

# Preceramic Polymers for Additive Manufacturing of Silicate Ceramics

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Contributor: Fateme Sarraf , Sergey V. Churakov , Frank Clemens

The utilization of preceramic polymers (PCPs) to produce both oxide and non-oxide ceramics has caught significant interest, owing to their exceptional characteristics. Diverse types of polymer-derived ceramics (PDCs) synthesized by using various PCPs have demonstrated remarkable characteristics such as exceptional thermal stability, resistance to corrosion and oxidation at elevated temperatures, biocompatibility, and notable dielectric properties, among others. The application of additive manufacturing techniques to produce PDCs opens up new opportunities for manufacturing complex and unconventional ceramic structures with complex designs that might be challenging or impossible to achieve using traditional manufacturing methods. This is particularly advantageous in industries like aerospace, automotive, and electronics.

preceramic polymer

polysilsesquioxane

silicate

additive manufacturing

3D print

## 1. Preceramic Polymers

The idea of using molecular precursors to produce ceramic structures was first introduced by Ainger and Herbert in 1960 <sup>[1]</sup>. Pyrolysis of organosilicon polymers to produce ceramic materials for use in high-temperature applications was presented by Verbeek in the early 1970s. The process was specifically designed to make Si<sub>3</sub>N<sub>4</sub>/SiC ceramic fibers <sup>[2]</sup>. The research study of Yajima et al. in 1975 on the synthesis of SiC-based fibers from polycarbosilane marked a major advancement in the area of polymer pyrolysis for the production of polymer-derived ceramics (PDCs) <sup>[3]</sup>. Since then, preceramic polymers (PCPs), more specifically organosilicon polymers, have been widely acknowledged as an effective method to create advanced ceramics. It is worthwhile to mention that different terms have been used for organosilicon polymers <sup>[4][5]</sup> such as Si-based polymers <sup>[6][7]</sup>, Si-based preceramic polymers <sup>[8][9]</sup>, and silicone resins <sup>[10][11]</sup>.

### 1.1. Si-Based Preceramic Polymers

The first step in the fabrication of Si-based polymer-derived ceramics is the synthesis of the proper organosilicon polymer. By grafting different elements such as oxygen, nitrogen, and carbon to the Si backbone structure, various types of Si-based polymers can be obtained <sup>[1][2]</sup>. These polymers serve as precursors for producing a wide range of ceramic compositions, including SiC, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiOC, SiCN, SiBCN, SiBOC, SiAlON, and other ceramics <sup>[2]</sup>.

Only high-molecular-weight polymers that are capable of crosslinking can be used for the fabrication of polymer-derived ceramics <sup>[3]</sup>. A brief description of the important classes of preceramic polymers including polysilane,

polycarbosilane, polysilazane, and polysiloxane are summarized below:

### 1.1.1. Polysilanes

Polysilanes having a one-dimensional silicon backbone are basic precursors for the synthesis of SiC ceramics. Each silicon atom is attached to  $R_1$  and  $R_2$  substituents, whereas the substituents are presenting molecules with different combinations of C, H, S, N, and O atoms. Polysilanes are typically prepared using the method known as Wurtz-type coupling of halosilanes [12]. This synthetic approach involves the reaction of chlorosilanes with sodium or lithium dispersion, resulting in the reduction process that leads to the formation of polysilane. The reaction occurs within a high-boiling-point inert solvent, such as toluene, benzene, or tetrahydrofuran, under reflux conditions. Polysilanes have been proposed for various applications such as photoresists, photoconductors, and semiconductors [5]. Their  $\sigma$ -conjugation due to electron delocalization on silicon–silicon bonds results in distinctive optoelectronic and photoelectric properties. The properties of polysilanes stem from two primary factors: the side chain groups attached to the backbone and the molecular weight of the polymer [2].

