ABSTRACT

TOSIN DAVID AJAYI. Tunable Multi-functional Properties of Polymer Derived Silicon Carbonitride (SiCN) Ceramic Composites for Advanced Aerospace Applications. (Under the direction of Dr. Cheryl Xu).

The emergence and need to always improve the performance of both commercial and military aircraft systems means that the stringent property demand by architectures that make up those systems must be met. This involves developing novel structural architectures that can effectively function in their respective work environments through flexible, cost effective manufacturing procedures.

This thesis aims at investigating the synergistic effect of different filler systems in improving the multifunctional properties (thermal, electromagnetic shielding, dielectric response and environmental protection) of polymer derived ceramics (PDC) - SiCN for applicability in high temperature environments. PDCs are a class of material that can be directly synthesized via thermal decomposition of polymeric precursors. Through the PDC process, thermally and chemically stable ceramic products in complex forms that are usually difficult to achieve through conventional ceramic processing routes, such as powder sintering can be easily prepared.

First, the boron nitride nanotubes (BNNT) were used to reinforce the PDC-SiCN and the thermal and dielectric properties of the resultant nanocomposite were investigated. Thermogravimetry analysis showed that nano-composites have good thermal stability up to 900°C in air. BNNTs in nanocomposites survived in an oxidizing environment up to 900°C, revealing that nanocomposites can be used for high temperature applications. Thermal conductivity of PDC reinforced with 35.4 vol.% BNNT was measured as 4.123 W/(m·K) at room temperature, which is a 2100 % increase compared to that of pristine PDC. The electrical resistivity of the pristine PDC increases from $10^6$
to $10^8 \, \Omega \, \text{m}$ after the addition of BNNTs. When the BNNT loading was increased to 5 wt.%, the average real relative permittivity of the PDC decreased from 2.94 to 2.80, while the quality factor (Q) of the PDC increased from 134.40 to 176.77. Results of this work show that BNNTs can improve the thermal properties of PDCs while also improving their electromagnetic transparency especially when the BNNT fraction is less than 10 wt.%.

Another approach involved using the PDC technology to prepare a multifunctional ceramic composite system for thermal protection while simultaneously shielding against electromagnetic wave interference to ensure overall aircraft safety. Thermal conductance of the multifunctional ceramic composite is about 22.5% lower compared to that of the carbon fiber reinforced polymer (CFRP) composites. Thermal insulation test reveals that the hybrid composite can be used up to 300 °C while keeping the surface temperature of CFRP around 167.8 °C. The average shielding efficiency $SE_T$ per thickness of the developed eight layered composite system was 16.57 dB/mm, showing high absorption dominant EMI shielding, which is distinctly different from the CFRP with reflection EMI shielding. Results of this study showed that materials with good thermal insulation and electromagnetic interference shielding can be obtained by allowing the movement of electrons inside the materials and restricting their movement in the material surface.

Another material system that was designed and fabricated is made up of cured polysilazane (PSZ) and YSZ fibers. Here, the thermal protection capability of the material system was only investigated without considering EMI shielding capability. The room temperature through-thickness thermal conductivity of the cured-PSZ is as low as 0.17±0.02 W/m·K, indicating good insulation capability. The thermal protection experiments showed that the coated CFRP (when skin material has been bonded on CFRP) can be heated up to 250 °C, proving that it can improve the survivability of CFRP high temperature environment.
The result of this thesis proved that through careful experimental approach and theoretical understanding, different functionalities such as thermal, dielectric, electromagnetic shielding etc. from PDC-SICN system can be obtained and improved by carefully choosing and incorporating suitable filler systems.
Tunable Multi-functional Properties of Polymer-derived Silicon Carbonitride (SiCN) Ceramic Composites for Advanced Aerospace Applications

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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DEDICATION

To God Almighty
BIOGRAPHY

Tosin David Ajayi was born and raised in Nigeria. He earned his bachelor’s degree in Metallurgical and Materials Engineering in 2014 and then proceeded to the United States to get his master’s degree in Industrial and Manufacturing Engineering at Florida A&M University. He joined Dr. Cheryl Xu’s group in the Spring on 2017 during his master’s program where he had the opportunity to explore the ‘world’ of advanced ceramic composite synthesis and fabrication. In the Fall of 2018, he moved with Dr. Xu’s research group to North Carolina State University to pursue his Ph.D. in Mechanical Engineering. His work during this time focused on how to suitably adjust the properties of polymer derived ceramic materials with different fillers for various functionalities. Tosin is passionate about using his interdisciplinary background to solving real-world problems. As they say in NC State, you can change the world just by “Thinking and Doing”.
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CHAPTER 1: INTRODUCTION

1.1. Motivation

The aerospace industry’s continuous effort to enhance the performance of commercial and defense aircraft is a great driving force behind developing improved high-performance structural materials [1]. These structures range from polymers to ceramics to metals and down to various composite systems. Specifically, the role and application of ceramics and their composites for aerospace applications cannot be over-emphasized, especially in applications where thermal stability, wear resistance and protection against other environmental conditions are greatly desired. Ceramics are materials with versatile usage in numerous engineering fields especially in high temperature applications. The distinct properties of ceramics are because of their structure and chemical composition.

Polymer derived ceramics (PDC) have been gaining a lot of attention for the past 40 years as an exceptionally formidable tool to manufacture advanced ceramics [2]. The PDC method involves the conversion of polymeric precursors (organometallic systems) into desired ceramic products with tailored chemical composition upon thermal treatment (pyrolysis), usually in inert environment [3, 4]. Through this process, thermally and chemically stable ceramic products in complex forms that are usually difficult to achieve through conventional ceramic processing routes, such as powder sintering can be easily prepared [5]. This method leads to a simple and cost-efficient approach to fabricate ceramic components/composites. Additionally, this method allows for the possibility to transform the PDC into different microstructure by changing the pyrolysis temperature. For instance, when the polymer precursor of SiC is pyrolyzed at 1200 °C, a biphasic microstructure is formed. However, at 1800 °C pyrolysis temperature, the biphasic structure transforms to a multiphasic structure of interdependent carbon and SiC crystals [6]. The
above mentioned and many more are the advantages the PDC process has over conventional ceramic processing method.

Composites are a combination of two or more chemically different materials with distinct interface between them. The combination of the constituent materials produces properties and characteristics that are different from those constituents [7]. One constituent known as the matrix usually forms a continuous phase, and the other constituent is labelled as reinforcement (fillers) which are added to improve the matrix properties. The most used types of fillers in metals, polymers and ceramics are fibers and particulates in micron size. However, in recent years, nano fillers such as carbon nanotubes and boron nitride nanotubes have been gaining more research attention and applications in ceramic composite systems because of their exceptional properties such as mechanical, thermal, electrical, and optical.

Therefore, as improved performance is continuously desired in both current commercial and defense aircrafts, the stringent property demands by the structures that make up such systems must be met. This involves developing new structures with cost effective manufacturing procedures. Therefore, this thesis aims at investigating the synergistic effect of different filler systems in improving the properties (thermal, electromagnetic shielding, dielectric response and environmental protection) of PDC for applicability in high temperature aerospace environment. The microstructure and interface between constituent materials in the ceramic composites will be characterized and correlated with the various investigated properties.

1.2. Research Objectives

The objective of this thesis is to investigate the effect different filler systems in improving the properties polymer derived silicon carbonitride (SiCN) ceramics for high temperature applications.
In respect to the different fillers, the properties of the PDC composite are fine-tuned to serve various purposes, specifically in high temperature environment. This research is filled with novel material design techniques and in particular, theoretical and experimental study with the following focuses:

i) Investigation on the effect of introducing boron nitride nanotube (BNNT) fillers to improve the thermal properties of polymer derived SiCN ceramic.

ii) Investigation on the effect of introducing boron nitride nanotube (BNNT) fillers to improve the dielectric properties of polymer derived SiCN ceramic.

iii) Investigation of multi-phase design and development of polymer derived ceramic composite system for improved and enhanced thermal protection, electromagnetic interference shielding and erosion resistance for carbon fiber reinforced polymer (CFRP) substrates.

iv) Investigation of design and development of cured polysilazane composite system for enhanced thermal protection of carbon fiber reinforced polymer (CFRP) substrates.

The theories and experimental data collected in this study will serve as a future guide in developing polymer derived SiCN ceramic composites by exploring different filler systems for improved thermal, electrical, dielectric, and electromagnetic interference shielding properties.

1.3. Dissertation Outline

This dissertation is composed of the following parts:

Chapter 2 is the literature review on polymer derived ceramics. This chapter also covers the structure of PDC-SiCN and its relation to their various properties. Chapter 3 discusses the effect of introduction boron nitride nanotube fillers into PDC-SiCN, which is aimed at improving the
thermal properties of the resultant nanocomposite. In chapter 4, the dielectric properties of the BNNT-PDC nanocomposite were studied. Chapter 5 discusses the development of a novel multi-phase PDC-SiCN composite structure that is an improvement upon the thermal, electromagnetic interference shielding and surface durability of traditional carbon fiber reinforced polymer (CFRP) composite. Chapter 6 covers a polymer composite layer developed from polysilazane precursor for enhanced thermal protection of traditional carbon fiber reinforced polymer (CFRP) composite. Chapter 7 gives general conclusion of the dissertation.
CHAPTER 2: LITERATURE REVIEW

2.1. Introduction to Polymer Derived Ceramics

Polymer-derived ceramics (PDCs) are a new class of advanced materials which is directly derived from the thermal decomposition of polymer precursors. PDC processing is an alternative and flexible route used to synthesize ceramic materials with a tailored chemical composition and well-defined nanostructure upon heat treatment under controlled environment. The resultant materials have a unique structure that is made up of an amorphous matrix and a mix of free-carbon phase. They possess excellent high-temperature properties such as high thermal stability and excellent oxidation and creep resistance [8-11].

Silicon nitride/silicon carbide (Si$_3$N$_4$/SiC) materials are now used for high temperature applications such as engine and turbine parts, and as microelectronic devices. The conventional method used to prepare these ceramics involves powder processing routes, which also makes use of sintering additives such as Al$_2$O$_3$ and Y$_2$O$_3$ at high temperature (1700 – 2100 °C), thereby limiting its usage. On the other hand, PDC technology presents a simple and cost-effective approach to prepare Si-based ceramic materials by carefully thermal decomposition of preceramic polymers. With the PDC route, the Si$_3$N$_4$/SiC ceramic products can be prepared as ceramic fibers [12, 13], coating layers [14, 15] and composite materials [16, 17], which is difficult to achieve with powder technology. Therefore, conventional polymer forming techniques such as polymer infiltration and pyrolysis (PIP), injection molding, extrusion or resin transfer molding can be utilized to process or shape the polymer. Afterwards, the polymer product can be converted into ceramic by thermal annealing process also known as pyrolysis. In general, the PDC fabrication process can be divided into three main steps and a visual representation is presented in Figure 1:
i) Polymer synthesis from mono- or precursor of silane compounds.

ii) Shaping of the product such as fiber drawing, PIP etc., achieved by thermal induced curing (usually between 150 and 250 °C) to prepare an unmeltable thermoset polymer.

iii) Pyrolysis at high temperature condition (usually 800 °C and above) in inert environment to form an amorphous ceramic structure.

Figure 1. Polymer to ceramic transformation

When PDC is formed, various characterization methods can be used to obtain information about its microstructure. Examples of those methods include X-ray photoelectron spectroscopy (XPS), Raman Spectroscopy, Nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and Electron paramagnetic resonance (EPR). These characterization techniques tell us the relationship between the chemical composition of the PDC with respect to its structure and properties.

2.1.1. Preceramic Polymer Synthesis

The molecular structure and chemistry of the precursor does not only determine the final composition of the PDC, but also the phase distribution and microstructure of the final ceramic product [18-22]. This makes the synthesis of preceramic polymers important in the field of PDCs. With this, the eventual macroscopic properties of the PDC can be modified and varied to a large extent during the preparation of the molecular precursor. To successfully synthesize silicon containing PDCs such as silicon carbonitrides and oxycarbides (SiCN and SiOC), a strong bonding between silicon and carbon atoms in the polymeric start-up compound is required to prevent
carbon from being given off in form of small hydrocarbon molecules during pyrolysis [23, 24]. PDCs are synthesized at relatively low temperature and they completely transform to ceramics under pyrolysis usually at or below 1100 °C [25, 26]. For a precursor to be considered ideal, it must have the following basic properties:

i) High molecular weight is important to prevent volatilization of low molecular compounds.

ii) Suitable viscosity and solubility to aid the shaping process.

iii) Precursor should be able to form thermoset after curing.

iv) Cage-like and ring structure in the polymer chain to give more rigidity to the Si backbone and reduce volatilization.

The two most important groups used to modify and design the polymeric precursor on the molecular level are:

i) The group (X) of the polymer backbone, and

ii) The substituents R\(^1\) and R\(^2\) attached to the silicon.

The difference in (X) results in different classes of Si-based polymers such as poly(organosilanes) formed with X=Si, poly(organocarbonsilanes) formed with X=CH\(_3\), poly(organosiloxanes) obtained from X=O, poly(organosilazanes) formed with X=NH, and poly(organosiloxanes) formed with X=[N=C=N]. Whereas R\(^1\) and R\(^2\) play an important role in controlling the viscosity, thermal stability, optical, electrical, and other properties of the resulting ceramics. Table 1 gives examples of preceramic polymer systems and their ceramic products [26-38].
Table 1. Some examples of polymeric precursors and their final products [27].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Nomenclature</th>
<th>Pyrolysis Temperature (°C)/Atmosphere</th>
<th>Final Product</th>
<th>Ceramic Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-Si-Si-]</td>
<td>Methylsilane</td>
<td>950/Ar</td>
<td>SiC</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Methylvinylsilane</td>
<td>1000/Ar</td>
<td>SiC</td>
<td>0.83</td>
</tr>
<tr>
<td>[-Si-O-]</td>
<td>Methylsiloxane</td>
<td>1000/He</td>
<td>SiO₂Cy</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Methylborosiloxane</td>
<td>1000/NH₃</td>
<td>SiBO₁.₃N₁.₄</td>
<td>0.62</td>
</tr>
<tr>
<td>[-Si-C-]</td>
<td>Silaethylene</td>
<td>1200/N₂</td>
<td>SiC</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Titanocarposilane</td>
<td>1300/N₂</td>
<td>SiC₄O₂Ti₂</td>
<td>0.75</td>
</tr>
<tr>
<td>[-Si-N-]</td>
<td>Hydridosilazane</td>
<td>1200/N₂</td>
<td>Si₃N₄</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>Hydridomethylsilazane</td>
<td>1000/Ar</td>
<td>Si₁.₇CN₁.₅</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Methylsilazane</td>
<td>800/NH₃</td>
<td>Si₃N₄</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Vinylsilazane</td>
<td>1200/N₂</td>
<td>SiC₄N₇/C</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Vinylphenylsilazane</td>
<td>1000/N₂</td>
<td>Si₃N₄</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Cyclomethylsilazane</td>
<td>1000/Ar</td>
<td>Si₃N₄/SiC</td>
<td>0.88</td>
</tr>
<tr>
<td>[-Si-N-B-]</td>
<td>Borosilazane</td>
<td>1000/Ar</td>
<td>BN/Si₃N₄</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Borosiliciumimide</td>
<td>1250/N₂</td>
<td>Si₃B₃N₇</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Borosilazane</td>
<td>1650/Ar</td>
<td>SiBN₃C</td>
<td>0.70</td>
</tr>
</tbody>
</table>

In this work, we used poly(organosilazanes), also referred to as polysilazane precursors to prepare the PDC material. Currently, there are series of polysilazane precursors that are commercially available. They serve as precursors for the synthesis of high-temperature resistant silicon carbonitride (SiCN) ceramics, SiNx dielectrics, and high-performance abrasive coatings. Most common polysilazane precursors are produced by KionCorp (Columbus, OH), which comprises
of various derivatives: Polysilazane HTT 1800, Ceraset® Polyureasilazane and Ceraset® Polysilazane [39]. Figure 2 shows a typical molecular arrangement of polysilazane.

![Molecular structure of polysilazane](image)

**Figure 2. Typical molecular arrangement of polysilazane**

### 2.1.2. Shaping and Crosslinking

Shaping is one of the areas the PDC process has tremendous advantage over conventional ceramic processing. The shaping process in conventional ceramic processing is greatly dependent on the size, shape and microstructure of powders involved in the process. Common ceramic shaping techniques are dry pressing, slip casting and plastic forming [40]. For instance, the powder pressing process is simple and cheap, however, the downside is the difficulty to fabricate intricate parts. Compared to powder pressing, slip casting can give a fine homogeneous shape but the structural strength of the final structure is usually low due to the porous nature of the structure generated by the process [41, 42]. Likewise, plastic forming can also be used to generate complex shapes, however, this is an expensive process due to the feedstock requirement.

On the other hand, the PDC process presents a cheap, less-complicated method to fabricate ceramic components from a polymeric precursor. Due to this, the precursors can be formed into the desired shape after curing before being then converted to ceramics. Ceramic matrix composites can also be prepared through a process known as polymer infiltration and pyrolysis (PIP) which is more environmentally friendly than chemical vapor infiltration (CVI) [43]. Moreover, polymeric
precursors do not encounter any drying problems thereby resulting in components with finer details compared to powder-based systems. Additionally, the precursors can be processed within a very short time compared to the gelation and drying of the sol-gel technique.

To transform the polymer precursor into ceramics, there are two main reactions that usually take place. The first reaction is called cross-linking. Here, the low viscous preceramic precursor cures to form a non-melted thermoset. The liquid precursor is converted into organic/inorganic material and this process avoids the loss of low molecular weight components of the preceramic. Cross-linking is achieved by annealing at 100 °C – 350 °C in air. The cross-linking temperature can be reduced by using catalysts, with the additional benefit of avoiding evaporation of oligomers with the formation of bubbles and increasing the ceramic yield. The addition of a catalyst also allows for the cross-linking to take place during shaping and not the subsequent pyrolysis treatment. After shaping and cross-linking, the material has to be converted to a ceramic. The second reaction takes place at a temperature above 400 °C, rearrangement and radical reactions occurs, which results in the cleavage of chemical bonding and release of organic functional groups (CH₄, C₆H₆, CH₃NH₂, etc.) [29]. Above this temperature, an open-pore channel network is formed and upon further heating up to 800 – 1000 °C, the pores diminish and form the ceramic structure.

2.1.3. Polymer to Ceramic Conversion

The polymer to ceramic conversion of preceramic polymers is a complex but flexible and important approach to the formation of ceramic components. The properties of the precursor influence its processing capability and therefore the shaping method to be used must fit the individual characteristic of the preceramic material. For example, preceramic polymers such as silazanes which are sensitive towards ambient humidity and tend to react by adding oxygen, must be handled, and processed accordingly.
Polymer to ceramic conversion consists of thermolysis and evolution of their organic groups at elevated temperatures (1000 – 1600 °C); at this temperature, the precursor is converted into amorphous covalent ceramics and at higher temperature, a crystalline ceramic material. Various forms of characterization such as X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR) and Raman spectroscopy have shown that after pyrolysis, part of the carbon is bonded to silicon-linking tetrahedral species and the excessive carbon present appear as carbon clusters at lower temperature (800-1200 °C) and graphitic carbon ribbons at higher temperature. Figure 3 displays the polymer to ceramic conversion of silicon-based polymers.

Figure 3. Thermal decomposition of silicon-based polymers (oversimplified representation of the molecular structure of the precursors) [2].

2.2. Microstructure of PDCs

Characterizing the microstructure of PDCs is an important activity since they undergo drastic structural changes during thermal treatment. Studies have indicated that properties of PDCs at high temperature such as resistance to thermal degradation greatly depends on the microstructure of the
amorphous phase of the material itself. According to previous reports, PDCs can maintain their amorphous phase up to a wide range of temperatures (1000–1800 °C) [44]. At higher temperatures, a devitrification process of the amorphous starts, resulting in phase separation, redistribution of chemical bonds and then to nucleation and growth of nanocrystals. In fact, decomposition can be followed by phase separation and crystallization with the bubble formation of gaseous products (CO, SiO, or N₂) [2]. A schematic representation of the molecular structure of PDC-SiCN is shown in Figure 4.

