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Mechanical Properties and Spectral Vibrational Response of Si-O-C With and Without Graphene Toughening

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MECHANICAL PROPERTIES AND SPECTRAL VIBRATIONAL RESPONSE OF Si-O-C WITH AND WITHOUT GRAPHENE TOUGHENING

by

ANTHONY VOZZA
B.S. Florida Polytechnic University, 2018

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Mechanical and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

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The mechanical behavior of silicon oxycarbide polymer derived ceramics (SiOC-PDC) without and with a graphene toughening phase was studied under uniaxial compressive load with zero dwell time and with 200 second dwell time step loading in combination with in-situ Raman spectroscopy to determine spectral vibrational response of SiOC under compressive stress. SiOC without and with graphene ceramic samples were produced through the replica templating technique. The compressive strengths of SiOC without and with a graphene toughening phase measured with zero dwell time was determined to be equal to 165.65 ± 54.21 and 163 ± 24.2 MPa, respectively, while compressive strengths of the selected ceramics measured with 200 second dwell time step loading was determined to be equal to 228.97 and 186.42 MPa, respectively. Weibull analysis of 27 pure SiOC ceramic samples and 31 SiOC-graphene ceramic composite samples tested with zero dwell time was performed to calculate their probability of failure. Weibull parameters, such as Weibull modulus and characteristic strength, were determined to be equal to \( m = 3.46 \) and \( \sigma_0 = 190.41 \) MPa for pure SiOC ceramics and \( m = 7.71 \) and \( \sigma_0 = 178.73 \) MPa for SiOC with graphene ceramic composite. In-situ Raman spectroscopy was performed during compression of SiOC without and with a graphene toughening phase dwelled for 200 seconds during step loading, which allowed the collection of Raman spectra of graphitic carbon nanodomains in SiOC at different applied compressive stresses. The properties of the D and G bands of the graphitic nanodomains in SiOC, such as peak intensity, peak area, peak position and FWHM, were analyzed as a function of applied compressive stress. Piezospectroscopic coefficients were then calculated to be equal to 10.994 and -10.269 cm\(^{-1}\)/GPa for the G band and
31.538 and 6.341 cm\(^{-1}\)/GPa for the D band of pure SiOC and SiOC with a graphene toughening phase, respectively.
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CHAPTER 1: INTRODUCTION

Silicon oxycarbide polymer derived ceramic is a promising material for a variety of industries due to its unique thermal [1, 2], mechanical [3, 4], and electrical [5, 6] properties in addition to an exceptional stability at high temperatures in harsh environments [7]. In recent years, piezoresistive effects in SiOC ceramics have been reported [8, 9], with gauge factors as high as 145 at temperatures up to 1400°C [8]. The values of SiOC electronic conductivity ranges from insulating to semiconducting [6, 10], with this variance in electrical conductivity attributed to the total degree of ordering of the segregated carbon phase within the overall SiOC matrix [11]. Despite the promising future of this material, for many ceramic composites such as SiOC there have been few studies on how stress transfer mechanisms as well as details on how piezoresistivity occurs within these ceramics. The main goal of this work is to contribute towards filling this gap in knowledge by studying the mechanical behavior of SiOC PDC without and with the addition of a graphene toughening phase under compression, and to determine the materials piezospectroscopic coefficients, providing insight into whether or not the spectral vibrational response of these ceramics is stress sensitive.

Silicon oxycarbide polymer derived ceramics without and with graphene were produced through the replica templating method in this study. SiOC without graphene was produced using a preshaped poly(vinyl alcohol) (PVA) foam template, which was infiltrated with a liquid SiOC preceramic polymer in order to produce SiOC/PVA green bodies, which were then cured and pyrolyzed. SiOC with graphene was produced through the same procedure, but the preshaped PVA foam was immersed into a graphene oxide – ethanol dispersion before the infiltration of the liquid
SiOC preceramic polymer to produce SiOC/GO/PVA green bodies. Produced SiOC PDC were machined after pyrolysis into 2mm x 2mm x 4mm samples for uniaxial compression and in-situ Raman spectroscopy testing. Uniaxial compressive tests were performed for SiOC without and with graphene utilizing zero dwell time and 200s dwell times at 12.5 MPa steps in order to analyze the time dependent mechanical behavior of the samples and provide enough time to perform in-situ Raman spectroscopy. Compressive strengths of SiOC without and with graphene were determined, and Weibull statistical analysis was performed in order to determine the probability of failure through parameters such as Weibull modulus (m) and characteristic strength ($\sigma_0$).

Raman spectra of SiOC without and with graphene were collected while selected samples were dwelled for 200s at 12.5 MPa steps until fracture occurred. Collected Raman spectra were analyzed through curve fitting procedures to determine Raman peak parameters, where the Raman spectrum of SiOC was defined by the graphitic carbon nanodomains within the overall SiOC matrix and was characterized primarily by intense D and G peaks. Peak parameters, such as peak position, peak area, peak intensity, and FWHM were analyzed as a function of applied compressive loading in order to determine if these peak parameters displayed a stress dependence in SiOC without and with graphene. In addition, piezospectroscopic coefficients were calculated for SiOC without and with graphene to characterize the stress sensitivity of the peak positions of the recorded Raman spectra.
CHAPTER 2: LITERATURE REVIEW

Many technical ceramics such as borides, nitrides, carbides and oxides have multiple applications in everyday life and in industry. Yttria-stabilized zirconia (YZP) [12] are commonly used as cutting knives, while lanthanum cobaltite (LaCoO₃) [13] has found applications as electrocatalysts in conversion reactions for chemical synthesis, doped cerium dioxide (CeO₂) [14] has found applications as a fast ionic conductor in fuel cells, lithium cobalt oxide (LiCoO₂) [15] is a major component of lithium-ion batteries, boron carbide (B₄C) [16] has found applications in protective shielding materials due to its high hardness and chemical resistance, silicon nitride (Si₃N₄) [17] is implemented in automotive engines and gas turbines due to its high strength and fracture toughness at high temperatures, while silicon carbide (SiC) [18] is used in high performance ceramic break discs and lightning arresters to protect electrical transformers. Ceramics can be processed using a variety of different approaches, such as pressureless sintering, hot pressing, injection moulding, or spark plasma sintering among many others [19-23]. One unique approach of processing ceramics is the pyrolysis of preceramic polymers to produce a polymer derived ceramic, where solid bulk ceramic samples can be simply processed from a soft or liquid polymer precursor [7]. Polymer derived ceramic (PDC) processing has many advantages, such as the ability to produce otherwise difficult to machine ceramic shapes and the ability to implement a variety of shaping and processing methods [7, 21]. Silicon oxycarbide (Si-O-C) is one unique polymer derived ceramic material with varied structure and properties, which depend on the processing route implemented [7, 24]. PDC processing also allows for the simple addition of filler materials to further enhance properties of silicon oxycarbide, with fillers such as graphene.
significantly improving material properties, such as electrical conductivity, to allow the implementation of SiOC PDC in state-of-the-art systems and engineering techniques [7, 25].

2.1 Si-O-C Polymer Derived Ceramics

Silicon-based polymer derived ceramics (PDC) have been produced through pyrolysis of precursor polymeric material for more than 60 years [7, 26]. The properties of the resulting ceramic can be developed through manipulation of the preceramic polymer chemistry, atomic networking, and pyrolysis process implemented [7, 24, 27]. Processing of SiOC PDC can be broken down into three fundamental steps, shaping, curing, and pyrolysis. There are a large variety of available processing methods, all of which will heavily influence the structure and properties of the final PDC product. For example, the replica templating method allows for the production of a bulk silicon oxycarbide ceramic with limited porosity and a homogeneous structure [7, 28].

Silicon oxycarbide ceramics have a complex microstructure, composed of silicon atoms tetrahedrally bonded with oxygen and carbon atoms. The carbon atoms of this tetrahedral structure have two possible hybridization bonds [27], sp²-hybridized carbon (free carbon), and sp³-hybridized carbon (carbidic carbon), the total degree of each heavily influencing material properties of the final ceramic product. The unique customizable microstructure of SiOC PDC leads to a variety of possible material properties, such as an electronic conductivity that ranges between semiconducting and insulating [6, 10], high piezoresistivity [8, 9], and significant variation in mechanical properties such as Young’s modulus [29], hardness [30], and bending strengths [31]. A detailed description of the processing, structure, and properties of PDC silicon oxycarbide ceramics are provided in the following paragraphs below.
2.1.1 Processing of Si-O-C

Silicon based polymer derived ceramics are a broad class of ceramics primarily produced through the pyrolysis of polymer precursors [7, 32], where pyrolysis is the process referring to the heating of a carbon-based material in the absence of oxygen. These polymer precursors are inorganic or organometallic compounds, which provide the developed ceramics with tailored chemical compositions and defined nanostructural organization through thermal treatment under a controlled atmosphere performed by curing and thermolysis processes [7]. Two common polymeric precursors utilized to produce silicon PDC are oligosilazanes and polysiloxanes [7, 10, 24, 28, 32-34]. Silicon oxycarbide ceramics are typically derived from polysiloxanes and they are carbon-rich [7, 10], where carbon-rich is defined as a material with a carbon content greater than 20 wt% [7]. The processing of polymer derived ceramics using polymer precursors can be broken down into a few fundamental steps, namely shaping, curing, and pyrolysis. In addition to these three basic steps of shaping, curing, and pyrolysis, the processing of PDC may also involve machining steps (Figure 1).

The first step of processing of polymer derived ceramics is shaping and it is described below. Preceramic precursors, which are used for processing of polymer derived ceramics, are polymeric in nature and can be either liquid or solid at the temperature at which they are shaped [7]. As a result, a number of forming methods are available, such as tape casting [35], injection molding [22, 36], or pressing (both cold and warm) [37-39]. It is possible to shape PDC components in the precursor stage before heat treatment required for their conversion into ceramic material [40], which allows the processing and shaping of complex structures such as ceramic fibers, layers, or composite materials [7]. One of the shaping methods of liquid polymeric
precursors is replica templating, where the liquid precursor is shaped by infiltration into a porous polymeric scaffold [7, 41]. Plastic forming technologies, such as resin transfer molding, warm pressing, fiber drawing, extrusion, and injection molding, can all be applied to preceramic polymers too [7], allowing the PDC process to produce near-net shape polymer ceramics [21].

The second step, curing process, is primarily designed to further cross-linking of polymer chains in the shaped polymer precursor and is typically performed by heating at lower temperatures for an extended period of time. Cross-linking is of specific importance in the processing of silicon
oxycarbide, as an increase in cross-linking will result in an increased ceramic yield during pyrolysis [42]. Curing typically takes place at temperatures in the range of 100 to 200°C [7, 21, 43, 44], but can be performed at higher temperatures for shorter times depending on the desired material properties [42, 45]. Besides simple heating, curing after shaping can also be achieved by oxidative curing, γ-radiation curing, or e-beam curing [7].

The final step of processing PDC ceramics is pyrolysis, which takes place at or below 1100°C in an inert atmosphere, resulting in the complete transformation of the silicon-based polymer precursor into silicon oxycarbide ceramic [42, 46, 47]. In the case of silicon oxycarbide, Argon gas is typically used as an inert atmosphere during pyrolysis [28, 33, 44]. The temperature at which pyrolysis is performed will vary depending on the desired properties of the ceramic produced [32, 48]. Pyrolysis temperature influences essential material properties, such as electrical and thermal conductivities as well as mechanical properties of the synthesized ceramic. Pyrolysis temperature also has a significant influence on the percentage of linear shrinkage of PDC ceramics during synthesis [28].

In the process of converting a polymer precursor to a ceramic, gasses are released during pyrolysis, causing significant linear isotropic volume shrinkage (20-30%) with porosity formed at micro and macroscopic levels [7]. As a result, both shrinkage and porosity lead to the presence of large defects within the ceramic, such as cracks or pores, which degrade the PDC properties tremendously [7]. To combat these issues, the replica templating method was developed [28, 41]. Replica templating is a simple method to produce crack-free bulk ceramics from preceramic polymers [41], which includes the infiltration of a sacrificial porous solid template with a liquid
polymeric precursor preceramic matrix material. The sacrificial template typically has a homogeneous microstructure and crack free struts [41], which helps to release gasses as to not form defects within the PDC structure. This infiltration is followed by pyrolysis, typically at temperatures above 1000°C [41]. In “soft template” replica techniques, the porous template decomposes at low temperatures, creating a porous sample. Soft template materials such as synthetic sponges and foams [28, 41, 49], or organic templates such as wood [50, 51] or rice bran [52] decompose nearly entirely at temperatures between 200°C and 500°C [28, 52]. In “hard template” replica techniques, the template does not decompose during heat treatment and requires additional processes to remove it, such as etching or milling [41]. Silica and carbon are commonly used as hard templates [53]. A schematic presentation of the replica templating technique is shown in Figure 2.

![Schematic illustration of the replica templating technique.](image)

**Figure 2**: Schematic illustration of the replica templating technique. [41]
The replica templating technique yields a bulk ceramic with limited porosity and a lack of defects, as the scaffolding allows for the release of gasses created through pyrolysis without pressure build-up, preventing cracks from forming \([7, 28]\). After completed pyrolysis, typically only a small percentage of template remains inside of PDC ceramics in the form of ash or char.

### 2.1.2 Structure of Si-O-C

The structure of any silicon oxycarbide material is heavily influenced by the structure of the preceramic polymer used in its processing. Figure 3 shows a schematic presentation of the formation of \(\text{Si}_x\text{C}_y\text{O}_z\) PDC ceramics based on the molecular structure of silicon-based polymer precursors. The structure of the preceramic polymer influences the number of phases, phase homogeneity, and microstructure of the final ceramic product \([7]\).

