Additive manufacturing of lightweight and high-strength polymer-derived SiOC ceramics

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ABSTRACT
Lightweight and high-strength polymer-derived SiOC ceramics with varied lattice structures have been successfully produced using different polysiloxanes as preceramic polymers (PCPs) via photopolymerisation-based digital-light-processing 3D printing and pyrolysis. Photocurable precursor resins were prepared by simple mixing of polysiloxanes with photosensitive acrylate monomers, achieving good flowability and preserving desirable stability under different heating and oscillation conditions. Complex micron-sized structures were manufactured with high precision via the optimisation of polymer formula and printing parameters. The printed PCPs pyrolysed at 600–1000°C preserved fine features with uniform shrinkage. The skeletons were almost fully dense, with smooth and flawless surfaces at macro/micro scale. Porosities and mechanical properties, including apparent compressive strength, elastic modulus, and indentation hardness, were characterised. XRD, FT-IR, Raman spectroscopy, and XPS were used to explore the chemical variations in elements and atomic bonds. High specific compressive strength to density ratios was obtained for the SiOC lattices compared with other porous ceramics.

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1. Introduction

3D printing (Yuan, Chua, and Zhou 2019), also known as additive manufacturing and rapid prototyping, is based on digital model files and uses the principle of material accumulation to construct objects via layer-by-layer printing (Pham and Gault 1998; Wong and Hernandez 2012). Compared with the use of resin and metal materials, the 3D printing of ceramics began comparatively recently and developed at a slower pace, yet it has still been popular among research institutes and enterprises because of its great potential for innovative and useful applications (Chen, Li, Li, et al. 2019).

The application of 3D printing technology to the shaping process of ceramic materials has many advantages (Janssen, Scheppokat, and Claussen 2008; Zhou et al. 2010; Tian et al. 2012; Chen, Li, Li, et al. 2019). First, it has no need for a mould, which can significantly shorten the development cycle. Second, it can realise the flexible design and manufacture of structural parts with complex shapes, breaking the limitations of the form in traditional ceramic processing technology, and third, it makes personalised designs and structures feasible, to meet the needs of different groups. At present, the main techniques for the additive manufacturing of ceramic parts are as follows: vat photopolymerisation, such as stereolithography (SL) (Jacobs 1992; Chen et al. 2010), material jetting, such as inkjet printing (UP) (Derby 2011; Tan, Tran, and Chua 2016; Saengchairat, Tran, and Chua 2017; Chen, Ouyang, et al. 2018), and binder jetting (Cheng et al. 2019), material extrusion (Tian et al. 2017), such as fused deposition manufacturing (FDM) (Danforth 2016; Cano et al. 2019) and direct ink writing (DIW) (Liu et al. 2019; Elsayed et al. 2019), powder bed fusion, such as selective laser sintering (SLS) (Yuan, Shen, et al. 2019; Chen, Wu, et al. 2018) and selective laser melting (SLM) (Minasyan et al. 2018; Chen, Li, Wu, et al. 2019; Yu et al. 2019), and binder jetting, such as three dimensional printing (Xiao et al. 2018; Huang et al. 2019). Digital-light-processing (DLP) (Felzmann et al. 2012; Chen, Liu, et al. 2019; Mei et al. 2019), as a derivative technology of stereolithography, is capable of curing a whole layer in one time period without the need for a laser light source, yet maintaining the high accuracy and surface quality of SL, which can greatly advance printing efficiency and reduce production costs at the same time.

To prepare a dense ceramic component by means of DLP 3D printing, slurries with high loadings of ceramic...
particles must be used. This can lead to reduced flowability, so that the levelling of the slurries during printing might be difficult. At the same time, both the particle size and the inhomogeneity of slurries limit its suitability for the manufacture of structures with much finer feature sizes, i.e. the printing resolution. In addition, the significant mismatch between the refractive index of the ceramic powder and that of the photocurable resin greatly reduces the curing depth, and, in addition, side scattering of the incident light can also cause problems with printing quality. Extensive work has been carried out on the preparation of simple binary oxide ceramic components using SL and DLP techniques, thanks to their reduced refractive index mismatch, including ZrO₂, SiO₂, Al₂O₃, and their mixtures (Zhou et al. 2016; Chen, Li, Liu, et al. 2019; Zhang et al. 2019). When it comes to high-performance non-oxide ceramics such as nitrides and carbides, much higher energy densities are required as the dark-colored materials show significant differences in refractive index according to the photosensitive polymers used (Griffith and Halloran 1996; Ding et al. 2019). Additionally, for other polynary ceramics such as SiCN and SiOC, their fine-powder feedstock can rarely be obtained (Colombo 2010).