![Figure 4. Schematic representation of PDC SICN [45]](image)

In order to understand these microstructural changes, there are various techniques that have been established to characterize PDCs. Some techniques such as XRD, FTIR, Raman and XPS give average information on the microstructure while techniques such as TEM and SEM provide information on morphology up to the nanometer scale.

a. **X-ray Diffractometry (XRD)**

XRD is a technique that can be used to determine the crystalline phases and chemical composition present in a material. The phases can be identified by comparing the acquired data to that in reference databases. To perform the test, an x-ray beam is directed at the sample and the scattered
intensity as a function of the outgoing direction is measured. When the beam is separated, the diffraction pattern (scatter) then indicates the sample’s crystalline structure. The Rietveld refinement technique is then used to characterize the crystal structure which most likely provides the observed pattern. From the pattern, determination like type of crystalline phases, quantity of crystalline phases and presence of amorphous can all be determined.

The XRD technique can quickly provide information on crystalline phases especially for high volume fraction crystalline material. In contrast, XRD does not provide much information for amorphous PDCs. With the Rietveld refinement, cluster sizes the α and β SiC, SiO₂, and Si₃N₄ phases can be determined. XRD also provides the opportunity to determine parameters such as in-plane crystallite size (Lₐ) and crystallite thickness for the carbon phases present in the material [2].

b. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical method used to establish chemical properties present in a material. It is a technique used to obtain infrared spectrum of absorption and emission of solid, liquid, and gas. Alterations in the characteristic pattern of absorption or emission bands clearly tell a change in the material composition. FTIR is useful in identifying and characterizing polymer precursors and their ceramic products. It works when a infrared radiation is send through a sample, where some radiation are absorbed and then some goes through the sample. The absorbed radiation by the sample’s molecules is then converted into a rotation/vibrational energy. A detector reveals the resulting signal, which represents the molecular fingerprint of the sample. A unique spectral is formed by each molecule or chemical structure.
c. Raman Spectroscopy

When light is irradiated on molecules, the molecules scatter the light. Most of the scattered light has the same frequency with incident light irradiated but some amount of the light has different frequencies because of the interaction that occurs between oscillation of light and molecular vibration. The phenomenon that the light is scattered with frequency change is called Raman scattering. Since frequency modulation is specific to vibration in molecules and phonon in crystal, it is possible to analyze the composition of the material or crystal lattice information by analyzing the spectrum of Raman. The information from the vibration of the molecule can be interpreted from the horizontal axis of the Raman spectrum, and the intensity of the activity can be read from the vertical axis. Moreover, the type and quality of the chemical bonds can be identified.

With Raman technique, the major features in the spectra for free carbon phase in PDCs are known by the presence of three major peaks. A peak of disorder-induced “D and D' bands” at around 1350 and 1620 cm\(^{-1}\) respectively. Another one called the “G band” at approximately 1582 cm\(^{-1}\) which is due to in-plane bond stretching of sp\(^2\) carbon, and also “G' band” at around 2700 cm\(^{-1}\). Another Raman feature is at about 2950 cm\(^{-1}\), which is associated with a D+G combination mode which is induced by disorder [46-52].

d. X-ray Photoelectron Spectroscopy (XPS)

XPS can be used to measure elemental composition, empirical formula, chemical state and electronic state of the elements within a material. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays while simultaneously measuring the kinetic energy of electrons that are emitted from the top 1-10 nm of the material being analyzed. A photoelectron spectrum is recorded by counting ejected electrons over a range of electron kinetic energies. Peaks appear in
the spectrum from atoms emitting electrons of a particular characteristic energy. The energies and intensities of the photoelectron peaks allows identification and quantification of all surface elements (except hydrogen). A surface layer is defined as being up to three atomic layers thick (~1 nm), depending upon the material. Layers up to approximately 10 nm are considered ultra-thin films, and layers up to approximately 1 μm are thin films. The remainder of the solid is referred to as bulk material. This terminology is not definitive however, and the distinction between the layer types can vary depending upon the material and its application.

The photon energy of the incident beam is known, using the value, the binding energy of the emitted electrons is calculated based on equation 1.

\[
E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \Phi) \tag{1}
\]

where \( E_{\text{binding}} \) is the binding energy (BE) of the electron, \( E_{\text{photon}} \) is the energy of the X-ray photons being used, \( E_{\text{kinetic}} \) is the kinetic energy of the electron as measured by the instrument and \( \Phi \) is the work function of the spectrometer (not the material).

e. **Transmission Electron Microscopy (TEM)**

Transmission electron microscopy is an important tool used to understand the distributions of carbon, the degree of crystallinity in a material. With TEM, people have been able to successful capture the stages of local crystallization, and to also visualize the nanocrystalline phases after the start of the devitrification process of the amorphous matrix.

In the amorphous state, TEM characterization has shown that PDCs are generally featureless. Although, the presence of nanosized turbostratic or graphitic carbon has been identified in many cases. Moreover, studies on the microstructural evolution of silicon oxycarbide (SiCO) and silicon carbonitride (SiCN) ceramics showed that they retain their amorphous structure up to a very high
temperature. However, this amorphous structure provides very intriguing ceramic-like properties such as good creep and oxidation resistance [53].

f. Scanning Electron Microscope

A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition. SEM produces images by scanning the sample with a high-energy beam of electrons. As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by one or more detectors to form images which are then displayed on the computer screen. When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. Generally, SEM technique has been largely employed to characterize the morphology of PDCs.

2.3. Properties of PDCs

2.3.1. Thermo-mechanical Properties

The PDC route was initially motivated by interest to fabricate ceramic fibers with high thermo-mechanical properties [54]. The corresponding SiC fibers displayed a tensile strength and Young’s modulus of 6.2 and 440 GPa, respectively. Nicalon fibers cured by iron irradiation process have also been developed and the fibers showed stability up to 1350 °C and elastic modulus up to 280 GPa [2]. BN and SiBCN fibers have also been synthesized form a boron modified polysilazane. The fibers exhibited stability up to 1500 °C and a tensile strength of 1.3 GPa and elastic modulus of 170 GPa [55]. A summary on the mechanical properties of PDC fibers is presented in Table 2.
<table>
<thead>
<tr>
<th>System</th>
<th>Precursor</th>
<th>Tensile strength (GPa)</th>
<th>Elastic modulus (GPa)</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(O)C</td>
<td>Polycarbosilane</td>
<td>3</td>
<td>200</td>
<td>2.55</td>
</tr>
<tr>
<td>SiC</td>
<td>Polycarbosilane</td>
<td>2.5</td>
<td>400</td>
<td>3.05</td>
</tr>
<tr>
<td>Si-Ti-C-O</td>
<td>Polytitanocarbosilane</td>
<td>3</td>
<td>220</td>
<td>2.35</td>
</tr>
<tr>
<td>Si-Al-C-O</td>
<td>Polyaluminocarbosilane</td>
<td>3</td>
<td>300</td>
<td>3.0</td>
</tr>
<tr>
<td>Si-B-C-N</td>
<td>B-modified polysilazane</td>
<td>1.3</td>
<td>170</td>
<td>-</td>
</tr>
<tr>
<td>BN</td>
<td>Poly[(methylamino)borazine]</td>
<td>1.48</td>
<td>365</td>
<td>1.95</td>
</tr>
<tr>
<td>Si-Al-O-N</td>
<td>Polyaluminocarbosilane</td>
<td>1.75</td>
<td>-</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Investigating the mechanical properties of bulk sample of PDCs has been hindered by the fabrication of appropriate ASTM sample dimensions. To solve this problem, two major methods have been introduced. First method is a powder route process used to prepare dense, crack-free monolithic PDC samples by direct pyrolysis of green compacts obtained by warm press of partially cross-linked preceramic polymers. The second method makes use of casting processes either from a sol-gel solution or a liquid polymer, thereby allowing the fabrication of fully dense, small rods or thin plates suitable for flexural strength and fracture mechanics measurements [56-58].

As previously mentioned, when PDCs are synthesized at relatively low temperature, they exhibit high temperature properties such as they resist thermal decomposition and large-scale crystallization up to 1800 °C (Figure 5a); excellent oxidation-resistant behavior (the oxidation rate is as low as that for CVD SiC and Si₃N₄ shown in Figure 5b; and good creep resistance. The
properties of PDC-SiCN (which was used in this study) compared with other ceramic materials is presented in Table 3.

![Image](image_url)

Figure 5. (a) TGA of polymer derived SiCN, SiBCN and commercial silicon nitride [53]. (b) Comparison of oxidation behavior of few Si-based materials at 1350 °C (PDC-SiCN has lowest oxidation rate, as low as CVD SiC and Si₃N₄ [59].

Table 3. Thermo-physical properties of SiCN-PDC compared with other high temperature materials [60].

<table>
<thead>
<tr>
<th>Properties</th>
<th>PDC-SiCN</th>
<th>SiC</th>
<th>Si₃N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.3</td>
<td>3.17</td>
<td>3.19</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>90-150</td>
<td>400</td>
<td>320</td>
</tr>
<tr>
<td>CTE (×10⁻⁶/K)</td>
<td>3</td>
<td>3.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.18</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>~1000</td>
<td>420</td>
<td>700</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>20</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>Thermal shock FOM*</td>
<td>~300</td>
<td>350</td>
<td>880</td>
</tr>
</tbody>
</table>

*strength/Modulus × CTE
2.3.2. Electrical Properties

PDCs also have many unique and outstanding electrical properties, which makes them become distinguished functional materials, especially for harsh environments. The electrical properties of PDCs were studied for the first time since their early discovery [61]. He studied the electrical conductivity of polycarbosilane-derived SiC as a function of pyrolysis temperature and suggested a possible application to fabricate small-size igniters. The room temperature DC conductivity (\(\sigma_{\text{dc}}\)) of PDC is dependent on the type of polymeric precursor, pyrolysis temperature and atmosphere used and can vary up to 15 orders of magnitude (usually from \(10^{-10}\) to \(1 \Omega\cdot\text{cm}^{-1}\)). PDCs synthesized at low pyrolysis temperature (< 600 °C) can be described as insulators because \(\sigma_{\text{dc}}\) is usually less than \(10^{-10} \Omega\cdot\text{cm}^{-1}\). For amorphous PDCs synthesized at higher pyrolysis temperature (> 800 °C), the conductivity increases with temperature, thereby displaying a semiconducting behavior.

Metallic-like (electron) conduction with \(\sigma_{\text{dc}}\), as high as \(0.1 - 1 \Omega\cdot\text{cm}^{-1}\) is found in \(\text{CH}_3\text{SiO}_{1.5}\)-derived Si–C–O pyrolyzed at high temperature (1400°C) when a percolation network of free carbon is formed. When high carbon (C) content is present in the PDC of SiOC such as the one in phenyl-containing polysiloxane, the formation of continuous C network can occur at lower pyrolysis temperature (1100 °C) [62]. A similar evolution of the electrical conductivity with the pyrolysis temperature is found for the Si–C–N system. For high C-containing Si–C–N ceramics pyrolyzed at temperatures above 1000 °C, the graphitic-like carbon is shown to be the main conductive phase [63-65]. Figure 6 shows the dependency of electrical conductivity amorphous PDC SiCN ceramics on annealing time and temperature.
The electrical conductivity of PDCs can also be tuned by adding filler particles into the ceramic matrix. For instance, by adding MoSi$_2$ particles to methyl-containing siloxanes, a drastic increase up to 14 orders of magnitude was observed in the conductivity of the MoSi$_2$/Si-O-C composites because the MoSi$_2$ particles formed a percolation network [67]. Also, the homogeneous dispersion of multiwalled CNTs into an insulating polysilazane derived SiCN ceramic resulted in a corresponding increase of conductivity up to 7 orders of magnitude for a volume fraction of CNTs less than 1% [68].

2.3.3. Electromagnetic Properties

The use of advanced materials such as microwave absorbers and radar-absorbing materials in electronic systems has become an integral part for both civilian and defense-oriented applications. The microstructure of PDCs is usually characterized by the homogeneous distribution of semiconducting or conducting nano-phases in the amorphous matrix. This can lead to the good
microwave absorbing properties since the electrical conductivity is equally improved. Therefore, those materials may not only satisfy the impedance matching but also rapidly attenuate electromagnetic (EM) waves. The absorption properties of PDCs can be easily tailored by the design of the molecular precursor, changes in morphology, and volume fraction of the filler particles [69]. In general, for a material to be considered an excellent EM absorbing material, it should possess the following features [69]:

i) It should have strong absorbing capability and impedance matching characteristic, i.e., it should have little reflection coefficient (RC).

ii) It should have wider efficient absorption bandwidth (EAB).

iii) It should possess low weight and high temperature stability

iv) It should have excellent mechanical property

The basic knowledge that leads to absorption and the design of absorbers has been published by many researchers for over the years. When the electromagnetic wave is incident on the surface of absorption materials, energy loss will occur through the interactions of the electromagnetic field with the material’s molecular and electronic structure [70]. The absorption materials transform electromagnetic energy into heat. The generated heat is related to the conductive and dielectric losses of materials. To obtain improved EM absorption properties, absorbing materials may have dielectric loss by polarization, and an appropriately high conductivity to attenuate the incident electromagnetic wave [71-73]. Generally, the absorption coefficient (A) and reflection coefficient (RC) are used to evaluate the performance of microwave absorption.

The schematic representation of EM wave propagation process through an absorbing material is shown in Figure 7. The absorption coefficient (A) is used to determine the capability of a material
to attenuate the EM wave. The absorption coefficient is defined as the ratio between absorbed power $P_A$ and incident power $P_I$. With a wave guide set-up, the value of $A$ can be calculated as:

$$A = 2\pi d \left(\frac{\varepsilon' \tan\delta}{\lambda}\right)$$

(2)

where $\varepsilon$ is $\varepsilon'$, $\lambda$ is the wavelength of microwave and $d$ is sample thickness. Absorption coefficient $A$ depends on the effective relative permittivity, dielectric loss of the material and the sample thickness.

![Figure 7. Schematic illustration of EM wave propagation process through a material [69]](image)

With the PDCs processing route, a microwave absorber that can offer a large flexibility for phase composition design and property control can be prepared. First, this is because this method offers the opportunity to tuned and optimized the PDC by the design of the molecular precursor. There are two methods to modify and design the chemistry and the architecture of the preceramic precursors: firstly, the group ($X$) of the polymer backbone, and, secondly, the substituent $R_1$ and $R_2$ attached to silicon [2]. The alteration of $X$ results in the formation of different classes of Si-based polymers. Second, with proper control of the processing steps, bi- or multiphase ceramic nanocomposites can be prepared at high temperature [74]. A bi- or multiphase structure can be
composed of electrically insulating matrix and pores (A phase) and electrically lossy phase (B phase) made up of turbostratic carbon and nanocrystalline SiC. This indicates that PDC can be excellent candidate for microwave absorption. Fillers can also be used to improve electrical and dielectric properties of PDCs for EM wave absorption applications. PDCs with fillers show multiple degrees of freedom to tune the dielectric constants which depending on the nature and the geometry of filler particles and the filler particles incorporation-mixing process [70]. For EM absorption applications, the fillers can be categorized into catalytic metal such as Fe, Ni, Co, etc. and electrical conducting phase.

i) PDCs with catalytic metal

When PDCs are prepared through catalyst assisted pyrolysis, formation of 1D nanostructures such as SiC nanowires/nanorods [75], Si$_3$N$_4$ nanowires/nanorods [76], C nanowires/nanotubes [77], BNNTs [78] and etch can be formed with respect to chemical structure of the precursor and temperature of pyrolysis. These 1D nanostructures exhibits unique and often superior properties when compared to their bulk and/or microscale counterparts. For instance, the 1D nanostructures of SiC and C both show the high electrical conductivity and surface area which can promote the conductance polarization and interfacial polarization [79, 80], which is beneficial to improvement of EM absorption in the PDC material. The main advantage of PDCs with 1D nanostructure is that they can reach wider EAB at thinner thickness [70].

ii) PDCs with electrically conductive phase

High electrically conducting fillers can be added into PDCs to improve their electrical conductivity, especially with those pyrolyzed at low temperature. The electrical behavior and dielectric properties of PDCs with electrically conductive phase is dominated among others by the
intrinsic filler conductivity, morphology of filler network and particle contacts [70]. For instance, Ionescu E. et al [81]. prepared a SiCN/CNT ceramic composite by adding MWCNTs into a cured polysilazane using a simple roll-mixing method and then combined with warm press and pyrolyzed at 1100 °C. The nanocomposite containing 5% volume fraction of CNTs exhibited a conductivity of 7.6 S/m. The permittivity corresponding to the minimum RC of PDCs modified with and without fillers at 10 GHz and 2.86 mm is shown in Fig. 8. It shows that the minimal RC of PDCs with free fillers can reach −10 dB which means beyond 90% EM waves area absorbed by the materials.

![Figure 8. Permittivity of PDCs modified with and without fillers when they reach minimal RC](image)

**2.3.4. Chemical Properties**

i) Oxidation Resistance: Since PDCs were intended for high temperature applications, their oxidation resistance has also been extensively studied [82]. In general, parabolic oxidation rates are observed when PDCs are pyrolyzed at a temperature high enough to completely remove the
hydrogen from the system [83-87]. They demonstrated that a formation of dense and continuous oxide layer with a sharp oxide/ceramic interface is introduced into the system. Modena et al. reported that the oxidation kinetics of SiCO glasses with different amounts of “‘free’” C (from ~ 0 % up to 60 %) have a parabolic αKp constants that increase with the amount of “‘free’” C present in the nanostructure. This means that the C activity in SiCO glasses is likely less than unity. Apart from that, the heats of dissolution in a molten oxide solvent showed that SiCO glasses possess a negative enthalpy relative to their crystalline constituents (silicon carbide, cristobalite, and graphite) in agreement with the proposed lower activity (<1) of C_{free} in SiCO PDCs [88]. Similar results, showing a negative enthalpy of formation, have also been reported for SiCNO derived from polysilazanes [89]. Investigations on the oxidation behavior after introducing extra elements to SiCN PDCs have also been carried out. When Al is added to Si–C–N–(O) PDCs, a nonparabolic oxidation curve (at T ≥ 1000 °C) which decreases more rapidly with time, down to a negligible level was observed. At T = 1400 °C, a stationary parabolic rate is observed for t > 420 h, with parabolic constants about ten times lower than those of the Al-free Si–C–N samples [2, 90].

ii) Chemical durability: Soraru G. D. et al [86] studied the chemical durability of silicon oxycarbide glasses with different amounts of “‘free’” C. in highly basic or acidic (HF) solutions. Compared to Silica glass, SiO₂, the SiCO network exhibits greater durability in both basic and acidic media because of the character of the bonding (Si–C bonds are less prone to nucleophilic attack) and a higher degree of compositional disorder and network cross-linking carbon (either bonded to Si atoms or present as a “‘free’”-carbon phase, impedes reactant transport locally). If the SiCO is pyrolyzed at high-temperatures (T > 1200 °C) it undergoes a phase separation into SiO₂-based, SiC and carbon regions and the chemical durability decreases since the SiO₂ species can be extracted [91].
2.4. Composites

The first uses of composites date back to about 10,000 B.C., as discussed by Ashby [92]. This was when early Egyptians and Mesopotamian settlers combined mud and straw together to create strong and long-lasting structures. Straws were also used to provide support as reinforcement to other structures like pottery and boats. The present evolution and development of composites started when polymers such as polyester, polystyrene, vinyl, etc. were discovered by scientists during the early 1900s. However, plastics could not provide enough structural properties such as high strength and hardness in some applications. Therefore, it was imperative that reinforcement was needed to provide additional strength and rigidity [93]. Other factors such as World War II, expansion of polymer industries and the discovery of high strength materials like glass fibers brought great technological advancement to composites through research and development by scientists and engineers.

