Development and Characterization of Thermally Conductive Polymeric Composites for Electronic Packaging Applications

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science and Engineering Graduate Department of Mechanical & Industrial Engineering University of Toronto

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Abstract

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Advancements in the semiconductor industry have lead to the miniaturization of components and increased power densities, resulting in thermal management issues. Due to this shift, finding multifunctional materials with excellent thermal conductivity and electrical resistivity are becoming increasingly important. For this research thesis, thermally conductive polymer composites were developed and characterized. In the first study, a LLDPE matrix was combined with hBN and SiC to determine the effects of both filler type and filler content. Novel porous composite materials were also fabricated to align thermally conductive fillers, improving $k_{\text{eff}}$ while significantly reducing the overall weight. In the second study, PPS was used as a high performance matrix material and combined with different types of hBN to investigate the effects of size, shape, and aspect ratio on the composite, as well as the effect of hybrid fillers. The composites were characterized with respect to their physical, thermal, electrical, and mechanical properties.
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Chapter 1

Introduction

As demand for smaller, faster microelectronics increases, the development of multifunctional materials with higher power densities becomes more significant. A material’s ability to dissipate heat is directly related to the reliability, performance, and potential miniaturization of electronics [2, 3]. Excess heat generated by high power densities can lead to elevated device operation temperatures, performance reduction, and hardware failure [4].

For the purposes of electronic packaging, a material with high thermal conductivity and electrical resistivity is necessary. Thermal conductivity’s relationship to heat dissipation bears importance for this application as the thermally conductive nature of the material is the main mechanism for cooling a device. High electrical resistivity is required in order to prevent leakage current, which introduces loss and can yield a nonfunctional circuit [5]. Other requirements for electronic packaging materials include, but are not limited to, low thermal mismatch, low-weight, small size, low cost, and ease of manufacturing [5]. Thermal mismatch between different materials, or a material and its environment, must be low in order to prevent debonding, bending, and delamination [6]. In regards to fulfilling the last suggested requirement, materials that are capable of being injection molded into parts with any possible three-dimensional
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geometry, such as polymeric composites, are beneficial.

As the electronics industry moves towards smaller, more portable devices, a lightweight material that has the ability to act as an enclosure or encapsulation surrounding the equipment, or as an independent heat management component, becomes more desirable.

1.1 Electronic Packaging Materials

The search for novel multifunctional materials with the aforementioned properties is a continuous pursuit for manufacturers in the semiconductor industry. The primary objective is to replace or enhance the existing materials used to make the components’ encapsulations, including electronic device enclosures, and embedded heat sinks.

Traditionally, thermal dissipation in encapsulated devices has been resolved through the use of embedded heat sinks [3, 7]. As component parts shrink in size, their power density increases requiring a more effective means of extracting heat from the device. If an appropriate solution is not found the device’s core temperature will increase beyond a safe limit. Further, embedded heat sinks are costly, susceptible to thermal cracking, and have limited use in thin packages [3]. In addition to embedded heat sinks thermal dissipation is commonly achieved through the use of epoxy molding compounds combined with silica. Silica is added to epoxy with the intention of not only improving the thermal properties of the composite, but also reducing the thermal expansion coefficient [8]. Silica has a relatively low thermal conductivity of 1.5 W/m-K, therefore providing only slight improvements in heat dissipation. Once again, advancements in technology resulted in higher power densities for component parts and caused increased heat dissipation, rendering epoxy-silica compounds insufficient.

Many solutions have been proposed in the search for alternatives to the current standards mentioned above. There are a number of materials that could satisfy the
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Figure 1.1: Schematic of modified heat sink to include electrically resistive composite.

The aforementioned requirements for electronic packaging, including metal-matrix composites (MMC), and polymer-matrix composites (PMC).

A more achievable goal in the short term relates to complimenting the existing heat sinks, instead of completely replacing them. As seen in Figure 1.1, an electrically resistive material can be combined with a standard aluminum heat sink to reduce the overall conductivity of the material. Currently, thermal insulating pads made of Kapton or mica are used for electrical insulation, mounting electronic parts to a heat sink. Although these materials may be electrically resistive, they have low thermal conductivities of approximately 0.37 W/m-K and 0.71 W/m-K, respectively [9]. By using a composite material with a much higher thermal conductivity, instead of mica or Kapton, heat dissipation through the heat sink can be greatly improved.

1.2 Thesis Objectives

One of the most common methods of improving thermal conductivity for a polymer composite is through the formation of a continuous conductive network of particles throughout the matrix material. By creating a stable path of particles that are thermally conductive, improvements can be made to a composite’s ability to dissipate heat. Significant enhancements to the thermal conductivity can be seen once a percolation
threshold has been reached. This threshold refers to the point at which the filler particulates come in contact with one another, creating interconnectivity throughout the composite.

For this research thesis, a number of different hypotheses were evaluated with the intention of improving the continuous conductive network of filler particles, in turn increasing the effective thermal conductivity. Initial studies were conducted in order to find the percolation threshold using specific matrix and filler combinations, and then subsequent analyses were performed in attempt to maximize both the thermal conductivity and electrical resistivity.

The two main objectives for this research thesis are as follows:

1. To fabricate thermally conductive, electrically resistive polymer-matrix composites with an enhanced continuous conductive network of filler particles, and evaluate the resulting structures in terms of their morphology, thermal, electrical, and mechanical properties.

2. To fabricate novel porous composites to investigate the effect of extensional biaxial flow fields on the alignment of thermally conductive filler materials.

1.3 Thesis Organization

The body of this thesis is separated into four chapters. A background and literature review is presented in Chapter 2 on the following topics: electronic packaging, thermally conductive materials, electrically insulating materials, polymer and ceramic composites, and foamed composite materials. In Chapter 3, the fabrication and characterization techniques of the composite materials are described. Chapters 4 and 5 present the fabricated composite materials, detailing various parametric studies conducted in this research. The thermal conductivity, electrical properties, mechanical properties, and the morphology are presented for these composites. Specifically, Chapter 4 describes
a series of linear low-density polyethylene (LLDPE)-based composites used to determine the impact of incorporating different filler materials at various concentrations. This chapter also includes a method for fabricating porous LLDPE composites, via foaming agents, and an analysis of the properties of the resulting material. In Chapter 5, the effect of filler size and shape, and hybrid fillers were studied with PPS-based composites. This chapter also contains mathematical modeling of the composite materials pertaining to the effect of filler content. Finally, the thesis concludes with an overview of this research and future recommendations.
Chapter 2

Background and Literature Survey

2.1 Electronic Packaging

The functionality of electronic packaging can be divided into four specific tasks: signal distribution, heat dissipation, package protection, and power distribution [10]. This broad range of applications means any material used for electronic packaging must have superior chemical, mechanical, thermal and environmental properties.

Multifunctional materials have great potential for this application due to their enhanced performance with respect to aforementioned tasks. This approach offers one material that serves multiple functions working synergistically, exceeding the sum of the individual component’s capabilities [11]. Reductions in size, weight, cost, and complexity are all possible while improvements in efficiency, and versatility can be achieved [11]. Electronic packaging requires multifunctional materials to provide structural support, mechanical and chemical protection, and thermal management. There are many factors which can contribute to the degradation of electronics such as, moisture, contaminants, mobile ions, radiation (including alpha particles, gamma photons and x-rays), and hostile environmental conditions including salt corrosion and oxidation [10]. Electronic packaging must protect devices from any adverse
environment and ensure long-term reliability. Often there are competing properties within multifunctional materials, therefore optimization of the desired characteristics must be investigated to obtain ideal attributes.

As a result of continued increases in power densities, manufacturers of semiconductor electronics are continuously searching for novel multifunctional materials to replace or enhance the existing standards mentioned in Section 1.1. Many alternatives have been proposed to replace the current heat sink materials, including metal-matrix composites (MMC) and polymer-matrix composites (PMC). MMCs are widely used in the aerospace and automotive industries [12]. These particle-reinforced isotropic composites have many attractive properties in relation to electronic packaging, including, high mechanical strength, low linear expansion ratio, and very high thermal conductivity [12]. Some of the MMCs that have been evaluated include Al-SiC [13, 14], Al-Si [15, 16], Cu-diamond [17–19], Al-diamond [20, 21], Cu-W [22], and Cu-Mo [23]. Although MMCs having many suitable properties, the high electrical conductivity of the composites limits application as an electronic packaging material [12, 24]. Other limitations of MMCs include their high density, susceptibility to corrosion, potential high cost, as well as thermal mismatch between filler and matrix metals [18, 25, 26].

Polymers are already standard in many electronic packaging components. These materials can be found acting as interlayer dielectrics on an integrated circuit (IC), die attachment adhesives, encapsulants, conformal coatings, passivation layers, and as the body of the package [10, 27, 28]. Recently, there has been a growing interest in the development of polymer-based composites for electronic packaging applications. Further discussion regarding the use of PMCs as a substitute for the current standard materials is presented in Section 2.4.
2.2 Thermally Conductive Materials

Thermal conduction is the phenomenon in which heat is transferred from high to low-temperature regions of a material \[29\]. Therefore, thermal conductivity is the property describing a material’s ability to transfer heat.

In a solid material, there are two main mechanisms of heat conduction: through lattice vibration waves, which are called phonons, and through free electrons. The movement of phonons is associated with a certain thermal energy, while free or conducting electrons participate in electronic thermal conduction \[29\]. Transport of heat within a non-metallic material occurs predominantly by phonon or lattice vibrations \[28\]. Phonon scattering leads to thermal resistance and occurs as a result of phonon-phonon scattering, boundary scattering, and defect or impurity scattering. Boundary scattering accounts for the majority of scattering occurrences due to the presence of an interfacial thermal barrier, which is associated with acoustic mismatch and flaws between the matrix-filler interface. By suppressing scattering events, phonon movement increases, in turn maximizing thermal conductivity \[30\]. Depending on the type of material, heat transfer will occur in variable manners.

In metals, the free electron mechanism is much more efficient at transporting heat compared to phonon movement since electrons are more resistant to scattering and move at higher velocities. The large number of electrons present within metals assists
in the thermal conduction process. In addition to promoting heat conduction, this mechanism increases the electrical conductivity in accordance to the Wiedemann-Franz law.

Ceramics are electrical insulators and inherently lack large amounts of free electrons. Due to the shortage of electrons, the heat transfer is predominantly through phonons. Even though free electrons are much more efficient at conducting heat, some ceramics have relatively high thermal conductivities. The thermally conductive nature of ceramics has been linked to the crystal structure. Adamantine materials, having a diamond-like structure, have high $k$-values comparable to those of face-centre cubic (FCC) metals. Ceramics with high $k$-values have been associated with the following characteristics: low atomic mass, strong interatomic bonding, and simple crystal structures to reduce the amount of phonon scattering [31–33].

Unlike ceramic materials, polymers typically have very low thermal conductivities, approximately between 0.2 to 0.3 W/m-K [29]. Polymers with a higher degree of crystallinity have been associated with greater thermal conductivities, in comparison to those with an amorphous structure. Coordinated vibrations of molecular chains that occur within a crystalline state prove to be an effective method of conducting heat [29]. A collection of thermal conductivity values for common metals, ceramics, and polymers can be found in Table 2.1.

In polymeric composites, thermal conductivity has been known to improve through the application of three different techniques. The first is by forming continuous networks using thermally conductive filler materials within the matrix [25, 28, 30, 34–36]. The next method is to decrease the number of thermally resistant junctions between adjacent filler particles by using particulates with increased size [3, 7, 36]. Lastly, the selection of a filler with fewer interfacial flaws can reduce the thermal contact resistance between fillers that are in contact with one another [28]. In addition to the above considerations, it is recommended to select fillers with multimodal particle size
### Material | Thermal Conductivity (W/m-K)
---|---
#### Metals
Aluminum (Al) | 234
Copper (Cu) | 400
Stainless Steel | 15
#### Ceramics
Silica (SiO$_2$) | 1.5
Aluminum Nitride (AlN) | 80 – 200
Silicon Carbide (SiC) | 70 – 490
Alumina (Al$_2$O$_3$) | 18 – 36
Boron Nitride (BN) | 300+
Diamond | 1000
#### Polymers
Linear Low Density Polyethylene (LLDPE) | 0.31
Polyether Ether Ketone (PEEK) | 0.29
Polyphenylene Sulfide (PPS) | 0.22
Liquid Crystal Polymer (LCP) | 0.20

Table 2.1: Thermal conductivity ($k$)-values of common materials at room temperature.
distributions, and use a polymer with a low melt viscosity to increase wetting and improve filler-matrix adhesion [30]. All of these suggestions are based on the assumption that good adhesion between the polymer and filler exists, otherwise air gaps could be introduced, reducing the effective $k$-value. Therefore, compatibility between the polymer and filler materials is also recommended to decrease the possibility of void formation.

One of the most common methods of improving thermal conductivity for a polymer composite is through the formation of a continuous conductive network of particles throughout the matrix material. By creating a stable path of particles that are thermally conductive, improvements can be made to a composite’s ability to dissipate heat. Significant enhancements to the thermal conductivity can be seen once a percolation threshold has been reached. This threshold refers to the point at which the filler particulates come in contact with one another, creating interconnectivity throughout the composite.

