Characterization of Carbon Nanostructured Composite Film Using Photothermal Measurement Technique

Kurt E. Harris
Utah State University

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CHARACTERIZATION OF CARBON NANOSTRUCTURED COMPOSITE FILM

USING PHOTOTHERMAL MEASUREMENT TECHNIQUE

by

Kurt E. Harris

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Mechanical Engineering

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UTAH STATE UNIVERSITY
Logan, Utah

2018
Characterization of Carbon Nanostructured Composite Film Using Photothermal Measurement Technique

by

Kurt E. Harris, Doctor of Philosophy
Utah State University, 2018

Major Professor: Dr. Heng Ban
Department: Mechanical and Aerospace Engineering

Graphene possesses impressive properties, including high strength, electrical conductivity, and thermal conductivity. Development of materials with graphene-like carbon nanostructures which exhibit these properties is actively being researched. This work focused on understanding how the microstructure influences thermal transport of thin-film samples in the through-thickness direction.

Various influences on thermal conductivity were studied, including overall carbon content, relative carbon nanotube content, porosity, and electrical conductivity. Measurement of thermal diffusivity for thin-film samples was performed with a back-detection photothermal radiometry setup, as standard techniques are not applicable. Density and specific heat capacity were measured and used to calculate thermal conductivity and effusivity. The uncertainties of the measured properties were then used to estimate the uncertainty of the calculated variables.

The microstructure was analyzed using Scanning Electron Microscopy and Raman spectroscopy, and the microstructure’s impact on the thermal conductivity was
analyzed. Increased carbon content improved thermal conductivity for low-porosity samples, but porosity was extremely detrimental to thermal conductivity in high-porosity samples. As air void formation during fabrication appeared to increase with carbon concentration, a negative correlation was observed between thermal conductivity and carbon content for unpressed samples. Hot pressing is fairly effective at removing voids, especially in higher carbon samples, with the result of improving thermal and electrical conductivity. The addition of carbon nanotubes to low-porosity samples resulted in an increase in thermal conductivity. Nanotubes also appeared to reduce variability in thermal conductivity between pressed and unpressed samples, and may allow for more predictable performance.
Characterization of Carbon Nanostructured Composite Film

Using Photothermal Measurement Technique

by

Kurt E. Harris, Doctor of Philosophy

Utah State University, 2018

Graphene is a form of carbon with unique thermal and structural properties, giving it high potential in many applications, from electronics to driveway heating. Advanced fabrication techniques putting small, graphene-like structures in a polymer matrix could allow for incorporation of some of the benefits of graphene into very lightweight materials, and allow for broader commercialization. Measuring the thermal properties of these thin-film samples is a technical capability in need of development for use with the specific specimens used in this study. Relating those thermal properties to the microstructural composition was the focus of this work.

Several conclusions could be drawn from this study which will help guide future development efforts. Among these findings, it was found that increasing carbon content only improves thermal and electrical conductivity if the samples were of low porosity. Samples of approximately identical overall carbon content and void content had higher thermal conductivity if some carbon nanotubes were added in place of graphite. Nanotubes also appeared to reduce variability in thermal conductivity between pressed and unpressed samples, allowing for more predictable properties in fabrication.
ACKNOWLEDGMENTS

I would like to thank Dr. Heng Ban for his mentorship throughout my education at Utah State University. I walk away from USU grateful for the influence he has had on me, both personally and professionally. I am also grateful for my committee members, and their willingness to help. I acknowledge the support from the Microscopy Core Facility at Utah State University for the SEM results I spent many hours procuring. I am also grateful to my various funding sources, without which I would not have been able to pursue my degree.

I was fortunate to have many good colleagues and friends in my time at USU. Though there are more than I can list here, I hope they understand that their help and friendship was priceless during the many difficulties I encountered in my research. These high-caliber individuals will succeed in whatever they undertake, and everyone involved in their education should be proud of them.

I am most grateful to my wife, Lenaye. She has been not only supportive of me in this undertaking, but has carried far more than her share of the parenting of our children, leaving me with a level of gratitude I cannot put into words.

Kurt E. Harris
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<td>1D</td>
<td>One dimensional</td>
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<td>2D</td>
<td>Two dimensional</td>
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<td>3D</td>
<td>Three dimensional</td>
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<td>AC</td>
<td>Alternating current</td>
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<td>BD-PTR</td>
<td>Back-detection photothermal radiometry</td>
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<td>BSE</td>
<td>Back-scattered electron</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
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<td>DC</td>
<td>Direct current</td>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>EDS</td>
<td>Energy dispersive x-ray spectrometry</td>
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<td>FD-PTR</td>
<td>Front-detection photothermal radiometry</td>
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<td>FTIR</td>
<td>Fourier-transformed infrared spectroscopy</td>
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<td>InSb</td>
<td>Indium antimonide</td>
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<td>IR</td>
<td>Infrared</td>
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<td>LFA</td>
<td>Laser flash analysis</td>
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<td>MCM</td>
<td>Monte Carlo Method</td>
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<td>PTR</td>
<td>Photothermal radiometry</td>
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<tr>
<td>RHS</td>
<td>Right-hand side</td>
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<td>SE</td>
<td>Secondary electron</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SERS</td>
<td>Surface-Enhanced Raman Spectroscopy</td>
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<td>TPS</td>
<td>Transient plane source</td>
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<td>Abbreviation</td>
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<td>TSM</td>
<td>Taylor Series Method</td>
</tr>
<tr>
<td>USU</td>
<td>Utah State University</td>
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<td>UV-Vis</td>
<td>Ultraviolet-visible spectroscopy</td>
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NOMENCLATURE

\( A \)  surface area, m²
\( \alpha \)  thermal diffusivity, m²/s
\( B \)  Biot number
\( \beta \)  useful parameter in thermal quadrupoles
\( \beta_n \)  the nth eigenvalue in Green’s function solution
\( C_p \)  volume-specific (or volumetric) heat capacity, J/m³-K
\( c_p \)  mass-specific heat capacity, J/kg-K
\( D \)  difference between a DSC sample measurement and empty crucible measurement, mW
\( e \)  effusivity, J·m⁻²·K⁻¹·s⁻¹/²
\( F \)  initial condition in Green’s function solution
\( f_i \)  boundary conditions in Green’s function solution
\( f \)  volume fraction in a composite
\( f \)  frequency, Hz
\( G \)  Green’s functions
\( h \)  heat transfer coefficient, W/m²-K
\( k \)  thermal conductivity, W/m-K
\( L \)  Lorenz number, 2.44x10⁻⁸ W·Ω·K⁻² (may also represent thickness)
\( L \)  thickness, m
\( \Lambda \)  mean free path of energy carriers, m
\( \lambda \)  wavelength in Raman spectroscopy, m
\( m \)  

mass, kg

\( \mu \)  

thermal diffusion length, m

\( \phi \)  

Laplace transformed heat flux, W/m\(^2\)

\( q \)  

absorbed energy at a surface or internally, used in Green’s function solutions, W/m\(^3\)

\( q_0 \)  

total energy in Green’s function solution, J

\( q'' \)  

heat flux, W/m\(^2\)

\( q''' \)  

volumetric heat generation, W/m\(^3\)

\( R \)  

radius of sample, m

\( r \)  

radial location in a sample, m

\( \rho \)  

density, kg/m\(^3\)

\( s \)  

complex Laplace variable

\( \sigma_e \)  

electrical conductivity, S/m

\( T \)  

temperature, K or \(^\circ\)C

\( t \)  

thickness, m

\( t \)  

time, s

\( \theta \)  

Laplace-transformed temperature, K

\( \Theta \)  

phase of Laplace-transformed temperature, degrees or radians

\( u \)  

distribution of absorbed energy along \( r \) in Green’s functions, m\(^{-2}\)

\( U_X \)  

expanded uncertainty (at 95%) confidence in variable \( X \) accounting for precision and bias

\( v \)  

distribution of absorbed energy along \( z \) in Green’s functions, m\(^{-1}\)

\( \nu \)  

average speed of sound in a material, m/s
\(w\)  heating function/duration in time in Green’s function solution, s\(^{-1}\)

\(w\)  wavenumber in Raman spectroscopy, m\(^{-1}\)

\(z\)  position through the thickness of a sample, m
CHAPTER 1
INTRODUCTION

1.1 Overview

The focus of this dissertation research is split into development of a photothermal measurement technique and characterization of an advanced carbon composite film. After an introduction of the motivation behind this work, the objectives and background literature are presented. The considerations for each of the various measurements are outlined, including experimental setups and uncertainty quantification.

1.2 Motivation

In this section, the motivating reasons for characterizing these samples and developing the photothermal technique are given.

1.2.1 Samples

An increasing number of electrical applications require development of advanced materials possessing useful thermal characteristics. High-power electronics require materials with high thermal transport capability, as increased temperature has a detrimental effect on component lifetimes. Overhead heating in portable shelters requires material flexibility [1]. Radiant floor heating in homes requires microstructural homogeneity to avoid hot and cold spots [2]. In developing these materials, the ability to customize properties while simultaneously minimizing costs is very important.

Carbon nanostructures in polymer matrices have shown impressive mechanical, electrical, and thermal ability [3]. New low-cost fabrication techniques allow for fabrication of these advanced thin-film materials [4]. Understanding the microstructure’s
effect on thermal transport allows this electrically conductive, flexible material to be compositionally tuned to exhibit desired thermal properties.

In this dissertation, analysis is performed on samples of differing carbon content, varying microstructural content (nanotubes and/or nanoflakes), and fabricated under different densification procedures. The thermophysical properties of these samples were measured and compared to the microstructure with the objective of understanding how the microstructural makeup affects thermal transport. This understanding allows for more accurate targeting of thermal properties in specimen fabrication for applications with defined heat transfer requirements.

1.2.2 Measurements

With regard to the technology development for thin-film thermal property measurement, the main measurement developed in this work is for through-thickness thermal diffusivity. This measurement – along with density and specific heat capacity measurements – allows for the calculation of through-thickness thermal conductivity and effusivity.

Commercial measurements of thermal diffusivity frequently rely on laser flash analysis (LFA), where a laser pulse heats one side of a sample, and the time-dependent backside temperature response is recorded, from which through-thickness thermal diffusivity can be extracted [5]. However, LFA is generally used for relatively thick samples and therefore is not applicable to thin film samples. An alternative technique is known as photothermal radiometry (PTR). Specifically, as the through-thickness thermal diffusivity is of interest, back-detection PTR (BD-PTR) is selected for development here. Front-detection PTR (FD-PTR) and other optical techniques are either less straight-
forward in determining through-thickness average thermal properties, or would only measure in-plane diffusivity.

This BD-PTR system uses an AC modulated laser to uniformly excite the front face of a sample. The laser switches back and forth from on to off, making a time-lapsed square-wave excitation that induces a change in the backside temperature. This temperature fluctuation affects the infrared (IR) radiation emitted from the backside, which is measured by an IR detector. The signal is measured by a lock-in amplifier, which determines the amplitude of the signal and the phase relative to a reference signal. The phase measurement allows for the determination of thermal diffusivity for this thin sample based on a thermal quadrupoles solution to the heat equation.

Complementary to the main measurement of thermal diffusivity, other property measurements allow for full characterization of the sample. An estimate of density can be made by measuring the surface area of a sample as well as its thickness and mass.

The specific heat capacity of a sample can be measured over a temperature range using a differential scanning calorimeter (Netzsch).

The thermal conductivity can then be calculated according to

\[ k = \alpha \rho c_p \]  \hspace{1cm} (1.1)

Thermal effusivity can be calculated from thermal conductivity and volumetric heat capacity

\[ e = \sqrt{k \rho c_p} \]  \hspace{1cm} (1.2)

Scanning electron microscopy (SEM) can be used to visualize the sample microstructure, which fundamentally controls the thermal performance of the film, and an associated technique can be used to verify elemental composition of the sample.
Raman spectroscopy can be used for qualitative analysis of the carbon structural quality, and to identify the relative performance of the polymer and the carbon in the vibrational modes of the composite.
CHAPTER 2

OBJECTIVES

The overall goal of the research was to understand how various aspects of the microstructure and composition of a nanostructured carbon composite film affect thermal transport in the through-thickness direction. Specific areas of study included the influence on thermal conductivity from carbon concentration, the ratio of carbon nanotubes to nanoflakes, the electrical resistivity, and the porosity.

These objectives were achieved by performing the following tasks:

1. Select a measurement technique for thermal diffusivity
2. Design and build a system
3. Measure a validation sample to ensure the system is working
4. Measure thermal diffusivities of various samples
5. Measure density
6. Measure specific heat capacity
7. Calculate thermal conductivity
8. Calculate thermal effusivity
9. Quantify the uncertainty on thermal diffusivity, density, specific heat capacity, thermal conductivity, and thermal effusivity
10. Image the sample microstructure
11. Discuss results to explain the influences on thermal transport

Results are reported in table and graphical format, with uncertainties reported at a 95% confidence level.
CHAPTER 3
BACKGROUND

The literature review and other background information relevant to both the main measurement technique and the sample will be covered in this chapter.

3.1 Samples

Materials with carbon nanostructures can have many interesting properties, including high thermal transport capability. In the early 1990s, carbon nanotubes (CNTs) were popularized and interest skyrocketed based on impressive energy transport capability [6, 7]. CNTs have even been reported to have conductivities as high as 3000 W/m-K [8]. Since its discovery in 2004 [9], graphene has been shown to have many remarkable properties, including electrical conductivity and thermal conductivity in the range of 3000-5150 W/m-K [10], which indicate great potential in future nanoelectronic applications. There are many fabrication techniques to produce graphene from natural graphite, including mechanical cleavage, liquid-phase exfoliation [11], chemical vapor deposition [12], atmospheric pressure graphitization [13], chemical reduction of exfoliated graphite oxide [14], and precursor-controlled thermolysis [15]. Each technique has strengths and weaknesses, and the tendency of graphene sheets to clump together, stack into graphite or roll into tubes [16] is often a problem.

Researchers have attempted to combine high conductivity carbon nanostructures with polymer composites. However, the interfaces between carbon and the polymer matrix scatter energy carriers, increasing interface resistances and decreasing conductivity. Pure polymers are generally around 0.2 W/m-K, and so research often focuses on adding carbon nanotubes to induce a percentage increase over this low value
Many of the reported nanostructured carbon-polymer systems are reported to have conductivities around 1-5 W/m-K [18-20], and it has been shown that thermal conductivity is a function of carbon content for [21]. An impressive conductivity of 6.44 W/m-K was reached by using graphite nanoplatelets in a polymer, likely due to a minimized geometric contribution to thermal interface resistance (Kapitza resistance) when compared to nanotubes [22]. Unfortunately, viscosity – a deterrent to non-lab-based fabrication [23] – is still problematic for this and other techniques [24]. It is thus important that development of these materials focus not only on thermal transport enhancement, but also on the ability to fabricate on a large-scale.

A new technique for fabricating electrothermal coatings decreased the percolation threshold by using nanostructured carbon [4]. The carbon nanostructure consists of low-dimensional nanostructures, 1D tubes and 2D flakes, dispersed in a polyurethane matrix. It is extremely flexible, contains no metal or oxide particles, and is almost entirely composed of carbon and hydrogen, giving it a low density. The choice of polyurethane as the primary polymer was to allow for high carbon loading while maintaining suitable viscosities for ease in manufacture. Thermal conductivity is sensitive to the morphology of the carbon, and preliminary but unverified measurements indicated relatively high sample performance, likely due to the decreased percolation threshold as well as the use of multilayer graphene sheets.

Samples were fabricated by tape casting with varying compositions, thicknesses, and densification processes. Preparation assumed a polyurethane resin density of 1.05 g/cc, per the manufacturer. The carbon composition (graphite flakes and carbon nanotubes) were assumed to have a density of 2.26 g/cc. In order to partially align the
structures in the x-y plane, tape casting was used. The casts were dried at 170°C for two days to remove the residual solvent. Geometrical measurements of the clear polyurethane resin indicated a density of 1.11±0.03 g/cc, which was then used to calculate the theoretical densities for the mixtures made in a rule-of-mixtures approach. Some of the samples were pressed at approximately 450 MPa uniaxial pressure using a silicone layer on one surface to transfer pressure at temperatures between 70 and 150°C. Pressing samples with more than 30 vol. % graphite resulted in substantially increased density, though a comparison with theoretical densities indicates a large amount of porosity, left over from the drying solvent. Sheet resistance was measured in units of Ω/square. This resistance can be converted to resistivity, which relates to electrical and thermal conductivity.

3.2 Measurements

With thermal conductivity dependent on thermal diffusivity and volumetric heat capacity, this section provides a background on needed thermophysical property measurements, as well as measurements of the microstructure.