The combination of the polymer-derived ceramic (PDC) technique and 3D printing technology is proposed as a way to address the above challenges. The PDC technique employs liquid preceramic polymers (PCPs) without the need for adding ceramic particles to the solution, making possible the decomposition of organic contents and their conversion into ceramic materials via pyrolysis (Colombo et al. 2010; Hundley et al. 2017; Fu, Zhu, and Zhu 2019). The advantages of the PDC technique lie in the control of composition and microstructure through design at the molecular level. In this way, high ceramic yields can be achieved following sintering with the cross-linked active groups present in PCPs. Moreover, both the liquid and solid polymer PDC forms possess simple shaping and machining ability, and their ceramic forms possess stability. This breaks the limitations of traditional ceramic materials and revolutionises the ceramic preparation process (Schulz et al. 2004; Colombo et al. 2010; Zaheer et al. 2012).

At present, research into the SL and DLP-based 3D printing of PDCs is still in its infancy (Pham et al. 2006). In 2016, Zanchetta and coworkers (Zanchetta et al. 2016) demonstrated the printing of some early examples of complex-shaped 3D polymer-derived SiOC ceramic structures with a 200 mm strut size by SL, inspiring new ideas and methods for ceramic printing. In the same year, Eckel et al. (2016) reported the fabrication of SiOC with a lattice structure by means of stereolithography, resulting in thermostability at 1700°C in air and higher specific strength over density compared with other ceramic forms. The feasibility of preparing PDCs by photopolymerisation-based 3D printing has been demonstrated. Although it has been a longstanding effort to create desirable high-temperature performance SL/DLP-printed SiOCs suitable for the production of lightweight high-strength porous ceramics used in extremely high-temperature environments, very few organic precursor formulations appropriate for SL/DLP have so far been reported. de Hazan and Penner (2017) developed a versatile new photocurable polycarbosilane to prepare SiC-rich complex structural ceramic parts at 1300°C. Schmidt and Colombo (2018) prepared three types of precursors by adjusting the ratio of the two organosilicone sources and obtained porous or densely structured SiOC ceramics. Wang, Schmidt, et al. (2019) utilised thiol–ene click chemistry to obtain three different formula of PCPs for the transformation into SiOC/SiC/SiCN ceramics, respectively. Brigo et al. (2018) fabricated micro/nano SiOC structures by means of two photon polymerisation. More recently, Wang, Xie, et al. (2019) demonstrated the DLP 3D printing of Si3N4 components using polysilazanes-based polymers.

There is still space for improvements in the mechanical properties and high-temperature stability of manufactured porous ceramics, which falls right in the scope of the current study. In contrast to our previous efforts applied to the PCP resin prepared by the sol–gel method (Fu et al. 2018, 2019), which required complicated processing and a lengthy synthesis period but had difficulty in maintaining good stability, in this study we developed a series of ceramic precursors for DLP 3D printing of SiOC by simple physical mixing, as inspired by the work of Schmidt and Colombo (Schmidt and Colombo 2018). After printing, the silicon-based resin was pyrolysed to generate lattice structures with fully dense skeletons. The microstructural, mechanical, and chemical properties of the ceramic samples obtained after pyrolysis at different temperatures were comprehensively studied, and the results showed that lattice-structured SiOC ceramics with great forming qualities, crack-free surfaces, and prominent specific strength were realised.

2. Material and methods

Figure 1 depicts the fabrication process of lattice-structured SiOC ceramic components, including the preparation of precursor resins, the design of 3D models with lattice structures, and DLP 3D printing and pyrolysis treatment.
2.1. Preparation of photocurable PCP resins

In this study, three kinds of polysiloxane powders with different functional substituents (SILRES MK, IC836, and 604, all from Waker, Germany) were used as silicon sources for the preparation of precursor photosensitive resins. Tetrahydrofuran (THF, Aladdin, China) and tripropylene glycol monomethyl ether (TPM, Aladdin, China) were chosen as dispersants. Trimethylolpropane triacrylate (TMPTA, Ryoji, Germany) and hexanediol diacrylate (HDDA, Ryoji, Germany), which exhibit high photopolymerisation reactivity for high printing precision, were used as diluent and monomer. Aliphatic polyurethane hexaacrylate (RJ423, Ryoji, Germany) was selected to improve the curing rate and cured strength of the resins. Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (819, Jiazhong, China) was used as a free radical photoinitiator. The schematic chemical structure of the polysiloxane (PSO) is shown in Figure 2.