### 2.3 Electrically Insulating Materials

Electrical resistivity ($\rho$) refers to a material’s ability to oppose conduction of electrical current, and is the inverse of conductivity. Materials are generally grouped into three categories: conductors, semiconductors, and insulators. Conductive materials typically have an electrical conductivity of $10^3$ (S/cm) or greater. To be considered an insulator, the electrical conductivity must not exceed $10^{-8}$ (S/cm) [29]; semiconductors encompass everything between conductive materials and insulators. Electronic conduction of current results from the motion of free charge carriers within the material.

Polymers characteristically have high electrical resistivities and are often used for applications where insulators are necessary [37]. For instance, polymers are used in flexible coatings on electrical wires and cables [38]. These materials can also be found
in printed circuit boards, transformers, end-fittings, and capacitors [39, 40].

In the context of polymeric composites, there is a proportion of filler content that once reached, improves the electrical conductivity significantly. This phenomenon is called the percolation threshold. At this point, filler particles come in contact with one another, in turn creating a connected three-dimensional conductive network through the composite. The interconnectivity of the particulates provides a continuous path for electrons to travel through the material. For cases where conductive polymer composites (CPC) are the target material, the filler content must exceed this threshold. For the purposes of this application, if electrically conductive fillers are added to a polymer matrix, the quantity must be below the percolation threshold to maintain high electrical resistivity.

2.4 Polymer/Ceramic Composites

Incorporation of ceramic fillers into a polymer matrix produces a composite with the thermally conductive properties of the ceramic, as well as the ease of processing and mechanical properties of the polymeric base. Previous research has been conducted on various polymer-ceramic combinations, as discussed in the following subsections.
2.4.1 Fabrication Methods

Studies have been conducted on the best method of combining a polymer with the filler particles in order to produce desirable properties. Agari et al. tested four methods of fabricating test specimen: powder, solution, roll-milled, and melt mixed [41]. Powder mixed referred to a dry-blend method where the materials are combined at room temperature and then melted into the appropriate shape. For solution mixing, the filler and matrix materials were dispersed within toluene until the solute was removed, and then was melted. Roll-milled samples had the filler mechanically kneaded into the melted polymer and melt mixing used a twin-screw compounder to combine the filler and matrix while the polymer was in a molten state. The thermal conductivity of the prepared specimen increased in the following order: melt mixture < roll milled = solution mixture < powder mixing [41]. These results suggest a non-uniform composite morphology encourages the formation of conductive networks through the material, increasing $k_{eff}$.

2.4.2 Common Issues

When fabricating polymer-ceramic composites, other researchers have reported a series of common complications. These issues are outlined below.

Achieving a homogeneous dispersion of filler particles within polymer composites has proven to be challenging. The ceramics have a tendency to form agglomerates resulting in a heterogeneous morphology. A non-uniform distribution of fillers will decrease the mechanical properties of the composite. Large agglomerates of filler particles have been shown to negatively affect the flexural and impact properties of a composite [42]. Reducing the average size of agglomerates within the composite aids in increasing the mechanical properties of the material [42].

Improvements in thermal conductivity have been exhibited at high loadings of
Ceramic fillers. Even though higher $k_{\text{eff}}$-values result, the ability to process the composites is compromised. The viscosity of the composite increases along with filler content, making the material more difficult to mix. This limit depends on the size, shape, aspect ratio, and ultimately the packing factor of the filler material [42]. Studies have suggested a maximum of 40 vol.% filler in order to maintain ease of processing [36, 43].

Achieving good interfacial adhesion between the polymer and filler has proven to be a difficult task. When compared to micromechanical models, the thermal performance of most of the polymer-ceramic composites is underwhelming. One of the major contributing factors is the interfacial barrier resistance. Lack of adhesion between the polymer and filler results in a high amount of phonon scattering, reducing the effective thermal conductivity of the material. In order to overcome this issue, phonon scattering events must be minimized.

2.4.3 Lessons Learned

Additional experimental work has been conducted in order to improve on the challenges mentioned in the previous section. The findings of these experiments are described below.

Through the use of coupling agents, improvements to both dispersion and interfacial adhesion between filler and polymer matrices have been achieved. The main purpose of a coupling agent is to functionalize the components within the composite, making it more reactive and willing to bind to both inorganic and organic fillers. Silane-[3, 28, 34], toluene-[44] and titanate-based [7, 8] coupling agents have been studied for use in polymer-ceramic composites. Enhanced mechanical properties have been noted as a result of improved adhesion. A lack of air gaps between the matrix and filler also increases the $k_{\text{eff}}$ [44].

The selection of filler materials is of great importance when producing polymer-
ceramic composites with high thermal conductivities. Materials with large particle sizes are recommended to reduce the thermal junctions within the material, and improve the effective thermal conductivity \([3, 36]\). Large particles create higher stability for conductive paths, but also increases the viscosity of the material. Therefore, a balance between improvements to \(k_{eff}\) with respect to particle size and viscosity must be obtained.

Composites containing more than one type of filler, which are referred to as hybrids, are also under evaluation for this particular application \([25, 28, 45]\). Ideally, the composite will retain the advantageous properties of each type of filler and minimize the disagreeable qualities, producing a material with the desired design criteria. Through the addition of multiple types of fillers, a synergistic effect can result. Modifications to the properties can be made easily by varying quantities of each type of material. Other studies have found that a combination of different sized fillers has improved the effective thermal conductivity \([7, 25, 28]\). The intention is to have a blend of small particles that occupy space between the larger particles, increasing the number of conductive paths through the composite.

### 2.5 Foamed Composite Materials

Due to the versatile nature of polymeric-based foams, they have been of interest within many different areas of research. These cellular materials are lightweight, have superior thermal insulating capabilities, and a high strength-to-weight ratio \([46, 47]\). Foamed composites have been utilized for various applications including packaging materials, sound insulation, thermal insulation, shock absorption, cushioning, and bioscaffolds for tissue engineering \([48, 49]\).

There are multiple methods of fabricating porous polymer composites. Most foams are formed based on the nucleation and growth of gas bubbles within a polymeric
matrix. The other well known method is the production of syntactic foams, which are formed when micro-beads of encapsulated gas are mixed into the matrix. Syntactic foams do not behave in a similar manner to those formed based on the principles of nucleation and growth.

The thermal conductivity of foamed materials is governed by four factors: conduction of heat through the solid polymer, conduction of heat through the gas, convection of heat through the cells, and finally, radiation through the cell walls and across the voids [50]. Convection generally only has a significant effect for foams containing cells larger than 10 mm, and is often ignored. The major contributor is usual conduction through the gas. Foam conductivity is generally quite low and is not much higher than the $k$ of air within the cell, which is $\sim 0.025 \text{ W/m-K}$.

Expancel® microspheres are hollow, polymeric microballoons, which expand when heated within a specific temperature range. The microsized bubbles consist of a polymer shell encapsulating a hydrocarbon gas. When heat is applied, simultaneously, the pressure of the gas inside the sphere increases, and the thermoplastic outer shell softens. The diameter increases from 18-24 $\mu$m to 120 $\mu$m, creating large pores within the material. This method of foaming is relatively new and as such has been deemed non-conventional.

Studies have been conducted using expandable polymeric microspheres to create porous materials. Multiple evaluations regarding the effect of temperature on the morphology of the foams have been conducted [51–53]. Density profiles showed an optimal processing temperature to obtain the lowest density for composites formed with Expancel® microspheres, which varied based on the grade of microsphere used. Below this optimal temperature, the viscosity of the polymer is too high and restricts bubble growth. Above this temperature, gas loss is inevitable, occurring at a high rate of diffusivity [53]. These studies outlined the importance of processing temperature in finding a balance between gas loss and expansion rate resistance for Expancel®
microspheres. In a study by Kim et al., closed-cell ceramic foams were fabricated using Expancel® \cite{54}. Variations in microsphere content were used to change the porosity of the material, showcasing the ability to tailor the bulk density of the material \cite{54}.

The concept of foaming a composite material to align filler materials, including fibres and particles, has been previously explored. Some studies have focused on using supercritical CO$_2$ as a foaming agent to align particles in the cell wall at the interface between the solid and gas phases \cite{55, 56}. Improvements in the mechanical and electrical properties for polymeric foams have been seen. Increased electrical conductivity, along with reduced foam density, have been attributed to a homogeneous distribution of conductive particulates, creating a conductive network throughout the composite \cite{55}. A novel concept was to use this same principle to create a three-dimensional interconnected pathway of thermally conductive particles throughout the polymer matrix, improving $k_{eff}$.

### 2.6 Micromechanical Modelling

Theoretical and empirical correlations are often used to predict the behaviour of composite materials. These micromechanical models can be used as a preliminary method for evaluating potential composites. Although the predictions may not be precise, they can be used to determine if the properties will be favourable, reducing the likelihood of failed, time consuming experimental work. Once a composite has been fabricated, the model can be fit to this empirical data for verification and validation.

Thermal conductivity is one of the crucial elements when determining the feasibility of a composite for use in electronic packaging. As such, there are a number of reference models available to forecast changes in $k$ with respect to any specified parameter, including filler content, size, shape and orientation. The ability of each model to predict the thermal conductivity is limited by the number of input parameters \cite{57}. 
Since no single model exists which accurately predicts the $k_{eff}$ of every composite, several theoretical correlations must be fit to the empirical data.

### 2.6.1 Basic Models: Series, Parallel and Geometric Mean Models

The series and parallel models determine the thermal conductivity of composites based on the direction of heat flow in relation to the fillers. These two models are used to represent the upper and lower bounds of the effective thermal conductivity [58]. The series and parallel models are described using Equation 2.1 and Equation 2.2.

\[
k_c = \frac{k_p k_f}{k_p(\phi) + k_f(1 - \phi)} \tag{2.1}
\]

\[
k_c = \phi k_f + (1 - \phi)k_p \tag{2.2}
\]

where, $k_f$, $k_p$, and $k_c$ represent the thermal conductivities of the filler, polymer matrix, and composite, respectively, and $\phi$ is the volume fraction of filler. The series model considers a case where the fillers are fully interconnected forming an internal network structure, generally overestimating the $k_{eff}$-value. For the parallel model, each particle is assumed to be an isolated entity, therefore minimizing the effect of the dispersed phase and underestimating $k_{eff}$.

The geometric mean model is a combination of the parallel and series models, assuming an equal proportion of each arrangement. This model is dependent on the weighted average of the filler and matrix materials, and has no physical basis.

\[
k_c = k_f^{\phi} k_p^{(1-\phi)} \tag{2.3}
\]
2.6.2 Maxwell Theoretical Model

Using the potential theory, Maxwell developed a relationship for conductivity of a two-phase mixture. This theory describing electrical conductivity was then adapted by Eucken for thermal conductivity [59]. This model is used for two-phase composites with randomly dispersed spherical particles. The spheres are assumed to be both homogeneous and non-interacting, within a homogeneous, continuous medium [60]. Predictions obtained using this model are generally more accurate for low filler concentrations, for scenarios where the particles do not network [8, 61].

\[
k_c = k_p \left[ \frac{k_f + 2k_p + 2\phi(k_f - k_p)}{k_f + 2k_p - \phi(k_f - k_p)} \right] \tag{2.4}
\]

2.6.3 Bruggeman Theoretical Model

Bruggeman adapted Maxwell’s theory to apply for cases of concentrated particulate composites [59, 61]. This model is also used for two-phase composites with randomly dispersed, isolated, spherical particles. Predictions obtained using this model are generally more accurate at higher filler concentrations [62].

\[
1 - \phi = \left[ \frac{k_f - k_c}{k_f - k_p} \right] \left( \frac{k_p}{k_c} \right)^{1/3} \tag{2.5}
\]

2.6.4 Lewis and Nielsen Theoretical Model

Many studies have found the Lewis and Nielsen semi-theoretical model to be the best fit for solid-solid compositions [60, 63]. A modified version of the Halpin-Tsai equation, this is one of the few models that accounts for the shape, orientation, and packing of fillers within a two-phase system [64].

\[
k_c = k_m \left[ \frac{(1 + AB\phi)}{(1 - B\phi\psi)} \right] \tag{2.6}
\]
where,

\[ B = \frac{k_f}{k_p} - 1 \]

\[ \psi = 1 + \left( \frac{1 - \phi_m}{\phi_m^2} \right) \phi \]

Equation 2.6 uses the \( A \) factor to take geometry into account, while \( \phi_m \) represents the packing factor. \( A \) is a function of the shape, aspect ratio, and direction of heat flow with respect to the dispersed phase, and is calculated in relation to the Einstein coefficient \( k_E \). This coefficient is generalized and depends primarily on particle geometry \[65\].

### 2.7 Summary

There are many approaches associated with electronic packaging and the materials used for its components. Each of these elements were discussed within this chapter including: a general overview of electronic packaging, thermally conductive materials, electrically insulating materials, polymer-ceramic composites, and foamed composite materials. Documentation on basic principles as well as a comprehensive review of previous research has been included as a guide for the selection of the best materials, fabrication techniques, and processing parameters for this research thesis. Polymer-matrix composites were selected for the basis of this work. Ceramic materials, paired with a coupling agent, were decidedly the best filler material due to their high thermal conductivity and electrical resistivity. Use of hybrid materials is also suggested to introduce a positive synergistic effect. With regards to fabrication, dry-blending was suggested as the best means of increasing thermal conductivity within PMCs. Finally, a technique used to increase the electrical conductivity of PMCs was modified for use
in novel porous thermally conductive materials, through the use of extensional flow fields as a result of microsphere expansion.
Chapter 3

Fabrication and Characterization

3.1 Material Selection

Polymer-based composites have been gaining attention within the electronic packaging industry as a substitute for the current standard materials. Polymers are of particular interest due to their electrical resistivity, lightweight, ease of manufacturing, and low cost [66]. Conventional polymers typically are thermal insulators, therefore requiring additional thermally conductive fillers within the matrix to improve their thermal conductivities [2, 3, 34, 67].