![Schematic presentation of SiOC development](image)

**Figure 3:** Oversimplified representation of the development of SiOC through the molecular structure of its precursor \([7]\).
Silicon oxycarbide PDC are composed of silicon atoms tetrahedrally arranged with oxygen and carbon atoms with short range order [27, 34, 54-56], where short range order refers to predictable and regular arrangement of atoms over a short distance, typically their first and second nearest neighbors, while lacking any consistent long distance arrangement. There is no significant carbon-oxygen bonding present throughout the Si-O-C structure [34, 56, 57]. The carbon atoms in this tetrahedral structure have two possible hybridization modes. The first is a sp\(^3\) hybridization for the C-Si bond found in the silicon based ceramic matrix, called carbidic carbon [27]. The second is a sp\(^2\) hybridization for the C-C bond found in the segregated phase, or the free carbon phase, referred to as graphitic carbon. These sp\(^2\) hybridizations make up the bulk of the carbon bonds, forming turbostratic carbon or graphene sheets. The free carbon section does not take part in the overall tetrahedral SiOC network, instead forming nanodomains of sp\(^2\) bonded carbon as exemplified in Figure 4 below [34]. When pyrolysis is performed at 1100°C, as shown in Figure 4, the single phase amorphous SiC\(_x\)O\(_y\) phase is formed as a result of such heat treatment.
The structure of silicon oxycarbide ceramics is also heavily influenced by the pyrolysis temperature, with samples prepared below approximately 1250°C characterized by their amorphous, glass-like structural network (Figure 4) [10, 24, 33, 58]. However, silicon oxycarbide ceramics pyrolyzed above 1250°C possess microstructure characteristic of glass-ceramics [33, 42, 59-61], where a standard glass-ceramic will have a microstructure consisting of small crystals surrounded by an amorphous “glassy phase”. In the case of silicon oxycarbide pyrolyzed above 1250°C, these glass ceramics consist of β-SiC nanoparticles and a segregated carbon phase homogeneously dispersed throughout a vitreous silica matrix [24, 42]. XRD readings from Bois et al. (Figure 5) [62] substantiate this, showing amorphous characteristics at temperatures lower than
1300°C, with peaks developing in the 1400°C sample due to the formation of β-SiC crystal nanodomains. The glassy silica matrix remains amorphous up to 1500°C [10, 63], which is a clear advantage over pure vitreous silica material, which begins to crystallize above 1200°C [60]. This increased resistance of SiOC to crystallization is likely due to the segregated carbon phase hindering crystallization by acting as a diffusion barrier [61, 63] and the presence of residual Si-C bonds within the glassy matrix hindering nucleation of crystalline phase [63].

![Figure 5: XRD patterns of SiOC pyrolyzed at various temperatures. [62]](image)

Silicon oxycarbide PDC also have a complex heterogeneous ordering at the nanoscale [55, 64], forming nanodomains at pyrolysis temperatures as low as 800°C, which persist even at annealing temperatures exceeding 1500°C [65]. High resolution transmission electron
micrographs of these nanodomains formed after SiOC pyrolysis at 1200°C is shown in Figure 6. The composition of these ordered nanodomains is varied depending on the initial preceramic polymer precursor used for processing of silicon oxycarbide [25]. The basic structural units (BSUs) of these silicon oxycarbide ordered nanodomains are typically small stacks of 2-3 layers of polyaromatic excessive carbon with approximately 1nm lateral extension homogeneously distributed throughout the amorphous glassy matrix (Figure 6, Insert) formed when pyrolyzed above 800°C [11, 66].

Figure 6: High-resolution transmission electron microscopy (TEM) image of SiCO pyrolyzed at 1200°C (with selected area diffraction insert in top right, indicating amorphous features). Basic structural unit enhanced in lower right inset [7].
2.1.3 Thermal and Electrical Properties of Si-O-C

2.1.3.1 Thermal Expansion and Thermal Conductivity of Si-O-C

Silicon oxycarbide glasses expand with a low linear coefficient of thermal expansion (CTE) of approximately $3.20 \times 10^{-6} \, ^{\circ}\text{K}^{-1}$ between 100-1000°C [2, 10, 33, 67]. While the CTE of SiOC glasses and glass ceramics are low, they are approximately one order of magnitude higher than that of pure vitreous silica ($5.7 \times 10^{-7} \, ^{\circ}\text{K}^{-1}$) [10, 42, 67]. Unfortunately, a systematic study on the impact of chemical composition and phase assemblage on the CTE of SiOC materials has not been performed [42]. Despite this, it is expected that the chemical composition will influence the CTE, as polycrystalline β-SiC displays higher CTEs, (with a mean CTE in a range between $4.3 \times 10^{-6} \, ^{\circ}\text{K}^{-1}$ [68] and $4.9 \times 10^{-6} \, ^{\circ}\text{K}^{-1}$ [69]) in comparison to vitreous silica [69] ($5.5 \times 10^{-7} \, ^{\circ}\text{K}^{-1}$ [70]) and thermal expansion is considered an additive property in glasses [71], where an additive property refers to a linear relation between a specific property and the composition of a glass material.

In amorphous material such as silicon oxycarbide, heat transfer is achieved through a heat diffusion mechanism [72]. Heat reaches the surface closest to the heat source which is then transferred to adjacent bulk atoms, slowly diffusing and causing disorderly vibration in atoms. Heat then disperses through these bulk atoms into adjacent atoms. This process is understood as the movement of phonons [72, 73]. Heat transport is reduced by any phonon scattering centers such as general defects or foreign ions within crystal lattices in a material [73]. Glasses and glass ceramics typically have lower heat transport due to their amorphous, disordered structure, in comparison with crystalline ceramics [24, 72]. Thermal conductivity of porous and near fully dense SiOC ceramics displays relatively low values for thermal conductivity (1.5 W/(m·K)), regardless of processing conditions [2, 25]. Qiu et al. [74] determined a thermal conductivity value
of roughly 0.041 W·m$^{-1}$·K to 0.078 W·m$^{-1}$·K at room temperature. Thermal conductivity values for SiOC glasses at room temperature have little reported data for comparison [5, 42, 75, 76]. As the effective size of SiC nanodomains within porous SiOC ceramics is approximately 1 nm, it was determined that they are too small to influence the thermal conductivity [66]. Instead, it has been suggested that thermal conductivity scales with density [25]. Gurlo et al. [1] further determined the temperature-dependent thermal conductivity of SiOC glass ceramic to be almost identical in behavior to vitreous silica, suggesting that the continuous glassy matrix governs thermal conductivity in SiOC glass ceramics containing at least 5 – 10 wt% of carbon.

For low porosity SiOC (7% closed) Stabler et al. [2] analyzed the effect of carbon content on thermal conductivity (Figure 7). As one can see in figure 7, when the total content of segregated carbon increased, the thermal conductivity of SiOC also increased, because segregated carbon (2.5 W·m$^{-1}$·K) has a higher thermal conductivity than the amorphous glassy matrix (1.75 W·m$^{-1}$·K [77]) [2].
Figure 7: Thermal conductivity of silicon oxycarbide glasses and glass ceramics. Standard deviation taken according to thermal diffusivity measurements. C1, C12, C16, and C17 denote the approximate volume fraction of segregated carbon. 1100 and 1600 denote the pyrolysis temperature. [2]

2.1.3.2 Electrical Conductivity and Piezoresistivity of Si-O-C

The electrical conductivity of SiOC ceramics is typically quite low and therefore SiOC is not typically implemented in applications requiring highly conductive materials [6, 10]. The values of SiOC electronic conductivity ranges from insulating ($4.3 \times 10^{-13} (\Omega cm)^{-1}$) to semiconducting ($7.1 (\Omega cm)^{-1}$) [6, 10]. Such large variance is mostly attributed to the content and the degree of ordering of the segregated carbon phase [11]. Efforts have been made to improve the electrical conductivity of silicon oxycarbide through two specific processes. First, through the conversion of sp$^3$ carbidic carbon into conductive sp$^2$ graphitic carbon. Second, through the percolation of sp$^2$
carbon phases [78-80]. During the initial polymer-ceramic conversion, carbon clusters grow and coagulate forming a percolation network, typically at temperatures between 800°C and 1400°C [11]. The percolation threshold is dependent on the total segregated carbon content in the polymer precursor and the processing method used, specifically the temperature at which the material is pyrolyzed [11]. For SiOC samples with a lower degree of segregated sp² carbon, higher pyrolysis temperatures are required to increase total electrical conductivity. Below the percolation threshold, electrical conduction takes place via the tunneling of localized electrons between excited states, known as the David-Mott model [11]. Above the percolation threshold, a percolation network of polyaromatic, turbostratic carbon provides electronic n-type conduction, as proposed by Cordelair et al. [11]. However, Kim et al. [79] proposed that SiOC exhibits p-type conduction character as determined through Hall-effect measurement.

In recent years, piezoresistive effects in SiOC ceramics have been reported [8, 9]. Piezoresistivity is defined as a change in electrical resistance of a material when a compressive or tensile stress is applied. Riedel et al. [8] prepared a SiOC ceramic using a commercial polysiloxane, poly(methylsilsesquioxane), synthesized at 1400°C, which exhibited high piezoresistivity (Figure 8). Samples with lower pyrolysis temperatures in the range of 1000° - 1300°C did not show any piezoresistive effect. To determine the piezoresistive properties of SiOC, gauge factor was measured for samples sintered at various temperatures [8], where gauge factor refers to the ratio of a change in electrical resistance to a change in length under an applied force, or strain. It was found that the observed piezoresistive behavior of SiOC was dependent on the percolated network of sp²-hybridized turbostratic carbon [8]. Gauge factor measurements of the ceramic samples pyrolyzed between 1100°-1300°C could not be determined due to high Ohmic resistances,
(100,000 kΩ), likely as a result of a lack of significant sp² carbon phase formation at this temperature and a lack of the development of a percolated network of the sp² carbon within the phases that were formed [8]. Measurement of the 1400°C sample determined a gauge factor of 145, indicating a very high sensitivity to piezoresistance.

Figure 8: Piezoresistive response of SiOC annealed at 1400°C. [8]

2.1.4 Mechanical Properties of Si-O-C Ceramics

2.1.4.1 Bending Strengths of Si-O-C

Soraru et al [31] successfully produced gel-derived monolithic silicon oxycarbide glasses at temperatures as low as 1000°C. These glass samples were created through the processing of gels
starting from triethoxysilane (HSi(OEt)$_3$, TREOS, $T^\text{H}$) and methyldiethoxysilane (HMeSi(OEt)$_2$, MDES, $D^\text{H}$). The two reagents were then mixed together in various MDES/TREOS molar ratios from 0 up to 1 in order to introduce differing carbon content between samples tested [31]. After processing and machining of SiOC PDC, the material was tested in three point bending to measure flexural strengths. Flexural strength values at 1000°C and 1200°C for each sample were quite high (Table 1), with a modulus of rupture (MOR) ranging from approximately 130 MPa up to 550 MPa [31], where the modulus of rupture represents the failure stress of the material. This large distribution of strength values is very typical of brittle materials such as ceramics, as the strength of brittle materials is sensitive to intrinsic flaws [81].

Table 1: MOR of SiOC samples tested through three point bending by Sorarù et al. [31]

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOR (MPa) 1000°C</th>
<th>MOR (MPa) 1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^\text{H}T^\text{H}0$</td>
<td>150 ± 84</td>
<td>143 ± 54</td>
</tr>
<tr>
<td>$D^\text{H}T^\text{H}0.1$</td>
<td>275 ± 101</td>
<td>129 ± 59</td>
</tr>
<tr>
<td>$D^\text{H}T^\text{H}0.3$</td>
<td>400 ± 150</td>
<td>350 ± 140</td>
</tr>
<tr>
<td>$D^\text{H}T^\text{H}0.5$</td>
<td>450 ± 260</td>
<td>520 ± 100</td>
</tr>
<tr>
<td>$D^\text{H}T^\text{H}0.75$</td>
<td>412 ± 270</td>
<td>380 ± 140</td>
</tr>
<tr>
<td>$D^\text{H}T^\text{H}1$</td>
<td>550 ± 230</td>
<td>450 ± 100</td>
</tr>
</tbody>
</table>

Figure 9 reveals a trend of increasing fracture strength as the amount of methyldiethoxysilane (HMeSi(OEt)$_2$) is increased in the precursor gel of the SiOC PDC. Bending strengths significantly increase even with a small ratio of methyldiethoxysilane (HMeSi(OEt)$_2$) content. Relating this trend to the composition of each sample reveals that the mechanical strength of oxycarbide glasses increases with an increase of substituted carbon in the silicon oxycarbide
network [31], indicated in Figure 9 as Carbon load. Average bending strength of SiOC pyrolyzed at 1200°C display the same trend, but had lower values compared to the SiOC pyrolyzed at 1000°C, with this discrepancy attributed to a higher degree of surface damage due to the double pyrolysis process performed, where double pyrolysis in this case refers to a second pyrolysis heat treatment performed at 1200°C with the aim of densifying the SiOC samples without the formation of β-SiC crystal nanodomains [31]. These results indicate significant benefit of carbon incorporation into the SiOC structure on the bending strength of silicon oxycarbide glasses [31].

![Graph showing average MOR values measured on oxcarbide glasses fired at 1000°C as a function of gel composition. Error bars are ± Standard Deviation. Carbon load as a function of gel composition is also expressed. [31]](image)

Figure 9: Average MOR values measured on oxcarbide glasses fired at 1000°C as a function of gel composition. Error bars are ± Standard Deviation. Carbon load as a function of gel composition is also expressed. [31]

### 2.1.4.2 Compressive Strengths of Si-O-C Ceramics

Uniaxial compression testing of SiOC samples fabricated utilizing the replica templating method using a liquid preceramic polymer (SILRES® H62C from Wacker Chemie AG) were
studied in [82]. Thirty samples were pre-loaded at 25N for 30 seconds, then compressed at a constant rate of 12 N/s (Approximately 3 MPa/s) until fracture occurred [82]. Scanning electron microscopy (SEM) analysis determined heterogeneous pores across all samples, a result typical of the replica templating method. The SEM micrograph of a typical SiOC PDC ceramic after machining is shown in Figure 10 [25].

![SEM micrograph](image)

Figure 10: SEM micrograph of an SiOC sample after machining created through the replica templating method. [25]

To determine possible trends, compressive stress of each sample was plotted as a function of its porosity (Figure 11) [25]. Compressive stress shows a slight increase with increasing porosity, determined to be a result of transgranular-like fracture, where fracture is not dictated by the borders of grains or pores but occurs through the dense SiOC ceramic itself [82].
Weibull analysis was then performed to determine the mechanical reliability of the tested samples, with results plotted in Figure 12 [82]. Weibull analysis makes it possible to determine failure consistency of a set of samples. The strength when failure occurs was found to be 165.65 MPa [82] (with 63.2% probability, the standard η probability for Weibull analysis). The Weibull modulus of the analysis was determined to equal $m = 3.57$ [82]. The higher the Weibull modulus, the more consistent the material sample set. For an engineered ceramic with controlled processing and small flaws, the Weibull modulus is typically $5 < m < 10$ [83].
Figure 12: Weibull analysis plot of SiOC. $\sigma_0$ represents the strength at failure (with 63.2% probability), m represents the Weibull modulus, F represents the rate of failure. [82]

2.1.4.3 Young’s Modulus of Si-O-C Ceramics

The Young’s modulus of silicon oxycarbide is dependent primarily on the atomic packing density and atomic bond energy of the material [29]. The atomic coordination, degree of crosslinking, and molecular organization (rings, layers, chains), have lesser effect [29]. Elastic moduli therefore reflect a mean volume energy density [29]. SiOC glasses exhibit higher Young’s moduli (typically between 96 and 110 GPa [3, 4, 31]) in comparison to vitreous silica (70 GPa [67]), even though the atomic packing density of SiOC glasses is lower than that of vitreous silica and the atomic bond energy of Si-C (447 kJ/mol) is lower than the atomic bond energy of Si-O.
(800 kJ/mol) [29]. This lowered bond energy leads to the conclusion that the stiffness of silicon oxycarbide glass is actually primarily a result of its 3D bonding architecture rather than the strength of its bonds [29]. Specifically, the primary cause of the increased Young’s modulus of various SiOC glass materials is the increase in the degree of crosslinking, which results in a higher mean volume energy density [29].