From the use of materials such as mud and straw to make buildings, to the use of polymers and synthetic fibers to manufacture advanced composite materials such as airplanes and cars; composites have undoubtedly generated a new way of thinking. A composite material is a material made from the combination of two or more constituent materials with significantly different properties. Each material brings a different quality to the overall performance of the composite. The combination of these materials acts as either matrix or reinforcement. The matrix helps to transfer stresses between the reinforcing fibers and serve as a barrier against adverse environment. On the other hand, the reinforcements are the load-bearing components. They are usually pre-massed into various forms to facilitate the fabrication of composite parts. The quality of the interface between the reinforcing fiber and the matrix determines the whether the properties of the composite will be good or bad. Thus, surface science has emerged as a new field of research [94].
2.4.1. Classification of Composites

Based on the matrix used, composites are classified as polymer matrix composites (PMCs), metal matrix composites (MMCs), or ceramic matrix composites (CMCs). Likewise, composites can also be classified based on the type and form of the reinforcement used such as fiber reinforced polymer (FRP), nanocomposite (nanotube-based composite, nano-particulate composites), hybrid composite, etc. The main advantages of composite materials are their high strength and stiffness, combined with their low density when compared with bulk materials, thereby allowing for a weight reduction in the finished products. The Composite industry is a $110 billion that keeps growing and have few advantages over other bulk materials because they:

- Are lightweight structural materials.
- Are highly anisotropic and designable materials.
- Have long service life and low life cycle cost.
- Possess flexural manufacturing technologies.
- Have multi-functionality by design.
- Are non-corrosive compared to metals.

When at least one of these phases has nanoscale dimensions (< 100 nm), the resultant composite product is called a nanocomposite and offers in addition a higher surface to volume ratio. The effectiveness of the addition of such materials results in a drastic improvement of properties that can include mechanical strength, toughness, electrical conductivity, and thermal stability. The physiochemical and biological properties of nanomaterials differ from properties of their individual atoms or bulk-sized equivalents due to their extremely high surface-to-volume ratios. Therefore, by creating nanoparticles it is possible to control the fundamental properties of
materials, such as their magnetic properties, charge capacity, melting temperature, and even their color without changing the materials’ chemical compositions. The properties of nanocomposite materials depend not only on the properties of their individual constituents, but also on their morphology and interfacial characteristics. By maximizing interface interactions, nanocomposites could be produced with a broad range of enhanced properties. Thus, nanocomposites promise new applications in many fields such as lightweight mechanical components, structural health monitoring systems, battery cathodes, sensors, and other systems.

2.4.2. Matrices

The matrix acts as a binder for the reinforcement while controlling the physical shape and dimensions of the part. Its primary purpose is to transfer the load, or stress applied to the part, to the reinforcement. The major roles of the matrix are:

- To transfer stresses between the fibers.
- To provide a barrier against an adverse environment.
- To protect the surface of the fibers from mechanical abrasion.
- To determine the processibility of composites.
- To determine heat resistance of composites.
- To determine inter-laminar shear, in-plan shear as well as damage tolerance properties of composites (non-reinforcement dominated properties).

The matrix also provides lateral support against the possibility of fiber buckling under compression loading, therefore increasing the compressive strength of the composite material to some extent. The interaction (interfacial bonding) between fibers and matrix is important in designing damage-tolerant structures.
2.4.3. Reinforcement

The reinforcement is the principal load-carrying component, such as fibrous materials. For structural composites, the reinforcements are stiffer and/or stronger than the matrix. Reinforcement for the composites can be fibers, fabrics, particles, whiskers or even nanomaterials. Though various composite materials, including fiberglass and fiber-reinforced plastics, are currently in wide use for numerous commercial applications, there has still been continuous demand for novel composites with desirable properties for other applications. Therefore, nano-based reinforcement such as nanotubes have been used to achieve this goal [95-97].

Carbon allotropes such as carbon nanotubes (CNTs) have been gaining wide attention over the past few years. CNTs show a much higher tensile strength of up to 100 GPa and modulus of up to 1.3 TPa [98, 99] with a typical diameter of sub-nanometer to tens of nanometer. Coupled with the exceptionally high electrical and thermal conductivities [100, 101], CNTs have shown that they are capable to be the next generation of strong, light, and multifunctional reinforcement materials. Also, Boron nitride nanotubes (BNNTs) are close structural analogues of carbon nanotubes (CNTs), made up of hexagonal B-N bonding network having partial ionic properties due to difference in the electronegativity of boron and nitrogen, while on the other hand, CNTs consists purely covalent C-C bonds [102]. Compared to CNTs, BNNTs also possess excellent mechanical properties (high tensile strength of 30 GPa and Young’s modulus of ~850 GPa) [103] and high thermal properties [104, 105].

Additionally, in opposite to CNTs, BNNTs do not absorb visible light due to wide band gap of ~5 – 6 eV [106], a property that has made them to be explored as additives in composites because they tend to improve the matrix’s mechanical and thermal properties while allowing it to retain its transparency [107]. Table 4 compares some of the properties between BNNT and CNT.
Table 4. Comparison between CNT and BNNT [103, 108]

<table>
<thead>
<tr>
<th>Properties</th>
<th>CNTs</th>
<th>BNNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical</td>
<td>Metallic or semiconducting</td>
<td>Always semiconducting (~5.5 eV)</td>
</tr>
<tr>
<td>Mechanical (Young Modulus)</td>
<td>1.33 TPa</td>
<td>900 TPa</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>60 – 40,000 W/mk</td>
<td>~ 3000 W/mk (Cu = 400 W/mk)</td>
</tr>
<tr>
<td>Thermal Oxidation Resistance</td>
<td>Stable between 300 – 600°C in air</td>
<td>Stable up to 800°C in air</td>
</tr>
<tr>
<td>Neutron scattering Cross-section</td>
<td>C = 0.0035</td>
<td>B = 767</td>
</tr>
<tr>
<td>Section</td>
<td></td>
<td>N = 1.9</td>
</tr>
<tr>
<td>Polarity</td>
<td>Covalent bond (no dipole)</td>
<td>Permanent dipole (Piezoelectric)</td>
</tr>
<tr>
<td>CTE</td>
<td>-1 x 10⁻⁶</td>
<td>1 x 10⁻⁶</td>
</tr>
</tbody>
</table>

2.4.4. Fabrication of Composite

The main manufacturing methods for polymer composites include:

Prepreg/vacuum bag/autoclave: Fabrics and fiber are pre-impregnated with resin by the materials manufacturer and then pre-cured. The prepregs can be laid up by hand or machine onto a mold surface, vacuum bagged and then heated to typically 120-180°C. This allows the resin to flow and then eventually to cure with the application of heat. Additional pressure for the molding is usually provided by an autoclave or press. The prepreg process is very simple, low cost, and the manufacturer has already set the fiber concentration.
Liquid composite molding (LCM): Liquid composite molding involves forcing liquid resin into the dry preformed reinforcing material. The main objective is to reach a full impregnation as the resin flows between the fibers. The impregnation driving force is usually resulting from pressure difference. Resin transfer molding, vacuum assisted resin transfer molding, and vacuum infusion are the most used types of LMC.

Sheet molding compound (SMC): Sheet Molding Compound (SMC) is a compression molding compound often used for larger parts where higher mechanical strength is needed. SMC is a mixture of polymer resin, inert fillers, fiber reinforcement, catalysts, release agents, and thickeners and possesses strong dielectric properties. Manufacture of SMCs is a continuous in-line process. The material is sheathed both top and bottom with a polyethylene or nylon plastic film to prevent auto-adhesion. The paste is spread uniformly onto the bottom film. Chopped glass fibers are randomly deposited onto the paste [110].
CHAPTER 3: THERMAL PROPERTIES OF BNNT-PDC NANOCOMPOSITE

3.1. Rationale

Boron nitride nanotubes (BNNTs) have attracted tremendous interest in the last decade thanks to their exceptional nanoscale properties. BNNTs are structural analogue of carbon nanotubes (CNTs), made up of a hexagonal B-N bonding network having partial ionic properties due to the difference in the electro negativity of boron and nitrogen [102], while CNTs consists of purely covalent C-C bonds. Similar to CNTs, BNNTs also possess excellent mechanical properties (high tensile strength of 30 GPa and Young’s modulus of 850-900 GPa [103, 111]) and high thermal properties [104, 105]. BNNTs do not absorb visible light due to their wide band gap of ~5.5 eV [106], which makes them an exceptional reinforcement candidate in application that require mechanical and thermal properties of the resultant composites. Most importantly, BNNTs show significant superiority in thermal and chemical stability compared to CNTs in air, since CNTs have oxidation resistance only up to 400 °C and can be substantially burnt off above 700 °C [112]. Chen et al. [113] studied and showed that the structures of individual BNNT can survive at up to 850 °C in air and exhibit the signs of their structural degradation at 900 °C or above. Han et al. [114] also studied the oxidation resistance of BNNTs by heating in an oxygen environment, proving that BNNTs were more stable than CNTs at 700 °C. In addition, the presence of boron makes BNNTs and BNNT composites excellent thermal neutron radiation shielding materials [115]. Another important property of BNNTs is their high thermal conductivity (200 W/(m·K)) [116], which makes BNNTs ideal reinforcements for improving the thermal conductivity of composites in harsh environment applications.

As previously mentioned, polymer derived ceramic (PDC) processing is a flexible route that can be used to synthesize ceramic composites with a tailored chemical composition and well-defined
nanostructure upon heat treatment. Different from conventional ceramics obtained by sintering powders, PDC is synthesized by direct thermal decomposition of polymeric precursors [117], which can either be liquid, melt, or organic solution. The PDC process gives the ability to manufacture complex shaped products with high volume fractions (up to 35.4 vol.% in this study) of the reinforcement (filler). The PDCs possess excellent oxidation and creep resistance up to exceptionally high temperatures [2] (the PDC silicon carbonitride (SiCN) ceramic has the oxidation resistance at 1350 °C similar to the best known resistance in crystalline material silicon nitride and silicon carbide [118] and has the creep resistance up to 1550 °C [24]). PDC silicoboroncarbonotride ceramic can even be stable to 2000 °C [119]. PDCs with nano reinforcements shows exceptionally improved mechanical and electrochemical performance. For instance, PDC SiCN with only 6.4 vol. % CNTs shows over 150 % increase in hardness relative to monolithic PDC SiCN [117]. PDC SiOC with 0.5 wt.% BNNT demonstrates a specific capacitance corresponding to 78.93 F·g⁻¹ at 1 A·g⁻¹ with a cyclic retention of 86% after 185 cycles [120].

In this chapter, we report the thermal properties of BNNT-reinforced ceramic composites with a high-volume fraction of BNNT filler (up to 35.4 vol.%) using the PDC processing routine. The synthesized ceramic composites in this work possess exceptional thermal properties, including high thermal conductivity of 4.123 W/(m·K) at room temperature, improved by 2100 % compared to that of pristine PDC.

3.2. Materials and Methods

Raw BNNTs (tube length over a few micrometers and diameter less than 5 nm synthesized by High Temperature Pressure (HTP) method [121] and supplied by NASA Langley Research Center were used as the reinforcement. Polysilazane (PSZ, KiON Defense Technologies, Inc.,
Huntingdon Valley, PA, USA), a liquid thermosetting resin with silicon and nitrogen atoms in repetitive units, was used as the liquid preceramic precursor of silicon carbonitride (SiCN) ceramic. The PSZ precursor was mixed with 4 wt.% dicumyl peroxide (thermal curing agent from Sigma-Aldrich). All materials were used as-received without carrying out any further purification.

Figure 9 illustrates the preparation steps to make BNNT reinforced PDC nanocomposites. The BNNT reinforced PDC nanocomposites were prepared by first mixing PSZ precursor and BNNTs, and then pyrolyzing the mixture at 1000 °C. The mixed PSZ precursor was poured into a ceramic crucible and then cured at 350 °C in a flowing argon atmosphere (step 1). After curing, the cross-linked product was milled in a planetary ball miller for 1.5 hours (step 2) to obtain cured PSZ powder (average size of powder 1 µm). After ball milling, different volume fractions of BNNTs were mixed with the cured PSZ powder (via additional ball milling for 30 minutes) to form a uniform homogeneous compound (step 3). The mixed BNNTs/cured PSZ powders were then compressed under uniaxial pressure (3.4 MPa) into a disk sample with a diameter of 25 mm (step 4) at room temperature. The compacted product was pyrolyzed at 1000 °C for 3 hours at a heating rate of 1 °C/min under the steady flow of a high purity 4.8 grade nitrogen environment to form a BNNT-PDC nanocomposite (step 5). Using this route, BNNT-PDC nanocomposites with BNNT volume fractions of 7.8, 15.2, 22.2 and 35.4 vol.% were successfully fabricated. The scanning electron microscopy (SEM) images of polished surfaces of the prepared pristine PDC and representative BNNT-PDC nanocomposites (reinforced with 15.2 vol.% BNNT) are shown in Figure 4, which reveals a typical morphology feature of a pristine PDC material, with angular dense sections, loose boundaries, and pores. In comparison, the BNNT-PDC nanocomposites show more dense sections, with much less loose boundaries and pores. The inset is a macroscopic photo
of BNNT-PDC nanocomposites (reinforced with 15.2 vol.% BNNT) which shows a black color after pyrolysis.

![Figure 9. Schematic diagram of preparation process of BNNT-PDC nanocomposite.](image)

### 3.3. Microstructural Characterization

The microstructure of the nano composites was characterized by Raman spectroscopy, X-Ray Diffraction (XRD), field emission scanning electron microscope (SEM, FEI Verios 460L) and transmission electron microscopy (TEM). Raman spectra were obtained on LabRAM HR Raman microscopes (HORIBA Scientific) with the 632 nm line of Ar⁺ laser as the excitation source. XRD data were acquired using a Malvern PANalytical Empyrean X-ray diffractometer with Cu K-alpha radiation (wavelength 0.15418 nm) in a 2-theta range of 10 to 80 degree. The step size and time per step used in these measurements are 0.026 degree and 87 sec/step, respectively. TEM observation was performed using a Talos F200X G2 (USA) microscope operated at 200KeV. TEM samples were prepared with Focused Ion Beam (FIB) milling by FEI Quanta 3D FEG (USA).

First, the scanning electron microscopy (SEM) images of polished surfaces of the prepared pristine PDC and representative BNNT-PDC nano-composites (reinforced with 15.2 vol.% BNNT) are
shown in Figure 10, which reveals a typical morphology feature of a pristine PDC material, with angular dense sections, loose boundaries, and pores. In comparison, the BNNT-PDC nanocomposites show more dense sections, with much less loose boundaries and pores. The inset is a macroscopic photo of BNNT-PDC nanocomposites (reinforced with 15.2 vol.% BNNT) which shows a black color after pyrolysis.

Figure 10. SEM images of (a) pristine PDC and (b) representative BNNT-PDC nanocomposites (reinforced with 15.2 vol.% BNNT). The inset is a macroscopic photo of BNNT-PDC nanocomposites (reinforced with 15.2 vol.% BNNT).

3.4. Effect of BNNTs on the Porosity and Density of BNNT-PDC Nanocomposites

The density of the nanocomposites ($\rho_0$) was calculated by measuring the weight and volume of the samples. The density of the fully dense PDC is 2.23 g/cm$^3$ [122], which is used as the theoretical density of PDC ($\rho_{PDC}$) and the theoretical density of BNNTs ($\rho_{BNNTs}$) is used as 1.38 g/cm$^3$ [123]. The theoretical density of the nanocomposites ($\rho$) is calculated as:

$$\rho = \rho_{PDC}v_{PDC} + \rho_{BNNTs}v_{BNNTs}$$ (3)
where \( \nu_{\text{PDC}} \) is the volume fraction of PDC, and \( \nu_{\text{BNNTs}} \) is the volume fraction of BNNTs. The porosity of the nanocomposites (\( P \)) is presented as:

\[
P = \left( 1 - \frac{\rho_0}{\rho} \right) \times 100\%
\]

The densities and theoretical porosity of pristine PDC and the nanocomposites with different volume fractions of BNNTs are listed in Table 5. The BNNT-PDC nanocomposites is denser than the pristine PDC and the density of the BNNT-PDC nanocomposites increases (the porosity decreases) with increasing BNNT volume fraction. The density of PDC is respectively increased by 13.3 % and 31.3 %, and the porosity of PDC is respectively reduced by 22.5 % and 69.2 % after addition of 7.8 vol.% and 35.4 vol.% BNNT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>True Density (( \text{g/cm}^3 ))</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PDC</td>
<td>1.28</td>
<td>42.6</td>
</tr>
<tr>
<td>BNNTs-PDC (with 7.8 vol.% BNNT)</td>
<td>1.45</td>
<td>33.0</td>
</tr>
<tr>
<td>BNNTs-PDC (with 15.2 vol.% BNNT)</td>
<td>1.61</td>
<td>23.4</td>
</tr>
<tr>
<td>BNNTs-PDC (with 22.2 vol.% BNNT)</td>
<td>1.62</td>
<td>20.6</td>
</tr>
<tr>
<td>BNNTs-PDC (with 35.4 vol.% BNNT)</td>
<td>1.68</td>
<td>13.1</td>
</tr>
</tbody>
</table>

A topography (FRTMicroProf®) measurement using the 3D mapping and w/shading technique is shown in Figure 11. The bright area in the images signifies the highest elevated points while the dark areas represent the lowest points of the scanned area. From the results, pristine PDC has an average pore height of 2.01 \( \mu \text{m} \) and an average pore diameter of 13.0 \( \mu \text{m} \), whereas with 15.2 vol.%
and 22.2 vol.% BNNT, the average pore height of the nanocomposites decreased to 0.84 µm and 0.82, respectively. The average pore diameter of the nanocomposites decreased to 9.22 µm and 9.73, respectively. The PDC materials always contain porosity after pyrolysis. Addition of filler can reduce the shrinkage and the porosity after the precursor is pyrolyzed [2], which can be expressed by the following equation:

Precursor + Inert filler = Ceramic + Inert filler + Free carbon + Gaseous products\[5\]

Figure 11. 3D mapping and w/shading topography (200×200 µm, Z scale = 50 µm, 60° Tilted) of (a) pristine PDC, (b) BNNT-PDC nano-composites (reinforced with 15.2 vol.% BNNT), and (c) BNNT-PDC nano-composites (reinforced with 22.2 vol.% BNNT).

BNNT can be viewed as inert filler during pyrolysis of the PDC precursor (BNNT does not react with PDC during preparation), and therefore, it has the effect of inhibiting shrinking and reducing the porosity and pore size of the nanocomposites. The total BNNT volume does not change, and the shrinkage of the total nano-composites entirely depends on the volume change of the polymer until it reaches a point (critical volume fraction of BNNTs) at which the BNNTs form a rigid network, and further shrinkage of the composites is impossible. Above the critical point, the shrinkage of the polymer results only in porosity. Therefore, the porosity decreases with increasing BNNT volume fraction before the BNNT rigid network forms.
3.5. Thermal Stability of Pristine BNNT and BNNT-PDC Nanocomposite at Elevated Temperature

Figure 12a shows TGA results of pristine BNNTs at temperatures from 20 °C to 900 °C in air and nitrogen. The 4% weight loss observed with samples in both environments from the starting point to around 200 °C is attributed to the removal of excess moisture confined in the sample. The weight of the sample is relatively stable from 200 °C to around 800 °C. Because the ‘as-received’ BNNTs used in this study contain boron impurities, thermal oxidation of these impurities is the source of some of the weight gain seen in TGA curves in air below 800 °C starting from just above 400 °C. The TGA spectra indicate that BNNTs are stable up to 800 °C. The SEM micrographs of pristine BNNTs after exposure in air and nitrogen at 900 °C are shown in Figures 12(b, c). BNNTs are viewed as thermally stable up to 800 °C because there is no morphology change at this temperature, which was also reported by Chen et al [113]. After exposed in air at 900 °C, BNNTs appear short because of damage by thermal oxidation, as shown in Figure 12b. Figure 12b also showed that the morphology was changed a lot after the TGA run. The remaining BNNTs appear more compact with granular morphology possibly because the oxidized boron that can be melted and resolidified to form granular morphology.
Figure 12. (a) Weight change of pristine BNNTs in air and in nitrogen at elevated temperatures.