3.1.1 Matrix Materials

Linear Low Density Polyethylene

Commercially available LLDPE from Exxonmobil (8555 series) was used as the primary matrix material. Since electronic packaging applications require a cost effective alternative to current component encapsulations and heat management parts, LLDPE was chosen. The melting temperature of LLDPE is 126 °C, and has an in-service temperature of approximately 50 °C. The density is low, 936 kg/m³, which aids in the reduction of the overall weight for packaging materials [68]. The properties of LLDPE
Polyphenylene Sulfide

High performance matrices were also used in an attempt to improve the material properties of the composites, as well as expand the potential market for the material. After compiling an extensive list of potential polymeric candidates, PPS Fortron 0203, obtained from Ticona, was selected for this study. This thermoplastic polymer is semi-crystalline and exhibits a high in-service temperature, ranging from 200-220 °C. Both the density and cost of PPS are slightly higher than that of LLDPE, but this material is stable at much higher temperatures. The properties of this matrix material are outlined in Table 3.1.

3.1.2 Filler Materials

Ceramic fillers were added to the two different matrices. These filler materials were SiC, obtained from Sigma-Aldrich, and hexagonal BN from Momentive Performance Materials. Both of the filler materials were chosen because they possess high thermal conductivities, while maintaining electrical resistivity. The physical properties of the fillers are outlined in Table 3.2.

Silicon Carbide

Silicon carbide (SiC) has been used for a wide variety of applications, including semiconductor electronics. SiC devices and circuits have been developed for high-temperature and high-power applications to replace semiconductors that do not function under these extreme conditions. The high thermal conductivity, high electric field breakdown strength and wide bandgap of this material makes it ideal for devices and circuits subjected to high-temperature, high-power, high frequency and high-radiation environments [70,71].
The silicon carbide used for this study was placed in the composites as-received. The particles have an irregular shape and vary in size from 32 to 74 µm. This filler has a thermal conductivity within the range of 70-490 W/m-K, which is much higher than that of a pure polymer. There are many different crystal structures of SiC, called polymorphs, each having their own electrical properties [71]. The material used has a hexagonal crystal structure, completely in the α-phase.

**Hexagonal Boron Nitride**

Boron nitride (BN), another wide band gap semiconductor, was also used as a filler material. BN is known to have a high thermal conductivity and performs well at high temperatures. This material is also lightweight and cost effective, which are both important qualities for electronic packaging materials [62].

Hexagonal boron nitride is comprised of planar sheets of covalently bonded boron and nitrogen atoms, which make up the in-plane structure of the crystal [72]. The different layers are held together in the through-plane direction through Van der Waals forces. Since the crystal structure is anisotropic, the thermal conductivity varies based on the direction. The in-plane thermal conductivity (k) has been estimated to be greater than 300 W/m-K, while the through-plane k is much lower, around 3 W/m-K [72]. Hexagonal boron nitride’s graphite-like structure also provides a lubricative effect which is desirable for processing. Minimal tangential resistance, seen with this type of structure, is attributed to shearing of the weak bonding between planes, in turn creating a low coefficient of friction and a high carrying load capacity [73].

Four different types of hexagonal BN were evaluated, varying in both size and shape, as seen in Figure 3.1. All four were used to determine the effect of the filler material’s size and shape on the properties of the composites. PTX25 and PTX60 have a spherical agglomerate shape with average diameters around 25 µm and 60 µm, respectively. PT110 has a platelet shape and an average diameter of 45 µm, while PT371
is a medium-density agglomerate varying in size from approximately 250-300 µm. The various sizes and shapes of the particles are directly related to the aspect ratio.

3.2 Fabrication Techniques

The composite materials were fabricated using one of two methods: melt-blend or dry-blend. Each method is outlined below and illustrated in Figure 3.2, with the melt-blend process represented in red and the dry-blend process in blue. All of the composites were created using the following methods unless otherwise mentioned.

3.2.1 Melt-Blend Process

The first method employed was melt-blend processing. In fabricating the solid samples, the polymeric matrix was combined with the filler material in the appropriate quantities. Then the mixture was placed into a DSM Xplore 15 twin-screw compounder and combined just above the melting temperature of the polymer. The material was mixed for a short time of 10 minutes in order to achieve homogeneous mixing and minimize thermal degradation. Once the material was purged from the compounder, it was pelletized and ground to fine powders using a freeze mill. The latter process was accomplished by quenching the material at –196 °C in liquid nitrogen and milling the pellets using a 6850 Freezer/Mill from SPEX CertiPrep Group.

Samples of varying sizes were prepared by compression-molding for an array of characterization analyses, including thermal conductivity (k), electrical impedance, and mechanical properties. For the aforementioned tests, discs 20 mm in diameter were created. Samples fabricated for k and mechanical properties measurements were 10 mm thick, while those prepared for dielectric analyses were 2 mm thick. During the compression molding process, the powders were first compacted in a mold at room temperature for approximately one minute, under a constant pressure of 6.7 MPa.
### Physical Properties

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>LLDPE [68]</th>
<th>PPS [69]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($\rho$)</td>
<td>936 kg/m$^3$</td>
<td>1350 kg/m$^3$</td>
</tr>
<tr>
<td>Melting Temperature ($T_m$)</td>
<td>126°C</td>
<td>280°C</td>
</tr>
<tr>
<td>Service $T_{max}$</td>
<td>50 °C</td>
<td>200 °C</td>
</tr>
<tr>
<td>Thermal Conductivity ($k$)</td>
<td>0.31 W/mK</td>
<td>0.22 W/mK</td>
</tr>
<tr>
<td>Dielectric Strength</td>
<td>25 kV/mm</td>
<td>385 kV/mK</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (CTE)</td>
<td>$\approx 400 \times 10^{-6} , (°C)^{-1}$</td>
<td>$520 \times 10^{-6} , (°C)^{-1}$</td>
</tr>
<tr>
<td>Resin Price</td>
<td>0.28 $/lb$</td>
<td>0.45-0.52 $/lb$</td>
</tr>
</tbody>
</table>

**Table 3.1: Physical Properties of the Matrix Materials**

![Figure 3.1: Variations of Boron Nitride. (a) PTX25, (b) PTX60, (c) PT371, and (d) PT110.](image)

### Physical Properties

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>SiC</th>
<th>hBN [74]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($\rho$)</td>
<td>3210 kg/m$^3$</td>
<td>2280 kg/m$^3$</td>
</tr>
<tr>
<td>Thermal Conductivity ($k$)</td>
<td>70-490 W/mK</td>
<td>300+ W/mK</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (CTE)</td>
<td>$2.77 \times 10^{-6} , (°C)^{-1}$</td>
<td>$0.6 \times 10^{-6} , (°C)^{-1}$</td>
</tr>
<tr>
<td>Size</td>
<td>32-74 µm</td>
<td>25-300 µm</td>
</tr>
</tbody>
</table>

**Table 3.2: Physical Properties of the Filler Materials.**
This compacting stage aimed to minimize the possibility of void formation within the sample. Subsequently, the samples were reheated just above the melting temperature of the polymeric matrix and held at this temperature for 15 minutes at 13.8 MPa (2000 psi). Lastly, all of the samples were cooled using an ice bath.

### 3.2.2 Dry-Blend Process

The second method used to mix the matrix and filler materials was dry-blending. For this processing technique, the matrix and filler materials were combined together in the appropriate quantities and mixed thoroughly at room temperature. The composite was then formed into the required sample size by undergoing the same compression-molding technique as mentioned in the melt-blend section. Although the preferred method of preparation was initially melt-blend processing, the simplicity of the dry-blending process proved to be effective.

### 3.3 Characterization Techniques

The thermal, electrical, mechanical and morphological characteristics of the composites were analyzed.

#### 3.3.1 Thermal Properties

**Thermal Conductivity**

The thermal conductivity of the samples was measured using an in-house built thermal conductivity analyzer [75], in accordance to ASTM E1225. This standard test method measures the thermal conductivity of samples through the comparative-longitudinal heat flow technique. The test is conducted at steady state and is effective within the range of 0.2-200 W/m-K [76]. The setup can be seen in Figure 3.3.
Figure 3.2: Flow Chart of Composite Processing.
In this method, a specimen with unknown thermal conductivity \(k_s\) is placed between two reference bars with a known thermal conductivity \(k_r\). A thermal gradient is established through the reference bars and sample. Once the setup reaches equilibrium conditions, the following equation is used to derive the thermal conductivity, given the temperature gradient:

\[
\frac{Q}{A} = k_s \frac{\Delta T_s}{\Delta Z_s} = k_r \frac{\Delta T_1}{\Delta Z_1} + \frac{\Delta T_2}{\Delta Z_2} \tag{3.1}
\]

where \(Q\) is the heat flow through the cross-sectional area \(A\), and \(\Delta T\) and \(\Delta Z\) correspond to the difference in temperature and the change in distance, respectively, between the top and bottom of the reference bar or sample. The LLDPE-based composites were evaluated for \(k\) at 67.5 °C, while the PPS-based composites were tested at 150 °C.

**Coefficient of Thermal Expansion**

The coefficient of thermal expansion (CTE) was measured for the solid composites. The dimensional stability as a result of change in temperature was measured using a Q400-series thermomechanical analyzer (TMA) from TA Instruments. The LLDPE-based composites were heated to 110 °C and the PPS-based composites were heated to 260 °C at a rate of 5 °C/minute. The CTE was determined from the slope of the plot, depicting change in dimension and temperature, from 30 to 100 °C for the materials with a LLDPE-matrix and 30 to 260 °C for the PPS-based materials. These bounds were selected to encompass the potential in-service temperatures for each set of materials.

### 3.3.2 Electrical Properties

The electrical properties of the composites were obtained using a dielectric/impedance analyzer from Alpha-N-Novocontrol Technologies. This analyzer is used to measure the complex impedance between two electrodes, in order to determine a material’s
dependence on frequency. The electrical conductivity and impedance of each sample were measured using a frequency sweep between $10^{-2}$ and $10^6$ Hz with an applied AC voltage of 1 V.

### 3.3.3 Mechanical Properties

The mechanical properties of the composites are important to the success of the packaging material. As an encapsulation to an electronic device, this material must be able to withstand high compressive forces. The samples were analyzed in terms of their compressive elastic modulus, measured from the linear elastic region of the stress-strain curves, as well as their compressive strength, determined by the 0.2% offset. Compression tests were performed using a Shimadzu Universal Tester Autograph AG-IS with a load cell of 50 kN at a strain rate of 1 mm/minute under ambient conditions. The samples were crushed between two metal plates, while the displacement of the crosshead and the compressive force were recorded. From the data collected, the stress was calculated using the applied force and the cross-sectional area of the sample, and the strain was calculated by taking the total displacement of the crosshead and dividing that by the non-deformed height of the sample. For each composition, three samples were tested and averaged.

### 3.3.4 Morphology

Polymer-filler morphology was obtained by a JEOL JSM-6060 scanning electron microscope. SEM micrographs allow images of the samples to be taken at higher magnifications than possible with a standard light microscope. Micrographs of the samples’ cross-sectional areas were captured to evaluate the dispersion of fillers within the matrix. These images also aided in the confirmation of the sizes and shapes of the particulates.
Preparation of the samples was necessary prior to placing the specimen in the SEM. In order to obtain an accurate representation of the material’s morphology, both thin and thick samples were fractured using liquid nitrogen (LN\textsubscript{2}). Freezing the composite pre-fracture produces a brittle sample, preventing distortion of the sample surface. Multiple samples previously used for dielectric analysis and thermal conductivity tests were both examined to confirm the repeatability of the morphology. The thinner dielectric samples were fractured in half, while the thicker thermal conductivity samples were sliced into several pieces using a bandsaw, and each of those individual pieces were subsequently broken into smaller pieces after being cooled in LN\textsubscript{2}.

Once the samples were fractured, they were mounted on metal studs and sputter coated with a thin layer of platinum (Pt) to create a conductive surface for imaging. An insufficient metallic coating will result in a charging effect within the SEM chamber. When a surface charges, the high intensity beam of electrons reacts with the surface of the material, in turn changing the morphology. Conversely, over coating the specimen with Pt will cover the features of the surface, and will have a smooth appearance under the SEM. The surface topography was evaluated using secondary electron imaging (SEI) at 50, 100, 250, 500 and 1,000× magnifications.

**Cell Morphology**

For the porous composite materials, the relative density, cell size, and cell density were measured. The pore size and density are a result of the processing parameters of the material, including the residence time and amount of filler placed in the material. These properties were measured to determine the optimal processing conditions.