The photocurable PCP resins were prepared as follows. First, a premix was obtained by dissolving commercially available silicone powders in a mixed solution of THF and TPM (volume ratio of 1:1). RJ423, TMPTA, and HDDA were slowly added to the premix while magnetic stirring at 500 rpm to lower the viscosity and enhance the photocuring intensity. After thorough mixing for 20 mins and rotary evaporation for 45 mins at 40°C and 0.095 mPa, vitreosol (i.e. transparent sol) was prepared. Vacuum pumping helped reduce the air pressure and the boiling point of THF decreased from 66°C to below 40°C, facilitating its evaporation. The evaporation of THF is beneficial to increasing PCPs concentration and generating higher ceramic yield. Finally, photoinitiator 819, which undergoes homolytic cleavage and the formation of radicals that could initiate the radical polymerisation once exposed to light in the near-UV range, was added to the vitreosol to prepare the PDC photosensitive resin. Table 1 lists the ingredients and their quantities used for the preparation of the slurry, and Figure 3 shows the flowchart of the preparation process.

2.2. DLP 3D printing and post-processing

3D printing experiments of PDC samples were carried out using a commercially available DLP 3D printer (Skyline, Longer, China), and the printing accuracy was improved by adjusting parameters such as exposure intensity,
curing time, layer thickness, support structure, and motor speed. After importing the STL files, the 3D model was divided into a series of sets of 2D images according to the geometric features and the predefined slicing thickness, followed by projection of the sliced shapes into the resin vat to cross-link the photosensitive organosilicone resin with LED UV light. After the curing of each single layer, the printing platform moved up and the trough inclined at a fixed angle to level off the resin at the same time. For the curing of the next adjacent layer, the platform descended into the vat, leaving a gap to the bottom corresponding to the slicing thickness, and the projection of the subsequent images continued on the cured part until the printing of the entire model was accomplished.

DLP 3D printing can also ensure high accuracy and surface quality. Compared with the stereolithographic 3D printing which proceeds in a point-line-layer scanning fashion, the DLP technique has the advantage of printing an integral layer at a time. This shortens the printing time considerably and thus improves efficiency. The DLP printer used in this study had a minimum lateral printing resolution of 50 μm and a preset slicing thickness of 100 μm. After printing, the PDC samples were taken down from the printing platform and the supports removed, followed by ultrasonic cleaning in deionised water for 3 mins prior to rinsing with absolute ethyl alcohol and blowing with compressed air. Post-curing in the UV curing box was carried out to ensure complete cross-linking of the resin (52 mW/cm², 60 s). Finally, the samples obtained were then pyrolysed to produce the final SiOC components in a tube furnace (OTF-1200X, Kejing, China) at 600/800/1000°C for 240 min under an argon atmosphere (≥ 99.9%) at a cooling rate of 2°C/min.

2.3. Characterisation

The dynamic viscosity of the PCP resin was measured using a rheometer (MCR 302, Anton Paar, Austria) using a rotary mode temperature scan to plot the viscosity–shear rate and the viscosity–temperature curves. In addition, the sol–gel transformation point was measured using an oscillating mode frequency scan to characterise the stability of the resin. The UV-curing properties of the resin, including the critical exposure intensity (E_c) and the transmission depth (D_p), were determined based on the empirical equation derived (Eq. (1)) from Beer–Lambert law, according to the extrapolation of a series of data points of cured depth (C_d) and exposure energy (E) measured using a UV-LED curing system (X-100, Yuntong, China) with LED light of 405 nm wavelength.

\[ C_d = D_p \ln E - D_p \ln E_c \]  

(1)

The critical exposure intensity and the transmission depth can be adjusted to be consistent with the predefined printing parameters.

Thermal gravimetric analysis (TGA) was carried out using a synchronous thermal analyzer (STA-8000, PerkinElmer, America) in a flowing nitrogen atmosphere where the temperature was gradually raised to a maximum temperature of 1000°C at a rate of 10°C/min. X-ray diffraction (XRD) analyses of the precursor/ceramic samples before and after pyrolysis were performed using an X-ray diffractometer (D8 Advance, Bruker, Germany). The microscopic morphologies of each lattice SiOC part were studied using a scanning electron microscope (SEM, Phenom Pro, Phenom, Netherlands). A Fourier transform infrared spectrometer (FT-IR, Frontier, PerkinElmer, USA) with a resolution of ± 4 cm⁻¹ over a scan range of 500–4000 cm⁻¹ was used to investigate the functional group information related to the variation in bonding structure before and after pyrolysis. Raman spectroscopy of 532 nm wavelength (iHR320, Horiba, Japan) over the range of 800–2000 cm⁻¹ was used to study the evolution of free carbon in SiOC

Table 1. Ingredients and their quantities for preparation of the photosensitive resin.

| Ingredient            | Quantity(wt%) | Organosilicone |
|-----------------------|---------------|----------------|
| Polysiloxane powder   | 40%           | 53%            |
| Dispersants THF and TPM | 28%          | 17%            |
| Oligomer RJ423        | 20%           | n.a.           |
| Diluent/monomer TMPTA | 8.0%          | 25%            |
| Diluent/monomer HDDA  | 2.0%          | 3.0%           |
| Photoinitiator 819    | 2.0%          |                |

