INTRODUCTION

Silicon carbide (SiC) is often the material of choice for numerous applications at high temperatures because of its unique combination of physical, thermal, and mechanical properties. For example, SiC retains mechanical strength up to 1500°C and has low density compared to most structural metals, high elastic modulus, high thermal conductivity, and low density compared to most structural metals.
thermal expansion relative to most engineering materials, \(^4\) and high resistance to creep deformation. \(^5\) When operating in air, SiC forms a silica scale that is durable and protective. \(^6\) These properties make SiC especially attractive for engineering applications under extreme environments such as heat exchangers in industrial processes and components in power generation technologies.

While its high hardness and high strength make silicon carbide an ideal candidate for structural applications, these properties also make machining operations difficult and expensive. As a consequence, significant efforts have been dedicated to the development of methods for manufacturing silicon carbide components with complex shapes without involving machining. These include, for example, slip casting, gelcasting, and injection molding. \(^9\) These methods utilize solvent-based slurries with dispersed powders to shape parts, typically with dies and molds. However, these fabrication methods cannot be used for fabricating components with controlled internal geometrical features, such as channels.

The advent of solid free-form fabrication (SFF) and additive manufacturing (AM) has provided additional degrees of freedom for manufacturing more complex designs including those of components with controlled internal geometrical features, which would be impossible to achieve using conventional processing methods. For ceramics, including SiC, there are three leading technologies for fabricating components by additive manufacturing \(^12,13\): (a) stereolithography based on light curing, sometimes called ceramic photolithography; (b) robocasting or gel (slurry, paste) extrusion and; (c) binder jet 3D printing (BJ3DP). Stereolithography is based on selectively curing 2D layers of monomer resins loaded with powder particles. One drawback of this approach when used to manufacture silicon carbide objects is that preforms tend to have low density due to low solid loading because of the opacity of SiC powders to light. \(^14,15\) Robocasting utilizes solvent, gel, or paste slurries that are extruded through a nozzle to obtain green objects. The drawbacks of this approach include limitations for printing detailed features and low deposition rates. \(^16\) BJ3DP utilizes a dry powder bed where a solvent and polymer mix is selectively sprayed onto the powder bed in 2D layers. \(^17,18\) BJ3DP can achieve much higher throughput with very high resolution compared to other methods, but the feedstock particulate size is normally larger than other methods (>5 \(\mu m\)). One reason for using larger particulates is that the flowability is better for larger powder when in dry form. Studies of flowability as a function of particle size have shown that the cutoff for good flowability in most powders is around 20 \(\mu m\). \(^19\)

Each method of powder shaping requires postprocessing to reach full density, such as sintering combined with reactive melt infiltration (RMI), chemical vapor infiltration (CVI), or polymer impregnation and pyrolysis (PIP). Fleisher et al. demonstrated the feasibility of fabricating geometrically complex thin-walled components by a combination of BJ3DP followed by phenolic resin binder impregnation, which provided a source of carbon for forming silicon carbide during reactive silicon melt infiltration. \(^20\) They showed that three phenolic resin impregnation cycles performed on the BJ3DP SiC body provide approximately half of the amount of carbon needed for forming SiC upon liquid silicon infiltration and reduced the amount of residual silicon content to 15% or less. They also showed that more than three phenolic resin binder impregnation cycles could cause clogging of pores, resulting in residual porosity. \(^20\)

Terrani et al. \(^21\) used BJ3DP followed by chemical vapor infiltration to fabricate simple and complex objects of high-purity, fully crystalline SiC with a density of ~91%. The resulting material had ambient temperature values of thermal conductivity and average characteristic equibiaxial flexural strength of 37 W/mK and 297 MPa, respectively. In contrast to reactive melt infiltration, which yields a composite material with two distinct phases, this method yields a pure single phase and components without significant shrinkage or geometrical distortions.

Polozov et al. \(^22\) and Singh et al. \(^23\) have demonstrated the use of SiC powders and fibers for printing objects using BJ3DP, followed by PIP with polycarbosilane. They reported that density values ~2.2–2.5 g/cm\(^3\) can be achieved after multiple PIP cycles. \(^23\) To address low yield and improve densification, many different polymeric SiC precursors with different backbone structure and different functional groups have been developed to obtain high SiC and Si-O-C yield. \(^24\)–\(^26\)

In this paper, we report results from an investigation to determine the effect of number of PIP cycles using polycarbosiloxane on the microstructure and properties of SiC composites manufactured by a combination of binder jet 3D printing and PIP. Because of the interest in using these materials for manufacturing gas-to-gas heat exchangers, special emphasis was on the effect of processing conditions on gas leakage.