Relative density, $\rho_r$, is the ratio of theoretical density, $\rho^*$, and the measured density, $\rho_m$, of each sample, as defined in Equation 3.2. The density was found by measuring the mass, thickness and diameter of each sample. That value was then compared to the theoretical, calculated density of a sample the same size. Three measurements were
taken for the thickness and diameter of each sample, and a minimum of three samples were used to obtain the average $\rho_m$. Using the calculated relative density, the actual filler content was also found.

$$\rho_r = \frac{\rho^*}{\rho_m} \quad (3.2)$$

The average cell size and cell density with respect to unfoamed volume were evaluated using SEM micrographs and ImageJ, an image processing software developed at National Institutes of Health of USA. Cell density, $N$, was calculated using Equation \ref{eq:cell_density}, where $n$ is the number of pores in the image within a measured area, $A$. Multiple images were used to confirm the pore density of each composition.

$$N = \left(\frac{n}{A}\right)^{\frac{3}{2}} \rho_r^{-1} \quad (3.3)$$
Figure 3.3: Thermal Conductivity Analyzer Setup.
Chapter 4

LLDPE Based Composites

This chapter investigates the fabrication of linear low-density polyethylene composites filled with ceramics and the characterization of their thermal, electrical, mechanical, and physical properties. The subsequent text is divided into two main topics: solid and porous composites. Each section contains the two parametric studies related to the different types of materials. Solid samples were used to determine the effect of different fillers, as well as the effect of content, on the aforementioned properties. Novel porous LLDPE composites were fabricated to evaluate the possibility of weight reduction while maintaining the thermally conductive properties of the polymer composite.

4.1 The Effect of Different Types of Filler

Linear low-density polythene-based composite materials were filled with SiC and hBN particulates. Parametric studies were conducted to investigate the overall effects of the aforementioned fillers within composite materials. Data was collected and analyzed with respect to their physical, thermal, electrical, and mechanical properties.

Table 4.1 outlines all of the compositions created with SiC, hBN and a combination of the both. The intention of these parametric studies was to determine whether a
percolation threshold exists for ceramic fillers within a polymeric matrix, along with variations in material properties due to different filler materials. A minor study on the effects of hybrid fillers was also conducted.

All of the samples in this study were fabricated using the melt-blend process, with the exception of LLDPE-33.3 vol.% SiC. Due to the abrasive nature of SiC particles, along with the high loading of filler within this composite, this composition was dry-blended.

4.1.1 Thermal Properties

4.1.1.1 Thermal Conductivity

Figure 4.1 displays the effective thermal conductivity ($k_{\text{eff}}$) measurements of the LLDPE-SiC, LLDPE-hBN, and LLDPE-hBN-SiC composites with various filler loadings. The general trend for all composites suggests that $k$ increases with higher filler content. These results were expected and are in accordance with other studies [2, 3, 34, 67].

Comparing the measured values of $k_{\text{eff}}$ for LLDPE-SiC and LLDPE-hBN composites, it can be observed that hBN was slightly more effective than SiC in enhancing the composite’s $k$. The slight difference could be attributed to the perfect lattice or crystal structure of hBN, which would lead to a decrease in the number of phonon scattering events and an increased thermal conductivity [3, 30]. Another advantage to using hBN is the soft nature of the filler when compared to the abrasive SiC. Processing of hBN is slightly easier and less destructive, compared to SiC. Among the three types of LLDPE composites, LLDPE-hBN-SiC exhibited the highest $k_{\text{eff}}$. This phenomenon demonstrates positive synergy between the hybrid fillers to promote heat transfer through the composite. It is believed that the increase in $k_{\text{eff}}$ from the hybrid fillers was not only caused by the higher total filler loading, but also by the better interconnectiv-
### Table 4.1: LLDPE-hBN-SiC Compositions

<table>
<thead>
<tr>
<th>Name</th>
<th>Vol.% of LLDPE</th>
<th>Vol.% of SiC</th>
<th>Vol.% of hBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE-2.46VF SiC</td>
<td>97.54</td>
<td>2.46</td>
<td>0</td>
</tr>
<tr>
<td>LLDPE-5.34VF SiC</td>
<td>94.66</td>
<td>5.34</td>
<td>0</td>
</tr>
<tr>
<td>LLDPE-9.36VF SiC</td>
<td>90.64</td>
<td>9.36</td>
<td>0</td>
</tr>
<tr>
<td>LLDPE-33.3VF SiC</td>
<td>66.67</td>
<td>33.3</td>
<td>0</td>
</tr>
<tr>
<td>LLDPE-2.46VF hBN</td>
<td>97.54</td>
<td>0</td>
<td>2.46</td>
</tr>
<tr>
<td>LLDPE-5.34VF hBN</td>
<td>94.66</td>
<td>0</td>
<td>5.34</td>
</tr>
<tr>
<td>LLDPE-9.36VF hBN</td>
<td>90.64</td>
<td>0</td>
<td>9.36</td>
</tr>
<tr>
<td>LLDPE-33.3VF hBN</td>
<td>66.67</td>
<td>0</td>
<td>33.3</td>
</tr>
<tr>
<td>LLDPE-33VF hBN-2.46VF SiC</td>
<td>64.24</td>
<td>2.46</td>
<td>33.3</td>
</tr>
<tr>
<td>LLDPE-33VF hBN-5.34VF SiC</td>
<td>61.36</td>
<td>5.34</td>
<td>33.3</td>
</tr>
<tr>
<td>LLDPE-33VF hBN-9.36VF SiC</td>
<td>57.34</td>
<td>9.36</td>
<td>33.3</td>
</tr>
</tbody>
</table>

Figure 4.1: Thermal conductivity (k) of LLDPE-hBN-SiC composites.
ity among the thermally conductive fillers of various sizes and shapes. Both factors would lead to a more dense packing of particulates. As a result, the secondary fillers would be able to bridge gaps among the primary fillers and create a more extensive three-dimensional thermally conductive network throughout the LLDPE matrix [62].

4.1.1.2 Coefficient of Thermal Expansion

For composites, the mismatch of thermal expansion within the material induces residual stress, which can result in debonding, bending, and delamination [6]. Through the reduction of thermal expansion of the composite, these stresses can be minimized. As such, the coefficients of thermal expansion for all of the composites were measured.

There is a general trend seen with regards to the thermal expansion of composites containing SiC. As seen in Figure 4.2, the coefficient of thermal expansion decreases for the materials containing SiC and hybrid fillers with increased amounts of inclusions. This trend is in accordance to the rule of mixtures (ROM), since the CTE of the filler material is much less than the polymer. The ROM is a simple, first-order method used to determine the overall effects of filler on the composite’s CTE, and is outlined in Equation 4.1.

\[
\alpha_c = \alpha_m (1 - \phi) + \alpha_f \phi
\]  

(4.1)

where \(\alpha_c\), \(\alpha_m\), \(\alpha_f\) represent the CTE of the composite, matrix and filler, respectively, and \(\phi\) is the volume fraction of filler. This approach is used to predict an approximate value, but takes neither the dispersion of fillers nor the interfacial interaction into account [6, 77]. The addition of filler particles also physically confines the polymer chains, reducing the overall expansion of the composite. By adding larger quantities of filler, increased constriction of polymer chains occurs. Factors affecting the degree of confinement include aspect ratio, orientation, bulk modulus, and dispersion of filler particles within the matrix [77, 78]. The aggregation of particles can have significant
effects on the properties of a composite, causing a reduction in the effective CTE \[79\], as seen with samples containing 33 vol.% SiC which were dry-blended.

For the composites containing hBN there was no significant change seen in the CTE values when varying the filler content. Even though this was the case, the overall CTE is much lower than the CTE of neat LLDPE, which is represented by the dotted line in Figure 4.2. The ROM predicts higher CTEs for the LLDPE-hBN composites when compared to the experimental results. This disconnect could be due to the poor interfacial strength between the filler and matrix materials, rendering the inclusions inefficient at constricting the free expansion of the matrix in a predictable manner \[80\]. The LLDPE-hBN composites exhibit thermal stability, regardless of the amount of filler added.

### 4.1.2 Electrical Properties

The electrical resistivity of the fabricated samples was evaluated through impedance (Z) curves obtained from the dielectric/impedance analyzer. At lower frequencies,
the impedance curves show linear, horizontal behaviour. Within this region, the impedance was frequency independent. This type of behaviour is a characteristic of resistive materials. At this particular point, the impedance value should be equivalent to the resistance of the material.

As seen in Figure 4.3, the impedance of the composites decreased as the filler content increased. When larger amounts of fillers were dispersed in the LLDPE matrix, the composite’s ability to resist AC current was reduced, slightly decreasing its resistivity. Although increasing filler contents led to a general downward shift in impedance, the values remained relatively close to one another, ranging from $10^{11}$ and $10^{16}$. In other words, both SiC and hBN would not compromise the electrical insulating properties of LLDPE.

In order to confirm the results seen in the impedance curves, the electrical conductivity of the composites was also analyzed. This data exhibited the same trends as the $Z$ curves. As the amount of filler increased there was a decrease in the electrical resistivity. The three-dimensional continuous conductive paths throughout the material that improve thermal conductivity likely encourage slight improvements in the electrical conductivity as well since the filler material has a higher conductivity than the polymer.

### 4.1.3 Mechanical Properties

#### 4.1.3.1 Compressive Elastic Modulus

The mechanical properties of LLDPE-SiC, LLDPE-hBN, and LLDPE-hBN-SiC were compared in terms of their compressive elastic moduli ($E$) and their compressive yield strength ($\sigma_y$). Figure 4.4 shows that, for both LLDPE-SiC and LLDPE-hBN composites, $E$ increased with filler content. At higher loading levels, particle-particle interactions would begin to influence the fracture mechanics. In composites, the elastic deformation
4. LLDPE Based Composites

**Electrical Property**

<table>
<thead>
<tr>
<th>Impedance</th>
<th>Conductivity</th>
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Figure 4.3: Electrical properties of LLDPE-hBN-SiC composites.
of the polymer component is controlled by the filler. As the volume percent of filler increased, less deformation of the polymer was seen and $E$ increased [81].

Comparing LLDPE-SiC and LLDPE-hBN composites, hBN has a stronger positive effect on the compressive modulus of the composite. One possible explanation for this is the dependence of elastic modulus on filler size. Vollenberg and Heikens found that there is a strong tendency for elastic modulus to increase with decreasing particle size of untreated fillers because the local solidification of the matrix activated at a free filler particle surface [82]. SEM micrographs in Section 4.1.4 revealed that the hBN agglomerates were broken into individual platelets during melt-compounding. These platelets were smaller than the SiC particles. Therefore, LLDPE composites filled with hBN platelets had a larger surface area for the potential activation of local solidification of the LLDPE, leading to more significant increases in their moduli.

4.1.3.2 Compressive Strength

Figure 4.5 shows the compressive strength of the various composite materials. In general, the strength of the material does not exhibit a drastic change with the addition of more filler. Large differences between the composites are not expected, since the variation in filler quantity does not vary significantly, except for the composites containing 33.3 vol.%. When comparing the strength of composites with different filler types, SiC and hBN perform quite similarly in most cases, with an exception for composites at high filler loadings. The composite containing 33.3 vol.% of SiC performed poorly compared to the 33.3 vol.% hBN composite. This is likely due to the formation of SiC agglomerates within the material as a result of the mixing method, reducing the overall strength of the material. The presence of inorganic particle agglomeration within the polymer matrix decreases the contact area and creates defects within the composite, in turn reducing the overall effectiveness of the interfacial interaction and the strength of the material [83].
The combination of SiC and hBN, to form a hybrid composite, has the best compressive strength. The addition of fillers with different sizes and shapes assists in improving $\sigma_y$. When the particles occupy the space between the larger particulates, a more efficient packing of fillers can help to improve the compressive yield strength of the composite. Increases in compressive strength can also be attributed to the improved transfer of stress between the polymer matrix and ceramic fillers [84, 85].

### 4.1.4 Morphology

Figures 4.6 (a) through (d) show the SEM micrographs for LLDPE-SiC composites of different SiC loadings. As evident in these figures, uniform dispersions of SiC particles within the LLDPE matrices were achieved. These results suggest that the processing conditions used for compounding the composites were appropriate.

From the SEM micrographs, it is apparent that some SiC particles had debonded from the LLDPE matrix, leaving irregularly shaped voids in different regions of the composites. This demonstrates that the interfacial adhesion between the SiC particles and the LLDPE matrix was weak, which may be due to the inability of the LLDPE melt to wet the crevices on the irregular surfaces of SiC particles. At higher magnifications, the SEM micrographs for the LLDPE matrices with 33.3 vol.% of SiC indicated a poor dispersion of the filler particles, as seen in Figure 4.7. The non-uniform filler distribution was a result of dry-blending the material instead of melt-compounding to prepare this LLDPE-SiC composite.

Upon evaluating the SEM images for the LLDPE-hBN composites, as seen in Figure 4.8, the hBN fillers are not as noticeable as the SiC particulates at 100× magnification. hBN$_{PTX60}$ particles were used in this particular composition, which are a spherical agglomerate shape. Even though the surface appears to look uniform at lower magnifications, upon increasing the magnification to 350×, the hBN particles are evident. The SEM images at higher magnifications, shown in Figure 4.9, reveal that the spherical
Figure 4.4: Compressive elastic modulus \((E)\) of LLDPE-hBN-SiC composites.

Figure 4.5: Compressive strength \((\sigma_y)\) of LLDPE-hBN-SiC composites.
Figure 4.6: SEM Images of LLDPE-based composites containing (a) 2.46VF SiC (b) 5.34VF SiC, (c) 9.36VF SiC (d) 33.3VF SiC

Figure 4.7: LLDPE-33VF SiC at 350× magnification.
agglomerates have been broken down into platelets. The agglomerates are comprised of boron nitride crystals formed into a spherical shape, but have separated into those smaller particulates during the melt-blend step. These results suggest that the processing conditions within the twin-screw compounder are too aggressive for mixing LLDPE and hBN spherical agglomerates.