SEM micrographs of pristine BNNTs after exposed in air (b), and in nitrogen (c) at 900 °C.

TGA results of pristine pre-ceramic polymer and representative pre-ceramic polymer with 35.4 vol.% BNNT in air are shown in Figure 13a. The pristine pre-ceramic polymer experienced about 18 % weight loss at 500 °C, which could be attributed to the porous nature of the material and loss of free carbon during oxidation [124]. The TGA results show that the mass loss of the pre-ceramic polymer in air is remarkably decreased by the introduction of BNNTs. The decrease is mainly due to the decreased pores and cracks, which reduce the oxidation of free carbon. Cracks (Figure 13c) form for pristine PDC when subjected to heating. When BNNTs are introduced, the cracks in the nanocomposites are decreased significantly (Figure 13d) during the TGA heating process in air.

Also, as seen from Figure 13b, the number and size of pores in BNNT-PDC nano-composites (reinforced with 35.4 vol.% BNNT) are significantly reduced compared to those of BNNT-PDC nano-composites (reinforced with 7.8 vol.% BNNT) (Figure 13d), and the porosity dropped from 33.0 to 13.1% dramatically (Table 5). The oxygen ingress therefore is reduced because of the
decreased crack size and pores. The oxidation of free carbon in the composites is reduced and the thermal stability is improved.

Figure 13. (a) TGA plots of pristine pre-ceramic polymer and pre-ceramic polymer with 35.4 vol.% BNNT up to 1000 °C. SEM image of BNNT-PDC nanocomposites (b) reinforced with 35.4 vol.% BNNT, (c) pristine PDC, (d) and 7.8 vol.% BNNT.

Although BNNTs are oxidized in air at 900 °C (Figure 13b), the nanocomposites may have potential application in harsh environments. The reason is that BNNTs inside the nanocomposites are protected from being oxidized. Raman spectra of the pristine BNNTs shows a h-BN peak at around 1396 cm⁻¹, as shown in the insert of Figure 14a. XRD analysis for the pristine BNNTs (in Figure 14g) shows (002) and (101) peaks for hexagonal boron nitride. Figure 14(a-g) are the SEM images, TEM images and XRD analysis of the BNNT-PDC nanocomposites (35.4 vol.% BNNT) before and after exposed to air at 900 °C for 1 h. The nanotubes are embedded in the PDC matrix before oxidation, as seen from SEM image (Figure 14a) and TEM image (Figure 14c). Figure 14e shows a Fast Fourier Transform (FFT) of the selected area (A) of the nanotubes. The (002) plane for BNNT verifies that the embedded nanotubes are BNNTs. After oxidation, there are still
undamaged nanotubes inside the nanocomposites, as seen from the SEM image (Figure 14b) and the TEM image (Figure 14d). XRD analysis (Figure 14g) before and after oxidation at 900 °C in air for 1 h reveals the (002) and (101) peaks for hexagonal boron nitride, indicating the presence of BNNTs in both oxidized and un-oxidized samples. The FFT of the selected area (B) of the nanotubes reveals the (002) plane for BNNT (Figure 14f), also verifying that BNNTs survive in the nanocomposites after oxidation at 900 °C, which make the nanocomposites thermally stable.
Figure 14. SEM images of BNNT-PDC nanocomposites (reinforced with 35.4 vol.% BNNT) before (a) and after (b) oxidation at 900 °C in air for 1 h. TEM images of BNNT-PDC nanocomposites (reinforced with 35.4 vol.% BNNT) before (c) and after (d) oxidation at 900 °C in air for 1 h. (g) XRD curves of the pristine BNNTs, the BNNT-PDC nanocomposites (35.4 vol.% BNNT) before and after exposed to air at 900 °C for 1 h. (e, f) are the Fast Fourier Transform (FFT) of the selected area A and B in Figure (c) and Figure (d), respectively. Insert of Figure (a) is the Raman spectra of Pristine BNNTs showing h-BN peak. The SEM image, TEM image and XRD pattern after oxidation are obtained after polishing the surface of the nanocomposites.
3.6. Thermal Conductivity Analysis of BNNT-PDC Nanocomposite

The thermal conductivity of the BNNT-PDC nanocomposites was studied as a function of volume fraction of BNNTs, which is illustrated in Figure 15. The thermal conductivity increased with increasing BNNT content. When the volume fraction of BNNTs is low, the thermal conductivity of the BNNT-PDC nanocomposites increased slowly with the increase of BNNT content. There is a significant increase in thermal conductivity when the BNNT content is higher than 22.2 vol.%, indicating a percolation transition (Figure 15).

![Graph showing thermal conductivity increase](image)

Figure 15. The BNNT-PDC nanocomposites fitted to the Single Exponent Phenomenological Percolation Equation (SEPPE). The SEPPE is obtained by putting the same value for the exponents $s$ and $t$ in the Two Exponent Phenomenological Percolation Equation (TEPPE).

The thermal conductivity of BNNT-PDC nano-composites (reinforced with 35.4 vol.% BNNT) was measured as 4.123 W/(m·K) at room temperature, which is a 2100% increase compared to that of the pristine PDC, as illustrated in Figure 10. The BNNT-PDC nanocomposites exhibit an improved thermal conductivity than other types of PDC composites reinforced with carbon fiber (Cf) and/or carbon nanotube (CNT) [125] as seen in Figure 16.
Figure 16. Room temperature thermal conductivity of pristine PDC and 35.4 vol.% BNNT-PDC nano-composites reported in this work compared to other PDC composites [126] (45 vol.% C/r/PDC, 45 vol.% C/r+10 vol.% CNT (short)/PDC, 45 vol.% C/r+10 vol.% CNT(long)/PDC).

3.6.1. Theoretical Model of Composite Material on Thermal Conduction

The transport properties, electrical conductivity (\(\sigma\)) [127-129], magnetic permeability (\(\mu\)) [130] as well as thermal conductively (\(\kappa\)), and diffusivity (\(D\)) of binary composites in relation to the volume fraction \(\phi\) and topology, can be described by a range of mixing rules (Effective Media Models). For a particular class of these composites, which undergo a percolation transition, the percolation equations can be used. Percolation systems are characterized in which the plots of log \(\sigma\) (or \(\epsilon\), \(\kappa\), \(D\) or \(\mu\)) versus \(\phi\) are sigmoid shaped. A rapid change in log \(\sigma\) (or \(\epsilon\), \(\kappa\), \(D\) or \(\mu\)) occurs at the critical volume fraction (percolation threshold) \(\phi_c\). While the classical percolation equations can only be fitted to the data below and above the percolation equations separately, the Single Exponent Phenomenological Percolation Equation (SEPPE) also known as the General Effective Medium Model (GEM) and the Two Exponent Phenomenological Percolation Equation (TEPPE) [127-130] can be used to across the ranges of \(\phi\) including in the cross-over region. For the TEPPE, the
curvature in the regimes below and above \( \varphi_c \) is characterized, by the two exponents \( s \) and \( t \), respectively. The SEPPE (GEM) can be obtained from the TEPPE by setting the exponent \( s = t \) [130]. For a binary composite consisting of a more thermally conductive filler and an insulating matrix, the TEPPE can be written as:

\[
\frac{(1-\varphi)(k^s_l-k^s_m)}{k^s_l+A k^s_m} + \frac{\varphi(k^s_h-k^s_m)}{k^s_h+A k^s_m} = 0
\]

(6)

with \( A = \frac{1-\varphi_c}{\varphi_c} \), \( \kappa_m \) is the conductivity of the composites, \( \kappa_h \) the conductivity of the more conductive component (filler) and \( \kappa_l \) the conductivity of the less conductive component (matrix). Note that the matrix conductivity term can incorporate any porosity.

The experimental results are fitted by the TEPPE using the least-square curve fitting method, which is shown in Figure 15. The best fit parameters are \( \kappa_h = 200 \pm 10 \) W/(m·K), \( \kappa_l = 0.2 \pm 0.03 \) W/(m·K), \( s = t = 1.5 \pm 0.6 \) and \( \varphi_c = 36 \pm 5 \% \) for the filler and matrix conductivities, exponents and percolation threshold respectively.

Thermal conductivity of the nanocomposites is determined by the phonon diffusion (phonon scattering). The thermal conductivity of pores can be viewed as 0, and that of BNNTs is much higher than pristine PDC. The pores will scatter phonons when they encounter each other, resulting in an increase of thermal resistance. The interfaces between BNNTs and PDC can also increase the thermal resistance due to the interface resistance. However, since BNNTs have a high thermal conductivity of 200 W/(m·K), an increase in BNNT content will result in the positive effect of from the conductivity provided by BNNTs thereby exceeding the negative effect in thermal resistance introduced by the conductivity inhibitors such as pores, defects and interfaces. When the volume fraction of BNNTs exceeds the percolation threshold (36 vol.\%), percolation network, which spans the nanocomposites is formed, leading to the jump in the thermal conductivity.
3.6.2. Thermal Conductivity of BNNT-PDC Nanocomposite at Elevated Temperature

The changes of thermal conductivity as a function of temperature for different BNNT-PDC nanocomposites and pristine PDC are illustrated in Figure 17a. Phonons play an important role in the thermal conduction of the nano-composites. Above room temperature, thermal conduction is mainly affected by phonon-phonon interactions, and phonon scattering by lattice defects, impurities, secondary phases, pores and grain boundaries.

The scattering frequency of phonon increases as the temperature rises. An increase in scattering frequency of phonon will result in a decrease of thermal conductivity of the nano-composites, due to the decrease of phonon mean free path. Thermal conductivity $k$ can be expressed by [131]:

$$k = \frac{1}{3} C \nu l$$  \hspace{1cm} (7)

where $C$ is heat capacity, $\nu$ is the phonon velocity and $l$ is phonon mean free path. For pristine PDC and PDC with low volume fractions of BNNTs (e.g. volume fraction less than 22.2 vol.%), the thermal conductivity of the nano-composites is low because of the amorphous state of PDC. The lower bound of phonon mean free path is the lattice spacing. The amorphous PDC can be considered to consist of small crystals with a size of several lattice spacing. The value of the phonon mean free path of PDC therefore is within several lattice spacing. Because the PDC is still in an amorphous state under the measuring temperature, the phonon mean free path of PDC cannot be decreased further when the temperature increases, implying that the thermal conductivity of PDC is not sensitive to the temperature change. For the nanocomposites with high volume fractions of BNNTs (e.g. 35.4 vol.%), the thermal conductivity decreases significantly when the temperature increases (Figure 17a). BNNTs are in a nanocrystal state. Their phonon mean free path is estimated to be 40-320 nm [132] at 290 K. At high temperatures, the phonon mean free path of BNNTs will
decrease when the temperature rises. The reduction will be within a large range from 40-320 nm to several lattice spacing. Meanwhile, the heat capacity of the BNNT-PDC nanocomposites is stabilized at around 1 ±0.3 J/g·K, as shown in Figure 17b when the temperature is increased. This means that the decrease in thermal conductivity is mainly induced by the decrease of phonon mean free path of BNNTs when the temperature is increased according to Equation 7. Although the thermal conductivity of the nano-composites reduces with the increase of temperature, the reduction becomes more and more slow as the temperature increases, indicating that BNNTs are still effective in improving the thermal conduction of the nano-composites at elevated temperatures.

Figure 17. Change of (a) thermal conductivity (b) and heat capacity as a function of elevated measurement temperature.

3.7. Conclusion

This chapter presents a polymer derived ceramic (PDC) processing technique to make BNNT-reinforced ceramic composites with a high-volume fraction of BNNT (up to 35.4 vol.%). The nanocomposites were fabricated by first mixing the cured polysilazane and BNNTs, and then pyrolyzing the mixture at 1000 °C. TGA results showed that the nanocomposites have good
thermal stability at 900 °C in air. SEM observation revealed that BNNTs survive in the nanocomposites after exposure in air at 900 °C. The thermal conductivity of BNNT-PDC nanocomposites (with 35.4 vol.% BNNT) at room temperature was measured as 4.123 W/(m·K), increased by 2100 % compared to pristine PDC. Thermal conductivity of the nanocomposites increased as the BNNT content increased. A thermal conductivity percolation threshold was calculated as 36 ±5 vol.%. 
CHAPTER 4: DIELECTRIC PROPERTIES OF BNNT-PDC NANOCOMPOSITE

4.1. Rationale

Radome materials used in harsh working environments require low relative permittivity, and excellent resistance to thermal shock [133,134]. Electromagnetic (EM) waves should not be altered significantly when transmitting through these materials, which requires the real relative permittivity and the quality factor (Q, the inverse of dielectric loss tangent) of the materials to be within a limited level as $\varepsilon^\prime < 5$ and $Q \geq 100$ [134].

The common EM transparent materials used in harsh working environments are ceramics such as SiO$_2$ [135-138], BN (h-BN) [139, 140], and Si$_3$N$_4$ [133-136, 138-141]. However, SiO$_2$ and BN ceramics suffer from poor thermal shock resistance [142], while the Si$_3$N$_4$ ceramic has high real relative permittivity of 9.0 [133], which limits their wide application. Therefore, searching for new ceramic composites that can meet the stringent demand has become an urgent requirement for developing EM transparent materials.

As mentioned in earlier chapters, Polymer derived ceramics (PDCs) are class of ceramics that can be synthesized by direct thermal decomposition of liquid, melt, or organic solution polymeric precursors [117, 143, 144]. Different from conventional ceramics, properties of PDCs can be tuned by tailoring the chemical composition upon heat treatment [2, 145]. PDCs are known to possess good oxidation resistance and creep resistance at high temperatures. The polymer derived SiCN has fracture strength $< 1100$ MPa [146], fracture toughness ($K_{IC}$) 2-3 MPa-m$^{1/2}$ [2], Vickers hardness (HV) 15-26 GPa [146] and elastic modulus (E) 155 GPa [146].

The PDCs (often contained free carbon) with or without fillers were often designed for EM absorption application because their conductivity is tunable when the pyrolysis temperature is
changed. However, there are limited research on the application of PDCs as EM transparent materials. In addition, the PDCs also suffer from low thermal shock resistance due to their brittle performance in the harsh environment and require the introduction of reinforcements.

As mentioned in previous chapter, Boron nitride nanotubes (BNNTs) have a wide-band gap and a similar structure to carbon nanotubes (CNTs). BNNTs have attractive properties, such as excellent mechanical properties and high thermal conductivity, and hydrogen storage capability. BNNTs also show significant superiority in thermal and chemical stability compared to CNTs in air. Additionally, BNNTs possesses perfect electrical insulation [147-149] and superb oxidation resistance [114], which can be used to adjust the real relative permittivity, dielectric loss tangent of materials [150]. BNNTs therefore are excellent candidate [151] for reinforcing polymers [152-156], ceramics [157-159] and metals [160].

Therefore, PDCs reinforced with BNNTs are expected to be excellent ceramic composites to meet the EM transparent application requirements. PDCs reinforced with BNNTs have shown improved thermal stability, thermal conductivity, and excellent electrochemical performance [120]. Herein, we report for the first time about the electrical and dielectric properties of BNNTs-reinforced PDCs. Results of this work showed that PDC-BNNT nano-composites are satisfactory materials for EM transparent applications.
4.2. Materials and Methods

The matrix in this work is polymer-derived SiCN ceramic synthesized by thermal decomposition of polysilazane (HTT-1800 THERMAL CURE) purchased from Extreme Environment Materials Solutions (EEMS), LLC. The molecular formula of the liquid precursor is shown in Figure 1. Raw BNNTs with tube length over a few micrometers and diameter less than 5 nm (manufactured by BNNT, LLC) were used as reinforcements. 0.5 wt.% catalyzer (CLC-PB058, EEMS) was added for efficiently curing the liquid precursor. Figure 18 also shows the detailed fabrication process of the PDC-BNNT nano-composites. The liquid precursor was first cured at 350 °C in a flowing argon atmosphere. The cross-linked precursor was ball milled in 8000D Mixer/Mill®-Dual High-Energy Ball Mill to be powders. The BNNT puffballs was then dispersed in ethanol using Q500 Sonicator. The ball milled powders were then mixed with the dispersed BNNT solution under stirring. The mixture was then dried under stirring and ball milled for 5 minutes to make sure uniformly mixed. The final mixture was compressed under uniaxial pressure (3.4 MPa) into a 25 mm disk at room temperature. The shaped product was finally pyrolyzed at 1000 °C for 3 hours with a ramping rate of 1 °C/min under a high purity 4.8 grade nitrogen environment to obtain the PDC-BNNT nano-composite. The PDC-BNNT nano-composites with BNNT weight fractions of 0, 5, 10, 15, 20, 25 and 30 were marked as PB0, PB5, PB10, PB15, PB20 and PB25, PB30, respectively.

![Figure 18. Fabrication process of the PDC-BNNT nano-composites.](image-url)
The relative complex permittivity of samples was measured through the waveguide method according to ASTM D 5568-08. The microwave scattering parameters were measured by a vector network analyzer (Keysight, N5225A PNA, 10 MHz to 50 GHz). The relative complex permittivity of the samples was calculated based on the Nicolson-Ross-Weir (NRW) algorithm. The dimension of the samples was 7.112 mm×3.556 mm ×3.018 mm and the frequency range was from 26.5 to 40 GHz (Ka band).

Direct current (DC) resistivity of the nano-composites was measured by the I-V curve on Keithley 6514 series multimeter (Tektronix, Inc. Beaverton, USA) at room temperature. Carbon paint (SPI, West Chester, Pennsylvania, USA) was then pasted on the surfaces as the electrodes. The voltage used in the conductivity measurements is 5 mV. Three samples of each kind were used for the conductivity measurement.

The microstructure of the nano-composites was characterized by Raman spectroscopy, X-Ray Diffraction (XRD), field emission scanning electron microscope (SEM, FEI Verios 460L) and transmission electron microscopy (TEM, Talos F200X G2 (USA)). Raman spectra were obtained on LabRAM HR Raman microscopes (HORIBA Scientific) with the 442 nm line of Ar+ laser as the excitation source. XRD data were acquired using a Malvern PANalytical Empyrean X-ray diffractometer with Cu K-alpha radiation (wavelength 0.15418 nm) in a 2-theta range of 10 to 80 degree. The step size and time per step used in these measurements are 0.026 degree and 87 sec/step, respectively.

The chemical state of the elements in the nano-composites was evaluated by X-ray photoelectric spectroscopy (SPECS FlexMod XPS with Hemispherical analyzer PHOIBIS 150) with Mg kα excitation (1254 eV). Base pressure in the analysis chamber is in 10^{-10} mbar range. X-Ray
incidence angle is ~30° from surface and x-ray source to analyzer ~60°. Energy calibration was established by referencing to adventitious carbon (C1s line at binding energy of 285.0 eV).

The density of the composites ($\rho_0$) was calculated by measuring the weight and volume of the samples. As earlier reported, the density of the fully dense PDC 2.23 g/cm³, and the density of 1.38 g/cm³, are used as the theoretical densities of PDC ($\rho_{PDC}$) and the BNNTs ($\rho_{BNNTs}$), respectively. Three samples of each kind were measured for the density and porosity.

4.3. Microstructural Characterization

Figure 19 shows the XRD patterns of the BNNT-PDC nanocomposites. There are no evident peaks detected in the pristine PDC sample (it is difficult to find a broad peak for the main peaks for the matrix (111) peak for SiCN at 20 around 35°, PDF 01-074-2309 and graphite at 20 around 26°), indicating an amorphous structure of the ceramic. BNNT peaks can be observed in all the PDC-BNNT nanocomposites, evidenced by the increasingly obvious peaks for (002) and (101) plane for h-BN with the increase of the BNNT content. Above observation reveals that crystalline BNNTs are dispersed in the amorphous ceramic matrix.