3.2.1 Densities

Volumetric mass density is a measure of the degree of compactness of a material. It is quantified as the mass divided by the volume, and usually reported in SI units of kg/m³ [25].

A useful method for calculating density is based on Archimedes’ principle. The famous anecdote relating the discovery of this principle [26] involves Archimedes pondering the measurement of density on behalf of royal commissioners. While in a bath he realized that the density of his body could be found by measuring the displacement of
the water, and then leaped out of the vessel and – while still naked – yelled “εὑρηκα” (I have found it out).

Though the anecdote is humorous, and the principle has been commercially applied, this project pursues a faster methodology that should provide sufficiently accurate results. Density is calculated from geometric measurements of thickness and surface area, and mass measurements.

\[
\rho = \frac{m}{At}
\]  

(3.1)

Here, \(\rho\) is density, \(m\) is the mean of several measurements of mass, \(A\) is the mean of various surface area measurements of a flat sample, and \(t\) is the mean of various thickness measurements of a sample.

3.2.2 Thermal diffusivity

Thermal diffusivity is a measure of the ability of a material to conduct thermal energy relative to its ability to store thermal energy [27]. It is frequently represented by the symbol \(\alpha\). Materials with large \(\alpha\) (like copper) respond quickly to changes in temperature in their environment, reaching equilibrium quickly. Small \(\alpha\) (like wood) means the material will respond slowly. It can be thought of as a measure of thermal inertia.

While there are methods for predicting the thermal diffusivity of advanced materials [28], measurements are generally preferred. There are several ways to do this, some more common than others, and each with advantages and disadvantages.

The transient plan source (TPS) technique [29] typically places a sensor/heating element between two halves of a sample. The temperature and time are monitored, from which thermal properties are extracted, with heating time and power adjusted for samples
based on geometry and thermal properties. However, due to probing depth requirements – the distance from any point on a heat section of the heating/detecting element must exceed the probing depth – this technique is not suitable for thin samples. More suitable are non-contact, optical methods.

One commercialized optical technique for thin discs is laser flash analysis (LFA). An intense light pulse is absorbed by the front of a sample, while the backside temperature is recorded over time. The shape of this data is used to calculate thermal diffusivity. The minimum thicknesses based on the fact that the backside temperature must not increase before the pulse ends, as the theory requires that the sample be “infinite”. With standard equipment, pulse times and power result in sample thicknesses roughly 1-3 mm [5], though measurements of polymers with thicknesses as low as 0.3 mm have been reported [30]. As most of the samples in this work are thinner than that, this technique is not suitable.

Photothermal radiometry (PTR) has wide potential applicability, including in the measurement of thin-film samples. Early efforts in 1962 [31] followed on the heels of LFA development and pursued a similar process, that is, pulse excitation with back-side detection of the response. Nordal and Kanstad are credited with developing modern PTR [32], where temperature-varying infrared emission (per Planck’s law) from a sample is detected and used to infer certain information about a sample. Pulsed excitation with front-detection was later developed to measure several properties, including absorption coefficients [33].

Later work utilized continuous modulation with back-side detection for photothermal probing of subsurface structures similar to commonly used ultrasonic
techniques [34]. This continuously modulated technique was expanded from metals to polymers by including front-detection [35].

With regard to measuring thermal diffusivity, there are thus four potential configurations: 1) pulsed excitation with front-detection, 2) continuous modulation excitation with front-detection, 3) pulsed excitation with back-detection, and 4) continuous modulation excitation with back-detection. In the literature, it seems that the second configuration is more commonly used to measure thermal properties [36]. However, the fourth configuration, referred to here as BD-PTR has been used to measure thermal diffusivity effectively [37], and due to its simplicity in setup and the ease of extracting through-thickness thermal diffusivity, it has been selected for development in this research.

3.2.3 Specific heat capacity

Volumetric heat capacity $C_p$ is a measure of a material’s ability to store thermal energy [27] while changing temperature but remaining in the same phase. It is usually reported in SI units of J/m$^3$-K. Specific heat capacity $c_p$ is the energy need to increase the temperature of a unit mass by one degree, usually reported in SI units of J/kg-K [38]. They are related by density $\rho$ by

$$C_p = \rho c_p \quad (3.2)$$

There are several systems for measuring heat capacity, such as bomb calorimeters and calvet-type calorimeters. A system utilizing differential scanning calorimetry (DSC) [39] from Netzsch will be used here.

DSC refers to the measurement of the change of the difference in the heat flow rate to a sample and to a reference sample while they are subjected to a controlled
temperature program [40].

3.2.4 Thermal conductivity

Thermal conductivity $k$ is the rate at which energy in a material is transferred by the diffusion process [27]. It is usually reported in SI units of W/m-K. It can be directly calculated from thermal diffusivity, density, and specific heat capacity according to

$$ k = \alpha \rho c_p $$ (3.3)

Thermal conductivity is a tensor, and a material may have different values in different directions. This project measures through-thickness thermal diffusivity and calculates the through-thickness thermal conductivity.

Thermal energy in solids is generally transported by the migration of free electrons and lattice vibrational waves known as phonons. In metals and other conductors, electron transport dominates. In other materials, phonon transport generally dominates. With electrons and phonons as energy carriers, thermal conductivity can be considered as the summation of the two carrier contributions

$$ k = k_e + k_{ph} $$ (3.4)

It should be noted that $k_e$ is approximately proportional to the inverse of electrical resistivity $\rho_e$ [27]. The sample manufacturer measured the electrical conductivity $\sigma_e$ (the inverse of $\rho_e$).

The Wiedemann-Franz law [41] relates the electron contribution to thermal conductivity to both the electrical conductivity $\sigma_e$ [S/m] and temperature through use of the empirically derived Lorenz number, where $L$ is $2.44 \times 10^{-8}$ WΩK$^{-2}$.

$$ k_e = \sigma_e LT $$ (3.5)

To ensure that bulk property estimation is valid, an estimate of the mean free path
of energy carriers – the average distance traveled before scattering collisions cause a loss in excess energy – can be made from simple kinetic theory [42]. Utilizing the average speed of sound in the material $v$, we have

$$\Lambda \approx \frac{3k}{\rho c_p v}$$  \hspace{1cm} (3.6)

While this is only an estimate, the approximate thermal conductivities expected result in a mean free path much smaller than the sample thicknesses near room temperature. Thus, aspects of nanoscale thermal transport need not be considered further in this work.

### 3.2.5 Thermal effusivity

Thermal effusivity is a measure of a material’s ability to exchange heat with its surrounding environment. It is normally calculated, not measured, as follows [43]

$$e = \sqrt{k \rho c_p}$$  \hspace{1cm} (3.7)

Effusivity is important to solutions of the heat equation for layered sample applications, as it is used to calculate interface temperature [44].

$$T_m = T_1 + (T_2 - T_1) \frac{e_2}{e_2 + e_1}$$  \hspace{1cm} (3.8)

An example of this interface temperature $T_m$ is often exemplified by touching metal and touching wood. Both are at room temperature, but upon contact from your warmer hand, the high-effusivity metal feels colder than the low-effusivity wood. This interface temperature is visualized in Fig. 3.1.
Fig. 3.1. Example of effusivity and its relation to the interface temperature between two materials or sample layers at different initial temperatures.

Though effusivity can be calculated based on the measured variables used to calculate thermal conductivity, the fact that thin-film carbon nanostructured polymers are used in multilayered applications, reporting effusivity directly is useful.

3.2.6 Microstructure

The section contains an overview of the two techniques utilized to understand the sample microstructures: scanning electron microscopy and Raman spectroscopy.

3.2.6.1 Scanning Electron Microscopy

Invented in the 1930s, SEM has been used commercially on electrically conductive samples since 1965 [45]. It is useful in visualizing the small features of conductive samples. In a vacuum, a focused beam of electrons is directed at a sample surface, and scanned in a raster pattern. A high-resolution image is made through software analysis of the beam position and the detected signal.

Features as small as 0.4 nm have been visualized with modern conventional equipment [46], and modern research is full of examples of its use.
3.2.6.2 Raman Spectroscopy

Named after an Indian physicist, Raman spectroscopy is based on inelastic scattering of photons, and is commonly used to identify molecules – a chemical fingerprint, of sorts. First put into practice in 1928 [47], it only became common with the commercialization of lasers in the 1960s, which simplified the instrumentation necessary for measurements.

Raman spectroscopy is a common technique in modern research. It is often used in studying the properties of graphene, allowing researchers to measure the number and orientation of layers, the quality and types of edges, the effects of perturbations from electromagnetic fields, and more [48]. Surface-Enhanced Raman Spectroscopy (SERS) enhances the Raman signal from samples with metal nanostructures by many orders of magnitude [49]. Thermal properties of atomically thin samples can even be measured with temperature-dependent Raman spectroscopy [50]. This technique is highly useful in understanding the quality of the carbon structures, as well as the relative impacts of carbon and polyurethane to the overall vibrational modes of the system.
CHAPTER 4
THEORY, EXPERIMENTAL SETUP, UNCERTAINTY

The theoretical development, experimental setups, and uncertainty quantification are outlined in this section.

4.1 Uncertainty Analysis

Uncertainty in a variable that is not directly measured can be calculated by propagating the uncertainties of the dependent parameters. In this work, two methods are used, the Taylor Series Method (TSM) and the Monte Carlo Method (MCM).

4.1.1 Taylor Series Method

Uncertainty propagation according to the TSM is rigorously outlined by Coleman and Steele [51], and a few key points are shown here.

The uncertainty of a measured variable $X$ can be thought of as the interval around the “best value” of $X$ where we expect the true value to lie within a certain confidence level. To calculate the uncertainty, the random (or precision) uncertainty is combined with the systematic (bias due to instrument) uncertainty, done by adding the variances (square of the standard deviations).

Regarding the bias uncertainty, an instrument with $k$ error sources has an estimated standard deviation of $b_k$. Regarding the precision uncertainty, the standard deviation estimate is $s_X$, given by

$$s_X = \frac{s_X}{\sqrt{N}} \quad (4.1)$$

where $s_X$ is the standard deviation of $N$ measurements. Note that the precision uncertainty on the average of the measurements goes down as the number of
measurements goes up. The combined uncertainty \( u_c \) for \( M \) significant systematic error sources is then

\[
    u_c^2 = s_X^2 + \sum_{k=1}^{M} b_k^2
\]

(4.2)

To assign a specific confidence level, a coverage factor is introduced based on the t-distribution. At the 95% confidence level used in this work, the expanded uncertainty \( U_{95} \) can be rewritten as

\[
    U_{95} = t_{95} u_c
\]

(4.3)

The \( t_{95} \) parameter can be found in a table based on the number of degrees of freedom.

Now, when a variable depends on several measured values, we must propagate those uncertainties with the TSM. Per Coleman and Steele, if

\[
    r = f(X_1, X_2, ... X_J)
\]

(4.4)

the general uncertainty in \( r \) from the variables it depends on can be given by

\[
    U_{r_{95}} = \left[ \sum_{i=1}^{J} \left( \frac{\partial r}{\partial X_i} \right)^2 U_{X_i}^2 \right]^{1/2}
\]

(4.5)

The TSM is useful when we have a data reduction equation, such as Equation (4.4), and we know the uncertainties of the dependent variables.

4.1.2 Monte Carlo Method

An alternative to the TSM is the MCM. This is useful in situations where a fitting procedure is used to solve for the variable of interest, whereas the TSM can be used with simpler, explicit calculations. The method has been made extremely useful in a wide range of applications due to modern computer power. This technique is outlined in more
detail elsewhere [51, 52], but is explained briefly here for completeness.

The MCM runs thousands of simulations with randomized inputs based on their specific uncertainty distributions. The results of those simulations are then analyzed by taking the average and standard deviation of the results, then sorting the results and identifying where the 95% confidence is defined – finding an upper and lower limit encompassing 95% of the results is important if the distribution is skewed to one side or another.

In this work, the uncertainties fed into the program were based on the measured thickness, the frequency of excitation set by the lock-in, and the phase measured by the lock-in, which are outlined in Table 4.1. Note that these uncertainties are “elemental”, relating to one standard deviation in the probability distribution. The expanded uncertainty (95% confidence level, or two standard deviations) is calculated post-simulation.

Table 4.1. Uncertainty parameter inputs to Monte Carlo calculation

<table>
<thead>
<tr>
<th>Input Description</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample thickness (m)</td>
<td>1.79E-05</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>2.50E-04</td>
</tr>
<tr>
<td>Phase (°)</td>
<td>5.00E-01</td>
</tr>
</tbody>
</table>

In the program, “true” values of $\alpha$, $L$, and an array of frequencies are set. In a loop through the simulations, these “true” values are randomized based on their uncertainty distributions, and then sent to the thermal quadrupoles calculation of $\theta_2$ which is used to calculate a “true” phase. This phase is then also randomized and fed (along with frequencies) into a least squares regression to fit an appropriate $\alpha$ to the data. This
“measured” $\alpha$ is then stored for every simulation, and the results are then statically analyzed. The expected result (no matter the shape of the input distributions) is that $\alpha$ should be distributed normally around an average value of thermal diffusivity, with the width of the bell curve indicating the expected “goodness” of our measurements. A tall, skinny bell curve indicates our measurements should be repeatable, while a broad distribution would indicate the input uncertainties are too high and should be reduced if possible.

The uncertainty in the thickness calculated from the bias and precision uncertainty was adjusted using penetration depths of the wavelengths of interest. On the front face, the excitation laser was 450 nm. On the back face, the peak emission wavelengths were 8-10 $\mu$m, and the peak detection wavelengths were 1-5.5 $\mu$m. Using ultraviolet-visible (UV-Vis) and Fourier-transformed infrared (FTIR) spectroscopy, the penetration depths of various samples were measured at several locations and wavelengths of interest (440-460 nm for the 450 nm excitation laser, 1-5.5 $\mu$m for the detector, and 8-10 $\mu$m for the peak emissions up to 70°C). Once calculated, two penetration depths on the front, and two penetration depths on the back were added to the thickness expanded uncertainty.

### 4.2 Densities

The expected density can be calculated from the rule of mixtures, as has been done in other polymer-based carbon composite research [37, 53].

$$\rho = f_c \rho_c + (1 - f_c)\rho_{pu} \quad (4.6)$$

Here, $\rho$ is the density of the composite, $f_c$ is the volume percentage of carbon, $\rho_c$ at 2260 kg/m$^3$ is the approximate density of the carbon filler, and $\rho_{pu}$ at 1250 kg/m$^3$ is the approximate density of the polyurethane matrix, as measured in a pure polyurethane
sample, though this is somewhat high when compared to literature values (which are generally closer to 1050 kg/m³).

Comparing the theoretical density to the measured density gives an indication of the porosity of the sample, which have the detrimental effect of scattering phonons and reducing thermal conductivity. From Equation (3.6), we note that the mean free path of the phonons is decreased, reducing the contribution to transport from phonons [54].

Based on Equation (3.1), density is calculated from measurements of mass, thickness, and surface area. To measure the mass, an A&D GR-202 Semi Micro Balance – capable of measuring as small as 0.01 mg – was used. Its bias uncertainty is taken to be one half the smallest digit readable, or 0.005 mg.

To measure thickness, a Brown & Sharpe Micromaster MM2000 – with capability of measuring as small as 1 µm – was used. Its bias uncertainty is taken to be one half the smallest digit readable, or 0.5 µm.

To measure surface area, a picture was taken of each sample from a tripod-mounted camera, and then Photoshop was used to determine surface area in square pixels, which was converted to SI units using a calibration imaged alongside the specimen of interest. Due to the high resolution camera, software accuracy, and clear imaging of the calibration, the bias uncertainty is neglected in the uncertainty analysis.

Overall uncertainty in density is quantified using the TSM outlined previously at a 95% confidence. Given Equation (3.1), we apply Equation (4.4) and (4.5) to get

\[
U_\rho = \left[ \left( \frac{\partial \rho}{\partial m} \right)^2 U_m^2 + \left( \frac{\partial \rho}{\partial A} \right)^2 U_A^2 + \left( \frac{\partial \rho}{\partial t} \right)^2 U_t^2 \right]^{1/2}
\] (4.7)

which can be rearranged by squaring both sides and dividing both sides by \(\rho^2\) to get
\[
\left( \frac{U_p}{p} \right)^2 = \left( \frac{U_m}{m} \right)^2 + \left( \frac{U_A}{A} \right)^2 + \left( \frac{U_t}{t} \right)^2
\]  

(4.8)

We know the uncertainty on the measured variables on the right-hand side (RHS) can be found by adding variances of bias and precision uncertainties, per Equation (4.2). The variables in the denominators of the RHS are the average of all measurements.