The Young’s modulus of SiOC glasses has a significant dependence on the temperature of the material as seen in Figure 13 and Figure 14. In addition, Figure 13 shows the significant influence of carbon on the Young’s modulus of SiOC as temperature changes. One remarkable behavior of SiOC as temperature varies is that the Young’s modulus increases as temperature increases. With no degradation of Young’s modulus, SiOC may be able to be applied in a variety of applications where high temperatures are an important consideration. This temperature dependence is very similar to that of a commercial vitreous silica (Figure 14) [67, 84]. For both silicon oxycarbide and vitreous silica, their Young’s moduli increase slightly up to 1100°C, at which point they begin to rapidly increase up to 1400°C [67]. In vitreous silica, the increase in Young’s modulus with increasing temperature is attributed to continuous atomic displacements during an amorphous-amorphous transformation [84]. Stabler et al. [84] determined that the temperature dependence of the Young’s modulus of SiOC glass-ceramics is therefore dependent on the silica glass matrix. This dependence supports the concept that both SiOC glasses and vitreous silica glass have similar atomic networking, causing the glassy silica matrix to undergo the same transformation mechanism as in vitreous silica [84].
Figure 13: Young’s modulus of SiOC samples pyrolyzed at 1600°C as a function of temperature. C1, C12, and C16 denote the approximate volume fraction of segregated carbon. [84]

Figure 14: Relative Young’s modulus as a function of temperature of a gel-derived SiOC glass sample (D^{HT}^{0.5}) [67]
Sorarù et al. also found that the increase in free carbon content of SiOC samples results in a decrease in Young’s modulus (Figure 15) [30]. This is likely due to the lower Young’s modulus of the free carbon phase (approx. 63 GPA) when compared to that of their tested SiOC glasses (approx. 117 GPa) [30]. The lower Young’s modulus value of free carbon helps to explain a lesser tendency for SiOC samples with high carbon content to crack during pyrolysis. Cracks during pyrolysis likely are caused by the development of stresses related to non-uniform shrinkage proportional to the elastic modulus [30], with lower elastic modulus values preventing high stress formation.

![Figure 15: Young’s modulus values of SiOC samples with varying degrees of free carbon content.](image)

Figure 15: Young’s modulus values of SiOC samples with varying degrees of free carbon content. [30]
2.1.4.4 Hardness of Si-O-C Ceramics

The Vickers microhardness values of SiOC glasses are typically between 6.4 and 9.3 GPa [3, 30, 31, 60]. These values are higher than that of vitreous silica with a hardness of roughly 6 GPa [3]. Hardness values determined by nanoindentation of SiOC materials are typically in the range of 10.5 – 11.4 GPa, higher than the value of vitreous silica at approximately 9.3 GPa [30, 42]. The enhanced atomic network connectivity is expected to be responsible for the increase in hardness value [42].

The chemical composition of the material is the primary factor determining the hardness of SiOC material. In samples with higher volume fractions of β-SiC, higher hardness values are found [42]. This is consistent with the higher hardness of polycrystalline β-SiC, with hardness values between 27.1 to 36.1 GPa [85]. Stabler et al. [42] concluded that the total amount of segregated carbon does not affect hardness, testing two samples with comparable amounts of β-SiC with 0 and 12 volume percent segregated carbon and receiving hardness values of 10.6 GPa and 10.5 GPa respectively. In contrast, Sorarù et al. [30] determined that the increase in free carbon content of SiOC samples results in a decrease in hardness (Figure 16). This is likely due to the fact that the hardness value of SiOC glass is approximately 10 GPa, while the hardness value of the free carbon phase is in the range of 5.5 – 6.0 GPa [30, 86].
2.2 Graphene Toughened Si-O-C

SiOC PDCs typically have a low electrical conductivity ranging between insulating ($4.3 \times 10^{-13} (\Omega \text{cm})^{-1}$) to semiconducting ($7.1 (\Omega \text{cm})^{-1}$) [6, 10]. These values are characteristic of PDC, which typically possess low electrical conductivities in the range of $10^{-13} - 10^{-1} (\Omega \text{cm})^{-1}$ [11, 87]. In order to increase the electrical conductivity of SiOC PDC composites, conductive components such as carbon fibers [88], carbon black powder [89], graphite flakes [90], and reduced graphene oxide [28] can be added to a SiOC matrix. There are many methods of introducing percolated networks of conductive filler into SiOC composites such as replica templating and aqueous phase transfer [28, 43, 91-93]. There is little information available on the thermoelectric properties and
performance of SiOC composites containing carbon nanomaterial, but there is much evidence that these ceramics will be able to be implemented in many future applications where high electrical conductivity is required [80, 94, 95]. Graphene is one of the most appropriate additives for SiOC PDC to improve electrical conductivity, which can be increased by many orders of magnitude through its inclusion, with reported electrical conductivities as high as 13 S/cm for SiOC/GO PDC [19], an extremely significant increase compared to SiOC without any graphene additive. Besides increasing electrical conductivity, the addition of graphene to the SiOC matrix leads to a decrease in thermal diffusivity [25], while mechanical properties of SiOC-graphene ceramic composites remain fairly similar to those without graphene, indicating that the addition of graphene does not lead to a significant degradation of mechanical strengths of SiOC ceramics.

2.2.1 Processing of Si-O-C with Graphene

The polymer-to-ceramic conversion process allows for filler material to easily be integrated into a PDC material, either by its inclusion in the structure of the preceramic precursor or through the introduction of filler particles during processing [7, 22, 32, 96]. Shen et al. [28] implemented the replica templating method illustrated in Figure 17, where preshaped polyvinyl alcohol (PVA) foam is immersed into a graphene oxide (GO) / ethanol dispersion. This immersion causes GO flakes to be deposited into the PVA foam walls. Liquid SiOC precursor, (in this case, SILRES 62C), is then filled into the voids of the PVA foam and cross-linked to form green bodies, where “green body” is a widely used term for raw, precursor ceramics.
Through pyrolysis of these green bodies, the PVA foam is decomposed, leading to varying shapes of Si-O-C/GO composites determined by the initial shape of the PVA foam. Pyrolysis of these samples can be undertaken in an inert atmosphere of argon, similar to the standard pyrolysis procedures of Si-O-C ceramics without filler [28, 33, 44, 96]. The linear shrinkage of the composites, as well as their electrical conductivity, is dependent on the pyrolysis temperature used when materials are produced (Figure 18) [28].
Figure 18: Linear Shrinkage and Electrical Conductivity as a function of Pyrolysis Temperature of a SiCO/GO composite. [28]

Additional benefit of an embedded graphene within Si-O-C materials is its impact on crack formation prevention inside of the SiOC bulk. In standard Si-O-C samples pyrolyzed from pure cross-linked SILRES 62C, cracks appear due to the thermal residual stresses appearing during pyrolysis. Meanwhile, SiOC/GO composites produced with SILRES 62C are fully dense and almost crack free [28]. Shen et al. [28] came to the conclusion that the graphene oxide network produced crack-free PDC composites due to two primary reasons. First, the graphene oxide network provides channels to release gas produced through the pyrolysis of SILRES 62C and the decomposition of the PVA foam. Secondly, the graphene oxide functions as a scaffold, holding together the SiOC matrix. This conclusion is further supported by the fact that the failure of SiOC/GO composites occurred at the interface of the SiOC matrix and graphitic domains [28].
In addition to the pyrolysis of green bodies, SiOC/GO ceramics can also be produced through the phase transfer of graphene oxide from an aqueous phase, where GO is dispersed in water, to an organic phase, where the diluted GO is combined with a copolymer precursor in diethyl ether, as implemented by Yu et al. [93] and shown in Figure 19.

Figure 19: Production schematic of SiOC/GO composites through phase transfer performed by Yu et al. [93]

This phase transfer method was developed in an attempt to achieve a SiOC/GO ceramic composite with more uniform graphene dispersion. The proper dispersal of graphene throughout the produced material is a challenge due to its high surface area and hydrophobic nature [93].
2.2.2 Structure of Si-O-C with Graphene

The structure of SiOC PDC developed with graphene filler material is primarily determined by the processing method used. When Shen et al. [28] implemented the replica templating method with a liquid preceramic polymer, SILRES 62C, multilayered edge-functionalized graphene oxide (EFGO) flakes, and a PVA foam, it significantly affected where graphitic domains developed within the microstructure of the material. It was determined that the addition of GO enabled the formation of a greater quantity of graphitic domains within the ceramic composite [28, 43]. These graphitic domains are formed during pyrolysis, with the total quantity of graphitic domains increasing as pyrolysis temperature increases. Graphitic domains have two mechanisms of formation, self-crystallization and GO-induced crystallization, illustrated in Figure 20 [28]. Self-crystallization occurs without the influence of any graphitic domain and is therefore spread throughout the material, while GO-induced crystallization occurs on the embedded GO particles and networks [28].
Figure 20: (a) Graphitic domain evolution unmodified SILRES 62C (self-crystallization), (b) SILRES 62C/GO composite (self and GO-induced crystallization), and (c) SILRES 62C/GO/PVA composite (self and GO-induced crystallization) during pyrolysis processes. [28]

When the replica templating method is implemented, a graphene oxide network is formed within the SiOC matrix. SEM imaging of the SiOC matrix and graphene oxide network is shown in Figure 21 [28]. GO randomly dispersed within the SiOC matrix does result in an increase in the quantity graphitic domains, but sees a much less significant variance in material properties such as electrical conductivity when compared to SiOC containing a GO network [28]. Although these SILRES 62C/GO/PVA composites have similar quantities of GO, the GO network facilitates the formation of graphitic domains upon the surface of the network, significantly enhancing electrical conductivity but reducing thermal conductivity [28].
In contrast to the replica templating method, Maheshwari et al. [19] developed SiOC ceramics with incorporated graphene nanoplatelets (GNP) through the implementation of spark plasma sintering (SPS). SPS processing can be performed very quickly, inhibiting crystallization within the matrix of the produced ceramic to some extent [97, 98]. Liquid polysiloxane precursor was combined with GNP and crosslinked at 230°C before pyrolysis in an argon atmosphere [19], producing a highly porous composite, which was then crushed, sieved, and densified. The resulting SiOC/GNP composite pellets contained a percolated network of GNP flakes with low porosity (< 0.5%) (Figure 22) [19].
Figure 22: HRSEM of spark plasma sintered SiOC ceramics. (a) shows the overall dense structure. (b) shows the presence of an interconnected network of GNP flakes, emphasized by black boxes. [19]

2.2.3 Properties of Si-O-C with Graphene Toughening

2.2.3.1 Thermal properties of Si-O-C with Graphene

Barrios et al. [25] analyzed two SiOC samples with varying amounts of graphene oxide and found that the inclusion of approximately 2 wt% of edge-functionalized graphene oxide (EFGO) resulted in a reduction in thermal diffusivity for their produced ceramic composite (Figure 23) [25]. Thermal diffusivity represents the ratio of the amount of thermal energy a material can conduct versus the amount of thermal energy a material can store, describing the rate of temperature spread throughout a material [99]. The diffusivity results shown in Figure 23 are therefore logical considering the heat capacity (C_\text{P}) of each sample, with the measured C_\text{P} value of
SiOC-7 (0.701 J/g·K) higher than that of SiOC-3 (0.068 J/g·K) [25]. SiOC-3 represents 3 mg/mL EFGO/ethanol solution used in processing, and SiOC-7 represents 7 mg/mL EFGO/ethanol solution used in processing (approx. 1.4-1.9 wt% EFGO) [25].

Figure 23: Thermal Diffusivity as a function of temperature in three SiOC/GO composites. [25]

Barrios et al. found that the thermal conductivity of SiOC/GO PDC decreased when compared to their SiOC PDC without graphene counterparts (Figure 24) [28]. SiOC-7 pyrolyzed at 1000°C had a thermal conductivity of 0.7654 ± 0.1091 Wm⁻¹K⁻¹ and 0.8676 ± 0.1289 Wm⁻¹K⁻¹ at room temperature (25°C) and 300°C, respectively [28], while the thermal conductivity of pure SiOC was measured to be 1.5 - 3 Wm⁻¹K⁻¹ [1, 74]. This decrease in thermal conductivity is likely due to an increase in phonon scattering at the SiOC matrix/GO interface [100]. Annealing at 1200°C did not significant impact the measured thermal conductivity of the SiOC-3 sample set. Both the SiOC-
3 sample pyrolyzed at 1000°C and the sample annealed at 1200°C had thermal conductivity values that were almost identical when measured at room temperature, with a room temperature value of 0.0689 Wm$^{-1}$K$^{-1}$ for SiOC-3 pyrolyzed at 1000°C and 0.071 Wm$^{-1}$K$^{-1}$ for SiOC-3 annealed at 1200°C [25]. Both SiOC-3 samples pyrolyzed at 1000°C and 1200°C also follow a similar trend to that of SiOC-7 pyrolyzed at 1000°C, with thermal conductivity gradually increasing with temperature, shown in Figure 24.

![Thermal Conductivity Graph](image)

Figure 24: Thermal conductivity of SiOC/GO composites tested by Barrios et al. [25]

2.2.3.2 Electrical properties of Si-O-C with Graphene

The inclusion of graphene filler material significantly influences the electrical conductivity of SiOC PDC. SiOC ceramic with 0 vol% GO developed by Yu et al. [93] was found to have an isotropic electrical conductivity of $4 \times 10^{-4}$ S/cm. The inclusion of GO resulted in a peak electrical conductivity of $3 \times 10^{-1}$ S/cm, an increase of three orders of magnitude compared to their pure
SiOC samples [93]. It was determined that the increase in electrical conductivity was due to the graphene networks formed during thermal reduction, causing the typically electrically insulating GO to transition into highly conductive graphene sheets [93]. The conductivity of these samples was also determined to be anisotropic, with increasing anisotropy as the total concentration of GO increases due to the alignment of the GO within the overall SiOC matrix [93]. Interestingly, the electrical conductivity was also dependent on the direction that current was applied, with electrical conductivity parallel to the pressing direction increasing only slightly with an increase in GO concentration from 0.5 to 2 vol%, (2.2 × 10^{-3} S/cm to 6.0 × 10^{-3} S/cm), while electrical conductivity perpendicular to the pressing direction increased significantly, (8.4 × 10^{-3} S/cm to 3 × 10^{-1} S/cm) [93]. This was determined to occur as a result of the anisotropic structure of the SiOC/GO sample, with parallel current flowing through the SiOC matrix, while perpendicular current primarily flows through the graphene sheets, illustrated in Figure 25 [93].