2 | MATERIALS AND METHODS

2.1 | Powder and printing

SiC powder (Sigma-Aldrich, ~400 mesh) was used for printing in the as-received condition, and the powder size and morphology are illustrated in Figure 1. The average particle size, or \(D_{50}\), was 15.92 \(\mu m\), and most of the particles had irregular shapes. The polycarbosiloxane preceramic polymer used in this study was MS-154 (EEMS, LLC Saratoga Springs). Liquid cross-linker CLC-PB055 (EEMS, LLC Saratoga Springs), which is a solution of a nonsolvent-based siloxane polymer, Pt, and peroxide, was used to increase cross-linking via hydrosilylation. A mixture of MS-154 and
CLC-PB055 was impregnated during the first step to facilitate curing at room temperature, thus improving mechanical strength of disks during the initial thermal cure of the MS-154. The printing binder used was an amine-based binder from ExOne.

An ExOne M-Flex printer was used to print preform samples. Powder for each layer was dispensed at 30 mm/s with an oscillator speed of 2600 rpm. The powder surface was leveled at 100-micron layer height with a counter-rotating 40-mm roller traveling at 10 mm/s across the powder bed. The powder packing density was estimated to be 40%, and a binder saturation (which is the volumetric ratio of the droplet to the pores, Saturation = $V_{droplet} / V_{pores}$) of 80% was used. Following binder deposition, a set time of 10 seconds was used before the heater passed over the surface at 10 mm/s. The heater output varied slightly with each layer to maintain a surface powder bed temperature of 60°C. Pucks of 55 mm diameter and 5 mm thickness as well as $15 \times 15 \times 5$ mm³ parallelepipeds were printed and postprocessed. Samples were cured at 200°C for 2 hours after printing.

2.2 Polycarbosiloxane preceramic polymer (MS-154) impregnation and pyrolysis (PIP)

After printing and curing, BJ3DP samples were transferred to aluminum trays or aluminum boats for MS-154 polymer impregnation and pyrolysis. The first PIP cycle is different from subsequent cycles because of the warping induced in green parts during the first impregnation due to their lack of structural integrity, so the use of catalyst helped obtain net-shaped parts with no warping and no large cracking.

The details of the first PIP cycle are as following.

1. The first impregnation was done with MS-154 polymer with 4 wt.% cross-linker until the samples were saturated with the polymer and cross-linker mix. Then, they were cured at room temperature for 12 hours to help improve the green strength of the parts. Then, a cure cycle was performed in air at 220°C for 2 hours where the samples experience negligible mass loss and became more robust because of polymer cross-linking. With improved green strength from the previous step, samples were then heated to 450°C in air for 2 hours to remove as much residual organic binder as possible.

2. A second impregnation was performed with un-cross-linked MS-154 to increase the amount of polymer infiltration followed by a second cure in air at 220°C.

3. A third impregnation was performed with un-cross-linked MS-154 followed by a third cure in air at 220°C. Then, the first pyrolysis was performed by heating at 2°C/min to 850°C and holding for 1 hour in nitrogen under a constant flow rate of 250 ccm.

During the second PIP step, samples were vacuum infiltrated with un-cross-linked MS-154 for 2 hours until saturation, and excess polymer was removed. Then, the samples were cured and pyrolyzed in one step by heating at 2°C/min to 850°C and holding for 1 hour in an environment of 250 ccm flowing nitrogen. This process was repeated for the third impregnation and pyrolysis step. A step-by-step illustration of the entire PIP process is shown in Figure 2.