![Figure 19. XRD patterns of the PDC-BNNT nanocomposites.](image)
To know the detailed composition of the PDC-BNNT nanocomposites, XPS analysis was conducted for the PDC-BNNT nanocomposites, as shown in Figure 20. The element survey of the pristine PDC indicates a composition of Si, C, N, O. The O was introduced during the dispersion of the catalyzer into the liquid precursor. The element survey also shows the introduction of BNNTs into the PDC-BNNT nanocomposites, evidenced by the B1s in Figure 20(b, c). To further investigate the atomic bond structure and the influence of O on the atomic bond structure of the nanocomposites, the C1s, N1s and Si2p peaks were fitted in Figure 20(d-i). The C1s spectrum can be split into C–Si, C=C, C–C, C–N/O, and C=N bonds, centered at around 282.7, 284.0, 285.1, 286.3, and 288.8 eV, respectively. The N 1s spectrum of the pristine PDC can be split into N–Si, N–C, and N=C bonds, centered at 397.2, 397.8, and 400.4 eV, respectively. The peak centered at around 398.6 eV in the PDC-BNNT nanocomposites can be attributed to the N–B bond for the BNNTs. The Si2p spectrum can split into Si–C, Si–N, and Si–O bonds, centered at 101.4, 102.6, and 103.7 eV, respectively. From these fitted results combined with the XRD results, the pristine PDC illustrates a amorphous Si–C–N network structure. The O mainly bonds with the PDC while not the BNNTs. The O might decrease the real relative permittivity of the PDC (FIGURE S1 in the Supplemental Materials). However, by the comparison of the Si2p of the pristine PDC and PDC with 25 wt.% BNNTs (FIGURE 20(f, i)), the O content is reduced and therefore the influence of O is reduced for the PDC-BNNT nanocomposites, which means that the dielectric property change of the PDC is mainly because of the BNNTs while not the O.

Figure 21(a-g) shows the SEM images of the PDC nanocomposites reinforced with different fractions of BNNTs. The pristine PDC reveals a morphology feature with angular dense sections, loose boundaries, and pores. Some of the BNNTs show bridging above the gaps in the PDC, as seen from the PDC nanocomposites reinforced with 5 wt.% BNNTs. Normally, the bridging of
BNNTs is beneficial for the toughness of the PDC. Some of the BNNTs lap together when the BNNT fraction increases to 10 wt.%. As the BNNT fraction increases to 25 wt.%, networks form in the PDC matrix. Such BNNT networks indicate that the nanotubes are well embedded and distributed uniformly in the PDC matrix.

Figure 21h is the TEM images and the corresponding selected area electro diffraction (SAED) of the PDC nanocomposites reinforced with 25 wt.% BNNTs. The (002), (100), (102) and (110) plane for h-BN verifies that the embedded nanotubes are BNNTs. The TEM image reveals that the BNNTs formed a percolation in the PDC matrix when the BNNT content is 25 wt.%. The percolation network will increase the difficulty for the electron to hop in the PDC matrix. Figure 21i shows a BNNT possessing clean interface with the PDC matrix, indicating that the BNNTs plays an inert filler role for the PDC system. The Fast Fourier Transform (FFT) of the framed area shown in Figure 21i reveals an amorphous structure of the PDC matrix.
Figure 20. XPS analysis of the PDC-BNNT nano-composites. (a, d-f) pristine PDC (PB0). (b) PDC with 10 wt.% BNNTs (PB10). (c, g-i) PDC with 25 wt.% BNNTs (PB25)
Figure 21. Morphology analysis of PDC-BNNT nano-composites reinforced with different fractions of BNNTs. SEM images for (a) 0 wt.%, (b) 5 wt.%, (c, d) 10 wt.%, (e-g) 25 wt.%. (h, i) TEM image of the PDC nano-composites reinforced with 25 wt.% BNNTs. The inset of Figure h is the corresponding selected area electro diffraction (SAED). The inset of Figure 21i is the Fast Fourier Transform (FFT) of the framed area.
The densities and porosity of pristine PDC and the nanocomposites with different weight fractions of BNNTs are shown in Figure 22. The PDC-BNNT nanocomposites is denser than the pristine PDC and the density of the PDC-BNNT nanocomposites slightly increases (the porosity slightly decreases) with the increasing BNNT weight fraction. The porosity of PDC reduces from 43.95 % to 35.11 % after addition of 25 wt. % BNNTs. BNNTs act as fillers during the pyrolysis of PDC precursor, which can inhibit the shrinking and reduce the porosity of the PDC.

![Figure 22. Porosity and density of the BNNT-PDC nanocomposites.](image)

**4.4. Electrical Properties of BNNT-PDC nanocomposite**

Figure 23a shows the Raman spectrum of the PDC-BNNT nano-composites. Two peaks around 1340 cm\(^{-1}\) and 1603 cm\(^{-1}\), associated with amorphous carbon and graphite respectively indicate the existence of free carbon in the PDC matrix. The peak at around 1375 cm\(^{-1}\) can be assigned to the h-BN. The electrical resistivity of PDC is associated with the sp\(^2\) carbon (G) in the PDC matrix. A percolation network of sp\(^2\) carbon will form when the pyrolysis temperature is above 1400 \(^{\circ}\)C [161]. In this work, because of the low pyrolysis temperature (1000 \(^{\circ}\)C), the percolation network is not formed, which results in a high electrical resistivity of the PDC matrix. Boron nitride
nanotubes (BNNTs) are electrically insulating materials as a result of the constant and wide band gap of about 5.5 eV for BN. Therefore, with the increase of BNNT content, the electrical resistivity sharply increases. Figure 23b shows the electrical resistivity of the PDC with different fractions of BNNTs. The electrical resistivity of the pristine PDC is around $10^6 \, \Omega \cdot m$. After addition of 5 wt.% BNNTs, the electrical resistivity of the nano-composites increases two order of magnitudes, reaching $10^8 \, \Omega \cdot m$. Further increasing the content of BNNTs does not drastically increase the electrical resistivity, indicating that the PDC-BNNT nano-composites have good insulating capability. The electrical resistivity change is mainly due to the charge carrier hopping within the PDC-SiCN matrix phase. The introduction of BNNTs might impede the electron hopping which originally can hop from the adjacent free carbon, as illustrated in the inset of Figure 23b.

![Figure 23. (a) Raman analysis of the PDC-BNNT nanocomposites. (b) Electrical resistivity of the samples as a function of BNNT fractions. Inset of figure illustrates the electron hopping.](image)

4.5. Dielectric Properties of BNNT-PDC nanocomposite

The relative complex permittivity and quality factor of the PDC-BNNTs with various fractions is shown in Figure 24. The average real ($\varepsilon'$) and imaginary ($\varepsilon''$) relative permittivity of the pristine
PDC is 2.94 and 0.026 in Ka band, which results in a high-quality factor (Q) of 134.40. The high Q factor suggests that the PDC matrix is a wave-transmitting material. After the loading of BNNTs, the real relative permittivity of the nano-composites decreases. The average real relative permittivity of the nano-composites decrease to 2.80 and 2.67, when the BNNT loading is increased to 5 wt.% and to 10 wt.%, respectively. The real relative permittivity of the nano-composites is further reduced when the BNNT content is higher than 10 wt.%, which is close to the value of BN reported in ref. [162]. The average imaginary relative permittivity (0.019) decreases, and the Q factor (176.77) increases when the BNNT content is 5 wt.% compared to that of the pristine PDC, which is due to the decreased porosity after introduction of the BNNTs. However, further increasing the BNNT content increases the imaginary relative permittivity and decreases the Q factor at low and middle frequency, which means that excess BNNTs cause material losses when interacting with the EM wave at these frequency range, although the real relative permittivity of the nano-composites further decreases. The Q factor shows an increase at high frequency when the BNNT content is high, which makes the average Q factor of the PDC further increase. For example, the average real relative permittivity decreases to 2.29, while the average Q factor increases to 208.60 when the BNNT content is increased to 30 wt.%. 
Figure 24. (a, b) Complex relative permittivity and (c) quality factor of PDC-BNNT with various weight fractions.
Effect of porosity on the real relative permittivity of the material can be described by the Lichtenecker–Rother equation [133]:

$$\log \varepsilon'_p = (1 - p) \log \varepsilon'_0$$

(8)

where $\varepsilon'_p$ and $\varepsilon'_0$ are the real relative permittivity of porous and dense materials, and $P$ is the total porosity. The real relative permittivity will decrease when the porosity is increased. Since the porosity in this work is decreased and the real relative permittivity is decreased when the BNNT content is increased, the decrease in the real relative permittivity of the PDC-BNNT nanocomposites is due to the introduction of BNNTs. However, the porosity influences the total real relative permittivity of the composites. The real relative permittivity of the pristine BNNTs was also measured using the PNA by pressing the BNNTs into disc samples. A density of 1.36 g/cm$^3$ was acquired after pressing the BNNTs, which is close to the theoretical density of BNNTs (1.38 g/cm$^3$). Therefore, the measured real relative permittivity of the pristine BNNTs should be close to the theoretical value in Ka band. The results are shown in Figure 25, which reveals that the average real relative permittivity of the pristine BNNTs is 3.57, almost similar to the experimental value of the pristine PDC (3.51, containing the porosity). Because the real relative permittivity of the PDC-BNNT nanocomposites is lower than that of the BNNTs, the porosity reduces the total real relative permittivity of the composites.
Figure 25. Calculated theoretical real permittivity of the pristine BNNTs and the pristine PDC

As fillers, the BNNTs can reduce the shrinkage and porosity of the PDC during pyrolysis [4]. Therefore, the main effect of the BNNTs is to increase the Q factor (decrease the loss tangent) of the nanocomposites according to the following equation:

\[ \tan \delta = (1 - P) \tan \delta_0 + P(AP^{n-1}) \]  \hspace{1cm} (9)

where \( \tan \delta_0 \) is the loss tangent of the fully dense material, \( n \) is a constant larger than 1, \( P \) is the volume fraction of pores, and \( A \) is a constant coefficient. Besides, the BNNTs can increase the electrical resistivity of the PDC according to the electrical property shown in Figure 23b.

The relationship between the real relative permittivity and imaginary relative permittivity of PDC-BNNT nanocomposites is plotted in Figure 26. As shown, the relationship between the real relative permittivity and imaginary relative permittivity of PDC without BNNTs and with 5 wt.% and 10 wt.% BNNTs reveals similar dielectric characters to that of the pristine PDC, indicating that there is no additional dielectric loss introduced in the PDC after addition of BNNTs. This phenomenon
verifies the electromagnetic transparent characteristic of PDC SiCN after reinforced by the BNNTs. The relationship between the real relative permittivity and the imaginary relative permittivity of PDC with BNNT content higher than 10 wt.% reveal helical lines, indicating that the dielectric loss might be caused by the Lorentz resonance relaxation process when the BNNT content is higher than 10 wt.%, which can be described by the following equation [163]:

\[
(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon'')^2 = \frac{(\varepsilon_0 - \varepsilon_\infty)^2}{[1 - (f / f_r)^2]^2 + (f / f_d)^2} \tag{10}
\]

where \(f_d\) and \(f_r\) are the Debye relaxation and natural resonance frequencies defining the shape of dispersion curve respectively. When the frequency increases, the locus of Eq. 10 becomes a helical line due to varying radius of the circle. The relationship between the real relative permittivity and the imaginary relative permittivity of PDC-BNNT nanocomposites indicates that dielectric loss occurs in the nanocomposites after addition of high fractions of BNNTs.

Figure 27 compares the dielectric properties of the PDC-BNNT nano-composites with other typical ceramic composites that can be used for EM transparent materials (dielectric loss meets the requirement for EM transparent application) in the literature overlapping with the Ka band (26.5-40 GHz). It can be seen that our ceramic composites have a lower real relative permittivity compared to that reported in these references, which means that more EM wave can enter into the materials. Also, the quality factor of the PDC-BNNT nanocomposites can be tunable based on the BNNT content to meet the requirement for EM transparent application. These features make it an attractive ceramic composite with good thermal shock, corrosion resistance and EM transparent properties.
Figure 26. Relationship between the real relative permittivity and imaginary relative permittivity of PDC-BNNTs with various weight fractions.
Figure 27. Comparing the dielectric properties of PDC-BNNT composites with other typical ceramics (ceramic composites) with similar dielectric property for EM transparent applications, frequency overlapping the Ka band [164-169].

4.6. Effect of Moisture on the Dielectric Property of BNNT-PDC Nanocomposite

To analyze the effect of moisture on the dielectric property of the PDC-BNNT nanocomposites, water was introduced into the samples by immersing the samples in a container with distilled water in vacuum at room temperature. The water content of the samples was calculated according to the weight gain periodically recorded by a high precision analytical balance. Before measurement, the residual surface water was removed using a lint-free cloth. Figure 28 shows the real relative permittivity and Q factor of the pristine PDC (PB0) and PDC with 5 wt.% BNNTs (PB10) under different water contents. As seen from the results, the moisture increases the real relative permittivity and decreases the Q factor of the materials. However, the moisture has a small effect on the dielectric properties of PB5 when the water content is low. The average real relative permittivity of the PB5 under water content of 0.69 wt.% and 1.37 wt.% is 2.81 and 2.91,
respectively (the value without moisture is 2.80). The average Q factor of the PB5 under water content of 0.69 wt.% and 1.37 wt.% is 108.21 and 48.20, respectively (the value without moisture is 134.40).

Figure 28. Effect of moisture on the dielectric properties of (a-c) the PB0 and (d-f) PB5 samples
4.7. Conclusion

Dielectric properties of different weight fractions of boron nitride nanotube (BNNT) reinforced ceramic composites fabricated by the polymer derived ceramic (PDC) processing route have been investigated in this paper. After the addition of 5 wt.% BNNTs, the electrical resistivity of the nanocomposites increases two orders of magnitudes, reaching to $10^8 \, \Omega \cdot m$. Further increasing the content of BNNTs does not evidently increase the electrical resistivity, indicating that the PDC-BNNT nanocomposites have good insulating property. The average real relative permittivity of the PDC decreased from 2.94 to 2.80, while the quality factor (Q) of the PDC increased from 134.40 to 176.77 when the BNNT content is 5 wt.%., which is due to the decreased porosity after introduction of the BNNTs. Further increasing the BNNT content decreases the real relative permittivity of the nanocomposites and increases the Q factor at high frequency. The average real relative permittivity decreases to 2.29, while the average Q factor increases to 208.60 when the BNNT content is increased to 30 wt.%. Relationship between the real relative permittivity and the imaginary relative permittivity of the PDC-BNNT nanocomposites showed that the dielectric loss with a high loading fraction of BNNTs may be caused by a Lorentz resonance relaxation process. Results of this work illustrated a satisfactory microwave transparent material system when the BNNT loading is lower than 10 wt.%.
CHAPTER 5: MULTIFUNCTIONAL CERAMIC COMPOSITE SYSTEM FOR SIMULTANEOUS THERMAL PROTECTION, ELECTROMAGNETIC INTERFERENCE SHIELDING FOR CFRPs

5.1. Rationale

Polymer matrix composites play an important role in aerospace and defense applications. For example, modern commercial airplane structures contain 20-70% of polymer matrix composites [170]. 35% of airframe weight of F-35 consists of structural composites [171]. The reason for the wide usage of polymer matrix composites is their exceptional strength-to-weight ratio and high specific modulus relative to metallic materials [172]. Carbon fiber reinforced polymer (CFRP) composites are one kind of polymer matrix composites commonly used in the above applications due to their exceptional strength and physical properties [173]. However, when CFRP is exposed to high temperatures, the polymer matrix is subjected to material degradation. Typical polymer matrixes are epoxy and bismaleimides (BMI), whose maximum service temperatures are around 180 °C and 232 °C, respectively [174]. Degradation in the mechanical properties occurs when these polymer matrixes are applied above their maximum service temperatures. The degradation includes decomposition of the polymer and delamination of fibers, resulting in the loss of structural integrity of the composites [175, 176]. For aerospace applications, at Mach 2.0, the skin temperature of the aircraft is usually above 100 °C while it can go up to 120 °C at Mach 2.2, and even further to 150 °C at Mach 2.4 [177]. Typically, thermal degradation of CFRPs is not a concern at Mach 2.0 and below. However, as aircrafts become more dependent on higher speed, temperature as a design parameter becomes more paramount. This therefore means that as the temperature of the aircraft’s skin increases (> 150 °C), the polymer matrix of CFRP becomes susceptible to thermal degradation. It is imperative to develop a light weigh protective material
that can protect CFRP structures in thermo-oxidative environment. To meet the requirement of thermal protection, the material should have low thermal conductivity as well as good thermal stability. The thermo-physical properties such as coefficient of thermal expansion (CTE), specific heat, thermal conductivity, heat flux [178], etc. are important in evaluating the material performance, especially those considered for high temperature applications [178, 179].

Electromagnetic (EM) radiation, such as lightning and other intentional EM interference, is another severe issue threatening the security of the aircrafts and their equipment [180-183]. These environments require the structures to be protected from the electromagnetic interference (EMI). High-performance EMI shielding properties for the materials are therefore highly required. To meet this requirement, the high electrical conductivity is required for the EMI shielding materials to reflect or absorb the EM radiation. For the absorption dominant EMI materials, both the skin depth (surface currents) and characteristic impedance are the key components. The skin depth should be small enough to make the coating as thin as possible [184]. And the characteristic impedance should match with the free space to allow the EM wave to enter into the coating.

Considering the above requirements, it is urgent to develop an effective coating system possessing thermal protection while simultaneously shielding against electromagnetic wave interference to ensure overall aircraft safety. However, the challenge for designing such multifunctional material systems is that most of the materials with high electrical conductivity also pertain high thermal conductivity. In open literatures, it is difficult to find such multifunctional systems that can offer such a dual protection mechanism for CFRP.

To address the aforementioned problems, a novel multi-layered ceramic composite system which can provide excellent thermal protection for the CFRP and simultaneously possesses excellent EMI absorption shielding ability was prepared. This system is different from common polymer
coatings which has limited-service temperature. This system contains polymer derived ceramic (PDC) silicon carbon nitride (SiCN) [117, 142]. The PDC SiCN has a room temperature specific heat 0.739 J/g·K, and thermal conductivity as low as 0.193 W/m·K [185]. The PDC SiCN prepared in our previous work was amorphous and will keep amorphous when the application temperature is below its pyrolysis temperature (1000 °C). However, the PDC SiCN has a thermal expansivity of 3.08-3.96 10-6 K-1 [186] and the amorphous PDC is brittle. Therefore, in order to toughen the PDC, the proposed system also contains YSZ fibers, which have low thermal conductivity (2.0 W/m·K (RT-400 °C)) and low specific heat (0.45-0.5 J/g·K (RT-400 °C) [187]), high thermal stability, and high resistance to spallation under thermal fatigue [188-190]. The YSZ reinforced PDC will provided the basic thermal protection for the CFRP via lattice vibrations because both YSZ and amorphous PDC are good thermal insulators. The system also contains CNTs which will provide the ceramic composites EMI shielding ability. The EMI shielding ability of the CNTs will depend on the free electron plasma oscillations. The plasma also acts as a microwave absorber. The free electron plasma oscillations are strongly coupled to the lattice vibrations and will reduce the thermal insulation ability of the composites. Therefore, to account for this effect, the composite system was designed as a multi-layered structure such that the YSZ reinforced PDC layer was used in the top and bottom of the composite to provide the thermal protection. The inter layers contain both YSZ reinforced PDC and CNTs to provide the EMI shielding for the CFRP. Because of its dielectric properties, the YSZ reinforced PDC layer also serves as impedance matching layer for the composites.
5.2. Materials and Methods

5.2.1. Materials

Unidirectional YSZ fiber (Zirca Zirconia, Inc. USA) with a bulk density and porosity of 1.02 g/cc and 87% respectively was used as the reinforcement. Rigidizer (Zirca Zirconia Inc. USA) having the same composition (90 wt% of ZrO₂ and 10 wt% of Y₂O₃) as the YSZ fibers was also used. The rigidizer is in the liquid state and it is comprised of sub-micron particles of yttria stabilized zirconia suspended in a zirconium acetate aqueous solution. Raw carbon fiber epoxy prepreg (AF254, Tg=135°C) from Stratton Composites Solutions was used to prepare the CFRP laminate. Durazane 1800 (Starfire Systems Inc.) was the polysilazane (PSZ) used in this work. PSZ is a type of preceramic precursor for silicon carbon nitride ceramics. Multi-walled carbon nanotubes (OD = 8-15nm, Length \( \sim \) 50 µm) was used as the electrical conducting phase for improved EMI shielding property.