Figure 3. Flowchart of the preparation process for the organosilicone resins. Note that for a general guideline purpose, detailed chemical names/amounts are not shown here, please refer to the text for the compositions. The boxes in light blue indicate raw materials, bright yellow boxes indicate intermediate or final mixture produced, light red boxes indicate processing operations executed.
ceramics after pyrolysis at different temperatures. The density and porosity of the parts were measured according to Archimedes’ method using a densimeter (MZ-Y120, Mayzun, China). Note that there are two types of densities. One is the ‘skeleton density’ which does not take any artificial porous space into account and is calculated through the division of the weight of the lattice sample over the actual volume of the lattice skeleton measured with Archimedes’ method. The other is the ‘cellular density $\rho_c$’ which includes the porous space within the models and can be calculated through the following equation,

$$\rho_c = \frac{m}{V_b}$$

where $m$ is the quality of lattice structure; $V_b$ is the volume of a box of the same three dimensional sizes as the lattice structure. The effective compressive strength of the lattice structure was measured using a universal mechanical testing machine (CMT4204, MTS, America). The effective elastic moduli of the structures were also derived from the stress–strain curves obtained. The localised elastic modulus and hardness of the dense skeletons were measured using a nanoindenter (Ti950, Hysitron, USA). Nanoindentation tests with a Berkovich tip were carried out with a maximum load of 5000 $\mu$N and a loading rate of 0.3 nm/s. The outer surfaces of the test lattice samples were finely polished to remove obvious asperity, where necessary, prior to nanoindentation experiments.

### 3. Results and discussion

#### 3.1. Thermogravimetric analysis of organic silicone powder

During the pyrolysis process, as the temperature rises the precursor polymer experiences weight loss, and the final ceramic yield depends on the type of polyoxysilane in the form of silicone powder used in the resin preparation. Three sets of organic silicone powder samples underwent TGA in the range 25–1000°C under a nitrogen atmosphere. The results are shown in Figure 4.

As can be seen from the TGA curves, the weight loss for the MK powder was smooth and achieved an overall loss of 18.0% at 1000°C. Since the theoretical SiOC content is 76%, the mass difference was assumed to be in the form of free carbon. The final weight loss for IC836 at 1000°C was 26.8%, with a sharp drop in the temperature range 400–700°C. This sudden release of large amounts of gas during the inorganic conversion process would create pores within the samples. Furthermore, significant thermal stress within the samples might also lead to the generation of cracks. The overall weight loss for 604 at 1000°C was 20.8%, lying between the values for MK and 836.

![Figure 4. TGA curves for MK, IC836, and 604 powders.](image)

#### 3.2. Rheological properties of precursor resins

The rheological properties of PCP resins, including flowability and stability, play a decisive role in the implementation of DLP 3D printing. Such properties rely, in turn, on the dispersants, oligomers, and diluents added to the system. The measured viscosities of the three types of photosensitive resins are shown in Figure 5. As the shear rate increased from 0.1 to 1000 s$^{-1}$, the viscosity decreased from 446.38, 398.93, and 395.27 mPa·s to 258.62, 216.36, and 140.98 mPa·s, respectively (Figure 5(a)). A significant number of C = C bonds break during the course of resin curing, with a large amount of heat released, which may lead to the production of gels and reduce the flowability of the resin system. Hence, the rheological properties above room temperature also need to be studied. As the temperature increased from 20 to 80°C at a shear rate of 50 s$^{-1}$, the viscosity decreased from 414.01, 316.50, and 202.47 mPa·s to 20.06, 18.11, and 15.01 mPa·s, respectively (Figure 5(b)). As the shear rate or temperature rose, shear thinning was exhibited in all of the resins, which is a feature of non-Newtonian fluids.

In order to avoid the gelation caused by the reaction of TMPTA with the unstable –CH$_3$ substituent attached to the MK backbone, the amount of MK powder used for the resin as the silicon source was relatively low (up to 40 wt %), while large amounts of organic solvents THF and TPM were added for dissolution. However, the MK resin still possessed a higher viscosity than the others in both viscosity–shear rate and viscosity–temperature plots, because RJ423, sticky aliphatic polyurethane acrylates with six functional groups, was introduced to increase the curing strength. Therefore, the MK resin still showed a greater viscosity even with a lower silicone content.

In the resins with IC836 and 604 as silicone source at the same ratio as other ingredients, the molecular weight
of the polysiloxane powder becomes a decisive factor in the viscosity of the two resins. With a relative molecular mass of 1350, 604 resin performed with greater flowability than IC836 resin (relative molecular mass of 1815), suggesting the former to be more suitable for DLP 3D printing.