2.3 Characterization and mechanical properties

Thermogravimetric analysis (TGA) was used to measure mass loss and decomposition of the polymers at different stages of the densification process. The polymers were heated in a TA Q50 (TA Instruments) at a 10°C/min ramp rate to 800°C (temperature limitation of this system) in nitrogen under flow rates of 40 and 60 mL/min for the balance and the furnace, respectively. Simultaneous thermal analysis (STA), which consists of simultaneous TGA and differential thermal analysis (DTA), was performed in a Netzsch STA 449 F3 Jupiter in a flowing argon atmosphere of 100 mL/min up to 1400°C at a rate of 3°C/min to assess high temperature stability. Fourier-transform infrared (FT-IR) spectra were recorded with a Nicolet iS50 FT-IR Spectrometer, and it measured the transmittance spectrum in the mid-IR region (4000–400 cm⁻¹) with a resolution of 4 cm⁻¹ using the FT-IR technique.

A Keyence VHX-1000 system was used to acquire light microscopy images of the entire cross section of the test specimens. Microstructures were analyzed by scanning electron
microscopy (SEM) in backscatter electron imaging mode using a Hitachi S4800. Geometric densities and Archimedes principle densities were also measured at ambient conditions. Crystallographic phase composition was determined by X-ray diffraction (XRD) using a PANalytical X’pert diffractometer with Mo K-α radiation ($\lambda = 0.709319 \text{ Å}$). The operating parameters were 40 kV and 40 mA, with a 20 step size of 0.02°. The XRD patterns were analyzed using the whole pattern fitting approach with the MDI Jade 2010 software database.

Flexural strength measurements were performed in a 4-pt. bending configuration using $50 \times 4 \times 3 \text{ mm}^3$ test specimens according to ASTM C1341 using an electro-mechanical test frame (Instru-Met, 1210AF-300-B) and a silicon carbide fixture. Young’s modulus was measured by impulse excitation according to $27,28$ using a commercially available system (Buzz-o-sonic, Glendale, WI).

Thermal expansion behavior between ambient temperature and 1000°C was investigated in air using a thermomechanical analyzer (TA Instruments Mod. Q400) at a heating/cooling rate of 3°C/min. For measurements of flexural strength, Young’s modulus and thermal expansion behavior, parallelepiped test specimens were obtained from the 55-mm diameter pucks with their longitudinal orientation orthogonal to the axis of the pucks. Thermal conductivity ($\kappa = \alpha \rho C_p$) was determined from measurements of thermal diffusivity ($\alpha$) using the laser flash method (Netzsch LFA 457) according to ASTM 14611-13 and specific heat ($C_p$) from differential scanning calorimetry (DSC) using a Netzsch Pegasus 404 system according to ASTM 1269-11.

There are two ASTM standardized test methods for determining air leak rates in flow systems that are most applicable, and the procedure used in this investigation is similar to that prescribed in ASTM standard E2930 but with vacuum [ASTM E2930—Standard Practice for Pressure Decay Leak Test Method]. The leak rate test in the current research is most closely related to ASTM D4991 Standard Test Method for Leakage Testing of Empty Rigid Containers by Vacuum Method. Air leak rate measurements were performed using a system schematically illustrated in Figure 3. The test setup consists of cavities on both sides of the test specimens and O-rings for sealing. One of the cavities is evacuated while the other is pressurized with air, and the system is held in place using a mechanical testing machine operating under load-control conditions. Once the base pressure is reached (~ –0.11 MPa), the vacuum is stopped, the system is allowed to reach equilibrium, and volumetric leak rate is calculated.

3 | RESULTS AND DISCUSSION

The structural evolution of the MS-154 preceramic polymer was investigated using the FT-IR spectra (Figure 4), including resin as received, after curing at 200°C for 2 hr, immediately after mixing after with 4% cross-linker and no heat, after curing with 4% cross-linker for 12 hours and no heat, and CLC-PB055 cross-linker as received. The bands in the FT-IR spectra were assigned to various functional groups with different highlighted colors. After mixing the cross-linker and polycarbosiloxane, the reduction in peak height of the vinyl absorptions bands (3056 and 1598 cm$^{-1}$) from the as-received resin to cross-linker-added resin indicated that the C=C double bond participated in cross-linking. The cross-linking of the preceramic polymers enables the impregnation of fragile, porous SiC 3D printed parts without washing away or slumping when impregnating large amounts of precursor. There was very little difference in FT-IR spectra between MS-154 immediately mixed with 4% cross-linker (no heat) and MS-154 mixed with 4% cross-linker with a curing time of 12 hours (no heat), indicating that curing for long periods of time is not necessary. Similar spectra of precursor and cross-linker suggest similar chemical structure of the cross-linker and polycarbosiloxane, because the cross-linker exhibits the same functional groups as the resin. The major difference was because the cross-linker had less Si-H and C-H functional groups with smaller molecular weight. The main difference between the spectra of the polycarbosiloxane resin and the cross-linker was the disappearance of the Si–H absorption (2160 cm$^{-1}$), indicating lack of Si-H in the backbone of the cross-linker. Therefore, the H atom position is taken by C=C, providing more cross-linking points for
polycarbosiloxane. What is even more important is that the additional presence of carbon from the C=C where H atoms had been positioned can contribute to more SiC formation and higher yield, but the atomic percents were left out as it is not in the scope of this work.