### 1.1.2. Polycarbosilanes

Polycarbosilanes with a Si-C backbone contain branched chains such as methylene, vinylidene, and phenylene which make them more complex compared to polysilanes [13]. The most common way to synthesize these polymers is thermal decomposition of polysilanes under pressure using the Kumada mechanism. However, the accumulation of decomposition gaseous products (e.g., methane,  $\text{Me}_3\text{SiH}$ ,  $\text{SiH}_4$ ) can lead to a dangerous increase in pressure in the autoclave. Synthesis of polycarbosilanes using pyrolysis of polydimethylsilane in a nitrogen atmosphere was performed at ambient pressure through catalytic processes (using polyborodiphenylsiloxane) in a reflux condenser [14]. This class of organosilicon polymers has been widely used for the fabrication of SiC-based components like fibers, composites, powders, and other non-oxide ceramic structures.

### 1.1.3. Polysilazanes

Using polysilazanes with carbon containing side chains attached to a Si-N backbone, SiCN ceramics are synthesized. If a C-free polysilazane polymer like perhydridopolysilazane is utilized,  $\text{Si}_3\text{N}_4$  ceramics can be produced. Fabrication of SiCN fibers from polycarbosilazanes was first demonstrated by Verbeek et al. in the 1970s [15] where oxidation resistance up to 1200 °C and a significant strength and elastic modulus were achieved.

### 1.1.4. Polysiloxanes and Polysilsesquioxanes

Polysiloxanes with a general formula of  $[\text{R}_2\text{SiO}]_n$  are an inexpensive, widely used class of Si-based PCPs for the synthesis of silicone oxycarbide and oxynitride ceramics [2].

Equation (1) describes the formation of polysiloxanes through the reaction of chlorosilane precursors with water.



Ring opening polymerization of cyclic trimers and tetramers has been reported as a successful alternative to the hydrolysis approach [16]. Crosslinked polysiloxanes and polysilsesquioxanes can be obtained using the sol-gel process via hydrolysis and condensation reactions of organically modified silicon alkoxides, depending on their functional side chain.

Polysilsesquioxanes with a chemical formula of  $[\text{RSiO}_{3/2}]_n$ , as implied by their name, consist of a silicon atom (sil-), bonded to one and a half (-sesqui-) oxygen atoms (-ox-), and a hydrocarbon group (-ane) [17]. R can be either an H atom or an organic functional group such as methyl, phenyl, ethoxy, or hydroxyl. The nature of the organic ligands attached to the Si atoms determines the packing of the molecules and the intermolecular forces between them, which ultimately determine the physical state of the material. As a result, pure polysilsesquioxanes can be found in the form of liquid, crystalline, or amorphous powder. These hybrid organic-inorganic materials can have random, ladder, double-decker, cage, and partial-cage structures [18][19].

Pyrolysis of polysiloxanes and polysilsesquioxanes results in the formation of siliconoxycarbide (SiOC) glasses [20]. Mechanical properties of carbon-rich SiOC glasses, particularly creep resistance, have been extremely improved compared to fused  $\text{SiO}_2$  [21]. The addition of ceramic or metallic particles allows for modification of the mechanical and physical properties of the SiOC matrix [22].

In addition to SiOC ceramics, silicate ceramics can be fabricated by introducing fillers to the polysiloxane/polysilsesquioxane polymers [1].

## 1.2. Properties of Si-Based Polymers

The unique properties of PCPs offer potential solutions for different applications where thermal stability is a necessity or the material experiences a harsh environment [5]. An intriguing aspect that encourages the utilization of PCPs is the possibility of modifying the functional groups within the starting precursor, thereby promoting its properties [2]. Using Si-based polymers, PDCs in the form of powders, fibers, coatings, composites, and complex three-dimensional (3D) structures can be produced. Diverse processing techniques have been implemented for fabrication of PDCs as they can be melted and crosslinked or dissolved in several solvents [2].

Due to their viscoelastic behavior above the melting point, and the miscibility with other polymers, various thermoplastic shaping methods can be utilized. Blending preceramic polymers with organic/inorganic additives facilitates the preparation of homogenous compounds for the fabrication of PDCs. Substituting PCPs for ceramic powders, it is feasible to mix the materials at lower temperatures, while also reducing abrasion within the machinery involved [23].

By dissolving PCPs in compatible organic solvents, mixed with other organic/inorganic additives, homogeneous ink, gel, or dried sediments (after drying) can be created. The obtained mixture can then be used for subsequent shaping or synthesis steps.