### 4.3 Thermal Diffusivity

Thermal diffusivity will be measured by BD-PTR, which requires sinusoidal heating on the front surface of a sample by a laser. The laser used is the 450nm 500mW Blue Laser Module/Industrial Design with cooling fan.

A Stanford Research Systems 850 lock-in amplifier is used to control the laser in a square-wave fashion (on or off states, set to a specific frequency).

As the laser periodically heats the front surface of the sample, a periodic temperature profile is induced through the sample. These oscillations are often called thermal waves. As the thermal waves propagate to the back-side, a slightly attenuated change in temperature is experienced on the back surface. This changing back-side temperature modulates the infrared radiation emission according to Planck’s law. An example of this is shown in Fig. 4.1.
An understanding of where the peak emissions occur allows for proper experimental design. This can be found from Wien’s Displacement Law

$$\lambda_{\text{max}} = \frac{2898 \, \mu m \cdot K}{T}$$

(4.9)

So we see that at room temperature (293.15 K is the lowest temperature our sample can possibly be during modulated laser excitation) peak emissions would occur at 9.89 μm. Increasing the back-side temperature increase results in shorter wavelengths as the peak emission, though higher intensity is seen. For example, emissions at 70°C average back-side temperature would be around 7.98 μm. Though the liquid nitrogen-cooled indium antimonide (InSb) detector best detects between 1-5.5 μm photons, the non-peak infrared emissions are still detectable. For back-detection, it is located directly behind the sample.

The 500 mW laser exits the housing as a small rectangle, roughly 6.35 mm x 0.635 mm, and then passes through attenuation lenses to control the heating. It then travels through a cylindrical lens to expand the beam to more of a square shape, and then goes through a circular iris to shape the spot to be similarly circular to the sample.
(prepared with a 6.35 mm hole punch). The laser provides roughly uniform heating of the front surface of the sample. The sample is held by a 3D-printed sample holder meant to minimize contact between the sample and the holder. This reduces the heat transferred to the sample holder, which could influence measurements negatively. The sample holder is placed in an add-on to the detector, which holds a germanium filter between the backside of the sample and the detector’s IR sensor. The filter protects the detector from any of the high-power laser that might pass around the sides of the sample. This setup can all be seen in Fig. 4.2.

Fig. 4.2. Image of BD-PTR setup, with, from right to left, laser, attenuation lenses, cylindrical expansion lens, circular iris

The detector signal is then passed through an inverted amplifier (adjust signal by 180°) before traveling to the lock-in amplifier. The lock-in amplifier is a band-pass filter with a very narrow band around a specified frequency, allowing it to “lock in” on a frequency of interest by filtering all other noise. The output of a periodic input signal is then analyzed and the lock-in outputs the amplitude of that signal, as well as the phase of the input signal relative to a reference signal (the same signal as is sent to modulate the laser). In this work, the input signal is from the detector, and it reflects the behavior of the
back-side temperature of the sample, which is oscillating at the same frequency as the excitation laser. More details on the inner workings of the lock-in amplifier are outlined elsewhere [55], but we note here that the frequency accuracy is given at 25 ppm, so at 10 Hz, that gives a bias uncertainty in the frequency at 0.25 mHz, and the precision uncertainty in frequency was found to be nearly zero. The phase bias uncertainty is 5E-4° and the precision uncertainty is around 0.05°. The lock-in’s phase measurement – which is generally preferred over amplitude measurements as they are not as susceptible to changes in ambient temperature – can be used to calculate the thermal diffusivity. The phase is corrected by subtracting off the measured phase of a signal sent by a photodiode detector excited directly by the laser. This detector has a fast enough response that the phase lag measured here is due to electronic error, and thus that signal must be taken off the sample measurements. The corrected phase signal of several frequency measurements is then used to estimate the thermal diffusivity using thermal quadrupoles.

4.3.1 Thermal quadrupoles

In its more basic version in heat conduction, a thermal quadrupole is based on 2 x 2 matrices that relate some transform (Laplace, Fourier, etc.) of both temperature and flux on one surface to the same quantities on another surface [56]. Development of a solution that can be used to find thermal diffusivity is outlined here. Starting from conservation of energy on a unit cell and using a Taylor series expansion that ignores higher order terms, the basic heat diffusion equation can be written as

\[
\frac{\partial}{\partial x} \left( k_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( k_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( k_z \frac{\partial T}{\partial z} \right) + q''' = \rho c_p \frac{\partial T}{\partial t}
\]  

(4.10)

Here, \( k_i \) is the thermal conductivity in the \( i \)-direction, \( T \) is temperature, \( q''' \) is the
volumetric heat generation (W/m³), ρ is density, and c_p is the specific heat capacity. This governing equation can be simplified to a 1D problem according to Fig. 4.3.

![Fig. 4.3. Square wave laser excitation uniformly illuminates a circular sample.](image)

For one-dimensional heat transfer with no heat generation, and assuming conductivity is constant through the thickness, we have the following differential equation

\[
k \frac{\partial^2 T}{\partial z^2} = \rho c_p \frac{\partial T}{\partial t}
\]  

(4.11)

Thermal diffusivity in the through-thickness direction is \( \alpha = k \rho c_p \), so we have the following simplification

\[
\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t}
\]  

(4.12)

Performing a Laplace transform of this results in

\[
\frac{\partial^2 \theta}{\partial z^2} = \frac{s}{\alpha} \frac{\partial \theta}{\partial t}
\]  

(4.13)

Here, \( \theta \) is the Laplace-transformed temperature, and \( s \) is the complex Laplace variable taking us from the time domain to the frequency domain, \( s = i\omega \), where \( \omega = 2\pi f \), and \( f \) is the frequency of periodic excitation, and the inverse of the period. We note that the Laplace transform is obtained from the Fourier integral by setting \( s = i\omega \) and under periodic excitation [43]. Letting \( \beta^2 = s/\alpha \), the solution to this 2nd order ordinary
differential equation is outlined below. We first take the characteristic equation

\[ r^2 - \beta^2 = 0 \quad (4.14) \]

We solve and get roots of \( r_1 = \beta \) and \( r_2 = -\beta \). A solution form can be assumed to be of the form

\[ \theta = c_1 e^{r_1 z} + c_2 e^{r_2 z} \quad (4.15) \]

Now, since \( e^{\beta z} = \sinh(\beta z) + \cosh(\beta z) \), and \( e^{-\beta z} = -\sinh(\beta z) + \cosh(\beta z) \), we can rework the above equation to get

\[ \theta = c_1[\sinh(\beta z) + \cosh(\beta z)] + c_2[-\sinh(\beta z) + \cosh(\beta z)] \quad (4.16) \]

\[ \theta = (c_1 - c_2) \sinh(\beta z) + (c_1 + c_2) \cosh(\beta z) \]

Renaming the coefficients, we get

\[ \theta = K_1 \sinh(\beta z) + K_2 \cosh(\beta z) \quad (4.17) \]

With Fourier’s law, we know the heat flux is defined as

\[ q'' = -k \frac{\partial T}{\partial z} \quad (4.18) \]

Now, taking a Laplace transform of the above equation, we have

\[ \phi = -k \frac{\partial \theta}{\partial z} \quad (4.19) \]

Substituting Equation (4.17) into Equation (4.19), we get

\[ \phi = -k\beta (K_1 \cosh(\beta z) + K_2 \sinh(\beta z)) \quad (4.20) \]

Assume the Laplace-transformed temperature and flux boundary conditions can be defined in the following equations

\[ \theta(z = 0) = \theta_1, \phi(z = 0) = \phi_1 \quad (4.21) \]

\[ \theta(z = L) = \theta_2, \phi(z = L) = \phi_2 \quad (4.22) \]

Plugging conditions in Equation (4.21) into Equation (4.17) and Equation (4.20),
the unknown coefficients are found to be \( K_1 = -\frac{\phi_1}{k\beta}, K_2 = \theta_1 \)

Plugging these back into Equation (4.17) and Equation (4.20) and rearranging, we get the following equations

\[ \theta = -\frac{\phi_1}{k\beta} \sinh(\beta z) + \theta_1 \cosh(\beta z) \]  

(4.24)

\[ \phi = -k\beta \left( -\frac{\phi_1}{k\beta} \cosh(\beta z) + \theta_1 \sinh(\beta z) \right) \]  

(4.25)

Now, plugging in conditions from Equation (4.22), we get

\[ \theta_2 = -\frac{\phi_1}{k\beta} \sinh(\beta L) + \theta_1 \cosh(\beta L) \]  

(4.26)

\[ \phi_2 = -k\beta \left( -\frac{\phi_1}{k\beta} \cosh(\beta L) + \theta_1 \sinh(\beta L) \right) \]  

(4.27)

Rearranging into matrix form, these equations become

\[
\begin{bmatrix}
\theta_2 \\
\phi_2
\end{bmatrix} =
\begin{bmatrix}
\cosh(\beta L) & -\frac{1}{k\beta} \sinh(\beta L) \\
-k\beta \sinh(\beta L) & \cosh(\beta L)
\end{bmatrix}
\begin{bmatrix}
\theta_1 \\
\phi_1
\end{bmatrix}
\]  

(4.28)

Inverting the matrix, we get

\[
\begin{bmatrix}
\theta_1 \\
\phi_1
\end{bmatrix} =
\begin{bmatrix}
\cosh(\beta L) & \frac{1}{k\beta} \sinh(\beta L) \\
-k\beta \sinh(\beta L) & \cosh(\beta L)
\end{bmatrix}
\begin{bmatrix}
\theta_2 \\
\phi_2
\end{bmatrix}
\]  

(4.29)

The thermal quadrupoles method thus allows for an easy calculation of back-side temperature and flux based on front-side boundary conditions, or vice versa. Two boundary conditions solve for the other two.

For BD-PTR, the front-side excitation flux \( \phi_1 \) is known, and the back-side excitation flux \( \phi_2 \) is zero. It should be noted that front- and back-side convection were
neglected, as the amplitude and phase at 10 Hz (a typical frequency used in measurements) varied by 0.03% and 0.06%, respectively, on a standard sample, and could thus be ignored. Looking at Equation (4.28), we have

\[ \theta_2 = \cosh(\beta L) \theta_1 - \frac{1}{k\beta} \sinh(\beta L) \phi_1 \] (4.30)

\[ 0 = -k\beta \sinh(\beta L) \theta_1 + \cosh(\beta L) \phi_1 \] (4.31)

Rearranging Equation (4.31), we have

\[ \theta_1 = \frac{\cosh(\beta L)}{\beta \sinh(\beta L)} \frac{\phi_1}{k} \] (4.32)

Plugging this into Equation (4.30) and rearranging, we get

\[ \theta_2 = \left( \frac{\cosh^2(\beta L)}{\beta \sinh(\beta L)} - \frac{\sinh(\beta L)}{\beta} \right) \frac{\phi_1}{k} \] (4.33)

Noting that \( \beta = \sqrt{i\omega/\alpha} \), the phase information related to the back-side temperature is independent of the amplitude of the front-side flux \( \phi_1 \) and thermal conductivity \( k \). A measurement of phase thus makes it so that a knowledge of the amplitude of the front-side flux \( \phi_1 \) – which depends on view factors and other complex issues – is unnecessary, as is knowledge of the thermal conductivity \( k \).

Because the back-side temperature is in phase with the infrared emission changes, the time-domain detector’s measurement and lock-in amplifier’s calculation of phase \( \Theta \) relative to the excitation signal is the same as the phase of the Laplace-transformed backside temperature \( \theta_2 \). Thus

\[ \Theta = \tan^{-1} \left[ \frac{\text{Im}\{\theta_2\}}{\text{Re}\{\theta_2\}} \right] \] (4.34)

Or we can write (noting that \( \phi_1 \) and \( k \) cancel out and are thus arbitrary values in the phase measurements)
\[ \Theta = \tan^{-1} \left[ \frac{\text{Im} \left\{ \frac{\cosh^2 \left( L \sqrt{\frac{i2\pi f}{\alpha}} \right)}{\sqrt{\frac{i2\pi f}{\alpha}} \sinh \left( L \sqrt{\frac{i2\pi f}{\alpha}} \right)} - \sinh \left( L \sqrt{\frac{i2\pi f}{\alpha}} \right) \sqrt{\frac{i2\pi f}{\alpha}} \sinh \left( L \sqrt{\frac{i2\pi f}{\alpha}} \right) \right\}}{\text{Re} \left\{ \frac{\cosh^2 \left( L \sqrt{\frac{i2\pi f}{\alpha}} \right)}{\sqrt{\frac{i2\pi f}{\alpha}} \sinh \left( L \sqrt{\frac{i2\pi f}{\alpha}} \right)} - \sqrt{\frac{i2\pi f}{\alpha}} \sinh \left( L \sqrt{\frac{i2\pi f}{\alpha}} \right) \right\}} \right] \]  

(4.35)

Now it can be seen that at any given frequency, a measurement of the back-side phase response of an excited sample can be used to estimate \( \alpha \) by a simple least squares regression.

The theoretical amplitude and phase response that could be recorded with the lock-in is shown in Fig. 4.4. A frequency range should be selected for each sample that avoids the low-phase-sensitivity region (avoid low frequencies), but achieves a sufficiently high signal-to-noise ratio (avoid high frequencies).

![Graph](image)

Fig. 4.4. The theoretical amplitude and phase responses of the back-side Laplace-transformed temperature, based on an application of thermal quadrupoles.

The amplitude decay as frequency increases is expected, as the thermal waves’ decay is often represented by the thermal diffusion length \( \mu \), where the amplitude of the thermal waves has decayed by about 1/e, or about 37%.
\[
\mu = \sqrt{\frac{\alpha}{\pi f}}
\] (4.36)

Uncertainty in diffusivity was determined by using the uncertainty of in phase measurements, thickness measurements, and frequency of excitation to feed Equation (4.35) into a MCM uncertainty analysis and propagate the input uncertainties to \(\alpha\) at 95% confidence level. This is necessary, as the simpler TSM cannot be used due to the required fitting procedure.

However, before proceeding with these measurements, it is important to understand what is physically happening to the sample. If the sample overheats mid-experiment and experiences a phase change, the data will be flawed and result in false estimates for diffusivity. Understanding and controlling the temperature rise in the sample is essential, and this is outlined in the following two sections, covering numerical and analytical models of the heat equation.

### 4.3.2 Numerical solution

A computational solution to the physics involved was performed with COMSOL Multiphysics Modeling Software. COMSOL utilizes finite element analysis to solve the heat equation in Equation (4.10) in the time domain. The 2D geometry was defined as a rectangle with certain thickness (0.1 mm) and radius (6.35/2 mm). The four boundaries were defined as follows: the left boundary is considered the centerline of the sample, and allows for axisymmetric simplification, and is also considered thermally insulated; the bottom, top, and right boundaries were convectively cooled; the bottom boundary experienced uniform heat flux periodically modulated in square-wave fashion at a defined frequency.
Several different mesh sizes and time steps were initially analyzed, and the results for coarse and fine discretization were compared. It was apparent that the default mesh size ("fine" gave 210 triangular elements) and the time step selected (0.002 seconds) were sufficiently accurate for use. The selected time step in the transient solution was sufficiently small to visualize not only the average steady-state temperature (considered the reference temperature for thermal diffusivity), but also the oscillatory behavior.

4.3.3 Analytical Solution in Time

The heat equation can be solved analytically using a Green’s functions [57]. A Green’s function is a simple solution to a differential equation with homogeneous boundary conditions, which can be used to construct many other solutions. Many of these basic solutions are tabulated, simplifying the math required to solve the partial differential equations of complex heat transfer problems. In transient heat transfer, a Green’s function describes the temperature distribution resulting from deposition of a pulse of energy.

