 400°C and high precision nozzles with diameters up to 100 microns[176].

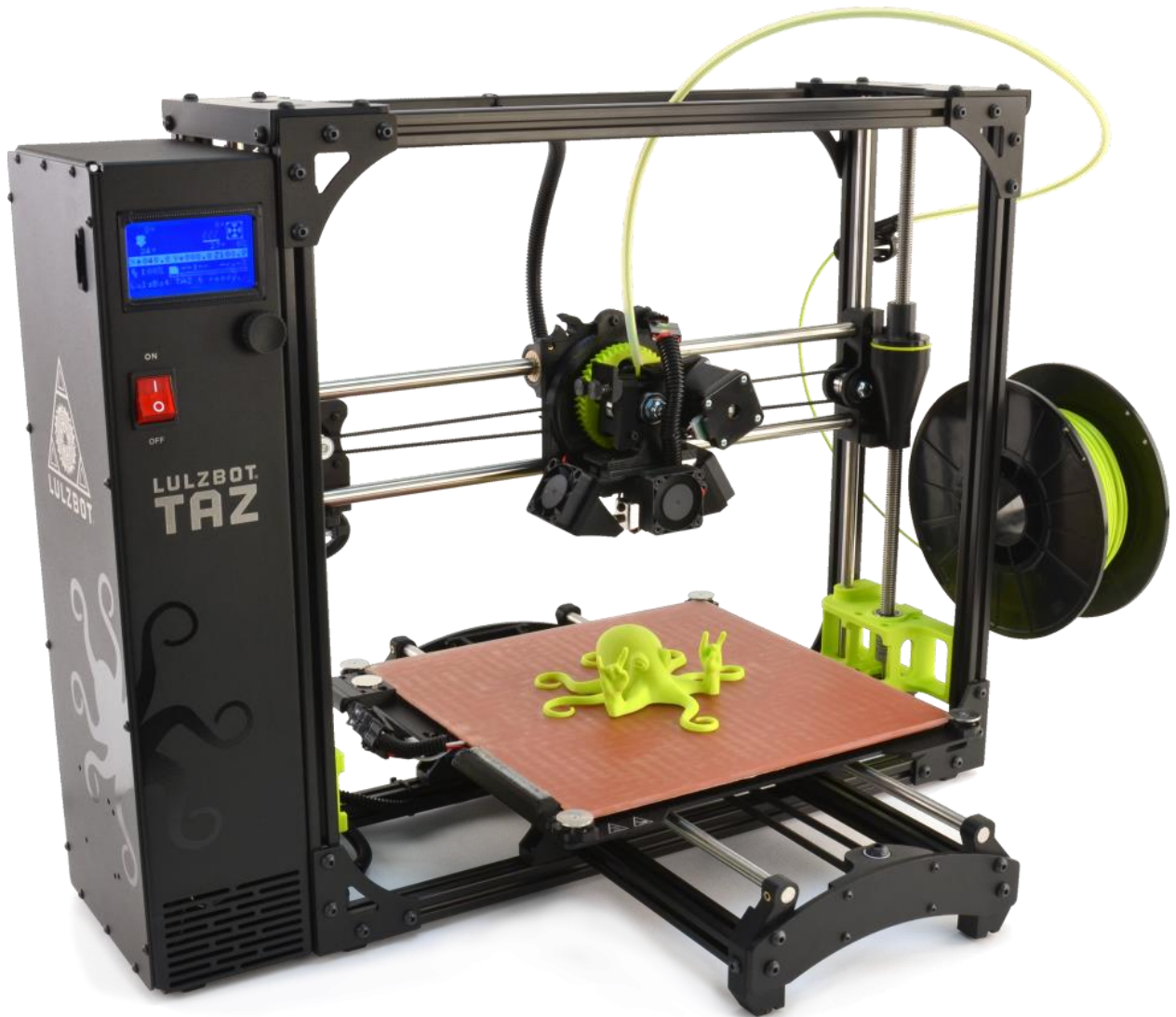


Figure 37: Lulzbot TAZ 6 3D printer (Fargo additive manufacturing) with automatic bed leveling and nozzle cleaning mechanism used in this project (lulzbot.com)

With the rise of open-source 3D printing and fall of prices, the open-source 3D printers offer incredible return on investment. Even a 3D printer bought for personal use can recover its cost between one and three years of ownership by printing various parts for home use [177], [178].

With the increased accessibility of 3D printers because of the RepRap project and open-source hardware, things like research equipment, medical hardware can be manufactured at a fraction of the cost [179], [180]. During the pandemic the open-source community came together to produce 3D printed ventilators and face shields [181].

The open-source hardware and 3D printing approach can be utilized to bring down costs for many other applications.

1.5 Scaffolds for bone regeneration

Bones, like most other body organs, heal themselves. However, some defects exceeding a critical size which may be caused by congenital or acquired pathologies, serious trauma and infections cannot be healed by the body. External intervention by surgical methods is needed in cases like this to aid the healing and regeneration process using substitute materials. In terms of tissue transplants, bone is considered the second most transplanted tissue [182].

The best possible option for such kind of substitute material is using the bone grafts patient's own body i.e., autografts. One of the main limitations to autografts as to how much of the healthy bone you can remove from the patient's body which requires a second surgical site. This comes with morbidity and possibility of infection and pain [183]. The other option is to use allografts, which are, tissues harvested from cadavers or living sources. But it comes with the downside of potential disease transmission and adverse immune response [184]. It can also result in uncertain bone resorption in the body and without the tissue being fully converted into

the bone. This might cause the repair to not be complete and the body to not regain the full strength at the site of the damage.

The viable option in this case is tissue engineering or tissue scaffolding. Until the 1970s, the method was to seed cartilage cells into bone spicules. Tissue engineering emerged in the 1990s to substitute bone grafting. The approach is to use a porous biodegradable scaffold material to transplant biofactors. The biofactors consist of stem cell and gene therapy methods, which eventually aid and stimulate tissue repair. Compared to allografts and autografts, bone tissue engineering might be able to provide a better solution in terms of superior mechanical properties, causing less stress shielding and decreasing vascular insult [185].

Bone is a complex tissue made of hierarchical architecture, formed by different components. The primary composition of bone is a composite of hydroxyapatite and type 1 collagen. There are two main parts of the bone: Cancellous bone and Cortical bone. Cancellous bone forms the internal part of the bone which is the porous structure. It contains the bone marrow abundant with stem cells. Cortical bone surrounds the cancellous bone forming the outer shell, which gives the bone its form [186], [187].

The scaffold should possess some particular characteristics in order to be ideal for bone tissue regeneration. The scaffolds should be biocompatible for the selected system and biodegradable. The material of the scaffolds should not produce toxic products upon degradation. The scaffold material should not promote any inflammatory response or any adverse immune response. The material should also be non-cytotoxic, meaning it should not kill the cells. The scaffolds should

also have osteoinductive and osteoconductive properties which aid in the diffusion of the osteoinductive elements and also help in the differentiation of cells [188].

The scaffolds should have a highly porous 3D architecture with interconnected porosities. The porosities in turn allow cell and nutrient diffusion, mitigation, and invasion of vasculature [189], [190]. It is even better if the pore size can be tailored for the targeted tissue and the cells, as the size of the pores and the density significantly affect the cell adhesion and proliferation [191], [192]. It has been showcased that the Bone Morphogenetic Proteins (BMP) induced osteogenesis was highly dependent on the geometry of the scaffolds. The scaffolds can be categorized into three types - bone inducing, cartilage inducing, and bone cartilage inducing. The pore size between 300-400 microns induced the bone formation directly and smaller sizes 90-120 microns induced cartilage formation first and then converted to the bone. Therefore, the optimal porosity for the bone forming was found to be 300-400 microns [193], [194].

Along with the porosity, the scaffolds should also have similar mechanical properties to the bone which the scaffold is to be implanted in. Since porosity can act against the mechanical strength, the scaffolds must have the right balance of porosity and the mechanical properties [195], [196]. Some researchers have shown that the best possible properties for the scaffolds would be comparable to that of the cortical bone. Where the ideal porosity would be around 60-90% pore size greater than 150 microns [197]. The scaffolds should have Young's modulus of 7-30 GPa with compressive strength of 100-230 MPa along the longitudinal axis and a tensile strength of 50-151 MPa [198]–[200]. Undesirable mechanical properties of the scaffolds can lead to undesirable results during osteogenic differentiation; thus it is preferable to have scaffold materials with properties similar to the bones themselves [201]–[203].

Different materials can be considered for scaffolds, such as - hydrogels, polymers, metals, bioactive glasses, and ceramics. Each of these materials have their own advantages and disadvantages. While natural polymers offer good biocompatibility and low toxicity, they lack load bearing strength and other mechanical properties. Synthetic polymers can be tailored to have better mechanical properties, but at times they are hydrophobic which results in poor cell adhesion [204]–[206]. Hydrogels are another option because of their high water content. They can be 3D printed to mimic the tissue architecture. The release of growth factors can also be controlled. But they have poor mechanical properties and loading each and every cell can be difficult [198], [207]–[209]. Metals have excellent mechanical properties and superior strength, and it can be advantageous in the case where the bone growth is slow providing the mechanical support [210], [211]. But the difference in the modulus of the bone and metal scaffold can lead to stress shielding. Also, release of metal ions can cause some local toxicity [212]. Bioactive glasses as described in the name are bioconductive and bioinductive and they are adapted for prosthetic use already [213]. But they are inherently brittle and the manufacturing of the prosthesis with exact shapes and architecture can be difficult [214], [215]. There is also the possibility of releasing the toxic metal ions.

Ceramics on the other hand are osteoinductive and osteoconductive allowing strong integration with the host tissue. Similar composition and architecture to the bone tissue can be obtained by 3D printing [216]. Even though they can be hard and brittle when used alone, when seeded with the tissue they provide optimum mechanical support [217]. The only downside is that there can be irregularities in the degradation and resorption rates, but it can be tackled with using composites [218].

Now, there are many manufacturing processes used to produce the scaffolds like solvent casting, gas foaming, phase separation and emulsification freeze drying, but the most popular one is 3D printing since it provides the flexibility of manufacturing different size, shapes and pore architectures of the scaffolds [219]–[223]. This results in a better capacity to incorporate the vascular structures into the scaffolds.

The ceramic scaffolds can be manufactured by various 3D printing methods such as, selective laser sintering (SLS) [224], [225], stereolithography (SLA) [226], binder jetting, material jetting, etc. The simplest of them all is material extrusion or fused filament fabrication (FFF) [227], [228]. Direct extrusion of ceramics is limited to a certain kind of materials which can be made into slurries or inks/gels. Even then the resolution and details obtained are not the greatest. Polymer FFF on the other hand is very evolved and resolutions up to 100 microns can be achieved.

Silicon based ceramics for scaffolds have certain advantages over other materials. Silicon possesses similar properties as phosphorus since it falls adjacent to it in the periodic table. It performs similarly to phosphorus when it comes to bone formation and development [229]. Previous research has shown that some of the osteogenesis related genes like ALP, BMP-2, Col I, are controlled by silicon [230]. Silicon also contributes to the promotion of early deposition of apatite, the growth of osteoblasts, and also some genes which control induction of cell cycles and progression which enhance osteogenesis [231]. Enhanced apatite mineralization ability, biocompatibility, and bioactivity is also seen. A significant increase in expression of angiogenic factors of BMSCs, osteogenic genes and alkaline phosphatase activity was seen due to the presence of silicon [232], [233].

1.6 Replica method

The replica method of producing ceramic foams has been demonstrated with impregnation of polyurethane foams with preceramic polymers. Regular polyurethane (PU) foams are dipped in a preceramic polymer solution with a solvent and a catalyst, where the solution is impregnated into the structure of the foams. The foams are then dried and pyrolyzed in an inert atmosphere to obtain ceramic replica of the PU foams.

Nangrejo and colleagues [234] showcased the replica method of PU foams by immersing them into a polysilanes precursor solution mixed with Si_3N_4 powders. The polysilanes precursors were synthesized starting from chlorinated silane monomers by alkali dechlorination. The obtained silanes were then mixed with Si_3N_4 powder (0.4g polymer + 2ml of dichloromethane mixed with 0.1g Si_3N_4 powder). The foams were then soaked in the suspension for 2 hours and dried overnight before pyrolyzing in the nitrogen environment. The percentage of the Si_3N_4 powder and the pyrolysis temperature was varied to assess the shrinkage of the foams after ceramization.

The weight loss of the ceramic increases as the pyrolysis temperature is increased from 1100C to 1500C with a very high increase between 1400 and 1500C. With the increase in the percentage of the Si_3N_4 powder in the composite, the shrinkage is reduced considerably but some cracks and defects start to occur as a result of the addition of Si_3N_4 .

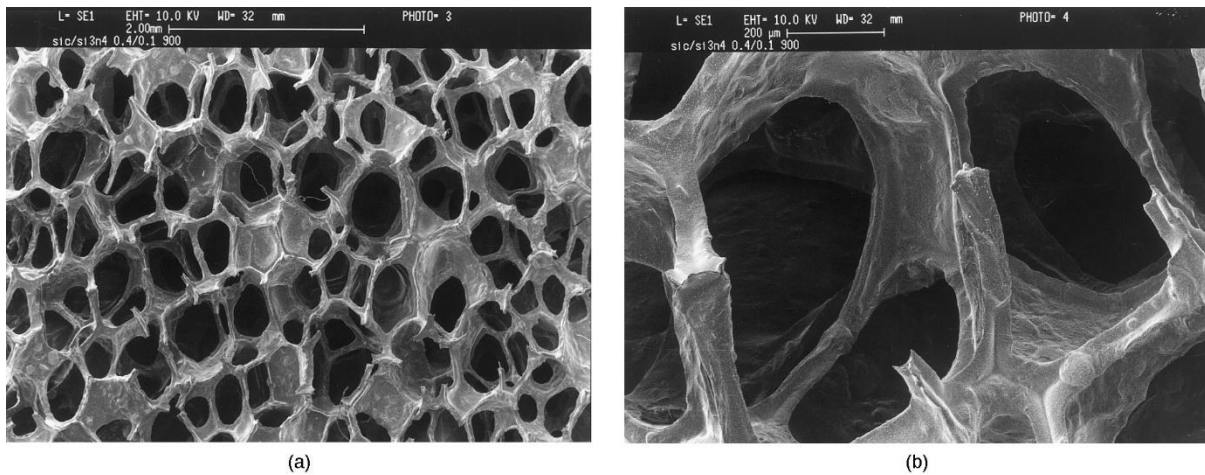


Figure 38: SEM images of the SiC-Si₃N₄ foams (polysilane/Si₃N₄ = 80/20 wt%) produced after pyrolysis at 900C [234].

Another similar experiment was performed by Nangrejo and colleagues [235], which demonstrated the production of composite ceramic foams by mixing polysilanes precursors with Si₃N₄ and TiC powders. The percentage of the powders was varied from 10 to 80% along with the change in the pyrolysis temperature. The results suggested the foams can be produced with 85 to 96% porosity when pyrolyzed at 1500C. With the increase in the amount of additives the shrinkage seemed to decrease. The particle size also affected the volume shrinkage as when the particles are more homogeneous and smaller in size, they blend in easier with the preceramic polymer solution and result in lower shrinkage values.

Compression testing performed on the ceramic foams of the porosity 85 to 96% resulted in the compressive strength of 1.1 to 1.6 MPa.

One key thing to note from the experiments by Nangrejo and colleagues is that the researchers did not explore the possibility of chemical interaction between the preceramic polymer and the PU foams which was later discovered in other experiments.

Soraru and colleagues [236] demonstrated that impregnating waste PU foams with polysiloxane preceramic polymer with a platinum catalyst and acetone solvent produces replica ceramic foams with dense struts after pyrolysis. The porous ceramic structures produced with these methods offer a very high porosity with high surface to volume ratio.

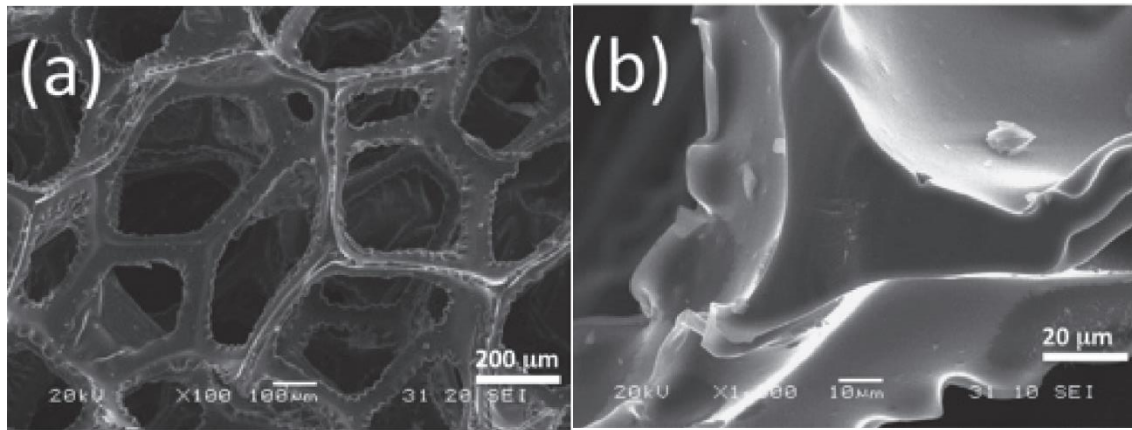


Figure 28: Cross sections of ceramic foams fabricated with the replica and impregnation of PU foams [236].

Replica method with 3D printed cellular components has also been demonstrated by Ortona and colleagues [237]. A cellular structure was printed using a stereolithography machine (Eden 260V, Object Ltd., Israel). The printer used 2 proprietary resins, one for the cellular structure and the other for the support between the cells which can later be removed. The primary resin was composed of acrylate-based polymers and the secondary resin was composed of acrylates mixed with polyethylene-glycols. After the part was printed the secondary resin was removed with water jet. The cellular structure was then coated with a slurry of a proprietary composition mainly consisting coarse and fine α -SiC powders, and a polymeric binder. The structure was then pyrolyzed at 1000C in argon atmosphere for 1 hour. The resulting cellular ceramic structure was left with an empty volume at the core of the struts where the 3D printed polymer was present. It also contained residual carbon and micro-porosities left by the decomposition

of the binder in the slurry. The structure was then infiltrated with liquid silicon by placing it on graphite plate painted with boron nitride and silicon flakes. The infiltration procedure was performed at 1500 under 10^{-2} mbar pressure for 1 hour. This resulted in struts with dense cross section of Si-SiC composition.

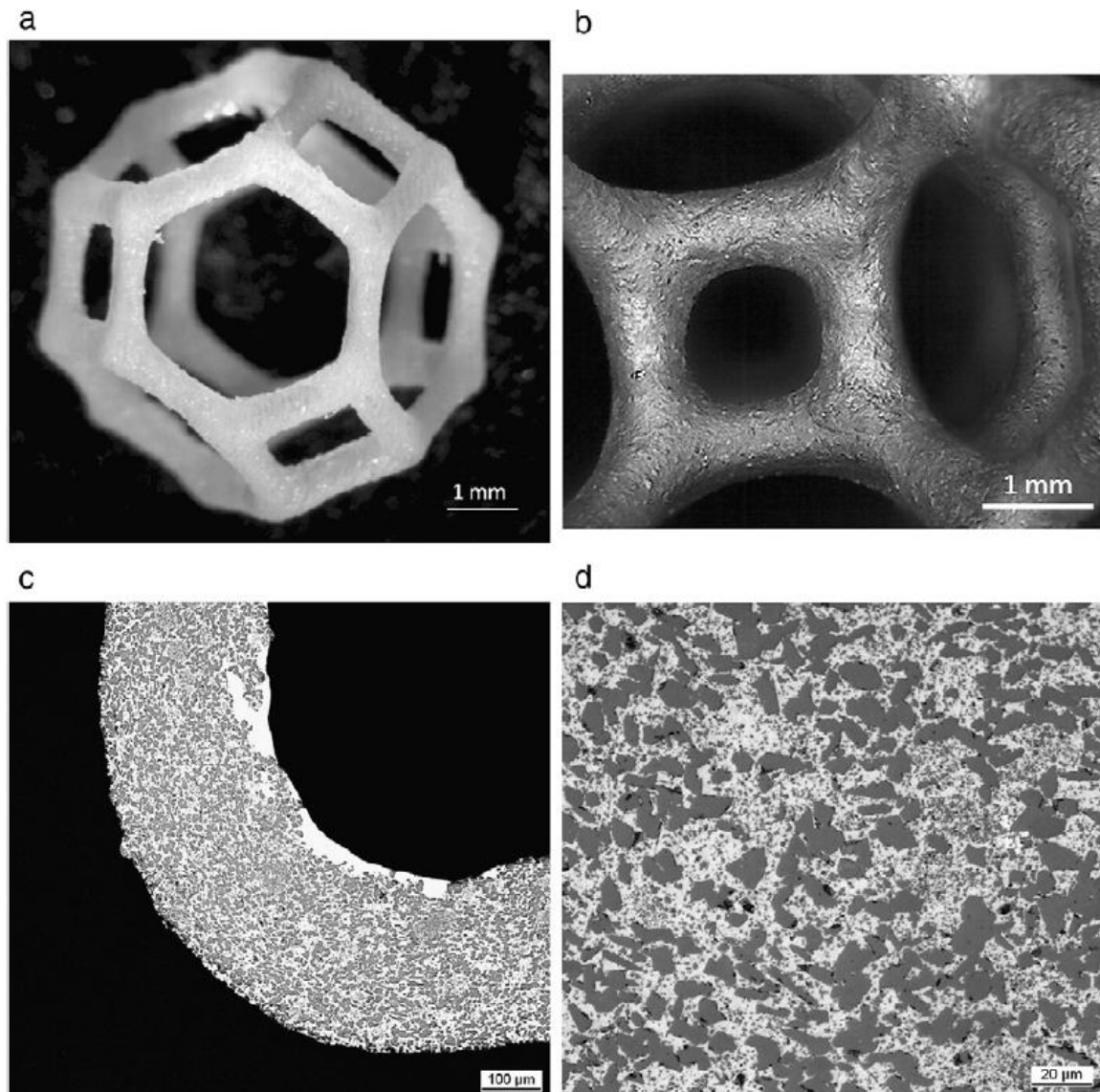


Figure 39: (a) polymeric 3D printed structure (b) pyrolyzed and silicon infiltrated structure (c) and (d) cross section of the ceramic struts showing the Si-SiC composition [237].

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Chapter 2

Polymer-derived SiOC Replica of Material Extrusion-based 3D Printed Plastics

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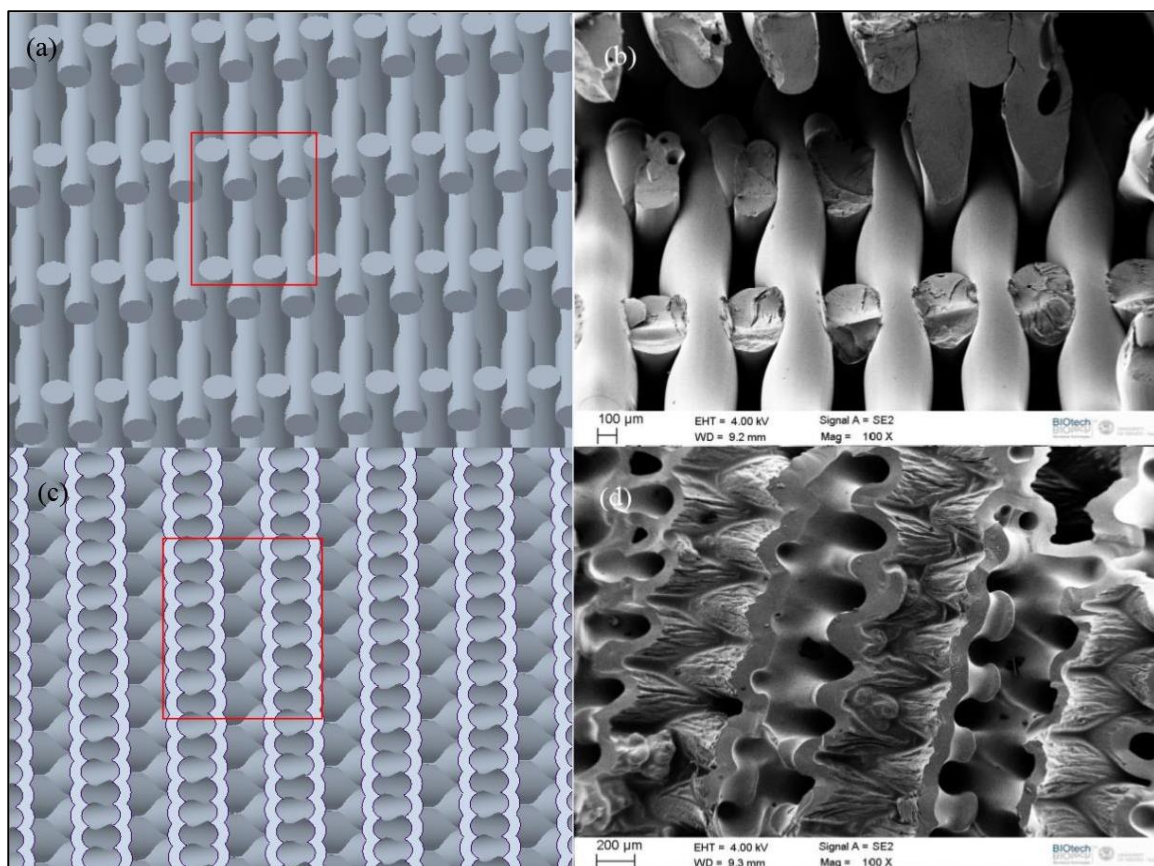
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Graphical Abstract



Abstract

A promising method for obtaining ceramic components with additive manufacturing (AM) is to use a two-step process of first printing the artifact in polymer and then converting it to ceramic using pyrolysis to form polymer derived ceramics (PDCs). AM of ceramic components using PDCs has been demonstrated with a number of high-cost techniques, but data is lacking for fused filament fabrication (FFF)-based 3-D printing. This study investigates the potential to use the lower-cost, more widespread and accessible FFF-based 3-D printing of PDCs. Low-cost FFF machines have a resolution limit set by the nozzle width, which is inferior to the

resolutions obtained with expensive SLA or SLS AM systems. To match the performance a partial PDC conversion is used here, where only the outer surface of the printed polymer frame is converted to ceramic. Here the FFF-based 3-D printed sample is coated with a preceramic polymer and then converting it into the corresponding PDC sample with a high temperature pyrolysis process. A screening experiment is performed on commercial filaments to obtain ceramic 3-D prints by surface coating both hard thermoplastics: poly lactic acid (PLA), polycarbonate (PC), nylon alloys, polypropylene (PP), polyethylene terephthalate glycol (PETG), polyethylene terephthalate (PET), and co-polyesters; and flexible materials including: flexible PLA, thermoplastic elastomer and thermoplastic polyurethane filaments. Mass and volume changes were quantified for the soaking and pyrolysis steps to form a hollow ceramic skin. All 3-D printing materials extruded at 250 microns successfully produced ceramics skins of less than 100 microns. Details on the advantages and disadvantages of the different 3-D printing polymer precursors are discussed for this processing regime.

The results are analyzed and discussed in order to provide guidance for more widespread application of additive manufacturing of PDCs.

Keywords: polymer derived ceramics, additive manufacturing, 3D printing, fused filament fabrication, ceramics

2.1. Introduction

Ceramic additive manufacturing (AM) is now well established and has been demonstrated with several technologies including: selective laser sintering (SLS) [1,2,3], stereolithography (SLA) [4], laminated object manufacturing (LOM) [5,6], direct ink writing (DIW) [7], binder jetting [8], directed energy deposition (DED) [9] and material (paste) extrusion [10,11].

Each of these methods has inherent challenges. SLS using powder substrates, results in low-density parts, and uses high energy densities requiring sophisticated laser equipment, which is costly [12]. Even though ceramic SLA provides high resolution, the cost of the feedstock (i.e. ceramic particles mixed with photocurable polymer) is high [13]. In LOM, decubing is the most difficult task as the ceramic parts can be severely damaged during this step as cutting occurs through strong and weak interfaces of ceramic and the adhesive [14]. The parts also need finishing after decubing that adds to the cost of the process [14]. Optimizing the rheology and in turn the layer uniformity is challenging in DIW [15]. Binder jetting is a multistep process where the binder needs to be removed from the manufactured part and it needs to be post processed to increase the density. The post-processing step can include sintering or isostatic pressing, which increases the total processing cost and time as well as the capital cost of the equipment [16]. DED of ceramics is difficult as it requires the feedstock to be heated to form a molten pool to fuse into the previous layer, which is a challenging physical process for many ceramics. In addition, DED requires a slow deposition rate increasing the build time of the process [17]. Finally, even though ceramic paste extrusion is inexpensive, it limits the resolution of the extrusion and the ability to manufacture complex geometric shapes due to rheological properties of the paste [18]. In addition, paste extrusion is hampered by drying of the paste inside the nozzle obstructing the extrusion and curling of the extruding paste [19]. Most detrimentally, cracks can also be introduced while drying the deposited paste compromising the mechanical properties of the part [20].

One approach that can enable AM of ceramics is to use the polymer pyrolysis route also known as polymer derived ceramic (PDC) route. It uses a two-step process of first printing the artifact using a polymer (preferably a preceramic polymer) AM (a much more mature AM material system that is now widespread among even consumers [21,22,23]) then converting the 3-D

printed structure into the polymer derived ceramic object via high temperature pyrolysis in controlled atmosphere. The PDC approach has many advantages compared to the conventional ceramic powder processing methods such as the lower processing temperatures, higher resolution and the possibilities to process multicomponent and multifunctional ceramic systems. [24,25,26,27].