To fabricate polymer-derived 3D ceramic structures, organosilicon precursors need to have certain properties in order to be effective. One of these properties is the ability to crosslink. Following the shaping process, these polymers undergo a crosslinking stage to maintain the shape during subsequent thermal treatment [24]. Preceramic polymers with high molecular weight are advantageous as more crosslinks can form, resulting in a thermoset that has a high shape stability during the thermal debinding process [5].

With pyrolysis and sintering of PCPs in either air or an inert atmosphere at relatively lower temperatures (800–1200 °C), a wide range of oxide and non-oxide ceramics can be obtained. Since the density values for the polymer (1–1.2 g/cm<sup>3</sup>) and ceramic phases (2–3.2 g/cm<sup>3</sup>) vary significantly, the resulting ceramic residue after pyrolysis may experience shrinkage of up to 70% in volume that leads to the development of considerable porosity or cracks. Therefore, achieving a ceramic yield above 60% is expected after pyrolysis [25].

To prevent the pore formation during crosslinking and pyrolysis, as well as the volume shrinkage of the PCPs during polymer to ceramic conversion [26], fillers have been commonly used for near-net-shape fabrication of PDCs by decreasing their freedom to shrink as was first introduced by Greil et al. in the 1990s [27][28]. By adding fillers to the PCP matrix, its mechanical, thermal, or other desired properties can be improved. The fillers are typically incorporated inside the matrix before the pyrolysis process. Depending on the specific application, desired characteristics, and compatibility with the PCP matrix, a wide range of fillers can be utilized [2][28].

Different shapes of fillers including powders, platelets, nanotubes, chopped and long fiber, and so on can be added to the PCP matrix before shaping.

- passive fillers: this group of fillers is not reactive. They only control the shrinkage and presence of macro defects during pyrolysis. Typical examples are SiC and Si<sub>3</sub>N<sub>4</sub>.
- active fillers: using active fillers, on the other hand, a new phase compared to the starting PCP can be achieved. Carbides, nitrides, silicates, oxides, and silicides can be produced as a result of a reaction between the filler and atmosphere or PCP residue after pyrolysis or the gaseous products during pyrolysis itself.
- meltable fillers: this category of fillers consists of meltable materials, typically glasses. When subjected to high temperatures, the glass phase melts or softens and effectively fills the available porosity which enhances the density. This approach protects the part against oxidation and corrosion. When meltable fillers are used in coatings, their softening at elevated temperatures reduces Young's modulus, allowing for the relaxation of thermomechanical stresses arising from mismatches in thermal expansion between the substrate, coating, and fillers within the precursor matrix. They may also undergo chemical reactions with other components in the system, acting as active fillers.
- sacrificial fillers: These organic compounds are mixed with the PCP and removed after crosslinking using thermal decomposition or dissolution in a solvent. Their main function is to create the porosity in the PDC parts.

The choice of fillers depends on the desired properties of the final ceramic material and the compatibility with the preceramic polymer matrix. The amount and dispersion of fillers within the polymer matrix also play a crucial role in determining the overall performance of the resulting ceramic material.

### 1.3. Synthesis of Silicate Ceramics Using Polysiloxane and Polysilsesquioxanes

In recent years, there has been a lot of interest in polymer-derived silicate ceramics by incorporating active fillers into the PCP matrix. Various types of silicate ceramics have been successfully produced using polysilsesquioxanes. It should be noted that the fabrication of silicates using organosilicon polymers requires handling and heat treatment in an air atmosphere [29][30][31]. Pyrolysis of PCPs in different atmospheres alters the ultimate composition. Using air atmosphere results in a SiO<sub>2</sub> residue, whereas working under an inert atmosphere (e.g., nitrogen or argon), silicon oxycarbide (SiOC) and residual carbon composition can be achieved [1][32][33].

By sintering at 1550 °C for 2.5 h, complete mullitization was achieved, with only a remaining volume fraction of 0.1% silicate glass. The presence of residual cristobalite was previously reported [34][35][36]. The absence of cristobalite impurity in this study was attributed to the effective dispersion of highly active nano-alumina within the PCP matrix. Colombo et al. reported the fabrication of different silicate ceramics using nano-active fillers [23]. Pure mullite, zircon, cordierite, forsterite, and yttrium-silicates with low grain size were achieved at low sintering temperatures and dwell times as a result of highly favorable reaction kinetics. However, the issue with densification in the polymer-derived silicates persists due to the typical poor ionic interdiffusion in silicates. Therefore, submicron pores appear between densified areas.