For our case, we start from the governing equation in cylindrical coordinates, where \( T = f(r, \phi, z, t) \) and \( q \) is the absorbed energy in the sample at the surface or internally, varying in both space and time, or \( q = f(r, \phi, z, t) \).

\[
\rho c_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( k_r r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \phi} \left( k_\phi \frac{\partial T}{\partial \phi} \right) + \frac{\partial}{\partial z} \left( k_z \frac{\partial T}{\partial z} \right) + q \quad (4.37)
\]

Assuming that the sample is isotropic and \( k \) is constant in all directions and over the full temperature range considered (small \( \Delta T \) assumed for constant properties), and we have
\[
\rho c_p \frac{\partial T}{\partial t} = \frac{k}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{k}{r^2} \frac{\partial^2 T}{\partial \phi^2} + k \frac{\partial^2 T}{\partial z^2} + q
\]  

(4.38)

Due to the axisymmetric nature of the problem, \( T = f(r, z, t) \), and we now have the following

\[
\rho c_p \frac{\partial T}{\partial t} = \frac{k}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + k \frac{\partial^2 T}{\partial z^2} + q
\]  

(4.39)

Because \( \alpha = k/\rho c_p \), we have our 2D axisymmetric model governing partial differential equation

\[
\frac{\partial T}{\partial t} = \alpha \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \alpha \frac{\partial^2 T}{\partial z^2} + \frac{\alpha}{k} q
\]  

(4.40)

We let

\[
q = q_0 u(r) v(z) w(t)
\]  

(4.41)

where, \( q \) is the absorbed/generated power [W/m^3], \( q_0 \) is the total energy [J], \( u(r) \) is the distribution along \( r \) [m^2], \( v(z) \) is the distribution along \( z \) [m^1], and \( w(t) \) is the heating function/duration [s^-1].

The initial and boundary conditions are

\[
T(r, z, t = 0) = F(r, z)
\]  

(4.42)

\[
k \frac{\partial T}{\partial n_i} + h_i T = f_i(t)
\]  

(4.43)

The \( n_i \) refers to an outward normal from the boundary of interest, with the subscript \( i \) indicating which boundary (the lateral surface or the axial surfaces), and gives the three boundary condition equations for convection or linearized radiation boundary conditions (at \( r = R, z = 0, z = L \)). \( F(r, z) \) and \( f_i(t) \) represent nonhomogeneities in the initial condition and the boundary conditions, respectively.

The general Green function solution is constructed by multiplying the two one-
dimensional Green functions, \( G_r \) and \( G_z \). This is one of the major advantages of using Green’s functions – one can take the “building blocks” from simpler solutions and apply them to more complicated solutions. We thus have for a sample of radius \( R \) and thickness \( L \)

\[
T(r, z, t) = \int_0^L \int_0^R G_z G_r F(r, z) 2\pi r \, dr \, dz + \frac{\alpha}{k} \int_0^t \int_0^L \int_0^R G_z G_r q(r, z, \tau) 2\pi r \, dr \, dz \, d\tau \\
+ \frac{\alpha}{k} \sum_{i=1}^S G_r G_z f_i(r, z, \tau) \, dS_i \, d\tau - \alpha \sum_{i=1}^S \left[ G_r G_z \frac{\partial (G_r G_z)}{\partial n_i} \right]_{bc} \, dS_i \, d\tau
\]

(4.44)

The first term is for the initial condition, the second term is for the source term, the third term is for 2\(^{nd}\) kind (prescribed heat flux, or Neumann) or 3\(^{rd}\) kind (convection, or Robin) boundary conditions, and the fourth term is for 1\(^{st}\) kind boundary conditions (prescribed temperature, or Dirichlet). If we let \( T \) represent the temperature rise from an arbitrary initial temperature, then \( F(r, z) = 0 \) and the initial condition is homogeneous. The boundary conditions in this model are also homogeneous, and \( f_i(t) = 0 \). This allows us to simplify the previous equation to be

\[
T(r, z, t) = \frac{\alpha}{k} \int_0^t \int_0^L \int_0^R G_z G_r q(r, z, \tau) 2\pi r \, dr \, dz \, d\tau
\]

(4.45)

Plugging in the definition of \( q \) from Equation (4.41), we have

\[
T(r, z, t) = \frac{\alpha}{k} \int_0^t \int_0^L \int_0^R G_z G_r q_0 u(r) v(z) w(t) 2\pi r \, dr \, dz \, d\tau
\]

(4.46)

We define the Green’s functions \( G_z \) and \( G_r \) by defining auxiliary problems in separated coordinates. The auxiliary equations replace the original heat conduction equation’s generation term with a Dirac delta function at location and time, \( r', z', \tau \), and has homogeneous boundary and initial conditions. The solution to the auxiliary problem
gives Green’s functions as follows [57]

\[
G_z(z, t|z', \tau) = \frac{2}{L} \sum_{n=1}^{\infty} e^{-\alpha \frac{\beta_n (t-\tau)}{L^2}} \left[ \beta_n \cos \left( \beta_n \frac{z}{L} \right) \right. \\
+ B_0 \sin \left( \beta_n \frac{z}{L} \right) \left\{ \beta_n \cos \left( \beta_n \frac{z'}{L} \right) + B_0 \sin \left( \beta_n \frac{z'}{L} \right) \right\} \\
\left( \beta_n^2 + B_0^2 \right) \left[ 1 + \frac{B_L}{\beta_n^2 + B_L^2} \right] + B_0 \right)
\]

with eigenvalues \( \beta_n \) from the eigenfunction

\[
\tan(\beta_n) = \frac{\beta_n (B_0 + B_L)}{\beta_n^2 - B_0 B_L^2}
\]

where the Biot numbers are \( B_0 = h_0 L/k \), and \( B_L = h_L L/k \), and

\[
G_r(r, t|r'|, \tau) = \frac{1}{\pi R^2} \sum_{n=1}^{\infty} e^{-\alpha \frac{\gamma_n (r-r')}{R^2}} \left[ J_0 \left( \gamma_n \frac{r}{R} \right) J_0 \left( \gamma_n \frac{r'}{R} \right) \right. \\
\left. \left( J_0^2(\gamma_n) + J_1^2(\gamma_n) \right) \right]
\]

with eigenvalues \( \gamma_n \) from the eigenfunction

\[
B_r J_0(\gamma_n) = \gamma_n J_1(\gamma_n)
\]

where the Biot number is \( B_r = h_r R/k \). We now note that \( G_z \) has units \([m^{-1}]\) and \( G_r \) has units \([m^{-2}]\). Substituting \( G_z \) and \( G_r \) into Equation (4.46) and simplifying, we get the following equation

\[
T(r, z, t) = \frac{\alpha q_0}{k} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} A_m B_m C_n D_n E_m F_n
\]

Which can be rewritten as

\[
T(r, z, t) = \frac{\alpha q_0}{k} \left( \sum_{m=1}^{\infty} A_m B_m E_m \right) \left( \sum_{n=1}^{\infty} C_n D_n F_n \right)
\]

Where
\[ A_n = \frac{2}{L} \left[ (\beta_n^2 + B_0^2) \left( \beta_n \cos \left( \frac{\beta_n z}{L} \right) + B_0 \sin \left( \frac{\beta_n z}{L} \right) \right) + B_0 (\beta_n^2 + B_L^2) + B_0 (\beta_n^2 + B_L^2)^2 \right] \] (4.53)

\[ B_n = \int_0^L \left( \beta_n \cos \left( \frac{\beta_n z'}{L} \right) + B_0 \sin \left( \frac{\beta_n z'}{L} \right) \right) v(z') dz' \] (4.54)

\[ C_n = \frac{J_0 \left( \gamma_n \frac{r}{R} \right)}{\pi R^2 [J_0^2 (\gamma_n) + J_1^2 (\gamma_n)]} \] (4.55)

\[ D_n = \int_0^R J_0 \left( \gamma_n \frac{r'}{R} \right) u(r') 2\pi r' dr' \] (4.56)

\[ E_n = \int_0^t e^{-\frac{\alpha \beta_n^2 (t-\tau)}{L^2}} w(\tau) d\tau \] (4.57)

\[ F_n = \int_0^t e^{-\frac{\alpha \gamma_n^2 (t-\tau)}{R^2}} w(\tau) d\tau \] (4.58)

We note that the distribution terms for our square wave heating is \( u(r) = 1 \, m^{-2} \) for uniform distribution in \( r \), \( v(z) = \delta(z - 0) \, m^{-1} \) for pulse heating at the front surface where \( z = 0 \), and \( w(t) \) is a square wave, or \( w(t) = \frac{\text{sign}(\sin(2\pi f t)) + 1}{2} \, s^{-1} \), oscillating between 0 and 1. This represents the square wave excitation on the front surface. Note that, in the experiment, letting \( u = 1 \) and \( w \) oscillate between 0 and 1 resulted in assigning \( q_0 \) the “false” identify of the front heat flux in W/m², where the power was measured by a power meter placed in front of the sample initially, and the surface area was calculated based on the sample.

The 2D solution can be reduced to the solutions of 1D problems, as is shown below. For 1D axial heat conduction, we have
\[ T(z, t) = \frac{\alpha q_0}{k} \sum_{n=1}^{\infty} A_n B_n E_n \]  

(4.59)

And for 1D radial heat conduction, we have

\[ T(r, t) = \frac{\alpha q_0}{k} \sum_{n=1}^{\infty} C_n D_n F_n \]  

(4.60)

The 1D axial heat conduction solution in Equation (4.59) suits our problem perfectly, where the aspect ratio (radius over thickness) is much greater than five, satisfying a rule of thumb that indicates a 1D solution method is applicable to a thin cylinder like our thin film geometry.

We can now address the parameters important to our problem. \( A_n \) is already simplified enough to program. The integral for \( B_n \) must be solved, and we start with

\[ B_n = \int_0^L \left( \beta_n \cos \left( \frac{\beta_n z'}{L} \right) + B_0 \sin \left( \frac{\beta_n z'}{L} \right) \right) \delta(z' - 0) \, dz' \]  

(4.61)

which rearranges to become

\[ B_n = \int_0^L \cos \left( \beta_n \frac{z'}{L} \right) \beta_n \delta(z' - 0) \, dz' + \int_0^L \sin \left( \beta_n \frac{z'}{L} \right) B_0 \delta(z' - 0) \, dz' \]  

(4.62)

Looking at Table 5.7 of [57], and noting that the Dirac delta function is an even function, and thus \( \delta(0 - z') = \delta(z' - 0) \), we can write

\[ B_n = \beta_n \cos \left( \frac{\beta_n 0}{L} \right) + B_n \sin \left( \frac{\beta_n 0}{L} \right) \]  

(4.63)

which simplifies to

\[ B_n = \beta_n \]  

(4.64)

There is no massive simplification possible to easily program \( E_n \), thus numeric integration was performed in Matlab using the intrinsic \texttt{integral} function, which employs
a vectorized adaptive quadrature [58]. An absolute tolerance of 1E-12 was specified as a stopping criterion.

With $A_n$ in Equation (4.53) as a function of position $z$ and eigenvalue $\beta_n$, $B_n$ in Equation (4.64) as a function of position $z$ and eigenvalue $\beta_n$, and numerical integration to get $E_n$ in Equation (4.57) as a function of time $t$ and eigenvalue $\beta_n$, we are able to program the temperature response $T(z, t)$ per Equation (4.59). It should be noted that the first eigenvalue is dominant in $E$ over higher eigenvalues.

4.4 Specific heat capacity

The specific heat capacity was measured using a Netzsch DSC 404 F3 Pegasus. The temperature profile consisted of two heating and cooling segments (20 K/min), with sufficiently long isothermal segments separating them. The first heating was recommended by Netzsch to remove moisture and potentially other impurities. The second heating curve was used to calculate specific heat capacity. The high-speed furnace consists of a gas outlet valve (for the inert nitrogen atmosphere), a heating element, a sample carrier, a protective tube, and a radiation shield.

The samples were prepared using a 6-mm hole punch, as it allows for ideal contact with the bottom of the platinum crucibles. For carbon materials, decomposition becomes an issue at about 600°C [59]. For temperature sweeps that high and higher, it is recommended to use highly conductive platinum as the crucible material. While an aluminum crucible would melt, platinum can go as high as 1700°C. An alumina liner can be used, but platinum and carbon or graphite materials will not generally react until around 1000°C. Alumina would react around 1400°C. It should be noted that DSC measurements are strongly influenced by crucible material, which is why a calibration
procedure must be followed to eliminate the induced uncertainty [60].

The testing follows ASTM standards [61], and Netzsch software following this standard is used to calculate specific heat at each temperature in the temperature sweep according to

\[ c_{p(s)} = c_{p(st)} \frac{D_s * m_{st}}{D_{st} * m_s} \] (4.65)

Here, \( c_{p(s)} [\text{J/g-K}] \) is the specific heat capacity of the specimen, \( c_{p(st)} [\text{J/g-K}] \) is the specific heat capacity of the sapphire standard provided by Netzsch, \( D_s [\text{mW}] \) is the difference between the DSC heating curves at a specific temperature of an empty crucible and a crucible with a sample inside, \( D_{st} [\text{mW}] \) is similar but with the sapphire standard, \( m_s [\text{mg}] \) is the mass of the specimen, and \( m_{st} [\text{mg}] \) is the mass of the sapphire standard.

In this work, the thin disc samples were placed in an alumina liner inside a platinum crucible. The system with this crucible selection is reported to have an uncertainty of about 10%. The temperature program swept from 70°C to 200°C. For the purposes of calculating thermal conductivity, the \( c_p \) value at 70°C was reported. Because only one measurement of uncertainty is taken, the precision uncertainty cannot be reported, and the bias uncertainty of 10% is used as the overall uncertainty.

### 4.5 Thermal conductivity

The thermal conductivity will be calculated based on the previous measurements, per Equation (1.1). The uncertainty will be propagated from previously determined uncertainties using the TSM [51] at 95% confidence. That is, because of Equation (3.3) and Equation (4.5), we get
\[
\left( \frac{U_k}{k} \right)^2 = \frac{U_\alpha}{\alpha}^2 + \frac{U_\rho}{\rho}^2 + \frac{U_{cp}}{c_p}^2 \tag{4.66}
\]

As noted in Equation (3.32), the contribution to thermal conductivity from electron transport is approximately inversely proportional to electrical resistivity. A comparison can be made between \( k \) and \( 1/\rho_e \) to determine the extent microstructural effect electrical and thermal transport.

### 4.6 Thermal effusivity

The thermal effusivity will be calculated from conductivity, density, and specific heat capacity per Equation (3.7).

Similar to thermal conductivity, the uncertainty on this calculation will be estimated at 95% confidence by propagating the underlying uncertainties using TSM. This is found to be

\[
\left( \frac{U_k}{e} \right)^2 = \left( \frac{1}{2} \right)^2 \left( \frac{U_k}{k} \right)^2 + \left( \frac{1}{2} \right)^2 \left( \frac{U_\rho}{\rho} \right)^2 + \left( \frac{1}{2} \right)^2 \left( \frac{U_{cp}}{c_p} \right)^2 \tag{4.67}
\]

### 4.7 Microstructure

This section outlines the samples as they were received from the manufacturer, as well as the theory behind the two measurement techniques utilized to understand sample microstructure: scanning electron microscopy and Raman spectroscopy.

#### 4.7.1 Sample Description

The samples received from the manufacturer were thin sheets of the composite bonded to Mylar (biaxially-oriented polyethylene terephthalate), and could be peeled off using a razor. They varied in their thicknesses, the densification process, the carbon content, and the ratio of “graphene” (mostly graphite flakes, and not single-atom-layer
graphene) to carbon nanotubes, as shown in the following figure.

![Figure 4.5. Samples as received, bonded to Mylar.](image)

Early measurements indicated achievable tensile strengths in excess of 1 MPa, and properties of specific samples received are outlined in the following table. Note that ratios of 1000 actually indicate a lack of carbon nanotubes in the sample.

**Table 4.2. Table of sample information as received from manufacturer.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vol. % C</th>
<th>&quot;graphene&quot;/CNT</th>
<th>Sheet Resistance, Ω/sq</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-9A(U)</td>
<td>16.8%</td>
<td>9</td>
<td>63±9</td>
</tr>
<tr>
<td>3-9A(P)</td>
<td>16.8%</td>
<td>9</td>
<td>44±4</td>
</tr>
<tr>
<td>3-9B(U)</td>
<td>20.7%</td>
<td>9</td>
<td>61±15</td>
</tr>
<tr>
<td>3-9B(P)</td>
<td>20.7%</td>
<td>9</td>
<td>33±4</td>
</tr>
<tr>
<td>3-9C(U)</td>
<td>25.7%</td>
<td>9</td>
<td>81±4</td>
</tr>
<tr>
<td>3-9C(P)</td>
<td>25.7%</td>
<td>9</td>
<td>41±6</td>
</tr>
<tr>
<td>3-9D(U)</td>
<td>30.3%</td>
<td>9</td>
<td>82±4</td>
</tr>
<tr>
<td>3-9D(P)</td>
<td>30.3%</td>
<td>9</td>
<td>26±2</td>
</tr>
<tr>
<td>3-9E(U)</td>
<td>34.9%</td>
<td>9</td>
<td>63±4</td>
</tr>
<tr>
<td>3-9E(P)</td>
<td>34.9%</td>
<td>9</td>
<td>19±4</td>
</tr>
<tr>
<td>11-18A(P)</td>
<td>25.4%</td>
<td>5.7</td>
<td>13±1</td>
</tr>
<tr>
<td>11-18C(P)</td>
<td>25.4%</td>
<td>5.7</td>
<td>10±2</td>
</tr>
<tr>
<td>11-29D(U)</td>
<td>30.2%</td>
<td>7.5</td>
<td>86±6</td>
</tr>
<tr>
<td>11-29E(U)</td>
<td>34.9%</td>
<td>7.5</td>
<td>71±4</td>
</tr>
<tr>
<td>12-28A(U)22um</td>
<td>17.1%</td>
<td>9.2</td>
<td>720±75</td>
</tr>
<tr>
<td>12-28A(U)30um</td>
<td>17.1%</td>
<td>9.2</td>
<td>455±35</td>
</tr>
</tbody>
</table>
Further correspondence with the manufacturer revealed that the “graphene-like” powder (graphite) used had an average characteristic length (x- and y-directions) of about 10 μm, and a thickness of 50-100 nm, with a density of less than 2.2 g/cc. It was 99% solid (1% moisture) and 97% carbon (with some oxygen and hydrogen impurities).