Figure 25: Illustration of parallel ($\sigma_{||}$) and perpendicular ($\sigma_{\perp}$) current flow in SiOC/GO samples developed by Yu et al. [93]

39
Maheshwari et al. [19] developed SiOC/GNP ceramic composites with an electrical conductivity of 13 S/cm. This value is extremely high for an amorphous PDC, with the electrical conductivity of a typical carbon rich SiOC sample having a value of approximately $1.0 \times 10^{-1}$ S/cm [78]. As discussed earlier, percolated GNP networks are formed within the SiOC ceramic matrix. This large value is attributed to the percolated GNP networks coupled with the low porosity of the PDC sample ($< 0.5\%$) and naturally high conductivity of GNP, (Approximately 600 S/cm), causing the GNP networks to act as charge carriers.

2.2.3.3 Mechanical properties of Si-O-C with Graphene

Uniaxial compression testing of SiOC/GO samples fabricated utilizing the replica templating method using a liquid preceramic polymer (SILRES® H62C from Wacker Chemie AG) with edge-functionalized graphene oxide were studied in [82] and denoted as SiOC-7, in reference to the 7 mg/mL EFGO/ethanol solution used in their processing. After processing of the bulk samples, they were machined to 2x2x4mm dimensions with their surfaces made flat and parallel ready for uniaxial compression testing. Thirty SiOC-graphene composite ceramic samples were pre-loaded at 25N for 30 seconds, then uniaxially compressed at a constant rate of 12 N/s (Approximately 3 MPa/s) until fracture occurred [82]. Prior to compression, selected ceramic samples were imaged using SEM with a typical micrograph of a machined surface presented in Figure 26. Microcracking was found to occur around some pores in SiOC-graphene ceramic composites, which was not the case in SiOC ceramic without graphene (Figure 10) [25]. Porous ceramics typically fail initially at weakened areas with local defects, so microcracking may result
in a greater likelihood of failure [101]. This microcracking is hypothesized to be a result of a high thermal mismatch between the added graphene and the SiOC/PVA material used during processing [82].

To determine possible trends, compressive stress of each sample was plotted as a function of its porosity (Figure 27) [25]. The porosity of the SiOC-7 samples ranged from 5 to 32%, with the addition of graphene leading to an independence of compression strength in respect to any variations in the porosity of SiOC, while for most ceramic materials porosity might lead to a decrease in the strength value, which was explained by the profound influence graphene has on the fracture mechanisms of porous SiOC PDC [82]. As discussed in Section 2.1.4.2, SiOC PDC without graphene fails through a transgranular-like mode, while the addition of graphene results
in a shift to an intergranular-like fracture, where cracks propagate through the material along the curves of pores and defects [82]. The compressive values of SiOC without graphene and SiOC with graphene are fairly similar, but the drastic shift in failure method suggests that the inclusion of graphene does impact the failure of the material in some way.

![Figure 27](image)

Figure 27: Porosity versus Compressive stress of SiOC-7 samples loaded continuously. [25]

In order to further analyze failure characteristics, Weibull analysis was performed (Figure 28). As mentioned in section 2.1.4.2, the strength value when failure is most likely to occur ($\sigma_0$) can be attained with 63.2% probability for a specific set of samples, (the standard $\eta$ probability for Weibull analysis). When graphene was added, the failure strength value of samples was found to be most likely to occur at 173 MPa, higher than that of SiOC without graphene (165 MPa) [82]. This increase is likely due to the development of the percolated graphene network within the SiOC-
7 samples, regardless of their porosity content [82]. The Weibull modulus \( m \) of SiOC-7 samples is also improved, at a value of \( m = 7.54 \) compared to SiOC without graphene \( (m = 3.57) \), and is a much more typical value for engineered ceramics.

![Weibull Analysis](image)

**Figure 28**: Weibull analysis of SiOC-7 [82]

### 2.3 Spectral Vibrational Response of Si-O-C Ceramics

The Raman spectrum of silicon oxycarbide shows features typical of a carbon-based material due to the significant presence of the graphitic carbon nanodomains in SiOC structure. A typical Raman spectrum of an Si-O-C sample is shown in Figure 29 [102]. Analysis of the Raman
spectrum of SiOC typically focuses on the graphitic carbon nanodomains, primarily through analysis of the first-order region (1000-1800 cm\(^{-1}\)), which contains two primary distinct bands (or peaks), called the D-band, or “Disordered” band, and the G-band, or “Graphitic” band [103]. The relationship between the D and G bands can reveal information about the total concentration of graphitic carbon, the total quantity of carbon defects, and the structure of the carbon phases within the SiOC ceramic matrix. The analysis of carbon-based materials through Raman spectroscopy is a complex process with numerous interpretations in its methodology that can make meaningful results difficult to identify and interpret. Despite these difficulties, there have been attempts to categorize typical properties of Raman spectra in order to develop a consistent methodology.

![Raman spectrum of Si-O-C displaying a disordered secondary carbon phase.](image)

Figure 29: Typical Raman spectrum of Si-O-C displaying a disordered secondary carbon phase. A\(_{1g}\) and E\(_{2g}\) vibration modes of sp\(^2\)-hybridized carbon are illustrated in the top right. [102]

Raman spectra are often analyzed through the deconvolution of peaks, typically performed through curve fitting, where curve fitting is one of the procedures that allows for the separation of
overlapping peaks. The number of curves applied is largely dependent on goodness of the curve fit where FWHM, position, intensity, and area of Raman bands are the four parameters identified and analyzed through curve fitting. The D and G bands of the Raman spectra of carbon-based materials are stress sensitive, with an application of stress resulting in a change in the properties of the Raman spectra, allowing the determination of stress transfer mechanisms during loading.

2.3.1 Raman Spectroscopy of Carbon-based Materials

Raman spectroscopy is a sensitive, nondestructive analysis tool for characterizing the free carbon within carbonaceous materials [24, 27, 104-109]. Raman spectroscopy is especially useful for the analysis of graphene-containing material, as graphene electrons behave as massless particles [110], therefore having zero band gap, leading the Raman spectrum to contain valuable information about electronic structure and electron-phonon interactions in addition to atomic structure [108].

Raman spectroscopy records information through the analyzation of the interaction of light with the chemical bonds that make up a material. A high intensity laser is aimed at a material, where incident light is then scattered surface molecules. The vast majority of this light is the same wavelength as the laser source, which does not provide useful information in Raman analysis, known as Rayleigh scatter. Approximately 0.0000001% of scattered light is scattered at different wavelengths due to the chemical composition of the material, known as Raman scatter [111]. Raman shift is the recorded energy difference between the incident light and the recorded scattered light. Raman data is typically presented in the form of a Raman spectrum, plotted as the recorded Raman shift (cm$^{-1}$) as a function of intensity (arbitrary units). Raman spectra of different material
can vary significantly, making it difficult to analyze Raman spectra between even two materials of the same composition with different processing methods. Despite this, a variety of different methods have been proposed for the systematic analysis of Raman spectra of carbon-based material, which are described below.

2.3.2 Curve Fitting and Mode Assignment of Carbon-Based Materials

Raman spectra data analysis relies heavily on subtle differences in the curvature and shape of spectral features, such as the intensity of recorded peaks and their wavelength position [112]. In order to preserve important information, background noise and artifacting must be eliminated, usually achieved through a process known as curve fitting, where a curve is created through the summation of smaller applied curves in order to develop a “best fit” for the overall Raman spectrum.

The appropriate methodology for curve fitting of carbon-based material is of some debate, with different carbon-based material producing varied Raman spectra that are difficult to quantify. The simplest possible fit is created using two Lorentzian fits, or two Gaussian fits [109], where each type of fit refers to a different line shape function which defines the applied curves. According to Ferrari and Robertson [109], a Breit-Wigner-Fano (BWF) line shape in combination with Lorentzian fits of the two main peaks, D and G, will provide a good fit for all carbon materials. In contrast, Sadezky et al. [113] found that a fitting using four Lorentzian fits for the G, D1, D2, and D4 bands in addition to a gaussian fit for the D3-band provides appropriate fits for first-order spectra of carbonaceous materials. In the fitting of a particularly complex Raman spectra of biomass char, Asadullah et al. [114] found it most appropriate to implement a fitting with 10
Gaussian bands. In an attempt to develop a geothermometer for application in the analysis of carbonaceous metasediment, Kouketsu et al. [115] devised various curve fitting methods for carbonaceous material, shown in Figure 30. While this study was primarily to determine the metamorphic temperatures of carbonaceous metasediment in the low to medium temperature range, their methodology and logic still provides useful information on the general shapes and protocol of curve fitting carbon-based Raman spectra. These methods are focused on the first-order region of carbonaceous materials, which was determined to be able to be broken down into seven fittings, A-G, with appropriate reasoning and methodology provided in Figure 31 [115].
Figure 30: Curve Fitting methods devised by Kouketsu et al. [115]
The curve fitting methods described by Kouketsu et al. [115] would provide the most effective fit for a variety of spectra, presented as a flowchart in Figure 31. Interestingly, in the proposed fittings G, F, and E, the center position of the D4-band is fixed at a value of 1245 cm$^{-1}$. Fixing the center of the D4-band was found to have no significant effect on other band parameters such as FWHM or intensity [115]. Another important distinction is found in possible differentiation in methods relating to the broad curve on the right side. In some cases, this broad curve is treated as a single G peak [103, 105, 106], while in others it is treated as two distinct bands, a G-band and a D2-band [113, 116, 117].

![Flowchart of peak fitting procedure created by Kouketsu et al. [115]](image)

Figure 31: Flowchart of peak fitting procedure created by Kouketsu et al. [115]
2.3.3 D and G Bands of Si-O-C Raman Spectra

As discussed in Section 2.1.2, the carbon atoms within SiOC PDC have two possible hybridization modes. The first is a sp$^3$-hybridization C-Si bond within the ceramic matrix, called carbidic carbon [27]. The second is a sp$^2$-hybridization C-C bond which forms a segregated phase of turbostratic carbon [27], also known as free carbon. As carbon atoms vibrations in SiOC PDC are Raman active, they can be easily studied using Raman spectroscopy. A typical SiOC PDC Raman spectrum is shown in Figure 29 [102].

Raman spectra of carbon-based material recorded in the near-infrared and visible light spectrums typically have two primary distinct bands (or peaks), called the D-band, or “Disordered” band, and the G-band, or “Graphitic” band [103]. The position of the D and G peaks, their intensity ratio (I_D/I_G), and the full width at half maximum (FWHM) reveal significant information about the total degree of disorder within carbonaceous ceramics, such as graphitic carbon, carbon black, graphene, carbon nanotubes, and others [103]. It is generally accepted that the G-band appears due to stretching vibrations of sp$^2$-hybridized in-plane C-C bonds [109], (E$_{2g}$-symmetry shown in Figure 29). The D-band represents the disordering of segregated free carbon, (A$_{1g}$-symmetry shown in Figure 29) [27, 109]. The D-band is located at approximately 1350 cm$^{-1}$, while the G-band is located at approximately 1580 cm$^{-1}$ in SiOC PDC [27].

It is also known that the Raman spectrum of carbonaceous material is composed of first-order and second-order regions [108, 115, 118]. The first-order region is located between 1000 – 1800 cm$^{-1}$. The second order region is located between 2500 – 3100 cm$^{-1}$. It was established that
the first-order region of SiOC Raman spectrum is composed of five discriminative bands (G, D (or D1), D2, D3, and D4) [27, 108, 115, 116]. The D bands were identified with increasing degree of disorder, where disorder in this case refers to defects such as bond length and angle disorder at the atomic scale [119]. with bands appearing at approximately 1350 cm\(^{-1}\) (D1-band), 1620 cm\(^{-1}\) (D2-band), 1510 cm\(^{-1}\) (D3-band), and 1245 cm\(^{-1}\) (D4-band) [115]. The origin of the D-bands has historically been contentious with many possible interpretations, but most recently has been attributed to double resonant Raman scattering [27, 120, 121], where double resonance is the process by which the initial incident laser creates an electron-hole excitation which creates a phonon. This phonon then proceeds to annihilate the electron-hole pair, creating another phonon [122]. The position of these Raman bands and their relative intensities changes with excitation wavelength (\(\lambda_0\)) due to the double resonance scattering process [123].

2.3.4 Stress Dependence of D and G Bands in Carbon Based Materials

It has been established that Raman bands in carbon-based materials, such as graphitic carbon, carbon nanotubes, and graphene, are stress sensitive [124-126], and therefore can be used for the determination of stress and stress transfer mechanisms which occur in these materials under external loading. The application of Raman spectroscopy for the determination of these stresses and stress transfer mechanisms is called piezospectroscopy [126-128]. Mu et al. [127] analyzed the stress transfer mechanism between the polymer and the reinforcing fibers in single-wall carbon nanotube (SWCNT) / Poly(methylmethacrylate) (PMMA) nanocomposites, processed through melt spinning into fibers with a diameter of approximately 50 μm and a gauge length of approximately 15.5 mm. These fibers were tested under tension while being monitored through Raman spectroscopy in order to determine changes in the Raman peak parameter values. In this
paper, the stress change and the parameters of the G-band in the Raman spectra were measured as a function of strain, with an emphasis on the small strain regime ($\varepsilon < 0.6\%$) and large strain regime ($\varepsilon < 21\%$). Raman measurements were recorded from the same spot on the sample while strain was applied to the nanocomposite fibers through tension until fracture [127]. In this study the G-band of the Raman spectrum was broken down into four peaks, $G_1$ (1589 cm$^{-1}$), $G_2$ (1585 cm$^{-1}$), $G_3$ (1565 cm$^{-1}$), and $G_4$ (1530 cm$^{-1}$), shown in Figure 32 below [127]. Despite that in the majority of papers these peaks are referred to as D bands, in this paper they are called G bands as SWCNT are unique among the spectra of other carbonaceous material, as it is more suitable to use the G band of the Raman spectra to study the influence of strain than the D band, hence the change in naming convention [125, 127, 129, 130]. Analysis was primarily performed on the $G_2$ peak, as this peak was the most intense and narrow and was determined to provide the most representative results [127].