Substituting a fraction of MK for SIRLES H62C, a relative density of 97% was achieved. The authors explained this observation by varying levels of network connectivity and defects in the amorphous silica phase of different organosilicon polymers, as a more defective silica network is favorable for accommodating the Si-O network containing fragments into the mullite structure [4].

The same approach has been successfully used to prevent the extensive cracking of zircon [37], forsterite [38], and cordierite [39] ceramics. Partial replacement of MK with SILRES H62C (H62C) enhanced the compactness due to the different molecular arrangement of the PCP, leading to diverse possibilities to rearrange the molecular structure. Also, H62C goes through different crosslinking reactions that avoid gas release during pyrolysis. In this way, local pressure accumulation from generated gaseous products is eliminated.

The microstructure of alumina-rich polymer-derived mullite ceramics (>74 wt% Al<sub>2</sub>O<sub>3</sub>) typically exhibits equiaxed grain morphology due to limited kinetics in solid-state cation interdiffusion. It has been demonstrated that the addition of B<sub>2</sub>O<sub>3</sub> can shift the mullitization to lower temperatures and encourage the anisotropic grain growth by lowering the viscosity of the intergranular phase [40].

To improve the relative density of mullite-based ceramics from 93% to 97%, Riedel et al. used an MK polymer filled with functionalized nano-γ-Al<sub>2</sub>O<sub>3</sub> (added octylsilane groups on the surface) [41] and obtained a high amount of mullite crystals already at 1300 °C, attributed to the better distribution of functionalized γ-Al<sub>2</sub>O<sub>3</sub> within the initial

PCP compared to unfunctionalized fillers. Due to heat treatment of the mixture in the nitrogen atmosphere, silicon oxycarbide (SiOC) was yielded from MK, which transformed into SiC crystals due to the interaction with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The resulting SiC-mullite monoliths can be an alternative for SiC/mullite nanocomposites derived from polymethylsiloxane gels filled with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The obtained crack-free monoliths can be potential candidates for complex-shaped ceramics, resistant to high temperatures and corrosion. A ternary SiC-mullite composite containing nano- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals was obtained by substituting nano-aluminum fillers for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [42].

In binary systems consisting of silica and a metal oxide, the formation of multiple silicate phases requires having a specific molar ratio between silica and the metal oxide. For instance, when silica is combined with CaO, various silicates such as CaO·SiO<sub>2</sub>, 3CaO·2SiO<sub>2</sub>, 2CaO·SiO<sub>2</sub>, and 3CaO·SiO<sub>2</sub> can be produced depending on the CaO/SiO<sub>2</sub> molar ratios. These silicates can be mainly used for biomaterial applications [43]. Using a filler like CaCO<sub>3</sub> can result in the formation of a silicate with a higher CaO/SiO<sub>2</sub> ratio than intended. For example, when micro-sized CaCO<sub>3</sub> is used in a filler/PCP formulation, the desired wollastonite (CaO·SiO<sub>2</sub>) phase is replaced with di-calcium silicate (2CaO·SiO<sub>2</sub>) due to localized concentrations of CaO. On the contrary, almost pure wollastonite was obtained using nano-sized CaCO<sub>3</sub> under the same conditions [44].

The choice of PCP has been found to influence the polymorphism of calcium silicates. Using H62C with a low molecular weight instead of MK, a trace of the  $\alpha$ -phase or “pseudowollastonite” was detected alongside the  $\beta$ -phase typically obtained at the temperature range of 900–1100 °C [43]. The polymer with a lower molecular weight consists of short Si-O fragments that promote the formation of ring-structured silicate variants like the  $\alpha$ -phase [45].

Synthesis of binary ceramic compositions such as forsterite and yttrium silicates has been reported as well. A highly reactive combination of PCP filled with nano-sized MgO enables the formation of forsterite for biomaterials [46] and dielectric applications [47] at temperatures as low as 800 °C. Biocompatibility and bioactivity observed in forsterite monoliths [48] and coatings [49][50] have made them a promising material for medical application. Moreover, forsterite has a low dielectric constant ( $\epsilon_r = 6.8$ ) which makes it attractive for submillimeter-wave applications. The low dielectric losses and the ability to transfer signals in a short time are interesting for high-frequency electromagnetic waves.