AM using PDCs has been demonstrated with powder based SLS, SLA and DIW [28,29]. DIW was effective using a solution of isopropyl alcohol and silicone resin powder [30]. A similar study was conducted to manufacture SiOC ceramics with ordered porosity [31]. SiOC ceramic microcomponents have also been manufactured with SLA by using photosensitive preceramic polymers and LED curing technology [32]. PDC parts were also manufactured by laser curing of SiC mixed with polysiloxane [33]. The primary challenges with 3-D printing ceramics using DIW are controlling the rheology of the ink mixture and stability of the deposited part, while with laser curing and SLA are inhibited from widespread adoption by the required expensive equipment. However, the most widespread form of AM is fused filament fabrication (FFF)-based 3-D printing made possible by the open source release of the self-replicating rapid prototyper (RepRap) project [34,35,36]. There is a dearth of knowledge on the potential for FFF-based 3-D printing to fabricate ceramic components using the PDC method.

To fill this knowledge gap and overcome the above-mentioned challenges this study investigates the potential to use the lower-cost, more widespread and accessible FFF-based 3-D printing of PDCs. Low-cost FFF machines have a resolution limit set by the nozzle width, which is much larger than the resolutions obtained with expensive SLA or SLS AM systems. To match the performance of more expensive and less accessible machines an FFF 3-D printed structure is replicated by coating and pyrolysis where the 3-D printed structure is coated with preceramic polymer. During pyrolysis, the organic 3-D printed polymer is decomposed, and

preceramic polymer is converted to ceramic resulting in a high-resolution structure. A screening experiment is conducted based on earlier work replicating polyurethane foams [37] and 3-D printed lattice with acrylic resin with SLA [38]. The PDC replica of a 3-D printed polymeric structure can, in principle, be possible if the pre-ceramic polymer swells and coats the struts of the organic polymeric structure. In this case the resulting ceramic object will have dense struts as in the case of the ceramic foams obtained from the impregnation of polyurethane foams. If the pre-ceramic polymer mainly coats without swelling the struts of the 3-D printed object then the resulting porous ceramic object will have two interconnected porosity channels, one originating from the decomposition of the organic polymer and the other one due to the porosity between the original 3-D printed polymeric struts.

In the present work we report the results of screening experiments conducted using the following commercial filaments both from the hard (poly lactic acid (PLA), polycarbonate (PC), nylon alloys, polypropylene (PP), polyethylene terephthalate glycol (PETG), polyethylene terephthalate (PET), and co-polyesters) and soft flexible (flexible PLA, thermoplastic elastomer and thermoplastic polyurethane filaments) thermoplastic materials.

In this experiment, samples were 3-D printed from filament materials, soaked in a preceramic polymer solution, dried at room temperature and then pyrolyzed to obtain a ceramic frame. Samples were characterized with scanning electron microscopy (SEM) to image and quantify the resultant 3-D hollow structures.

The results are analyzed and discussed in order to provide guidance for more widespread application of additive manufacturing of PDCs.

2.2. Materials and Methods

The following filaments material (with suppliers) were tested: PLA (Ultimaker), Polycarbonate (eSUN), Ally 910 (Taulman), PETG (eSUN), t-glase (Taulman), Inova 1800 (Chromastrand), nGen (Colorfabb), polypropylene (Verbatim), n Gen Hard (Colorfabb) PRO series TPU (Matterhackers), Pro series TPE (Matterhackers), nGen Flex (Colorfabb), NinjaFlex (NinjaTek), PORO-LAY LAYFOMM 60, RUBBERLAY SOLAY, Flexfill 98A (Fillamentum), Flexsolid (Madesolid), PCTPE (Taulman), and SoftPLA (Matterhackers). The filaments were 3-D printed on a Lulzbot TAZ 6 (Aleph Objects) using an E3D SL 0.25mm extruder and standard 0.5 mm extruder using the parameters summarized in Table 1 for hard thermopolymers and Table 2 for flexible thermopolymers.

The samples were designed as 10mm × 10mm × 10mm cubes in OpenSCAD 2015.03. The cubes were then prepared as a mesh with line type infill and 40% infill density (distance between two lines is 625 microns) using Cura Lulzbot 3.6.3 open source slicer.

Table 1: List of hard thermoplastic filaments and their printing parameters

Hard								
Filament	PLA (Ultimaker)	Polycarbonate (eSUN)	Alloy 910 (Taulman)	PETG (eSUN)	t-glase PETT (Taulman)	Inova 1800 (Chroma strand)	Polypropylene (Verbatim)	nGen (Colorfabb)
Color	Clear	Black	Natural	Clear	Blue	Red	Clear	Green
Printing Temperature upper limit (°C)	210	290	260	245	230	240	260	240
Printing Temperature lower limit (°C)	180	250	250	220	210	230	230	220
Bed Temperature (°C)	55	120	55	55	60	50	print on polypropylene tape	85
Printing Speed (mm/sec)	40	30	45	17	22	35	15	55
Bottom layer print speed (mm/sec)	15	15	15	15	10	15	15	15
Layer height (mm)	0.2	0.25	0.2	0.2	0.2	0.2	0.25	0.2
Bottom layer height (mm)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Nozzle diameter (mm)	0.25	0.5	0.25	0.25	0.25	0.25	0.5	0.25

Table 2: List of soft flexible thermoplastic filaments and their printing parameters

Flexible										
Filament	PRO Series TPU (Matterhackers)	PRO Series TPE (MatterHackers)	nGen Flex (ColorFabb)	NinjaFlex (Ninjabot)	PORO-LAY LAY-FOMM 60 Porous Filament	RUBBERLAY SOLAY Elastic Filament	Flexfill 98A (Fillamentum)	FlexSolid (Madesolid)	PCTPE (Taulman)	Soft PLA (Matterhackers)
Color	Blue	Red	Dark Grey	Green	White	White	Black	Black	Natural	White
Printing Temperature upper limit (°C)	260	235	260	235	230	195	220	250	245	230
Printing Temperature lower limit (°C)	240	230	240	225	220	175	200	230	230	
Bed Temperature (°C)	60	50	80	45	no heated bed	use glue stick	50	70	50	45
Printing Speed (mm/sec)	15	15	15	15	15	5	15	15	15	15
Bottom layer print speed (mm/sec)	5	5	10	10	5	5	10	5	10	10
Layer height (mm)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Bottom layer height (mm)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Nozzle diameter (mm)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25

A commercial liquid polysiloxane, precursor for silicon oxycarbide (SiOC) ceramics, (Polyramic SPR-036, Starfire Systems) was selected. Platinum divinyltetramethyldisiloxane complex, ~Pt 2% in xylene (CAS number: 68478-92-2, Sigma-Aldrich, St. Louis, MO, USA) was further diluted to 0.1% before using. Pt catalyst promotes the crosslinking of the preceramic polymer *via* hydrosilylation reaction between the Si-H and the C=C moieties present in the silicon polymer [39]. 100 microliters of the catalyst solution per 1 gram of preceramic polymer were used. The preceramic polymer was dissolved in acetone (50:50 by weight). Acetone was selected as a solvent as it is less detrimental to the various polymers used in this experiment compared to other solvents [40]. The 3-D printed structures were soaked for a 30 mins in the SPR-036/acetone/Pt solution. The samples were then taken out and left to dry in air at room temperature for 24 hours on a ceramic foam before pyrolysis.

The impregnated samples were then pyrolyzed in an alumina tube furnace (Thermolyne 5400 High Temperature tube furnace) at 1200°C in nitrogen flow (400 cc/min) with a heating rate of 10°C/min with 1 hour dwelling at 1200°C. The samples were then cooled freely to the room temperature. To remove any oxygen and moisture from the system, the furnace was purged for 45 mins before heating, with the samples inside the tube [41].

To characterize the polymer-to-ceramic transformation, the samples were weighed with a digital scale (Mettler AT20, ± 0.00006 gm), and their volume was measured with a digital Vernier caliper (VINCA, ± 0.01 cm) before and after pyrolysis. The morphology of 3-D printed polymeric samples and of the corresponding ceramic samples after pyrolysis characterized by scanning electron microscopy (Zeiss Supra 40) after coating the samples with a thin Pt/Pd film. In order to get a clean fracture surface, the 3-D printed polymeric samples were dipped in liquid nitrogen before cutting them with a knife.

The decomposition process of selected (Ninjaflex, PRO TPU, Polycarbonate, Alloy 910, PETG and Rubberlay) 3-D printed polymeric samples (not impregnated with the pre-ceramic polymer), and of the starting SPR-036 polymer before and after addition of the Pt catalyst (100 μ l of Pt for 1 g of Si-polymer), was studied recording differential thermal analysis and thermogravimetric analysis, DTA/TGA using a Netzsch STA 409 equipment (Netzsch GmbH, Selb, Germany) at 10°C/min up to 1200°C in flowing N₂ (150 cc/min).

2.3. Results

A weight increase ranging from 6% to 35% percent for hard filaments and 8% to 30% for flexible filaments was observed after soaking and drying the samples as seen in Figure 1.

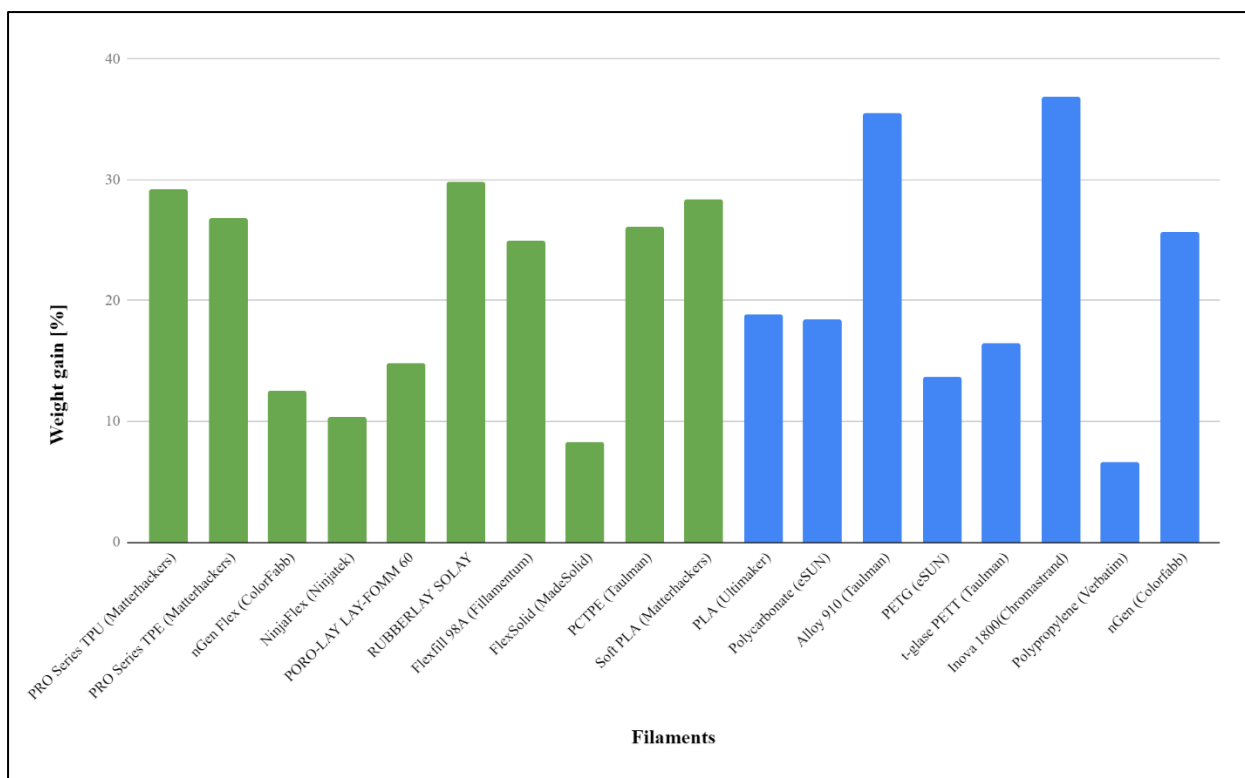


Figure 1: Percentage weight gain of 3-D printed samples after soaking in preceramic polymer solution and drying.

The materials that increased in weight the most were Nylon alloy Alloy 910 (Taulman), Soft PLA (Matterhackers) and thermoplastic elastomers PRO TPU, PRO TPE (Matterhackers), Rubberlay. While the materials that gained the least amount were PP (Verbatim) and PETG (eSUN). The weight increase is the result the Si-based compound forming a coating on the surface of the 3-D printed filament struts. No swelling of the samples was measured after drying therefore suggesting that the main reason for the observed weight increase of the samples after soaking in the pre-ceramic polymer solution was the formation of a coating on the surface of the 3-D printed struts.

TGA curves recorded on selected 3-D printed polymeric structures and their derivative (DTG) are shown in Figure 2.

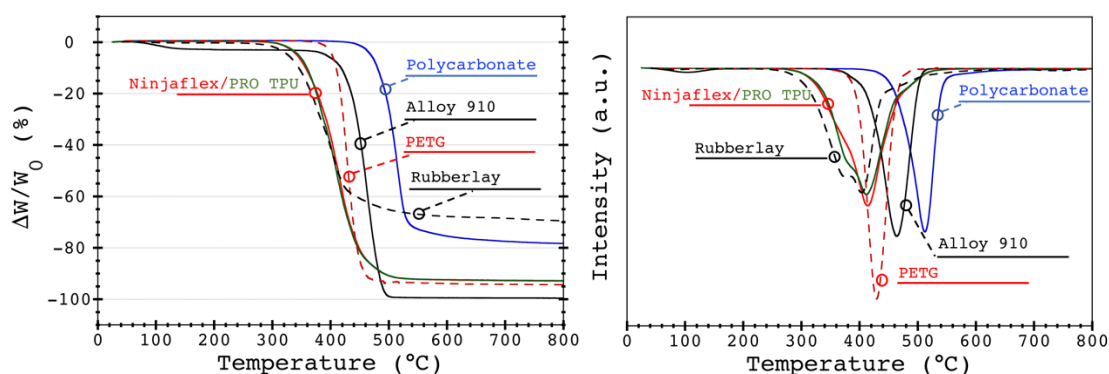


Figure 2. DTA (left) and TGA (right) curves recorded on selected 3-D printed polymeric samples.

The pyrolysis of the polymeric structures leads to an almost complete decomposition (weight loss above 95%) and only for two polymers, namely Polycarbonate and Rubberlay, the carbonaceous residue is of the order of 20-30%. The temperature range in which this decomposition occurs goes from a minimum of ca 300°C to a maximum of ca 550°C. At these temperatures the pre-ceramic polymer is already crosslinked, and its pyrolysis leads to a volume shrinkage (and weight loss) without losing the initial shape. Indeed, DTA/TGA experiments performed on the as received SPR-036 and on the siloxane resin after addition of 100 mL/g of Pt catalyst (see Figure 3) indicate that crosslinking occurs readily at around 100 °C with a strong exothermic effect. After crosslinking, the weight loss of the pre-ceramic polymer is reduced to ca 30% compared to the 45% of weight loss associated to the non-crosslinked polymer. Not only the Pt-catalyzed siloxane polymer crosslinks before the decomposition of the 3-D printed structure but also before the melting of the polymeric struts (all the polymeric filaments used in the experiment have their melting region starting well below 275°C). Accordingly, without using catalyst the polymeric samples would lose their structure and start melting before the preceramic is cured. In this case a replicated structure of ceramic will not be obtained after pyrolysis.

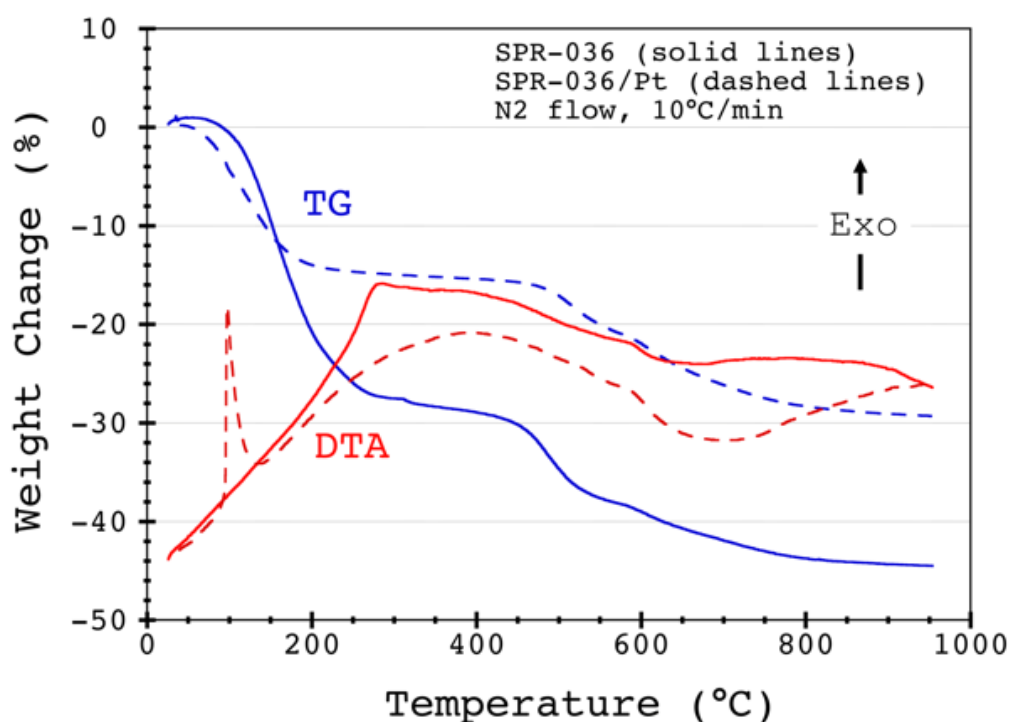


Figure 3. DTA/TGA curves recorded on the “as-received” SPR-036 and on the same polymer after addition of 100 mL/g of Pt catalyst (0.1%).

The volume shrinkage after pyrolysis measured for the impregnated 3-D samples (Figure 5) ranges from 33% to 67% and the corresponding weight loss (Figure 4) varies between 50% and 93%. The weight loss is the combined result of the thermal decomposition of the organic polymer and of the Si-based pre-ceramic compound. Since the decomposition of the organic polymer occurs with a nearly 95-100% weight loss the percentage of ceramic residue is directly related to the relative amount of the SPR-036 polymer coated on the surface of the 3-D printed polymeric objects. A high weight loss value during pyrolysis should be correlated to a thinner coating and should lead to thin ceramic structures. The sample that shows the lowest weight loss during pyrolysis (50%) is the Rubberlay, which must also be due to the high carbonaceous residue that this polymer shows (ca 30 wt%, see Figure 2).

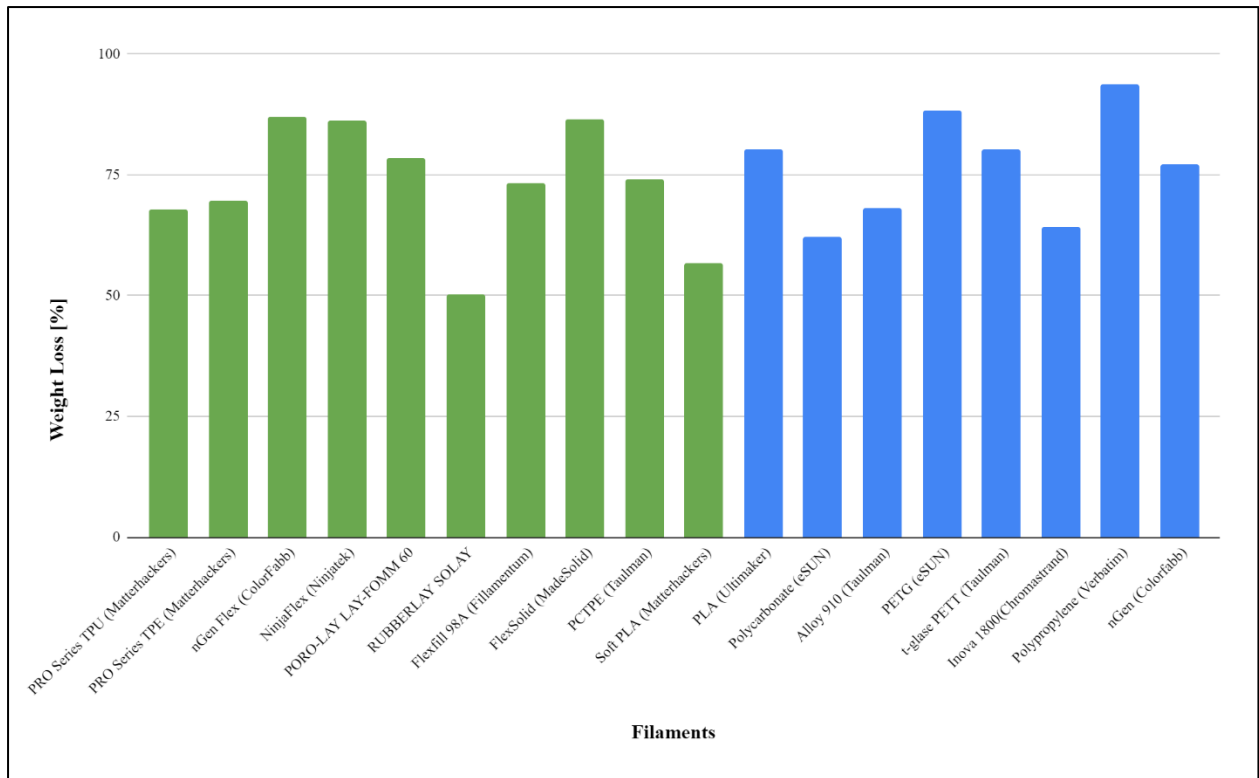


Figure 4: Percentage weight loss measured for the 3-D printed impregnated samples during the polymer-to-ceramic conversion.

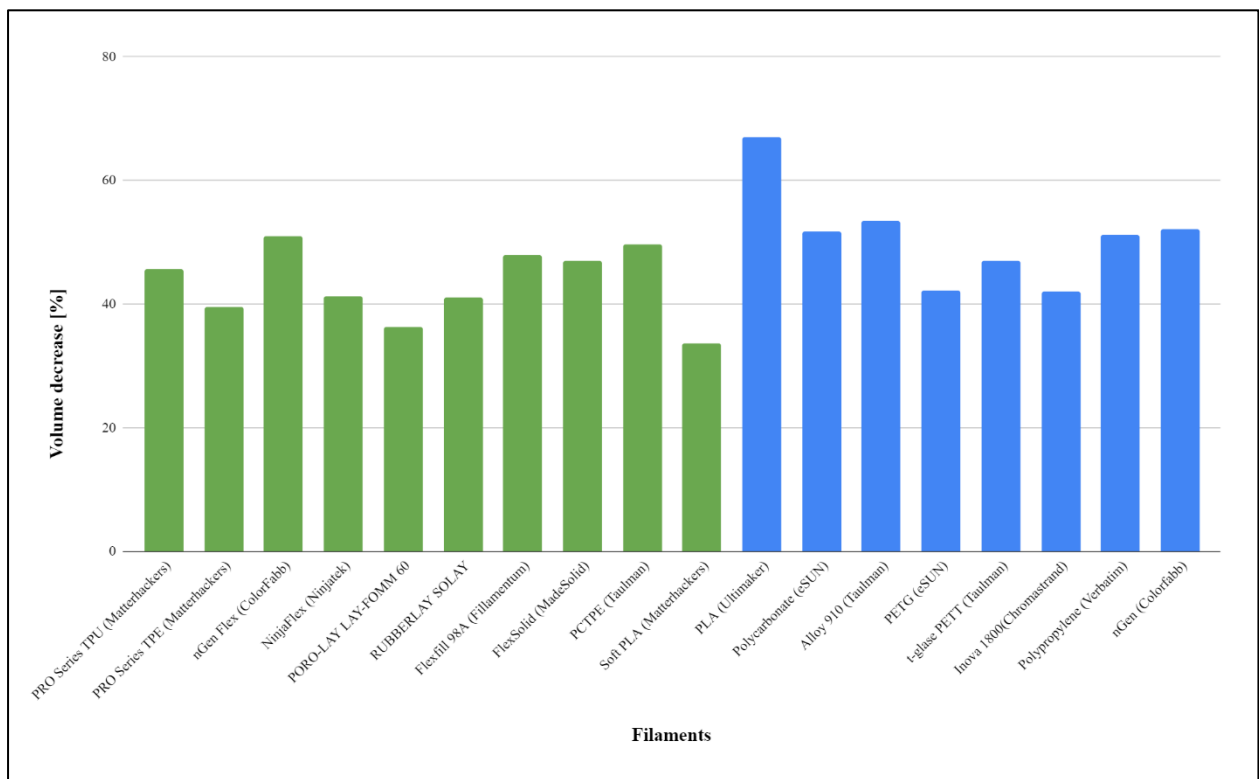


Figure 5: Percentage volume shrinkage measured for the 3-D printed impregnated samples during the polymer-to-ceramic conversion

The ceramic samples obtained after pyrolysis are compared to the initial polymeric ones in Figures 6-23. The ceramic samples held their structure without any major visible damage. However, depending on the type of polymer used in the FFF process there was some small distortion. PLA and PET (Figure 6 and 10) displayed some highly reflective areas that can be ascribed to the excess pre-ceramic solution forming a continuous film on the face of the 3-D cube. In a similar manner, PC and PETG in Figure 7 and 9 shows some extra materials on the exterior which can be explained as extra preceramic polymer retained on the surface of the sample. This type of defect can be removed by further optimizing the soaking/drying process. Several materials provided nearly perfect replica of the structure such as Alloy 910 (Figure 8), PP (Figure 12), nGen (Figure 13), Pro TPU (Figure 14), Pro TPE (Figure 15), Ninjaflex (Figure 17), Poro-Lay LayFomm (Figure 18), Rubberlay Solay (Figure 19), FlexSolid (Figure 21), PCTPE (Figure 22), and Soft PLA (Figure 23). NGen Flex (Figure 16) and Flexfill 98A (Figure 20) had a non-uniform distortion of shape.