![Figure 32: Raman spectra of purified SWCNT (solid blue line) and SWCNT/PMMA nanocomposite (dashed red line) with $G_{1-4}$ bands shown. [127]](image_url)
In order to determine the stress dependence of the G-band at small strains (0 – 0.6%), stress-strain, peak position-strain, and FWHM-strain plots were created (Figure 33). The G$_2$ peak shifts downwards gradually until yielding begins at approximately $\varepsilon_y = 0.2\%$, at which point the rate of decline decreases, suggesting that load transfer is less effective at this point [127]. This decline is consistent with a decrease in slope of the stress-strain plot at the same yielding point of $\varepsilon_y = 0.2\%$. The maximum average stress value ($\sigma_{\text{max}}$) corresponds to stronger interactions between the SWCNTs and PMMA polymer [127]. At $\sigma_{\text{max}}$ peak position displays a downshift of 2.5 cm$^{-1}$, indicating that only small amounts of stress are transferred to the SWCNTs. The full width at half-maximum provides insight into the stress distribution in the composite fibers. As the FWHM remains fairly constant with strain, it was concluded that the stress distribution remains constant with applied small strains [127].

Figure 33: Properties of the G$_2$ peak of the SWCNT/PMMA composite as functions of strain from 0-0.7% (a) Stress-strain curve for SWCNT/PMMA nanocomposite fibers. (b) Raman peak position of the G$_2$-band. (c) Raman peak FWHM of the G$_2$ band. [127]
Mu et al. also attempted to determine stress dependence of the G-band at high strains (0-21%) through the creation of stress-strain, peak position-strain, and FWHM-strain plots for this strain region (Figure 34) [127]. Interestingly, after reaching maximum peak downshift, the peak position of the G band begins to gradually increase with increasing strain until failure at 19% strain [127]. This is likely due to the SWCNT/PMMA interface failing and the total stress on the SWCNTs decreasing [127]. In addition, FWHM gradually increases as strain increases, which suggests that the stress applied to the SWCNTs is becoming more heterogeneous, likely a result of slippage at SWCNT/PMMA interfaces, additionally resulting in a reduction of transfer efficiency [127].

Figure 34: Properties of the G₂ peak of the SWCNT/PMMA composite as functions of strain from 0-21% (a) Stress-strain curve for SWCNT/PMMA nanocomposite fibers. (b) Raman peak position of the G₂-band. (c) Raman peak FWHM of the G₂ band. [127]
It has been clearly established that the Raman spectra of carbon-based materials are stress sensitive, with changes in applied stress resulting in a change in the properties of the Raman spectra, such as peak position, FWHM, or peak intensity. These changes in spectral properties allow for the determination of piezospectroscopy coefficients and to determine the stresses and stress transfer mechanisms during loading.

2.4 Application of Si-O-C

The piezoresistive properties of SiOC make it a promising material for high temperature piezoresistive applications [9, 24, 131]. Roth et al. [131] tested the high temperature piezoresistivity of carbon containing SiOC nanocomposites (C/SiOC) and determined a gauge factor of $80 \pm 20$ at $1200^\circ$C. This property makes SiOC a unique possibility for high temperature application ($T > 400^\circ$C), as few other piezoresistive materials operate at such high temperatures [8, 24]. With the addition of filler materials, it is likely that SiOC ceramic matrix composites will allow for the development of high-temperature-resistant, electrically conductive ceramics with integrated pressure sensor functions [8]. SiOC PDC is also promising in the field of electrochemical energy storage applications due to the disordered carbon phase and the hybrid bonding of silicon atoms with oxygen and carbon atoms [95, 132, 133]. Typically, graphitic carbon is used as an anode material, which unfortunately often suffers from shortcomings such as low specific capacity, inferior rate capability, and poor cycling ability which limits implementation in commercial products [134]. As a result, SiOC has been turned to as an acceptable substitution, particularly in the implementation of high-performance Li-ion batteries, with silicon electrodes delivering as much as 5-10 times higher discharge capacity in comparison to a standard graphite electrode [95]. In addition, SiOC PDC have been used to produce ceramic joints between reaction-
bonded silicon carbide parts [135], which are commonly implemented in metallurgy, abrasives, and refractories. This joining method is possible at relatively low temperatures (1000-1200°C) and highly tailorable composition and properties through the addition of filler material [135]
CHAPTER 3: EXPERIMENTAL

3.1 Processing of SiOC Without and With Graphene Toughening

SiOC samples were produced as described in [25] through a facile replica templating method [136-138]. Two different sets of samples were produced. The first sample set was produced through the pyrolysis of SiOC/PVA green bodies. Green bodies were produced by infiltration of a liquid SiOC preceramic polymer (SILRES® H62C from Wacker Chemie AG) into a clean preshaped PVA foam [25, 28]. These green bodies were then cured at 160°C for 16 hours. After curing, pyrolysis was performed with a 0.5°C/min heating rate, holding at 300°C and 350°C for two hours each. After these holds at 300°C and 350°C, the samples were heated with a 1.0°C/min heating rate to 600°C, where they were held for two hours dwell time, and again at 1000°C for another two-hour dwell time, after which the SiOC PDC processing was considered completed. The second set of SiOC based PDC was made through the pyrolysis of SILRES 62C/GO/PVA green bodies produced using the same method as the first set of samples, however it contained an added 2.6 vol% percolated graphene network obtained by immersing the preshaped PVA foam in a GO-ethanol dispersion before the infiltration of the liquid SiOC preceramic polymer [25, 28]. The stoichiometry of samples was determined through LECO combustion (C, O) and wet chemistry (Si) (NSL Analytical, Cleveland, Ohio). The density of produced samples was measured using the Archimedes’ technique in accordance with [139]. After pyrolysis all samples were machined to dimensions of 2 mm x 2 mm x 4 mm (Bomas Machine Specialties, Massachusetts, USA) in accordance with [140].
3.2 Uniaxial Compression

Produced SiOC based samples were tested under uniaxial compression to determine strength using an MTS universal testing machine Criterion® Model 43 (MTS Systems Corporation, Minnesota, USA) (Figure 35). The universal testing machine was equipped with a 2kN load cell (MTS Systems Corporation, Minnesota, USA) which was used to measure the load during experiments. 6mm compression platens were installed onto the universal testing machine to secure the samples during compression (Figure 37). Displacement was recorded by the crosshead movement of the MTS testing machine. In addition, an optical probe camera with a 20x objective lens (Renishaw plc, Wotton-under-Edge, UK) (Figure 35, 36, and 37) was used to record images of the SiOC based samples during compression.

Two loading profiles were implemented for the uniaxial compression testing of the SiOC samples without graphene, referred to below as profiles (1) and (2). The samples in compression were preloaded up to 1.04 MPa at a 0.05 MPa/s loading rate, after which the load, displacement and time were zeroed. The loading used in Profile (1) was applied in a load-controlled compression mode with a continuous 12 N/s loading rate until fracture. Profile (2) involved the same load-controlled compression mode as profile (1), however at each 50N (12.5 MPa) load increment a dwell of 200s was applied during which the load was kept constant. After this dwell, loading was then continued at 12N/s up to the next 50N increment, at which point another 200s dwell began during which the load was kept constant. This process was then repeated at every 50N until fracture occurred. Twenty-seven samples of SiOC without graphene were tested using profile (1), and two samples were tested using profile (2).
The loading profiles of the SiOC with graphene sample set were presented in [25] and summarized below. Two loading profiles were implemented for the compression of the SiOC samples with graphene, referred to here as Profiles (A) and (B). For each profile, a preload-force of approximately 25N (6.25 MPa) was applied. After preload the values of time and crosshead displacement were zeroed. Profile (A) involved the implementation of a load-controlled compression mode with a loading rate of 20 N/s (5 MPa/s) until fracture. Profile (B) implemented the same load-controlled compression mode with a loading rate of approximately 12 N/s until reaching 50N (12.5 MPa), at which point a 200 second dwell was implemented where load was kept constant. After this dwell period, loading was applied at a 12 N/s rate up to the next 50N increment, where another 200s dwell period began where load was kept constant. This process was repeated until fracture occurred. Thirty-one samples of SiOC with graphene were tested using profile (A), with two samples tested for profile (B).
Figure 35: Criterion® Model 43 MTS Universal Testing Machine with Raman probe. [141]
Load readings were obtained by the 2kN load cell attached to the universal testing machine. Once obtained, load values were recalculated into stress through the standard procedure of dividing the applied load by the cross-sectional area of the sample. Displacement of the sample was measured by recording the movement of the crosshead. Strain was then calculated by using Equation 1:

\[ \epsilon = \frac{\delta}{L} \]  

(1)

In this equation \( \delta = L_1 \), where \( L_1 \) is the original length of the sample minus the changed length of the sample measured under compression, where \( L \) is the original length of the sample. As the measured crosshead displacement involved not only the sample displacement but also the displacement of the spring in the load cell as well as the attached metal compression platens, such measurements are not precisely accurate and cannot compute a perfectly accurate value of strain.
3.3 In-situ Raman Spectroscopy under Applied Compressive Load

An optical probe (Renishaw, Gloucestershire, UK) with a 20x objective lens attached to a motorized XYZ-stage (Velmex Inc., Bloomfield, New York, USA) was used to collect in-situ Raman spectra of SiOC based samples under uniaxial compression. A computer modeled representation of the experimental set-up is shown in Figure 36 [141], with the actual experimental set-up used for Raman spectra collection shown in Figure 37. The motorized stage was controlled by two Vexta stepping motors (Oriental Motor, Tokyo, Japan) [141]. One Vexta motor provided control over the Y- and Z-axis motion of the probe, while the other controlled motion along the X-axis with a 0.005 mm/step resolution in the X- and Y- directions and a 0.0016 mm/step resolution in the Z-direction [141]. The motion of the probe was controlled by a designed Virtual Basic software, which could define the collection area on the sample surface and signal the collection of Raman data [141]. This optical probe was connected to a Renishaw® inVia Raman microscope system (Renishaw, Gloucestershire, UK). The Renishaw microscope system was equipped with a 532 nm Si laser with a maximum power of 300 mW and a single spectrograph fitted with holographic notch filters, connected to an optical microscope (Leica Microsystems GmbH, Wetzlar, Germany). The spectrometer was calibrated before use with a standardized silicon (100) wafer reference sample to ensure appropriate system health.

Raman spectra of SiOC were recorded between 800-2000 cm\(^{-1}\) Raman shift values in order to collect the spectral response of the graphitic carbon nanodomains in SiOC. The SiOC samples were loaded in the universal testing machine and Raman spectra were collected at each load during the 200s dwell times in loading profiles (2) and (B) described in section 3.2. For the SiOC samples without graphene tested through profile (2), the first Raman spectrum was collected during the
initial preload dwell. For the SiOC samples with graphene tested through profile (B), the first Raman spectrum was collected during the 200s dwell at the first 50N loading step. In order to collect the Raman spectra, the optical probe was focused on the 2mm x 4mm side of SiOC sample at a certain location. During loading, the sample was deformed and the location of spectrum collection on the sample surface was slightly changed at the next load with a dwell time, thus each spectral response recording of SiOC was not collected from exactly the same location as the previous collection.

After Raman spectra were collected, they were analyzed utilizing WiRE 3.4 software (©2002 Renishaw plc, build 2377) following the detailed procedure described in section 4.4 below. Before analysis, a baseline was subtracted from each recorded spectrum. Curve fitting of the collected spectrum was then implemented, with the entire procedure of baseline subtraction and curve fitting described in section 4.4 below.
Figure 36: A) Computer modeled representation of experimental set up. B) Closer view of sample data collection in experimental computer model. [141]

Figure 37: Photograph of Raman probe during data acquisition.
CHAPTER 4: RESULTS AND DISCUSSIONS

The goal of the research presented in this thesis is to analyze the spectral response of SiOC and SiOC with a graphene phase to applied uniaxial compressive stress using \textit{in-situ} Raman spectroscopy. The properties of the processed SiOC, such as stoichiometry, density, porosity, and ceramic yield, are presented in Table 2 [82]. A comparison of uniaxial compressive strength of SiOC without and with graphene was made and their probability of failure was analyzed by Weibull statistics. Raman spectra of SiOC without and with graphene were collected \textit{in-situ} at various stress levels during uniaxial compression. Curve fitting procedure of the collected SiOC Raman spectra were developed in order to extract parameters of the peaks, such as peak intensity, peak position, FWHM, and peak area. These peak parameters were further analyzed to determine their dependence on the applied compressive stress during SiOC uniaxial loading. The comparison of spectral vibrational response of SiOC without and with a graphene phase was then made to determine if the addition of a graphene phase contributes to the strengthening of SiOC. Analysis of these Raman spectra presented in this work in an attempt to understand the strengthening that the addition of a graphene phase would bring to SiOC PDC. Therefore, the results and discussion chapter will include the following subsections: (1) Loading Profiles of Si-O-C in Uniaxial Compression (2) Si-O-C Compressive Strengths, (3) Weibull Analysis of Si-O-C Strength Results, and (4) \textit{In-situ} Raman Spectroscopy of Si-O-C.
Table 2: Properties of SiOC composite samples produced by Barrios et al. [82]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stoichiometry Composition</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Ceramic Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOC</td>
<td>SiC₃.₀₆O₁.₂₇</td>
<td>1.42 ± 0.11</td>
<td>14.₄ ± 7.₀₆</td>
<td>42.₅ ± 1.₉₉</td>
</tr>
<tr>
<td>SiOC/GO</td>
<td>SiC₃.₀₈O₁.₃₁</td>
<td>1.₃₉ ± 0.₁₀</td>
<td>1₉.₃ ± 6.₆₂</td>
<td>61.₁ ± 2.₈₈</td>
</tr>
</tbody>
</table>

4.1 Loading Profiles of Si-O-C in Uniaxial Compression

SiOC without and with graphene samples were tested through uniaxial compressive loading with four different loading profiles, ((1), (2), (A), and (B)), to determine the time dependent mechanical behavior of the samples. Loading profiles (1) and (2) were implemented for SiOC without graphene. Loading profiles (A) and (B) were implemented for SiOC with graphene. The stress vs time and strain vs time of selected samples tested implementing these four loading profiles are presented in Figure 38.