5.2.2. Multifunctional composite fabrication

Firstly, YSZ fiber preform is infiltrated with low concentration CNT solution (2.5 mg/ml) by dipping the preform in the solution and subsequently dried at 100 °C. This process was repeated seven times to achieve uniform distribution of CNT on the fiber. Afterwards, the preform was further infiltrated with high concentration CNT solution (5.0 mg/ml) by the vacuum assisted method with the aid of a filtration set-up. The preform was turned over when one filtration cycle is completed to ensure CNTs are coated on both sides thereby forming a YSZ-coated CNT layer.

A second layer was prepared by infiltrating the YSZ preform with the rigidizer to increase the volume fraction of YSZ in that layer. Then, the YSZ-coated CNT layers were sandwiched between two YSZ-infiltrated rigidizer layers to form a multi-layered structure. The multi-layered structure
was placed in an oven at 150 °C for 3 hours to convert the rigidizer into fully stabilized YSZ ceramic structure. Afterwards, the liquid PSZ solution was infiltrated into the multi-layered structure. The infiltration was carried out under vacuum for 30 minutes and samples were cured immediately at 140 °C for 3 hours. The product was finally pyrolyzed at 1000 °C for 3 hours with a ramping rate of 5 °C/min under a high purity 4.8 grade nitrogen environment to obtain the multi-layered ceramic composite (interchangeably referred to as multi-functional composite layer in this study). For detailed analysis of this study, the sandwiched YSZ preforms were prepared under different states (high CNT concentration, low CNT concentration and no CNT). Six kinds of samples were fabricated based on the composition shown in Table 6. The unique structural design of the multifunctional composite consists is to ensure that the thermal protection and EMI absorption goals are achieved. The two outer layers of our multi-layered composite structure are made up of YSZ and SiCN phases, which helps to impede the thermal flux from the environment for improved thermal protection and improve impedance match which allows more EM wave to transmit into the sample. The inner layers which are consist of CNT, YSZ and SiCN phases. The CNT phase has good mobile charge carriers due to its high electrical conductivity that can interact with the incoming EM radiation, thereby improving EMI shielding. However, in other to have a systematic study of the effect of increased CNT content in EMI shielding performance, the number of YSZ-coated with CNT layers were subsequently varied. This was represented as “N” in Figure 29. Sample A, B, C and D represents multi-functional composite with 1, 2, 4 and 6 YSZ-coated with CNT layers, respectively. For further detailed study on the effect of CNT in property performance, the inner layers were also prepared with low CNT content and no CNT at all. Sample E and F represents multi-functional composite with 4 layers each of YSZ-coated with low CNT content and pure YSZ (no CNT), respectively.
Through a hand-layup process, the multi-functional composite layer was carefully placed on stacked plies of carbon fiber prepreg. The lay-up was then housed in a vacuum bag system for the co-curing process under isothermal compression molding using a hot press. This was done by preheating the hot press chamber at 275 °F followed by immediate vacuuming before applying pressure at 30 psi for 30 minutes. Through this way, the epoxy resin from the prepreg is forced out to bond with the multi-functional ceramic composite. Afterwards, the mold and part were cooled below 200 °F before demolding. The product from the co-curing process bonds the multi-functional ceramic composite onto the CFRP, which is referred to as the hybrid composite.

Figure 29. Fabrication process of the multi-layered ceramic composite.
Table 6. Composition of different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT/YSZ mat layer (high conc.)</th>
<th>CNT/YSZ mat layer (low conc.)</th>
<th>YSZ layers</th>
<th>Top YSZ layer</th>
<th>Bottom YSZ layer</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.6</td>
</tr>
<tr>
<td>D</td>
<td>6</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2.4</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.6</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

5.2.3. Characterization Techniques

The S parameters of the samples were measured in Ka band (26.5–40 GHz) through the waveguide method using a vector network analyzer (Keysight, N5225A PNA, 10 MHz to 50 GHz). The dimension of the samples was 7.112 mm × 3.556 mm × (0.600-3.018) mm. The permittivity of samples was calculated based on the NRW algorithm.

The direct current (DC) conductivity was measured at room temperature by the I-V curve on Keithley 2000 multimeter (Tektronix, Inc. Beaverton, USA). Resistance was measured from the I-V curves, and the electrical conductivity was calculated. The sample surface was polished to 1 µm finish. Carbon paste (SPI, West Chester, Pennsylvania, USA) was applied on the sample’s surface as the electrodes.

The microstructure of the samples was characterized by Raman spectroscopy, field emission scanning electron microscope (SEM, FEI Verios 460L) and Transmission electron microscopy
(TEM, Talos F200X G2 (USA) microscope operated at 200 KeV, samples were prepared with Focused Ion Beam (FIB) milling by FEI Quanta 3D FEG (USA)). Raman spectra were obtained on LabRAMHR Raman microscopes (HORIBA Scientific) with the 442 nm line of Ar$^+$ laser as the excitation source.

The bonding strength of the multi-functional composite on CFRP at room temperature was measured using a PosiTest adhesion tester (AT-A DeFelsko Corporation, Ogdensburg, US). The instrument conforms to international standards such as ASTM C1583 and ISO 4642. The instrument is made up of an electronically controlled hydraulic pressure system (with ±1% calibration accuracy) that can grip onto a self-aligning aluminum dolly (20 mm diameter) which ensures accurate measurement on uneven and smooth surfaces. The aluminum dolly is attached of the sample’s surface via a cyanoacrylate glue and a precut deep into the coating layer is made around the dolly. Then the hydraulic pump automatically applied smooth and continuous pull off pressure (0.2 MPa/s) on the dolly and the corresponding pressure value is shown on a display panel. The pull-off strength is automatically recorded when pull-off happens. The equipment and method used to measure the pull-off bonding strength of the hybrid were shown in the Supporting Information (Figure 30).

![Figure 30. Equipment and method used to measure the pull-off bonding strength of the hybrid.](image-url)
The thermal conductance test can help give a good insight into the multi-layered ceramic composite’s ability to resist or allow the flow of heat through it. Two aluminum blocks (19.05 × 19.05 × 38.10 mm, 19.05 × 19.05 × 127 mm) are used to sandwich the test sample and facilitate the heat flow across it. The base of the bottom aluminum block is supplied with a constant heat flux source (Joule heating) with the help of a heater connected to a power source. All surfaces of the two aluminum blocks except for the surfaces in contact with the test sample and top surface of the upper aluminum block were insulated with glass fiber to minimize the heat loss in the lateral direction. To reduce contact resistance between the aluminum and the test piece, a high thermal conducting (6 W/mK) silicone pad (AIYUNNI thermal pad, Amazon Inc.) that conforms and fills surface gaps was used. The material system contains top and bottom YSZ/PDC layers which have lower thermal conductivity than the silicone pad. The increase of the number of the YSZ/PDC/CNT (CNT contained) layer will not significantly increase the superficial conductance of the material, because the CNT contained layers are sandwiched between the two thermal insulation layers. Therefore, the white noise (large fluctuations) in thermal measurements will not dominate the results. All surfaces of the two aluminum blocks except for the surfaces in contact with the test sample and top surface of the upper aluminum block were insulated with glass fiber to minimize the heat loss in the lateral direction. The experimental setup is similar to that used by Lee et al. [191]. With the insulation on the sides of the aluminum block, heat flux at the bottom is driven upwards (top aluminum block is opened to ambient) making the heat transfer (conduction) in the system in only one direction (along the x-axis in Figure 31a). A steady state heat conduction experiment was performed to measure the overall conductance of the material system. Temperature in the two aluminum blocks were measured at eight different points at a time interval of about 30 minutes until two successive readings differed by less than ±0.1 °C. The thermocouples
were located along the intersection of the centerline. The 1D heat equation (Eq. 11) from the linear temperature distribution at steady state conditions within the aluminum block can be solved as:

\[
\frac{d^2T}{dx^2} = 0
\]  

(11)

\[T(x) = c_1 x + c_2\]  

(12)

Linear extrapolation was used to calculate the temperature on the hot surface \(T_h\) and the cold surface \(T_c\) of the test sample using the lower and upper aluminum block temperature distributions, respectively. The heat conduction from bottom to upper aluminum block through the test material can be written as shown in Eq. 13.

\[q_{\text{conduction}} = \frac{T_h - T_c}{R_t}\]  

(13)

where \(T_h\) and \(T_c\) are the temperatures, and \(R_t\) is the thermal resistance of the test material. The current study focuses on the total material systems’ ability to conduct temperature across CFRP base material, which has been represented in terms of thermal conductance along the through-thickness direction as shown in Eq. 14. The setup of the measurement is illustrated in Figure 31a. Three samples for each category were measured.

\[h_c = \frac{q_{\text{conduction}}}{T_h - T_c} = \frac{1}{AR_t}\]  

(14)

The set-up for the flame tests is shown in Figure 31b to evaluate the thermal protection performance of the multi-functional composite in high temperature conditions. A propane cylinder with its torch (Ace Hardware Corp. U.S.A.) served as the temperature source for heating the surface of the test piece. The set-up was arranged in a way that the flame is perpendicular to the surface of the test piece and then the IR camera was placed in a position where the heated area can be captured. A k-type thermocouple was attached to the back of the sample and connected to a
multimeter and then to a DAQ unit to take real time temperature readings. The IR camera was calibrated with a thermocouple before the start of the tests. The test piece was housed in a stainless-steel holder.

Figure 31. (a) Thermal conductance measurement setup of the samples, (b) Schematic drawing of the flame test set-up, (c) infrared (IR) camera image of the sample during the flame test.

5.3. Microstructural and Bonding Strength Characterization

Figure 32a shows the optical images of different materials. The YSZ mat is white in color. After infiltrated with low concentration CNT solution, a small weight change of 2.3% was recorded and it is evident by the color change from white to gray (YSZ/CNT\textsubscript{L}). Further infiltrating CNTs of high concentration gives a weight change of 12.92% and the color changes to complete black (YSZ/CNT\textsubscript{H}), indicating high content of CNTs in the mat. The pyrolyzed ceramic mats reveal dark color because of the presence of PDC in the samples (conversion of polysilazane to ceramics). Figure 32b shows the porosity and density of different samples. The porosity of CNT containing samples A-D show similar values of around 24-28%, while the density displays a decreased trend with the increase of the CNT containing layers in samples B, C and D due to increased CNT content in the samples. Finally, the bonding morphology of the interface was also characterized. Figure 32c shows cross section of the hybrid composite under SEM. The two layers can be clearly
seen to display good bonding behavior without any form of defects such as voids indicating that the co-curing method was effective.

Figure 32. Optical images (a), porosity and density (b) of different samples and (c) SEM cross-section of hybrid composite showing the bonding interface.
Figure 33 shows the TEM images of the cross section of sample D. In Figure 33a, the YSZ-PDC layer (top) and YSZ-CNT-PDC layer (bottom) can clearly been seen, which can be verified by the corresponding enlarged views of selected areas A and B. In Figure 33b (enlarged view of area A), the SAED image reveals that the particle-like phase shown in area A is YSZ fiber, evidenced by the (111), (200), (220) and (311) for c-ZrO$_2$. The phases between the particle-like phase in area A in Figure 33a are composed of PDC and rigidizer, as shown in Figure 33b and the corresponding enlarged view in Figure 33c. In Figure 33d (the enlarged view of area B in Figure 33a), the SAED image also reveals c-ZrO$_2$, which verifies that area B is composed of YSZ fiber, PDC and CNTs (shown in the following enlarged views).

PDC is present between the YSZ fibers. A CNT layer can be clearly seen between area A and area B in Figure 33a. The YSZ fiber is composed of many small grains, as shown in Figure 33b and Figure 33d. The CNT network (the d-space of the CNT is 0.34 nm [192]) can be observed by the enlarged view of the area between the YSZ fibers (Figure 33e). Free carbon (d-space 0.34 nm) can also be observed from this area. The existence of CNT network and free carbon largely connects the YSZ fibers and improves the electrical conductivity of among the YSZ fibers. CNTs can also been found in the gaps within the YSZ fiber bundles, as shown in Figure 33f, which also increases the electrical conductivity of the YSZ fibers.
Figure 33. TEM images of sample D. (a) Lower magnification image showing the two different layers that make up multi-layer ceramic composite, (b) Enlarge view of Area A from Figure 33a, (c) Enlarge view of Figure 33b, (d) Enlarge view of Area B in Figure 33a, (e) Enlarge view of Figure 33d, (f) CNTs present between YSZ fiber gaps. Inset of figure b and d are the SAED images, inset of figure e shows the enlarged views of the representative free carbon area and CNT area, respectively.
The bonding strength of the co-cured sample (Sample HA) was recorded and compared to a commercially available epoxy adhesive (Aremco Bond 526N, Aremco Inc. USA) (Figure 34a). The Aremco bond was applied between the composite layer and CFRP and then cured at 94 °C for 2 hours under constant pressure of 30 psi. Three samples were measured for each case. According to the result, the bonding strength of the co-cured sample is recorded as 3.1 ± 0.1 MPa which is about two folds greater than that of the commercial adhesive-bonded sample (1.5 ± 0.2 MPa). The pulled-off surface was characterized with the optical microscope to understated the failure mode after pull-off. Figure 34b presents the surface of the co-cured sample after pull-off bonding test showing a rough morphology and some fiber pull out. This indicates a cohesive failure mode because major failure occurred in the substrate [193, 194]. On the other hand, the commercial adhesive-bonded sample shows an adhesive failure since much of the failure occurred at the adhesive region (Figure 34c), which is why the bonding strength value was relatively lower.

It is believed that the multifunctional composite is held on CFRP through an interlocking mechanism which directly influence the bonding strength. The interlocking occurs because of the irregularities and unevenness on the multifunctional composite’s surface. Therefore, the excess epoxy from the prepreg is forced to occupy those surface gaps during the co-curing process. After the co-curing process is complete, the cured epoxy acts as an effective adhesive between the two layers.
Figure 34. (a) Bonding strength of co-cured sample compared to adhesive-bonded sample.

Optical images of (a) co-cured sample and (b) Aremco bonded sample after bonding test.

5.4. Thermal Protection Investigation of Composite Layer

5.4.1. Thermal Insulation Test

Figure 35a shows the temperature distribution of different samples measured by the set up shown in Figure 31a. The temperature drops evidently at the connections between the samples and the blocks. The temperature difference (Figure 35b) of sample D is large and is obviously larger than that of the CFRP, illustrating the good thermal protection of our sample. The good thermal protection results in the large temperature difference of the hybrid composite sample HD (after sample D has been bonded on CFRP). Thermal conductance of different samples is shown in Figure 35c. The CFRP has a thermal conductance of more than 530 W/m²K. With the ceramic
composites, the thermal conductance is effectively reduced. Sample D has a conductance of less than 411 W/m²K, which is about 22.5% reduction relative to the CFRP. Sample E and F have conductance as low as around 352 W/m²K and 355 W/m²K, respectively due to little and no presence of CNTs in the samples. These results reveal that the composite layer can effectively improve the thermal insulation ability of the CFRP. From Figure 35c, the superficial conductance reduces from sample A-D to sample D-F and temperature difference occurs in A-C to D-F to the next class of samples. Generally, the thickness of the composite is directly proportional to its thermal resistance. Besides, the thermo-physical properties of materials play an important role in the heat transfer. In this study, three kinds of materials (YSZ, PDC, CNTs) with different thermo-physical properties were used. Since the top and bottom layer of composite are composed of thermal insulating material of YSZ/PDC, when the number of CNT containing layer (YSZ/PDC/CNTs) is small, the superficial conductance is dominated by these two layers. The superficial conductance and temperature difference are not sensitive to thickness when the number of CNT containing layer is small. Even with an increase by one or two CNT containing layers, it will not result in significant increase of superficial conductance and temperature difference. For the samples E and F, they both have the same thickness (1.6 mm) as sample C. Sample C consists of four layers of YSZ-coated with high CNT content (CNT₇). This means the resultant composite for this thickness with exhibit higher superficial conductivity compared to samples E and F. Sample E and F consist of 4 layers each of YSZ-coated with low CNT content (CNT₈) and pure YSZ (no CNT), respectively. Lower or no CNT content means lower superficial conductance of the resultant composite and hence the trend observed.
Figure 35. Thermal conductance results (a) temperature distribution profiles used to calculate $T_h$ and $T_c$ (b) Temperature difference ($T_h - T_c$) of different samples and (c) thermal conductance ($h_c$) of different samples
In addition, the effect of combined composite layer and CFRP system has been studied under typical operating conditions of $T_h \approx 300$ °C at steady state conditions. The multi-functional ceramic composites were bonded onto CFRP separately and will be referred to as hybrid composites. Performing a simple energy balance on each of the hybrid system gives an interesting insight into the effect of the thermal protection layer on the CFRP base. Using the 1D conduction model, similar to a composite wall on the hybrid system, we can estimate the temperature at the interface ($T_{int}$) between composite material and CFRP using Eq. 15. Table 7 depicts the temperature distribution for the hybrid systems. It can be observed from Figure 35 that the ceramic composite’s layers perform the task of insulation by drastically reducing the temperature at the interface of ceramic composites and CRFP. For example, when the surface temperature hybrid composite D (HD) is 300 °C, its interface temperature is 167.8 °C. Thus, performing the required function of protecting the CFRP from harsher thermal conditions.

$$k_{ceramic\ layer}(\frac{T_h-T_{int}}{l_1}) = k_{CFRP}(\frac{T_{int}-T_c}{l_2})$$

(15)

where $l_1$ and $l_2$ are the thicknesses of the ceramic layer and CFRP, respectively.

Table 7. Temperature distribution across the hybrid composite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hybrid composite thickness (mm)</th>
<th>Multi-functional composite layer thickness (mm)</th>
<th>$T_h$ (°C)</th>
<th>$T_{int.}$ (°C)</th>
<th>$\Delta T$ (°C)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>2.9</td>
<td>1.1</td>
<td>301.3</td>
<td>208.5</td>
<td>92.8</td>
<td>114.1</td>
</tr>
<tr>
<td>HD</td>
<td>3.8</td>
<td>2.4</td>
<td>300.0</td>
<td>167.8</td>
<td>132.2</td>
<td>90.2</td>
</tr>
<tr>
<td>HF</td>
<td>3.4</td>
<td>1.6</td>
<td>304.8</td>
<td>178.9</td>
<td>125.9</td>
<td>1.98.3</td>
</tr>
</tbody>
</table>
5.4.2. Flame Test

To further illustrate the thermal insulation ability of the multi-layered ceramic composites during transient conditions, flame test was conducted for the hybrid composite samples. The front and back surface temperatures of the samples are plotted in Figure 36. The front temperature represents the temperature that the hybrid composites or CFRP is exposed to. It can be seen that the ceramic layer can obviously reduce the heat penetrating into the CFRP as shown by the back-surface temperature of the samples during the flame test, which illustrates the effectiveness of the ceramic layer. For example, after about 85 seconds burning time, the temperature difference of HD is around 72.9 °C (shown by the arrows in Figure 36c) while CFRP’s temperature was 25.1 °C during that same period. The insulation performance of the HD investigated under high temperature settings also show a maximum temperature difference of 280.7 °C. CFRP was not investigated under high temperature settings due to its limitation to survive under that condition.