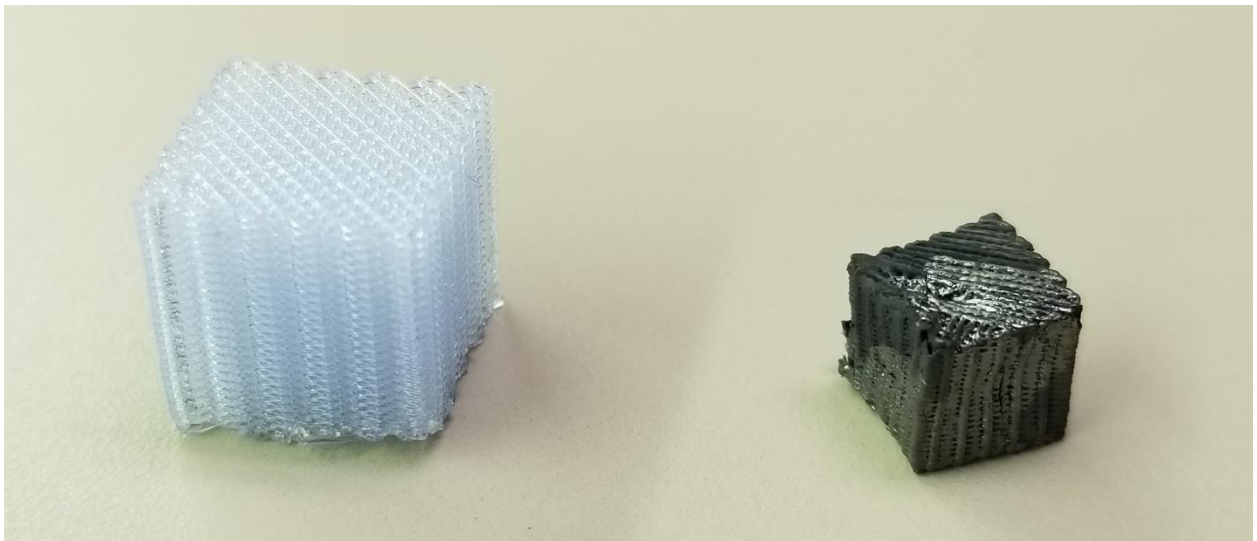


Figure 6: PLA (Ultimaker)

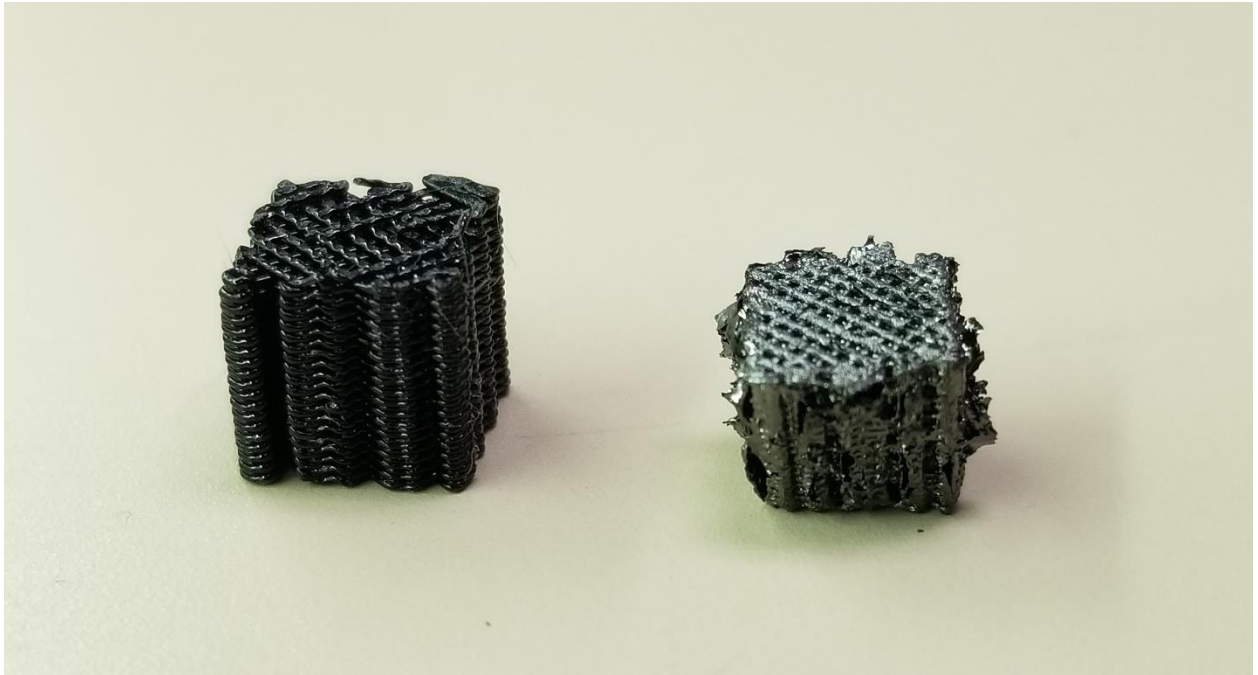


Figure 7: Polycarbonate (eSUN)

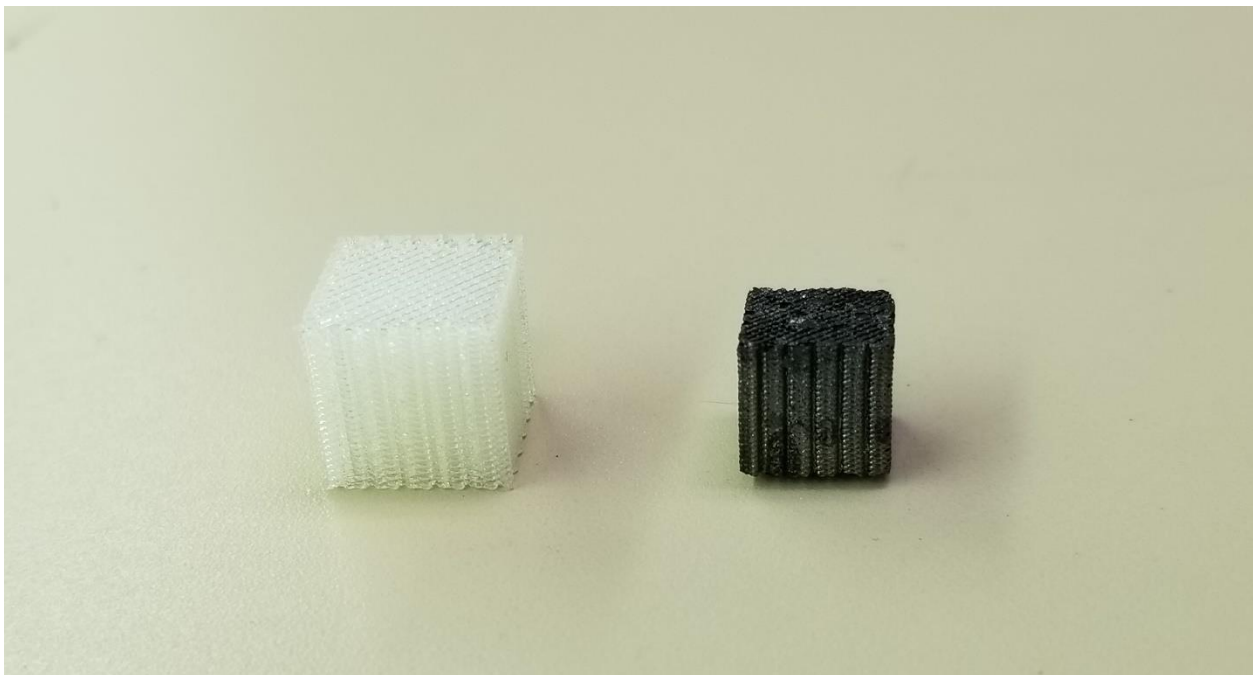


Figure 8: Alloy 910 (Taulman)

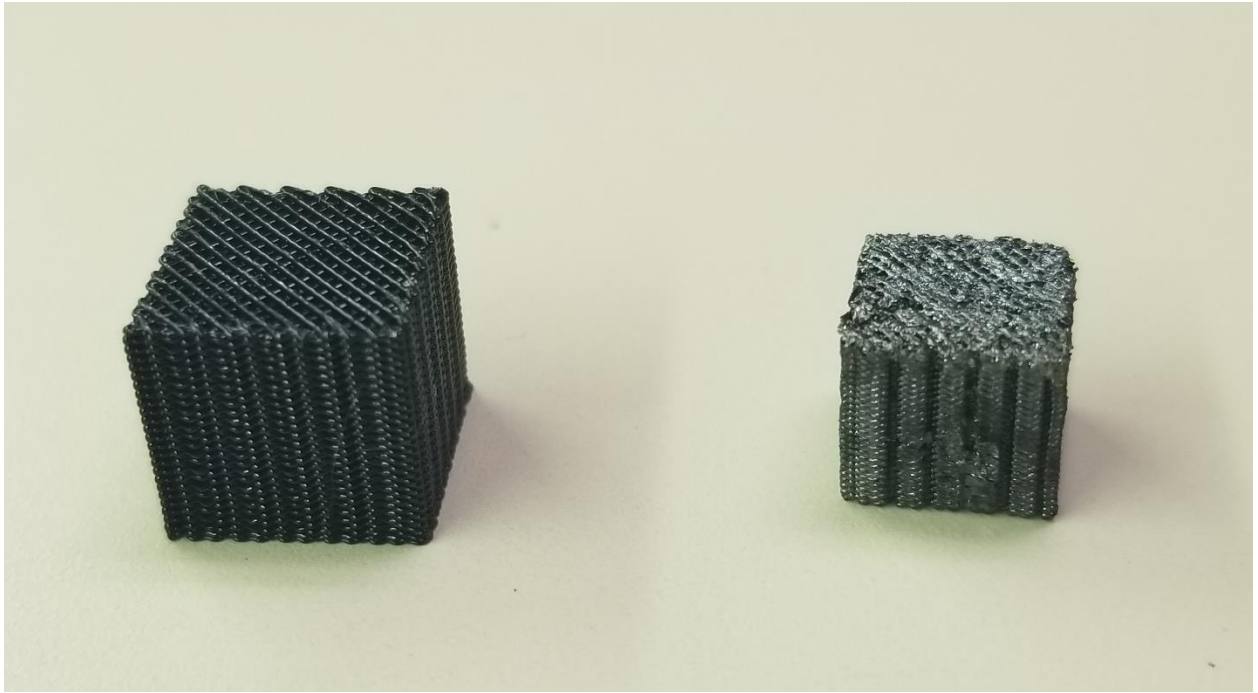


Figure 9: PETG (eSUN)

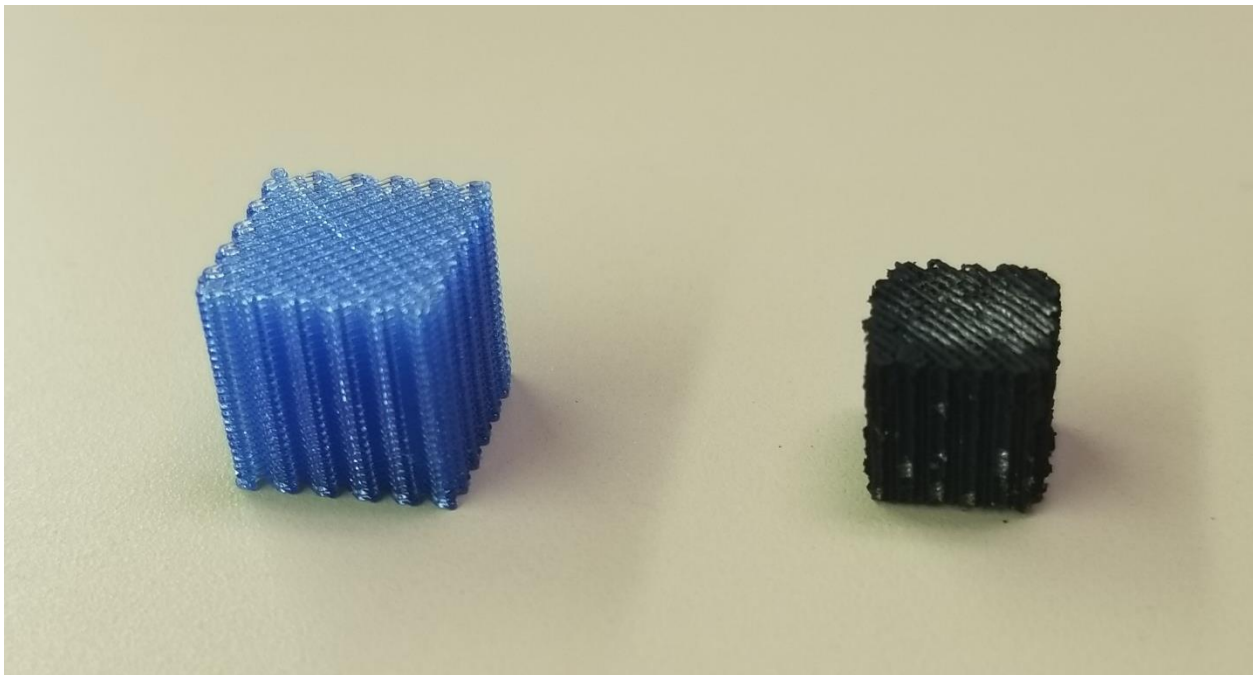


Figure 10: t-glase PETT (Taulman)

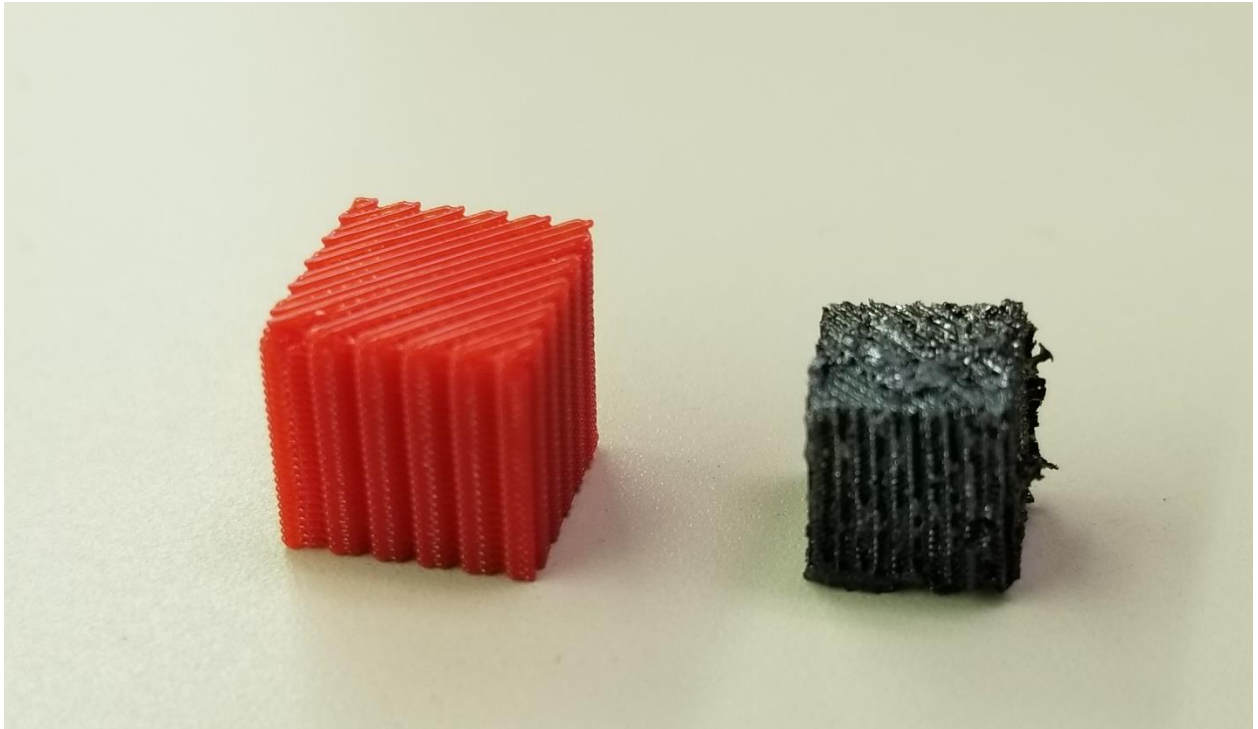


Figure 11: Inova 1800 (Chroma Strand)

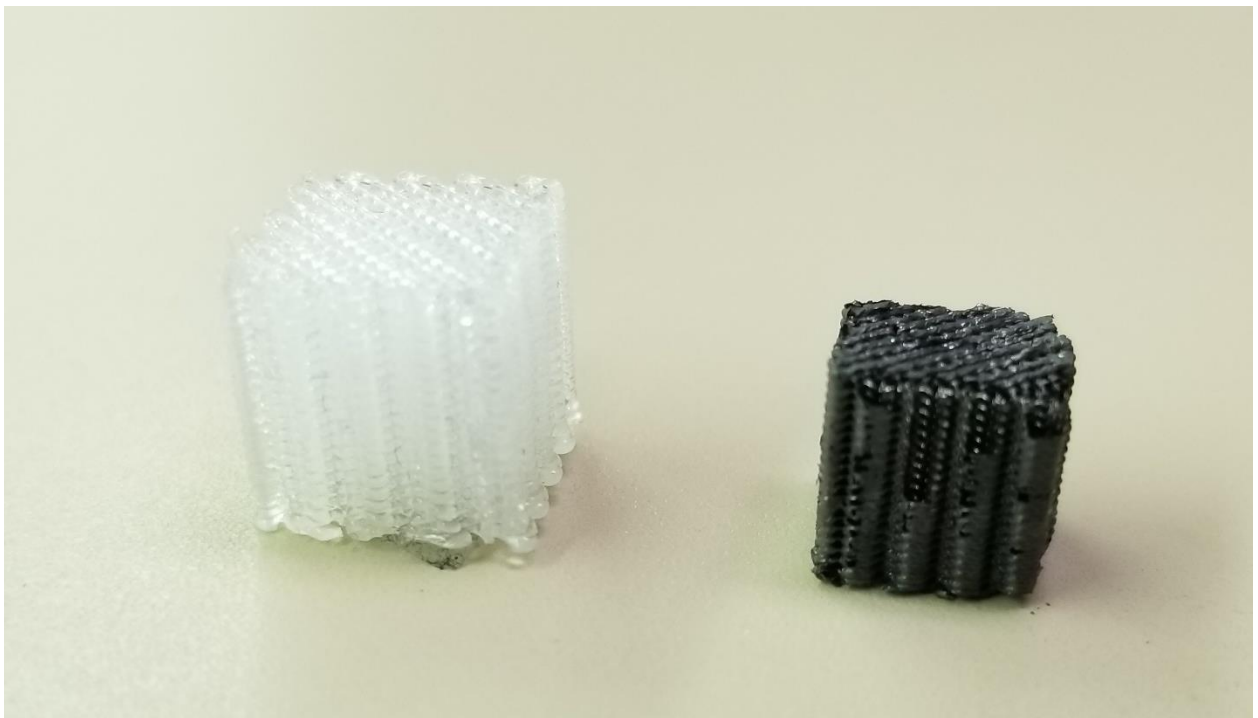


Figure 12: Polypropylene (Verbatim)

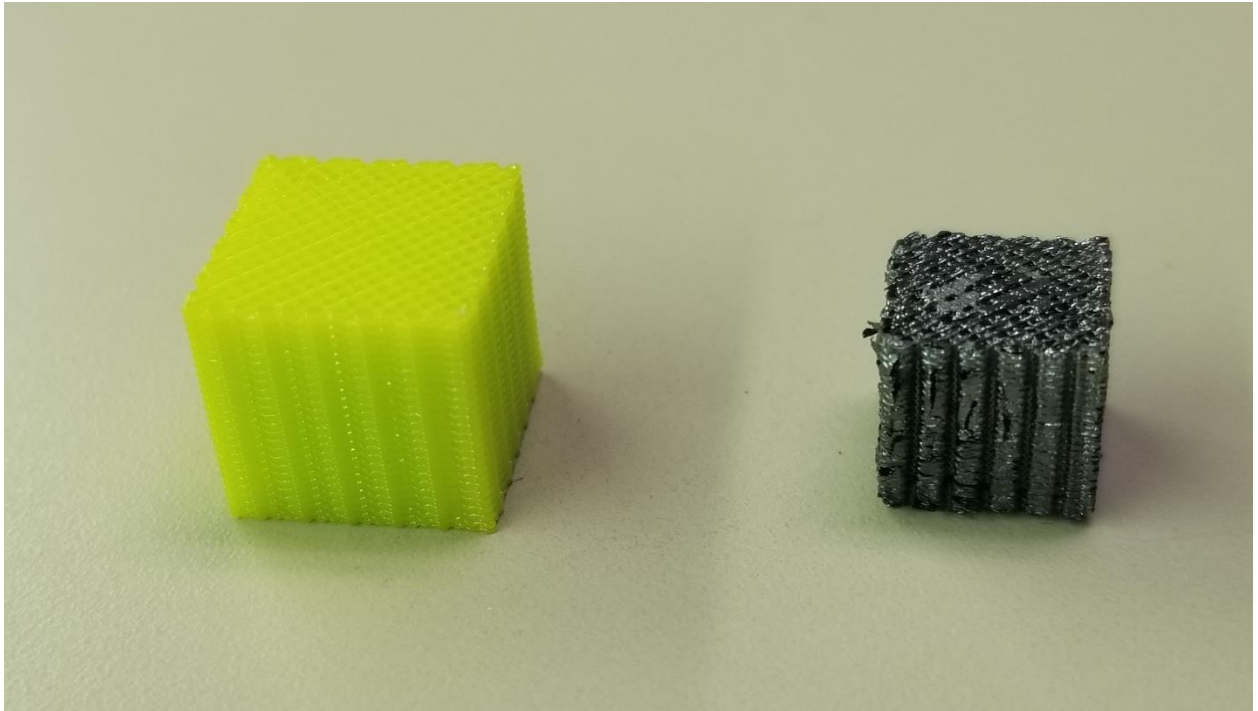


Figure 13: nGen Hard (Colorfabb)

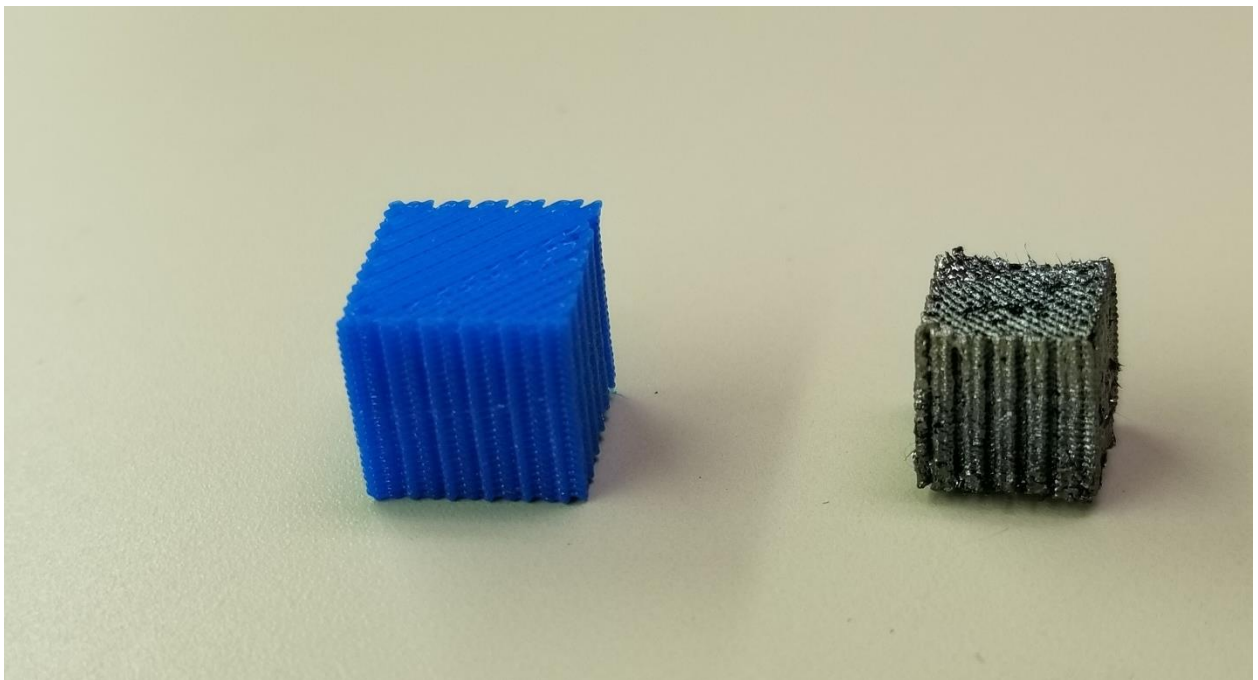


Figure 14: PRO TPU (Matterhackers)

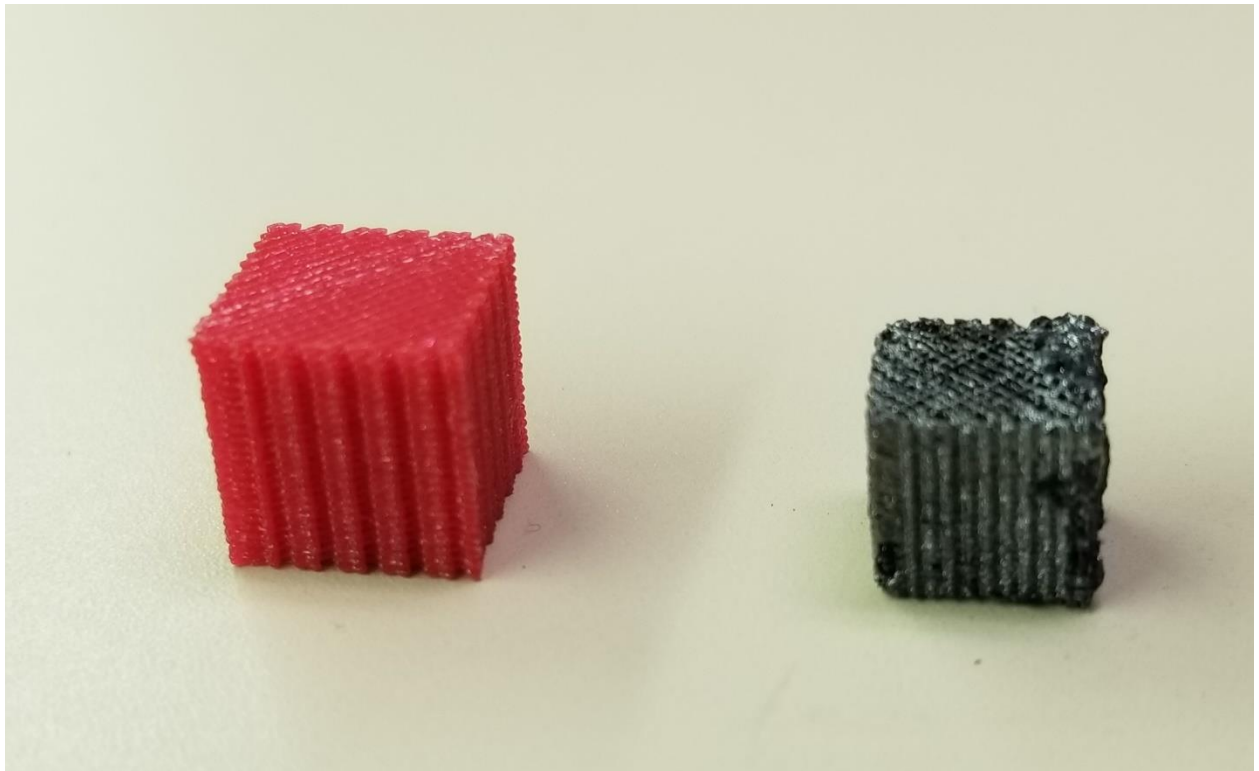


Figure 15: PRO TPE (Matterhackers)

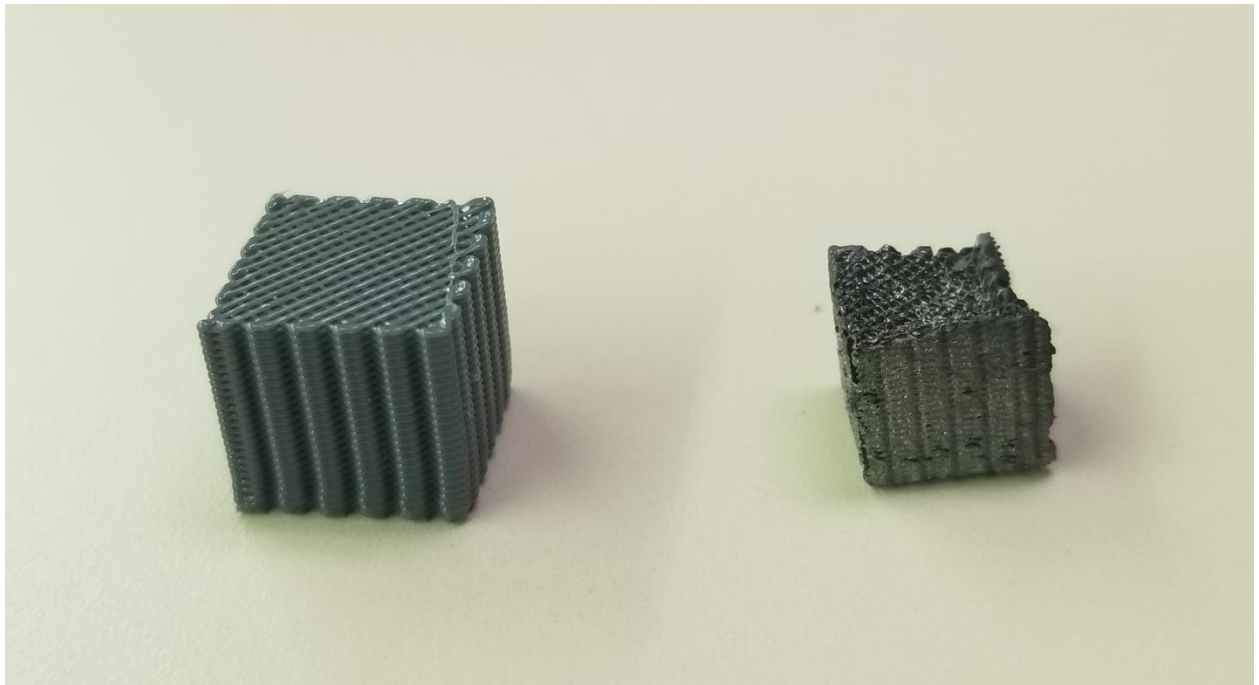


Figure 16: nGen Flex (Colorfabb)

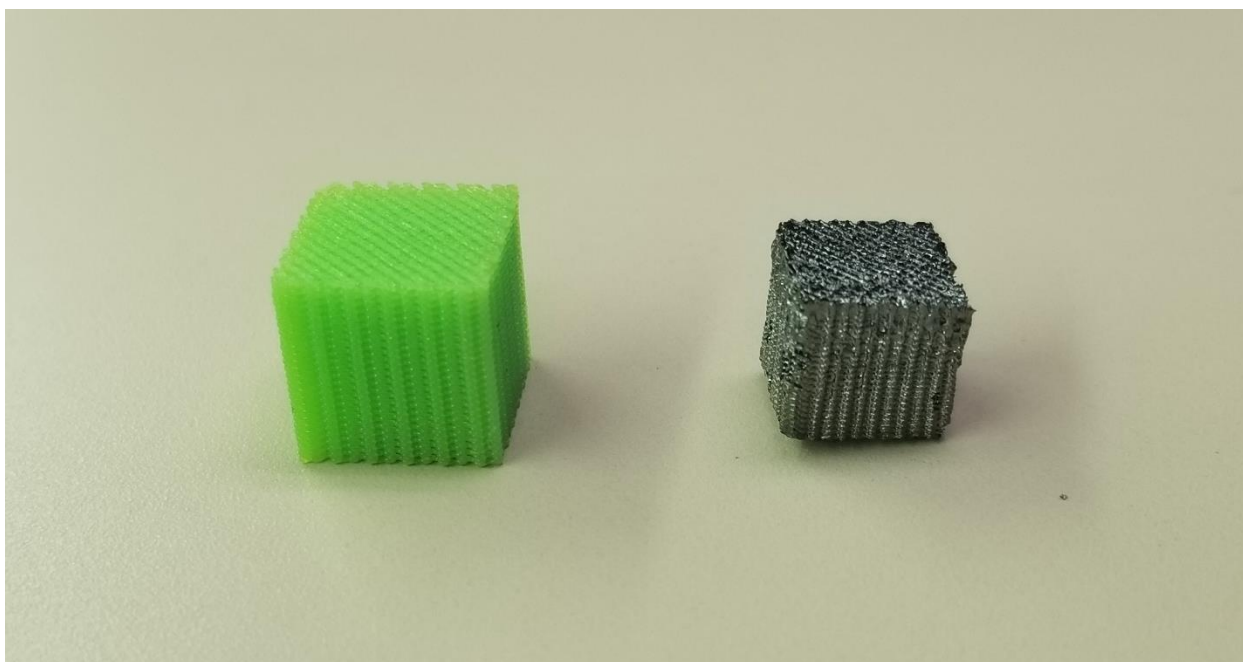


Figure 17: NinjaFlex (NinjaTek)