Similar to the LLDPE-SiC composites, SEM micrographs of the LLDPE-hBN composites also revealed that some hBN platelets had been detached from the LLDPE matrix. This again demonstrates the poor adhesion force between the LLDPE and the ceramic fillers. With limited adhesion, it is expected that phonon scattering would be significant at these interfacial regions. To take advantage of the full potential for these thermal conductive fillers, in turn enhancing the composite’s $k$, an effective strategy to improve the compatibility between the polymer matrix and the ceramic filler is needed.

Finally, the polymer-filler morphology of hybrid composites filled with both SiC and hBN particulates were also evaluated, and the SEM micrographs are shown in Figure 4.10. These images depict good dispersion of both SiC and hBN particles in the LLDPE matrix. In Figure 4.10 (d) it can also be observed that the inclusion of SiC particles among the smaller hBN platelets helped to bridge the individual platelets. The formation of a more interconnected thermally conductive network led to an increase in the composite’s $k_{\text{eff}}$ when hybrid fillers were used. Once again, the hBN spherical agglomerates appear to have split into smaller crystals and did not retain their original shape.

### 4.1.5 Micromechanical Modelling

Micromechanical models, as described in Section 2.6, were compared to experimental data for both the LLDPE-SiC and LLDPE-hBN composites. The series and parallel models represent the maximum and minimum theoretical $k$-values, while the remain-
Figure 4.8: SEM images of LLDPE-based composites containing (a) 2.46VF hBN (b) 5.34VF hBN, (c) 9.36VF hBN (d) 33.3VF hBN.

Figure 4.9: LLDPE-33VF hBN at 1,500× magnification.
Figure 4.10: SEM images of LLDPE-based composites containing 33VF hBN and (a) 2.46VF SiC (b) 5.34VF SiC, (c) 9.36VF SiC at 100× magnification, and (d) 9.36VF SiC at 350× magnification.
Figure 4.11: Theoretical predictions compared to experimental data for the effect of different fillers (a) hBN, and (b) SiC.

The curves are contained within these limits. Due to the similar thermal conductivities of SiC and hBN, the models for each material do not vary significantly.

Most of the models underestimate the thermal conductivity of the composites when compared to the experimental data. These models assume that the spherical particles are independent of one another. Even though the distribution of particles within the matrix is considered to be relatively uniform, small clusters of SiC and hBN still exist, assisting in the formation of continuous paths and increasing thermal conductivity.

For the hBN samples, as confirmed by the SEM micrographs, the spherical agglomerates have broken down into small crystals. This change in structure would affect the thermal conductivity and cause deviation from the theoretical models.

Between 10-15 vol.% of filler, the geometric mean model predicts higher $k_{eff}$-values for these composites. At this point, the thermal interfacial resistance must be large enough to lower the effective thermal conductivity. Phonon scattering, which occurs at the surface between the matrix and filler, is amplified along with filler content due to increased surface area to volume ratio.
4.1.6 Summary

On the basis of the parametric studies conducted in this work, the effects of a single ceramic filler and hybrid fillers on thermal conductivity, electrical resistivity, and compressive elastic modulus were investigated. Mechanical testing showed an increase in compressive modulus corresponding to an increased filler content. Dielectric analysis revealed that the ceramic fillers used in this work, regardless of the loadings, did not compromise the electrical resistivity of the polymer, making them good candidates as thermally conductive fillers. Experimentally measured thermal conductivities of the fabricated composites suggested that hBN seemed to be a more effective than SiC in promoting the composite’s $k_{eff}$. In addition, the use of hBN together with SiC, which have different shapes and sizes, demonstrated a synergistic effect, thus increasing the composite’s $k_{eff}$. Therefore, optimization of $k_{eff}$ in composite materials may result from the use of hybrids fillers with different geometries.

However, it can be observed from the polymer-filler morphologies that the interfacial adhesions for both composites were weak. This means significant phonon scattering would occur at the interfaces, producing a much lower $k$-value when compared to a calculated, theoretical thermal conductivity.

Micromechanical modelling of the composites yields results that underestimate the actual $k$-values of the materials. This is likely due to the general assumptions made by the models, which do not encompass all of the variables of the various filler types, including size, shape and agglomeration.

4.2 The Effect of Content

A study was conducted in order to determine the effect of filler content on the properties of a composite. Solid samples containing 5, 10, 20, 30, 40 and 50 vol.% of hBN$_{PT110}$ in a LLDPE-matrix were fabricated with the intention of determining whether the
percolation threshold for this material system exists within these bounds. All of the samples fabricated in this study were dry-blended and compared to the values obtained in Section 4.1.

4.2.1 Thermal Properties

4.2.1.1 Thermal Conductivity

The thermal conductivity values are displayed in Figure 4.12. In general, the $k$ increases along with filler content, confirming that the addition of hBN within the composite positively influences the thermal conductivity. A significant increase in $k_{\text{eff}}$ is found when compared to neat LLDPE which has thermal conductivity of 0.31 W/m-K. The highest $k_{\text{eff}}$ achieved in this study was 4.34 W/m-K for the LLDPE-50 vol.% hBN composite.

At lower filler loadings, the hBN particles are surrounded by thermally-insulating LLDPE and do not come in contact with one another, preventing the formation of a conductive path. Composites with reduced filler content have much lower $k_{\text{eff}}$-values. As the amount of filler increases, the $k_{\text{eff}}$ improves, but is still smaller than the bulk properties of hBN. The interfacial resistance between the matrix and fillers in the composite is believed to be high, preventing even larger improvements in $k_{\text{eff}}$. Once the particles started to come in contact with one another, the $k_{\text{eff}}$-values increased since the amount of LLDPE between each platelet decreased. Once the filler particles form a continuous thermally-conductive path through the materials, the percolation threshold has been reached. Since the relationship between filler content and thermal conductivity is relatively linear, this threshold is difficult to determine for these particular composites, suggesting that the interfacial resistance among individual fillers is significantly high.

A dry-blend technique was employed for mixing these composites. As seen in
Section 4.2.4, the platelets have maintained their size and shape. This particular mixing method is not as destructive when compared to melt-blending and the platelets are able to maintain their aspect ratio. These large platelets have decreased surface area in contact with the matrix material, reducing the thermal interfacial resistance. Also, with larger particulates, less filler material is required to create interconnectivity, improving $k$.

### 4.2.1.2 Coefficient of Thermal Expansion

Changes in the coefficient of thermal expansion with respect to filler content were evaluated and the results can be seen in Figure 4.13. The general trend exhibited a decrease in CTE along with filler content. Neat polymers typically have higher susceptibility to dimensional instability due to increased chain mobility. When inclusions are added to a plastic, they inhibit chain movement, decreasing CTE. This study confirms the decrease in CTE with growing quantities of filler material, further constricting polymer chains. Unlike the coefficient of thermal expansion data seen in Section 4.1, there is a visibly decreasing trend for the CTE containing hBN. These differences are believed to be a result of both the mixing method, as well as the particle size and shape. Dry-blending has a tendency of forming agglomerates, which decreases the CTE, and particles with larger aspect ratios are associated with an increased effect with respect to dimensional change. Platelets also have a tendency of aligning, which exhibits much greater changes in the measured CTE.

### 4.2.2 Electrical Properties

The electrical resistivity of the composites is evaluated using the impedance and conductivity curves obtained from the dielectric analyzer. The electric properties of the LLDPE-hBN composites with varying filler content can be found in Figure 4.14. Both the electric impedance and conductivity curves show a decrease in the electrical re-
Figure 4.12: Thermal conductivity ($k$) of LLDPE-hBN composites with varying filler content.

Figure 4.13: Coefficient of thermal expansion (CTE) of LLDPE-hBN composites with varying filler content.
sistivity with increasing quantities of hBN. This phenomenon is expected since the electrical conductivity of hBN is greater than LLDPE. That being said, both components are still electrical insulators, where LLDPE and hBN\textsubscript{PTX60} have an electrical resistivity of $10^{17}$ $\Omega$-cm and $10^{14}$ $\Omega$-cm, respectively \cite{86}. The insulation properties of each individual material suggests that the composite will not be conductive. The impedance graph shows a slight fluctuation in electrical resistivity, varying by only one order of magnitude from $10^{15}$ to $10^{14}$.

4.2.3 Mechanical Properties

4.2.3.1 Compressive Elastic Modulus

The volume fraction of the matrix to fillers influences the behaviour of a composite. The general trend for the compressive elastic modulus shows an increase along with filler content, displayed in Figure 4.15. In general, as more ceramics are added to the composite, the stiffness of the material increases.

Polymers typically have a low compressive modulus, and are often combined with fillers to improve the mechanical properties, creating a stronger material. Neat LLDPE has a $E$ of 107 MPa, which increases to 366 MPa when 50 vol.% hBN is added. As seen in Section 4.2.4, the cross-sections of the dry-blended samples are not uniform. Due to the inconsistent morphology, the mechanical properties vary slightly, even between the same composition.

4.2.3.2 Compressive Strength

The compressive strength does not change significantly with change in filler content. The results of this study can be seen in Figure 4.16. The strength of the composites ranges from ~ 10 to 14 MPa and shows little variability with respect to change in filler. At higher hBN loadings, a slight decrease is seen in comparison to the initial values.
Figure 4.14: Electrical properties of LLDPE-hBN composites with varying filler content. (a) electrical impedance, and (b) electrical conductivity.
Since dry-blending was used as the mixing method, variability between samples is common. This mixing technique also increases the possibility of the formation of agglomerates. Clusters of particles within a composite are known to reduce the compressive strength. The presence of ceramic agglomerates within a polymer can decrease the effective contact area, reducing the overall interfacial interaction between the matrix and filler material, causing a reduction in strength.

### 4.2.4 Morphology

The cross-sections of the LLDPE-hBN composites are displayed in Figure 4.17. As previously discussed, these samples were fabricated using a dry-blend technique, which accounts for the irregular morphology displayed in the micrographs. The hBN platelets seem to agglomerate and are not dispersed evenly within the LLDPE matrix. This non-uniform structure is more visible in composites with lower filler content. Once the composites contain 30 vol.% of hBN or more, the filler appears to dominate, and minimal amounts of LLDPE are visible. Starting around 20 vol.% hBN, a network of filler particles through the material is seen, aiding in the improvement of $k_{\text{eff}}$. The micrographs show platelets randomly dispersed in all direction within the three-dimensional matrix, which will also help form a thermally conductive network.

The hBN$_{PT110}$ platelets are easily distinguishable in the SEM micrographs. Since the composites were dry-blended there is a decreased chance of damage to the fillers as a result of processing, which is an issue when the material undergoes the melt-blend process.

### 4.2.5 Micromechanical Modelling

The theoretical models discussed in Section 2.6 were compared to the experimental data found within the LLDPE-hBN effect of content study. As seen in Figure 4.18, the
Figure 4.15: Elastic compressive modulus ($E$) of LLDPE-hBN composites with varying filler content.

Figure 4.16: Compressive strength ($\sigma_y$) of LLDPE-hBN composites with varying filler content.
Figure 4.17: SEM Images of LLDPE-hBN composites with different filler content at varying magnifications.
similarities between these models and the experimental data are limited. As expected, the series and parallel models depict the upper and lower bounds of the thermal conductivity. Most of the models have $k_{\text{eff}}$-values lower than the experimental results until 35 vol.% hBN, at which point the geometric-mean model and Nielsen model prediction exceed the tested composites.

All of the models assume a homogeneous mixture with non-interacting particles. From the SEM micrographs, we can discern this is not the case. The composites were fabricated using a dry-blend process, resulting in the formation of agglomerates due to the uneven dispersion of particles throughout the material. The mixing technique and morphology of the composites account for the discrepancy seen in $k_{\text{eff}}$-values below 35 vol.% hBN. After this point, the Nielsen and geometric mean models show a steep increase for thermal conductivity. These models assume there is little to no thermal interfacial resistance, which is not the case. Assuming zero phonon scattering at the barrier between the matrix and filler would result in much higher thermal conductivity values than the actual experimental results.

These models, with the exception of the Nielsen model, all assume the discrete phase are spherical, which is not the case in this study. PT110, which is a platelet shape and has a much larger aspect ratio compared to a typical spherical filler, was added into an LLDPE matrix. In the Nielsen model, a correction factor $A$ accounted for the change in shape and the related packing factor. These considerations shifted the $k_{\text{eff}}$-values to reflect these modifications. The fit of each model to the empirical data was not ideal, suggesting additional correction factors are necessary to provide more accurate mathematical models. Other studies have found discrepancies in Nielsen’s model with respect to platelet-shaped fillers [57]. In a study by Hill et al., the mathematical modelling results were similar to those found in this section. For platelets, they had to modify the $A$ factor and the $\phi$ to 30 and 0.85, respectively, before the Nielsen predictions mimicked the experimental results. The soft nature of hBN allows it to be compressed
4.2.6 Summary

A parametric study was performed to determine the effect of content on the thermal, electrical, mechanical, and morphological properties of a polymeric composite filled with hBN. The thermal conductivity was found to increase from 0.31 W/m-K to 4.34 W/m-K through the addition of 50 vol.% hBN into an LLDPE matrix. The relationship between filler content and thermal conductivity follows a linear trend, increasing with higher filler content. The coefficient of thermal expansion exhibited a decreasing trend along with filler content which is likely due to the addition of hBN inclusions within the composite, inhibiting polymer chain movement. The electrical resistivity decreases slightly with increasing amounts of hBN. Even though this is the case, only a minor decrease in impedance results, and the electrical insulating properties of LLDPE were not compromised with the addition of hBN. Compression testing
showed an increase in the modulus of the composites with higher filler content. The $E$ increased from 107 MPa, for neat LLDPE, to 366 MPa, for LLDPE-50 vol.% hBN. SEM micrographs displayed irregular morphology. These heterogeneous cross-sections were expected due to the dry-blend method used for these composites. At compositions with filler content greater than 20 vol.%, hBN is more prominent within the micrographs, resulting in the formation of continuous pathways through the material.