Raman analysis of different samples is shown in Figure 36f. The spectrum exhibits three major bands corresponding to carbon (D band centered at 1350 cm⁻¹, G band centered at 1580 cm⁻¹, and 2D band centered at around 2700 cm⁻¹). The D peak originates from the breathing of the sp² carbon atoms in rings and the G peak results from the in-plane bond stretching of the sp² carbons. The 2D peak is the second order of the D peak and caused by the double resonant Raman scattering with two-phonon emissions. The spectrum of CNTs exhibits the major bands G and 2D while with small D peak, indicating well crystallization of the CNTs. The spectrum of the PDC exhibits the major bands G and D with D band the major peak, revealing the existence of amorphous carbon in the PDC. The spectrum of multi-layered ceramic composite reveals similar peaks to the CNTs, indicating that the CNTs were successfully introduced into the system.
Figure 36. Front and back temperature of different samples during the flame test. (a) sample CFRP at low temperature setting, (b) sample A at low temperature setting, (c) sample D at low temperature setting, (d) sample D at high temperature setting, (e) sample F at high temperature setting, (f) Raman analysis of different samples.
A control experiment of the CNTs before and after heat treated at 1000°C for 3 hours with a ramping rate of 5°C/min under a high purity 4.8 grade nitrogen environment was conducted to compare the characterization results. The results (Raman spectra of the CNTs before and after heat treated) have been shown in Figure 37. Three measurement points were taken for the CNTs before and after heat treated, respectively. The average value of $I_G/I_D$ was calculated. The $I_G/I_D$ of the CNTs before heat treated is 5.86, while that after heat treated is 6.29. The two values are close, and the formation of graphitic structures are possible but not the main reason for the improved conductivity. The broad D and G bands from the composites is because of the PDC which has low crystallinity of free carbon, as shown from the comparison between the Raman spectra of pure PDC and CNTs shown in Figure 36f. Besides, from Figure 37, the CNTs before and after heat treatment show the similar broad D and G bands. Therefore, CNTs should be maintained inside the material.

![Raman spectra](image)

Figure 37. Raman spectra of the CNTs before and after heat treated at 1000°C for 3 hours with a ramping rate of 5°C/min under a high purity 4.8 grade nitrogen environment.
The Raman spectrum of the samples (C and D) after flame test shows similar characterization to the multi-layered ceramic composite before flame test. The G and D peaks are broadened, and their ratio is reduced, indicating damage to CNTs by the flame when the temperature is higher than the oxidation temperature of CNT (370 °C). However, our composite layer can be used at temperatures above the application temperature of CFRP.

To further observe the microstructural change of different samples before and after flame test, SEM images of the cross section of the samples before and after flame test are shown in Figure 38. The samples before flame test (sample D and sample E shown in Figure 38 (a, b) and Figure 38(c, d)) show compact structure except for some voids that were not infiltrated during the fabrication process. The corresponding enlarged views (Figure (b, d)) reveal good bonding between the fibers and matrix. Figure (38e-j) are the images for sample A, sample D and sample E after low temperature flame test, which indicate similar structures compared to those before flame test. These observations suggest good structural stability of our materials at elevated temperature. Our materials also have the potential to protect other substrates used in higher temperature applications. From Figure 38(k, l), the composites after the high temperature flame test still have similar structure to those before flame test.
Figure 38. SEM images of the cross section of the samples before and after flame tests. (a) sample D before the flame test (low magnification), (b) sample D before the flame test (high magnification), (c) sample E before the flame test (low magnification), (d) sample E before the flame test (high magnification), (e) sample A after flame test (low temperature setting, low magnification), (f) sample A after flame test (low temperature setting, high magnification), (g) sample D after flame test (low temperature setting, low magnification), (h) sample D after flame test (low temperature setting, high magnification), (i) sample E after flame test (low temperature setting, low magnification), (j) sample E after flame test (low temperature setting, high magnification), (k) sample C after flame test (high temperature setting, low magnification), (l) sample C after flame test (high temperature setting, high magnification).
5.5. EMI Shielding Performance

The total EMI shielding efficiency \( SE_T \) can be characterized as follows [132]:

\[
SE_T = SE_R + SE_A + SE_M
\]

(16)

in which \( SE_A \), \( SE_R \) and \( SE_M \) denote the EMI shielding efficiency due to reflection, absorption, and multiple reflections, respectively. \( SE_T \), \( SE_R \) and \( SE_A \) were calculated from the S-parameters \( S_{11}(S_{22}) \) and \( S_{21}(S_{12}) \) as follows [132]:

\[
R = |S_{11}|^2 = |S_{22}|^2
\]

(17)

\[
T = |S_{21}|^2 = |S_{12}|^2
\]

(18)

\[
SE_R = -10\log(1 - R)
\]

(19)

\[
SE_A = -10\log(T / (1 - R))
\]

(20)

where \( R, T \) represent the reflectivity and transmittivity, respectively.

Figure 39 shows the frequency dependence of \( SE_R \), \( SE_A \), and \( SE_T \) per thickness of the composites. The \( SE_T \) per thickness of YSZ mat is low due to the absence of absorption phases in the samples. The \( SE_T \) per thickness of the CNT coated YSZ mat is improved and the values for samples A and B are the highest ones among these samples. The average \( SE_T \) per thickness of samples A, sample B, sample D and CFRP is 16.72 dB/mm, 21.45 dB/mm, 16.57 dB/mm, and 16.87 dB/mm, respectively. Both the \( SE_R \) and \( SE_A \) per thickness of sample A and B are high compared to pure CFRP which has higher value than the rest samples. The \( SE_A \) per thickness of sample D is high due to the high content of CNT in the composite. The skin depth of sample D is small, implying a high conductivity of the sample. In order to understand the EMI shielding mechanism of the
composites, the DC conductivity, frequency dependence of reflectivity and absorptivity of different composites are shown in Figure 40. DC conductivity of the YSZ mat was increased after coating the YSZ fibers with CNTs. The DC conductivity of the composites with CNT layers is significantly improved after the introduction of the CNT inner layer. The DC conductivity of the composites with CNT inner layers has a similar value of around 1 S/m, indicating that the CNTs are homogeneously distributed in the composites.

The reflection coefficient (RC) of the nanocomposites was calculated by the following equations (21 and 22) [195]:

\[ R_L = 20 \log \left( \frac{Z_{in} - 1}{Z_{in} + 1} \right) \]  

(21)

\[ Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left[ j2\pi\sqrt{\mu_r\varepsilon_r}fL / c \right] \]  

(22)

where \( R_L \) is the reflection coefficient of the composites, \( c \) is light velocity in the vacuum, \( f \) is frequency, \( Z_{in} \) is the normalized input impedance, \( \varepsilon_r \) and \( \mu_r \) are relative permittivity and permeability of materials, respectively.

The reflectivity of the CFRP is high, which clearly indicates that CFRP is a reflection dominant shielding material. Figure 40 also clearly shows that our sample C and D are absorption dominant shielding materials due to the high absorptivity of these composites. The absorption by the CNTs is the main contribution to the shielding, as compared to the YSZ composites without CNTs. To further illustrate the EM absorption ability of the sample D, the frequency dependence of RC is shown in Figure 40d, which indicates that our composite has the absorption ability covering the entire Ka band (26.5-40 GHz). The average RC of sample D is -15.26 dB. These results indicate excellent absorption ability of our multi-layered ceramic composites.
The surface impedance of the materials was characterized by the following equation [195]:

\[
Z_1 = Z_0 \sqrt{(1 + |S_{11}|^2 + 2|S_{11}|\cos\phi) / (1 + |S_{11}|^2 - 2|S_{11}|\cos\phi)}
\]  \hspace{1cm} (23)

where \(Z_1\) the surface impedance of the materials, \(S_{11}\) is the ratio between the voltage of reflected electromagnetic wave and that of source electromagnetic wave, \(\phi\) is the phase angle and \(Z_0\) is the characteristic impedance of the transmission line.

Figure 39. Frequency dependence of (a) \(SE_R\) (b) \(SE_A\) (c) \(SE_T\) per thickness (d) skin depth of different composites. Inset of figure shows the enlarged view.
The surface impedance of the samples is shown in Figure 41a. Sample A and B reveal larger impedance mismatch with free space compared to other samples. Sample C and D have better impedance match among these samples. The good impedance match with free space allows more EM wave to transmit into the ceramic layers for absorption. Figure 41 (b, c) shows the SEM images of the surface layer of sample B and D, which reveals different porosity for the two samples. The porosity observed by the SEM of sample D is higher than that of the sample B. Higher porosity means more EM wave can transmit into the material. Therefore, the reason why sample D has higher absorption shielding ability than sample B.

From the DC conductivity of the multifunctional composite (Figure 40a), samples with CNTs (A-D) have higher conductivity compared to samples E and F (only YSZ/PDC, without CNTs). This
result reveals that the electrons can freely move in the percolated CNTs within the inner layers of the composite material. Since the top and bottom layers of the composite are all composed of YSZ/PDC (insulating layers), the moving of electrons is impeded by the top and bottom layers. Consequently, when the EM wave interacts with the material, conducting paths form [196] inside the YSZ/PDC/CNT inner layer and the induced current loss of the material will only occur inside these layers. The coupling mechanism of the lattice vibrations (phonons) and electrons are shown in Figure 41d. Each conducting path contains enough induced current loops because of the percolation of the CNTs (Figure 33e) and the electron movement induces the occurrence of the electrical loss. The top and bottom layers’ thermal conduction relies on the phonon movements, resulting in the good thermal insulation of the multifunctional materials. The top and bottom layer will act as impedance matching layers with the free space, which facilitates the entering of EM for absorption. With the increase of EMI layers, the conducting paths will increase and lead to increase of the conductivity and EMI ability.

Therefore, the top and bottom YSZ layers provide the thermal protection for the CFRP because of the low thermal conductivity of both the PDC and YSZ phases, while the YSZ/PDC/CNT layers absorb the EM wave and shield the CFRP from EMI due to the existence of CNT network. The fibers in the YSZ/PDC/CNT layers also can provide thermal protection, which is the reason for low thermal conductance of sample D (six YSZ/PDC/CNT layers) relative to sample A and B.
Figure 41. (a) Surface impedance of different materials. (b) SEM images of the surface layer of (b) sample B and (c) D showing different porosities. (d) Illustration of the thermal protection and EMI shielding of the multi-functional layers.

Table 8 compares of the densities of the multifunctional composite with CNT, YSZ and PDC. The resultant composite should have acceptable density for aerospace application. Airframe structures such as aluminum and CFRP have densities of 2.7 g/cm$^3$ and 1.3-1.6 [197] respectively. The average density of our multifunctional composite is 2.28 g/cm$^3$. This is an evident that the composite is a lightweight material that can be used for aerospace applications. The bonding of the multi-functional composite on CFRP does not compromise the weight of CFRP because of the low density of the composite. For instance, after bonding the composite on CFRP, the average density of the resultant hybrid composite is 2.02 g/cm$^3$ which is well suitable for aerospace applications.
Table 8. Comparison of the densities of the multifunctional composite with CNT, YSZ and PDC

<table>
<thead>
<tr>
<th>Material</th>
<th>CNT</th>
<th>YSZ</th>
<th>PDC</th>
<th>Multifunctional Composite</th>
<th>Hybrid Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.3-1.4</td>
<td>1.03</td>
<td>1.28</td>
<td>2.28 (ave)</td>
<td>2.02 (ave)</td>
</tr>
</tbody>
</table>

Figure 42 compares the $SE_T$ per unit thickness of our materials with that of the typical PDC-based composites reported in recent literature [198-203]. It was reported that the commercial copper mesh with areal density of 107.4 g/m² has the attenuation below 10-20 dB at frequency range 20-30 GHz [200], while our material (density of 2.32 g/cm³) has an attenuation $SE_T$ of 16.57 dB/mm in the Ka-band (26.5-40 GHz). Although the copper mesh has lower areal density, its porosity and high thermal conductivity make it difficult to apply as thermal protection material. The manufacturability of our material system is simple and more economical when compared to other commercial solutions such as copper meshes which usually require series of machining operations to manufacture. For instance, the manufacturing a copper mesh requires drawing down the bulk copper in a series of die to achieve desired wire diameters. These wires are then welded together at intersections or woven over each other to form a continuous network called mesh. Besides, there are other limitations to using these types of materials for shielding. The copper mesh has lower melting point than our composite because of its metallic property. While our composite can be used at even higher temperature inert environment due to the ceramic property.
Figure 42. Comparison of the EMI shielding property with other PDC-based materials reported in the literature (note: comparison is not in the same frequency range).

5.6. Chapter Summary

To obtain simultaneous thermal protection and high electromagnetic interference shielding property for CFRPs in the adverse environments, a multifunctional ceramic composite system has been developed in this study. The ceramic composite is a multi-layered system. The YSZ fiber reinforced PDC acts as the thermal protection and impedance layers, while the YSZ fiber reinforced PDC with CNTs provides EMI shielding. The multifunctional ceramic composite system is bonded onto CFRPs through a co-curing process. The thermal conductance of the ceramic composite is about 22.5% lower than that of the CFRP. Steady state thermal insulation test reveals that the hybrid composite can be used up to 300 °C while keeping the interface temperature at around 167.8 °C. During the flame test, the temperature difference of the hybrid
composite is 72.9 °C and 280.7 °C during the low and high temperature settings, respectively. The satisfactory insulation capability of the ceramic composite can be attributed to the low thermal conductivity of the YSZ and PDC phase. SEM observation reveals that there are no changes to the structure of the ceramic composite after flame. The four-layered ceramic system has an average $SE_T$ per thickness of 21.45 dB/mm indicating high reflection dominant EMI shielding. The average $SE_T$ per thickness of the eight-layered ceramic system was 16.57 dB/mm, revealing high absorption dominant EMI shielding, which is different from the CFRP. Typical CFRP reveals reflection EMI shielding property. The high absorption dominant EMI shielding is attributed to the free movement of electrons in the percolated CNTs within the inter layers of the composite material and the restriction in electron movement in the surface layer, which provides impedance matching with the free space. The surface layers whose thermal conduction relies on the lattice vibrations also acts as thermal insulation for the CFRPs. This study provides new insights in designing multifunctional materials for high temperature aerospace and defense applications.
CHAPTER 6: ENHANCED THERMAL PROTECTION OF CFRP WITH CURED-PSZ AND YSZ COMPOSITE SKIN MATERIAL

6.1. Rationale

The aerospace industry’s continuous effort to enhance the performance of commercial and defense aircraft is a great driving force behind developing improved high-performance structural materials. Just like in previous chapter, the goal of the work in this chapter is to improve the survivability of carbon fiber reinforced polymer in high temperature environments. Up to now, many systems can be used for the potential thermal protection for CFRP, such as metal-based coatings [205-207], ceramics [208, 209] and ceramic with polymers [193, 210]. However, the compatibility of these systems with the CFRP is poor because of their heterogeneity relative to the CFRP. Therefore, searching for a new system possessing good compatibility and high thermal stability is important to the protection for CFRP.

In this chapter, a novel polymer system which has good compatibility with CFRP and can provide excellent thermal protection (TP) for the CFRP is reported. This system is different from the common polymers which has low service temperature. This system contains cured polysilazane (PSZ), which is a preceramic polymer precursor for silicon carbon nitride ceramics [2, 117, 143]. The curing (cross-linking) of PSZ allows the conversion of the polymeric precursor into infusible materials at low temperatures (<500 °C). For preceramic polymer precursor, many works have focused on the investigation of the thermal properties of the derived ceramic (PDC) products [185, 211, 212] and not on the polymer-state products. However, for the first time, the application of the cured precursor as thermal protection system is investigated. The cured precursor illustrates high thermal stability up to the cured temperature. The system also contains YSZ fibers which have low thermal conductivity, chemical and thermal stability and high resistance to spallation under thermal
fatigue [188 - 190].

6.2. Materials and Methods

6.2.1. Materials

Durazane 1800 (Starfire Systems Inc.) was the polysilazane (PSZ) used in this work. PSZ is a type of preceramic precursor for silicon carbon nitride ceramics, which is usually made of silicon and nitrogen in repetitive units. Unidirectional YSZ fiber (Zirca Zirconia, Inc. USA) with a bulk density and porosity of 1.02 g/cc and 87% respectively was used as the reinforcement. Rigidizer (Zirca Zirconia Inc. USA) having the same composition (90 wt% of ZrO$_2$ and 10 wt% of Y$_2$O$_3$) as the YSZ fibers was also used. The rigidizer is in liquid state and it is comprised of sub-micron particles of yttria stabilized zirconia suspended in a zirconium acetate aqueous solution. It forms a fully stabilized zirconia body upon curing. Raw carbon fiber epoxy prepreg (AF254, Tg=135 °C) from Stratton Composites Solutions was used to prepare the CFRP laminate.

6.2.2. Coated composite fabrication

Figure 43 shows the schematic illustration of the coated composite preparation process. The YSZ preform was first infiltrated with the rigidizer to increase the volume fraction of YSZ in the final composite. The preform was dried in the oven at 150 °C for 3 hours to convert the rigidizer into a fully stabilized YSZ body. Afterwards, PSZ solution was infiltrated into the preform. The infiltration was carried out under vacuum for 30 minutes and samples were cured immediately after infiltration at 300 °C for an hour. After the preparation of the YSZ/cured-PSZ skin layer, the coated composite was then fabricated. First, through a hand-layup process, the YSZ/cured-PSZ composite skin layer was carefully placed on stacked plies of prepreg (four plies). The lay-up was then housed in a vacuum bag system for the co-curing process under isothermal compression.
molding using a hot press. This was done by preheating the hot press chamber at 135 °C followed by immediate vacuuming before applying pressure at 30 psi for 30 minutes. Afterwards, the mold and part were cooled below 93 °C before demolding.

![Image of fabrication steps](image)

Figure 43. Schematic illustration of the fabrication steps in making the coated composite.

### 6.2.3 Characterization Techniques

The thermal stability of the cured-PSZ samples was investigated with a DSC/TGA system thermal analyzer (SDT 650, TA Instruments), which delivers simultaneous heat flow and data. The samples (140 °C and 300 °C cured-PSZ) were analyzed in a platinum pan at a heating rate of 5°C/min from room temperature to 400 °C under air flow. Both the cured PSZ and skin layer were also kept at 300 °C with different time durations in a horizontal furnace in air to further investigate the thermal stability.

Fourier transform infrared (FTIR) spectroscopy was utilized to analyze the chemical structure of the cured-PSZ samples. The spectra of the samples were recorded using a frontier FT-IR 94235 spectrometer equipped with a universal attenuated total reflection (ATR) accessory with a diamond/ZnSe crystal combination. The spectra were collected between 4000 cm⁻¹ and 650 cm⁻¹.

The microstructure of the YSZ/cured-PSZ composite skin layer and the coated composite were characterized using the scanning electron microscope (SEM, FEI Verios 460L) and confocal laser
scanning microscope (Kenyense VKx1100). Samples were polished before characterization. The chemical state of the elements in the nano-composites was evaluated by X-ray photoelectric spectroscopy (SPECS FlexMod XPS with Hemispherical analyzer PHOIBIS 150) with Mg $\kappa$ excitation (1254 eV). Base pressure in the analysis chamber is in $10^{-10}$ mbar range. X-Ray incidence angle is ~$30^\circ$ from surface and x-ray source to analyzer ~$60^\circ$. Energy calibration was established by referencing to adventitious carbon (C1s line at binding energy of 285.0 eV).

The room temperature through-thickness thermal conductivity of the cured-PSZ polymer was characterized using the $3\omega$ method [213]. For our experiment, 50 nm of aluminum heater/thermometer was thermally evaporated on the sample surface. Silver plates were used to make electrical connections to the deposited heater thermometer. The electrical resistance of circuit was measured to be 1.8 ohms. The sample was connected in a 4-point configuration to the experimental set-up. An AC current with a 1$\omega$frequency was sent to the heater and the 3$\omega$ voltage response from the thermometer was measured to extract the thermal conductivity. The AC source was from Keithley 6221 and SR830 lock-in amplifier was used to measure the 3$\omega$ voltage. A $V_{3\omega}$ amplification circuit was constructed to reduce the 1$\omega$ noise. The flow chart of the 3-omega measurement is shown in Figure 44a. The thermal conductivity of YSZ fiber and particles (~ 0.1 W/mK) was taken from the supplier’s data sheet.