The storage modulus $G'$ and the loss modulus $G''$ of the resins are shown in Figure 6. As the angular frequency $\omega$ increases to 100 rad/s, $G''$ increases from 4.06 to 30.33 Pa, indicating that the resin system is in a high potential energy state. Meanwhile, the values of $G'$ of the IC836 and 604 resins rise to maxima of 0.01 and 1.66 Pa, respectively, which are much lower than the minimum for $G''$. According to the above relationship between $G'$ and $G''$, gelation occurs in neither the IC836 resin nor the 604 resin, proving that the high stability of these two types of resins make them suitable for DLP 3D printing.

For MK resin, $G'$ reached 18.94 Pa when $\omega$ was 46.4 rad/s, while the corresponding value of $G''$ was 17.56 Pa, and the storage modulus remained higher than the loss modulus at larger values of angular frequency. In other words, MK resin transforms into gel in the vibration test, and $\omega = 46.4$ rad/s is the sol–gel inversion point of the system. This is because energy derived from oscillations exerts itself inside the resin system, leading to destruction of molecular chains such as -CH$_3$ and C = C (Figure 7). The backbone cross-links and polymerises to form a space network of colloidal particles with Si–O–Si as the frame, resulting in a gel with poor flowability.

Following the above comprehensive analyses, taking into account flowability, stability, and ceramic yield, polysiloxane SILRES 604 was selected as the preferable silicon source of PCP resin in the subsequent experiments.

### 3.3. Photocuring properties of precursor resins

The photocuring properties of the as-prepared organosilicone resins are another decisive factor in the feasibility of...
of DLP 3D printing, which is also related to reactive dilu-
ents and photoinitiators.

The effect of the concentration of TMPTA diluent/
monomer on $D_p$ is shown in Figure 8(a). As the con-
centration of TMPTA increases from 14.29% to 32.14%, $D_p$
decreases from 467.95 to 147.11 μm, and $E_c$ decreases
from 32.0501 to 15.2409 mJ/cm². This is because the con-
centration of the photosensitive substance per unit
volume increases with increasing TMPTA concentration.
As the concentration of monomer TMPTA increases,
the reactivity of resin rises and thus $E_c$ decreases. When
the UV light reaches the resin, the energy is fully
absorbed by the superficial radicals while the radicals
inside the resin would not trigger polymerisation. This
contributes to a lowering of the value of $E_c$ and prevents
the polymerisation of further radicals created by the
photoinitiators in the neighbouring resin, resulting in a
marked reduction in $D_p$.

As shown in Figure 8(b), the photoinitiator 819 signi-

cantly influences the values of $D_p$ and $E_c$ of the resin.
When the concentration of 819 rises from 0.5% to
3.0%, $D_p$ decreases from 706.6 to 209.6 μm and $E_c$
decreases from 26.0 to 7.5 mJ/cm², suggesting good
curing behaviour.

According to the above reasoning, a low $E_c$ value
suggests that there is no requirement for excessive
energy in polymerisation and ensures an easier 3D
printing process. However, an excessively low value
of $D_p$ could prevent the generation of a sufficiently
thick cured layer. In contrast, a much higher value of
$D_p$ is also unsuitable since UV light penetrates the
resin and causes post-curing of the cured layers. Both
these cases would dramatically reduce the printing
accuracy of the sample. Thus, the optimal concen-
trations of TMPTA and 819 were determined to be
25.0 wt% and 2.0 wt%, respectively, for the subsequent
experiments.

3.4. Ceramisation process

The ceramisation process of the PDCs was studied using
thermal gravimetry in a nitrogen atmosphere, and the
results are shown in Figure 9, including those for the
organosilicone powder (SILRES 604), the cured resin,
TMPTA, HDDA, and a mixed solution of THF and TPM
(volume ratio of 1:1). The TGA curves suggest that the
weight-loss period of the cured resin can be divided
into three main regions, with an overall loss of 69.3 wt
% at 1000°C. From room temperature to 100°C, the
weight loss ($\approx 1$ wt%) is caused by the evaporation of
residual THF. Most of the loss occurs during the second
part (100–600°C), reaching approximately 66 wt%, due
to the further evaporation of residual TPM and the sub-
sequent release of ingredient byproducts from TMPTA
and HDDA. The third region (600–800°C) showed a
small weight loss ($\approx 2$ wt%), resulting from the removal
of hydrogen, hydroxy, methyl, and phenyl from 604.
The weight changed only very slightly ($< 0.3$ wt%)
when the pyrolysis temperature exceeded 800°C.