4.7.2 SEM

An SEM system generally consists of an electron column and a control console, along with a computer and monitoring for viewing the results [62]. The electron column influences the path of electrons traveling down a high-vacuum tube towards a sample.
specimen at the base. A computer with appropriate software and monitor allow one to visualize in real-time the results.

When the electron beam interacts with a sample, several types of signals are produced, including secondary electrons (SE), back-scattered electrons (BSE), and characteristic X-rays, as seen in Fig. 4.6.

Fig. 4.6. Types of electrons that leave a sample excited by an electron beam include secondary electrons, back-scattered electrons, and characteristic x-rays.

For the simple topographical imaging needed here, the SEs emitted from the surface of the sample are detected with the Everhart-Thornley detector. Operating at pressures less than 5E-05 Torr and with features larger than 50 nm, imaging is very feasible.

An FEI Quanta FEG 650 was available for this work. The system uses a NavCam and software to position the sample stage. The spot size, voltage, working distance, and stigmation can all be controlled to enhance image clarity. Furthermore, the system comes with a detector for energy dispersive x-ray spectrometry (EDS), for use in determining
elemental composition. This system will allow for the verification of sample purity and imaging of the polyurethane, carbon nanotubes and graphite flakes.

4.7.3 Raman Spectroscopy

Physically, when a photon interacts with a molecule, there is a temporary excitation of the molecule up to a virtual energy state, before the photon then scatters inelastically – that is, the photon may be higher or lower energy than the incoming photon, and thus there is a detectable shift in the photon wavelength. This is called a Stokes or anti-Stokes shift, depending on whether the photon loses energy (Stokes) or gains energy (anti-Stokes). In a Stokes shift, the energy gained by the molecule alters the rotational or vibrational state. In anti-Stokes, the molecule already has excess energy above the ground state, and adds some of that energy to the scattering photons. This is contrasted with Rayleigh scattering, which represents elastic scattering of photons, and it should be noted that Raman measurements of samples at room temperature generally start in the ground state, and Stokes shifts are induced.

The change in energy is often reported in terms of wavenumbers, which relate to wavelength, per the following equation, where the change in energy $E$ is related to the wavenumber $\omega$ change by either wavelengths or by Planck’s number $\hbar$ and the speed of light $c$:

$$\frac{E_0 - E_1}{\hbar c} = \Delta \omega = \frac{1}{\lambda_0} - \frac{1}{\lambda_1}$$

(4.68)

So for an excitation laser wavelength of $\lambda_0 = 633 \, nm$, and a Stokes shift resulting in an inelastically scattered photon of wavelength $\lambda_1 = 675.8 \, nm$, the change in wavenumber is reported as $\Delta \omega = 1000 \, cm^{-1}$. For any given sample, a Raman sweep of
all the shifted photons may produce a figure like the following. As discussed previously, the anti-Stokes shifts (negative wavenumber shifts) are less common than the Stokes shifts for most room temperature samples.

The instrument available for this work is a Renishaw inVia Raman Microscope with a 633 nm, 15 mW laser.
CHAPTER 5
RESULTS AND ANALYSIS

The results for all measurements are presented and analyzed in this section.

5.1 Densities

The average of all mass measurements and their respective uncertainties are given in the following table and figure.

Table 5.1. Averages and 95% confidence uncertainties associated with measurements related to the density calculation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>m (mg)</th>
<th>( U_m ) (mg)</th>
<th>t (cm)</th>
<th>( U_t ) (cm)</th>
<th>( A ) (( cm^2 ))</th>
<th>( U_A ) (( cm^2 ))</th>
<th>( \rho ) (g/( cm^3 ))</th>
<th>( U_\rho ) (g/( cm^3 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-9A(U)</td>
<td>5.280</td>
<td>0.0132</td>
<td>0.0156</td>
<td>0.000190</td>
<td>0.299</td>
<td>0.00480</td>
<td>1.133</td>
<td>0.0230</td>
</tr>
<tr>
<td>3-9A(P)</td>
<td>4.753</td>
<td>0.0197</td>
<td>0.0139</td>
<td>0.000215</td>
<td>0.297</td>
<td>0.00679</td>
<td>1.157</td>
<td>0.0324</td>
</tr>
<tr>
<td>3-9B(U)</td>
<td>4.808</td>
<td>0.0135</td>
<td>0.0205</td>
<td>0.000232</td>
<td>0.299</td>
<td>0.00199</td>
<td>0.786</td>
<td>0.0106</td>
</tr>
<tr>
<td>3-9B(P)</td>
<td>4.723</td>
<td>0.0232</td>
<td>0.0156</td>
<td>0.000193</td>
<td>0.296</td>
<td>0.00452</td>
<td>1.025</td>
<td>0.0208</td>
</tr>
<tr>
<td>3-9C(U)</td>
<td>4.631</td>
<td>0.0199</td>
<td>0.0225</td>
<td>0.000141</td>
<td>0.299</td>
<td>0.00333</td>
<td>0.690</td>
<td>0.0093</td>
</tr>
<tr>
<td>3-9C(P)</td>
<td>4.422</td>
<td>0.0200</td>
<td>0.0173</td>
<td>0.000172</td>
<td>0.296</td>
<td>0.00366</td>
<td>0.865</td>
<td>0.0143</td>
</tr>
<tr>
<td>3-9D(U)</td>
<td>3.461</td>
<td>0.0150</td>
<td>0.0193</td>
<td>0.000151</td>
<td>0.300</td>
<td>0.00282</td>
<td>0.598</td>
<td>0.0078</td>
</tr>
<tr>
<td>3-9D(P)</td>
<td>4.174</td>
<td>0.0145</td>
<td>0.0216</td>
<td>0.000151</td>
<td>0.299</td>
<td>0.00583</td>
<td>0.646</td>
<td>0.0136</td>
</tr>
<tr>
<td>3-9E(U)</td>
<td>3.527</td>
<td>0.0200</td>
<td>0.0217</td>
<td>0.000154</td>
<td>0.297</td>
<td>0.00294</td>
<td>0.549</td>
<td>0.0074</td>
</tr>
<tr>
<td>3-9E(P)</td>
<td>3.522</td>
<td>0.0169</td>
<td>0.0156</td>
<td>0.000201</td>
<td>0.295</td>
<td>0.00577</td>
<td>0.764</td>
<td>0.0182</td>
</tr>
<tr>
<td>11-18A(P)</td>
<td>14.634</td>
<td>0.0183</td>
<td>0.0101</td>
<td>0.000169</td>
<td>1.129</td>
<td>0.00548</td>
<td>1.289</td>
<td>0.0227</td>
</tr>
<tr>
<td>11-18C(P)</td>
<td>27.512</td>
<td>0.0290</td>
<td>0.0197</td>
<td>0.000154</td>
<td>1.091</td>
<td>0.00421</td>
<td>1.283</td>
<td>0.0113</td>
</tr>
<tr>
<td>11-29D(U)</td>
<td>14.022</td>
<td>0.0211</td>
<td>0.0191</td>
<td>0.000217</td>
<td>1.251</td>
<td>0.00674</td>
<td>0.586</td>
<td>0.0074</td>
</tr>
<tr>
<td>11-29E(U)</td>
<td>13.594</td>
<td>0.0244</td>
<td>0.0216</td>
<td>0.000176</td>
<td>1.097</td>
<td>0.00189</td>
<td>0.573</td>
<td>0.0467</td>
</tr>
<tr>
<td>12-28A(U)22um</td>
<td>0.712</td>
<td>0.0169</td>
<td>0.0027</td>
<td>0.000025</td>
<td>0.267</td>
<td>0.00070</td>
<td>0.988</td>
<td>0.0787</td>
</tr>
<tr>
<td>12-28A(U)30um</td>
<td>1.263</td>
<td>0.0132</td>
<td>0.0039</td>
<td>0.000178</td>
<td>0.280</td>
<td>0.00078</td>
<td>1.162</td>
<td>0.0548</td>
</tr>
<tr>
<td>12-28A(U)62um</td>
<td>1.469</td>
<td>0.0204</td>
<td>0.0049</td>
<td>0.000365</td>
<td>0.289</td>
<td>0.00030</td>
<td>1.041</td>
<td>0.0792</td>
</tr>
<tr>
<td>12-28A(U)85um</td>
<td>2.858</td>
<td>0.0278</td>
<td>0.0085</td>
<td>0.000276</td>
<td>0.302</td>
<td>0.00300</td>
<td>1.114</td>
<td>0.0393</td>
</tr>
<tr>
<td>12-28A(U)118um</td>
<td>4.027</td>
<td>0.0195</td>
<td>0.0123</td>
<td>0.000341</td>
<td>0.296</td>
<td>0.00225</td>
<td>1.104</td>
<td>0.0321</td>
</tr>
<tr>
<td>1-13C(U)56um</td>
<td>9.228</td>
<td>0.0158</td>
<td>0.0078</td>
<td>0.000156</td>
<td>1.159</td>
<td>0.00276</td>
<td>1.028</td>
<td>0.0209</td>
</tr>
<tr>
<td>1-13C(U)124um</td>
<td>13.909</td>
<td>0.0199</td>
<td>0.0119</td>
<td>0.000576</td>
<td>1.037</td>
<td>0.00255</td>
<td>1.124</td>
<td>0.0543</td>
</tr>
<tr>
<td>5-24A(P)</td>
<td>31.317</td>
<td>0.0344</td>
<td>0.0163</td>
<td>0.000267</td>
<td>1.625</td>
<td>0.01171</td>
<td>1.181</td>
<td>0.0211</td>
</tr>
<tr>
<td>7-5A(U)</td>
<td>9.433</td>
<td>0.0304</td>
<td>0.0272</td>
<td>0.002448</td>
<td>0.278</td>
<td>0.00107</td>
<td>1.249</td>
<td>0.1126</td>
</tr>
<tr>
<td>7-5A(P)</td>
<td>8.518</td>
<td>0.0175</td>
<td>0.0295</td>
<td>0.003814</td>
<td>0.282</td>
<td>0.00062</td>
<td>1.024</td>
<td>0.1327</td>
</tr>
<tr>
<td>7-5B(U)</td>
<td>9.466</td>
<td>0.0293</td>
<td>0.0323</td>
<td>0.005861</td>
<td>0.291</td>
<td>0.00461</td>
<td>1.007</td>
<td>0.1835</td>
</tr>
<tr>
<td>7-5B(P)</td>
<td>9.448</td>
<td>0.0165</td>
<td>0.0288</td>
<td>0.000765</td>
<td>0.289</td>
<td>0.00210</td>
<td>1.137</td>
<td>0.0314</td>
</tr>
<tr>
<td>7-5C(U)</td>
<td>9.739</td>
<td>0.0146</td>
<td>0.0285</td>
<td>0.003571</td>
<td>0.285</td>
<td>0.00157</td>
<td>1.197</td>
<td>0.1501</td>
</tr>
</tbody>
</table>
The rule of mixtures from Equation (4.6) provides an expectation of the density. As a percentage of this theoretical density, the samples – both pressed and unpressed – are shown in Fig. 5.2. We note that the lower carbon content results in samples closer to the theoretical density, whether pressed or unpressed. The pressing process may not have much influence on the polyurethane, and the voids may be primarily due to carbon concentration. In the figure, there are two zero-carbon samples, one pressed the other.
unpressed. The unpressed polyurethane sample was used as the theoretical density of polyurethane in the calculations for composite theoretical densities, though it is slightly higher than literature values.

The apparent density decrease with increasing carbon content is likely due to voids or air pockets formed. The existence of porosity will decrease thermal conductivity, and act to counter the increased thermal transport that would occur from carbon addition. It also appears that carbon exacerbates the formation of voids, as the unpressed, as-cast samples have increasing porosity with increasing carbon content.

Fig. 5.2. Sample densities presented as a percentage of the theoretical density and as a function of the mixture volume percentage of carbon.

We can also note that pressing samples appears to be quite effective – though not perfectly so – at removing voids, especially at higher carbon concentrations.

The four pressed samples that appear to follow the unpressed samples’ trend were all a part of the same series, series 3-9, and contained CNTs. It may be that this series was poorly pressed during fabrication.

This can also be visualized by giving the actual densities measured and compared
to the theoretical density, as shown in the following figure.

![Figure 5.3](image)

**Fig. 5.3.** Sample densities compared to theoretical densities.

It appears that the densification process has an upper bound and a lower bound. The pressed samples become more distant from the theoretical density with higher carbon concentrations, and the unpressed samples begin to deviate less and less with higher carbon content.

### 5.2 Specific heat capacity

The specific heat capacity at $70^\circ$C with its associated uncertainty is given in the following table and figure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$c_p$ (J/g-K)</th>
<th>$U_{c_p}$ (J/g-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-9A(U)</td>
<td>1.650</td>
<td>0.165</td>
</tr>
<tr>
<td>3-9A(P)</td>
<td>1.675</td>
<td>0.168</td>
</tr>
<tr>
<td>3-9B(U)</td>
<td>1.542</td>
<td>0.154</td>
</tr>
<tr>
<td>3-9B(P)</td>
<td>1.483</td>
<td>0.148</td>
</tr>
<tr>
<td>3-9C(U)</td>
<td>1.485</td>
<td>0.148</td>
</tr>
<tr>
<td>3-9C(P)</td>
<td>1.433</td>
<td>0.143</td>
</tr>
</tbody>
</table>

Table 5.2. Results from DSC measurements of specific heat capacity, with associated uncertainty.
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3-9D(U)</td>
<td>1.551</td>
<td>0.155</td>
</tr>
<tr>
<td>3-9D(P)</td>
<td>1.572</td>
<td>0.157</td>
</tr>
<tr>
<td>3-9E(U)</td>
<td>1.423</td>
<td>0.142</td>
</tr>
<tr>
<td>3-9E(P)</td>
<td>1.349</td>
<td>0.135</td>
</tr>
<tr>
<td>11-18A(P)</td>
<td>1.538</td>
<td>0.154</td>
</tr>
<tr>
<td>11-18C(P)</td>
<td>1.584</td>
<td>0.158</td>
</tr>
<tr>
<td>11-29D(U)</td>
<td>1.324</td>
<td>0.132</td>
</tr>
<tr>
<td>11-29E(U)</td>
<td>1.317</td>
<td>0.132</td>
</tr>
<tr>
<td>12-28A(U)22um</td>
<td>1.285</td>
<td>0.128</td>
</tr>
<tr>
<td>12-28A(U)30um</td>
<td>1.425</td>
<td>0.142</td>
</tr>
<tr>
<td>12-28A(U)62um</td>
<td>1.186</td>
<td>0.119</td>
</tr>
<tr>
<td>12-28A(U)85um</td>
<td>1.256</td>
<td>0.126</td>
</tr>
<tr>
<td>12-28A(U)118um</td>
<td>1.407</td>
<td>0.141</td>
</tr>
<tr>
<td>1-13C(U)56um</td>
<td>1.943</td>
<td>0.194</td>
</tr>
<tr>
<td>1-13C(U)124um</td>
<td>1.809</td>
<td>0.181</td>
</tr>
<tr>
<td>5-24A(P)</td>
<td>0.995</td>
<td>0.100</td>
</tr>
<tr>
<td>7-5A(U)</td>
<td>1.800</td>
<td>0.180</td>
</tr>
<tr>
<td>7-5A(P)</td>
<td>1.800</td>
<td>0.180</td>
</tr>
<tr>
<td>7-5B(U)</td>
<td>1.824</td>
<td>0.182</td>
</tr>
<tr>
<td>7-5B(P)</td>
<td>1.843</td>
<td>0.184</td>
</tr>
<tr>
<td>7-5C(U)</td>
<td>1.653</td>
<td>0.165</td>
</tr>
<tr>
<td>7-5C(P)</td>
<td>1.670</td>
<td>0.167</td>
</tr>
<tr>
<td>7-5D(U)</td>
<td>1.522</td>
<td>0.152</td>
</tr>
<tr>
<td>7-5D(P)</td>
<td>1.462</td>
<td>0.146</td>
</tr>
<tr>
<td>7-5E(U)</td>
<td>1.338</td>
<td>0.134</td>
</tr>
<tr>
<td>7-5E(P)</td>
<td>1.403</td>
<td>0.140</td>
</tr>
<tr>
<td>7-5F(U)</td>
<td>1.230</td>
<td>0.123</td>
</tr>
<tr>
<td>7-5F(P)</td>
<td>1.243</td>
<td>0.124</td>
</tr>
<tr>
<td>7-5G(U)</td>
<td>1.243</td>
<td>0.124</td>
</tr>
<tr>
<td>7-5G(P)</td>
<td>1.519</td>
<td>0.152</td>
</tr>
<tr>
<td>7-5H(U)</td>
<td>1.481</td>
<td>0.148</td>
</tr>
<tr>
<td>7-5H(P)</td>
<td>1.500</td>
<td>0.150</td>
</tr>
<tr>
<td>7-5I(U)</td>
<td>1.329</td>
<td>0.133</td>
</tr>
<tr>
<td>7-5I(P)</td>
<td>1.437</td>
<td>0.144</td>
</tr>
</tbody>
</table>
Fig. 5.4. Results from DSC measurements of specific heat capacity, with associated uncertainty bands.