Micromechanical modelling was used to predict the behaviour of the composites. The models that were used did not match the empirical data exactly, which could be due to a number of reasons. Platelets were used in this particular study, which have been known to need additional modifications to the Nielsen model for accurate results. Interfacial resistance between the filler and matrix material also is not accounted for within any model, which can increase the error between the model and experimental results.

### 4.3 Comparison of Mixing Techniques

Thermal conductivity is one of the most important properties when it comes to electronic packaging. One goal within this project was to create a material with the highest possible $k_{eff}$-value using polymeric composites. When dealing with this type of material, thermal resistance at the interface between polymer and filler is a large issue. By modifying the processing parameters, the properties of the composite vary. The following outlines variations in thermal conductivity due to mixing technique, especially at high filler content.

Figure 4.19 shows the differences in $k_{eff}$ for similar compositions, varying only in the preparation method. The composites discussed in Section 4.1 underwent the melt-blend process, while those in Section 4.2 were dry-blended. The effective thermal conductivity values of the dry-blended composites are consistently higher than
those fabricated by melt-blending. The non-uniform morphology produced from dry-blending causes agglomeration and grouping of filler particles, which appears to be advantageous with respect to thermal conductivity. As the filler content increases, the differences in $k_{eff}$ between the two processing techniques is even greater. The twin-screw compounder is effective at breaking up agglomerates, even at high filler loadings, creating a homogeneous mixture. For dry-blending, regardless of the amount of filler, uniform mixtures are difficult to fabricate, and ultimately large clusters of hBN will form within the composite. This particular characteristic of dry-blended composites, which initially seems undesirable, aids in the formation of thermally conductive networks throughout the material, increasing $k_{eff}$.

Even though hBN$_{PTX60}$ was used in the melt-blend study and hBN$_{PT110}$ was used in the dry-blend study, the differences with respect to type of hBN are considered to have a minimal effect on the overall effective thermal conductivity. The difference between the $k_{eff}$-values of hBN$_{PTX60}$ and hBN$_{PT110}$, processed using the exact same methodology, is less than 0.12 W/m-K. All of the values presented in Figure 4.19 are greater than this value, with the exception of 5 vol.%. Therefore, the results still suggest an improvement in $k_{eff}$ for composites fabricated using the dry-blend process. An in-depth discussion regarding the effect of the size and shape of a filler can be in Section 5.1.

4.4 The Effect of Porosity

The following section outlines the fabrication of linear low-density polyethylene-based composite foams filled with hBN$_{PT110}$ platelets and Expancel® 950 DU120 microspheres. Two parametric studies were conducted to investigate the effects of varying residence time, as well as the concentration of microspheres within the composites. Data regarding the physical, thermal, and morphological properties of each material
was collected. The primary objective of this work was to show that constrained polymeric foaming processes are a feasible method of aligning filler materials within the polymer matrix to maintain high thermal conductivity, while reducing the overall mass of the composite. The theory behind this method suggests that the extensional flow fields associated with the expansion of the microspheres could assist in aligning the thermally conductive filler particles, forming a three-dimensional conductive network throughout the matrix and increasing the effective thermal conductivity.

The fabrication method employed in these studies varied from all of the other composites to accommodate the addition of Expancel® microspheres. A dry-blend technique was utilized in order to mix the composites. Due to the similarities in the melt temperature of LLDPE and the activation temperature of the Expancel® microspheres, melt-blend processing was not an option. The LLDPE, Expancel® and hBN were measured out in the appropriate quantities and blended together at room temperature to create a homogeneous mixture. A summary of the material compositions studied
in this work are shown in Table 4.2.

During the compression molding process, the dry-blended mixtures were compacted at room temperature, and then heated to 130 °C. The samples remained at this temperature for 15 minutes, at which point they were heated to 180 °C and compressed at 13.8 MPa (2000 psi) for the desired length of time. All of the samples were fabricated using constrained foaming molding, which means that they were unable to expand beyond the dimensions of the mold cavity which has a 20 mm diameter and is 10 mm in height.

Expancel® microspheres are comprised of a hydrocarbon particles surrounded by a thermoplastic shell, which is activated when a predetermined elevated temperature is reached. This particular grade of Expancel has an initial diameter of 18-24 µm and can expand up to 120 µm. The manufacturer determined the activation temperature to be between 138 to 210 °C, so for this study the composites were heated to 180 °C. The residence time refers to the length of time the samples were heated at this elevated temperature.

### 4.4.1 Morphology

SEM micrographs were used as visual evidence of the foamed structure, as well as the enhanced alignment and interconnectivity of the hBN platelets within the LLDPE matrix.

The microstructure of all of the composites can be found in Figures 4.20 to 4.23. In all of the micrographs, a random distribution of voids is seen, which can be attributed to the dry-blending procedure used to fabricate these samples. Although the dispersion of hBN platelets and the voids were not uniform, studies have associated high $k_{eff}$ with dry-blending techniques, therefore deeming this method appropriate for this particular application [41].

As seen in Figures 4.20 and 4.21 the addition of greater amounts of Expancel®
Table 4.2: Porous LLDPE-hBN Compositions

visibly increases the number of pores within the composite. The composites containing 0.5× and 1.0× the theoretically-calculated amount of Expancel®, necessary to fill the specified void (either 20 or 40 vol.%), appear to have not enough microspheres to create interconnectivity between pores, while the composites containing 1.5× and 2.0× the theoretically-calculated amount do. As expected, the samples containing 40 vol.% voids have a higher number of pores in comparison to the 20 vol.% void samples. Double the amount of Expancel® were added to the 40 vol.% void samples, therefore increasing the porosity of the material. In general, the pores seen in the composites containing high quantities of filler are smaller than those with lower amounts of hBN.

Figures 4.22 and 4.23 show the effect of varying residence time. As seen in other studies [51, 53], there is an optimal residence time for maximum expansion of the microspheres. Before this ideal time, the microspheres will not have ample time to expand fully, and after this point the bubbles will begin to lose gas and contract. These figures indicate that increasing the residence time to 5 minutes did not affect the pore
size, but increasing the time to 8 minutes was detrimental to the constrained foam expansion. After 8 minutes at 180 °C, excessive gas loss from the expanded Expanscel® resulted due to high gas diffusivity through LLDPE.

From the micrographs, an average cell size and cell population density were calculated. The cells were observed to be almost spherical and uniform in shape, with cell sizes ranging from 50 to 130 µm. The uniform nature of the cell structure can be attributed to the use of Expanscel® microspheres as the foaming agent. If gas was directly injected into the composite melt during a physical foaming process, the cells would not be as readily dispersed in the system. Likewise, if chemical blowing agents were used to create the porous composite, then severe cell coalescence would result, since there is no physical constraint related to a maximum expansion of spheres like Expanscel®. Therefore, this method of creating a cellular structure is most desirable for this particular application. As seen in the micrographs, these composites consist of two solid phases, the LLDPE matrix and the hBN platelets, and a gaseous phase.

Figure 4.24 displays the cellular structure within the composite along with the successful alignment of hBN around the expanded microsphere. At higher magnifications, the hBN platelets can easily be seen interconnected and aligned along the cell walls amongst the adjacent cells. It is theorized that the extensional flow field, generated within the cell wall upon the expansion of the Expanscel® microspheres, oriented the hBN platelets and aligned them along the cell walls throughout the LLDPE-hBN composite foams. The highly-interconnected and perfectly aligned hBN network led to thermally conductive pathways throughout the cellular composite structure, overcoming the thermal insulation property of typical plastic foams and promoting the $k_{eff}$.
Figure 4.20: SEM Images of LLDPE Foamed Composites with varying amounts of microspheres, containing 33 vol.% with 20 and 40 void percent.
Figure 4.21: SEM Images of LLDPE Foamed Composites with varying amounts of microspheres, containing 50 vol.% with 20 and 40 void percent.
Figure 4.22: SEM Images of LLDPE Foamed Composites with varying residence time, containing 33 vol.% with 20 and 40 void percent.
Figure 4.23: SEM Images of LLDPE Foamed Composites with varying residence time, containing 50 vol.% with 20 and 40 void percent.
4.4.2 Thermal Conductivity

The thermal conductivities of the cellular composite materials were measured. The effect of various properties on the $k_{eff}$ was compared and contrasted, and can be seen in the following figures.

In Figure 4.25 (a) and (b), the effects of cell size and cell population on $k_{eff}$ are illustrated. LLDPE-hBN composites fabricated containing both 20% and 40% volume fraction of voids are included. All of these samples were kept in the mold for a 2 minute residence time once the temperature reached 180 °C. The variation in cell size and cell density were a direct result of the Expancel® content, ranging from 0.5× to 2.0× the theoretically-calculated amount of microspheres to fill a 20 vol.% or 40 vol.% void in the composite foams, once fully expanded. The amount of hBN content within the cell walls varies between 33 vol.% and 50 vol.%. It can be observed that an optimal cell size and cell density both exist, to promote the $k_{eff}$ of the LLDPE-hBN composite foams, except in the case containing 40 vol.% voids and 33 vol.% hBN in the cell wall. When the fabricated cellular materials containing 20%-unfilled space and 40%-unfilled space are compared, the optimal cell size decreases and the optimal cell density increases, along with an increase in unfilled volume within the mold cavity. The existence of both optimal cell size and cell density to promote $k_{eff}$ implies that there are at least two

Figure 4.24: SEM Images of LLDPE Foamed Composites with 1.5× the calculated amount of Expancel necessary to fill 20 void% at (a) 250×, and (b) 1,000× magnification.
competing factors affecting the thermal conductivity of the composite foams. These two factors are speculated to be the number of voids, as well as the hBN alignment.

The composites with 40%-unfilled volume contain double the amount of Expancel® microspheres than the 20%-unfilled volume samples. Upon expansion, the additional microspheres may restrict the overall growth of the each cell and encourage contact with one another, which will promote the overall thermal conductivity through the formation of continuous conductive pathways within the polymer matrix. On the other hand, the presence of too many thermally insulative voids would be detrimental to the overall effective thermal conductivity of the composites.

In general, the LLDPE composites containing 50 vol.% hBN had a smaller cell size with respect to the unfoamed volume compared to the composites with 33 vol.% hBN because of the smaller void fraction. This is possibly a result of increased viscosity of the material with filler content, hindering cell growth [48]. The force required for the microspheres to expand, in turn aligning the hBN platelets, must be higher for a composite with greater filler content. According to the manufacturer specifications, the maximum final diameter of the expanded microspheres is 120 µm, but few pores grew to that size. As the cell size decreases, the cell density increases, which is both expected and congruent with literature [87].

To further investigate the effects of foam morphology on the effective thermal conductivity, the $k_{\text{eff}}$ was plotted against the percentage of volume expansion, as shown in Figure 4.26. Regardless of the hBN content in the cell wall, the $k_{\text{eff}}$ of the composite foams first decreased as the percentage of volume expansion increased, from about 20% to 50%. Once the volume expansion exceeded 50%, the $k_{\text{eff}}$ of the cellular composites started to improve. The initial reduction in $k_{\text{eff}}$, as the volume expansion increased from 20% to 50%, was attributed to the greater amount of voids, which were filled with thermally insulative gas (air). However, beyond this critical percentage, the continued expansion of the microspheres within the foams began promoting $k_{\text{eff}}$. 


Figure 4.25: Effect of cell morphology on $k_{\text{eff}}$ of LLDPE-hBN composite foams. (a) Effect of cell size on $k_{\text{eff}}$ (b) Effect of cell population on $k_{\text{eff}}$. 
The $k_{eff}$-values were also compared to the $k_{eff}$ of solid samples, with the same LLDPE matrix and hBN filler, as described in Section 4.2. The corrected hBN quantities were used for this comparison. As an example, the LLDPE-hBN foams containing 33.3 vol.% hBN within the cell walls have a corrected hBN content of 27 vol.% and a void fraction of 0.17. The corrected hBN content was determined through the use of void fractions of the corresponding foams, determined through the use of mass density as described in the previous chapter. Figure 4.27 indicates that the $k_{eff}$ of the foams with their corrected hBN content is quite close to the solid samples containing a similar quantity of filler. Deviation from the solid samples became more apparent when the volume expansion increased and the $k_{eff}$ of the foamed samples started to decrease.

In addition to variations in the amount of Expancel® content and the unfilled volume of the mold cavity, residence time of the dry-blended mixture was also modified to investigate the effects. Residence time was varied from 2, 5, and 8 minutes to determine the change in expansion. As seen in Figure 4.28, an increase to 5 minutes did not change the microstructure, although a residence time of 8 minutes did not yield desirable results. After 8 minutes at an elevated temperature of 180 °C, excessive gas loss from the expanded microspheres resulted due to high diffusivity through LLDPE. This data suggests that an optimal residence time exists, and that compression molding for a length of time greater than 5 minutes is not recommended.