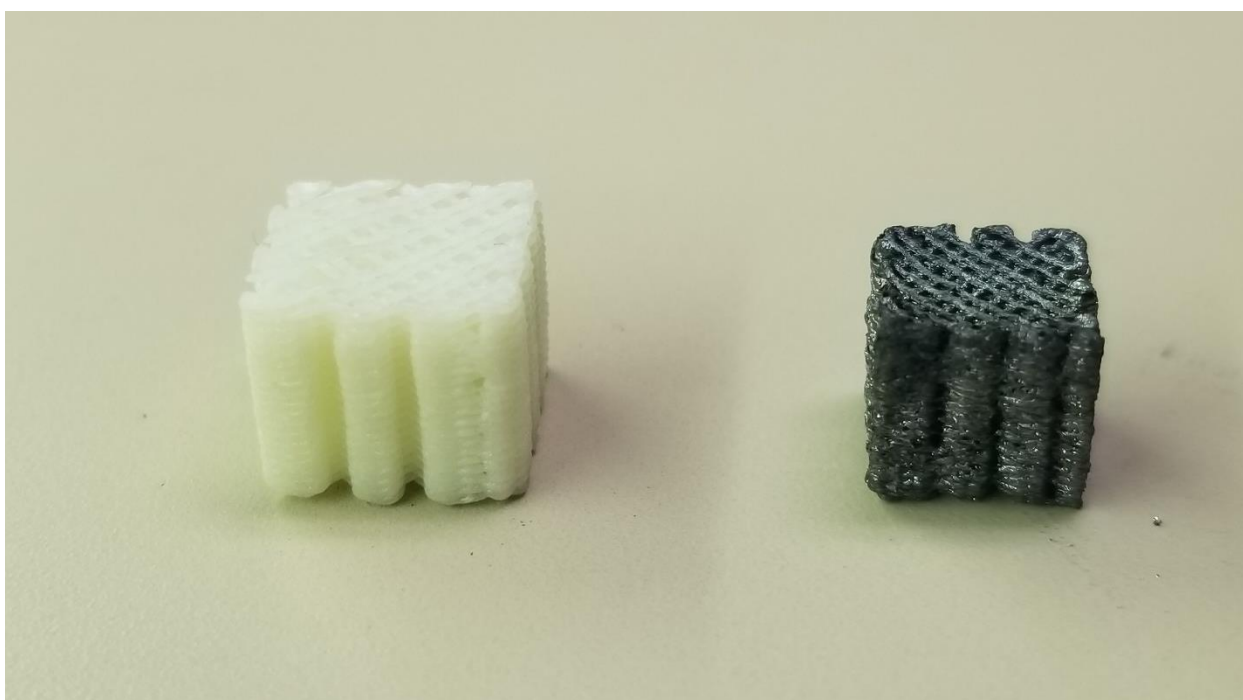


Figure 18: PORO-LAY LAYFOMM 60

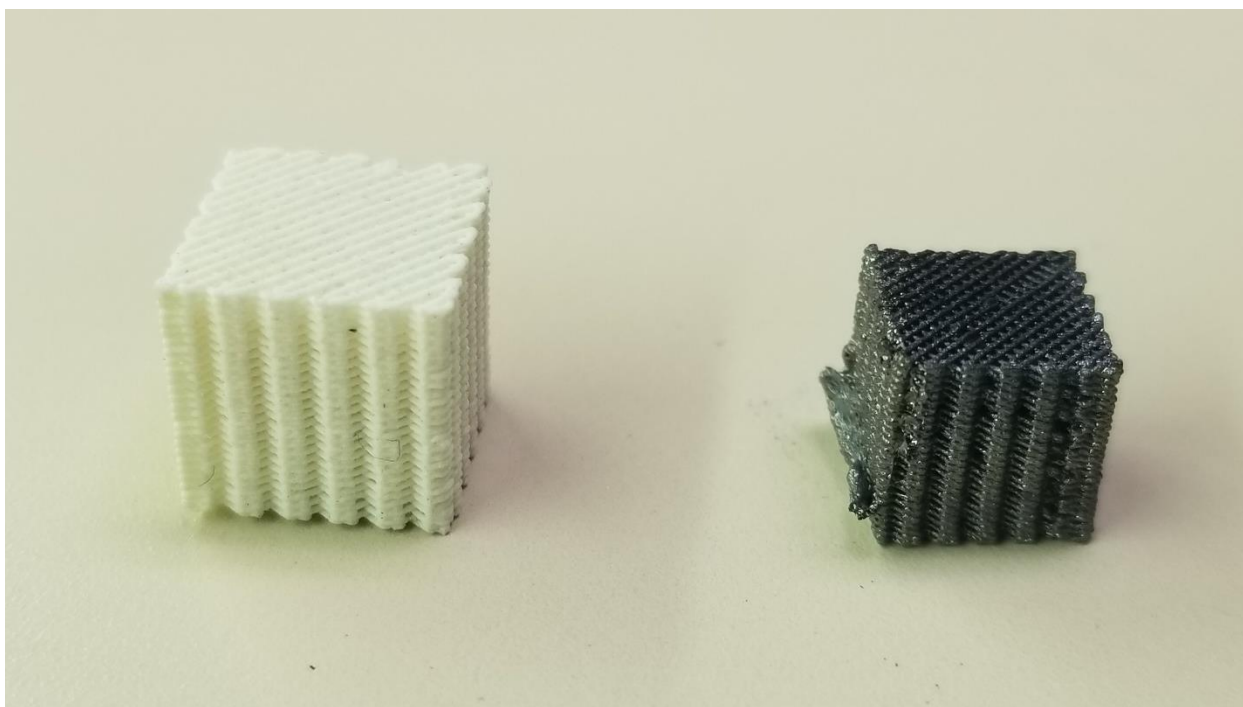


Figure 19: RUBBERLAY SOLAY

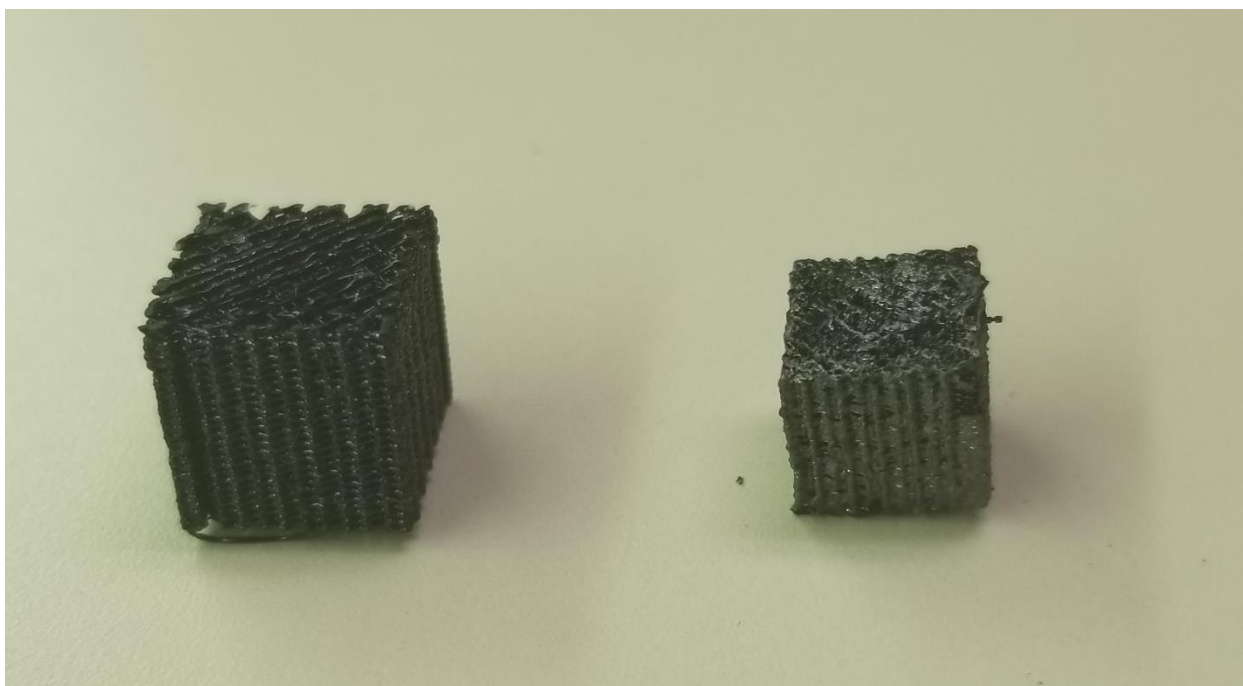


Figure 20: Flexfill 98A (Fillamentum)

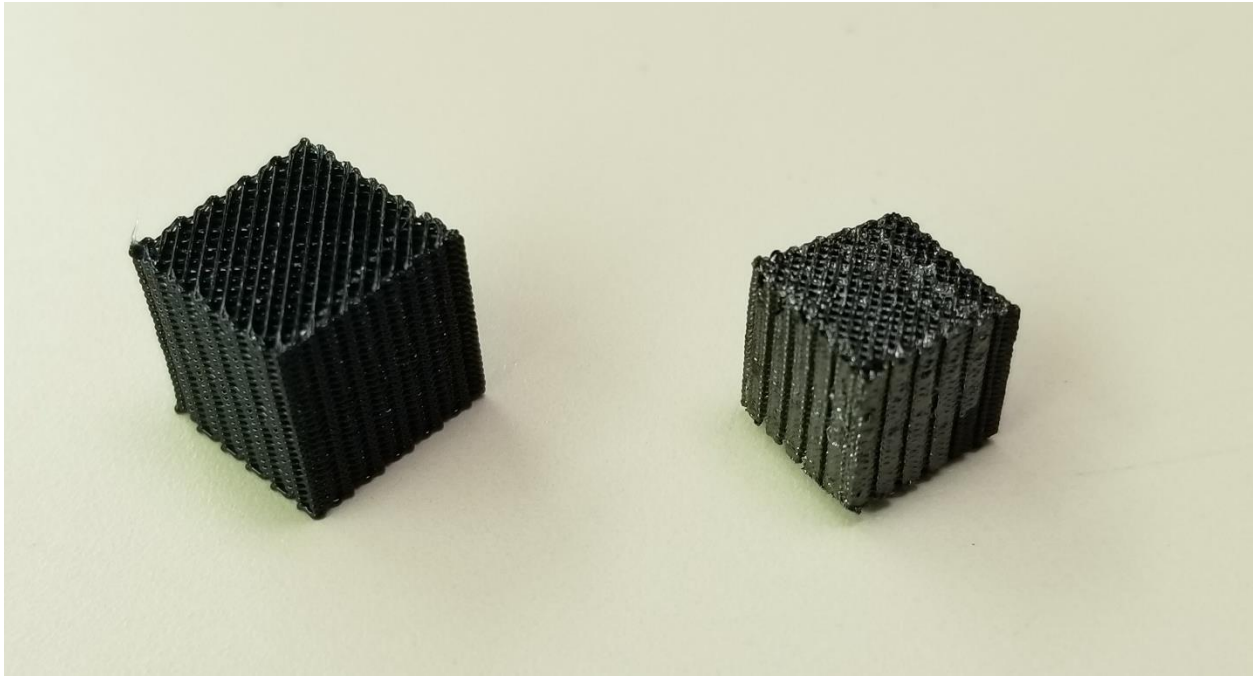


Figure 21: FlexSolid (MadeSolid)

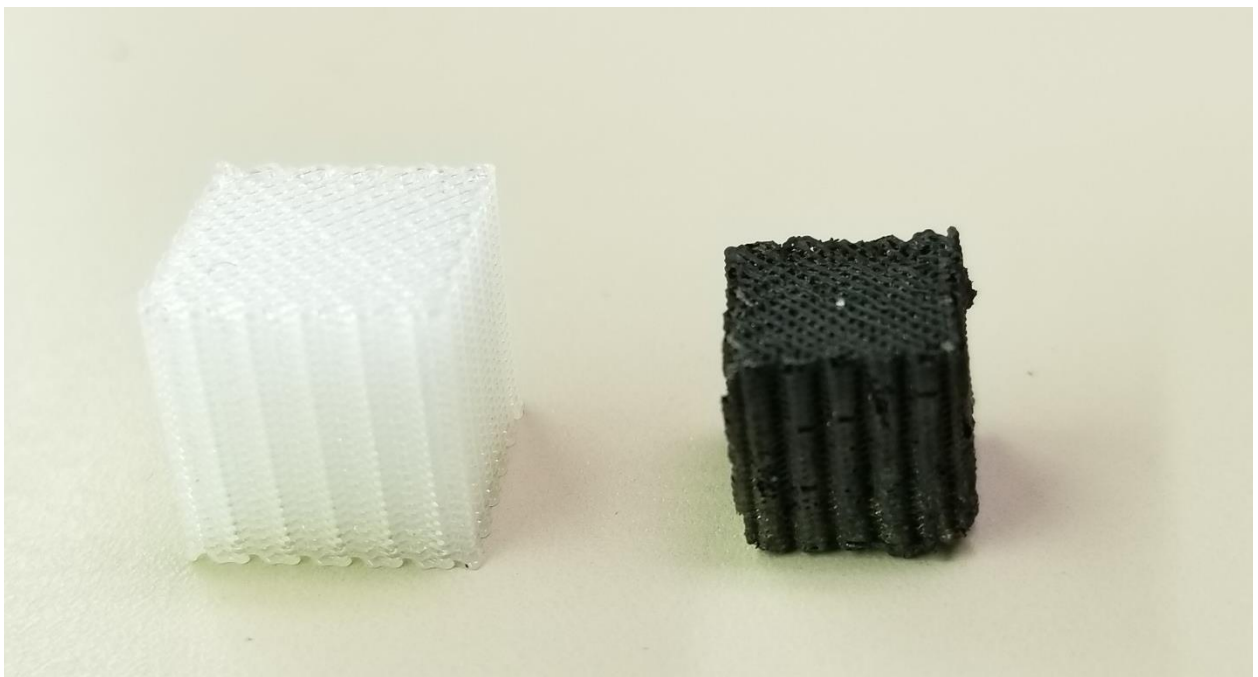


Figure 22: PCTPE (Taulman)

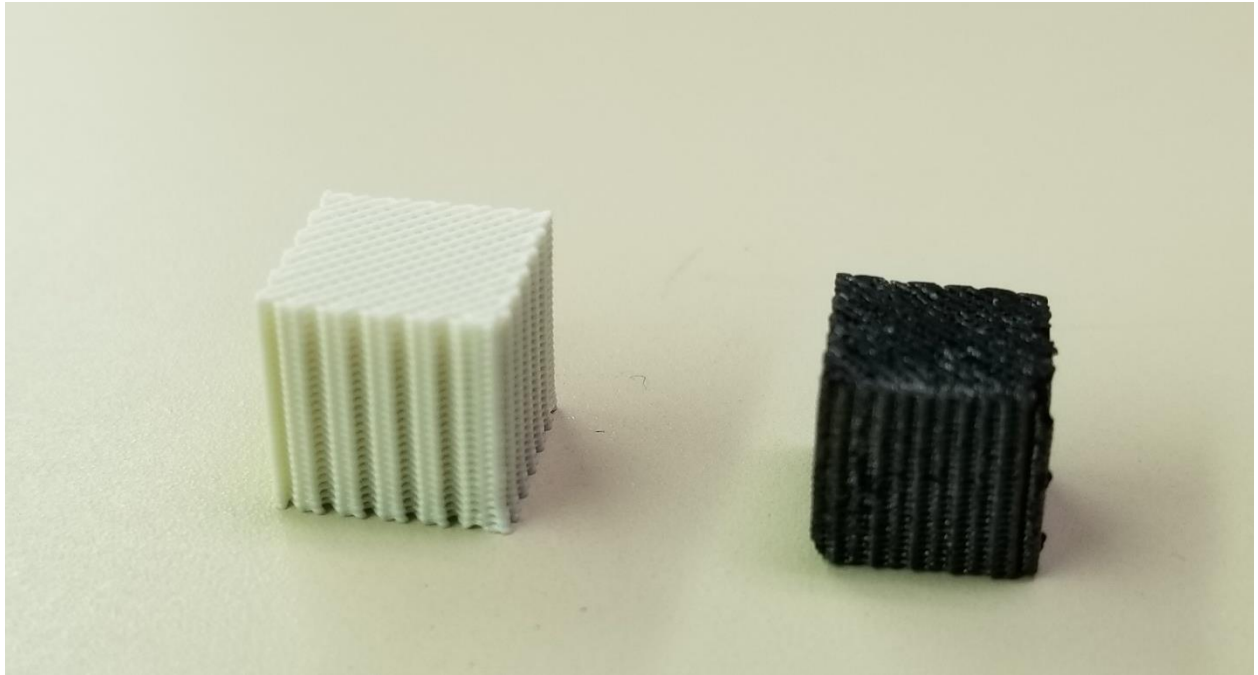


Figure 23: Soft PLA (Matterhackers)

Figure 24 (a) shows the CAD model of the 3-D printed sample and then in (c) the theoretical cross section after pyrolysis with the remaining material representing only the thin surface layer of ceramic present. As can be seen by the cross-sectional SEM images the theoretical prediction was shown to be accurate. Figure 24 (b) shows the SEM of the as-printed PC and then the remaining ceramic is shown after processing in Figure 24 (d). It can be clearly seen that the space initially occupied by polymer filaments is completely empty and ceramic coating is being applied on the surface of the struts creating a thin ceramic structure with far more surface area than the parent 3-D printed structure.

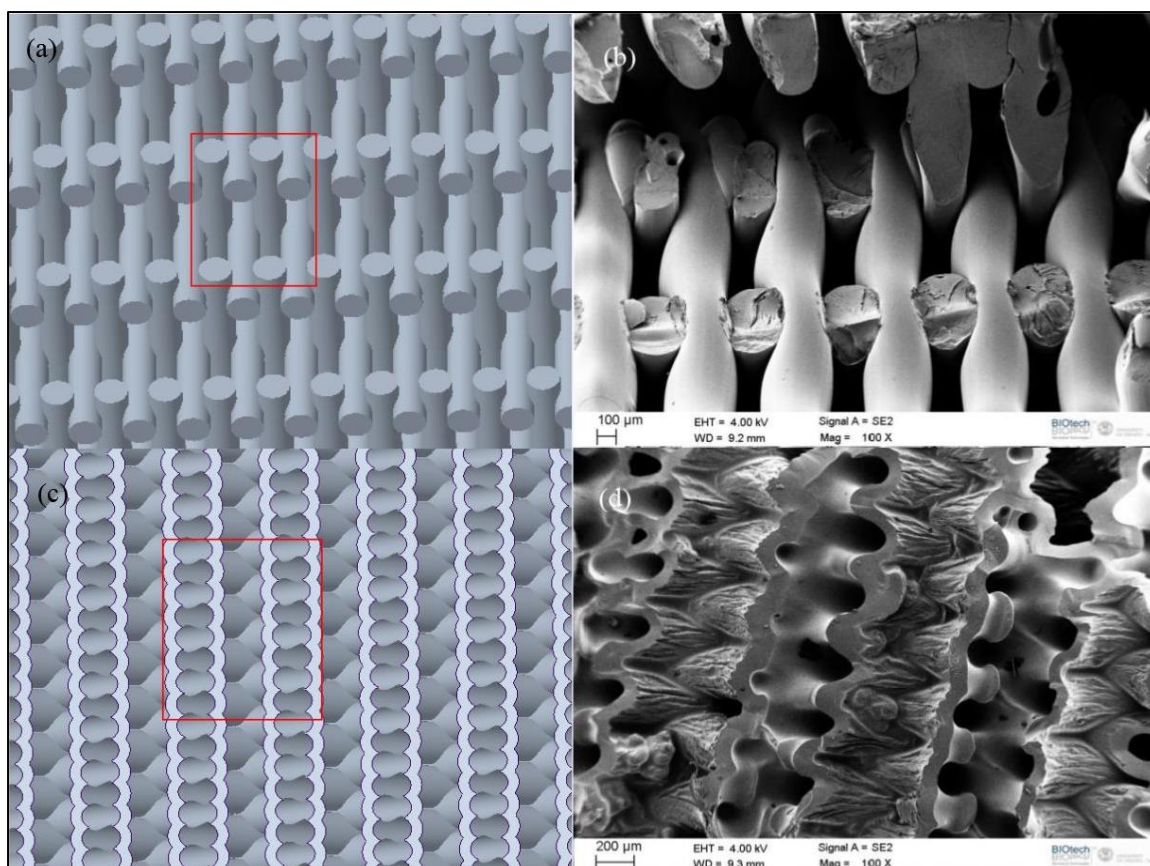


Figure 24: (a) Section of a CAD model of the 3-D printed sample (b) SEM image of a section of polycarbonate (eSUN) sample (c) Section of a CAD model after pyrolysis (d) SEM image of a section of ceramic sample obtained from polycarbonate.

Different filaments/ polymers were observed to produce different results in terms of weight loss, which directly relates to the thickness of the ceramic coating. The ability of the 3-D printed filament to retain the preceramic polymer on its surface can be affected by different parameters such as chemistry of the 3-D printing polymers and the preceramic polymer and also the surface texture of the 3-D printed polymers. It can be seen that Rubberlay (Figure 25(a)) having a very rough surface, produced a thicker coating of the ceramic. Even though Soft PLA (Figure 25(c)) is not as rough as the Rubberlay filament it produced thicker coating than relatively smooth filaments like PP and PETG (shown in Figure 26) which were observed to have a very thin coating on the surface after pyrolysis.

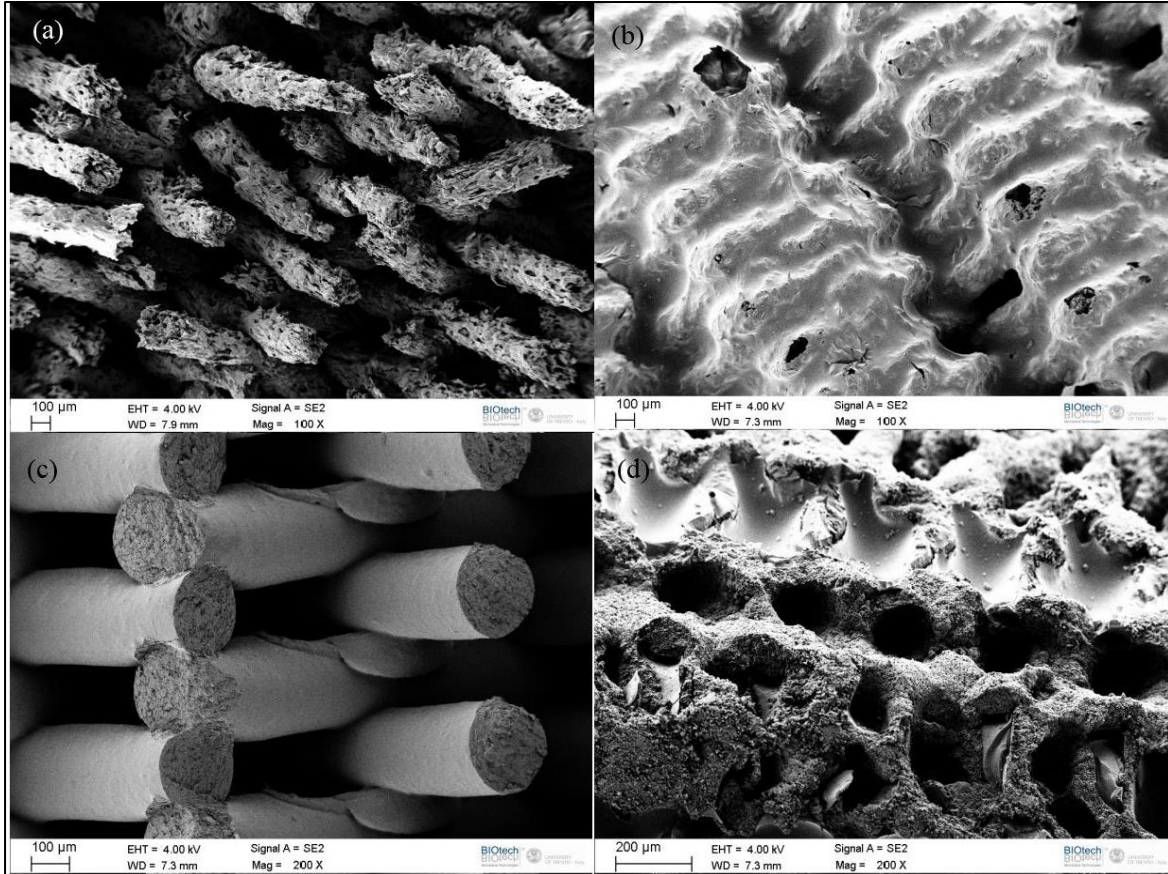


Figure 25: (a) SEM image of a section of the sample printed with RUBBERLAY filament
 (b) SEM image of section of ceramic sample obtained from RUBBERLAY filament (c) SEM
 image of a section of the sample printed Soft PLA filament (d) SEM image of section of
 ceramic sample obtained from Soft PLA filament

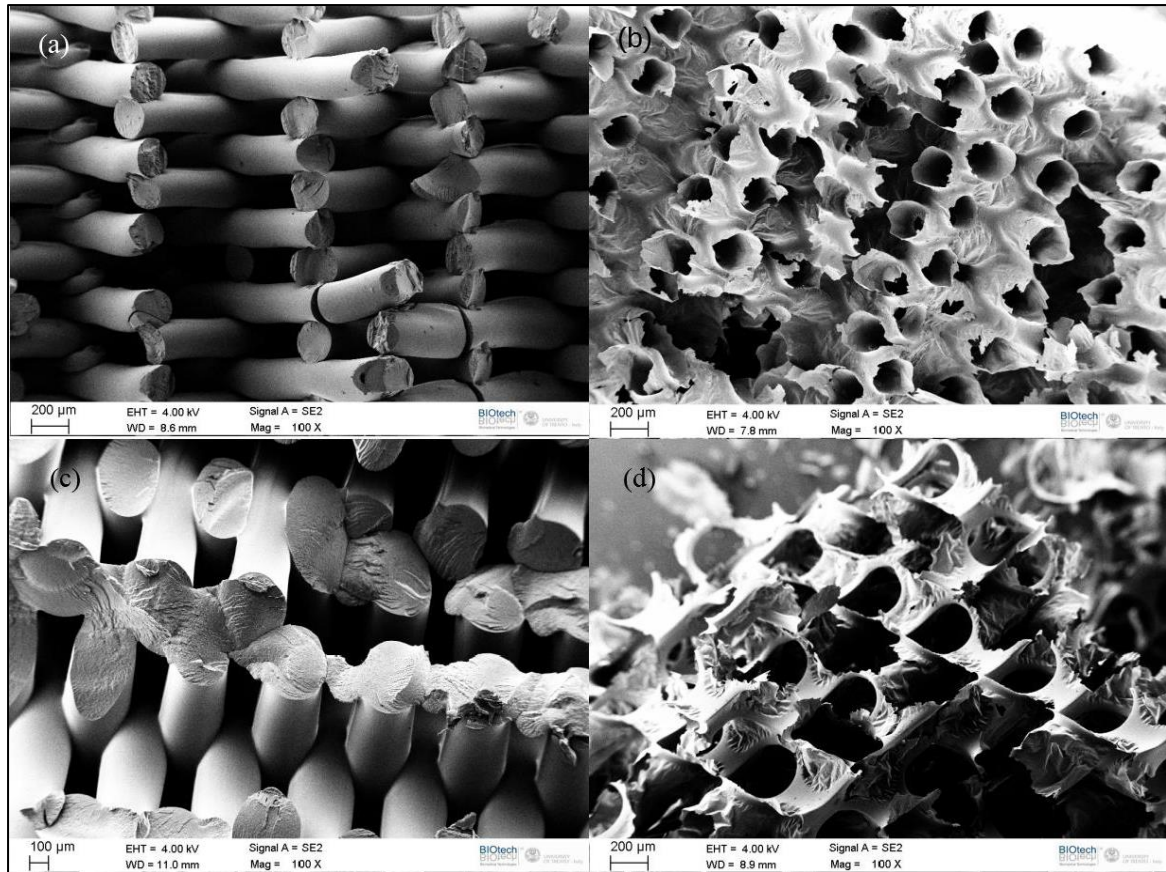


Figure 26: (a) SEM image of a section of the sample printed with PETG filament (b) SEM image of section of ceramic sample obtained from PETG filament (c) SEM image of a section of the sample printed PP filament (d) SEM image of section of ceramic sample obtained from PP filament.

2.4. Discussion

The results of this experimental study open up a whole new avenue in low-cost 3-D printing of ceramic structures with FFF based methods. The cost of materials used for FFF 3-D printing are much less compared to the cost of powder feedstock required for the laser sintering of the ceramics or the resin slurry required for stereolithography [42]. The equipment itself used for FFF based 3-D printing is much less expensive than any of the other methods with reliable DIY

kits costing a few hundred dollars [43] and the Lulzbot printers used in this study costing \$2500. This makes the ability to AM in ceramics accessible for a much wider range of individuals, schools, fab labs, makerspaces, community centers, libraries, and small and medium sized enterprises.

As the studied preceramic polymer only coats the outer surface of the 3-D printed polymers, the output ceramic structure consists of two porous systems. One being the designed porosity in the cellular structure and other being the porosity created by decomposition of the polymer filaments during pyrolysis. This type of method is being employed for the first time to create a multi-level porous system using FFF 3-D printing. The ability of the method to apply thin coat of ceramic on to a 3-D printed structures, provides ceramics with high surface to volume ratio having high geometric stability.

The ceramic structures produced in this study (silicon oxycarbides) can withstand very high temperatures up to 1400°C [44], however, since this process is not restricted to the use of polysiloxane - precursor for SiOCs -, if polysilanes or polycarbosilane are employed, SiCN and SiC ceramics are obtained which are stable up to even higher temperature, in case of SiC up to 1900°C.