Sample specific heat capacities – which are not a strong function of temperature – were measured to be between 1-2 J/g-K at 70°C, with higher carbon content generally resulting in lower specific heat capacity, as expected and shown in

![Specific heat capacity vs volume % carbon](image)

Fig. 5.5. Specific heat as a function of carbon content.

The overall uncertainty is approximately 10%, with pure polyurethane measuring 1.8 J/g-K (both pressed and unpressed), in line with literature values. At ~20 vol.% C,
four of the unpressed samples are very thin, and the low $c_p$ values may be a result of a loss of contact between the sample and the bottom of the DSC crucible due to sample curling.

5.3 Thermal diffusivity

5.3.1 MCM Results

Performing the MCM analysis with 10,000 simulations as outlined in Section 4.1.2 on the thermal quadrupoles model, the uncertainty in $\alpha$ measurements from the lock-in amplifier’s phase measurement at 95% confidence is around 1.06%, as shown in Fig. 5.6.

![Fig. 5.6. Histogram of simulations from Monte Carlo analysis.](image)

Because the analysis does not take into consideration all underlying uncertainty factors (convective heating coefficient uncertainty, surface roughness, etc), a safety factor of 10 is applied to the calculated 1.06%. This can be compared to the uncertainty in new ultrafast laser flash methods for sub-micrometer thick metal films, where uncertainty is
estimated at 8% for picosecond pulse heating [63].

We note that the thickness expanded uncertainty was adjusted for two penetration depths on the front (2 x 3.1 μm) and back (2.2 μm), per the results from UV-Vis and FTIR spectroscopy at the wavelengths of interest. These estimates are conservative, as the spectroscopy results used to calculate penetration depths were based on measurements of the most transmissive sample (12-28A(U) was 26 μm thick, 17.1 vol.% C), which showed a transmittance of nearly 0% (with some noise above 0%). This barely nonzero measurement was used to calculate 3.1 μm and 2.2 μm penetration depths for 440-460 nm, and infrared wavelengths (average of 1-5.5 μm and 8-10 μm), respectively.

The calculations of penetration depth were performed by averaging the transmittance across the wavelengths of interest, and averaging those values across locations. The optical depth $\tau$ was then calculated from transmittance percentage $T$ according to

$$\tau = -\ln(T)$$ \hspace{1cm} (5.1)

Then the attenuation coefficient $\alpha \ [m^{-1}]$ was calculated from thickness $L$ assuming the optical depth was linear through $z$, according to

$$\alpha = \tau / L$$ \hspace{1cm} (5.2)

The penetration depth $\delta_p \ [m]$ is then calculated as the inverse of the attenuation coefficient.

5.3.2 Numerical Solution Results

The approximate thermal property values and other inputs in COMSOL are outlined in Table 5.3.
Table 5.3. Input parameters to COMSOL numerical model.

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>$1.50 \frac{W}{mK}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$950 \frac{kg}{m^3}$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>$1.83 \frac{J}{gK}$</td>
</tr>
<tr>
<td>$q_0$</td>
<td>$0.1 \frac{W}{\pi R^2 \frac{mm^2}{m^2}}$</td>
</tr>
<tr>
<td>$q''(t)$</td>
<td>$\frac{q_0}{2} \left(\text{sign}(\sin(2\pi ft)) + 1\right)$</td>
</tr>
<tr>
<td>$h$</td>
<td>$5 \frac{W}{m^2K}$</td>
</tr>
<tr>
<td>$f$</td>
<td>$1 \text{ [Hz]}$</td>
</tr>
<tr>
<td>$R$</td>
<td>$\frac{6.35}{2} \text{ [mm]}$</td>
</tr>
<tr>
<td>$L$</td>
<td>$100 \text{ [\mu m]}$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>$293.15 \text{ [K]}$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>$0.002 \text{ [s]}$</td>
</tr>
<tr>
<td>$t_{max}$</td>
<td>$50 \text{ [s]}$</td>
</tr>
</tbody>
</table>

These inputs result in a 2D solution shown in Fig. 5.7.
Fig. 5.7. COMSOL’s 2D numerical solution at t=50s portrayed in 3D by rotating the solution around the sample centerline.

The temperature varies little from the center to the outer edge, and thus using the centerline node as a representation of the entire front and back surface is reasonable. Plotting these two temperatures versus time, we have Fig. 5.8. The first image shows the temperature increase over time, slowly converging on a “steady-state” temperature (the average of the oscillations). We can see in the second image the small difference between the front and back surface temperatures due to the propagated thermal wave.
Fig. 5.8. COMSOL numerical solution to heat equation at the nodes located along the sample’s centerline on the front and the back surfaces. The right image is zoomed in on the last oscillation’s peak.

The default mesh consisted of 210 triangular elements, and this appeared to give reasonable results which complement the results found in the next section using Green’s functions.

5.3.3 Analytical Solution Results

The input parameters to a Matlab code of Green’s function solution to this heat transfer problem are initially identical to those used in Table 5.3 for COMSOL. The $z$ position were specified as $z = 0$ for the front surface and $z = L$ for the back surface. The results for the temperature rise are shown in Fig. 5.9. Note that 293.15 K was added so that the starting point was identical to COMSOL’s initial temperature.
Fig. 5.9. Green’s function solution to heat equation at $z = 0$ (front surface) and $z = L$ (back surface). The right image shows a zoomed-in on the last oscillation’s peak. The randomness is an artifact of the numerical integration.

Comparing this solution to the COMSOL finite element solution in Fig. 5.10, we see that Green’s functions are very comparable, with the small discrepancy where COMSOL has about 0.8% lower peak temperature in its final oscillation, likely due to the convective heat loss in the radial direction considered in COMSOL but neglected in the Green’s function solution. We can also note that the response is similar to the transient response experienced by a sample under DC heating – or by a sample under pulse heating over very short time periods, as in LFA.
Fig. 5.10. Green’s function solution compared to COMSOL solution for front and back surfaces indicates validity of 1D Green’s functions solution, which can more easily be used to experimental parameters affecting sample temperature.

Given that the 1D Green’s function solution was comparable to COMSOL’s 2D solution at the center nodes, it was used to control parameters of the BD-PTR experiments, such as the frequencies of excitation (controls magnitude of oscillations, and thus signal size) and the heating power (to approximately control the reference temperature of the sample, with a goal of 50-80°C).

First, an analysis of various frequencies is performed. At low frequency, oscillations are larger than higher and give a larger, more stable signal. High frequencies give lower signals. This is shown in Fig. 5.11. This complements the discussion in the section on thermal quadrupoles, and we recall that the trade-off is that low frequencies have less phase sensitivity and give worse measurements of $\alpha$. 
Fig. 5.11. Low frequencies give larger oscillations and larger signals than high frequencies.

Turning attention to the free convection heat transfer coefficient, which is unknown. Typical free convection with gases can range anywhere from 2-25 W/m²-K [27], but an industry recommendation [64] of 5 W/m²-K was used, meant for free convection from a vertical plate in air with a 30°C temperature difference. Varying this coefficient can have a dramatic effect on the reference temperature, as indicated in Fig. 5.12. This indicates that the level of uncertainty on the reference temperature is quite large.

Fig. 5.12. Green’s function solution for various convection coefficient, indicating wide uncertainty the reference temperature.
Using a coefficient $h$ of 5 W/m²-K a laser power of 25 mW was selected for use on all samples, with power thus oscillating between 0 and 25 mW, in order to approximately raise the temperature of the sample to 70°C. One sample is analyzed to demonstrate this. Using real, measured data (outlined in Table 5.4) for sample 3-9B(P) with 25 mW peak power heating, the Green’s function solution for the temperature increase was calculated.

Table 5.4. Input parameters to Green’s function solution in Matlab.

<table>
<thead>
<tr>
<th>Name</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>1.3182 $[\frac{W}{mK}]$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>1024.32 $[\frac{kg}{m^3}]$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>1483.45 $[\frac{J}{kgK}]$</td>
</tr>
<tr>
<td>$q_0$</td>
<td>$\frac{0.025}{\pi R^2} [\frac{W}{mm^2}]$</td>
</tr>
<tr>
<td>$q''(t)$</td>
<td>$\frac{q_0}{2} \left( \text{sign}(\sin(2\pi ft)) + 1 \right)$</td>
</tr>
<tr>
<td>$h$</td>
<td>5 $[\frac{W}{m^2K}]$</td>
</tr>
<tr>
<td>$f$</td>
<td>10 [Hz]</td>
</tr>
<tr>
<td>$R$</td>
<td>$\frac{6.35}{2} [mm]$</td>
</tr>
<tr>
<td>$L$</td>
<td>156.7 [$\mu m$]</td>
</tr>
<tr>
<td>$T_0$</td>
<td>25 [$^\circ C$]</td>
</tr>
</tbody>
</table>

The results of these inputs are shown in Fig. 5.13.
Under these conditions, the average steady-state temperature is approximately 64.4°C, very much in-line with the 70°C reference temperature for the previously reported $c_p$ values (allowing for calculation of $k$) and we see oscillations smaller than 0.1 K peak-to-peak. In experiment, these were detectable, though the signal-to-noise ratio (indicated by stability of the lock-in measurement) was near its limit.

5.3.4 BD-PTR Results

To verify that the system works, a reference sample of Inconel 600 was used. The sample has a measured thickness of 2.560 mm, a measured density of 8347 kg/m$^3$, literature values for specific heat capacity of 444-465 J/kg-K (at 20-100°C), and a thermal conductivity of 14.9-15.9 W/m-K (20-100°C) [65]. This leads to an expected diffusivity of between 4.02-4.10E-6 m$^2$/s. Note that a peak heating power of 95 mW was required to attempt 70°C average temperature, and a lower frequency range than the range used for carbon polymer samples due to the difference in thermal properties. The result of curve-fitting $\alpha$ to the lock-in’s phase measurements is shown in Fig. 5.14, and
we measure the Inconel 600 sample to have an $\alpha$ of 4.068E-6 m$^2$/s – right in line with the literature values (4.07E-6 m$^2$/s at 70°C from [65]).

Fig. 5.14. Curve fitting the phase measurements on Inconel 600 result in a value very close to that reported in literature.

Given the apparent accuracy of this method, the carbon nanostructured polymers were all measured, with results shown in Fig. 5.15 for the fit of $\alpha$ that best matches the phase measurements, along with 95% confidence uncertainty bands determined from the previous MCM analysis.
Fig. 5.15. Measured sample thermal diffusivities, with associated uncertainty bands from MCM analysis.

The thermal diffusivities of the samples that vary only in their thickness (same mixture, but cast at different thicknesses) are the series 12-28A(U) and the series 1-13C(U) samples. While the diffusivities were not measured to be identical, they do mostly fall within each other’s uncertainty bounds, as expected.

There were a few samples that could not be measured. Samples 7-5A were transparent and pure polyurethane, which complicates IR measurements. Samples 7-5H and 7-5I were too brittle for handling, and could not be placed in the sample holder for measurement.

5.4 Thermal Conductivity

With $\alpha$, $\rho$, $c_p$ all measured, $k$ can be calculated. The results along with a TSM uncertainty analysis are shown in Fig. 5.16. The uncertainty averaged 10.6%.
Fig. 5.16. Thermal conductivities calculated from measurements of $\alpha$, $\rho$, $c_p$, with uncertainty bands from a TSM analysis.

Looking at the thermal conductivity of the samples with identical thickness (12-28 series, and 1-13C series), we see that the thermal conductivities mostly fall within each other’s uncertainty bands, as expected.

5.5 Thermal Effusivity

The data necessary to calculate effusivity and its uncertainty bands at 95% confidence are shown in Table 5.5. These numbers also indicate, according to Equation (3.6), that nanoscale heat transfer is negligible. For example, sample 7-5B(U) has a mean free path $\Lambda$ estimated to be less than 1 nm – much smaller than the samples thicknesses which average 213 $\mu$m.