4.4.3 Summary

In this study, a novel foam structure of PMC filled with thermally conductive and electrically insulative ceramic platelets was successfully fabricated using a simple and effective processing technology. Thermal conductivity measurements of the fabricated LLDPE-hBN composite foams indicated the unique cellular structure led to a significant increase in $k_{eff}$ when compared to LLDPE. This work also demonstrated that the
Figure 4.26: Effect of foam volume expansion on \( k_{\text{eff}} \) of LLDPE-hBN composite foams.

Figure 4.27: Comparison of \( k_{\text{eff}} \) of LLDPE-hBN composite foams to that of LLDPE-hBN solid composites.
percentage of volume expansion is a critical factor in the promotion of $k_{eff}$. The alignment of hBN platelets within the composite is induced by the extensional flow fields during the expansion process of the microspheres. This foaming process also aids in the formation of a three-dimensional thermally conductive network throughout the composite foam.

This initial study demonstrates that a thermally conductive foam structure can be fabricated for lightweight electronic packaging applications. It is also proposed that this processing strategy be extended for use in other polymer matrix and filler systems in order to tailor the multifunctional properties of the PMC foams for additional applications.
Figure 4.28: Effect of residence time on the foam volume expansion.
Chapter 5

PPS Based Composites

This chapter examines polyphenylene sulfide-based composite materials filled with different types of hBN particulates. Two different parametric studies were conducted to investigate the effects of hBN within this high performance matrix material. The first study pertained to the effect of filler size, shape, and aspect ratio on the composite’s properties. The second study focused on hybrid fillers and the effect of combining multiple ceramic fillers in one composite. The overall performance of the matrix material was also compared to that of LLDPE. Data was collected and analyzed with respect to their physical, thermal, electrical, and mechanical properties.

5.1 The Effect of Filler Size and Shape

Polyphenylene sulfide-based composite materials were filled with four different types of hBN particulates. A study was conducted to investigate the effect of filler size, shape, and aspect ratio on the properties of composite materials. Data was collected and analyzed with respect to their physical, thermal, electrical, and mechanical properties.

The four types of hBN were discussed in Section 3.1 and are referred to in terms of the name given by the manufacturer: PTX60, PTX25, PT110, and PT371. All of the
compositions had PPS as a matrix material and contained 33.3 vol.% of hBN in order to provide a consistent base for comparative purposes.

5.1.1 Thermal Properties

5.1.1.1 Thermal Conductivity

The effective thermal conductivity of composites containing each of the four types of hBN were evaluated. The thermal conductivity of the bulk material does not vary, since the base filler material remains as hBN, but when added into a PPS matrix the effects were unknown. From Figure 5.1, the $k_{eff}$-values do not appear to fluctuate significantly, although slight differences can be seen. These changes are likely due to the size, shape, and aspect ratio each type of hBN is manufactured into.

Out of the four composites, PPS-hBN$_{PT371}$ has a marginally higher $k_{eff}$ than the other three. This grade of hBN is a medium-density agglomerate with the largest particle size. PT371 is 275 $\mu$m, while the other grades range from 25 to 60 $\mu$m. Even though these particles are initially larger, the SEM micrographs show that the hBN have broken down into small particles. From the SEM micrographs, the composites containing PT371 appear to have a mixture of large and small hBN platelets, which may aid in the formation of continuous conductive paths, leading to higher $k_{eff}$-values.

When comparing the grades of hBN, those formed into spherical and medium-density agglomerates are more fragile in comparison to the PT110 platelets. The delicate nature of the agglomerates resulted in the breakdown of these clusters, as seen in Section 5.1.4. For the three grades of hBN that have broken down into small crystals, a decreasing trend is apparent with increasing particle size. The PPS-hBN$_{PTX25}$ and PPS-hBN$_{PTX60}$ broke down into similar sized particulates, resulting in a similar $k_{eff}$.

For the composites containing PT110 platelets, the $k_{eff}$ values are slightly higher
than the two composites containing spherical agglomerates. This difference could be related to the size of the platelets, which are larger than the other hBN crystals. This larger particle size is believed to account for the increase in $k_{\text{eff}}$, due to decreased phonon scattering as a result lowered surface area between the particle and matrix, in turn lowering interfacial resistance.

As previously discussed, in an anisotropic material the in-plane thermal conductivity is much higher than the through-plane. In the interest of reducing the anisotropic nature of composites spherical agglomerate were selected for use in these materials. These isotropic fillers could assist in promoting the effective thermal conductivity of the composite since there is no directional dependence. Therefore, if the spherical agglomerate was maintained the overall $k$ would increase in all directions. Since the PTX25 and PTX60 broke down into smaller platelets, this effect could not be seen.

5.1.1.2 Coefficient of Thermal Expansion

The coefficients of thermal expansion for the PPS-based composites with varying types of hBN were obtained, as seen in Figure 5.2. Both the CTE before and after the glass transition temperature ($T_g$) were found. The values for the CTE below to the $T_g$ were observed to be much lower than those above. All of the composites contained equivalent amounts of hBN, but varied with respect to the size, shape, and aspect ratio. There is no significant variation between the CTEs for the materials containing different types of hBN. These results are expected and are in accordance with the rule of mixtures. The ROM does not take size, shape, orientation or aspect ratio into account, and as such only varies with respect to filler content. For a composite containing 33.3 vol.% of hBN in a PPS matrix, the ROM predicts a CTE of $\sim 350 \times 10^{-6}/°\text{C}$. Discrepancies between the ROM and the measured values are likely a result of not taking the aforementioned filler characteristics into account, along with poor adhesion between the matrix and inclusions.
Substantial differences are seen for the CTE found before and after the $T_g$. The $T_g$ represents the point at which the CTE undergoes a significant change, above which expansion of the material begins to occur at more rapid rate. The rigidity of the composite decreases, along with the adhesive strength, resistance to moisture, dielectric strength and volume resistivity [88].

Since the PPS-based composites are being evaluated for high temperature applications, the CTE above the $T_g$ is more relevant. To ensure the composite is well-suited for electronic packaging applications, the CTE above the $T_g$ must be studied. At higher temperatures, the CTE is on average $125 \times 10^{-6}/\circ C$.

### 5.1.2 Electrical Properties

The electrical impedance and conductivity of these composites were measured and are displayed in Figures 5.3 (a) and (b). The impedance curves show slight variations in the electrical resistivity of the composites. Since the bulk properties of each of the hBN types is similar, the electrical properties should be congruent with one another. Once again PTX25 and PTX60, both of the hBN particles that are spherical agglomerates, behave in a very similar manner. All of the composites remained electrically resistive, with values ranging from $10^{12}$ to $10^{15}$. Therefore, the addition of the thermally conductive fillers improved the $k_{eff}$ of the composite without compromising the electrical resistivity.

### 5.1.3 Mechanical Properties

#### 5.1.3.1 Compressive Elastic Modulus

The compressive elastic modulus values of the PPS-hBN composites with different size and shaped fillers are seen in Figure 5.4. Out of the agglomerate-based particles, PTX25 has the highest compressive modulus. This grade appears to have broken down
Chapter 5. PPS Based Composites

Figure 5.1: Thermal conductivity ($k$) of PPS-hBN composites with different size/shape fillers.

Figure 5.2: Coefficient of thermal expansion (CTE) for different sizes and shapes of hBN, above and below the $T_g$. 
Figure 5.3: Electrical properties of PPS-hBN composites with different sizes and shapes of hBN. (a) electrical impedance, and (b) electrical conductivity.
into the smallest size particles, which is likely the cause for the improvements in $E$. For the composites containing PTX60, although there is a large deviation between values obtained for different samples of the same composition, the general trend shows results similar to those of PTX25. PTX25 and PTX60 performed quite similarly within all of the tests, which suggests that the hBN agglomerates broke down into comparable sizes during the composite processing and had analogous particle distributions. Similar studies have also found large deviations in data collected from compression testing [89]. Smaller particles are associated with higher compressive moduli due to their enhanced dispersion with the polymer matrix. The presence of agglomerates reduces the mechanical properties of a composite.

From the SEM micrographs, the composites with PT371 appear to have a range of particle sizes containing both smaller and larger hBN crystals within the matrix. The aggressive processing conditions for the composites caused the medium-density agglomerates to break down. The combination of small hBN crystals dispersed between larger particulates is believed to create a synergistic effect, improving $E$.

The composites containing PT110 have the lowest compressive elastic modulus. As expected, the composites containing large particles have the least desirable mechanical properties.

### 5.1.3.2 Compressive Strength

Figure 5.5 exhibits the compressive strength values for PPS-hBN composites containing various size and shaped fillers. The compressive strengths show slight variability, similar to the compressive elastic moduli. Once again, PTX25 and PTX60 have similar properties, likely due to the comparable size of hBN crystals, along with the homogeneous dispersion of these particulates within the composites. The highest $\sigma_y$ values were found for the composites containing PT371. The mixture of small and large hBN crystals are believed to be the cause of positive synergy, increasing $\sigma_y$. Similar to the
compressive elastic modulus, the PPS-hBN_{PT110} composites have the lowest compressive strength. The larger-sized platelets are believed to be the cause of the decrease in mechanical properties.

5.1.4 Morphology

The morphologies of PPS-33.3 vol.% hBN with different grades of filler can be seen in Figure 5.6. While PT110 has appeared to retain the shape, PTX25, PTX60, and PT371 all have not. The original platelet shape of PT110 is still visible in the SEM micrographs, but the other three grades have broken down into small hBN crystals. The latter three grades are all comprised of small crystals formed into different shapes, but are quite vulnerable to separation. The processing conditions used in the manufacturing process were too severe, causing this breakdown. Even though short melt-blend times were used, at low mixing speeds, the original shape of the hBN was not maintained. Many of the hBN crystals are <10 µm in size, which is much smaller than the manufacturer’s specifications for the various grades, ranging from 25-275 µm. Other studies have also seen agglomerate disintegration associated with melt-blend and compression molding processes [72].

In terms of relative sizing, the filler sizes appear to increase in the following order: PTX60, PTX25, PT371, and PT110. These sizes have been related to the performance of the composite materials and therefore bear immense importance within this study.

5.1.5 Micromechanical Modelling

Figure 5.7 depicts the results of Nielsen’s model compared to the experimental data. Since this was the only model that took filler shape, orientation and packing factor into account, it was selected for this analysis. There is no variability between the values computed for PTX25 and PTX60 because both are spherical fillers. An increased
Figure 5.4: Compressive elastic modulus ($E$) of PPS-hBN composites with different size/shape fillers.

Figure 5.5: Compressive strength ($\sigma_y$) of PPS-hBN composites with different size/shape fillers.
Figure 5.6: SEM Images of PPS-hBN composites with different size/shape filler, at varying magnifications.
thermal conductivity is seen with Nielsen’s model with change in shape and packing factor, as seen for PT110. The platelets have a much larger aspect ratio and as such improve the composite’s $k_{eff}$. Since the Nielsen model accounts for filler differences, the calculated values reflect the variability.

Discrepancies between the calculated values and the experimental data are likely a result of the hBN particle breakdown, for PTX25, PTX60, and PT371. Since the original shape of the particulates is not maintained, the measured $k_{eff}$ will inevitably deviate from the micromechanical model.

Figure 5.7: Theoretical predictions compared to experimental data for different sizes and shapes of hBN.
5.1.6 Summary

PPS-based composites with 33.3 vol.% of different size and shape hBN filler particles were fabricated in this study. The intention was to determine the effects of filler size, shape, and aspect ratio on the thermal, electrical, mechanical and physical properties of the composites. Even though the bulk properties of the hBN particulates were all similar, the results showed variability. SEM micrographs showed that the processing conditions used in this study were too aggressive for the delicate nature of hBN. The spherical and medium-density agglomerates brokedown from their original shape into small hBN crystals. PPS-hBN\textsubscript{PT371} exhibited marginally higher thermal conductivity values compared to the other three types of hBN. The range of different sized hBN particles within this composite is believed to improve the interconnectivity of filler materials in the polymer matrix, lowering the thermal interfacial resistance and resulting in increased $k_{\text{eff}}$. The electrical conductivity of the material also showed similar results. All of the composites remained electrically resistive, which was expected, since hBN is an insulator. In regards to the mechanical properties, the composites with PT371 have the best $E$ and $\sigma_y$ likely due to the range in hBN particle sizes, creating a synergistic effect. PTX25 and PTX60 also exhibited high mechanical properties, since the spherical agglomerates brokedown into small hBN and were dispersed in a homogenously throughout the composites.

5.2 The Effect of Hybrid Fillers

The following compositions were fabricated to determine whether a positive syner-gistic effect exists when multiple ceramic fillers are combined in a polymeric matrix. As outlined in Table 5.1, predetermined ratios of hBN\textsubscript{PTX60} and hBN\textsubscript{PT110} were added to PPS in a melt-blending process to form PPS-hBN\textsubscript{1:0}, PPS-hBN\textsubscript{4:1}, PPS-hBN\textsubscript{3:1}, PPS-hBN\textsubscript{2:1}, and PPS-hBN\textsubscript{0:1} composites. The primary goal was to determine whether
Table 5.1: PPS-hBN Hybrid Compositions

smaller PTX60 spherical agglomerates would fit in between larger PT110 platelets to create interconnectivity throughout the polymer matrix, and increase the effective thermal conductivity of the composites.