Figure 5 shows parts after one PIP cycle. Figure 5A shows how the shape was retained because the dimensions are nominally the same as those of the as-printed object with diameter ~55 mm and thickness ~5 mm. Also, no visible cracks were observed in the majority of samples. The print lines from the printing binder can be seen along the top surface of the puck. The fine features obtained can also be seen with the clear number “7” that had been printed onto the samples. Without cross-linker in the first impregnation, it was difficult to achieve high resin loading while retaining preform shape with no warping. Thus, the addition of the cross-linker was important for the first impregnation of MS-154. Figure 5B shows a larger, more complex gyroid part. It shows how the method can translate to larger parts. It also shows how complexity, curvature, and overhangs are highly achievable with this method.

Figure 6 shows TGA results for the MS-154 resin in the as-received and after curing conditions; MS-154 resin with 4% cross-linker directly after mixing and after 12 hours of curing; and the binder used during printing. All samples were run in nitrogen at the same heating rates.

The behavior of the MS-154 resin in the as-received condition consists of a sharp decrease (~50%) in mass up to 200°C due to the breaking of the side carbon chains, which results from the low thermal stability of less cross-linked polycarbosiloxane. A more gradual decrease in mass from 200°C to 500°C was due to the breakdown of the main carbon-silicon chain. The same resin was cured and heated in TGA again and showed a similar mass loss behavior compared to the
as-received resin. From the mass of the residual solids, a conversion yield of 49% was achieved for the oxidation cured resin and as high as 80% in resin with cross-linker.

Since a cross-linker was needed to achieve the first impregnation without deforming and warping green printed parts while also achieving high content of MS-154, the behavior of the MS-154 resin with 4% cross-linker was analyzed directly after mixing and after curing. The cross-linker made the resin more stable and rigid due to the increased cross-linking, which is reflected by the limited mass loss during heating during the TGA test, and shape retention as illustrated in Figure 5. The results also revealed that the cross-linker acts fast enough resulting in similar thermal processing for mixtures that were immediately mixed and those that were cured for 12 hours. These findings are consistent with the FT-IR results where little difference was observed in the chemical structure between an immediate mixture or a mixture that was allowed to cure for 12 hours. Heating does not cross-link the precursor as well as the cross-linker does, which is concluded from the lower ceramic yield and lower temperature degradation obtained in samples processed without a cross-linker.

The TGA of the binder was performed for comparison and for curing cycles after printing. The amount of binder used was roughly 80 vol.% of the powder printed, and most of the solvent in the binder evaporated during layer drying or curing. This means that the amount of polymer is low (1%–2%) because its concentration is only a small percentage of the binder. Thus, it is concluded that it has a very small contribution toward densification during postprocessing.

Table 1 lists values of the mass at each step in the processing, along with percent mass gain during each step, and percent mass gain from the beginning. The mass of the SiC powder was measured after printing by burning out the printing binder at 600°C. For all samples processed through the PIP cycles, the printing binder is not burned out because the preforms became too weak to handle. Multiple cures and impregnations can be performed before pyrolysis, especially the first pyrolysis step, because some residual organic material burns out, the cross-linking or solidification of the resin results in a decrease in volume; thus, more volume is available to fill in the BJ3DP part. The mass gain after curing the MS-154 with cross-linker was negligible, which demonstrates the benefits of using the cross-linker because significant mass loss occurs when curing the MS-154 without a cross-linker. This is consistent with the results from TGA. The curing step at 450°C is used to allow more MS-154 resin impregnation before the first pyrolysis. Since the density of SiC parts with additional pyrolyzed SiC with PIP leveled off after a few cycles, it is important to get as much material into the preforms before performing a full pyrolysis heating cycle. Overall, a mass gain from printed to processed through three PIP cycles was ~63 wt.%. 