Table 5.5. Results for the measured and calculated values of $\alpha$, $\rho$, $c_p$, $k$, and $e$, with uncertainty bands at 95% confidence.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\alpha \pm U_\alpha \left( \frac{m^2}{s} \right)$</th>
<th>$\rho \pm U_\rho \left( \frac{kg}{m^3} \right)$</th>
<th>$c_p \pm U_{c_p} \left( \frac{J}{kg , K} \right)$</th>
<th>$k \pm U_k \left( \frac{W}{m , K} \right)$</th>
<th>$e \pm U_e \left( \frac{J}{m^2 , K , \sqrt{s}} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-9A(U)</td>
<td>9.70e-07±1e-07</td>
<td>1133±23</td>
<td>1650±165</td>
<td>1.81±0.15</td>
<td>1841±120</td>
</tr>
<tr>
<td>3-9A(P)</td>
<td>9.36e-07±9.9e-08</td>
<td>1157±32</td>
<td>1675±168</td>
<td>1.81±0.15</td>
<td>1876±124</td>
</tr>
<tr>
<td>3-9B(U)</td>
<td>9.92e-07±1.1e-07</td>
<td>786±11</td>
<td>1542±154</td>
<td>1.20±0.15</td>
<td>1208±95</td>
</tr>
<tr>
<td>3-9B(P)</td>
<td>8.63e-07±9.1e-08</td>
<td>1025±21</td>
<td>1483±148</td>
<td>1.31±0.15</td>
<td>1412±107</td>
</tr>
<tr>
<td>3-9C(U)</td>
<td>1.14e-06±1.2e-07</td>
<td>690±9</td>
<td>1485±148</td>
<td>1.17±0.15</td>
<td>1095±88</td>
</tr>
<tr>
<td>3-9C(P)</td>
<td>1.02e-06±1.1e-07</td>
<td>865±14</td>
<td>1433±143</td>
<td>1.27±0.15</td>
<td>1254±96</td>
</tr>
<tr>
<td>3-9D(U)</td>
<td>1.22e-06±1.3e-07</td>
<td>598±8</td>
<td>1551±155</td>
<td>1.13±0.15</td>
<td>1023±84</td>
</tr>
<tr>
<td>3-9D(P)</td>
<td>1.23e-06±1.3e-07</td>
<td>646±14</td>
<td>1572±157</td>
<td>1.25±0.15</td>
<td>1127±88</td>
</tr>
<tr>
<td>3-9E(U)</td>
<td>1.66e-06±1.8e-07</td>
<td>549±7</td>
<td>1423±142</td>
<td>1.30±0.15</td>
<td>1007±76</td>
</tr>
<tr>
<td>3-9E(P)</td>
<td>1.16e-06±1.2e-07</td>
<td>764±18</td>
<td>1349±135</td>
<td>1.19±0.15</td>
<td>1107±89</td>
</tr>
<tr>
<td>11-18A(P)</td>
<td>1.03e-06±1.1e-07</td>
<td>1289±23</td>
<td>1538±154</td>
<td>2.05±0.15</td>
<td>2015±125</td>
</tr>
<tr>
<td>11-18C(P)</td>
<td>1.11e-06±1.2e-07</td>
<td>1283±11</td>
<td>1584±158</td>
<td>2.25±0.15</td>
<td>2140±128</td>
</tr>
<tr>
<td>11-29D(U)</td>
<td>1.17e-06±1.2e-07</td>
<td>586±7</td>
<td>1324±132</td>
<td>0.91±0.15</td>
<td>839±80</td>
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<tr>
<td>11-29E(U)</td>
<td>1.08e-06±1.2e-07</td>
<td>573±47</td>
<td>1317±132</td>
<td>0.81±0.17</td>
<td>783±95</td>
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<tr>
<td>12-28A(U)22um</td>
<td>1.20e-06±1.3e-07</td>
<td>988±79</td>
<td>1285±128</td>
<td>1.52±0.17</td>
<td>1389±117</td>
</tr>
<tr>
<td>12-28A(U)30um</td>
<td>1.13e-06±1.2e-07</td>
<td>1162±55</td>
<td>1425±142</td>
<td>1.86±0.15</td>
<td>1757±121</td>
</tr>
<tr>
<td>12-28A(U)62um</td>
<td>1.30e-06±1.4e-07</td>
<td>1041±79</td>
<td>1186±119</td>
<td>1.61±0.16</td>
<td>1408±114</td>
</tr>
<tr>
<td>12-28A(U)85um</td>
<td>9.82e-07±1e-07</td>
<td>1114±39</td>
<td>1256±126</td>
<td>1.37±0.15</td>
<td>1386±105</td>
</tr>
<tr>
<td>12-28A(U)118um</td>
<td>9.79e-07±1e-07</td>
<td>1104±32</td>
<td>1407±141</td>
<td>1.52±0.15</td>
<td>1536±110</td>
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<tr>
<td>1-13C(U)56um</td>
<td>8.25e-07±8.7e-08</td>
<td>1028±21</td>
<td>1943±194</td>
<td>1.65±0.15</td>
<td>1813±123</td>
</tr>
<tr>
<td>1-13C(U)124um</td>
<td>7.91e-07±8.4e-08</td>
<td>1124±54</td>
<td>1809±181</td>
<td>1.61±0.15</td>
<td>1807±132</td>
</tr>
<tr>
<td>5-24A(P)</td>
<td>1.72e-06±1.8e-07</td>
<td>1181±21</td>
<td>995±100</td>
<td>2.02±0.15</td>
<td>1541±96</td>
</tr>
<tr>
<td>7-5A(U)</td>
<td>0.00e+00±0</td>
<td>1249±113</td>
<td>1800±180</td>
<td>0.00±0</td>
<td>0±0</td>
</tr>
<tr>
<td>7-5A(P)</td>
<td>0.00e+00±0</td>
<td>1024±133</td>
<td>1800±180</td>
<td>0.00±0</td>
<td>0±0</td>
</tr>
<tr>
<td>7-5B(U)</td>
<td>5.86e-07±6.2e-08</td>
<td>1007±183</td>
<td>1824±182</td>
<td>1.08±0.23</td>
<td>1406±211</td>
</tr>
<tr>
<td>7-5B(P)</td>
<td>4.84e-07±5.1e-08</td>
<td>1137±31</td>
<td>1843±184</td>
<td>1.01±0.15</td>
<td>1458±131</td>
</tr>
<tr>
<td>7-5C(U)</td>
<td>1.11e-06±1.2e-07</td>
<td>1197±150</td>
<td>1653±165</td>
<td>2.20±0.19</td>
<td>2088±191</td>
</tr>
<tr>
<td>7-5C(P)</td>
<td>1.43e-06±1.5e-07</td>
<td>1215±14</td>
<td>1670±167</td>
<td>2.91±0.15</td>
<td>2428±137</td>
</tr>
<tr>
<td>7-5D(U)</td>
<td>1.36e-06±1.4e-07</td>
<td>786±15</td>
<td>1522±152</td>
<td>1.63±0.15</td>
<td>1395±95</td>
</tr>
<tr>
<td>7-5D(P)</td>
<td>1.31e-06±1.4e-07</td>
<td>1279±28</td>
<td>1462±146</td>
<td>2.46±0.15</td>
<td>2144±127</td>
</tr>
<tr>
<td>7-5E(U)</td>
<td>1.58e-06±1.7e-07</td>
<td>594±10</td>
<td>1338±134</td>
<td>1.25±0.15</td>
<td>998±77</td>
</tr>
<tr>
<td>7-5E(P)</td>
<td>1.48e-06±1.6e-07</td>
<td>1312±15</td>
<td>1403±140</td>
<td>2.72±0.15</td>
<td>2239±128</td>
</tr>
<tr>
<td>7-5F(U)</td>
<td>1.63e-06±1.7e-07</td>
<td>514±3</td>
<td>1230±123</td>
<td>1.03±0.15</td>
<td>808±70</td>
</tr>
<tr>
<td>7-5F(P)</td>
<td>1.59e-06±1.7e-07</td>
<td>1346±17</td>
<td>1243±124</td>
<td>2.67±0.15</td>
<td>2112±121</td>
</tr>
<tr>
<td>7-5G(U)</td>
<td>1.52e-06±1.6e-07</td>
<td>481±6</td>
<td>1243±124</td>
<td>0.91±0.15</td>
<td>736±70</td>
</tr>
<tr>
<td>7-5G(P)</td>
<td>1.89e-06±1.2e-07</td>
<td>1336±14</td>
<td>1519±152</td>
<td>3.82±0.15</td>
<td>2786±150</td>
</tr>
<tr>
<td>7-5H(U)</td>
<td>0.00e+00±0</td>
<td>476±10</td>
<td>1481±148</td>
<td>0.00±0</td>
<td>0±0</td>
</tr>
<tr>
<td>7-5H(P)</td>
<td>0.00e+00±0</td>
<td>1314±14</td>
<td>1500±150</td>
<td>0.00±0</td>
<td>0±0</td>
</tr>
<tr>
<td>7-5I(U)</td>
<td>0.00e+00±0</td>
<td>469±12</td>
<td>1329±133</td>
<td>0.00±0</td>
<td>0±0</td>
</tr>
<tr>
<td>7-5I(P)</td>
<td>0.00e+00±0</td>
<td>1328±19</td>
<td>1437±144</td>
<td>0.00±0</td>
<td>0±0</td>
</tr>
</tbody>
</table>

The results for effusivity shown in Fig. 5.17.
5.6 Microstructure

A Coulter LS Particle Size Analyzer was used by the manufacturer on the graphite particles and the carbon nanotubes used in producing samples, and gives an approximation of the nanostructures in the film samples. For graphite, the median particle “diameter” was 9.8 μm, confirming the manufacturer’s previous estimate of 10 μm. The distribution in particle size was skewed towards smaller particles, however, as the average size was 12.5 μm. The Sauter mean diameter – which represents the diameter of a sphere that has the same ratio of volume to surface area as the particles – was found to be approximately 2.7 μm, indicating graphite particles are flat compared to a round sphere. 80% of the graphite particles were between 1.6-26.6 μm in their largest dimension. Regarding the results for CNTs, it was found that the median length was 57.7 μm, with 80% of CNTs between 27.6-151.6 μm.

These particle sizes were influenced by the dispersion, however, as the system measures agglomerates. The previous measurement indicates the CNT agglomerates are
roughly 4-5 times as large as the graphite flakes in raw material form.

A multipoint BET measurement of mass-specific surface area was taken with a TriStar 3000. As nitrogen can absorb on surfaces within the agglomerates, it can be used to estimate mean particle diameter by assuming monosized spheres. In this case, the graphite was found to be 24 m²/g, and the CNTs were 224 m²/g. By using a density of 2.2 g/cc, we estimate equivalent sphere diameters for graphite and CNTs would be 114 nm and 12 nm, respectively, in raw material form.

In examining the microstructure, a subset of the samples from Table 4.2 were selected and SEM and Raman Spectroscopy were used, as outlined in the following few sections, with associated analysis.

5.6.1 SEM

EDS measurements on a sample containing polyurethane, graphite flakes, and CNTs indicated a high level of purity, as only carbon, nitrogen, and oxygen were detected (hydrogen can’t be detected with EDS). This is shown for several different locations in Fig. 5.18.
Fig. 5.18. Results for EDS on sample containing polyurethane, graphite, and CNTs are as expected.

To image pure polyurethane, the nonconductive sample had to be put in a low vacuum, which unfortunately allows atmospheric particles to scatters the electron beam and reduces image quality, as seen in the somewhat amorphous polyurethane of the following figure. These images still help distinguish polyurethane from graphite and nanotubes in further images, however.
Fig. 5.19. SEM image of sample 7-5A(B), which is pure polyurethane. The sticky sample was contaminated with random particles, and can be seen in these image surfaces. The polyurethane itself is somewhat amorphous at this scale and resolution.

Contrasting this sample with a sample 5-24A(P), which has 86.9 vol. % graphite and no carbon nanotubes, we see in the following figure the sharp-edged, plate-like graphite contrasts with amorphous polyurethane. We also note that while the sizes of the graphite particles vary greatly, the manufacturer’s reported sizes of 10 μm x 10 μm x 0.1 μm is reflected in SEM. We also see the graphite appears to be predominantly oriented in the x-y plane.
Fig. 5.20. SEM images of sample 5-24A(P), which contains 86.9 vol.% graphite in polyurethane. The graphite sheets are approximately the size indicated by the manufacturer, sizes vary greatly. The amorphous polyurethane with its rounded edges contrasts with the sharp-edged graphite.

However, in a sample with less graphite and more polyurethane – like sample 7-5C(P) at 20.9 vol.% graphite – we see that the graphite flakes appear oriented more randomly, as seen in the following figures. It is also more difficult to distinguish polyurethane from graphite, as the polyurethane appears to bond to the surface of the carbon and distort the previously sharp-edged shape of the flake.
Looking at a sample with a similar amount of carbon, but with carbon nanotubes included, we see in imaging of sample 3-9B(P) – which has 9x as much graphite as CNTs – that the CNTs appear to protrude from the polyurethane in agglomerates. The distribution of CNTs is not uniform, and may impact the bulk thermal transport of the sample if agglomerates provide only localized benefit. Furthermore, if the clustering of CNTs results in large sections of carbon-less polyurethane, the overall thermal conductivity may be reduced.
Fig. 5.22. SEM images of sample 3-9B(P), which contains 20.9 vol.% carbon, and 9x as much graphite as CNTs.

In sample 11-18C(P), there is a slightly higher concentration of carbon, but only 5.7x as much graphite. The clustering of CNTs appears even more pronounced, and the surface seems more defined, possibly indicating a reduced coating of polyurethane. The apparent diameter of the nanotubes in this figure are all between 10-50 nm.
Looking at sample 11-29E(U) – which with 34.9 vol.% carbon and 7.5x as much graphite as CNTs has the most CNTs of all the samples – we see that the large amount of graphite results in more flakes oriented in the x-y plane. And despite having most CNTs than other samples, the graphite and polyurethane still obscure CNTs. Only the last image of Fig. 5.24 shows CNTs well, and that cluster was difficult to find. It is possible that CNTs preferentially cluster internally to the sample, with the graphite flakes forming an outer wall.
Fig. 5.24. SEM of sample 11-29E(U), which contains 34.9 vol.% carbon and 7.5x as much graphite as CNTs, resulting in the sample with the largest amount of CNTs. The graphite and polyurethane obscure CNT agglomerates on the surface.

With regard to hot pressing samples, we can see in the following images that pressing does indeed appear to have the effect of aligning graphite flakes in the x-y plane, at least on the surface.
Fig. 5.25. Unpressed sample 3-9B(U) on the left and pressed sample 3-9B(P) on the right show an alignment of structures in the x-y plane for the pressed vs unpressed sample.

5.6.2 Raman Spectroscopy

Measuring the normalized scattering intensity across a Raman shift (wavenumber) spectral range from 100-3200 cm\(^{-1}\), we observe several important differences between the various sample compositions. Starting with a pure polyurethane sample, 7-5B(P), we see in the following figure peaks at wavenumbers corresponding to published values for polyurethane.

Fig. 5.26. The measured Raman spectrum for sample 7-5A(P) (pure polyurethane) closely matched published data.
Turning to a mostly graphite sample in Fig. 5.27, we see peaks at wavenumbers corresponding to published values.

![Graph showing Raman spectrum](image)

**Fig. 5.27.** The measured Raman spectrum for sample 5-24A(P) (86.9% “graphene” in polyurethane) closely matched published data for both graphene and graphite, which respond similarly. The G mode (from graphite) is apparent at 1581 cm\(^{-1}\), and the D mode (from defects) is at 1333 cm\(^{-1}\).

The largest peak at 1581 cm\(^{-1}\) (1580 cm\(^{-1}\) in literature) is often referred to as the G mode (for graphene), and relates to the planar vibrations of carbon atoms, or stretching of C-C bonds [66]. The peak to the left of it at 1333 cm\(^{-1}\) is the disorder band, or D mode, and is not visible in perfect graphene. It arises when an excited charge carrier is inelastically scattered by a phonon, followed by an elastic scattering due to a defect or zone boundary. In literature, it is usually reported at 1350 cm\(^{-1}\). The larger the G mode is relative to the D mode, the fewer structural defects exist. The peak to the right is the G’ mode, and it is actually an overtone of the D mode, and is sometimes referred to as the 2D mode. Its location depends heavily on the wavelength of the excitation laser, though 2690 cm\(^{-1}\) is often cited [67]. The G’ mode is always visible regardless of the presence of defects, as it arises because in the second scattering described for the D mode is also an
elastic scatter from a second phonon.

The defects that can exist in graphene-based structures are generally categorized as extrinsic if they involve foreign atom impurities. As SEM indicated high purity, the defects that exist here are intrinsic and involve point defects like vacancies or interstitial atoms, dislocations, grain boundaries, or stacking faults.

Pure polyurethane and nearly-pure graphite can be compared to samples with different compositions. Looking at a sample with less graphite relative to the polyurethane (Fig. 5.28), we see some influence from the polyurethane at 2932 cm\(^{-1}\) which was not apparent in the 86.9 vol.% graphite sample. But the small amplitude peak from polyurethane indicates graphite dominates the rotational and vibrational states of the sample, despite being only 20.9 vol.% of the sample mixture.

Fig. 5.28. The measured Raman spectrum for sample 7-5C(P) (20.9% “graphene” in polyurethane). The graphite dominates the response, though polyurethane is detectable at its peak wavenumber.

This no-CNT sample can be compared to sample 3-9B(P), which has nearly the same overall carbon content, but also has a small amount of carbon nanotubes. With a 2 \(\mu\)m diameter laser spot size, four different locations on the sample were measured and are
shown in Fig. 5.29.

![Raman Spectrum Fig. 5.29](image)

Fig. 5.29. The measured Raman spectrum for sample 3-9B(P) at four different locations. This sample has similar overall C content (20.7 vol.% C), and most of that is graphite (9x as much graphite as CNT). The ratio between the G and D modes varies tremendously, indicating structural defects in the graphite dominate the Raman response, and the polyurethane and the carbon nanotubes have less impact in overall sample behavior.

The G/D mode ratio of the amplitudes varies by location from 0.72 up to 3.45 – none of which are high enough to indicate graphene-like structure (which would have a G/D ratio of at least 10-100). Though the carbon structure defects vary in their effect on the rotational and vibrational states of the sample, they are found at the four locations sampled and support the random distribution of materials seen in SEM.

The G band occurred on average at 1575 cm$^{-1}$, and the D band occurred on average at 1328 cm$^{-1}$. Neither the G mode nor the D mode location is significantly shifted from the graphite-only sample. This indicates there may be little to no influence from the carbon nanotubes in this sample, compared to a similar sample with graphite making up all the carbon content.

This can be compared to a sample with similar overall carbon content, but with more CNTs (only 5.7x as much graphite).
Fig. 5.30. The measured Raman spectrum for sample 11-18C(P) at four different locations. This sample has slightly higher overall C content (25.4 vol.% C), but only 5.7x as much graphite as CNTs. The ratio of the G mode to the D mode does vary less than in 11-29E(U), indicating defects in the graphite and not the nanotubes may dominate.

The G band amplitudes which occur at average wavenumber 1579 cm$^{-1}$ divided by the D mode amplitudes at average wavenumber 1332 cm$^{-1}$ are between 2.4-7.4. As this is less than the sample with 9x as much graphite as CNTs, this indicates a higher presence of defects in graphite than in CNT clusters. We also note that the G mode wavenumber is shifted closer to literature values for graphene, indicating the nanotubes themselves (rolls of graphene) have high-quality, graphene-like structure. The G’ mode occurs on average at 2683 cm$^{-1}$, similar to the previous sample with less CNTs, but with larger amplitude, again indicating more graphene-like structure.