The changes in functional groups after photocuring
and pyrolysis at different temperatures was studied
using FT-IR spectroscopy, as shown in Figure 10. The
peak at 699.48 cm$^{-1}$ corresponds to the out-of-plane
bending vibration of C–H from phenyl, and the peaks
at 2934.01 and 3073.29 cm$^{-1}$ correspond to the stretch-
ing vibrations of C–H from methyl and phenyl, respect-
ively. All three peaks weaken as the pyrolysis
temperature increases, and almost disappear at 600°C.
The decrease in the ratio between the transverse and
longitudinal optical components of the Si–O–Si asym-
metric stretching vibrations, at 1059.32 (network struc-
ture) and 1128.28 cm$^{-1}$ (cage structure), indicates the
densification of the inorganic network structure deriving
from cured resin. The disappearance of the peaks at
1267.36 and 1727.38 cm$^{-1}$ shows the extinction of the
-OH and -O–CH$_3$ groups. The reduction and planarisation

![Figure 8. Penetration depth and critical exposure energy for the prepared PCPs as functions of the amounts of (a) TMPTA and (b) 819.](image-url)
of the peaks at 806.31 and 920.40 cm\(^{-1}\) demonstrate the transformation of the Si–CH\(_3\) group to small-molecule gases such as CH\(_4\) and CO\(_2\). When the pyrolysis temperature increases, the structural rearrangement leads to an energy increment for the vibration of every bond, resulting in a blueshift and broadening of almost all of the absorption peaks.

Figure 11 shows the Raman spectra of the cured resin and pyrolysed PDCs. The main peaks located at 1335 and 1605 cm\(^{-1}\) pertain to the D mode and G mode of free carbon, respectively. The quantity of amorphous structure is measured by \(L (I_D/I_G)\), which is the intensity ratio of the D and G modes. From the spectra of resin and SiOC ceramics pyrolysed at 1000°C, \(I_D\) and \(I_G\) decrease from 2668 and 2416 to 2036 and 1822, respectively, and \(L\) increases from 1.1043 to 1.1175, which indicates a decline in the quantity of free carbon and an increase in the quantity of amorphous structure, as expected.

As verified by X-ray photoelectron spectroscopy (XPS) in Figure 12, the element composition of PDCs was determined of 18.64 atomic percent at% Si, 23.78 at% O and 57.57 at% C, or SiO\(_{1.28}\)C\(_{3.08}\). C/O ratio plays a pivotal role in both physical form and performance, and therefore SiOC ceramics with high C/O value behaves similarly to amorphous-SiC materials, benefiting to the enhancement of mechanical properties (Ryan et al. 2010). The differences between chemical composition can be ascribed to PCPs used for manufacturing (Table 2).

The phase changes of the PCPs and SiOC ceramics after pyrolysis at 600–1000°C were studied using XRD analysis, as shown in Figure 13. With increasing pyrolysis temperature, PCP changed into amorphous SiOC ceramics, with only one broad peak observed at 16–25°. Similar results were also found by de Hazan and
It is worth noting that when the temperature reached 800°C, a very weak absorption peak appeared at 43°C corresponding to the characteristic diffraction of β-SiC, suggesting the possible crystallisation of the SiOC ceramic.

3.5. DLP 3D printing and characterisation of lattice structures

Lattice structures were designed and successfully printed, as shown in Figure 14(a–c). By controlling the amount of TMPTA diluent/monomer in the appropriate range, sufficient curing strength of the precursor resin can be guaranteed and DLP 3D printing of complex structural parts can be achieved. After post-curing in UV light of 52 mW/cm² intensity for 60 s, the resin models were pyrolysed at 600, 800, and 1000°C, respectively in an argon atmosphere. Intact lattice-structured SiOC ceramic components with a high surface quality and a fine internal structure were obtained (Figures 14(d–f)). The inner channels were well interconnected, without clogging, suggesting that structural details were maintained (Figure 14(g–i)).

The microstructures of lattice-structured SiOC ceramics are shown in Figure 15, where (a, d, g) show the octet truss structure, (b, e, h) the trunc octa structure, and (c, f, i) the rhombus dodecahedron structure at different magnifications. The skeletons of the printed SiOC ceramic components are of high density and good shape, with no obvious defects (Figure 15(h and i)). The thickness of each layer after contraction was about 60 μm. The distinctive step effect can be observed on the contoured surfaces of the samples, which resulted mainly from the software slice profile data (Figure 15(e and f)). Such effects can be prevented by means of thinning of the layer thickness or optimisation of the slicing procedure. Nevertheless, very few pores at microscale can be identified at high magnification since the escape of small-molecule gases occurs during pyrolysis, which may have only a small effect on the mechanical properties of SiOC ceramics (Figure 15(g)).