Thermal conductance gives a good insight into the material’s ability to reduce the heat flow to the CFRP base at the desired operating condition (temperature difference). The thermal conductance setup used here is the same as the one described in Chapter 5; Section 5.2.3 of this dissertation as shown in Figure 44b.

The pull-off bonding strength test on the hybrid composite at different temperatures and after insulation test were carried out using a PosiTest adhesion tester (AT-A DeFelsko Corporation,
Ogdensburg, US). This setup used here is the same as the one described in Chapter 5; Section 5.2.3 of this dissertation (shown in Figure 44c). Two samples were measured for each of the conditions and the average was taken. For the high temperature measurement, the sample (held by the hydraulic pump) was placed in a box furnace (Neytech Vulcan furnace) for 30 minutes after it has achieved steady state, with the controller placed outside the furnace. To verify the temperature, a k-type thermocouple was attached to the sample surface and connected to a thermometer outside the furnace. For all measurements, the thermometer reading was ±5 °C relatively to the furnace temperature.

Figure 44. (a) Arrangement of thermal conductivity measurement by 3ω method. (b) Experimental set-up for the thermal conductance measurement of the coated composite. (c) Equipment and method used to measure the pull-off bonding strength of the coated composite.
6.3. Thermal Stability of Cured Polysilazane

FTIR spectroscopy analysis was used to study the chemical structure of the PSZ after curing, as presented in Figure 45c. The sample showed characteristic N-H stretching between 3500 and 3200 cm\(^{-1}\). The appearance of a Si-H stretching band around 2100 cm\(^{-1}\) implies that there were some hydrosilane groups present in the polymer. Peaks at around 1250 cm\(^{-1}\) shows characteristic of the asymmetric mode of \(\text{CH}_3\) bonded to silicon. The peak at around 1169 cm\(^{-1}\) can be assigned to the absorption band of Si-O-Si [214-217], since the curing of HTT1800 was carried out in ambient environment. Moisture from hydrolysis reaction can help to cure the precursor and react with the Si-H bond to form silanol groups which subsequently undergoes condensation to produce siloxane units [215, 217], as shown in Figure 3e. Formation of Si-O bond is also illustrated by XPS analysis of the cured precursor (shown in Figure 46d). The main component of the Si2p is Si-O bond at around 104.3 eV [218]. The Si-N bond, which is the main line of the Si2p for PSZ [215], located at around 103.1 eV. The position of the Si-N bond shift compared to the standard position for Si-N [218] due to the formation of Si-O bond [219].

The thermal stability of the cured-PSZ matrix was first investigated by TGA. The TGA analysis of PSZ precursor shows that the precursor experiences weight loss when the temperature is above 300 °C. However, when the precursor was cured, the PSZ can be stable up to its cured temperature. In this study, the HTT1800 precursor was cured at 140 °C and 300 °C, respectively. Figure 45a shows the results of the thermal stability investigation of the PSZ material after curing at the two representative temperatures. According to the TGA result, both samples display good thermal stability (no significant weight change) from room temperature up to the curing temperatures. The resulting cured-PSZ material is a non-meltable thermoset which is usable up to its curing temperature. The cured PSZ (at 300 °C) and the skin layer were also kept at 150, 200, and 300 °C.
in air for different time to test the thermal stability, respectively. As seen from Figure 45b, the weight of both kinds of samples is almost unchanged when kept at constant temperatures (150, 200, and 300 °C) with the increase of heating time, revealing that both the cured PSZ and the skin layer were stable at the cured temperature. The stability of cured-PSZ can also be seen via FTIR analysis. Samples were cured at 300 °C and held at different times, starting from 3 hours to 24 hours. All the spectra shown in Figure 45c displays similar absorption bands as the holding time increases, indicating no new bonds formed. The Si-O-Si absorption shifted from ~1170 cm\(^{-1}\) to lower wavenumber (~1130 cm\(^{-1}\)) as the curing time is increased from 3 hours to 24 hours. This could be an indication of increasing intermolecular interactions between the oxygen atoms and the hydrogen from N-H groups of the precursor during chain scission of the bond [220].

The through-thickness thermal conductivity of the cured-PSZ was measured by the 3-omega method. The in-phase and out-of-phase signals were fitted by the heat diffusion model to derive the thermal conductivity of the material. The volumetric heat capacity value used for the fitting was 1.63 J·K\(^{-1}\)·cc\(^{-1}\), which was from measured from differential scanning calorimetry (DSC) method. Through this way, the room temperature thermal conductivity of the 300 °C cured-PSZ was extracted as 0.17±0.02 W/m·K, which has the same order of magnitude with other known low thermal conductivity polymers such as silicone (k = ~0.2 W/m·K [221]) and epoxy (k = 0.15-0.25 W/m·K [222]). The experimental and systematic uncertainties are combined to calculate total error bars. This result proves that the cured-PSZ material is a candidate material for thermal insulation applications.
Figure 45. (a) Thermogravimetric analysis (TGA) of PSZ precursor and samples cured at 140 °C and 300 °C, respectively. Inset of figure are optical images of the cured PSZ at 140 °C and 300 °C, respectively. (b) Time dependent of weight change at 300 °C in air for the cured PSZ and skin layer. (c) FTIR spectra of cured PSZ at 300 °C at various holding time. (d) XPS analysis of Si2p for the 300 °C cured PSZ. (e) Illustration of moisture curing of PSZ precursor in air [215].
6.4. Microstructural Characterization

The initial porosity of the as-received YSZ preform was around 87%. However, after infiltration, the porosity of the composite skin is measured to be around 3%. The density of the final composite skin was 1.67 g/cm³, which is about 60% increment compared to the density of the pure YSZ preform. Our skin layer is light in weight and can be used for both aerospace and defense applications. Figure 46 shows the cross-sectional SEM images of the YSZ/cured-PSZ composite skin and coated composite. According to the images, the large pores in the YSZ preform was completely closed in the final composite skin layer, further proving that the infiltration process is effective. The cured PSZ exists as the matrix and the YSZ fibers are well embedded inside of it. At a higher magnification, no significant voids can be observed in the sample, indicating that the structure of the sample is dense (inset of the figure). The thickness of the YSZ/cured-PSZ layer was about 200 µm.

The cross-section of the entire coated composite was also characterized to understand the bonding status between the different layers. Figure 46(b-d) present the SEM micrographs of the cross-section of the final coated composite. The final coated composite structure can be divided into three parts: the YSZ/cured-PSZ layer, the bonded region and the CFRP substrate. The bonded region is fabricated by the co-bonding process and is the excess epoxy from the prepreg bonding with the surface the YSZ/cured-PSZ composite skin. As shown in the figure, the YSZ/cured-PSZ layer bonds seamlessly with the CFRP without any defects. The thickness of the bonded region is around 100 µm. This good bonding behavior will ensure the structural integrity of the coated composites.
Figure 46. Cross-sectional SEM images of (a) the YSZ/cured-PSZ composite skin and (b – d) coated composite.

6.5. Thermal Insulation Performance of Skin Material

An effective thermal barrier should be able to prevent or minimize the transfer of heat through its body. The thermal conductance of the composite skin layer and cured PSZ was characterized and compared with CFRP under the same operating conditions. Two samples were measured for the composite skin based on the composition of the starting phases. The composite skin containing 5.3% and 11% volume fraction of cured-PSZ is labeled as “skin 1” and “skin 2” respectively. The
higher temperature ($T_h$) was kept below 180 °C in order not to exceed the service temperature for CFRP. The thickness of the sample used here is 0.5 mm.

The test sample was placed between the bottom and upper aluminum blocks without any external bonding agents. In order to check the repeatability of the experiments, the CFRP sample with 0.5 mm thickness was tested under similar conditions four different times. During each repetition, the sample was rotated 90° in the clockwise direction while the aluminum blocks were held stationary in order to nullify any effect of surface finish. Table 9 presents the result from this experiment. From the table, the repeatability of the experiments is good, as similar $T_h$ results in similar $T_c$ and conductance. The conductance of CFRP in these experiments is large and varied by a maximum of ± 0.5% from an average value of 1735W/m²·K. The cured PSZ shows good thermal insulation properties, which can significantly impede the heat transfer. For example, the when the $T_h$ of the PSZ cured at 300 °C is 250 °C, the $T_c$ is only 182.2 °C and the corresponding conductance is only 316.63 W/m²·K. The conduction of other materials is showed in Figure 47c. Under similar operating conditions (higher temperature $T_h$), the two novel skins (skin 1 and skin 2) of similar thickness have about 45% reduction in thermal conductance compared to CFRP. Lower the conductance, higher the insulating property of the material. The $T_h$ and $T_c$ of different materials are also plotted in Figure 47b, which shows the comparison of temperature differences between front and back surfaces of the skin materials with CFRP of similar thickness under same operating conditions. It can be observed that the skin materials have about 56% larger temperature drop than CFRP under this operating condition.
In addition, the effect of combined skin layer and CFRP system has been studied under typical operating conditions of $T_h \sim 200$ °C. The two skin layers were bonded onto CFRP separately and the coated CFRP were referred to as H1 and H2 respectively. The thickness of the skin layer was maintained at 0.5 mm and the overall thickness of the coated systems were 1.2 mm. As seen from Figure 47c, the conductance of the coated composites is low, with the values of 838.48 and 660.84 W/m²·K for the coated CFRP H1 and H2, respectively. Therefore, the skin layers provide excellent thermal protection for the CFRP and can improve the survivability of CFRP in high temperature environment. The superior thermal insulation performance experienced by the skin layer can be attributed to the low thermal conductivities of cured PSZ. The service temperature of the material system can be significantly improved by using our skin layer.
Figure 47. (a) Temperature distribution profiles calculated $T_h$ and $T_c$ (b), conductance (c) for different materials.
6.6. Bonding Strength of Skin Material on CFRP Substrate

The bonding strength was first measured for hybrid composite samples at different temperatures (room temperature, 100 °C and at 150 °C). Temperature higher than 150 °C could not be measured due to the limitation of the PosiTest equipment to survive at such condition. For the high temperature measurement, the sample (held by the hydraulic pump) was placed in a box furnace (Neytech Vulcan furnace) for 30 minutes after it has achieved steady state, with the controller placed outside the furnace. To verify the temperature, a k-type thermocouple was attached to the sample surface and connected to a thermometer outside the furnace. For all measurements, the thermometer reading was ± 5 °C relatively to the furnace temperature. Furthermore, the bonding integrity of the hybrid composite was also characterized after insulation test. Two samples were measured for each of the conditions and the average was taken.

The result of the pull-off bonding strength is presented in Table 10. The bonding strength of the skin material on CFRP at room temperature is 0.73 MPa. At high temperature conditions, the bonding strength experienced no significant change. For example, at 100 °C and 150 °C, the bonding strength was recorded as 0.75 MPa and 0.69 MPa, respectively. Furthermore, the bonding strength of skin material on the CFRP substrate was also established after insulation test at 150 °C and 200 °C. Similarly, the skin material displayed excellent bonding durability with the CFRP substrate such that its bonding strength does not significantly change after insulation test. For instance, after insulation test at 200 °C, the bonding strength was recorded as 0.67 %, which is about 8 % drop in relative to bonding strength before insulation test. This result can be attributed to the excellent insulation capability of the skin material ensuring that interface is protected from thermal damages such as delamination.
Table 10. Pull-off bonging strength of hybrid composite

<table>
<thead>
<tr>
<th>Condition</th>
<th>Bonding strength (MPa)</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp</td>
<td>0.730</td>
<td>-</td>
</tr>
<tr>
<td>At 100°C</td>
<td>0.750</td>
<td>-</td>
</tr>
<tr>
<td>At 150°C</td>
<td>0.690</td>
<td>5.48</td>
</tr>
<tr>
<td>After insulation test at 150°C</td>
<td>0.710</td>
<td>2.74</td>
</tr>
<tr>
<td>After insulation test at 200°C</td>
<td>0.670</td>
<td>8.22</td>
</tr>
</tbody>
</table>

6.7. Chapter Conclusion

A composite skin layer was developed for the thermal protection of CFRPs. The skin layer was made of cured PSZ reinforced with yttria stabilized zirconia (YSZ). Thermogravimetry analysis and heat treatment of the sample in air showed that the cured PSZ material was stable at a higher temperature. Fourier transform infrared (FTIR) spectroscopy further confirmed the thermal stability and structure of the material in ambient environment with respect to increasing holding time. The room temperature through-thickness thermal conductivity of the cured-PSZ is as low as 0.17±0.02 W/m·K, indicating good insulation capability. The skin layer has a density of 1.67 g/cm³, which is light in weight and can be used for both aerospace and defense applications. Thermal conductance of the skin layer is around 940 W/m²·K, which is about 45% reduction in conductance compared to the CFRP. The thermal protection experiments showed that the coated CFRP can be heated up to 250 °C, proving that it can improve the survivability of CFRP high
temperature environment. The pull-off bonding strength test on the hybrid composite at different temperatures and after insulation test showed that the skin material displayed excellent bonding durability with the CFRP substrate. The excellent insulation of the composite skin can be attributed to the low thermal conductivity of the cured PSZ.
CHAPTER 7: CONCLUSION

7.1. Major Finding of Dissertation

This dissertation establishes the relationship between polymer-derived SiCN ceramics and different filler system and the resultant composite’s properties especially for aerospace applications. Through careful experimental approach and theoretical understanding, this work established that different functionalities such as thermal, dielectric, electromagnetic shielding etc. from PDC-SiCN system can be obtained and improved by carefully choosing and adding appropriate filler materials. The microstructure and performance of the resultant composite with respect to the fillers added were studied and analyzed. This dissertation, “Tunable Multi-functional Properties of Polymer Derived Silicon Carbon Nitride (SiCN) Ceramic Composites for Advanced Aerospace Applications” demonstrates several original accomplishments.

Chapter 4 reported the addition of boron nitride nanotube (BNNT) fillers into PDC-SiCN and processed at 1000 °C. The aim of this work is to improve the thermal properties such as thermal conductivity, heat capacity and oxidation resistance of PDC-SiCN by adding BNNTs at elevated thermal environments. Some of the new findings in this chapter include:

- Reported highest volume fraction value (35.4 %) of BNNT in a matrix system. Usually, it is difficult disperse nanomaterials such as BNNT in another phase especially micro or macro-sized phases like the PDC system especially at high volume fraction. This is because BNNT are always synthesized in bundles and the bundling is caused as a result of attractive intermolecular forces between the nanotubes themselves. And poor dispersion prevents effective load transfer from the matrix to the nanotube reinforcements of the nanocomposite material, yielding significantly lower values in the properties than
theoretically predicted. Through the PDC processing route, we were able to achieve the better uniform dispersion at high volume fraction.

- The synthesized ceramic composites in this work possess high thermal conductivity of 4.123 W/(m·K) at room temperature, improved by 2100 % compared to that of pristine PDC. The composite also showed excellent oxidation resistance up to 900 °C. There was an observation of significant increase in thermal conductivity when the BNNT content is higher than 22.2 vol.%, indicating a percolation transition. A conduction model was also used to fit our experimental result to further prove the correctness of our result.

Chapter 5 studied the electrical and dielectric properties of the BNNT with PDC-SiCN system. Since PDCs are transparent materials, it is expected that introducing BNNTs due to their perfect electrical insulation and superb oxidation resistance, the resultant composite will possess properties to meet EM transparent application requirements in high temperature application. In this chapter, we have achieved significant new findings:

- We report for the first time about the electrical and dielectric properties of BNNTs-reinforced PDCs. The electrical resistivity of the pristine PDC is around $10^6 \, \Omega \cdot m$. But after adding 5 wt.% BNNTs, the electrical resistivity of the nanocomposites increases two order of magnitudes, reaching $10^8 \, \Omega \cdot m$. BNNTs in the PDC-SiCN is believed to impede electron hopping that occur from adjacent free carbon, thereby improving electrical resistivity.

- The average real relative permittivity of the PDC decreased, while the quality factor (Q) increases when 5 wt.% of BNNT was added. Relationship between the real relative permittivity and the imaginary relative permittivity of the nanocomposites showed that the
dielectric loss with a high loading fraction of BNNTs may be caused by a Lorentz resonance relaxation process.

Chapter 6 investigated the multi-functional properties of a ceramic composite system for simultaneous thermal protection and electromagnetic shielding for carbon fiber reinforced polymers (CFRPs) which is a common material for airframe design. In here for the first time, we designed a dual protection system for CFRP used in aerospace applications. The uniqueness of this work includes:

- In this project, we designed a dual protection system for CFRP that can offer thermal shielding ability and electromagnetic shielding capability. Because materials with high thermal conductivity also have high thermal electrical conductivity, such system has never been reported. However, through our novel design and fabrication technique, the system was fabricated. The system was fabricated as a multi-layered structure of YSZ/PDC layer for thermal protection and YSZ/SiCN/CNT for EMI shielding due to existence of CNT network.

- The thermal conductance of the ceramic composite is about 22.5% lower than that of the CFRP. Steady state thermal insulation test reveals that ceramic composite can offer thermal protection to CFRP up to 300 °C. Our eight-layered ceramic composite has average SET per thickness of 16.57 dB/mm revealing high absorption dominant EMI shielding while CFRP reveals reflection EMI shielding property.

- The high absorption dominant EMI shielding can be attributed to the free movement of electrons in the percolated CNTs within the inner layers of the composite material and the restriction in electron movement in the surface layer, which provides impedance matching
with the free space. On the other hand, the outer layers whose thermal conduction relies on the lattice vibrations also acts as thermal insulation for the CFRPs.

- This study provides new insights in designing multifunctional materials for high temperature aerospace and defense applications.

Chapter 7 investigated the thermal protection properties of a novel composite skin layer for carbon fiber reinforced polymers (CFRPs).

- The skin material consists of YSZ and cured polysilazane (PSZ) phase. The cured PSZ is a thermoset obtained by curing liquid polysilazane at 300 °C. The cured-PSZ material is a non-meltable thermoset which is usable up to its curing temperature.

- The room temperature through-thickness thermal conductivity of the cured-PSZ is as low as 0.17±0.02 W/m·K, indicating good insulation capability. Thermal conductance of the skin layer is around 940 W/m²·K, which is about 45% reduction in conductance compared to the CFRP. The thermal protection experiments showed when the skin material is coated on CFRP, the resultant hybrid composite can be heated up to 250 °C, thereby improving the survivability of CFRP in high temperature environment.
7.2. Future Works

Identification of several avenues for further research and developmental work on PDC-SiCN and filler systems has been made so that it can be applicable to a wider range of experimental systems. Some of these developments will require additional physical mechanisms and property characterization to be incorporated as summarized below:

- Mechanical properties such as of toughness, hardness, flexural strength, etc of the BNNT-PDC nanocomposite can also be investigated in the future. Mechanical properties investigation is also an important tool in evaluating the performance of materials used in high temperature since these materials can be subjected to thermal shock and other physical impact during operation.

- Investigating the in situ electrical and dielectric property of BNNT-PDC nanocomposite with increasing temperature could create an avenue to use material as a temperature sensor. The dielectric constant of the PDC systems is also a function of temperatures. So, investigating this property at elevated temperature via free space measurement could be an exciting premise to be explored.

- In chapter 6, the EMI shielding performance of the multi-functional composite can also be investigated in other frequency bands such as X, V, and W band. The X-band is particular interesting in the defense industry for stealth application. V and W-bands also have promises in satellite applications. Additionally, another thermophysical property that can be investigated is coefficient of thermal expansion (CTE). The CTE of the ceramic composite layer and CFRP should be compatible to avoid debonding during cyclic thermal operations.
• In chapter 7, another important area that needs attention is the investigation of the relationship between thermal conductivity of the skin material and curing temperature. It is well established that the thermal conductivity of material changes with respect to temperature which could influence the thermal properties of the skin material.
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