![Figure 5](image-url) **Figure 5** Photographs of (A) SiC puck and (B) gyroid processed by binder jet 3D printing followed by one PIP cycle with MS-154 resin. Note the number “7” that was printed onto the top side to assess the degree of distortion during processing as well the excellent shape retention in the complex gyroid part.

![Figure 6](image-url) **Figure 6** TGA of MS-154 as-received, MS-154 after curing, MS-154 and cross-linker directly after mixing, MS-154 and cross-linker after air curing, and the ExOne printing binder.
Figure 7 shows optical and SEM images of cross sections of the parallelepiped samples. After the first PIP cycle, the porosity was evenly distributed throughout the part. Cracks were evident from the analysis of the SEM image. Also, in the first PIP cycle, the newly formed material from the conversion of MS-154 can be seen around SiC powder particles. This newly converted material is Si-O-C (silicon oxy carbide), as it will be shown later in the paper from additional microstructural characterization. In these micrographs, the SiC powder particles appear light gray, whereas Si-O-C appears with two shades of darker gray color, and cracks and pores are the darkest shade almost showing up as black. The Si-O-C around the SiC particles with lighter color was from the material that was cured with cross-linker, and the outer Si-O-C with the darker gray color was from all other treatments in the first PIP cycle. No further differentiation in

| PIP # | Mass of SiC powder | Mass change (%) | Total mass gain (%) |
|-------|--------------------|-----------------|---------------------|
| 1     | 23.81              | 39.57           | 41.05               |
|       | Initial cure (220°C in Air) | 23.81              | 0.00                | 41.05               |
|       | Residual organic binder burnout (450°C in air) | 22.57              | −5.21               | 33.71               |
|       | 2nd impregnation of MS-154 (no cross-linker) | 26.54              | 17.59               | 57.23               |
|       | 2nd Cure (220°C in air) | 25.40              | −4.30               | 50.47               |
|       | 3rd impregnation of MS-154 (no cross-linker) | 27.17              | 6.97                | 60.96               |
|       | 3rd cure (220°C in Air) | 26.40              | −2.83               | 56.40               |
|       | First pyrolysis (850°C in N₂) | 25.79              | −2.31               | 52.78               |
| 2     | Vacuum impregnation | 27.82              | 7.87                | 64.81               |
|       | Cure (220°C in Air) | 27.24              | −2.08               | 61.37               |
|       | Second pyrolysis (850°C in N₂) | 26.67              | −2.09               | 58.00               |
| 3     | Vacuum impregnation | 28.37              | 6.37                | 68.07               |
|       | Cure (220°C in Air) | 28.03              | −1.20               | 66.05               |
|       | Third pyrolysis (850°C in N₂) | 27.51              | −1.86               | 62.97               |

Note: Variability values are not listed, but standard deviations are in the 0.05–0.1 range.
microstructure based on gray scale tone can be observed with successive cures of PIP cycles, which confirms that the only difference was in Si-O-C with resin that was cross-linked. In the second PIP cycle, the density of samples increased, but some pores and microcracks remain. However, the Si-O-C appears as a single shade of gray. The results were similar after the third PIP cycle, with increases in density and remaining pores and microcracks. In this case, the Si-O-C appeared as a single shade of gray. The larger pores observed in the first PIP cycles are not eliminated with successive PIP cycles because those pores became closed pores, so no resin material can diffuse to fill them in. The pores are mostly concentrated in the center of the sample processed with three PIP cycles as a result of increased tortuosity for the flow of the liquid phase after successive infiltrations. The density of samples processed three PIP cycles was $2.33 \pm 0.08 \text{ g/cm}^3$ as shown in Figure 8, which illustrates the evolution of density and open porosity as a function of number of PIP cycles.

It is worth noting the significant increase in density after the first PIP, which changed from $1.2 \text{ g/cm}^3$ for the porous SiC preform to $2.05 \text{ g/cm}^3$ at the end of the cycle. Conversely, open porosity decreased from 62% to ~10%. The ability to significantly increase the density after the first PIP cycle is important for reducing manufacturing times and costs. It was also found that the increase in density starts to level or taper with increasing PIP cycles, and this is because the amount of open porosity decreased with each additional PIP cycle making and more tortuous path for resin infiltration.