The variation in phase organisation and microstructure resulting from different pyrolysis temperatures may lead to varied linear shrinkage and mass loss at the macroscopic scale. The linear shrinkage results shown in Figure 16(a) were calculated as averaged values with standard deviations based on the linear shrinkages measured along the three directions of the samples. The very small standard deviations (i.e. error bars) shown in Figure 16(a) for all the three pyrolysis temperatures further indicate a uniform shrinkage occurred during pyrolysis along the three directions. From the observation of pictures (Figure 14) and SEM images (Figure 15), it can be further confirmed that no obvious cracks were found in the pyrolysed samples at either macro- or micro-scales.

The linear shrinkage with increasing temperature increased from 36.49% to 42.01%, while the mass loss increased from 65.92% to 70.37% (Figure 16(a)), suggesting a progressive densification of lattice-structured SiOC ceramics. However, both linear shrinkage and mass loss varied only slightly in the range 800–1000°C, proving that the phase organisation and microstructure tend to be stable in this temperature range. The density and porosity were measured according to Archimedes’ method (Figure 16(b)). As the pyrolysis temperature rose from 600 to 1000°C, the skeleton density increased from 1.06 to 1.60 g/cm³, overlapping the SiOₓCᵧ theoretical density range of 1.17–2.13 g/cm³ to a reasonable extent. As shown in Figure 13, the crystallisation of the SiOC took place at temperatures above 800°C, resulting in the growth and rearrangement of the ceramic grains. It would decrease the number of particles surrounding the pores, which finally disappeared when the number is lower than the coordination number. Thus, the porosity decreased from 7.09% to 3.64%, while the relative density increased from 92.91% to 96.36%, suggesting that high densification of the SiOC lattice-structure was achieved.
The mechanical properties of the octet truss lattice-structured SiOC ceramics, including the skeleton’s localised hardness and elastic modulus as well as the effective structural compressive strength and effective elastic modulus, were measured, and the results are given in Table 3 and shown in Figures 17 and 18, respectively. Nanoindentation tests were carried out with a maximum load of 5000 μN and a loading rate of 2.5 N/s.

**Figure 14.** (a, b, c) CAD models of the designed lattice structures; (d, e, f) front views and (g, h, i) side views of the printed polymer and pyrolysed ceramic components with different structures.

**Figure 15.** SEM images of the surfaces of lattice-structured SiOC ceramics after pyrolysis at 1000°C: (a, d, g) octet truss; (b, e, h) trunc octa; and (c, f, i) rhombus dodecahedron structures.
0.3 nm/s. As a result of the step effect and stratification, discrete and irregular data were obtained for the indentations along the hierarchical direction, i.e. the lifting direction of the building platform, while the data obtained for the direction perpendicular to the lifting direction were relatively accurate, as given in Table 3. Due to the gradual densification of SiOC ceramics as the pyrolysis temperature increased, the indentation displacement decreased from 395.3 to 247.7 nm, the hardness and elastic moduli increased, as expected, from 2.21 and 19.7 GPa to 5.82 and 46.4 GPa, respectively. With regard to the same sample, both the hardness and elastic moduli showed a decreasing trend as the displacement increased, suggesting the appearance of the strain softening phenomenon. That is, the material softens when strain appears in the specimen during the loading process, resulting in nonuniform properties between the surface and the subsurface. Therefore, the stress required for further deformation decreases and the strain growth rate accelerates with an increase in stress. As can be seen from Figure 17, the load–displacement curves in both the perpendicular (Figure 17(a)) and hierarchical directions (Figure 17(b)) are all typically smooth, suggesting a dense and uniform solid state of the pyrolysed samples.

Three typical stress–strain curves for the samples pyrolysed at different temperatures are shown in Figure 18(a). On the other hand, the effective uniaxial compressive strength increased significantly from 1.54 to 19.08 MPa, showing an order of magnitude improvement when the pyrolysis temperature rose from 600 to 1000°C (Figure 18(b)). The effective elastic modulus of the whole lattice structure, which was extrapolated by fitting the stress–strain curve, increased from 7.98 to 38.96 GPa.

The specific compressive strength to density ratios of the SiOC lattices prepared in this study were compared with those of other lattices, as well as honeycombs made from Al2O3, ZrOC, SiOC, and SiC, as shown in Figure 19 (Colombo, Hellmann, and Shelleman 2001; Agrafiotis et al. 2007; Bird and LaPointe 2013; Bauer et al. 2014; Meza, Das, and Greer 2014; Eckel et al. 2016; Zanchetta et al. 2016; Fu et al. 2018, 2019; Liu et al. 2018). The silicon oxycarbide lattice manufactured in this study showed a prominent specific compressive strength to density ratio of up to $5.74 \times 10^4$ N·m/kg, which is distinctly higher than that of other materials of similar density. Compared with the SiC honeycomb (Agrafiotis et al. 2007), the compressive strength of 19.09 MPa found in the current study is approximately two times higher at only one third of the density. The superior performance of the SiOC lattices in this study is due to their compact and flawless printed structures.