By choosing from 3-D printing polymers with different potential to retain the preceramic polymer solution provides (as shown in this screening study), an optimum and consistent thickness of ceramic struts can be obtained for the desired application. If thick struts with more structural strength are needed, polymers like RUBBERLAY and SoftPLA can be used. Any application where the strength of the ceramic is secondary and very thin ceramic layers are needed, polymers such as PETG and PP can be selected. This selection is based on the processing parameters used, clearly future work could increase or decrease the thickness of the ceramic by adjusting the process parameters.

The components produced in this study can find further applications like ceramic heat exchangers where more surface area is required for heat dissipation [45]. The high resolution of the structures can also enable the use of the study in applications like chemical or gas filters such as catalytic converters [46,47,48]. The structures can be used in biomedical applications as scaffoldings for bone tissue growth as ceramics have been proven to be compatible as implant materials [49,50].

This study did not attempt to fabricate monolithic ceramic parts with the help of 3-D printed PDCs, since the soaking recipes investigated here will only coat the outer surface and will not impregnate the solid 3-D printed part. Future work is needed to look in more detail to choose the optimum polymer/pre-ceramic polymer system in order to maximize the swelling of the 3-D printed struts and, together with optimum heating, soak times and catalyst concentrations, achieve a dense solid part.

The shrinkage during the conversion from 3-D printed polymer structure to the final ceramic structure needs to be quantified to determine the impact on the geometric integrity of different types of ceramic parts. Also, the resolution of the FFF based 3-D printing process can be limiting in certain applications. In this study the smallest head used was 0.25 mm. However, with only the surface PDC method results of thickness less than 100 microns were obtained on the walls as seen in Figure 26 (d).

Future work of the study includes producing finer structures by increasing the 3-D printing resolution by using 3-D printing nozzles smaller than 250 microns. In addition, changing the recipe for the PDCs to make the surface coating even thinner. In order to decrease the cost of the process crosslinking with photoinitiator and curing it with UV light instead of the platinum catalyst should be explored. In the other direction, different preceramic polymers such as

polysilazanes or polysilanes, which might be more compatible with the 3-D printing polymers can be used to try and produce 100% dense ceramic cellular structures.

2.5. Conclusions

In summary, the results of this study show that low-cost FFF-based 3-D printing can fabricate 3-D ceramic structures with line widths of 200-250 microns using the PDC process. This also enables accessibility to produce custom ceramics fabricated with geometric stability and high temperature and strength. All of the 3-D printing polymers (PLA, PC, nylon, PP, PETG, PET, copolyesters, TPE, flexible PLA, and TPU) produced definite ceramic structures with varying weight and volume reductions. The filaments with the ability to retain the preceramic such as SoftPLA and Rubberlay produced better results whereas filaments such as PP and PETG were not able to retain the preceramic polymer after soaking as well compared to other filaments. The low-cost processes outlined in this study enable hollow ceramic skins to be fabricated (from all 3-D printing FFF materials) successfully producing ceramics skins of thickness less than 100 microns in thickness. The novel results developed here can be used to choose FFF-based polymers to use for PDC processing on a wide range of applications such as heat exchangers, heat sinks, scaffoldings for bone tissue growth, chemical/ gas filters and custom scientific hardware.

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2.6. References

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Chapter 3

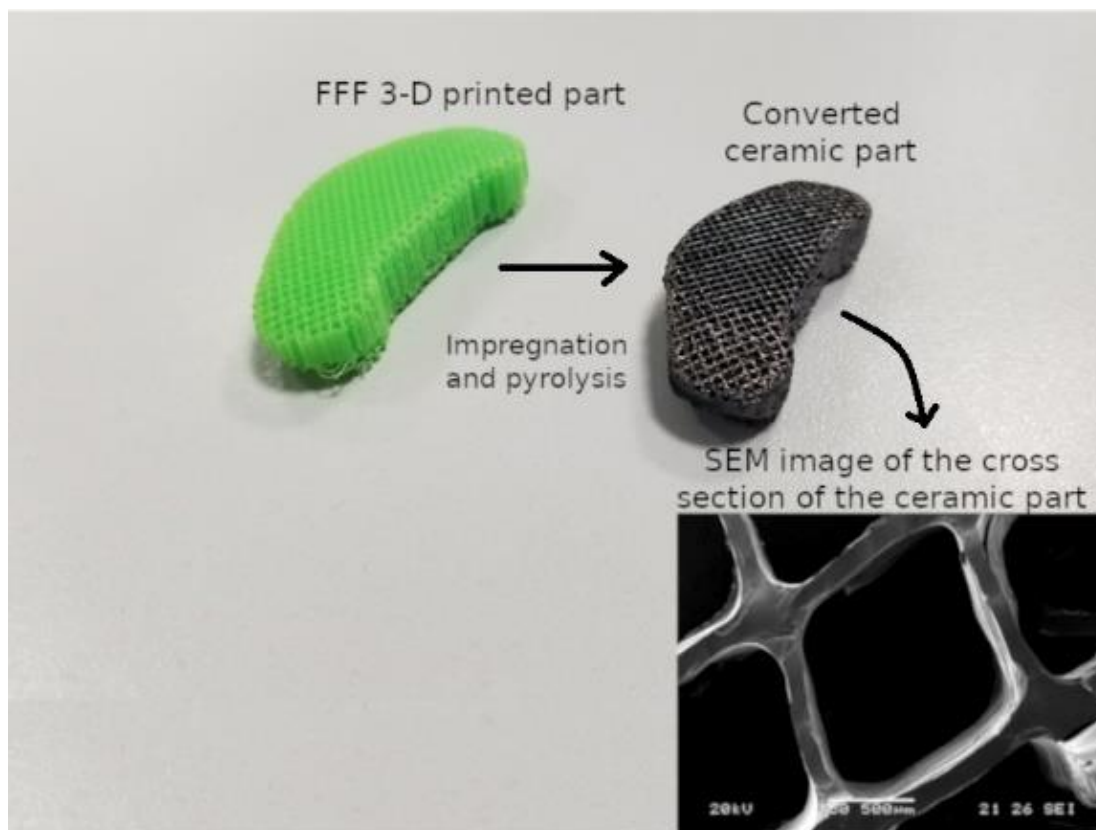
SiOC(N) cellular structures with dense struts by integrating FFF 3-D printing with polymer derived ceramics.

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Graphical Abstract



Abstract

Great advances have been made in various 3-D printing methods for ceramics [1], [2]. Fabrication of Si-based ceramics using polymer derived ceramics (PDC) is gaining popularity [3], [4]. Using this route, preceramic polymers can be shaped in the polymer state and then pyrolyzed to produce different type of ceramics [5], [6]. Cellular ceramics can be manufactured using this technique [7]. This study reports on the novel fabrication of cellular ceramics with a two-step process using PDCs. First cellular structures are 3-D printed with fused filament fabrication (FFF) using thermoplastic polyurethane and impregnated with preceramic polymer polysilazane. Second, pyrolysis of the impregnated structure produces a self-similar ceramic

cellular structure. This study systemically evaluates the impact of i) catalysts, ii) curing environment and iii) pyrolysis sequence optimization to form cellular ceramics with fully-dense SiOC(N) struts. The resultant custom ceramic components can tolerate operating temperatures of 1500°C and can be manufactured for less than 5% of the cost of competing methods. The ceramic material is shown to be biocompatible and promotes fast cell adhesion. Finally, early-stage cell activation on the SiOC(N) structure is shown to be tunable by adjusting the porosity with this 3-D printing to mimic the bone tissue geometry for bone regeneration.

Keywords: Additive manufacturing, Polymer derived ceramics, preceramic polymers, Fused filament fabrication, Open source 3-D printing, Polysilazane, Thermoplastic polyurethane

3.1. Introduction

Several AM technologies have been proposed for producing fully-dense ceramics including selective laser sintering (SLS) [8]–[10], stereolithography (SLA) [11], laminated object manufacturing (LOM) [12], [13], binder jetting [14], extrusion-based printing (robocasting) [15], [16], directed energy deposition (DED) [17], and direct ink writing (DIW) [18].

PDC cellular ceramics have been proposed for applications in various fields such as catalysis [19], metal, liquid and gas filtration [20], [21], drug delivery [22], thermal insulation/ thermal protection systems [23], [24], and scaffoldings for bone regeneration [25], [26]. Mechanical properties [27], [28], thermal behavior [29], chemical and oxidation resistance [30] for cellular ceramics has been successfully reported. Unfortunately, the use of relatively expensive AM processes has limited access to the new opportunities for digitally manufacturing ceramic components.

Additive manufacturing (AM) of polymer derived ceramics (PDCs) has been demonstrated with various methods using preceramic polymers in liquid or solid form as a feedstock combined with various AM technologies [31], [32]. Stereolithography (SLA) techniques have been showcased using liquid ceramic precursors such as polysiloxanes, polysilazanes, and polycarbosilanes. To make the preceramic polymers compatible with the SLA process they must be chemically modified to add photosensitive functionalities or combined with photosensitive resins [33], [34]. In this latter case, careful control over the composition of the chemical mixture is required to obtain optimum rheological and optical attributes [35]. Binder jetting type AM has also been used with solid preceramic polymer powders as the feedstock of the process. The powders are then bound layer by layer using a binder solution [36]. The binder solution has to be optimized to have a suitable rheology and concentration of polymer binders and crosslinking agents for the preceramic polymers [37]. Direct ink writing (DIW), which can be considered a subtype of FFF printing, uses preceramic polymers combined with solvents to obtain the optimum rheology for 3D printing [38], [39]. Ceramic composites can also be manufactured using DIW by including additives in the ink solution. Ceramic structures were obtained by adding boron nitride powder to polysilazane ink solution to achieve superior mechanical properties [40]. Similarly, ceramic composites were obtained by adding silicon carbide powder and carbon fiber chops to the polysiloxane ink solution [41]. A novel method is also described where a solution of polysiloxane preceramic polymer was printed in a support bath/gel made from mixing fumed silica and mineral oil. The rheological properties of both the support gel and the printing solution have to be controlled and optimized to have decent printability [42]. A method similar to the one proposed in this paper was reported by some of us using FFF 3-D printing where 3-D printed structures were coated with polysiloxane preceramic to obtain hierarchically porous cellular ceramics [43]. Selective laser sintering

(SLS) using preceramic polymers was also successfully showcased where polysiloxane powder mixed with SiC filler was selectively cured and pyrolyzed using laser sintering [44].

The above-mentioned processes, however, are limited by some inherent challenges. Such as in SLA, even though very good resolution can be obtained, the resin has to be chemically modified to obtain the suitable rheological and optical properties. Also, the process has to be conducted under controlled environment to avoid crosslinking of the liquid resin and to avoid the toxic fumes from releasing into the environment. With DIW the rheology of the inks has to be maintained to achieve good printability. The method also lacks in resolution compared to other processes due to the same reason. Similar consideration to the binders in the binder jetting process has to be given to maintain printability. Parts made from binder jetting contain porosity since the process starts from powders and the sintering post processing does not close all the porosities in the ceramic parts. The process also has to be conducted in a controlled environment since the micron sized powders can be a health hazard.

Fused filament fabrication (FFF) is the most accessible and widespread method of AM, which was made possible by the open source release of the self-replicating rapid prototyper (RepRap) project [45]. Yet, there is a lack of research in the area of integrating FFF 3-D printing with PDCs. This study aims to fill the gap utilizing PDCs with the low cost and simple process control of the FFF 3-D printing method to produce cellular ceramics with dense struts [46]–[48]. The method uses similar approach of replicating acrylic lattice 3-D printed with SLA [49].

The proposed method uses a two-step process, first to 3-D print cellular structures with FFF 3-D printing using thermoplastic polyurethane (TPU)-based filaments and impregnating the

structure with preceramic polymer (polysilazane). Second, pyrolysis of the impregnated structure produces a self-similar ceramic cellular structure. The method successfully attempts to overcome the drawbacks of previously mentioned AM methods using preceramic polymers by using low cost FFF open source 3-D printing. Since the method uses a desk top 3D printer with commercially available filaments, the printing process does not need to be conducted under a controlled environment unlike SLA and binder jetting. The method also uses commercially available preceramic polymers and solvents which do not require any chemical modification to be suitable for the process. Usage of commercially available polymer filament also avoids production of rheologically controlled ink unlike DIW process. The method also utilizes less power compared to the high-power laser used in SLS.

This study systemically evaluates the impact of i) catalysts, ii) curing environment and iii) pyrolysis sequence optimization to form cellular ceramics with fully dense SiOC(N) struts via the combination of FFF-based 3-D printing with polysilazane-based PDCs. The resultant materials are quantified by hardness depth profiles and compressive strength of completed parts. The results are discussed in the context of three applications that are demonstrated with low-cost ceramic components for medical, aerospace, and high temperature systems.

3.2. Experimental

The initial tests were done using TPU filaments with varying shore hardness; Matterhackers Pro TPU (90A), Matterhackers TPE (98A), Ninjabot NinjaFlex (85A) Fillamentum Flexfill (98A), Colorfabb nGen Flex (95A). The samples were printed as cellular structures with 1.2

mm square cells. The samples were then impregnated with the preceramic polymer (Durazane) solution and then pyrolyzed at 1200°C to obtain the final ceramic (see Methods).

The 1.2 mm cell size forms a vertical channel, which creates a capillary structure for the preceramic polymer solution to rise through the channels. This in turn reduces the necessity to have the excess amount of solution to totally submerge the sample nearly eliminating chemical waste.

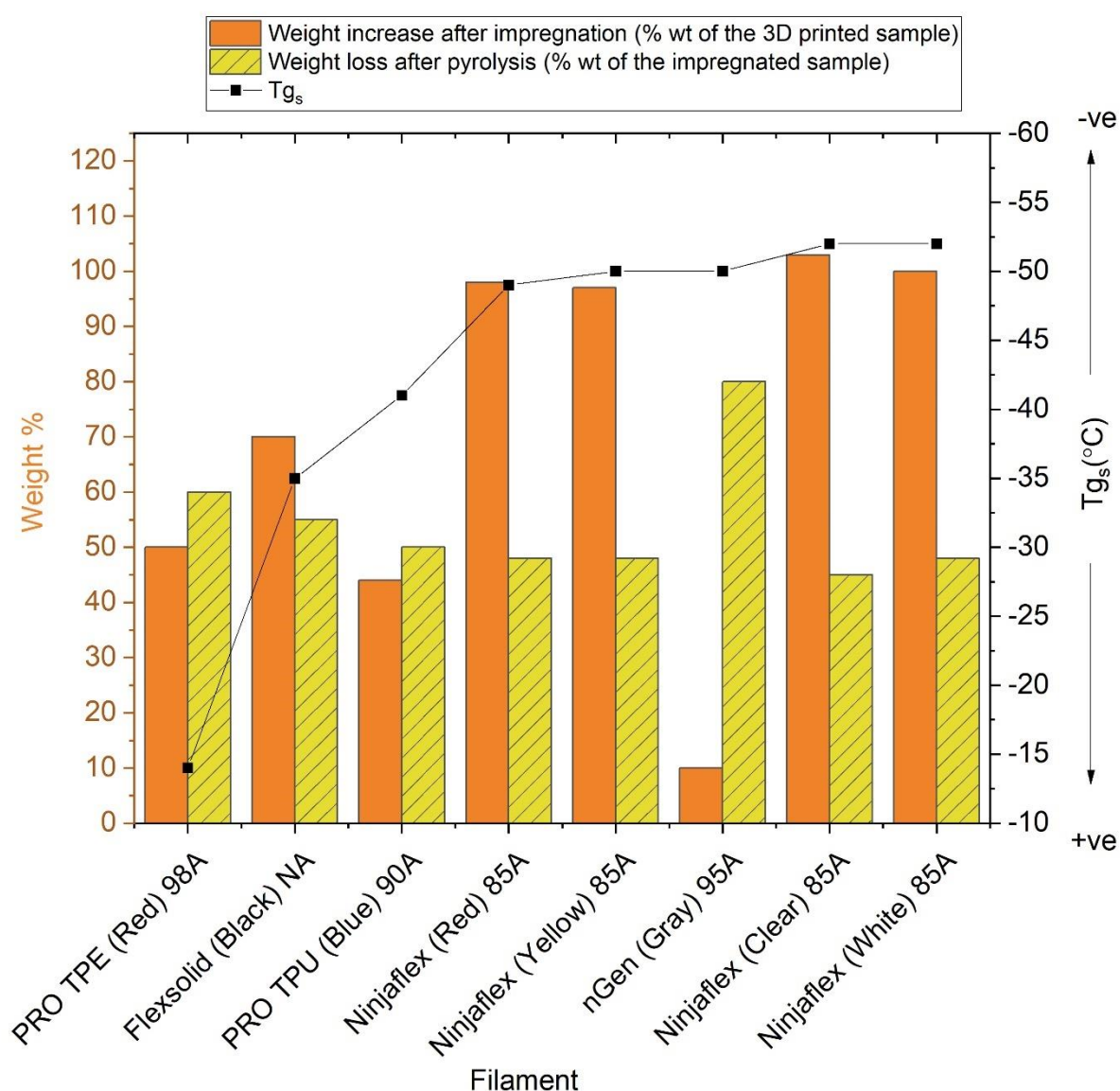


Figure 1: Comparison of TPU filaments of different shore hardness with their glass transition temperatures (T_g s) with increase in weight after impregnation with the preceramic polymer and weight loss after the pyrolysis.

Characterization of the TPU filaments with DSC (**Figure 1**) reveals that the lower the shore hardness the lower the glass transition temperature (T_g). T_g s represents the glass transition of the soft segments [50]. The T_g s ranges from $-52.5\text{ }^{\circ}\text{C}$ (Ninjaflex 85A) to $-13.7\text{ }^{\circ}\text{C}$ (PRO TPE 98A). The glass transition temperature is affected by many factors. Lower T_g indicates higher amounts of amorphous phase in the semicrystalline polymer. T_g also depends on length of the linear polymer chains. The lower the T_g , the greater the length of the chain, which gives the polymer more flexibility [51]. Finally, T_g can also depend on the additives put into the commercial filaments to give them their specific properties such the surface texture and color. The impregnation tests also showed that the more flexible the TPU filament the higher the amount of preceramic polymer retained and, subsequently, the higher the final ceramic yield (Figure 1).

The clear Ninjaflex TPU filament presented the best results regarding the weight increase and final ceramic yield. $100 \pm 5\%$ weight increase after impregnation, $65 \pm 5\%$ volume increase and $17.5 \pm 2.5\%$ increase in linear dimensions were noted after the impregnation indicating successful diffusion and interaction between TPU and polysilazane.

Since the 3-D printed part after impregnation contains both TPU and Durazane in the same amount, the thermal behavior of the TPU filament as well as Durazane precursor must be considered. The DSC analysis of the NinjaFlex TPU filament shows that it starts melting around 165°C . The DTA analysis of the liquid polysilazane precursor mixed with Pt catalyst (100 microliters/g precursor) with constant heating rate of $10^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere,

shows an exothermic peak at 250°C suggesting that it crosslinks into a thermoset polymer around this temperature. This means that, at a constant heating rate, the impregnated PU part will melt and lose its structure before the crosslinking of the Durazane. This implies that a modified heat treatment is necessary for the polysilazane to be crosslinked before the TPU filament reaches the melting onset. According to recent studies [52], polysilazanes can be crosslinked at lower temperatures in air atmosphere. The moisture in air helps activate the crosslinking at temperatures as low as 120°C when exposed for long times by promoting hydrolysis and polycondensation reactions. Following the modified heat treatment schedule, with the isothermal curing at 160°C, the 3-D-printed structures were successfully pyrolyzed into self-similar ceramic structures.

50 ± 2% weight loss was observed during the polymer to ceramic transformation. The ceramic yield from pure Durazane is reported to be 65 to 70%. The Ninjaflex filament decomposes up to 95% above 500 °C. If there was no interaction between the TPU and the polysilazane, expected ceramic yield of the system would be only 35 to 40%. The 50% final yield from the NinjaFlex and Durazane system indicates the existence of some chemical reaction forming intermediate products, which contribute to the extra 10% ceramic yield.

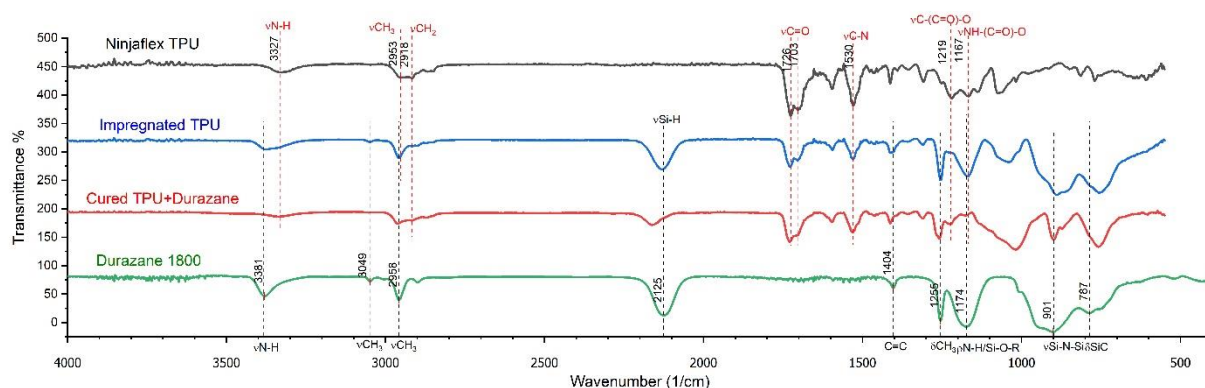


Figure 2: Comparison of FTIR spectra of i) Ninjaflex TPU filament ii) TPU filament impregnated with Durazane precursor iii) Impregnated filament cured at 160°C for 3 hours iv) Pure Durazane 1800 precursor

Further investigations with the FTIR (**Figure 2**) show that, in the cured sample, the Si-H peak coming from the polysilazane is shifted towards higher wavenumber and the -NH-(C=O)-O (urethane) peak disappears after crosslinking. N-H peak at 3380 cm^{-1} coming from Durazane are reduced after crosslinking. Taken all together this information indicates that there might be some chemical interaction occurring between the TPU polymer and the polysilazane, which further promotes the impregnation and increases the ceramic yield.

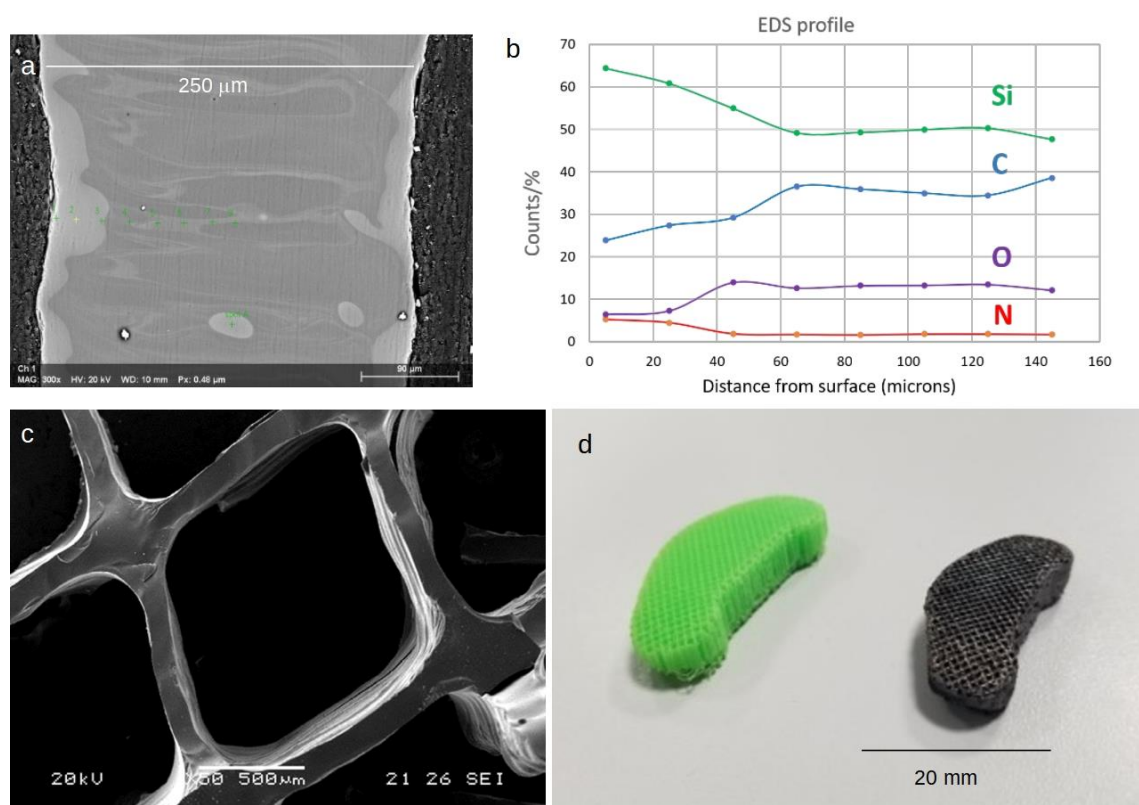


Figure 3: (a) Backscatter image of cross section of the strut of the final ceramic component with points for EDS analysis. (b) EDS profile of Si, C, O and N going from the surface to the center. (c) SEM image of the fracture surface of the ceramic sample. (d) 3-D printed

prototype spinal disc for potential prosthetic use in human spine and the converted ceramic counterpart. Note: the EDS profile is not quantitative but provides a qualitative view on the change in composition of elements from the surface to the core.

The SEM images (**Figure 3a and 3c**) show that the struts are completely dense indicating that the impregnation was successful.

The elements profile (Figure 3b) demonstrate that Si is present in high amount even at 140 microns beneath the surface, which means at the center of the struts (thickness around 280 – 300 microns). This is the result of Durazane easily diffusing in the TPU structure. Indeed, a similar EDS study conducted on the impregnated TPU component (see supporting information) confirmed the presence of Si through the strut cross section and, also, evidenced a localized higher concentration of Si at the surface of the struts which should be related to the deposition of a thin Durazane coating.

Moreover, the SEM (Figure 3a) shows some bright regions near the surface of the struts and the EDS scan of the cross section (Figure 3b) reveals a Si gradient in the first 60 microns with a higher concentration close to the surface. The reason can be that, together with the diffusion of polysilazane in the PU structure, also a thin layer of polysilazane can deposit on the surface of the struts explaining the formation of the bright, Si-rich, regions.

The easy diffusion of Durazane into the TPU structure is probably due to a good chemical affinity between the two polymers which have similar functional groups (N-H and Urethane groups), unlike the polysiloxane which has less chemical similarity with the TPU and the impregnation process results into a thin coating on the surface of the surface compared to the

diffusion to the core. This leads a formation of hollow ceramic struts instead of a fully dense strut [43].

The carbon and oxygen profiles (Figure 3b) show an increase towards the center of the struts. The oxygen presence cannot be attributed to the oxidation occurring during the curing process in air. Indeed, if this was the case then a reverse oxygen profile, with higher concentration near the surface and decreasing toward the core would have been found. Most probably oxygen comes from a reaction between the decomposing urethane groups, producing CO₂ [53] and the polysilazane. Such reaction would also explain why the amount of nitrogen measured was low compared to the expected SiCN ceramic composition from polysilazane precursors [54]. Indeed, it is known that pyrolysis of polysiloxanes in CO₂ flow results in cleaving the Si-C bonds and formation of new Si-O bonds [55], [56]. Thus, it can be tentatively assumed that a similar reaction occurs between the in-situ produced CO₂ and Si-N bonds of polysilazane resulting into an increase of oxygen in the ceramic residue and an elimination of nitrogen as N₂ or NH₃.

3.2.1. Testing

Chemical analysis shows the average composition of the ceramic samples. Nitrogen was observed to be no more than 2 mass percent. The average phases of the ceramic were calculated as (mass%) 56% SiO₂, 4.3% Si₃N₄, 9.2% SiC and 30.5% free carbon making the final composition SiO_{1.5}C_{0.18}N_{0.1} + 2 C_{free}.

The density of the material was found to be 2.12 g/cm³, which is similar to SiOC ceramics reported in the literature.[57] The hardness of the silicon and nitrogen rich surface region was

found to be 8.6 ± 0.5 GPa and that of the oxygen + carbon rich core regions were found to be 7.1 ± 0.2 GPa.

20mm $\times$ 20mm $\times$ 10mm compression samples (see supporting information) were tested with two different types of infill grid and tri-hexagonal with 1.2 mm cell size (25% infill density). The infill pattern was exposed along the direction of the load. The average compressive strength for tri-hexagonal infill was 24 ± 1.5 MPa while for grid type samples was 22 ± 1.8 MPa.

45mm $\times$ 6mm $\times$ 3mm samples (see supporting information) for 4-point bending tests were printed with 25% dense grid and tri-hexagonal infill, with the infill pattern perpendicular to the direction of the load. The average flexural strength of the grid infill samples was 17 ± 3 MPa and for tri-hexagonal infill it was 18 ± 0.7 MPa.

One of the main areas where silicon-based ceramics can be utilized are high temperature applications. Taking advantage of the PDC route ultra-high temperature resistant ceramic materials can be obtained [58]. Silicon-based PDCs, for example, can be high temperature resistant for temperatures greater than 1000°C [59]. Cellular ceramics are beneficial in many fields as they possess better thermal and physical properties than the bulk ceramics in some cases [60]. Open cell ceramic structures also possess better thermal conductivity as heat transfer is improved because of the fluid flow through the cells [61]. Silicon-based ceramics have a higher specific heat capacity compared to alumina and zirconia as well as higher thermal conductivity and thermal shock resistance. Therefore, silicon based cellular ceramics can find applications in fields as porous burners and high temperature catalyst carriers [62]. For applications such as heat shields and heat exchangers the ceramic parts need to fit industrial tolerances [63].