Figure 9 shows the air volumetric leak rate as a function of the number of PIP cycles. The leak rate was found to decrease with the number of PIPs and reached a value of ~4 mbar-L/s, although this value could be relatively high for certain applications. Hermetic materials have leak rates lower than $1 \times 10^{-6} \text{ mbar-L/s}$, but for most flow applications, a pressure loss of 2% is often deemed acceptable, and in some cases, leak rates of up to 10% of the inlet flow in heat exchangers have been reported. The leak rates reported here are higher than those reported for SiC composites made by BJ3DP followed by silicon RMI.

Figure 10 shows an SEM image and EDS maps of the cross section of a parallelepiped sample processed with two PIP cycles. From the EDS maps, the particles are identified as SiC. The carbon signal was high inside the pores as a result of infiltration by epoxy used to metallographically prepare the samples. The matrix around the SiC particles is clearly a mixture of Si, C, and O. This is because the SiC-forming preceramic polymers converted to a Si-O-C compound.

Figure 11 shows the XRD and FT-IR patterns of the 3D printed sample after three PIP cycles, starting powder, and plain pyrolyzed resin without the powder. The FT-IR of as-received resin was included to compare to processed parts to identify residual organic material or possible Si, O, and C bonds of solid material. The SiC powder was single crystal $\alpha$-SiC, specifically, and the peaks for $6H$-SiC are indicated in the figure. Similarly, the XRD of the printed sample processed with MS-154 PIP has the same XRD pattern as the powder, so the XRD of plain, pyrolyzed MS-154 was included. The XRD of the plain, pyrolyzed MS-154 resin was amorphous and does not display distinct crystalline peaks, so further investigation is needed to characterize the material that formed around SiC particles from the PIP process. FT-IR spectra show that the printed sample after PIP has Si-O-Si and SiC bonds that are shifted from the same peaks found in the powder, which is most likely from the amorphous Si-O-C phase detected in XRD or some residual organics. The FT-IR also shows that the 3D printed sample has some residual organic trimethylsilyl function group, Si-CH$_3$.

Figure 12 shows 4-pt. bending testing results and a typical fracture surface. Figure 12A shows the flexural stress vs cross-head displacement curves as a function of the number of PIP cycles. Values of flexural strength after the first,
second, and third PIP cycles were 26.1 ± 3.1, 40.2 ± 3.9, and 66.8 ± 2.5 MPa, respectively. The inset in Figure 12A illustrates the orientation of deposited layers with respect to the loading direction. The cross-head displacement at failure was also very similar regardless of the number of PIP cycles. The strength values reported here are comparable to values reported by others.²²,²³ It is also clear from the analysis of the stress vs cross-head displacement curves that the stiffness of the samples increased with the number of PIP cycles, as expected considering the increase in density with the number of PIP cycles. Also, the sharp drop off in stress seen in all samples indicates that these failed in a brittle manner. Figure 12B shows an optical image of a typical fracture surface. The dimples, ridges, and craters are typical features seen in fracture from large pores and microcracks, which is consistent with the microstructure of polish surfaces in Figure 7. Young's
modulus and CTE values were measured, and the results are listed in Table 2. It was found that the stiffness values increased with the number of PIP cycles from $43.2 \pm 2.8$ GPa after one cycle to $69.5 \pm 2.8$ GPa after three PIP cycles.

Figure 13 shows an SEM micrograph and EDS elemental maps of a fracture surface of a sample processed with three PIP cycles. There are large pores and microcracks in the amorphous matrix. The fracture surface shows clear areas of the amorphous Si-O-C matrix and the SiC particles from BJ3DP. The cracks appeared to propagate through the amorphous phase and around SiC particles, producing debris from the amorphous Si-O-C. More evidence that fracture is only through the amorphous Si-O-C phase is the SiC particles seem to have the same morphology as the powder meaning they were not fractured.