Figure 38: A) Loading profiles of stress v time and strain v time with 0s and 200s dwell time used during uniaxial compression of SiOC without graphene. B) Loading profiles of stress v time and strain v time with 0s and 200s dwell time used during uniaxial compression of SiOC with graphene presented in [25].
When loading profiles with zero second dwell time ((1) and (A)), were implemented the compressive testing lasted between 30.35 and 102.35 seconds. When loading profiles with 200 second dwell times ((2) and (B)) were implemented, the total test time was extended considerably, with compressive testing lasting between 1841.85 and 3712.45 seconds. The maximum load applied to the selected SiOC without graphene sample with zero dwell presented in Figure 38A was 952.12 N, while the maximum load applied to the selected SiOC with graphene sample with zero dwell presented in Figure 38B was 771.35 N, with calculated stress values of 186.42 MPa and 228.04 MPa respectively. The maximum load applied to the selected sample of SiOC without graphene presented in Figure 38A was 476.27 N, while the maximum load applied to the selected sample of SiOC with graphene tested with 200s dwell times presented in Figure 38B was 501.31 N, with calculated stress values of 125 MPa and 115.38 MPa, respectively.

It is known that SiOC PDC behave in a linear elastic manner, where stress is directly proportional to strain, according to Hooke’s law[30, 67, 142]. The total magnitude of deformation increases proportionally to the applied loading values, where such a stress-strain relationship should represent Hooke’s law \((\sigma = E\varepsilon)\), which states that force and displacement scale proportionally in linear elastic materials. Although loading was applied in a load-controlled mode, the proportional increase in strain with increasing values of stress indicate that there is no phase lag between the stress input and strain response observed. The samples tested through loading profiles (2) and (B) with 200s dwell times do show some minor deviances in stress and strain proportionality in the form of small “pop-in” events, where the deformation values change while loading is constant, especially noticeable as the material approaches fracture. This is possibly due
to microcracking developing around the pores of the material or due to more significant cracking occurring before fracture.

4.2 Si-O-C Compressive Strength

Stress-strain curves for the previously selected SiOC without graphene and SiOC with graphene samples loaded with zero seconds dwell time and 200 seconds dwell time are presented in Figure 39. These plots are obtained from combining the stress v time and strain v time graphs shown in Figure 38. As SiOC PDC is linear elastic [30, 67, 142], the stress-strain deformation plots are linear, however at small loads there is a deviation from this linearity.

Figure 39: A) Stress-strain curves for tested SiOC without graphene presented in [25]. B) Stress-strain curves for tested SiOC with graphene presented in [25].
Young’s modulus was calculated from the slope of the linear portion of the stress-strain curve, with values of 13.98 GPa and 8.26 GPa for the selected SiOC without graphene zero dwell and 200 second dwell samples respectively. The slope of the selected SiOC with graphene samples stress-strain curve gave Young’s modulus values of 12.89 GPa and 11.60 GPa for zero seconds dwell and 200 second dwell respectively. These values are significantly lower than typically reported Young’s modulus values of dense SiOC PDC, which are usually measured to be between 96 and 110 GPa [3, 4, 31, 107]. Such significant discrepancies between the reported values and our calculated values are due to inaccurate displacement measurements as a result of using displacement data measured from the position of the crosshead of the universal testing instead of sample displacement in our test, resulting in stress-strain deformation plot slopes that are not representative of the actual values of SiOC PDC which produced significantly lower values of Young’s modulus. As we are dealing with very small measurements (< 4mm), the addition of the column mounts on the machine, the spring within the load cell, and the compression platens that hold the sample all will contribute to the measured displacement during loading and do not allow for accurate measurement of displacement values.

The stress-strain deformation curve of the 200 second dwell SiOC sample without graphene (Figure 39A) shows numerous instances of discontinuous yielding in the form of “pop-in” events, likely a result of spontaneous microcrack growth occurring without the full failure of the material. These “pop-in” events likely are one of the primary causes of the reduced overall compressive strength of the SiOC samples tested with 200 second dwell time. The stress-strain deformation curve of the SiOC with graphene sample (Figure 39B) utilizing loading profile (B)
with 200s dwell times also displays an abnormal “staircasing” pattern as a result of a software problem, which was eliminated in all other loading profile data.

When SiOC without graphene was loaded through profile (1), average compressive strength ($\sigma_c$) was determined to be 165.65 ± 54.21 MPa, with values for each individual sample tested presented in Appendix B. SiOC with graphene samples provided similar results, with a $\sigma_c = 163 \pm 24.2$ MPa determined for samples loaded through profile (A), with values for each individual sample tested presented in Appendix B. As only two samples were tested for profiles (2) and (B), no meaningful average compressive strength values could be determined. The strength of SiOC without graphene loaded through profile (1) with zero dwell time were plotted as a function of their density (Figure 40). Density measurements for SiOC with graphene have not been performed. Density values were provided by Elizabeth Barrios [25], measured through the Archimedes’ technique in accordance with [139]. It was determined that an increase in sample density typically resulted in an increase in compressive strength, indicating that samples with high compressive strength have a lower porosity, resulting in the ceramic matrix carrying more of the applied load and, thereby, increasing strength of the material.
4.3 Weibull Analysis of Si-O-C Strength Results

Weibull analysis was implemented to determine the probability of failure of SiOC, with two Weibull parameters such as characteristic strength ($\sigma_0$) and the Weibull modulus ($m$) were determined. The characteristic strength ($\sigma_0$) represents the strength of the material at which the probability of failure is 63.2%, and the Weibull modulus represents the variability of material failure, with higher Weibull modulus representing more consistent strength values of the material. $R^2$, the goodness of fit of the trendline of the strength values, was also calculated, representing the degree of variation between recorded and expected strength values, with numbers closer to 1 indicating less variation. Weibull analysis results for SiOC without and with graphene loaded with zero dwell time are shown in Figure 41. The strength values used for Weibull analysis of SiOC without and with graphene loaded with zero dwell time are presented in Appendix B.
Figure 41: A) Weibull analysis of SiOC without graphene tested in zero second dwell loading profile (1). B) Weibull analysis of SiOC with graphene tested in zero second dwell loading profile (B). Weibull analysis results were originally presented in [25], however, dwell time tested samples have been removed in this work leading to different results.

Weibull analysis of the SiOC without graphene sample set shown in Figure 41A determined a characteristic strength of 190.41 MPa for the data set. A Weibull modulus of $m = 3.46$ was determined, a low result for an engineered ceramic, which are typically in the range of $5 < m < 10$ [83]. This low Weibull modulus coupled with a calculated $R^2 = 0.9122$ indicates that the strength values follow an appropriate model and that this material is not very reliable. Weibull analysis of SiOC with graphene, shown in Figure 42B, determined a characteristic strength of 178.79 MPa for the data set. The characteristic life value of this sample set was 11.62 MPa lower than that SiOC samples tested without graphene, a decrease of approximately 6.29%. A Weibull modulus of $m = 7.22$ was determined, a value considerably higher than that of SiOC without graphene and more in line with a typical engineered ceramic. In addition, an $R^2$ of 0.9821 was calculated, a noticeably higher value, which coupled with an increased Weibull modulus indicates
that the addition of graphene will result in a more consistent method of failure than samples without the addition of graphene.

4.4 In-situ Raman Spectroscopy of Si-O-C

Raman spectra of SiOC without and with graphene at 12.5 MPa stress levels are presented in Figure 42. While many factors contribute to the overall shape of a material’s Raman spectrum, it is understood that the ratio of intensities of the D and G bands (I_D/I_G) in carbonaceous materials is influenced by the total presence of carbonaceous nanodomains [27, 103, 109, 117]. As this I_D/I_G ratio increases, the size and quantity of graphene nanodomains are decreased, with the D band growing more intense in the Raman spectrum, indicating a greater degree of disorder [103]. The inverse is also true, with the G band growing more intense in the Raman spectrum as the total quantity of graphene nanodomains is increased. This ratio change is visible in Figure 42, as the ratio of I_D/I_G decreases with the addition of graphite into SiOC samples, indicating an increase in the total graphitic nanodomain content.

![Raman spectra of SiOC without and with graphene at 12.5 MPa stress levels.](image)

Figure 42: A) Raman spectra of SiOC without graphene at 12.5 MPa. B) Raman spectra of SiOC with graphene at 12.5 MPa.
The recorded Raman spectra of SiOC without and with graphene were analyzed through the deconvolution of peaks using curve fitting. As discussed in section 2.3, due to the significant presence of the graphitic carbon nanodomains in the overall SiOC structure, the Raman spectrum of SiOC shows features typical of a carbon-based material, for which there are a variety of curve fitting procedures available [108, 109, 112, 115]. For example, Ferrari and Robertson [109] state that fitting only the two primary peaks, (D and G), will give a good fit for all carbon material at a broad laser energy range, while Sadezky et al. [113] found that fitting using five peaks, (G, D1, D2, D3, D4), provides appropriate fits for first-order (1000-1800 cm\(^{-1}\)) spectra of carbonaceous materials. In order to determine which method would provide the best results, curve fitting of SiOC without and with graphene was implemented utilizing 2, 3, 4, and 5 curves, with the methodology of each of these curve fitting processes presented below. The spectra of SiOC without and with graphene were curve fitted through each method, (2, 3, 4, and 5 curves), where spectra were in-\textit{situ} recorded at varying stress levels during loading. After determining the best curve fitting procedure, the peak intensity, peak area, peak position, and FWHM were plotted as a function of stress to determine if there is any significant change in spectral properties during deformation.

\textit{4.4.1 Curve Fitting of Si-O-C Raman Spectra}

Curve fitting of the Raman spectra of SiOC without and with graphene began with baseline subtraction, where a baseline was subtracted from each recorded Raman spectra in order to eliminate background noise or fluorescence present. This baseline removal process is illustrated in Figure 43. Renishaw’s WiRE 3.4 software initializes a straight baseline between the ends of the spectrum, which is then adjusted manually to ensure the baseline applies an appropriate offset to the intensities of the spectrum while also minimizing changes to the spectrum’s peak intensity
ratios. In order to ensure consistent methodology between spectra collected at each stress level, only linear polynomial fit baseline subtraction was applied in each case of the curve fitting.

After baseline subtraction, curve fitting of each spectrum was performed with mixed Gaussian-Lorentzian curves. Curve fitting was performed in the WiRE 3.4 software by manually placing the desired number of curves at the approximate location of known Raman bands, such as the D1 (~1350 cm$^{-1}$), D2 (~1620 cm$^{-1}$), D3 (~1510 cm$^{-1}$), D4 (1245 cm$^{-1}$), and G (~1580 cm$^{-1}$) bands [27, 108, 115, 116]. Curves height and width can then be modified to fit more appropriately with the recorded Raman spectra. Once an approximate fit has been manually achieved, the WiRE software runs a curve fitting algorithm, which performs many iterations until the best fit is reached. Curve fit parameters along with the summation of the applied curves are then reported by the software for analysis as seen in Figure 44, 45, 46, and 48. Goodness of fit for applied curves was determined through their reduced chi-squared ($\chi^2$) value. Reduced chi-squared values are
calculated automatically through the WiRE 3.4 software. A $\chi^2$ of 1 indicates an ideal fit with true parameter values, a $\chi^2$ significantly greater than 1 indicates a poor fit for a set of data, a $\chi^2$ slightly greater than 1 indicates that the fitting has not captured all of the data, or that the data has been underfit, and a $\chi^2$ less than 1 indicates that the data has been overfit [143]. The details of curve fitting procedures of the D and G bands of SiOC without and with graphene using 2, 3, 4, and 5 curves are described below.

4.4.1.1 Curve Fitting of Si-O-C Raman Spectra Using Two Peaks

An example of a typical SiOC Raman spectrum curve fitted with two curves is shown in Figure 44. Through the two-curve method, the Raman spectra is broken down into two discriminative bands: D (~1330 cm$^{-1}$) and G (~1580 cm$^{-1}$). A two curve fit is the simplest fitting implemented for Raman spectra of carbonaceous materials, as they show two prominent peaks (D and G) [109]. The applied curve fit presented using this method below is not ideal, with significant variance in the experimental data and the summation of the curves applied, especially visible at the portion of the spectrum between the two curves.
Figure 44: Example curve fitting of an SiOC Raman spectrum using 2 curves. The solid line (in blue) represents the best fit to the experimental data (in red) through the sum of the two applied curve components (G and D).

For the curve fitting procedure with two peaks, an average $\chi^2$ of 5.86 and 2.87 were determined for SiOC without and with graphene respectively. These high values indicate a poor fit for the spectrum. In an attempt to account for this, curve fitting was performed a second time, with a second baseline applied in conjunction with the applied curves. This second baseline is generated by the WiRE 3.4 software and implemented automatically using the first and last points of the Raman spectrum. Through this method, an average $\chi^2$ of 5.07 and 2.59 were determined for SiOC without and with graphene respectively. While there is some improvement, these values are still high, indicating that this fitting method is not optimal for the Raman spectra collected.
4.4.1.2 Curve Fitting of Si-O-C Raman Spectra Using Three Peaks

An example of a typical SiOC Raman spectrum curve fitted with three curves is shown in Figure 45. Through the three-curve fitting procedure, the Raman spectrum is broken down into three discriminative bands: D1 (~1330 cm⁻¹), D2 (~1600 cm⁻¹), and a third D3 band, approximately located at ~1540 cm⁻¹. It was reported that the D3 band is located at 1510 cm⁻¹ in [115, 144], however in the case of the recorded SiOC without and with graphene spectra, the best fit was produced when the band was located at 1540 cm⁻¹. Despite this discrepancy, the addition of this D3 band to the curve fitting process does result in a noticeably improved summation-fit when compared to the two-curve procedure described in section 4.4.1.1.

Figure 45: Example curve fitting of an SiOC Raman spectrum using 3 curves. The solid line (in blue) represents the best fit to the experimental data (in red) through the sum of the three applied curve components (D1, D2, Misc.).
For the curve fitting procedure with three peaks, an average $\chi^2$ of 1.93 and 1.31 were determined for SiOC without and with graphene respectively. As these values are higher than 1, indicating that the data has been under-fit, a second round of curve fitting applying a second baseline to the data was implemented. This resulted in an average $\chi^2$ of 0.96 and 0.80 for SiOC without and with graphene respectively, a significant improvement compared to the implementation of only one baseline. The application of a second baseline causes these curve fits to over-fit the data.