Table 3. Results for indentation displacement, localised hardness, and elastic modulus for the SiOC ceramic lattice structures after pyrolysis at different temperatures.

| Direction     | Pyrolysis temperature (°C) | Displacement (nm) | Hardness (GPa) | Elastic modulus (GPa) |
|---------------|----------------------------|-------------------|----------------|-----------------------|
| Perpendicular| 600                        | 395.3             | 2.21           | 19.7                  |
|               | 377.5                      | 2.53              | 20.8           |                       |
|               | 370.2                      | 2.56              | 22.1           |                       |
|               | 320.0                      | 3.10              | 33.7           |                       |
|               | 313.3                      | 3.17              | 34.3           |                       |
|               | 310.7                      | 3.23              | 34.7           |                       |
|               | 279.0                      | 5.28              | 39.3           |                       |
|               | 265.2                      | 5.55              | 39.7           |                       |
|               | 247.7                      | 5.82              | 46.4           |                       |
| Hierarchical  | 600                        | 355.1             | 2.83           | 23.5                  |
|               | 349.3                      | 2.89              | 24.5           |                       |
|               | 321.6                      | 2.99              | 32.5           |                       |
|               | 411.8                      | 1.54              | 27.1           |                       |
|               | 232.2                      | 7.38              | 49.1           |                       |
|               | 210.3                      | 0.05              | 1.8            |                       |
|               | 241.9                      | 6.32              | 47.4           |                       |
|               | 235.2                      | 4.99              | 67.6           |                       |
|               | 175.0                      | 10.86             | 94.8           |                       |
Lattice matrices consisting of period and regular arrays of multi rods, are a type of stretching dominated structures and their carrying capacity can be given full play when the rods are bearing compressive loads. The pyramid unit in each octa cell disperses the axial stress into the rods located in four orthogonal directions, avoiding stress concentration at the loading point and transforming failure modes from collapse of the whole structure to buckling of the rods. In this strain condition, the maximum compressive strength $\sigma_{\text{max}}$ equals to the Euler critical load $\sigma_{\text{cb}}$, which can be calculated according to the following equation (Zok et al. 2004),

$$\sigma_{\text{max}} = \sigma_{\text{cb}} = \frac{E_a \pi d \delta}{l(\sqrt{2}\cos \omega + t)} \left[ \sin^2 \omega \frac{3}{16} \left( \frac{d}{l} \right)^2 \cos^2 \omega \right]$$  \hspace{1cm} (3)

where $E_a$ represents elastic modulus of axial compression, $d$ is the diameter of the rod, $\delta$ refers to the

![Figure 18. (a) Stress-strain curves; (b) compressive strength and elastic modulus of lattice-structured SiOC ceramics pyrolysed at different temperatures.](image)

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amount of ultimate displacement before destruction, \( l \) is the length of rod, \( \omega \) is the inclining angle of rod, \( t \) is the spacing between adjacent rods (Figure 20).

Nevertheless, the strength to density ratio found in this study is not as exceptional as the SiOC matrix nanocomposites (NCs) honeycomb since the latter was transformed from elastomeric poly(dimethylsiloxane) matrix NCs (Liu et al.2018). In addition, in that study, enriched SiC nanocrystalline precipitated from SiOC after pyrolysis at 1300°C, and the resultant ceramics would have had strength enhancement with a dual amorphous-crystalline phase. As can be seen from Figure 19, the specific strength of SiOC lattices can be further promoted toward the theoretical limit by choosing precursor polymers with a higher C–O ratio and a suitable pyrolysis temperature to facilitate the formation of nanocrystalline SiC.

4. Conclusions

In summary, three types of polysiloxane were tested as silicon sources, and a ceramic precursor with high stability, superior flowability, and appropriate curing properties suitable for additive manufacturing was developed by simple mixing of high ceramic yield organosilicone powder with dispersant, diluent, monomer, and photoinitiator. Following synthesis, the silicon-based precursor was cross-linked via DLP vat photopolymerisation 3D printing, post-cured, and pyrolysed to generate dense and crack-free polymer-derived SiOC ceramics with complex lattice structures. Increasing the pyrolysis temperature contributed significantly to linear shrinkage, mass loss, density, compressive strength, and elastic modulus. The as-prepared SiOC components, after pyrolysing at 1000°C, were almost fully dense, with a theoretical density of 96.5%. In addition, SiOC lattices with a cellular density of 0.33 g/cm³ exhibited a specific strength of \( 5.74 \times 10^4 \) N m/kg, surpassing the compressive strength to density ratios of ceramics based on various other materials or structures of similar density. The successful manufacture of lightweight and high-strength lattice-structured SiOC ceramics also provides valuable inspiration toward further enhancement of their mechanical properties by optimising material formulas, regulating printing parameters, and optimising pyrolysis conditions.

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