A combination of yttria (Y<sub>2</sub>O<sub>3</sub>) and silica (SiO<sub>2</sub>) can produce mono- and di-silicates such as Y<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub> (or Y-MS) and Y<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> (Y-DS) [51]. Y-MS is monophasic, undergoing a dislocative transformation between the X1 (low temperature) and X2 (high temperature) phases. Y-DS, however, exhibits multiple polymorphs ( $\gamma$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $z$ ), with each form stable within a specific temperature range. Depending on the processing, different polymorphs can be obtained [52].

## 1.4. Processing of Preceramic Polymers

### 1.4.1. Shaping

One of the advantages of PCPs is their viscoelastic behavior rising from their polymeric nature. As a result, PCPs are well-suited for a wide range of thermoplastic shaping techniques such as casting, injection molding, pressing,

tape casting, extrusion, fiber drawing, and coating [24]. More recently, using additive manufacturing (AM) techniques for shaping PCPs attracted interest among researchers as well.

### 1.4.2. Crosslinking

Crosslinking is the process by which polymer chains are linked together, forming a three-dimensional network. This process is important for almost all the fabrication processes of PDC structures because it allows the precursor to transform from a flexible, thermoplastic organic material (necessary for shaping) into a rigid and insoluble thermoset and preserve the structure during post processing [18]. Crosslinking can occur through a variety of mechanisms, most commonly by thermal crosslinking in the range of 100–250 °C under airflow, crosslinking with chlorosilane, or curing with radiation [26]. With the presence of functional groups such as Si-H, Si-OH, and Si-vinyl, PCPs can be spontaneously crosslinked below 200 °C using hydrosilylation (addition) or silanol–silanol reactions (condensation) [24]. Crosslinking in an air atmosphere has traditionally been a popular method for curing PCPs to provide SiO<sub>2</sub> yield. This process, however, is not suitable for the fabrication of non-oxide ceramics due to the drawback of leaving up to 15 wt% oxygen in the final PDC [53][54][55]. This residual oxygen content can adversely affect the thermal stability of the non-oxide PDCs, weakening their overall performance.

### 1.4.3. Pyrolysis

Shaping and crosslinking of PCPs is followed by a pyrolysis step, known as ceramization, in which the PCP is transformed into a ceramic material through various thermal processes. These processes include hot pressing, spark plasma sintering, chemical vapor deposition, plasma spraying, rapid thermal annealing, laser pyrolysis, microwave heating, and the most commonly used method, pyrolysis in an argon or nitrogen atmosphere. Pyrolysis in such inert atmospheres leads to the formation of amorphous covalent ceramics with the decomposition of organic side chains (methyl/phenyl/vinyl groups) or Si-H, Si-OH, or Si-NH<sub>x</sub> groups and the gradual removal of the gaseous byproducts at elevated temperatures (600–1000 °C). The reaction mechanisms during pyrolysis have been studied using solid-state nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and a thermogravimetric analysis (TGA) coupled with mass spectroscopy. The use of ion irradiation to eliminate hydrogen atoms through the cleavage of C-H bonds is an alternative non-thermal process for ceramization where any remaining carbon is transformed to diamond-like carbon clusters. The pyrolysis atmosphere can modify the composition of the final ceramic component. Pyrolysis of a preceramic polymer under an inert atmosphere (argon or nitrogen) is required to create SiC, Si<sub>3</sub>N<sub>4</sub>, SiCN, SiBC, or SiCBN (depending on the starting PCP composition) whereas pyrolysis in air can be employed for the formation of silicate ceramics using active metal oxide fillers.