4.4.1.3 Curve Fitting of Si-O-C Raman Spectra Using Four Peaks

An example of a typical SiOC Raman spectrum curve fitted with four curves is shown in Figure 46. Through the four-curve fitting procedure, the Raman spectrum is broken down into four discriminative bands: D1 (~1350 cm$^{-1}$), G (~1600 cm$^{-1}$), D3 (1510 cm$^{-1}$), and D4 (1245 cm$^{-1}$). This procedure was similar to the one outlined by Kouketsu et al. [115] and illustrated in Figure 30(g). Through this procedure, the D3 curve position is fixed at 1510 cm$^{-1}$ and the D4 curve position is fixed at 1245 cm$^{-1}$. In this curve fitting procedure the broad band located at approximately 1600 cm$^{-1}$ is treated as a single peak, referred to here as the “G band”, although this terminology is not used in [115] and is instead substituted with “D2 band”. It was proposed by Kouketsu et al. in [115] that the lattice vibration mode which attributes to the D2-band is attributed to the same vibration mode as the G-band (E$_{2g}$ mode), further justifying this naming convention.
Figure 46: Example curve fitting of an SiOC Raman spectrum using 4 curves. The solid line (in blue) represents the best fit to the experimental data (in red) through the sum of the four applied curve components (D1, G, D3, D4).

For the curve fitting procedure with four peaks, an average $\chi^2$ of 1.12 and 0.93 were determined for SiOC without and with graphene respectively, both acceptable values for a good fit. As the $\chi^2$ of SiOC was greater than 1, indicating that the data was slightly under-fit, curve fitting was performed again with the addition of a second baseline in conjunction with the applied curve. Through this method, an average $\chi^2$ of 0.98 and 0.80 were determined for SiOC without and with graphene, respectively. The addition of a second baseline resulted in significant improvement of the $\chi^2$ of SiOC without graphene equal to 0.98, a difference between 1 and $\chi^2$ of only 0.02, indicating a very good fit for this method. Despite this improvement for SiOC without graphene, the $\chi^2$ of SiOC with graphene through this method was overfit significantly with a value equal to 0.804, a predictable result when considering the $\chi^2$ with only one baseline was less than 1, indicating a small degree of overfitting.
The curve fitting of the Raman spectrum of SiOC with graphene collected at the highest (125 MPa) compressive stress just before sample failure did not provide good curve fitting results utilizing the four curve fit one baseline procedure, with a $\chi^2$ of 1.72. This significant underfitting in the spectrum collected at 125 MPa was due to an increased background recorded between 800 cm$^{-1}$ and 880 cm$^{-1}$ Raman shift values (Figure 47), which could not be removed through the one baseline procedure, which resulted in a higher $\chi^2$ value. However, when the four curve fit two baseline procedure was performed, this increased background was resolved and the $\chi^2$ value improved to 0.98. Therefore, for the Raman spectrum of SiOC with graphene collected at 125 MPa, the two baseline procedure was used in both the one and two baseline analysis methods.

Figure 47: SiOC with graphene Raman spectra at the Lowest 12.5 MPa and Highest 125 MPa stress levels. A red box was added around the 800 – 880 cm$^{-1}$ region of increased background of for emphasis.
The curve fitting procedures implementing one baseline for curve fitting of SiOC with graphene tested at all other stress levels (12.5 MPa to 112.5 MPa) did not experience any form of increased background in this 800 cm$^{-1}$ to 880 cm$^{-1}$ range and the one baseline procedure produced results with $\chi^2$ values close to 1. When implementing the four curve fit two baseline procedure for the spectrum recorded at 125 MPa compressive stress, a new average $\chi^2$ of 0.86 (Table 3) was determined for the four curve method implementing one baseline.

4.4.1.4 Curve Fitting of Si-O-C Raman Spectra Using Five Peaks

An example of a typical SiOC Raman spectrum curve fitted with five curves is shown in Figure 48. Through the five-peak fitting procedure, the Raman spectrum is broken down into five discriminative bands: D1 (~1350 cm$^{-1}$), D2 (~1620 cm$^{-1}$), D3 (~1510 cm$^{-1}$), D4 (1245 cm$^{-1}$), and G (~1580 cm$^{-1}$), where the peak around 1600 cm$^{-1}$ has been decomposed into G and D2-bands. Through this method, the D4 peak position is fixed at 1245 cm$^{-1}$. This method was outlined by Kouketsu et al. [115] and illustrated in Figure 30(e). In order to determine if the fixing of the D4 peak position provides appropriate results, curve fitting was performed with and without fixing this band for comparison.
For the curve fitting procedure with five peaks, an average $\chi^2$ of 0.90 and 0.84 were determined for SiOC without and with graphene, respectively, when the D4 peak position was fixed at 1245 cm$^{-1}$ during curve fitting. For comparison, an average $\chi^2$ of 0.87 and 0.84 were determined for SiOC without and with graphene, respectively, when the D4 peak position was left free for optimization during curve fitting. The decreased $\chi^2$ values when the D4 peak is left free indicated that fixing the D4 peak is an appropriate procedure for the curve fitting of these Raman spectra, as reported in [115]. For consistency with previous procedures, curve fitting was also implemented with a second baseline applied. This procedure resulted in an average $\chi^2$ of 0.71 and
0.71 for SiOC without graphene with the D4 peak locked and unlocked, respectively. An average $\chi^2$ of 0.69 and 0.70 were found for SiOC with graphene with the D4 peak locked and unlocked, respectively. These lessened $\chi^2$ values indicate that the application of a second baseline resulted in significant overfitting, an expected result as the $\chi^2$ value before the application of a second baseline was less than 1. The $\chi^2$ values obtained by the curve fitting of the Raman spectra of SiOC without and with graphene using 2, 3, 4, and 5 curve procedures are presented in Table 3. Average $\chi^2$ value for each procedure was calculated by performing the specified curve fitting procedure on the Raman spectra of both SiOC without and with graphene and taking the average of all $\chi^2$ values obtained through curve fitting at each compressive stress level.

Table 3: Average $\chi^2$ value of the two, three, four, and five curve fitting methods for SiOC without and with graphene implementing one and two baselines.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>2 Curves</th>
<th>3 Curves</th>
<th>4 Curves</th>
<th>5 Curves</th>
<th>5 Curves (D4 locked)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOC With Graphene (1 Baseline)</td>
<td>2.87±0.51</td>
<td>1.31±0.37</td>
<td>0.86±0.07</td>
<td>0.84±0.28</td>
<td>0.84±0.28</td>
</tr>
<tr>
<td>SiOC Without Graphene (1 Baseline)</td>
<td>5.86±1.85</td>
<td>1.93±0.41</td>
<td>1.12±0.19</td>
<td>0.87±0.12</td>
<td>0.90±0.13</td>
</tr>
<tr>
<td>SiOC With Graphene (2 Baselines)</td>
<td>2.59±0.32</td>
<td>0.80±0.09</td>
<td>0.80±0.07</td>
<td>0.70±0.06</td>
<td>0.69±0.06</td>
</tr>
<tr>
<td>SiOC Without Graphene (2 Baselines)</td>
<td>5.07±1.56</td>
<td>0.96±0.10</td>
<td>0.98±0.13</td>
<td>0.71±0.04</td>
<td>0.71±0.04</td>
</tr>
</tbody>
</table>

As one can see from table 3, the average $\chi^2$ value was closest to one when the four curve fitting procedure was applied, with a $\chi^2$ value of 0.985 with two baselines and a $\chi^2$ value 0.860 with one baseline respectively, compared to the most appropriate two curve (5.077 without graphene, 2.591 with graphene), three curve (0.967 without graphene, 0.809 with graphene), and five curve (0.907 without graphene, 0.846 with graphene) methods. This indicates that the curve fitting procedure where four peaks are curve fit was the most appropriate and provided the best fit
for the collected Raman spectra for SiOC both without and with graphene. The curve fitting results of the four curve fitting procedure applied to in-situ recorded SiOC without and with graphene Raman spectra at varying stress levels are presented below with all other curve fitting data presented in Appendix A.

4.4.2 Raman Spectra Peaks of Si-O-C as a Function of Applied Compressive Stress

In-situ Raman spectra of SiOC ceramics without and with graphene additive collected during uniaxial compression at different stress levels are presented in Figure 49. SiOC without graphene Raman spectra are presented for every other stress level for consistency, with all stacked Raman spectra presented in Appendix A. From these stacked graphs, it appeared that there is a decrease in the intensity and broadening of the Raman peaks as compressive stress is applied to the SiOC ceramic without graphene, especially noticeable when comparing the lowest 4.1 MPa and highest 217.3 MPa stress levels, but even at 120.7 MPa this broadening and decrease in peak intensity is already significant (Figure 49). However, the spectra of SiOC ceramic with graphene does not show such visible pronounced intensity decrease and peak broadening as compared to SiOC ceramic without graphene. In order to attain more detailed information about the Raman peak parameters, such as the total change in peak intensity, peak area, peak position, and FWHM as a function of increasing compressive stress, curve fitting was performed through the methods described in section 4.4.1.3. Curve fitting will allow the determination of small peak shifts that are not clearly visible in the stacked Raman spectra as they represent rather small changes. The peak position shift is an important spectroscopic parameter as it allows the determination of the piezospectroscopic coefficient of the material when plotted as a function of compressive stress. In
addition, the ratio of the intensity of the D and G bands, or $I_D/I_G$ ratio, (here named $I_{D1}/I_G$), can be calculated to determine if there are changes in the disorder of the carbonaceous domains within the SiOC matrix.

Figure 49: A) Offset Raman spectra of SiOC without graphene. B) Offset Raman spectra of SiOC with graphene. The dashed lines in both plots are placed vertically from the position of the D and G bands in the Raman spectrum at the lowest stress level.

The peak intensity, peak area, peak position, and FWHM for D1, G, D3, and D4 Raman bands of SiOC ceramics without and with graphene were obtained through the curve fitting
procedures discussed in section 4.4.1.3 in order to see how they change as a function of applied compressive stress and to determine if the addition of a graphene phase results in any strengthening during loading of SiOC PDC. Intensity ratio $I_{D1}/I_{G}$ was calculated using the peak intensities of the D1 and G bands in order to determine any change in the total degree of disorder of the carbon domains within the SiOC matrix as compressive stress was applied. The plots of peak intensity vs applied compressive stress, peak area vs applied compressive stress, peak position vs applied compressive stress, and FWHM vs applied compressive stress, as calculated using the four curve fitting procedure of SiOC without graphene, are presented in Figure 50, 52, 53, and 54. Similar plots of four curve fitting parameters as a function of applied compressive stress for SiOC with graphene phase are presented in Figures 55, 57, 58, and 59. The plots of peak intensity vs applied compressive stress, peak position vs applied compressive stress, and FWHM vs applied compressive stress for SiOC with and without graphene produced for the two, three, and five curve fitting procedures described in section 4.4.1 are presented in Appendix A.

The peak intensity of the D1, G, D3, and D4 bands of SiOC without graphene plotted as a function of applied compressive stress is presented in Figure 50. As one can see from Figure 49, at low applied stress values there is a small increase in intensity for all four bands, however between the initial 4.1 MPa and final 217.3 MPa applied compressive stress there is a significant reduction in intensity for all four bands of the Raman spectra, with the D1 band decreasing 53.59%, the G band decreasing 51.66%, the D3 band decreasing 43.03%, and the D4 band decreasing 36.12%.
Figure 50: Peak intensity of the D1, G, D3, and D4 bands of SiOC without graphene vs applied compressive stress.

$I_{D1}/I_G$ was calculated by dividing the intensity of the D1 band by the intensity of the G band [103, 108, 109, 123, 145], with $I_{D1}/I_G$ of SiOC without graphene plotted as a function of applied compressive stress presented in Figure 51. While there is a significant reduction in intensity of the D1 and G bands, there is only a minor reduction in $I_{D1}/I_G$ ratio, from 1.134 at the lowest stress level 4.1 MPa to 1.129 at the highest stress level 217.3 MPa. The $I_{D1}/I_G$ ratio remains fairly consistent between each applied compressive stress level, with a standard deviation of 0.017, with this consistent intensity ratio indicating that there is no significant change in the total degree of disorder as compressive stress is increased [108, 145].
Figure 51: Intensity ratio of the D1 and G bands of SiOC without graphene as a function of applied compressive stress.

The peak area of the D1, G, D3, and D4 bands of SiOC without graphene plotted as a function of applied compressive stress (Figure 52) appear very similar to the previously described peak intensity as a function of applied compressive stress plots (Figure 50), repeating the same general trends. This is an expected result as peak intensity and peak area are widely known to be closely related, with some publications using the two parameters interchangeably for analysis, such as using peak area in the calculation of $I_D/I_G$ [106, 109, 123]. Each of the four bands display a small increase in peak area at low stress levels before decreasing as further stress is applied. As compressive stress further increases, there is a decreasing trend in peak area values for all four bands. Between the initial 4.1 MPa and final 217.3 MPa applied compressive stress there is a significant reduction in area values, with the D1 band decreasing 55.13%, the G band decreasing 47.54%, the D3 band decreasing 40.17%, and the D4 band decreasing 33.89%.
Figure 52: Peak area of the D1, G, D3, and D4 bands of SiOC without graphene vs applied compressive stress

Peak position shift of Raman bands is one of the important parameters, which allows the use of piezospectroscopy [146], where piezospectroscopy refers to the analysis of stress sensitive Raman peak shift occurring during applied compressive or tensile loading to determine information about stress transfer within the material [147]. The peak shift of Raman active bands is connected to the applied or residual stress by Equation 2 [146-149]:

\[ \Delta \nu = \Pi_{ij} \sigma_{ij} \quad (2) \]

Where \( \Delta \nu \) represents the Raman peak shift, \( \sigma_{ij} \) represents the applied stress, and \( \Pi_{ij} \) is the piezospectroscopic coefficient. The piezospectroscopic coefficient measures the stress sensitivity of a tested material by relating the peak position shift of its Raman bands with stresses applied. The piezospectroscopic coefficient is typically calculated through the slope of the peak shift vs applied compressive stress plot and provides insight into how efficiently the material will transfer stress [149-151].
In order to determine the piezospectroscopic coefficients, the peak positions of the D1, G, D3, and D4 bands of SiOC without graphene plotted as a function of applied compressive stress (Figure 53). The peak positions of the D3 and D4 bands are fixed, therefore they do not show dependence on the applied stress in Figure 53. Both the D1 and G bands show a clear trend of increasing peak position as increased compressive stress is applied, where shift towards higher wavenumbers is known as a “blue shift” and a shift to lower wavenumbers is known as a “red shift” [152]. Blue shift is typical for the D and G bands of carbonaceous materials when compressive stress is applied, as the atoms within the carbon nanodomains within the SiOC matrix move closer together resulting in higher wavenumber values [153-155].

![Graph showing peak positions of D1, G, D3, and D4 bands vs stress](image)

Figure 53: Peak position of the D1, G, D3, and D4 bands of SiOC without graphene vs applied compressive stress.