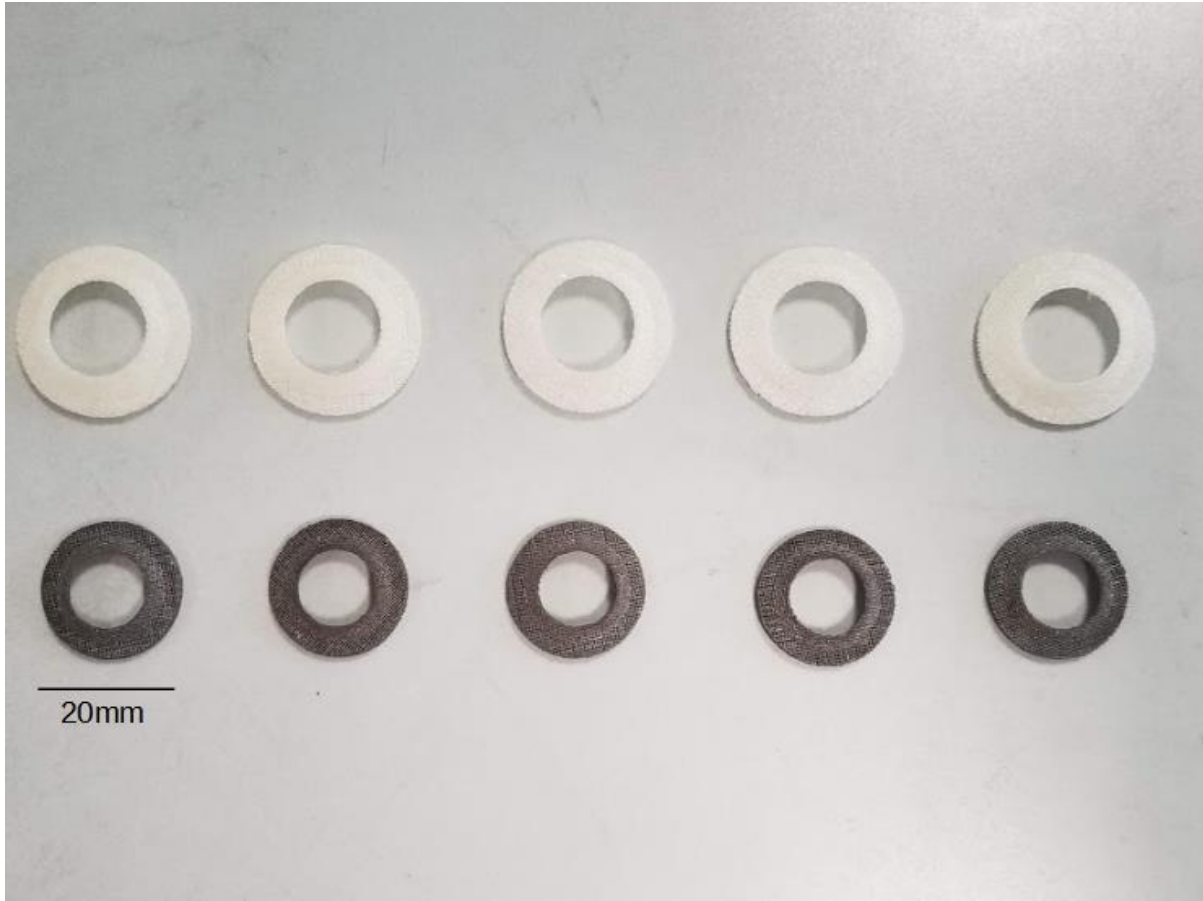


Figure 4: Ring shaped spacer parts to test the fitting tolerances

To check the fitting tolerances, a ring-shaped part to fit between two metal plates (**Figure 4**) was designed with final dimension requirements of 20 mm outer diameter, 15 mm inner diameter and 4 mm thickness. Since from the previous experiments the average increase in linear dimensions was 17.5% during impregnation and the average decrease in after pyrolysis was 32%. The parts were printed in the dimension 25mm diameter and 5mm thickness. These measurements were then increased to $29.3 \pm 0.1\text{mm}$ in diameter and $5.9 \pm 0.1\text{mm}$ in thickness. After the pyrolysis, the standard deviation in the diameter measurement was 0.11 with the mean being 19.87mm and for the thickness measurement standard deviation and mean being 0.05

and 4.01mm, respectively. The mechanical tolerance of the parts was within 0.1mm, which is the limit set by the FFF printer used.

3.2.2. Testing for applications

3.2.2.1 High temperature applications

The same samples were used for high temperature stability testing. After 12 hours at 1500°C, $0.5 \pm 0.15\%$ weight loss and $2 \pm 0.25\%$ shrinkage in the linear dimensions was observed with a reflective layer formed on the structure. This suggest that the structure is not losing mass, which might affect the performance at high temperatures. The reflective layer can be a result of the oxidation and formation of a thin, passivating, silica layer. SEM pictures of the ceramic components before and after the oxidation are shown in **Figure 5**. The component after oxidation for 12 h at 1500 °C in air does not show any major modification. In order to get more insights into the oxidation behavior a TGA was performed in flowing air up to 1500°C (see supporting information). This experiment showed the presence of only one weight loss step between 600 and 1200°C of ca 2 wt% which can be attributed to the oxidation of free carbon. The 0.5 wt% loss measured in the bulk samples after the oxidation in air for 12 hours must therefore be the results of the 2 wt% weight loss due to C oxidation and an opposite weight increase due to the formation of a silica scale.

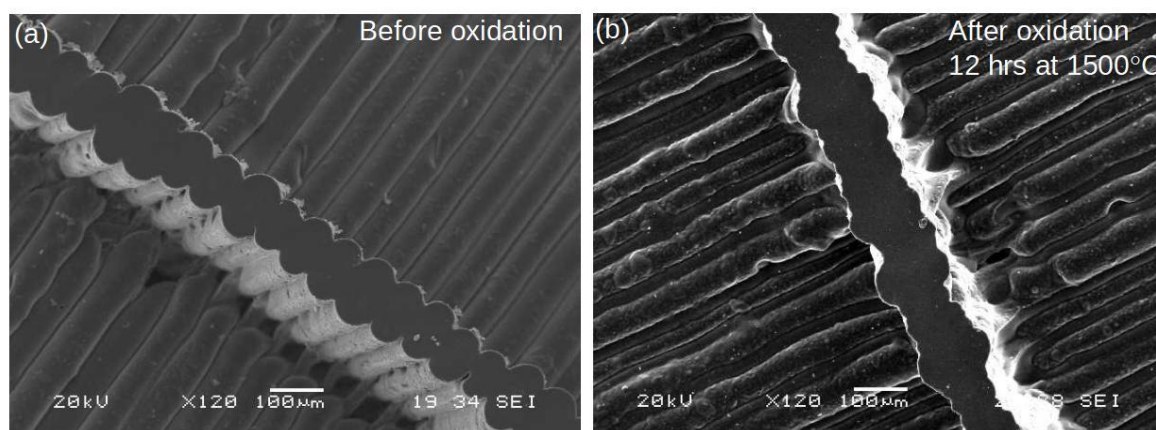


Figure 5: SEM image of the fracture surface of the ceramic (a) before oxidation and (b) after oxidation on the left.

Other oxidation studies done on polymer derived SiOC ceramics show that the system undergoes passive oxidation as the activity of the free carbon present in the ceramic is very low [64]. The outer layer being rich in silicon and nitrogen as well as most of the free carbon being in the center of the strut might help preventing the oxidation of the free carbon. Previous research also shows that SiOC (N) ceramics exhibit a higher thermal stability due to inclusion of nitrogen [65], [66].

3.2.2.2. Scaffoldings for bone tissue regeneration

One of the main applications the cellular ceramic can be used for is scaffoldings for bone regeneration [67], [68]. Ceramic AM with materials like hydroxyapatite, bioactive glasses, polylactic acid, zirconia, calcium phosphate has already been demonstrated [26], [69]. Moreover, SiOC ceramic nanowires in the form of scaffolds have already been tested for biocompatibility. SiOC ceramic structures have been shown not to be cytotoxic and to support cell growth and activity beneficial for tissue regeneration [70]. SiOC material has also been

tested for blood contact applications resulting in good hemocompatibility due to the presence of pyrolytic carbon [71]. Similarly, the 3-D printed ceramic scaffolds need to satisfy the cytotoxicity and cell proliferation tests as a first step to be considered compatible as scaffolds for bone tissue regeneration [72].

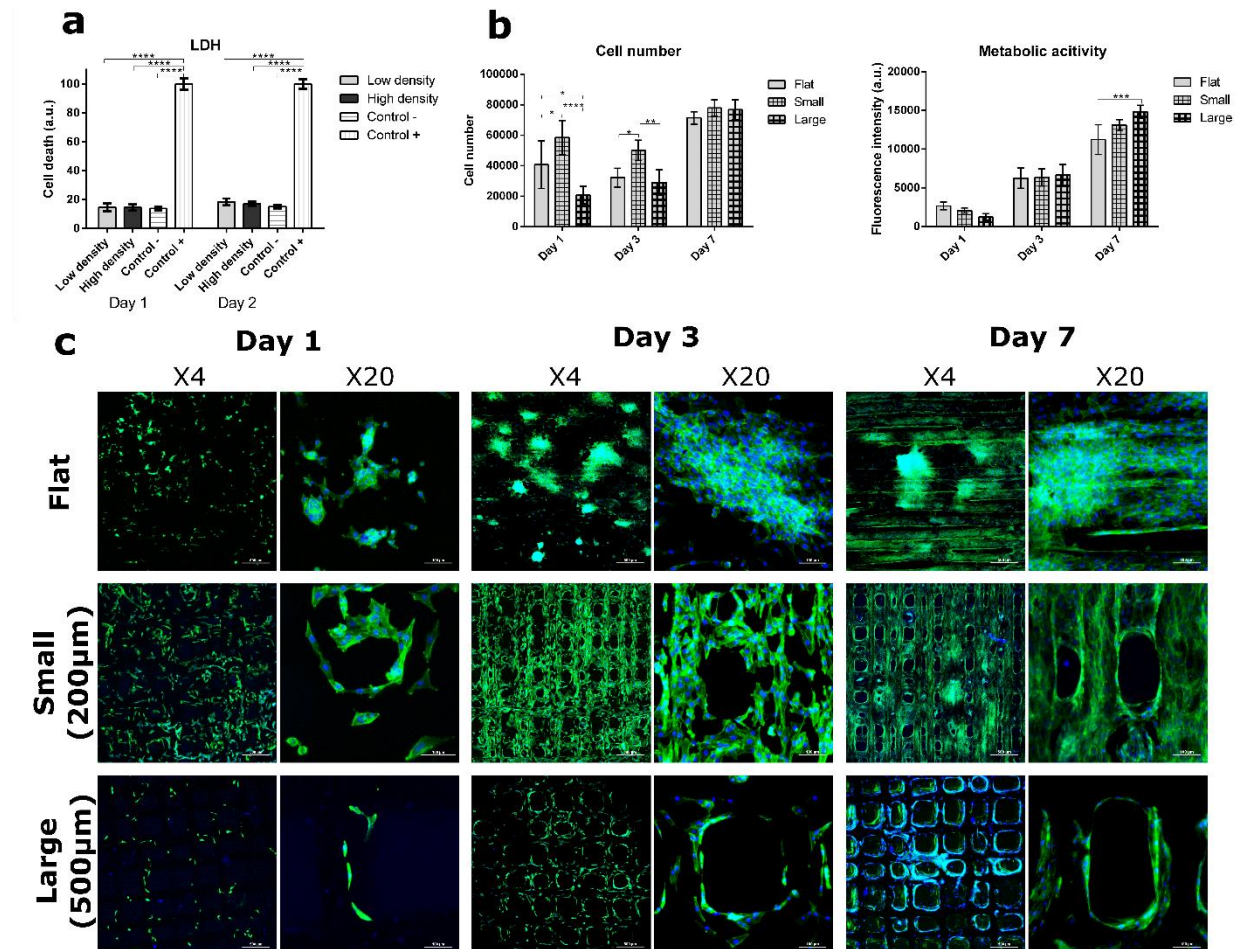


Figure 6: (a)Cell death ratios on low density (500µm pores) and high density (200µm pores) samples compared to the negative control sample (b)Increase in cell number and cell metabolic activity on flat, small pore, large pore samples on day 1, day 3 and day 7 (c) Confocal images of cell growth on flat, 200µm pore and 500µm pore samples after day 1, day 3 and day 7.

Figure 6a shows the results of the cytotoxicity test for the high density (200 μm) and low density (500 μm) samples. The cell death ratios after 24 and 48 hours are close to the negative control samples, indicating the materials are not cytotoxic, and the infill density does not affect the cytotoxicity. Figure 6b shows that from day 1 to 7, the total cellular metabolic activity increased gradually in general; however, samples with larger porosity showed the highest activation if compared with the reference system, flat sample. Figure 6c shows the results of cell adhesion, metabolism and proliferation. The cells seemed to proliferate when cultured with smaller porosity, however they grew in a monolayer on the top surface bridging the pores. The lower density samples with 400 μm pores seemed to help the cell adhesion and together cell migration growth inside the pores, instead of forming the surface layer, but with a slower proliferation rate. In all the samples the cell-to-cell connections is clearly visible.

3.2.3. Cost Calculation

The main concern when it comes to specialized materials and custom applications is the cost. Even if AM saves costs in inventory, assembly, retailing and distribution compared to the conventional manufacturing processes, AM methods such as laser sintering and thermal jetting have high capital and operating costs associated to them. This study has shown that the distributed manufacturing model using low-cost FFF-based 3-D printing, which has proven to consistently reduce costs fabricating open source designs [73], also reduces the materials costs of custom ceramic components to less than 5% of those currently commercially available.

The machine costs for SLS printers constitute almost 60% of the total production costs over its lifetime, with the machines costing around \$500,000 [74]. The cost of energy consumption for laser-based systems can be as high as 500% compared to the FFF 3-D printing [75], which have been shown to be even less energy intensive than conventional manufacturing when used

for distributed manufacturing [76]. This energy efficiency in production also reflects in the cost of the commercial product when one needs to get a part printed from a company.

To compare the production costs, quotes were obtained from commercial manufacturers of ceramic 3-D printed parts for a spinal disc (bio-ceramic part) and a micro satellite nozzle (high temperature application part) (Figure S2) with the materials that would satisfy the application requirements. A simple model to analyze the production cost of the parts with this method was used.[77] The cost of the build can be calculated as:

$$C_{\text{build}} = (C_{\text{energy}} \times T_{\text{build}})_{\text{printer}} + (M \times P_{\text{raw material}}) + (C_{\text{indirect}} \times T_{\text{pyrolysis}})$$

Where,

C_{energy} = cost of energy consumption for the printer per hour.

T_{build} = Time for the build.

M = Amount of raw material used (this consists of the TPU filament, Durazane 1800, Acetone solvent, Pt Catalyst, p-Xylene solvent)

$P_{\text{raw material}}$ = Price of the raw material.

C_{indirect} = Indirect costs for the furnace (this consists of the energy consumption, the purging gas, and the cooling water).

$T_{\text{pyrolysis}}$ = Time the furnace is operated for the pyrolysis.

Table 1 describes the costs estimation for a single part and a batch of 10 parts.

The nozzle is also manufactured as a cellular structure with the impregnation method as it provides more surface area for better heat dissipation without losing any functionality as a heat shielding component.

Table 2 shows the material costs for the parts from commercial ceramic AM companies. It shows that the distributed manufacturing ceramics with the impregnation approach reduces the cost by as much as 200 – 300%.

Table 1: Cost analysis of manufacturing 1 component and 10 components

Consumables	Cost	Spinal Disc (150 micron nozzle)	Cost (Euro s)	Spinal Disc (10 pieces)	Cost (Euro s)	Nozzle (250 micron nozzle)	Cost (Euro s)	Nozzle (10 pieces)	Cost (Euro s)
Electricity for printer (500W)	€0.25/kWh	25 min (0.208 kWh)	0.05	17 hours (8.5 kWh)	2.125	3 hrs 54 mins (2 kWh)	0.5	39 hrs 18 mins (20 kWh)	5
TPU filament	€40/750 g	0.001 g	0.01	92 g	5	9 g	0.53	98 g	5.24
Durazane	€200/1Kg	10 g	2	100 g	20	30 g	6	300 g	60
Pt Catalyst	€150/5ml	25 µl	0.75	250	7.5 µl	75 µl	2.25	750 µl	22.5

Acetone	€50/lit	10 ml	0.5	100 ml	5	30 ml	1.5	300 ml	15
p-Xylene	€100/lit	475 µl	0.04	4.75 ml	0.4	1.425 ml	0.12	14.25 ml	1.2
Electricity for furnace (7500 W)	€0.25/kWh	6.16 hrs (46.25 kWh)	11.5	6.16 hrs (46.25 kWh)	11.5	6.16 hrs (46.25 kWh)	11.5	6.16 hrs (46.25 kWh)	11.5
Nitrogen (300cc/min for 9 hours)	€110/(8 liter 150 bar)	162 lit	15	162 lit	15	162 lit	15	162 lit	15
Total cost			29.85		66.525		37.4		135.44
Cost per piece					6.6525				13.54

Table 2: Cost comparison of commercial ceramic AM and FFF 3DP

	AM method	Spinal disc 1 piece (Euros)	Spinal disc batch (Euros)	Nozzle 1 piece (Euros)	Nozzle batch (Euros)
Steinbach AG (Alumina)	Stereolithography	745	220/piece (for 10 pieces)	1900	1145/ piece (for 5 pieces)
Creatz 3D (Alumina)	Stereolithography	780	282/piece (for 5 pieces)	780	282/ piece (for 5 pieces)
Creatz 3D (Zirconia)	Stereolithography	1380	584/piece (for 5 pieces)	1380	584/ piece (for 5 pieces)
Formatec (Silica)	Digital Light Processing	Cannot make.	Cannot make.	950	NA
Protiq marketplace (Alumina)	Stereolithography	1927	NA	3117	NA
UniTrento	TPU replica	29.85	6.6525/ piece (for 10 pieces)	37.4	13.544/ piece (for pieces)

3.3. Conclusion

In conclusion, it has been demonstrated for the first time, that SiOC (N) cellular ceramic structures with fully dense struts can be manufactured by impregnating preceramic polymers into FFF 3-D printed TPU structures in fraction of the cost of the competing methods.

With the use of an open source 3-D printing technique, the principal cost of investing in expensive machinery is saved [78]. The method uses commercially available materials, which brings the operating costs down. The same part can be manufactured at 5% of the material cost compared to the commercial manufacturers using a distributed manufacturing technique.

The novel method demonstrated in the research, eliminates the possibility of having pores with complete impregnation of the preceramic polymer in the TPU structure, which can be manufactured with industrial tolerances. The material of the ceramic is biocompatible and promotes fast cell adhesion, and early-stage cell activations which gives the possibility to mimic the bone tissue geometry for bone regeneration.

In the future, the method can be modified to manufacture ceramic composites by either adding nano fillers in the preceramic polymer solution or modifying the TPU filament to expand the use of the structures in applications such as active filters, catalytic converters, or electrically conductive applications.

3.4. Methods

FFF printing: The filaments were printed on an open source Lulzbot TAZ 6 (Fargo Additive Manufacturing Equipment 3D, LLC, USA) with nozzles of size 0.15 mm and 0.25 mm.

Design of Samples: The samples were designed as 20 mm × 20 mm × 10 mm cubes using OpenSCAD 2015.03 and prepared as cellular structures with line type infill and line distance (cell size) of 1.2mm using the open source Lulzbot Cura 3.6.21 slicer.

Impregnation: A commercial polysilazane (Durazane 1800; CAS: 503590-70-3; Merck, Darmstadt, Germany), precursor for silicon carbonitride (SiCN) ceramic, was used along with the catalyst platinum divinyltetramethyldisiloxane complex, ~Pt 2 % in xylene (CAS number: 68478-92-2, Sigma-Aldrich, St. Louis, MO, USA) diluted to 0.1 %. Pt catalyst promotes the crosslinking of the preceramic polymer *via* hydrosilylation reaction between the Si-H and the C = C moieties present in the silicon polymer [79]. The TPU sample was first submerged in a solution of 5g acetone and 500 microliters of catalyst. After 15min. 5g of the preceramic polymer was added and kept for 4 hours changing sides after 2h. The samples were then taken out and dried for 24h in air at room temperature.

Heat Treatment: The samples were then treated in an alumina tube furnace (GERO tube furnace) at 160°C (10°C/min) in air flow (400cc/min) for 3 hours and then free cooling back to room temperature. The furnace was then purged with nitrogen flow (400cc/min) for 2 hours following a pyrolysis to 1200 °C with 1-hour dwelling at the maximum temperature. The samples were then cooled to room temperature at 10°C/min. For biological evaluations, the samples were rinsed by deionized water (DI water) and then sterilized by autoclave at 121°C for 15min.

Characterization of TPU filaments: For the characterization of the TPU filaments for their thermal behaviour, differential scanning calorimetry (DSC) (Mettler DSC30) and infrared spectroscopy (ATR, Varian 4100 FTIR, Agilent Technologies Inc., USA) were performed. Fourier transform infrared spectroscopy was also done on the as received Durazane 1800 (Nicolet Avatar 330 FTIR spectrometer, Thermo Fisher Scientific, Waltham, MA, USA).

The crosslinking of the preceramic polymer and decomposition of TPU filaments was examined using simultaneous differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) (Netzsch STA 409 Netzsch GmbH, Selb, Germany) at 10°C/min up to 1200°C in flowing Air/N₂ (150 cc/min).

Mechanical Testing: Density of the final ceramic is measured with a helium pycnometer (AccuPyc 1330TC, Micromeritics, Norcross, GA, USA). Hardness testing was also done along polished section of the struts with FM-310 microhardness tester (Future Tech). Compression tests and 4-point bending tests were performed using Instron 5969 testing machine with 10kN load cell with displacement 1mm/min.

Electron Microscopy and EDS: The ceramic morphology and elemental composition from the surface to center of the struts were characterized using energy dispersive spectroscopy (EDS) with scanning electron microscope Jeol JSM-IT300LV.

High Temperature stability: To check the high temperature stability the samples were held in air for 12 hours at 1500°C and the weight and dimension changes were observed.

Biocompatibility for scaffoldings as bone tissue regeneration: The samples were also tested for biocompatibility for the purpose of regeneration of bone tissue. The samples were designed as discs of diameter 13mm and thickness 1.5mm with pore sizes of 200µm and 500µm.

The cytotoxicity was evaluated on sample extracts by using the lactate dehydrogenase assay (LDH assay-TOX-7 Sigma) on NIH 3T3 cell lines (murine embryo fibroblast, ATCC) in vitro cultures, by following ISO 10993-5 protocol with experimental time points on day 1 and 2 against a control group of cells cultured in the standard medium.w

The cell behavior on porous samples was evaluated by culturing MG63 (human osteosarcoma, ATCC) cells up to 7 days and measurements were done at day 1,3 and 7.

To evaluate the cell proliferation PicoGreen DNA quantification assay (Quant-iT PicoGreen dsDNA Assay, Invitrogen, Carlsbad, USA) was used. For both the cell behavior and the cell proliferation tests, flat samples of the same material were used as control and measurements were taken after day 1, 3 and 7.

Cell metabolic activity was determined by AlamarBlue Cell Viability assay (Invitrogen, Carlsbad, USA), that quantifies cellular metabolic activity and in turn determines the concentration of viable cells in each sample. Measurements were taken after day 1, 3 and 7. Cell morphology and distribution was visualized by Oregon green phalloidin (cytoskeleton filament) and 4'6-diamidino-2-phenylindole (DAPI) (nuclei) staining and observed using Zeiss LSM 510 Meta confocal laser scanning microscope.

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3.5. Supporting Information

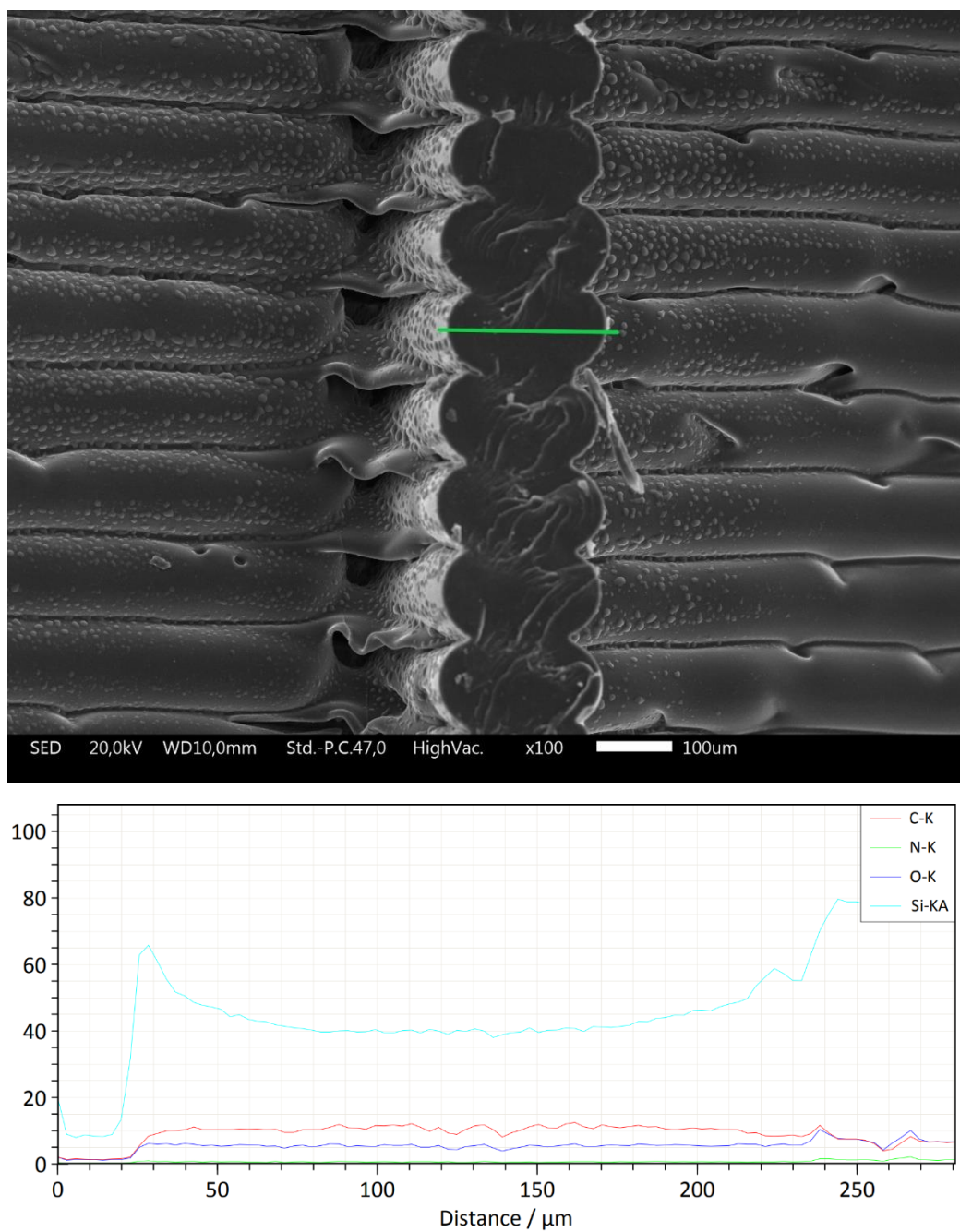


Figure S1: EDX line scan across the cross section of the strut of TPU structure impregnated with Durazane 1800.

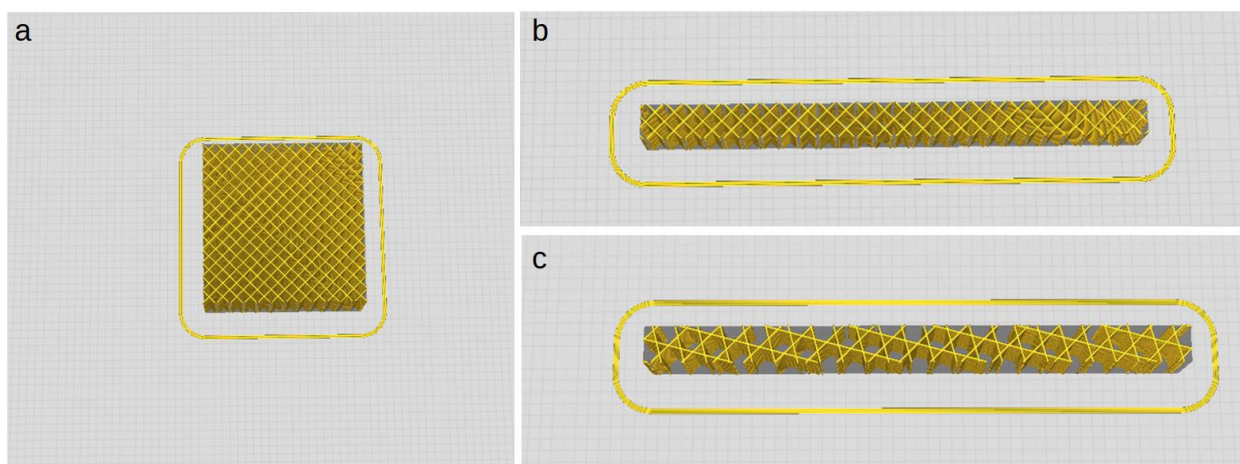


Figure S2: (a) Schematic for compression test (grid infill) (b): Schematic for 4-point bending test (grid infill) (c) Schematic for 4-point bending test (tri-hexagonal infill).