## 2. Additive Manufacturing of Preceramic Polymers

The versatility of polymer-forming technologies allows for shaping preceramic polymers in various ways and thereby overcoming the limitations and drawbacks associated with a traditional ceramic shaping process like pressing, extrusion, or injection molding. The pressing method, followed by pyrolysis and sintering, is an effective

method to produce PDCs without or with very low content of porosity. However, it is limited to simple shapes. When this method is employed for more complex structures, a subtractive machining step is necessary, which is expensive and time-consuming, and results in significant material waste [56]. To fabricate more complex structures, extrusion and injection molding have been employed [57]. Nevertheless, the extrusion process is limited to circular symmetric objectives and for the injection molding, designing of molds is required, which makes prototyping economically unreasonable due to the cost of the molds. Even though the complexity of ceramic parts increases from pressing to injection molding, additive manufacturing (AM) has the highest freedom of geometrical design. Using AM, a 3D computer model with complex and tiny geometry can be converted into a three-dimensional (3D) structure by depositing the material layer by layer. In this way, even dense structures with controlled inner porous structure designs can be achieved easily without using pore formers. In addition, the need for costly molds and material waste can be avoided.

## 2.1. Light-Assisted AM (Vat Photopolymerization)

Vat photopolymerization techniques including the first invented stereolithography (SL) method [58] followed by digital light processing (DLP) and two-photon polymerization (TPP) as derivatives of the SL technique can provide accurate 3D replicas with fine details and utilize similar principles but have some key differences in their implementation [59].

PCPs are highly compatible with AM involving vat photopolymerization [60]. In SL of PCPs, precise patterning of PCPs and subsequent conversion to ceramics through pyrolysis result in complex PDCs with a high resolution. The PCP needs to be photosensitive, soluble in compatible solvents, and providing proper rheological behavior. Ensuring a homogeneous dispersion of PCPs in the liquid phase also helps minimize scattering, resulting in a high-quality surface finish for the final PDC components.

### 2.1.1. Stereolithography (SL)

Stereolithography (SL) enables the creation of precise objects with defined edge quality. The SL method is based on photopolymerization of liquid resins containing monomers and oligomers that are sensitive to a specific wavelength of light [61]. These so-called photopolymers undergo a chemical reaction using exposure to a specific wavelength and the liquid transforms into a solid polymer. In this process, a thin layer of the photopolymer is deposited on the build platform. This layer of resin is exposed to a specific pattern of light, typically ultraviolet (UV) light, using a point-by-point scanning method, where the laser beam sequentially cures the resin. The photoinitiator in the resin absorbs the light energy and cures the resin in the defined areas to form a solid layer. After curing one layer, the platform moves down to create space for the next layer of liquid resin. Each cured layer bonds to the previous layer, creating a cohesive structure. This process continues layer by layer until the desired 3D structure is built. After printing, the printed form is treated with the proper solvent to remove the extra uncured resin. Using the SL technique for 3D printing of PCPs, a high printing resolution (20  $\mu\text{m}$  or less) can be achieved [62]. However, the full potential of this method is still not fully explored due to a limited number of proper photocurable PCPs.

### 2.1.2. Digital Light Processing (DLP)

The digital light processing (DLP) technique shares similarities with SL. However, it uses a different approach to achieve layer-by-layer printing [63]. In DLP, the light source is a digital projector with a digital micromirror device (DMD) that projects a patterned image of an entire layer onto a vat (the container of liquid resin) that allows for higher resolutions without the need for complex scanning processing. That is why DLP offers a higher printing speed compared to SL since the whole layer can be exposed to light simultaneously. Here, a photopolymer resin sensitive to light, specifically to a certain wavelength such as ultraviolet (UV) or visible light, is used. To start the printing process, the build platform is lowered into the vat, submerging a thin layer of liquid resin. The digital projector then projects the patterned image onto the resin surface. Selective curing of the resin happens in the illuminated areas. The exposed resin undergoes photopolymerization, transforming from a liquid to a solid state to create the desired pattern. The platform is then incrementally raised or lowered to deposit a new layer. The process is repeated until the 3D form is completed. Then, the printed object is typically removed from the vat and rinsed to remove any excess or uncured resin.