The piezospectroscopic coefficients of the D1 and G bands found in SiOC without graphene were determined to be 31.538 cm\(^{-1}\)/GPa and 10.994 cm\(^{-1}\)/GPa respectively. Detailed piezospectroscopy experiments on SiOC PDC have not been published to the best of my knowledge, however, comparison with carbon-based materials can be performed, with a variety of materials piezospectroscopic coefficients listed in Table 4. Reports of the piezospectroscopic
coefficient of carbon-based materials typically focus on the Raman peak located around the 1580 – 1600 cm\(^{-1}\) wavenumber, which characterizes an E\(_{2g}\) vibration mode.

Table 4: Piezospectroscopic Coefficients of the peak located at Raman shift 1580 – 1600 cm\(^{-1}\) of a variety of carbonaceous material

<table>
<thead>
<tr>
<th>Material</th>
<th>Piezospectroscopic Coefficient (cm(^{-1}) / GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOC without graphene</td>
<td>10.9</td>
</tr>
<tr>
<td>SiOC with graphene</td>
<td>-10.2</td>
</tr>
<tr>
<td>Graphite [156]</td>
<td>4.7</td>
</tr>
<tr>
<td>Graphite Oxide [157]</td>
<td>3.8</td>
</tr>
<tr>
<td>Highly Oriented Pyrolytic Graphite [158]</td>
<td>4.1</td>
</tr>
<tr>
<td>Graphene [159]</td>
<td>7.47</td>
</tr>
<tr>
<td>Exfoliated Graphene [160]</td>
<td>7.4</td>
</tr>
<tr>
<td>Monolayer Graphene [161]</td>
<td>9 – 10.5</td>
</tr>
<tr>
<td>Unsupported Monolayer Graphene [162]</td>
<td>5.4</td>
</tr>
<tr>
<td>Single Wall Carbon Nanotubes [163]</td>
<td>10.1 ± 1.2</td>
</tr>
<tr>
<td>Tetrahedral Amorphous Carbon [164]</td>
<td>4.1 ± 0.5</td>
</tr>
</tbody>
</table>

The piezospectroscopic coefficient of the G band of SiOC without graphene was calculated to be 10.994 cm\(^{-1}\)/GPa, a relatively high value when compared to other carbon-based materials [156-164]. As seen in Table 4, there is considerable variance between the piezospectroscopic coefficients of carbon-based materials, with the most comparable piezospectroscopic coefficient to the reported SiOC without graphene being that of monolayer graphene, with values in the range of 9-10.5 cm\(^{-1}\)/GPa [161]. The piezospectroscopic coefficients of the D1 band of SiOC without and with graphene were calculated as 31.538 cm\(^{-1}\)/GPa and 6.341 cm\(^{-1}\)/GPa, respectively, but no published data were identified to make a meaningful comparison.
The FWHM of the D1, G, D3, and D4 bands of SiOC without graphene plotted as a function of applied compressive stress is presented in Figure 54. Each of the four bands display an increasing trend in FWHM as compressive stress is applied, with the G band showing the clearest increasing trend with increasing stress. This increasing FWHM for each of the four bands is indicative of the broadening of all peaks, which can be attributed to an increase in strain and disorder within the material as a result of the applied compressive stress [108, 119, 165]. In addition, an increase in the FWHM of all Raman bands indicates that the strain throughout the material is becoming more heterogeneous as applied stress is increased [127].

![Graph of FWHM vs Stress](image)

Figure 54: Full width at half max of the D1, G, D3, and D4 bands of SiOC without graphene vs applied compressive stress.

The peak intensity of the D1, G, D3, and D4 bands of SiOC with graphene plotted as a function of applied compressive stress are presented in Figure 55. Each of the four bands experiences a decrease in intensity at low stress levels, with the D1 and D3 bands then increasing in intensity roughly to their original value as compressive stress is increased, with a difference between the lowest 12.5 MPa stress and highest 125 MPa stress peak intensities of just 0.6 % and 1.9% for the D1 and D3 bands respectively. The G and D4 bands of SiOC with graphene do not
fully recover from this reduction in intensity, with a decrease between the lowest and highest stress peak intensities of 11.2% and 14.2% for the G and D4 bands respectively.

![Graph showing peak intensity changes](image)

**Figure 55:** Peak intensity of the D1, G, D3, and D4 bands of SiOC with graphene vs applied compressive stress.

The ratio of the intensity of the D1 and G bands of SiOC with graphene plotted as a function of applied compressive stress is presented in Figure 56. As applied compressive stress increases there is a clear increase in $I_{D1}/I_{G}$ ratio, with a standard deviation of 0.062, almost four times that of SiOC without graphene, with the increase in $I_{D1}/I_{G}$ ratio reflected in the lowered intensity values of the G band as compared to the D1 band previously presented in Figure 55. At the lowest 12.5 MPa stress level, $I_{D1}/I_{G}$ has a value of 1.12, with this value increasing to 1.25 at the highest 125 MPa stress level, an increase of 11.6%. This increase in $I_{D1}/I_{G}$ indicates an increase in the total disorder of the material as compressive stress is applied [166], indicating that the addition of graphene to the SiOC ceramic matrix resulted in the material becoming more susceptible to an increased number of structural defects under applied compressive loading [108, 167].
Figure 56: Intensity ratio of the D1 and G bands of SiOC with graphene vs applied compressive stress.

The peak area of the D1, G, D3, and D4 bands of SiOC with graphene plotted as a function of applied compressive stress (Figure 57) appear similar to the previously described peak intensity as a function of applied compressive stress plots (Figure 55), repeating the same general trends, similar to the peak intensity and peak area of the D1, G, D3, and D4 bands of SiOC without graphene as a function of stress described above (Figure 50 and 52). Each of the four bands shows an initial decrease in peak area values, with the D1 and D3 bands then increasing to a peak area roughly equivalent to their initial recorded values, with a difference between the lowest 12.5 MPa stress and highest 125 MPa stress peak areas of 6.3% and 2.0% for the D1 and D3 bands respectively. As was the case in the peak intensity of the G and D4 bands of SiOC with graphene, the G and D4 peak area does not recover from this initial reduction in area, with a decrease between the lowest and highest stress peak areas of 18.6% and 15.6% for the G and D4 bands respectively.
The peak positions of the D1, G, D3, and D4 bands of SiOC with graphene plotted as a function of applied compressive stress are presented in Figure 58. The peak positions of the D3 and D4 bands were fixed, so they do not show any dependence on the applied stress in Figure 58. As applied compressive stress increased during SiOC-graphene composite loading, the D1 band experienced a slight shift towards higher wavenumbers, from an initial value of 1338.22 cm$^{-1}$ to a final value of 1339.15 cm$^{-1}$, while the G band experienced a slight shift towards lower wavenumbers, from an initial value of 1595.54 cm$^{-1}$ to a final value of 1594.85 cm$^{-1}$. The piezospectroscopic coefficients of the D1 and G bands of SiOC with graphene were determined to be 6.341 cm$^{-1}$/GPa and -10.269 cm$^{-1}$/GPa for D1 and G, respectively. The piezospectroscopic coefficient of the D1 band of SiOC with graphene is significantly lower than that of SiOC without graphene, which had a piezospectroscopic coefficient of 31.548 cm$^{-1}$/GPa. The reason for the change to a negative value in the G band of SiOC with graphene is unknown and more research is required to clarify the nature of such difference.
Figure 58: Peak position of the D1, G, D3, and D4 bands of SiOC with graphene vs applied compressive stress.

The FWHM of SiOC with graphene Raman spectra plotted as a function of stress is presented in Figure 57. As stress increases the FWHM of each band have little variation, with a difference in peak area at the lowest 12.5 MPa and the highest 125 MPa compressive stress of 3.3% for the D1 band, 2.6% for the G band, 3.3% for the D3 band, and 1.1% for the D4 band. In addition, the standard deviation in FWHM for each band was below 5%. Such consistent FWHM as compressive load is increased for each of the four bands is indicative of a consistent strain distribution throughout the material [127].

Figure 59: Full width at half max of the D1, G, D3, and D4 bands of SiOC with graphene vs applied compressive stress.
CHAPTER 5: CONCLUSIONS

Silicon oxycarbide polymer derived ceramics without and with graphene were produced through the replica templating method. SiOC without graphene was produced through the pyrolysis of SiOC/PVA green bodies, where these green bodies were produced by infiltrating a liquid SiOC preceramic polymer into a clean preshaped PVA foam. SiOC with graphene was produced through the pyrolysis of SiOC/GO/PVA green bodies, where graphene was added through the immersion of the preshaped PVA foam into a GO-ethanol dispersion before the infiltration of the liquid SiOC preceramic polymer. Produced SiOC PDC were machined into 2mm x 2mm x 4mm samples for uniaxial compression and in-situ Raman spectroscopy tests.

Compressive strength was determined for SiOC without and with graphene samples tested with zero dwell time until fracture occurred. In addition, two SiOC samples were tested with a 200s dwell time during compressive loading applied at every 12.5 MPa loading step to determine the time dependent behavior of the samples and to provide the necessary time to collect Raman spectra. Compressive strength of SiOC without and with graphene, when tested with zero dwell time, were calculated to be $165.65 \pm 54.21$ MPa and $163 \pm 24.2$ MPa, respectively. The compressive strength of selected SiOC without and with graphene samples tested with 200s dwell times was measured to be 228.97 MPa and 186.42 MPa, respectively. Weibull statistical analysis was performed on the obtained compressive data of SiOC samples tested with zero dwell time in order to determine the probability of failure of SiOC without and with graphene, with a Weibull modulus for SiOC without and with graphene of 3.46 and 7.71 respectively, and their characteristic strengths calculated to be $190.41$ MPa and $178.73$ MPa respectively.
Raman spectra were collected \textit{in-situ} for some SiOC without and with graphene samples during the 200s dwell times implemented at every 12.5 MPa step. The collected stress dependent Raman spectra were analyzed through standard curve fitting procedures to determine the spectral parameters of the graphitic carbon nanodomains present within SiOC. Peak parameters of the four applied bands, (D1, G, D3, D4), such as peak intensity, peak area, peak position, and FWHM, were then analyzed as a function of stress in order to determine their parameters. The Raman spectra of SiOC without graphene exhibited a consistent decrease in peak intensity and peak area, while peak position shifted to higher wavenumbers and FWHM increased slightly as the applied stress increased. Such material’s behavior is fairly consistent with the effect compressive stresses have on the spectral vibrational response, where a decrease in the peak intensity, broadening of the peaks, and a shift of the peak position to a higher wavenumber is indicative of the presence of imposed compressive strain in SiOC ceramics during compressive loading. In addition, the ratio of intensity of the D1 and G bands, (I\textsubscript{D1}/I\textsubscript{G}), remained fairly constant, indicating that there is no significant increase in the degree of disorder within the material’s graphitic carbon nanodomains when increasing compressive load was applied. The piezospectroscopic coefficients of the D1 and G band of SiOC without graphene were determined to be equal to 31.538 cm\textsuperscript{-1}/GPa and 10.994 cm\textsuperscript{-1}/GPa, respectively.

Unlike the spectral behavior of Raman bands of SiOC without graphene, the Raman spectra of SiOC with graphene showed very little, if any, stress dependence of peak intensity and peak area for all four fitted bands (D1, G, D3, D4). The peak position of the D1 band experiences a slight increase in wavenumber and a slight increase in peak area, while the peak position of the G band experiences a slight decrease in wavenumber and slight decrease in peak area. The peak
position of the D3 and D4 bands is fixed, and therefore shows no dependence on applied stress. The peak area of the D3 band shows a slight increase, while the D4 band peak area shows a slight decrease. The FWHM of each band increased slightly as applied compressive stress was increased. The $I_{D1}/I_G$ ratio of SiOC with graphene gradually increased, indicating that the addition of graphene to SiOC PDC results in an increase in the degree of disorder within the material’s carbon nanodomains as applied compressive loading increases. The piezospectroscopic coefficients of the D1 and G bands of SiOC with graphene were determined to be equal to 6.341 cm$^{-1}$/GPa and -10.269 cm$^{-1}$/GPa, respectively.
APPENDIX A: RAMAN SPECTROSCOPY DATA
Figure 60: Stacked Raman graphs for SiOC without graphene toughening
Table 5: SiOC Without Graphene $\chi^2$ Values Implementing One Baseline

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Average: 5.865789 1.932474 1.128368421 0.8714211 0.907315789
± from 1: 4.865789 0.932474 0.128368421 -0.128579 -0.092684211
Table 6: SiOC Without Graphene Two Baseline $\chi^2$ Values Implementing Two Baselines

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Average: 5.077316 | 0.967011 | 0.985684211 | 0.712526316 | 0.71473684
± from 1: 4.077316 | -0.03299 | -0.014315789 | -0.287473684 | -0.2852632
Table 7: SiOC With Graphene $\chi^2$ Values Implementing One Baseline

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± from 1: 1.8749 | 0.31789 | -0.1395 | -0.1553 | -0.1532

Table 8: SiOC With Graphene $\chi^2$ Values Implementing Two Baselines

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Average: 2.59168 | 0.8093 | 0.80422 | 0.7008 | 0.6986

± from 1: 1.59168 | -0.1907 | -0.19578 | -0.2992 | -0.3014
Figure 61: SiOC Without Graphene Curve Fitting Implementing Two Curves Results
Figure 62: SiOC Without Graphene Curve Fitting Implementing Three Curves Results
Figure 63: SiOC Without Graphene Curve Fitting Implementing Five Curves Results
Figure 64: SiOC With Graphene Curve Fitting Implementing Two Curves Results
Figure 65: SiOC With Graphene Curve Fitting Implementing Three Curves Results
Figure 66: SiOC With Graphene Curve Fitting Implementing Five Curves Results
APPENDIX B: COMPRESSIVE STRENGTH DATA
Table 9: SiOC with graphene toughening recorded strength values

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Table 10: SiOC without graphene toughening compressive testing data values. Samples 19, 20, and 22 all had noticeable defects as a result of their machining process resulting in greatly reduced strengths and were therefore excluded from data analysis.

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### Table 11: Weibull values for SiOC without graphene toughening samples

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Table 12: Weibull values for SiOC with graphene toughening samples

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LIST OF REFERENCES


M. Mashhadi, H. Khaksari, and S. Safi, "Pressureless sintering behavior and mechanical properties of ZrB2–SiC composites: effect of SiC content and particle size," *Journal of


[133] Y. Xia et al., "Supercritical fluid assisted biotemplating synthesis of Si–O–C microspheres from microalgae for advanced Li-ion batteries," RSC Advances, vol. 6, no. 74, pp. 69764-69772, 2016, doi: 10.1039/C6RA13560A.