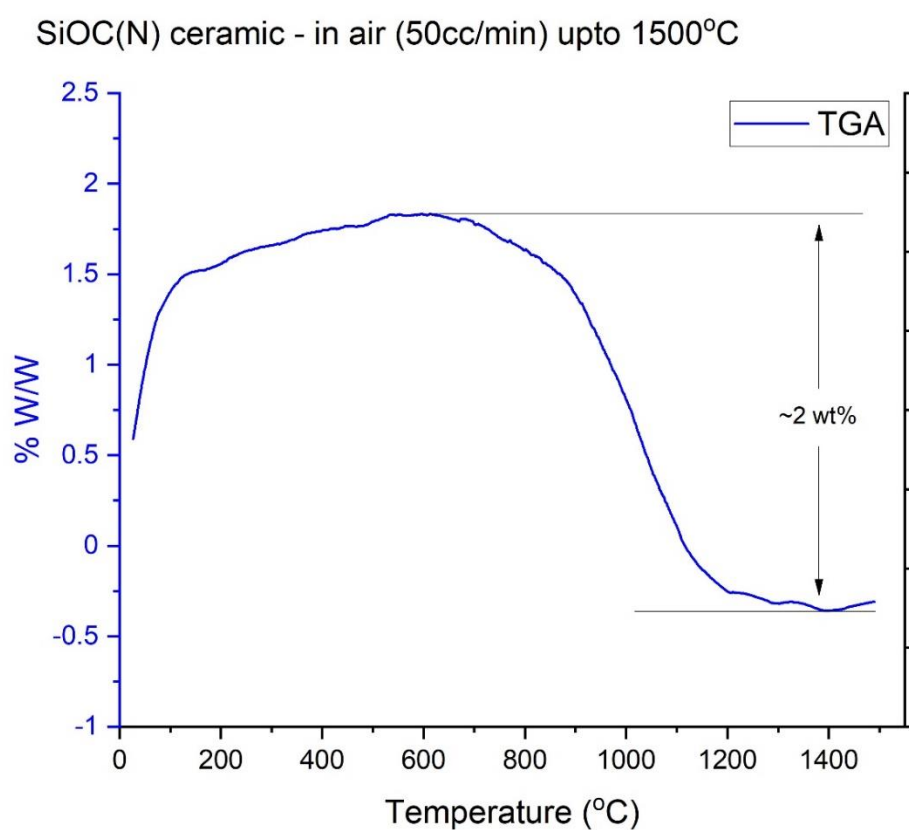


Figure S3: Thermogravimetry and Differential thermal analysis of the SiOC(N) ceramic samples from room temperature to 1500°C with the heating rate 5°C mm⁻¹.

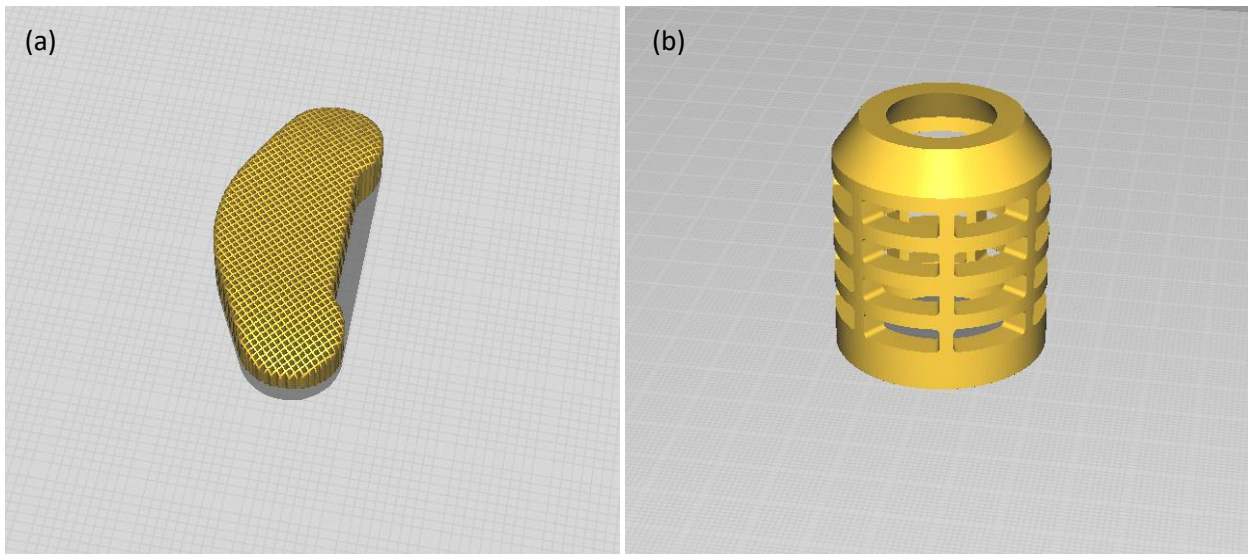


Figure S4: STL models for cost comparison (a) spinal disk (b) nozzle

5.6. References

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Chapter 4

3D Printed SiOC(N) Ceramic Scaffolds for Bone Tissue Regeneration: Improved Osteogenic Differentiation of Human Bone Marrow-Derived Mesenchymal Stem Cells

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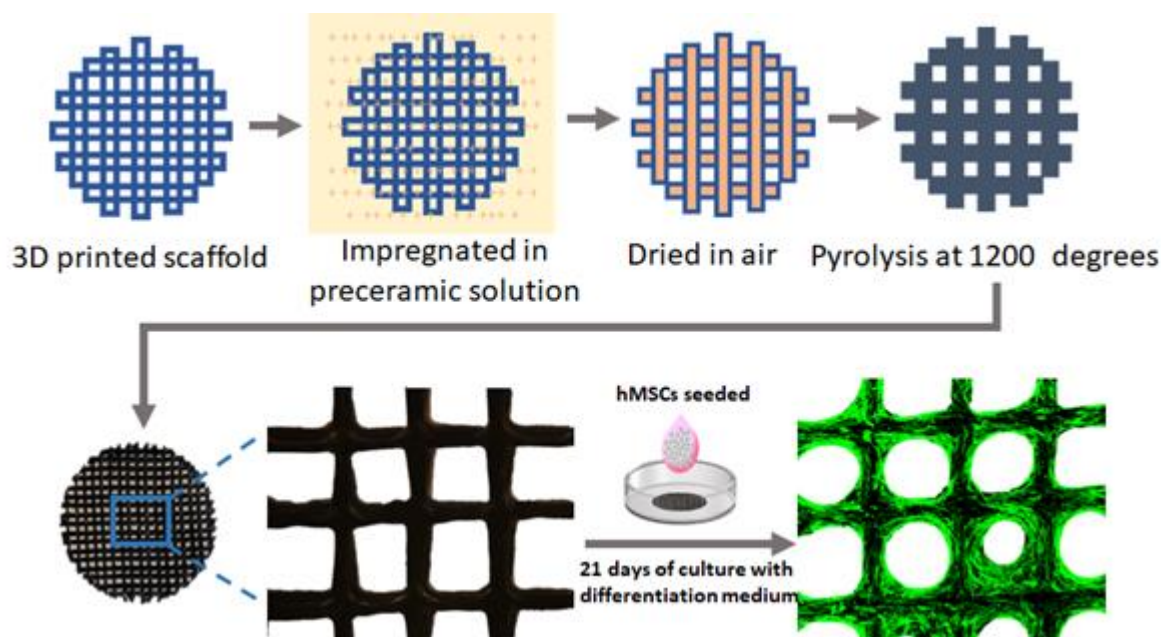
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Graphical Abstract



Abstract

Bone tissue engineering has developed significantly in recent years as there has been increasing demand for bone substitutes due to trauma, cancer, arthritis, and infections. The scaffolds for bone regeneration need to be mechanically stable and have a 3D architecture with interconnected pores. With the advances in additive manufacturing technology, these requirements can be fulfilled by 3D printing scaffolds with controlled geometry and porosity using a low-cost multistep process. The scaffolds, however, must also be bioactive to promote the environment for the cells to regenerate into bone tissue. To determine if a low-cost 3D printing method for bespoke SiOC(N) porous structures can regenerate bone, these structures were tested for osteointegration potential by using human mesenchymal stem cells (hMSCs). This includes checking the general biocompatibilities under the osteogenic differentiation

environment (cell proliferation and metabolism). Moreover, cell morphology was observed by confocal microscopy, and gene expressions on typical osteogenic markers at different stages for bone formation were determined by real-time PCR. The results of the study showed the pore size of the scaffolds had a significant impact on differentiation. A certain range of pore size could stimulate osteogenic differentiation, thus promoting bone regrowth and regeneration.

Keywords: Bone tissue regeneration, polymer derived ceramics, biocompatibility, stem cells, osteogenic differentiation, additive manufacturing, fused filament fabrication, cellular ceramics, open source 3D printing

4.1. Introduction

Silicon-based ceramic scaffolds for bone regeneration are one of the main strategies used for the treatment of bone loss and large-scale bone defects [1]–[5]. Current studies show that silicon is an essential element for bone development and formation [6], [7]. Silicon-based materials play an important role in the surface bioactivity through the exchange of ions at the scaffold–tissue interface, which results in the formation of a layer, similar to the mineral phase of bone [8]. Silicon possesses similar properties to phosphorus when it comes to bone formation and development [9]. Previous research has shown that the expression of some osteogenesis-related genes, e.g., alkaline phosphatase (ALP), bone morphogenetic protein-2(BMP-2), and collagen type I (Col I), are affected by silicon [10]. Silicon also contributes to the promotion of early deposition of apatite, the growth of osteoblasts, and some genes that control the induction of cell cycles and progression which enhance osteogenesis [11]. Enhanced apatite mineralization ability, biocompatibility, and bioactivity are also seen. A significant increase in

the expression of angiogenic factors of human bone marrow-derived mesenchymal stem cells (BMSCs), osteogenic genes, and alkaline phosphatase activity were seen due to the presence of silicon [12].

Moreover, the silicon-based ceramic scaffolds for bone regeneration have a highly porous 3D architecture with interconnected porosities, which is a similar architecture to that of bone. These porosities allow cells to adhere, proliferate, migrate and invade the vasculature [13], [14]. The pore size, however, can be tailored for the targeted tissue and the cells, as the size of the pores and the density significantly affect cell adhesion, proliferation, and spatial distribution [15], [16]. It has been shown that the osteogenic differentiation of human mesenchymal stem cells (hMSCs) was highly dependent on the geometry of the scaffolds [17], [18]. Along with the porosity, the scaffolds should also have similar mechanical properties to the bone in which the scaffold is to be implanted. Since porosity can act against the mechanical strength, the scaffolds need to have the right balance of porosity and mechanical properties [19], [20]. Some studies have shown that the best possible properties for scaffolds would be comparable to the cortical bone, where the ideal porosity would be around 60–90%, with a pore size greater than 150 microns [21]–[23]. Undesirable mechanical properties of scaffolds can lead to undesirable results during osteogenic differentiation. Thus, it is preferable to have scaffold materials with properties similar to the bones [24]–[26].

Thanks to the development of additive manufacturing technology, the complex structure and various pore sizes of the silicon-based ceramic scaffold can be easily obtained. Various 3D printing methods have showcased the fabrication of ceramic scaffolds, such as selective laser sintering (SLS) [27], [28], stereolithography (SLA) [29], binder jetting, material jetting, etc. The simplest, most widespread and lowest-cost method of 3D printing is material extrusion or fused filament fabrication (FFF) [30], [31]. Direct (material) extrusion of ceramics, however,

is limited to certain ceramics that can be made into slurries or inks/gels, and the resolution and details obtained from them are not adequate for many applications. Polymer-based FFF, on the other hand, has been undergoing rapid open source technical evolution [32], [33] and resolutions better than 100 microns can be achieved [34].

Polymer-derived ceramics, PDCs, are novel multifunctional ceramics obtained from pyrolysis in a controlled atmosphere of preceramic polymers [35]. PDCs can be processed in different shapes including porous foams and aerogels [36], [37]. PDCs have already been showcased for biomedical applications such as multidrug delivery systems [38], [39]. A novel method of fabricating SiOC(N) cellular structures with dense struts by integrating FFF 3D printing with polymer-derived ceramics was reported in our previous paper. The method utilizes the simplicity of the polymer FFF combined with the polymer-derived ceramics to obtain high-resolution ceramic scaffolds [40], [41] with both tunable pore size and low-cost fabrication on a RepRap-class 3D printer able to print thermoplastic elastomer [42], [43]. Moreover, the preliminary biological evaluations in a previous study showed that the ceramic material has good cytocompatibility, promoting fast cell adhesion and early-stage cell activities [40]. This makes it possible to apply the scaffold to mimic the bone tissue geometry and microenvironment for bone regeneration.

The study presents in vitro testing of the SiOC(N) porous ceramic scaffolds for bone regeneration applications. Ceramic scaffolds with two different pore sizes (300 μm and 500 μm) were tested here to demonstrate the impact of the pore size on cell behavior. Human bone marrow-derived mesenchymal stem cells (hMSCs) were seeded on the top of the scaffolds and cultured in the osteogenic differentiation medium for 21 days. The cell metabolism, proliferation, alkaline phosphatase (ALP) activity, and morphology were evaluated. Finally,

the gene expression level of the main osteogenic differentiation markers was investigated by quantitative real-time PCR.

4.2. Materials and Methods

4.2.1. Preparation of Ceramic Scaffolds

The samples were designed [44] (OnShape, PTC) as porous discs of 13 mm diameter and 1.5 mm thickness. The samples were designed with different pore sizes of 300 microns (small pores) and 500 microns (large pores) to analyze the effect of pore size on bioactivity (Figure 1). They were first printed on an open source RepRap-class FFF 3D printer (Lulzbot TAZ 6, Fargo Additive Manufacturing Equipment 3D, Fargo, ND, USA) using NinjaFlex TPU with a 0.15 mm nozzle. The scaffolds were printed with the pore sizes of 500 and 700 microns since the pyrolysis process results in 25–30% shrinkage. They were then impregnated with a solution of acetone, polysilazane preceramic polymer (Durazane 1800, Merck GmbH, Darmstadt, Germany), and catalyst platinum divinyltetramethyldisiloxane complex, Pt 2% in xylene (CAS number: 68478-92-2, Sigma-Aldrich, St. Louis, MO, USA). The discs were then dried for 24 h in the air and pyrolyzed in a tube furnace (Gero tube furnace) at 1200 °C for 1 h in a nitrogen atmosphere with 400 cc/min flow. The obtained scaffolds were first rinsed with deionized water (DI water) and then sterilized by autoclave at 121 °C for 15 min.

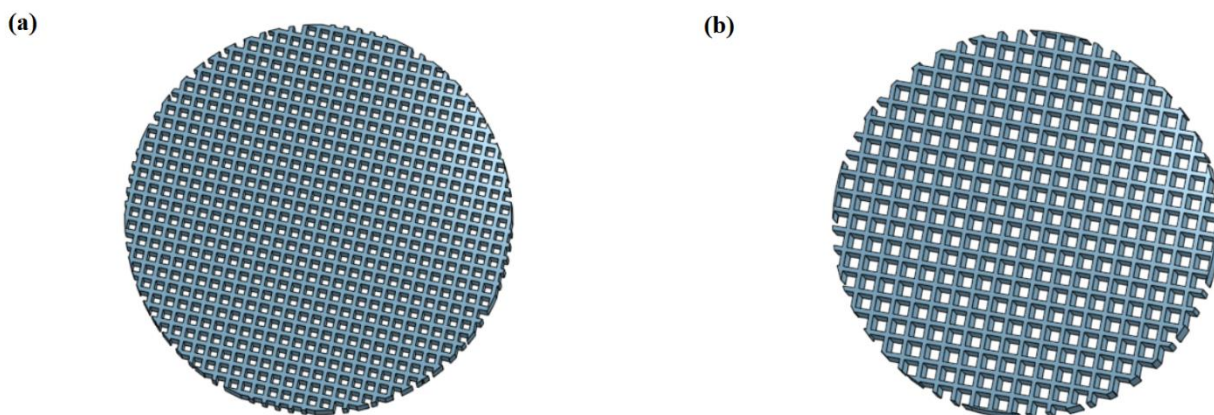


Figure 1. (a) 3D representation of the 300-micron pore size test sample; (b) 3D representation of the 500-micron pore size test sample.

4.2.2. Silicon Release

The release of silicon ions was tested by submerging the samples in PBS solution (EuroClone). The samples were submerged into 5 mL of PBS solution and kept in the incubator at 37°C. At each time point, a 2 mL solution was extracted and replaced by a fresh PBS solution. The extracted solution was tested for silicon ions using ion coupled plasma employing optical emission spectroscopy (ICP-OES) (SPECTRO Analytical Instruments, Kleve, Germany). Eight replicates were used for each pore size at each time point. The final results were calculated as the total released amount.

4.2.3. Cell Culture

Human bone marrow-derived mesenchymal stem cell line (hMSCs, ATCC number: PCS-500-012) was cultured in α -MEM medium supplemented with 10% Fetal Bovine Serum (FBS, EuroClone) and 1% Antibiotic/Antimycotic (AA, EuroClone), in a humidified atmosphere of 5% CO₂ at 37 °C. The medium was changed every two days. Once they reached 70%

confluence, the cells were detached by 1% trypsin-EDTA solution, counted, and re-suspended in standard medium with the concentration of 500,000 cells/mL.

4.2.4. Cell Seeding and Differentiation

After placing sterilized samples into 24-well plates, 0.6 mL cell suspensions (standard medium) were added directly to the samples (300,000 cell/well) and tissue culture plates (TCP), which were the control group (only cells without samples). The plates were incubated in a humidified atmosphere of 5% CO₂ at 37 °C to promote cell adhesion. Twenty-four hours after the seeding, the samples with cells were moved to new plates and the medium was switched into the differentiation medium: standard medium with 0.1 µM dexamethasone (DEX), 0.1 mM ascorbic acid 2-phosphate (AP) and 10 mM β-Glycerophosphate (BGP). The differentiation medium was changed every two days until 21 days.

4.2.5. AlamarBlue Assay

The cells' viability activity on different pore sizes (300 µm and 500 µm) after 7 days, 14 days, and 21 days of culture was determined with AlamarBlue Cell Viability assay (Invitrogen, Carlsbad, CA, USA), which quantifies cellular metabolic activity. AlamarBlue reagent was added directly to each well at 10% of the cell culture medium volume. Then, the well plates were incubated at 37 °C in a humidified atmosphere with 5% CO₂ for 3 h. From each well, 100 µL of the solution was collected. The fluorescence signal was measured with a Tecan Infinite 200 microplate reader (Tecan Group, Männedorf, Switzerland) with an excitation wavelength

of 560 nm and an emission wavelength of 590 nm. TCP was used as the control group and eight replicates were considered for each experimental condition.\

4.2.6. DNA Quantification Assay

To evaluate cell proliferation on the different pore sizes (300 μm and 500 μm), a PicoGreen DNA quantification assay (Quant-iT PicoGreen dsDNA Assay, Invitrogen, Carlsbad, CA, USA) was used. TCP was used as the control group. After 7 days, 14 days, and 21 days of culture, the culture medium was removed, and the samples were washed with PBS. Samples were then covered with 300 μL of 0.05% Triton-X PBS solution and incubated at 37 °C for 1 h. Before analysis, the samples were sonicated for 10 s with a Hielscher ultrasonic homogenizer (UP400S, 400 W-24 kHz, cycle 1, amplitude 40%, from Hielscher Ultrasonics, Teltow, Germany). Subsequently, 100 μL supernatant of each sample was placed in a black 96-well plate and mixed with 100 μL of PicoGreen working solution, prepared following the manufacturer's instructions. Fluorescence intensity was measured with a Tecan Infinite 200 microplate reader (Tecan Group, Männedorf, Switzerland) using an excitation wavelength of 485 nm and an emission wavelength of 535 nm. A calibration curve was created using a double-stranded DNA standard provided by the kit and was used for the calculation of the DNA content. Finally, the approximate number of cells per sample was determined from DNA content by the conversion factor of 7.7 pg DNA per cell. Eight replicates were considered for each pore size at each time point.

4.2.7. Alkaline Phosphatase (ALP) Activity Assay

ALP activity of the cells on scaffolds with different pore sizes was evaluated by the Alkaline Phosphatase assay kit (abcam, Cambridge, UK). The preparation procedure of the samples is the same as for the DNA quantification assay, in which the supernatant was obtained after washing, incubating, and sonication. Non-fluorescent 4-methylumbelliferyl phosphate disodium salt (MUP) substrate and MUP reaction solution were prepared following the instructions of the manufacturer. The reaction wells were set up in a black 96-well plate by mixing supernatant with MUP reaction solution and stop solution, using the volume suggested by the instruction. A standard curve was also created using the ALP enzyme. The fluorescence intensity was measured at excitation wavelength 485 nm and emission wavelength 535 nm. The readings of the samples were applied to the standard curve to obtain the amount of MUP generated by the ALP sample, and the activity of ALP in the tested samples was calculated by dividing the amount of 4-MU by the volume of the sample. Eight replicates were considered for each pore size at each time point.

4.2.8. RNA Isolation

Total mRNA was isolated from the scaffolds directly by NucleoZLO reagent (MACHEREY-NAGEL, Düren, Germany) according to the protocol from the manufacturer. The isolated RNA of the samples was dissolved in 20 μ L RNase-free water; the final concentration of RNA was determined by a NanoDrop (ND-1000 Spectrophotometer, Thermo Fisher Scientific, Waltham, MA, USA) and then diluted into 10 ng/ μ L.

4.2.9. cDNA Synthesis

The isolated RNA was reverse transcribed into cDNA by iScript Reverse Transcription Supermix kit (BIO-RAD, Hercules, CA, USA). Then, 4 μ L iScript RT Supermix was mixed with 16 μ L of isolated RNA (total RNA 160 ng) for each reverse transcription reaction well. Then, the complete reaction mix was incubated in Bio-Rad CFX96 Touch (BIO-RAD, Hercules, CA, USA) using a thermal cycling protocol provided by the manufacturer.

4.2.10. Gene Expression by Quantitative Real-Time PCR (RT-qPCR)

The quantification of gene expression was performed by Bio-Rad CFX96 Touch (BIO-RAD, USA). SsoAdvanced Universal SYBR Green Supermix kit was used, and the primer assays used in this study were listed in Table 1. The tested samples were mixtures that consisted of 5 μ L SsoAdvanced Universal SYBR Green Supermix, 0.5 μ L primer, and 5 μ L cDNA sample, which led to a final amount of 40 ng cDNA per well. The PCR amplification was carried out as follows: polymerase activation and DNA denaturation at 95 °C for 42 s, followed by 40 cycles at 60 °C and 30 s for each cycle. Then, the melt curve was performed between 95 to 65 °C with 0.5 °C increments at 2 to 5 s/step. The PCR results were relatively quantified with the comparative $\Delta\Delta C_T$ method by CFX Manager Software, comparing to the housekeeping mRNA expression of glyceraldehyde-3 phosphate dehydrogenase (GAPDH). The analysis of each gene was processed in duplicate and there were eight replicates for each sample.

Table 1. Selected primers for gene expression.

Code	Gene	Primer	Catalog No.
ALP	Alkaline phosphatase	ALPL, human	qHsaCID0010031
COL1	Collagen type I	COL1A1, human	qHsaCED0043248
RUNX2	Runt-related transcription factor 2	RUNX2, human	qHsaCED0044067
SPARC	Osteonectin	SPARC, human	qHsaCID0010332
GAPDH	glyceraldehyde-3 phosphate dehydrogenase	GAPDH, human	qHsaCED0038674

4.2.11. Cell Morphology, Distribution, and Immunofluorescence Staining

Cell morphology and distribution were visualized by Oregon green phalloidin and 4'6-diamidino-2-phenylindole (DAPI) staining. Oregon green phalloidin stains actin filaments of cytoskeleton resulting in green fluorescence while DAPI stains nuclei resulting in blue fluorescence. After 7 days, 14 days, and 21 days of culture, the cell-seeded samples were fixed with 4% paraformaldehyde, washed three times with PBS, and then were permeabilized using 0.2% Triton X-100 PBS solution for 30 min. After washing with PBS 3 times (15 min each time), cells were incubated in Oregon green phalloidin (5.0 μ L/well) and DAPI (1.0 mL/well,

5.4 μL dilute in 25.0 mL PBS) solution for 1 h at room temperature. After three rinses with PBS, samples were observed using Zeiss LSM 510 Meta confocal laser scanning microscope.

4.2.12. Statistical Analysis

GraphPad Prism 9 (La Jolla, CA, USA) was used for statistical analysis for all the data obtained from each independent experiment. Where applicable, data were expressed as mean $\pm$ SD. The statistical analysis was performed by two-way ANOVA using the all-pair-wise multiple comparison procedure, in which * $p < 0.05$ were set as the level of significance.

4.3. Results

4.3.1. Structural Characterization of SiOC(N) Ceramic Scaffolds

Two different pore sizes (500 μm and 300 μm) (Figure 2) were selected to mimic the pore size of human bone. The theoretical surface area of the porous discs was calculated using OnShape and the results are shown in Table 2. The structure of the final products was observed by an optical microscope. Theoretically, the total surface of discs with small pores is 1.26 times larger and the top/bottom surface is 1.36 times larger, compared to the total surface area of discs with large pores.

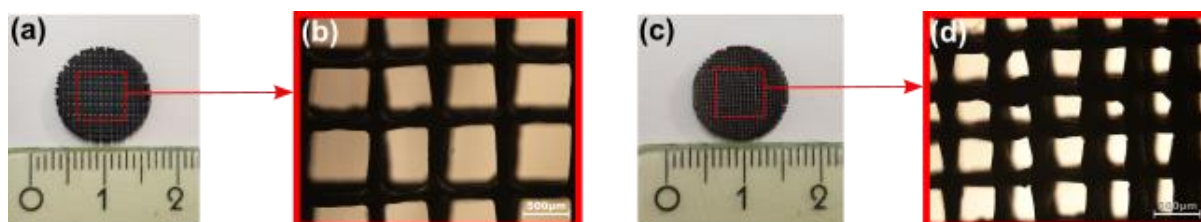


Figure 2. Large (a) and small (c) pore size SiOC(N) scaffold; the scaffold structure under the optical microscope (b,d). The scale bars in (b,d) are 500 μm .

Table 2. Sample information.

	Large Pore Size	Small Pore Size
Diameter (mm)	13	13
Thickness (mm)	1.5	1.5
Pore size (μm)	500	300
Theoretical total surface area (mm^2)	1077.00	1358.84
Theoretical top/bottom surface area (mm^2)	53.88	73.81

4.3.2. Silicon Ion Release of SiOC(N) Ceramic Scaffolds

The release of silicon ion was monitored for 21 days by ICP-OES, and the total amount of the released silicon ion was calculated and plotted in Figure 3. Scaffolds with large pore size and small pore size had almost the same releasing curve and amount. Until day 10, the amount of released silicon kept increasing, and after 10 days of release, the released amount of Si ion reached a plateau.

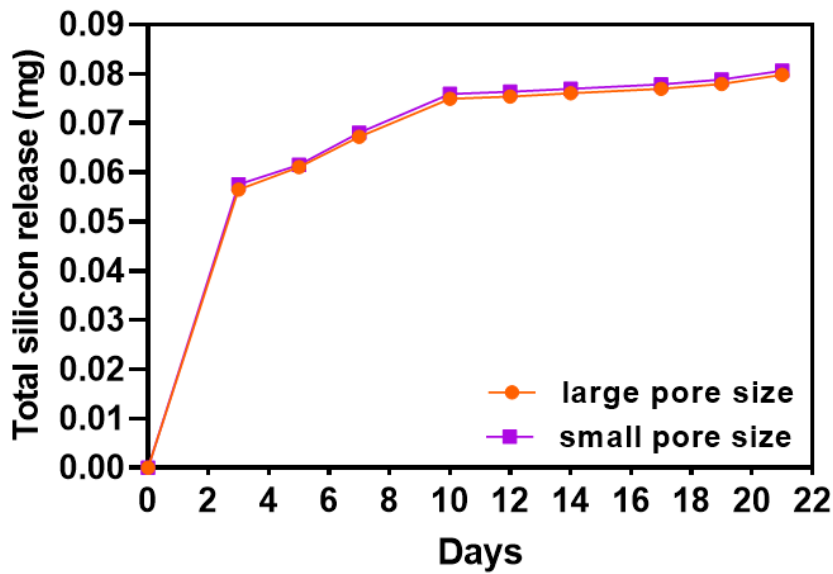


Figure 3. Silicon ion release curve. $n = 8$.

4.3.3. Characterization of Proliferation, Metabolism of hMSCs during Osteogenic Differentiation

Cell proliferation and metabolic activity of hMSCs seeding on SiOC(N) ceramic scaffolds with different pore sizes were performed on day 7, day 14, and day 21 in the presence of the osteogenic medium, using PicoGreen DNA quantification assay and AlamarBlue assay, respectively. The results are shown in Figure 4. The small pore size scaffolds induced a higher proliferation rate than the large ones. Interestingly, the cell number did not change over time in all the groups during 21 days of culture. Metabolic activity was normalized by cell numbers for each group at each time point. Except for day 7, in which the data of large and small pore size scaffolds showed no significant difference, cells cultured on the large pore size scaffold

showed, in general, a higher metabolism activity than those cultured of small pore size scaffold, in particular on day 21.