### 2.1.3. Two-Photon Polymerization (TPP)

Using two-photon polymerization (TPP), high-resolution, complex three-dimensional micro to nanoscale structures can be obtained [64]. In this method, a photosensitive material absorbs a femtosecond laser beam in the near-infrared range with a high photon energy density. The material molecules enter the excited state at irradiated locations and create a voxel (volume pixel) with the two-photon absorption process [65]. In this way, each layer is built by curing the photopolymer point by point until the full 3D form is obtained. Using this method, the fabrication of unique 3D structures with two-photon polymerization is an ideal technique for various applications in fields such as microelectronics, photonics, biomedicine, and other areas that require precise fabrication at the micro- and nanoscale. These applications encompass tissue-engineered scaffolds, micro medical devices like micro swimmers and needle arrays, optical devices, and more [65]. Using the TPP method, only SiOC ceramics were obtained [66][67][68].

## 2.2. Selective Laser Sintering (SLS)

Using the selective laser sintering (SLS) technique, a laser beam facilitates the fusion or sintering of powdered materials together to build 3D structures [69]. First, a thin layer of powder is deposited on the build platform. A high-powered laser beam is exposed on the powder bed, accurately tracing the desired object shape. Consequently, particles stick together because of the material's partial melting and selective fusion in defined areas. After sintering each layer, the platform is lowered to prepare a new layer of powder for sintering. Once the sintered 3D structure has undergone cooling, it is taken out for subsequent processing, e.g., remove the excess powder and finish the surface followed by heat treatment, depending on the material and desired specifications.

## 2.3. Laminated Object Manufacturing (LOM)

In this method, thin sheets of material bond together to form 3D objects. A stack of sheets can be first laminated and then cut (cut-off-the-stack) or each sheet can be cut and then laminated (cut-then-bond) together [70]. The cutting is computer-controlled and follows the contour of the object's shape in each sheet and removes the excess

part to achieve the desired shape. In the cut-then-bond method, a layer of adhesive is applied to bind the sheets together. After that, heat and pressure are applied using heated plates or rollers to ensure firm fusing of the sheets. The sequence of the cutting to binding step is repeated until the full 3D object is built. Trimming with mechanical or laser cutting, depending on the material and desired specifications, may be required. LOM is commonly used for simple geometries and large-scale object fabrication in various industries.

## 2.4. Extrusion-Based AM

As mentioned earlier, PCPs exhibit thermoplastic behavior because of their polymeric nature. As a result, extrusion-based additive manufacturing techniques can be utilized to create PDC parts [71]; however, they behave differently compared to the typical engineering polymers due to their low glass transition temperature and lack of chain entanglements [5]. Additionally, temperature significantly influences their viscoelastic properties [72]. To preserve the printed shape during the pyrolysis step, it is important to crosslink the PCP. It is worth noting that the introduction of fillers to PCPs can improve the shape stability regardless of crosslinking, as the fillers themselves can provide a higher viscosity and a network that will result in a yield point to retain the form [5].

### 2.4.1. Direct Ink Writing (DIW)

Direct ink writing (DIW), also called robocasting [73], involves a controlled deposition of inks and pastes to create 3D objects [74]. The ink or paste is typically a mixture of polymers and fillers such as ceramics, metals, or composites with a careful formulation to achieve the desired rheological properties. In this process, a deposition system controls the flow and pressure of the ink extruded from the nozzle. The extruded material flows as a stream or filament and is deposited on a build platform. Movements of the extrusion system in multiple axes are controlled through a computer and follow a specific path to achieve the desired shape. The ink should have the necessary flow characteristics, including a proper yield stress and storage modulus to be extruded through a printing nozzle.

An ideal ink is extruded by applying a high shear rate and at low viscosity [75], exhibiting a shear-thinning behavior. After deposition on the printing bed, the viscosity yield point should be immediately achieved by building a network structure to reduce deformation of the printed structure. As a result, a time-dependent oscillating viscosity analysis is of great importance.

To achieve a suitable rheology, the following methods are outlined below:

- High solid loading of the ink/paste formulation: Using a high solid content, forming a network of the extruded material happens fast [76]. However, only nozzles with a diameter of approximately 500  $\mu\text{m}$  are applicable to avoid clogging of the nozzle.
- Addition of polymeric binder: Organic binders such as polyvinyl butyral (PVB) or polyethylene glycol (PEG) can be added to the ceramic phase (maximum of 23 wt%) [77]. In this way, the rheology of the ink can be justified without manipulating parameters such as pH.