Figure 14 shows TMA (thermal strain and CTE) data from a sample processed with two PIP cycles. The thermal strain data are very similar among samples and overlap for several samples processed with two PIP cycles as well as samples processed with 1 and 3 PIP cycles, and thus, only the sample processed with two PIP cycles is shown. The as-processed samples experienced nonlinear thermal strain from room temperature to 200°C, and then, they experienced an inflexion point around 200°C, and then, they experienced a steady increase in thermal strain up to 0.5% at 1000°C. To understand the nature of the thermal expansion behavior, a sample was annealed at 1400°C for 30 minutes and tested again. The thermal expansion behavior of the annealed sample was similar, suggesting that the anomalous thermal expansion behavior is intrinsic to the materials. Current work has been focused to understand the mechanisms responsible for this behavior. TGA was performed on samples in argon and air to understand stability up to 1400°C, and samples experienced mass loss in both cases recorded in Table 2. The mass loss is mostly likely from partial decomposition of the matrix while some of it crystallizes.34

![Figure 13](image13.png)

**Figure 13** SEM image and EDS mapping of a fracture surface of a sample processed with three PIP cycles

**Figure 14** Thermal strain as a function of temperature obtained with thermomechanical analyzer

| TABLE 2 Results of bend tests, impulse excitation showing the flexural strength, stiffness or modulus of elasticity tested in ambient atmosphere and temperature |
|----------------------------------------------------------------------------------|
| Flexural strength (MPa) | Elastic modulus (GPa) | TGA mass loss in air up to 1400°C (%) | TGA mass loss in Ar up to 1400°C (%) |
|-------------------------|-----------------------|---------------------------------|---------------------------------|
| 1 PIP                   | 26.1 ± 3.1            | 43.2 ± 2.8                      | 2.1 ± 0.1                       | 2.1 ± 0.1                       |
| 2 PIP                   | 40.2 ± 3.9            | 54.1 ± 2.7                      | 2.5 ± 0.2                       | 2.3 ± 0.1                       |
| 3 PIP                   | 66.8 ± 2.5            | 69.5 ± 2.8                      | 2.6 ± 0.2                       | 2.5 ± 0.2                       |

![Figure 15](image15.png)

**Figure 15** Values of thermal conductivity as a function of temperature for the sample processed with MS-154 PIP. The thermal conductivity was determined from the product of separate measurements of heat capacity, thermal diffusivity, and mass density. The increase in PIP cycles correlated with higher thermal conductivity, as a result of the increase in densification. The increase in conductivity from room temperature to about 250°C is from the large increase in heat capacity.
dominating the thermal conductivity calculation, and that is from the amorphous nature of the matrix material as seen in other studies.\textsuperscript{35,36} The decrease in thermal conductivity after 300°C is due to phonon scattering in the particle’s lattices and from pores, which is most likely dominating the transport properties up to higher temperature around 800°C. Overall, the thermal conductivity is low relative to bulk, sintered or CVD-made SiC because of the amorphous nature of the matrix material, the porosity of the composite, and the multiple interfaces with the α-SiC particles in the composite.\textsuperscript{5}

4 | CONCLUSIONS

A process for fabricating SiC components by a combination of BJ3DP and impregnation and pyrolysis of polycarbosiloxane with and without cross-linker is reported. It was found that by performing more low temperature cures and impregnations before pyrolyzing, it was possible to achieve significant increases in yield and density after the first PIP cycle, in contrast to traditional techniques. Specifically, the density achieved after three cycles (2.33 g/cm\textsuperscript{3}) was greater than that obtained using the conventional process. The microstructure shows the decrease in pores and cracks with increasing number of PIP cycles, and the concentration of pores was near the center, indicating that there is a minimum part thickness to achieve high density without closing off pores. Also, some pores become closed even after one PIP cycle. The air leak rate decreased with increasing PIP cycles and while the material was not hermetic after three PIP cycles, the air leak rate was found to be adequate for some applications. The values of flexural strength and Young’s modulus at room temperature after three PIP cycles were 66.8 ± 2.5 MPa and 69.5 ± 2.8 GPa, respectively, which are comparable to those reported by others. The newly formed phase was amorphous and consisted of Si-O-Si, SiC, and Si-O-C bonds. The thermal expansion behavior was independent of number of PIP cycles. The composites showed thermal stability with only ~2% mass loss in air and Ar atmospheres up to 1400°C. The thermal conductivity was lower compared to bulk SiC but increases with increasing PIP cycles.

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