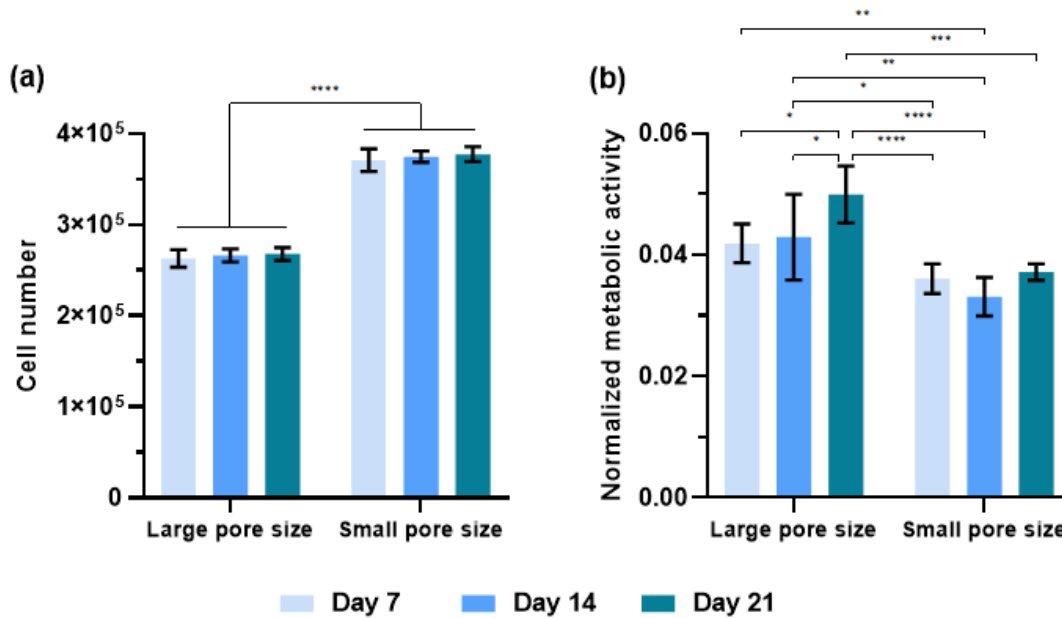


Figure 4. (a) Cell proliferation and (b) Metabolic activity of hMSCs in 7 days, 14 days, and 21 days of cell culture. $n = 8$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; **** $p < 0.0001$.

4.3.4. Visualization of Cell Morphology and Distribution by Confocal Laser Scanning Microscopy

The confocal images were taken in both low and high magnification on scaffolds with different pore sizes (Figure 5). Cell morphologies during the osteogenic differentiation were evaluated by staining the cell cytoskeleton with Oregon green phalloidin (green). In general, the scaffolds could promote very good cell adhesion during the cell culture period. In the first week, the adhered cells morphology exhibited a high degree of spreading with many cell/cell connections due to filopodia and lamellipodia formation (Figure 5b,d) in all groups, which was even more

evident on small pore size scaffolds (Figure 5d). Instead, at 2–3 weeks of culture, adhered cells of all the groups penetrated in the pores, colonizing the 3D structure. A difference in cell behavior, however, was observed during the 3 weeks of culture. Despite a large number of cells on the scaffolds, the spatial organization of cells was quite different. On the large pore size scaffolds, the cells were aligning on the surfaces, but were not able to cross the empty space. However, the cellular structure of the small pore size scaffold was small enough for the cells to bridge the pore and the pores were almost filled by cells over time.

4.3.5. Characterization of ALP Activity of hMSCs during Osteogenic Differentiation

ALP production is widely used as a marker of bone cells because it is associated with osteoblastic differentiation. In this work, ALP activity was measured by the Alkaline Phosphatase assay kit, and the results are presented in Figure 6. In the first two weeks of differentiation, both groups had similar levels of ALP activity. A dramatic increase in the ALP activity occurred on day 21, which was more than two times higher than on day 7 and day 14, which is particularly relevant on the small pore size scaffold on day 21.

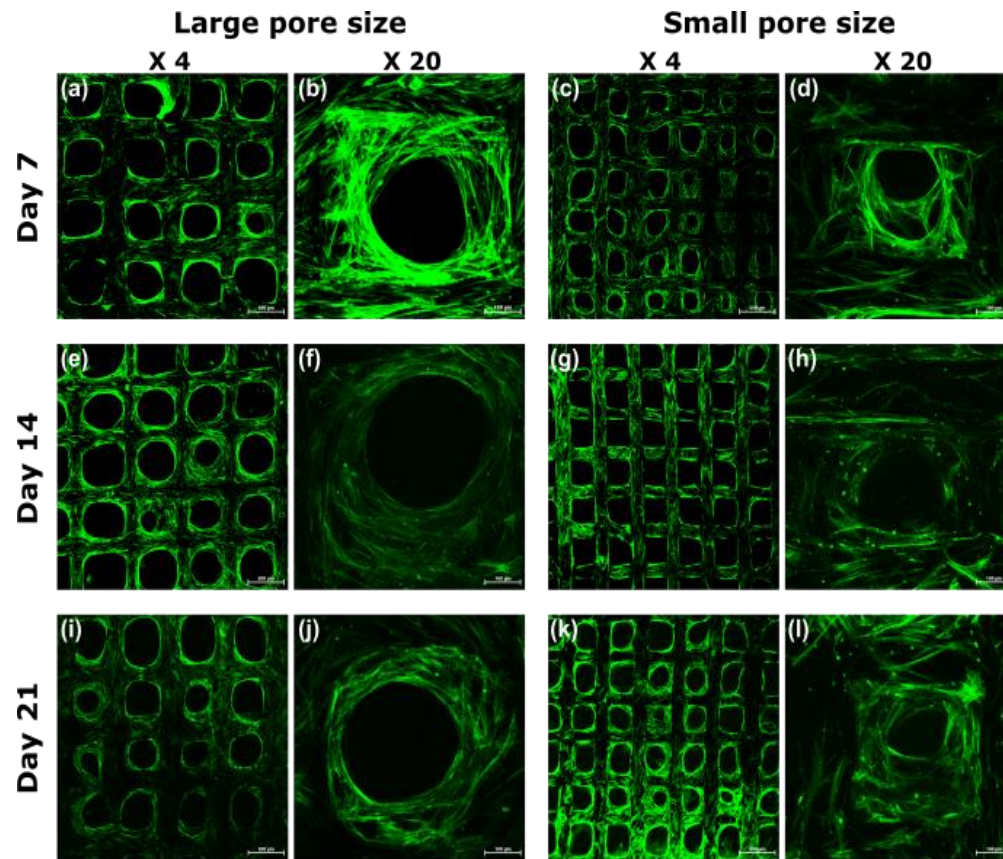


Figure 5. (a)-(l) Confocal images of hMSCs morphology on the scaffolds with different pore sizes cultured in the osteogenetic medium for 7, 14, and 21 days. Each sample was presented in low ($\times 4$) and high ($\times 20$) magnification. The scale bars in the images of $\times 4$ columns are 500 μm , and the scale bars in the images of $\times 20$ columns are 100 μm .

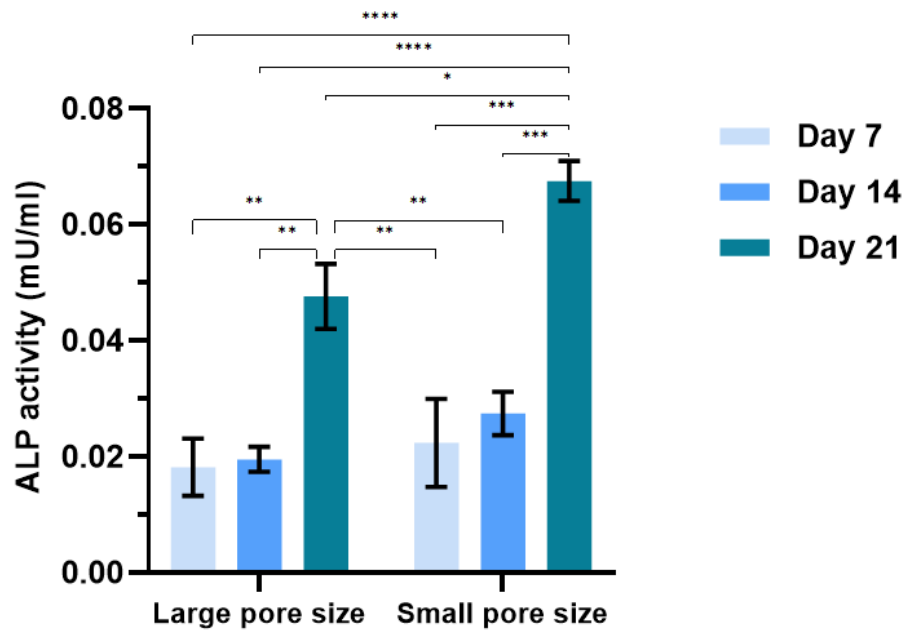


Figure 6. ALP activity of hMSCs on large and small pore size SiOC(N) ceramic scaffold in osteogenic medium for 7, 14, and 21 days. $n = 8$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; **** $p < 0.0001$.

4.3.6. Expression of Osteogenic Marker Genes in the Presence of the SiOC(N) Ceramic Scaffold

The relative mRNA expression levels of the osteogenic markers: alkaline phosphatase (ALP), collagen type I (COL 1), runt-related transcription factor 2 (RUNX2), and osteonectin (SPARC) were monitored on day 7, 14, and 21 using RT-qPCR. The total RNA was isolated from cells seeded on SiOC(N) scaffolds with different pore sizes and cultured in the osteogenic medium. The results were presented in Figure 7 and the heat map of the gene expression overview were presented in Figure 8.

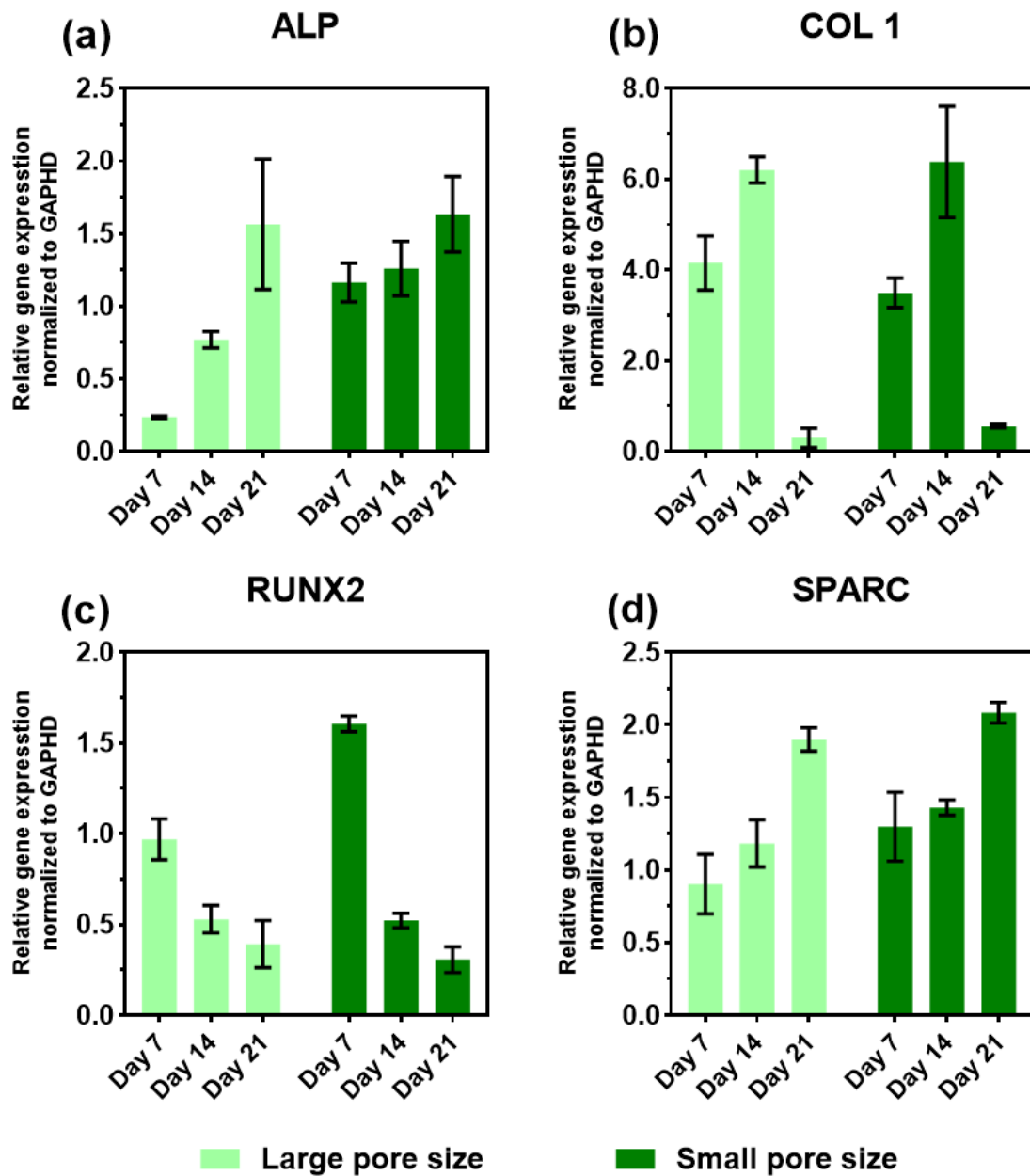


Figure 7. Relative gene expression of ALP (a), COL 1 (b), RUNX2 (c), and SPARC (d) of hMSCs on SiOC(N) ceramic scaffolds with different pore sizes after culturing in osteogenic medium for day 7, 14, and 21. TCP with hMSCs was used as a reference group. GAPDH was used as a housekeeping gene. $n = 8$.

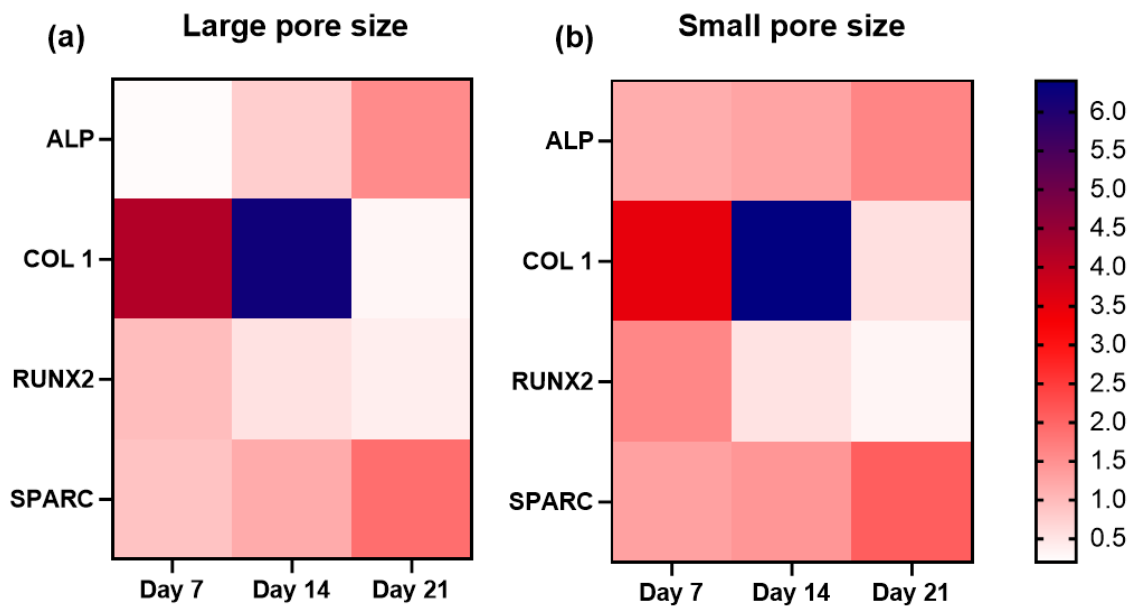


Figure 8. Heat map of gene expression of small (a) and large (b) pore size SiOC(N) ceramic scaffolds. $n = 8$.

Generally, the gene expression trends of the selected markers were similar in both sample groups (Figure 7) and these trends were different from TCP during the 21 days of culture (Supplementary Materials, Figure S1). An increasing level of ALP expression was observed in both groups. It should be noted that the ALP expression of the small pore size scaffold was significantly higher at the first experimental time point (day 7), compared with the large pore size samples. Additionally, both groups reached a similar expression level of ALP on day 21. The expression of COL 1 for both groups showed a peak on day 14 and dropped almost to zero on day 21. No significant differences showed in the expression of COL 1 during 21 days between the two groups at the same time point. A downregulation of RUNX2 was observed in both groups during the three weeks, but the small pore size scaffold showed a higher level in the first week compared with the large pore size group. The expression of osteonectin

(SPARC), for both groups, showed the same trend along with the three weeks of culture and similar levels.

4.4. Discussion

Tissue engineering is based on the use of instructive scaffolds that should provide 3D templates for initial cell attachment, proliferation, and subsequent tissue formation. Therefore, the materials used as well as the geometry of the scaffold have relevant impacts on the biological performance. In our previous study [40], the fabrication procedures were optimized and the physical, mechanical, chemical, and preliminary biological properties of the SiOC(N) ceramic scaffolds were already thoroughly characterized. The results demonstrated that the novel method eliminates the possibility of having pores or defects inside the struts with complete impregnation of the preceramic polymer in the TPU structures. Another issue with biomedical implant structures is that they are very expensive to manufacture. The research also showed that the scaffolds can be manufactured, with high reproducibility and industrial tolerances, at an affordable and thus accessible price. The preliminary biological studies proved the material to be non-cytotoxic, promote fast cell adhesion, and early-stage cell activations [40]. In the present study, the research is focused on the impact of the geometry of the scaffold on the osteogenic differentiation of hMSCs.

Different biological results were obtained by comparing two groups of scaffolds that are different in total surface areas and pore sizes, and, according to the literature, these differences can affect the releasing amount of silicon ions. In the current work, despite the scaffold with the small pore size having a larger surface area (26% more) the results of silicon ion release showed that there is no significant difference in the release amount between the two groups

(Figure 3). This suggests that the only parameter that causes differences in cell behaviors is the pore size (in terms of morphology, proliferation, metabolic activity, ALP activity, and gene expression).

The ability of the materials to induce good cell adhesion and proliferation was confirmed with a higher cell number on small pore size scaffolds due to the larger surface area available. It is interesting to observe that, for both groups, cell numbers (Figure 4a) from one week to three weeks remained constant, demonstrating that the cells were differentiating in the very early stage (first week). As reported in the literature [45], during the differentiation process, cell proliferation and differentiation are two interdependent processes that have a counteracting relationship, and this correlated with the obtained results. Cell spatial organization, detected by confocal images (Figure 5), shows that the cells on the small pore size scaffolds were able to build a 3D network, migrating into the structure and connecting to each other crossing the pores (Figure 5d,h,i). The 3D cell distribution is a more physiological cell organization, promoting stem cell differentiation into the bone cells [46]. When the pore size is too large, the 3D structure is not able to drive cells forming the 3D organization, slowing down the differentiation. In fact, this is confirmed by the gene expression (Figure 7) that the cells on small pore size scaffolds were able to differentiate in an earlier stage, particularly in the expression of ALP (Figure 7a) and RUNX2 (Figure 7c).

The geometry differences in the scaffolds also had an impact on the cell activities during the osteogenic differentiation. In the presented work, general and phenotypic-specific metabolism were determined by AlamarBlue assay and ALP production, respectively. It is reported in the literature that an increase in ALP activity should be associated with osteoblastic differentiation. ALP is thought to increase and then decrease when mineralization is well progressed [47]. The cells on small pore size scaffolds showed a lower general metabolic activity (Figure 4b), but

higher ALP activity (Figure 6) compared to cells on large pore size scaffolds, especially on day 21. The significant increase in this enzyme between the second and third week suggested that cells on small pore size scaffolds were shifting to a more differentiated state.

The mRNA levels of osteogenic genes (ALP, COL 1, RUNX2, and SPARC) were evaluated during the 21 days of differentiation, using RT-qPCR. The positive impact of Si-based materials on osteogenic differentiation has been investigated in numerous studies [48], in which the water-soluble silicon was proved to enhance osteoblast proliferation and differentiation under in vitro conditions. The investigated expression levels of osteoblast-specific marker genes in terms of osteoblast differentiation, have shown a special pattern that could help to have a perception of the functional bone construct (Figure 8). RUNX2, a member of the runt homology domain transcription factor family, plays a crucial role in osteoblast development. It is a major gene responsible for the early orientation of stem cells towards osteoblastic lineage and directly activates the transcription of genes such as osteocalcin, COL 1, and ALP. Moreover, it is typically downregulated in three or four weeks of culture, which is an important indicator of matrix maturation and mineralization [49]. In fact, there was a significant decrease in the expression of RUNX2 observed in both groups during the second and the third week, suggesting the acceleration of the differentiation. COL 1 plays an important role in biomineralization. It is expressed in high levels near the end of the proliferation state and during the period of matrix deposition. It is also known to decrease with time and an ongoing calcification of the bone tissue [50]. The increase in COL 1 expression showed a peak on day 14 and then dropped to a very low level in both scaffolds between the second and the third week. This observation is in accordance with the expression profiles reported in the literature for the osteogenic differentiation of hMSCs [51]. The ALP gene is first detected in osteoblast progenitor cells which are committed to differentiate into osteoblasts. The expression of ALP is dependent on the maturation stages of osteoblasts. It increases when mineralization is well

progressed and then decreases in later stages [52]. In this case, upregulation of ALP expression was observed in both scaffolds in 21 days. Although, the expression level showed significant differences on day 21 between the samples with large pore size and small pore size. It is worth noting that hMSCs on small pore size expressed a significantly high level of ALP on day 7 compared to that on large pore size, suggesting the cells on the small pore size scaffolds had an earlier differentiation. Osteonectin (SPARC) is a phosphorylated glycoprotein that plays a role in regulating the initiation, and promotion of mineralization as well as crystal growth [53]. In this work, it is revealed that the expression of osteonectin is increased in hMSCs during differentiation on both groups, this may be due to the osteoprogenitor culture conditions.

4.5. Conclusions

In summary, the bioactivity and osteogenic differentiation ability of this open-source 3D printing process for SiOC(N) ceramic scaffolds with different pore sizes was investigated by in vitro cell culture of hMSCs. The results showed that the material of the scaffold has a good ability to release water-soluble silicon ions and the total amount of released silicon ions was not affected by the pore size. Moreover, the scaffolds were able to improve the differentiation while retaining the cell number. It has been demonstrated that the pore size of the scaffold has a strong impact on cell behaviors including cell number, metabolism, ALP activity, distribution, and the speed of osteogenic differentiation. This open-source 3D printing process for SiOC(N) ceramic scaffolds is promising and provides opportunities to have more complex and precise structural matrices with controllable bioactivity for bone regeneration applications. Future work, including in vivo testing, is warranted in order to improve the technology to be used as bone implants.

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Conclusions

The present work describes the approach of combining polymer derived ceramics with the open source FFF 3D printing. Polymer derived ceramics were utilized because their ability to be shaped in polymeric state. FFF 3D printing provides the benefit of producing objects with complex geometries. The open-source part of it makes it easily accessible, repairable and more importantly affordable.

The aim of the thesis was to develop a novel and affordable method to produce cellular ceramics combining the methods.

The first approach was to coat the polymer 3D printed parts using FFF 3D printers with polysiloxane preceramic polymer. The ceramic resulting after pyrolysis has the composition SiOC and exhibits a multi-level porous structure. Since the preceramic polymer does not react the organic 3D printing polymers, the 3D printing polymers are decomposed. This leaves the already cellular structures with hollow channels where the organic polymers were present. The produced ceramics posses very high surface to volume ratio as the insides double the surface area. The tests conducted with 20 different types of 3D printing polymers show that the surface texture of the 3D printing polymer governs the amount of preceramic polymer retained on the surface of the printed part. This in turn dictates the thickness of the wall of the hollow strut of the final cellular ceramic produced.

The second approach uses thermoplastic polyurethane (TPU) as the 3D printing polymer and polysilazane preceramic polymer pair. With this approach, instead of coating the printed part with the preceramic polymer, the polysilazane reacts with the TPU and completely impregnates the 3D printed structure. This results in a fully dense ceramic struts of the composition

SiOC(N). The mechanical tests conducted, show that the ceramic components possess very high mechanical strength. The components subjected to extreme high temperatures for 12 hours resulted in no change in the properties, indicating that the ceramic can withstand very high temperatures. With these excellent properties, the novel method can be utilized to produce cellular ceramic components for applications such as liquid metal filters, supports for catalytic converters, heat shields for high temperature applications.

The cost analysis for the production of the ceramic cellular parts produced with the 3D printing replica method was done. The cost was compared to the quotations received from different companies who manufacture ceramic 3D printed parts using similar materials. The production cost of the proposed method was found to be only 10% of the commercially available options. The comparison does not take into account the profit margins and other cost incurred for logistic and operations but, even with 100 to 200% addition to the production cost, the proposed method would still be 70 to 80% cheaper than the available alternatives.

One of the main applications the cellular ceramics can be used are implantable scaffolds for bone tissue regeneration. Research has been going on for affordable options for implant materials with desirable mechanical properties for this application. The primary tests of the material that needs to be done to test the biocompatibility of the material for the particular application are in vitro tests. The in vitro tests start with cytotoxicity which determine whether living cells can survive on the material. The further tests include cell adhesion and cell proliferation, which determine if the cells can adhere to the material and if they can multiply with the provided structures. The final in vitro test is differentiation which determines if the stem cells seeded on the cellular scaffolds start to turn into bone cells.

The in vitro studies showed that the material is not cytotoxic and allows the cells to proliferate freely. The cell differentiation i.e. bone formation depends on a variety of factors, one of which

is the pore size of the scaffolds. With the accurate pore size, the scaffold provides the stimulus to the stem cells to start the differentiation into bone cells and mineralization. This is identified by different gene expressions. The 21 days in vitro testing indicated that the differentiation was accelerated, and the bone was starting to mineralize.

The material can be characterized as bioactive material between the four biomaterial classes (biotolerant, bioinert, bioactive and bioresorbable). The quality that classifies the material as bioactive is that the material reacts with the stem cells and provides the stimulus for the cells to start the osteointegration process by means of physical and chemical stimuli, i.e., the porosity and silicon release.

One of the benefits of using 3D printing as a fabrication method is that the porosity and the pores size can be controlled with high precision to match the required value and to promote the bone regeneration. The other major benefit being the cost. The open-source 3D printing approach brings the cost of fabricating scaffolds down to 1/10th.

The analysis of the manufacturing costs showed that cellular ceramic components can be manufactured at a fraction of the cost quoted by the commercial manufacturers of ceramic components.

This shows the successful development and implementation of the novel manufacturing process which integrates FFF 3D printing and polymer derived ceramics.

Future work

The future work on the research includes improving the reliability and repeatability of the method. As the process involves volume change going from polymer 3D printed part to a

ceramic, the control of the final dimensions is critical. The dimensions can be controlled now for components smaller than 4 cm. The precision needs to be improved for bigger components.

In terms of applications, collaborative efforts can be taken on testing the cellular ceramics for applications such as filters for casting/ foundries and bases for catalytic converters.

The next step in the biocompatibility testing is to test the scaffolds in vivo i.e., animal testing.

A collaboration with the University of Texas at Arlington is ongoing where the scaffolds are being tested with mice specimen and are being compared to the traditional ceramic material (hydroxyapatite) used for 3D printing the scaffolds.

Annex A

The results showed that different 3D printing polymers and preceramic polymers produce different results. To obtain a ceramic structure with dense struts the “must” is to have a successful impregnation of the preceramic polymer into the 3D printing polymer.

Now, with this method there are three polymer systems interacting with each other. The 3D printing polymer, the preceramic polymer and the solvent. As the solvent needs to be compatible with the 3D printing polymer it also needs to dissolve the preceramic polymers being used. The successful combination would be a solvent that dissolves the preceramic polymer and a 3D printing polymer which is able to swell in presence of the solvent.

The impregnation of preceramic polymer into the 3D printed structure seems to be linked to the swelling of the 3D printed polymer after soaking/ submerging the samples in the preceramic polymer solution. One of the key factors that contribute to the soaking is the solvent used. The right solvent is the one which does not completely dissolve the 3D printed polymer and also is not completely inert to the 3D printing polymer. It should interact with the 3D printed polymer just enough to breach into the structure and expand it. This swelling allows the preceramic polymer to successfully impregnate the 3D printed structure.

This can depend on multiple factors such as:

- a. Different functional groups present in each of the chemicals
- b. Chemical affinity of the functional groups towards each other
- c. Chemical and physical interaction between the chemicals

There are multiple solvents which produce different results combined with different preceramic polymers. The list of solvents includes acetone, n-hexane, cyclohexane, tetrahydrofuran,

chloroform, isopropyl alcohol. These all can be used as solvents in different capacities for the preceramic polymers polysilazanes, polysiloxanes, polycarbosilanes etc.

Experiments were performed with different combinations of the chemicals such as:

3D printing polymer	Solvent	Dissolution	Swelling
PLA	Acetone	No	No
TPU	Acetone	No	High
TPU	2-Propanol	No	No
TPU	n-Hexane	No	No
TPU	Cyclohexane	No	No
ABS	Acetone	Complete	No
ABS	O-xylene	Mild	Very little
PC	Acetone	No	No
PP	O-xylene	No	No

Out of these combinations the best combination that worked was TPU 3D printing polymer, acetone solvent and polysilazane preceramic polymer. Acetone acts as a perfect solvent for TPU where it swells the TPU and does not dissolve it completely, thus allowing the preceramic polymer to interact with the 3D printing polymer.

Now, only swelling does not help the impregnation either. There should be chemical interaction between the 3D printing polymer and the preceramic polymer. The chemical affinity between the polymers and the functional groups present in both the polymers will affect this interaction.

In case of TPU + polysilazane, the theory is that the urethane (from TPU) and NH group (from polysilazane) are the ones that interact with each other.

Further research needs to be done to investigate the actual chemical interaction between these polymer systems.

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Publications

- **A. Kulkarni**, G. D. Sorarù, and J. M. Pearce, “Polymer-derived SiOC replica of material extrusion-based 3-D printed plastics,” Additive Manufacturing, vol. 32, p. 100988, Mar. 2020.
- **A. Kulkarni**, Y. Yang, A. Motta, J. M. Pearce and G. D. Sorarù, “SiOC(N) cellular structures with dense struts by integrating FFF 3-D printing with polymer derived ceramics.”, Advanced Engineering Materials 2021, 2100535.
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Conference Presentations

- **“Integrating Polymer Derived Ceramics with FFF 3D printing for producing scaffoldings for bone tissue regeneration”** 46th International Conference and Expo on Advanced Ceramics and Composites, Daytona Beach, Florida, USA, January 2022
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