- Reversible gel transformation: In this approach, ink is extruded in a non-wetting bath, often oil [78]. To achieve a reversible gelling effect, ceramic suspension is flocculated in a controlled manner by introducing polyelectrolytes, manipulating pH or ionic strength of the solvent. Addition of a gelling aid, like inverse thermoreversible gels, can be used alternatively.
- Use of preceramic polymers: Polysiloxanes and polysilsesquioxanes can be incorporated to control the rheology of the ink PCPs and offer a dual role [75]. The PCPs have the potential to serve as reactive binder additives, since they result in SiO<sub>2</sub> and SiOC ceramics after pyrolysis in air or an inert atmosphere, respectively. When active fillers are added to the yielded SiO<sub>2</sub>, various silicate ceramics can be produced.

### 2.4.2. Fused Deposition Modeling (FDM)

Fused deposition modeling (FDM), also called fused filament fabrication (FFF), is based on extruding and deposition of thermoplastic materials [79][80]. FDM is one of the most widely used and accessible methods of 3D printing. In this method, thermoplastic feedstocks containing an organic binder and ceramic powder in the form of filaments or pellets are fed into an extrusion chamber inside a heat zone where the feedstock is melted [81][82]. The melted filament/pellets are pushed further and extruded through a small nozzle on a build platform layer by layer. The movements of the nozzle along the X and Y axes follow the pre-determined path of the object's digital model. Each layer solidifies directly after deposition and bonds with the previous layer to ensure the structural integrity of the object. This layer-by-layer approach continues until the entire object is formed. After that, the printed object requires a debinding step to remove the organic thermoplastic component.

FDM printing of PDCs remains an underexplored area because the commonly used filament printers require spooling of the feedstock into filaments. Considering the high glass transition temperature (>50 °C) and melting temperature (ranging approximately from 70 °C to 250 °C) of PCPs, their filaments can be brittle and hard to spool. On the other hand, the thermoplastic nature of PCPs is favorable for adjusting the viscosity and elastic properties of filaments.

Thermal processing under both air and inert atmospheres during the crosslinking and pyrolysis steps of a commercial methyl-silsesquioxane preceramic polymer (MK) has been investigated by Sarraf et al. [83]. They reported that employing low heating rates (below 2 K/min) under an air atmosphere has a notable impact on the SiO<sub>2</sub> yield of MK. Using a heating rate of 0.3 K/min and 0.6 K/min resulted in SiO<sub>2</sub> yields of 69.1 wt% and 75 wt%, respectively, in contrast to the standard yield of 82 wt%. They concluded that slower heating rates provided more time to evaporate volatile species before the crosslinking occurred. In the FDM process, low heating rates and dwell times are necessary to remove binders without causing defects like cracks, blisters, and bubbles. To overcome this issue, mixing of feedstocks above the crosslinking temperature of MK (190 °C) was suggested. In this way, a stable yield of 81 wt% SiO<sub>2</sub> was achieved, regardless of the heating rate.

## 3. Conclusions

The introduction of the polymer-derived ceramic (PDC) route in 1975 opened up a new door to explore novel possibilities in ceramic synthesis. Although most of the available studies on the fabrication of PDCs are performed in an inert atmosphere to obtain non-oxide ceramics, the synthesis under air to produce several oxide ceramics has been reported as well.

The possibility to combine the shaping and synthesis steps is an attractive aspect of polymer-derived ceramics. Preceramic polymers can be dissolved in many organic solvents and also be processed with thermoplastic shaping methods due to their polymeric nature. As a result, there is a continuous and growing adoption of various additive manufacturing (AM) techniques for the production of PDC structures. Various studies have presented interesting findings regarding the additive manufacturing (AM) of PDCs, indicating a promising future for these materials. Several studies have investigated the fabrication of bioactive ceramics/glass ceramics, SiOC, and mullite-based foams and scaffolds using vat polymerization and direct ink writing techniques. Also, the fabrication of mullite honeycomb structures has been reported via the fused deposition modeling technique. Vat polymerization and direct ink writing have been only used for the fabrication of thin and detailed PDC structures, foams, and scaffolds. Using the fused deposition modeling technique, however, there are first reports on the fabrication of bulk PDCs by modifying the binder system. There is a great potential in development of bulk and large PDC structures with high temperature stability and shock and creep resistance by using this method.

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