We conclude the Raman observations by stating that the carbon dominates the response from the rotational and vibrational states of the sample, as the response from the polyurethane is barely detectable. CNTs appear to provide more graphene-like structure than graphite, possibly due to a decrease in defects such as stacking faults more present in multi-layered graphite flakes. Despite this, it appears that graphite dominates the overall Raman spectra.
5.7 Analysis of $k$

There are many factors that may influence thermal transport. This section covers the overall carbon content, the relative carbon nanotube content, the porosity, and the electrical conductivity. While the average uncertainty was found to be 10.6%, the uncertainty bands are not plotted here to avoid clutter. The conclusions are drawn with uncertainty considered. In Fig. 5.31, the thermal conductivity for samples with no CNTs is shown.

![Graph showing thermal conductivity versus volume percent carbon of samples with no CNTs.]

Fig. 5.31. Thermal conductivity versus volume percent carbon of samples with no CNTs.

Looking at Fig. 5.2 and Fig. 5.31, we postulate that unpressed samples are negatively correlated with graphite content due to increasing porosity induced by the graphite, overriding the inherently high thermal conductivity of carbon.

For the pressed samples, the positive correlation reflects expectations, though the randomized behavior may be due to defects, such as voids. In the 86.9 vol.% C sample, which is difficult to handle due to its friability, the decrease in $k$ may be due to unseen fractures, which inhibit the propagation of thermal energy.

From the Raman spectroscopy results, CNTs appear to have higher-quality carbon...
structure than graphite. They should also provide more thermal conduction paths, given the reduced electrical percolation observed. Theoretically, additional CNTs would then improve $k$. Turning to measurements of samples containing CNTs, we see in Fig. 5.32 at ~25 vol.% carbon a positive effect from increasing CNT concentration, as $k$ nearly doubles when the ratio of graphite to CNTs, $r$, decreases from 9.1 to 5.7. However, at 30-35 vol.% carbon, increasing the CNT concentration slightly by reducing the ratio from 9.1 to 7.5 has a detrimental effect, likely due to porosity in the unpressed higher-CNT samples overriding the benefits of CNTs.

![Fig. 5.32. Thermal conductivity versus the overall volume percentage of carbon, with varying ratios of graphene to CNTs.](image)

We also note that the variability in $k$ between unpressed and pressed CNT-containing samples shown in Fig. 5.32 is less than the variability seen in the graphite-only samples of Fig. 5.31. One possible explanation would be that large graphite flakes induce larger voids during casting than CNTs, and by replacing some of the graphite with CNTs, more conduction pathways are able to form to bypass the voids. Though this would need further investigation, there would be a benefit to knowing that adding CNTs
during sample fabrication would provide more predictable thermal conductivity.

There are many models to predict the effective thermal conductivity of composite materials, though none consider graphene-like particles as constituents, and all require knowledge of the thermal conductivity of the constituents, which are unknown here [28]. The famous Maxwell model predicts that small additions of spherical carbon particles would most dramatically increase the thermal conductivity. This is seen in the pressed samples with no CNTs, where the lowest carbon sample has a conductivity near 1 W/m-K, and the next lowest sample with around 20.7 vol.% more has a nearly 3-fold increase.

Overall, all samples containing carbon nanostructures do show higher thermal conductivity than polymers like polyurethane, expected to be about 0.33 W/m-K [68].

With porosity apparently a major issue in the thermal behavior of these samples, a FIB-Dual Beam SEM was used to image beneath the surface of an unpressed sample containing 34.9 vol.% C and 7.5x as much graphite as CNTs, shown in Fig. 5.33.

Fig. 5.33. Porosity is apparent in imaging the cross section of unpressed sample that has been milled, with arrows indicating several voids.
The porosity through-the-thickness is apparent in this unpressed, as-cast sample, and the observed detriment to $k$ can be minimized by pressing these voids out.

Additional samples were fabricated with an attempt to control porosity. At 20.9 vol.% carbon, samples with and without CNTs were pressed at various levels. The density and diffusivity were measured, and the specific heat capacity was estimated using the average value measured in previous samples with the same carbon content. The thermal conductivity as a function of the percentage of the theoretical density at varying densification levels and graphite to CNT ratios is shown in the following figure. The densification was performed at three pressures: unpressed (UP) at 0 MPa, half-pressed (HP) at 56 MPa, and fully-pressed (FP) at 210 MPa. Pressing was performed at approximately 80°C for one minute. The CNT levels were similar to those previously analyzed, at $r = \infty$ (no CNTs), $r = 9.0$ (9x as much graphite as CNTs), and $r = 5.6$ (5.6x as much graphite as CNTs).

![Graph showing thermal conductivity](image)

Fig. 5.34. Thermal conductivity of 20.9 vol.% C samples with varying levels of densification and CNT content. The densification is indicated for unpressed (UP), half-pressed (HP), and fully-pressed (FP) samples, along with the ratio of graphite to CNTs, $r$.

The overall densification is similar to previously-measured samples 7-5C(U) and
7-5C(P), which contained the same carbon content. For samples with 9x as much graphite as CNTs, there is the clear trend that pressing increases thermal conductivity, likely due to void removal.

The samples with the most CNTs (only 5.6x as much graphite) had the least porosity at all levels of pressing, as well as the least variability in $k$. This further supports the discussion from Fig. 5.32 that CNTs affect void formation during fabrication differently than the graphite flakes.

There is also a clear benefit to CNT addition in the fully-pressed samples, where the highest $k$ was seen in the $r = 5.6$ sample, and was over 42% higher than its no-CNT counterpart. CNTs also appear to benefit the half-pressed and unpressed samples even more significantly, but the addition of voids makes quantifying CNT benefit difficult.

### 5.7.1 Electrical Conductivity

The Wiedemann-Franz law was derived for metal conductors, where both heat energy and electrical energy are transported by free electrons. Carbon itself has six electrons, with four in the outer shell. Three of those outer shell electrons bond to other carbon atoms in graphene, leaving one electron “free” (often called a $\pi$ electron), similar to a metal, and giving graphene its high electrical conductivity. Given that the samples measured here are not pure graphene, and only “graphene-like” with CNTs and graphite flakes, associated structural defects likely restrict the mobility of the $\pi$ electron and reduce its energy transport capability. This non-metal aspect means Wiedemann-Franz likely overestimates the electron contribution, again resulting in Wiedemann-Franz’s conservative use as a maximum estimate of the electronic contribution to thermal transport.
The Wiedemann-Franz law predicts the electron transport to be very small, according to the calculations of electrical conductivity from reported sheet resistance measurements for samples at 70°C. The contributions of $k_e$ range from 206E-6 to 103E-3 W/m-K, while total conductivity $k$ ranges from 0.814-3.82 W/m-K, as seen in Fig. 5.35. There does appear to be a weak correlation to the logarithm of electrical conductivity, supporting the expectation that electrical and thermal percolation go hand-in-hand.

![Graph](image)

**Fig. 5.35.** Thermal conductivity as a function of the logarithm of electrical conductivity, with a first order polynomial fit, with distinctions between densification and CNT presence. Dots were unpressed, circles were pressed, with lines for respective model fitting.

There are a few possible conclusions that can be drawn from the weak correlations. In all cases, increasing electrical conductivity results in higher thermal conductivity, as expected. There is, however, a larger increase for unpressed samples than for their pressed counterparts. This may be due to variations in the sample porosity, as the unpressed samples exhibited a wider range of densification than the pressed samples. Thus, a very porous unpressed sample would have very low electrical conductivity, while a slightly porous sample would perform significantly better. The sample with the highest
electrical and thermal conductivity had 61.3 vol.% C (graphite only).

We note here that the electrical conductivity was derived from measurements of the sheet resistance using a four-point probe. Though this in-plane measurement may not reflect the through-thickness electrical conductivity, it is likely an upper bound. This allows it to be used as an estimate of a maximum possible through-thickness electrical conductivity.
CHAPTER 6
CONCLUSION

This work developed a photothermal radiometry technique with back-side
detection to measure the through-thickness thermal diffusivity of thin-film samples,
allowing for the successful characterization of the thermophysical properties of an
advanced composite film of carbon nanostructures in polyurethane.

The bulk thermophysical properties of samples with varying composition,
microstructure, and densification were measured and calculated, along with the
associated property uncertainties. Film thicknesses ranged between 27 and 520 μm. For
pressed and unpressed samples containing graphite flakes and CNTs, through-thickness
thermal conductivity was found to be 0.81-3.82 W/m-K across an overall volumetric
carbon content of 10.5-61.3%, with an average of 10.6% uncertainty at a 95% confidence
level. This demonstrated an increase in thermal conduction from the approximately 0.33
W/m-K of pure elastomeric polyurethane.

The microstructure and composition were examined in order to understand their
influence on thermal conductivity. It was apparent that the porosity of the film had a
detrimental effect on thermal conductivity. Pressing during fabrication effectively
reduces the pore volume and is likely to increase thermal conductivity.

Increased graphite content exacerbated pore formation and reduced thermal
conductivity. However, with highly densified samples, adding graphite flakes increased
thermal conductivity.

Measurements of low-void samples showed that CNT addition improved through-
thickness thermal conductivity. A 20.9 vol.% C sample with 5.6x as much graphite as
CNTs had a 42% higher thermal conductivity than a counterpart with no CNTs. This may be due to an increase in conduction pathways or by the improved carbon structure of the CNTs. It was also observed that the samples with the highest CNT content had less variability in porosity and thermal conductivity between samples of varying densification.

In the samples studied, the highest thermal conductivity (3.8 W/m-K) was seen in a pressed sample with 61.3 vol.% graphite and no CNTs. While increasing carbon content generally improves thermal conductivity, increasing much beyond this level results in a reduction in thermal conductivity, likely due to the friable structure forming fractures across conduction pathways.
CHAPTER 7

REFERENCES


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Curriculum Vitae

KURT HARRIS

Department of Mechanical & Aerospace Engineering
Utah State University

EDUCATION

<table>
<thead>
<tr>
<th>Year</th>
<th>Institution</th>
<th>Degree</th>
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<tr>
<td>2017</td>
<td>Utah State University</td>
<td>Ph.D. in Mechanical Engineering</td>
<td>Logan, Utah</td>
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<tr>
<td></td>
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<td>• Dissertation: <em>Characterization of Carbon Nanostructured Composite Film Using Photothermal Measurement Technique</em></td>
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<tr>
<td></td>
<td></td>
<td>• Advisor: Dr. Heng Ban</td>
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</tr>
<tr>
<td>2012</td>
<td>Utah State University</td>
<td>B.S. in Mechanical Engineering</td>
<td>Logan, Utah</td>
<td>3.94</td>
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<tr>
<td></td>
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<td>• Minors in Math and Portuguese</td>
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WORK EXPERIENCE

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<th>Date</th>
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<tr>
<td>08/2012 – current</td>
<td><em>Utah State University</em> – Graduate Researcher</td>
<td>Back-detection photothermal radiometry (BD-PTR) for thermal diffusivity measurements of advanced thin-film samples</td>
<td>Atomic Force Microscopy (AFM) for topology and thermophysical property characterization through Scanning Thermal Microscopy (SThM)</td>
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<tr>
<td></td>
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<td>Experience using contact, thermo resistive, and thermocouple probes on unique dual tower AFM system both in atmosphere or vacuum</td>
<td>Differential Scanning Calorimetry for specific heat measurements</td>
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<tr>
<td></td>
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<td>Thermal conductivity, specific heat, and thermal diffusivity measurements using Transient Plane Source method with Hot Disk TPS 500</td>
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<tr>
<td>Summer 2015</td>
<td><em>Universities Space Research Association</em> – Center for Space Nuclear Research Fellow</td>
<td></td>
<td>Performed research supporting USRA at their CSNR location at Idaho National Lab</td>
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<td></td>
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<td>For a future Mars colony, designed the surface fission power conversion cycle (supercritical CO2 Brayton)</td>
</tr>
<tr>
<td>Summer 2014</td>
<td><em>Silesian University of Technology</em> – NSF International Research Fellow in Poland</td>
<td></td>
<td>Fellowship funding for international collaboration at prestigious laboratory</td>
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<td></td>
<td>Atomic Force Microscopy, Scanning Thermal Microscopy (SThM), photothermal methods</td>
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<tr>
<td>Summer 2012</td>
<td><em>Sandia National Laboratories</em> – SIP Graduate Professional Technical Intern</td>
<td></td>
<td>Theorized and validated improvements to current models relevant to photovoltaic power plants, including temperature models, spectral analysis, and instrumentation</td>
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<td>Began development on a performance model for large photovoltaic plants, including research into a model to predict spatial variation in module temperature based on limited meteorological data</td>
</tr>
<tr>
<td>01/2011 – 05/2012</td>
<td><em>Utah State University</em> – Graduate Researcher</td>
<td></td>
<td>Initial thermophysical property characterization on advanced materials fabricated</td>
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by NASA for use in custom-engineered thermoelectric devices meant for harsh environments

- Properties of interest: Seebeck coefficient, thermal conductivity, electrical conductivity
- Plane Source method with Hot Disk TPS 500

**Summer 2011 Westinghouse Electric – Intern/Extractions Engineer at Western Zirconium**

- 10 different projects in the areas of piping, earthquake safety, stress, corrosion
- Directed and supervised drafters to improve mechanical/structural drawings and P&ID’s
- Inspected equipment and piping used to produce zirconium and hafnium for fuel and control rods
- Proposed changes to existing processes, considering both safety, the environment, and cost
- Prepared environmental changes, process hazard analyses, scopes of work, and requests for quote

**Summer 2010 Idaho National Laboratory – Intern/Researcher**

- Fabricated new hafnium-aluminum composite to be used in future nuclear reactor designs
- Composed 50+ page quality control plan outlining fabrication, validation, characterization
- Performed qualitative analysis, as well as mechanical, and thermophysical property analyses on composite specimens using laser flash analysis (LFA), Archimedes density tests, and differential scanning calorimetry (DSC)
- Documented runs of casting, powder processing, hot pressing, and property characterizing
- Trainings: radiation working (Rad Worker II), laser safety, cryogenic materials

**AWARDS**

2017 ANS Michael J. Lineberry Graduate Scholarship
2017 ANS John and Muriel Landis Scholarship
2016 ASME Elisabeth M. and Winchell M. Parsons Scholarship
2015 USU Graduate Enhancement Award
2015 USU Student Association Distinguished Service Award
2013 NSF’s International Center for Materials Research (ICMR) Fellowship
2012 DOE Nuclear Energy University Programs (NEUP) Fellow
2012 USU Presidential Doctoral Research Fellowship
2011 ASME Nuclear Division Scholarship
2011 USU Harold V. Peterson Scholarship
2011 Engineering Undergraduate Research Program scholarship
2010 Nuclear Energy University Programs Scholarship from U.S. Department of Energy
2009 Tau Beta Pi Stabile Scholarship
2009 Rio Tinto Scholarship in Engineering
2006 USU Richard and Moonyeen Anderson Scholarship
2006 Utah’s New Century Scholarship
2006 Robert C. Byrd Honors Scholarship from U.S. Department of Education
2006 USU Presidential Scholarship
PEER-REVIEWED JOURNAL PUBLICATIONS


CONFERENCE PRESENTATIONS AND POSTERS


CONFERENCE PUBLICATIONS


**RESEARCH INTERESTS**

Molten salt reactors, thorium fuel cycle, supercritical carbon dioxide Brayton cycles, nuclear applications in space, thermal property characterization, nano- and micro-scale heat transfer, thermoelectrics

**PROFESSIONAL SOCIETY ACTIVITIES & SERVICES**

**Membership**
- American Society of Mechanical Engineers (ASME)
- American Nuclear Society (ANS)
- Tau Beta Pi (TBP) – The Engineering Honor Society
- Utah Nuclear Engineering Student Delegation (UNESD)

**Leadership**
- UNESD
  - Summer 2015 – Invited to join NESD in DC and learn about nuclear advocacy
  - Spring 2016 – Founded and chaired the state-level advocacy group, UNESD. Focus to legislators: general benefits of nuclear technology, and introduce UNESD. Partnered with local nuclear companies.
  - Spring 2017 – Chair. Focus to legislators: the benefits of thorium molten salt reactors and other advanced reactors, and specific opportunities in Utah.
- ANS
- TBP
  - 2009 – Member
  - 2010 – Webmaster
- GRC – Government Relations Council at USU 2015-16
  - Promoted higher education in Utah to legislators; encouraged voting among students, participated in County Council and City Council meetings; participated in USU presidential search, Student Regent application process, Regents’ and Trustees’ meetings.