5.2.1 Thermal Properties

5.2.1.1 Thermal Conductivity

Figure 5.8 shows the effect of hybrid fillers on the thermal conductivity of PPS-based composites with 33.3 % hBN. Neat PPS has a low thermal conductivity of 0.22 W/m-K, which was increased through the addition of hBN. As discussed in Section 5.1, composites with a single type of hBN (ie. PTX60 and PT110) had similar thermal conductivities. PPS-hBN composites filled with either hBN\(_{PTX60}\) or hBN\(_{PT110}\) increased from 0.22 W/m-K to 1.75 W/m-K and 1.89 W/m-K, respectively. As seen in Figure 5.13, the SEM images show the microstructure of PPS-hBN\(_{PTX60}\) samples. Although this particular grade of hBN should be in a spherical agglomerate, the filler particles seem to have broken down into smaller crystals, approximately 10 µm or less in size, during the melt-blend and compression molding processes. Smaller particulates of hBN\(_{PTX60}\) led to higher thermal contact resistance between the PPS matrix and the hBN fillers, resulting in a lower \(k_{eff}\) for PPS-hBN\(_{PTX60}\) composites compared to that of hBN\(_{PT110}\).
The addition of multiple types of hBN had a positive synergistic effect on the composites. Hybrids of hBN\textsubscript{PTX60} and hBN\textsubscript{PT110} in ratios of PPS-hBN\textsubscript{4:1}, and PPS-hBN\textsubscript{3:1} resulted in an increased $k_{\text{eff}}$ compared to single-filler composites. The initial goal was to use hBN\textsubscript{PT110} platelets to bridge the gaps between hBN\textsubscript{PTX60} spherical agglomerates, creating interconnectivity throughout the material. The smaller particles have the ability to occupy space the larger hBN\textsubscript{PT110} platelets cannot, resulting in a more efficient packing of the fillers within the composite. Despite the hBN\textsubscript{PTX60} agglomerates breaking down into smaller crystals, a synergistic effect was seen, increasing the thermal conductivity. The $k_{\text{eff}}$-values of 4:1 and 3:1 were 1.97 W/m-K and 2.04 W/m-K, respectively. A slight decrease in the $k$ was seen for PPS-hBN\textsubscript{2:1}.

An optimal volume ratio of small to large hBN particulates, with regards to thermal conductivity, was found to be PPS-hBN\textsubscript{3:1}. When the filler ratio was increased to 2:1, a reduction in $k_{\text{eff}}$ was found. This decrease is due to an insufficient amount of fine, or small particles dispersed within the PPS matrix, between the larger platelets. With both the PPS-hBN\textsubscript{3:1} and PPS-hBN\textsubscript{4:1}, the smaller crystal aided in the formation of a three-dimensional continuous conductive pathway, thus increasing $k_{\text{eff}}$.

### 5.2.1.2 Coefficient of Thermal Expansion

Figure[5.9] shows the change in CTE for PPS-hBN composites with hybrid fillers. Once again, large differences are not seen between composites. The overall amount of hBN within the polymer matrix is consistent at 33.3 vol.%. Since the bulk CTE of hBN is the same, regardless of grade, the effect of size and shape on the material’s CTE is not assumed to be considerable.

A noticeable difference is seen between the CTEs above and below the $T_g$. At this point the composite changes from a hard, glassy state below the $T_g$ to a soft, rubbery state above the $T_g$. For a polymer above the glass transition temperature, the motion of polymer chains are adjusted through thermal vibration, therefore allowing free volume
to dominate [91]. When the polymer tries to expand or contract, the filler particles resist the change and create stress within the material, reducing the dimensional change.

The CTE for the PPS-hBN composite containing PT110 was slightly lower than the other composites above the \( T_g \). Some studies have shown an increased effect through the addition of fillers with high aspect ratios [92]. If the fibers or platelets are aligned, reduction in CTE can be much greater. Even though the SEM micrographs show a relatively random ordering of platelets for this composite, there is a slight orientation within the material, which could account for the minor decrease in CTE.

### 5.2.2 Electrical Properties

Figures 5.10 (a) and (b) show the effects of filler composition on the electrical properties of PPS-bases composites filled with 33.3 vol.% hBN. The electrical impedance curves exhibit very similar behaviour for all of the composites. Regardless of the amount of hBN added of either PTX60 or PT110, the impedance remained high. As confirmed by the electrical conductivity curves, the electrical resistivity is not compromised through the addition of these fillers.

### 5.2.3 Mechanical Properties

#### 5.2.3.1 Compressive Elastic Modulus

The compressive elastic moduli of the PPS-hBN hybrid composites are displayed in Figure 5.11. The \( E \) for PTX60 and PT110 are among the lowest, with PTX60 yielding the lowest value. When comparing PTX60 to PT110, the platelets that make up PT110 have a larger aspect ratio, which is associated with increased compressive elastic moduli and strength [93].

The mechanical properties follow a similar trend to those found for thermal conductivity. When evaluating the three hybrid composites, an optimal value exists and
Figure 5.8: Thermal conductivity ($k$) of PPS-hBN composites with hybrid fillers.

Figure 5.9: Coefficient of thermal expansion (CTE) of PPS-hBN composites with hybrid fillers.
Figure 5.10: Electrical properties of PPS-hBN composites with hybrid fillers: (a) electrical impedance, and (b) electrical conductivity.
is seen for PPS-hBN$_{3:1}$. When the smaller hBN$_{PTX60}$ particles occupy the space between the larger hBN$_{PT110}$ platelets, a more efficient packing of filler can help to improve the compressive elastic modulus of the composite. The $E$ is the highest for PPS-hBN$_{3:1}$ and then declines when a 2:1 ratio of PTX60:PT110 is added. As the amount of hBN$_{PT110}$ increases past the optimal quantity, the mechanical properties begin to deteriorate.

In general, finer particles are advised for improved mechanical properties [36, 81]. The primary rationale behind this logic is improved dispersion within composites with smaller particles. The formation of agglomerates in composites prevents homogeneity within a material, and reduces its mechanical properties. Smaller particles have a tendency of forming agglomerates that have a lesser effect on the mechanical properties, due to their reduced size. A trade-off between the effects of increased aspect ratio and uniform dispersion of smaller particulates exists. Therefore, an ideal balance for the two must exist, which is seen in the PPS-hBN$_{3:1}$ hybrid composites.

5.2.3.2 Compressive Strength

The compressive strength of the composite materials shows a similar trend to the compressive elastic modulus, and can be seen in Figure 5.12. An optimal ratio of PTX60 to PT110 appears to exist. The composites containing 4:1 and 3:1 have the highest compressive strength, while 2:1 has a significantly lower $\sigma_y$. Both PPS-hBN composites containing a single type of filler have lower $\sigma_y$ values, which suggests a hybrid effect with respect to compressive strength. PT110 has a larger aspect ratio when compared to PTX60. As the amount of PT110 increases, there is an increased interfacial area. A higher contact area is associated with poor interfacial bonding, therefore resulting in delamination and failure, ultimately leading to a lower $E$ [94].
Figure 5.11: Compressive Elastic Modulus ($E$) of PPS-hBN composites with hybrid fillers.

Figure 5.12: Compressive strength ($E$) of PPS-hBN composites with hybrid fillers.
5.2.4 Morphology

SEM micrographs of the cross-sections are seen in Figure 5.13 at both 250× and 1000× magnifications. Upon inspection of the images, as the amount of hBN_{PT110} increases from PPS-hBN_{4:1} to PPS-hBN_{2:1}, there is a visible difference in the number of platelets. Since hBN_{PT110} has a much larger aspect ratio in comparison to hBN_{PTX60}, they are more visible within the composites.

The morphology is uniform for all of the composites, which suggests that the processing conditions are ideal for producing a homogeneous material. A uniform microstructure was expected since the composite was melt-blended. Unlike dry-blending, shear mixing within the twin-screw compounder generally creates excellent dispersion. Even though this is the case, at higher magnifications there is a lack of spherical agglomerates, which is unexpected due to the presence of hBN_{PTX60} in the composites. hBN_{PTX60} is fabricated by forming an agglomerate out of small hBN crystals, which have broken down during the processing of the composites either during the melt-blend or compression molding stage. The SEM micrographs show these smaller hBN_{PTX60} particles dispersed between the larger hBN_{PT110} particles. In order to maintain the spherical agglomerate shape of hBN_{PTX60}, alternative mixing techniques must be employed.

5.2.5 Summary

Hybrids of hBN were added into a PPS matrix to determine the effects of adding multiple types of filler into a composite. The filler content was kept consistent at 33.3 vol.%, but three different combinations were tested. Filler was added in ratios of 4:1, 3:1, and 2:1 (hBN_{PTX60}:hBN_{PT110}), and compared to composites containing 33.3 vol.% of only one type of hBN. The thermal conductivity of the composites increased from that of neat PPS, 0.22 W/m-K, to 2.04 W/m-K for PPS-hBN_{3:1}. An optimal ratio of PTX60 to
Figure 5.13: SEM Images of PPS-hBN hybrid composites at varying magnifications.
PT110 exists, creating synergy and promoting thermal conductivity. With increased amounts of PT110, above this ideal mixture the $k_{eff}$ decreases. The electrical properties of the single and hybrid filler composites do not vary significantly. Since the bulk properties of all the fillers are consistent, these similar results are expected. The compressive elastic moduli of the composites follow the same trend as the $k$ properties. The ideal combination of PTX60 to PT110 is also PPS-hBN$_{3:1}$. Particles with a larger aspect ratio have better interfacial adhesion between the matrix and filler materials, but smaller hBN has a decreased tendency of forming agglomerates affecting the mechanical properties. SEM micrographs confirm the presence of PTX60 and PT110 in the hybrid filler composites. Although PTX60 has broken down into small hBN crystals, they still assist in bridging gaps between PT110 platelets. The amount of platelets visibly increase when comparing the PPS-hBN$_{2:1}$ to PPS-hBN$_{4:1}$. A positive synergistic effect was found to exist when multiple ceramic fillers are combined in a PPS matrix.

### 5.3 Comparison of Matrix Materials

Multiple base materials were utilized within this project in order to determine the effect of a matrix on the properties of a composite. LLDPE was selected as a low temperature, cost effective matrix material, while PPS was chosen since it is stable at high temperatures. As previously mentioned, thermal conductivity is one of the most important parameters for electronic packaging. Even though polymers typically have very low thermal conductivities, their ease of processing and low cost makes them attractive for this particular application. Slight variations exist between matrix materials, and this section describes differences seen between LLDPE and PPS with hBN filler particles.

An effect of content study was conducted on the thermal conductivity of PPS-hBN composites, and the results are displayed in Figure 5.14. PPS-based composites containing
33.3, 50, and 74 vol.% of hBN\textsubscript{PTX60} were fabricated. The upper limit selected for this study was 74 vol.% hBN because of the filler shape. The theoretical maximum amount of spherical agglomerates is related to the atomic packing factor of a hexagonal close-packed (HCP) structure. Assuming the spheres all have the same diameter, the packing factor is 0.74 where each particle is in contact with its nearest neighbours, leaving the absolute minimum volume of voids.

As seen in Figure 5.14, the thermal conductivity increased along with filler content. The results from this study show that there is significant increase in $k_{\text{eff}}$, $34 \times$ that of neat PPS. The PPS-74 vol.% hBN composite yielded the highest $k_{\text{eff}}$-value out of all of the materials fabricated. At lower filler loadings, the relationship between volume percent of hBN and thermal conductivity in linear. Between 50 vol.% and 74 vol.% this trend no longer exists, suggesting that the percolation threshold has been reached within this range.

A comparison between PPS- and LLDPE-based composites can be seen in Table 5.2. Both of the values for the neat polymers were found in literature, while the mixing methods were kept consistent for comparative purposes for 33.3 vol.% and 50 vol.% hBN. The data suggests that the differences due to matrix materials are not significant. The results are similar for both LLDPE and PPS. The thermal conductivities of the neat matrix materials vary by less than 0.1 W/m-K, therefore large changes in the composite’s $k_{\text{eff}}$ were not anticipated. Therefore, an appropriate matrix material can be selected for each particular application with minimal effects on the thermal

<table>
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<th>LLDPE-matrix</th>
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<td>0.22</td>
<td>0.31</td>
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<tr>
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<td>1.90 ± 0.2</td>
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<td>3.48 ± 1.5</td>
<td>4.34 ± 0.5</td>
</tr>
<tr>
<td>74</td>
<td>7.52 ± 1.2</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 5.2: Comparison between PPS and LLDPE Matrix Materials on $k$
5.3.1 Micromechanical Modelling

Theoretical models were compared to the experimental results, seen in Figure 5.15. As seen in the other studies, large differences exist between the calculated values and the collected data. In this particular case, the geometric mean model closely follows the experimental data at lower thermal conductivities, but deviates after 33.3 vol.%. As
seen in many of the models, steep increases in thermal conductivity are seen between 33.3 and 50 vol.\%.

Below 33.3 vol.\% the majority of the models predict $k_{eff}$-values less than the measured data. As previously mentioned, the model assumes randomly distributed, discrete particles within a homogeneous medium, which is generally not the case. Interaction between particles increases the thermal conductivity of the composite, accounting for slight improvements in the experimental data.

At higher concentrations, Bruggeman’s model appears to be the most similar to the experimental data. Most of the models predict large increases in thermal conductivity at high concentrations of filler. The experimental data does not reflect this extreme increase in $k_{eff}$ due to issues with high thermal resistance at the interface between the matrix and filler. These models predict very high thermal conductivity values, which would result if an effective method of reducing interfacial phonon scattering was discovered.

### 5.4 Other Studies

#### 5.4.1 The Effect of a Coupling Agent

Amino silane ($((C_2H_5O)_3SiC_3H_6NH_2)$) is a common coupling agent used to improve the bond between inorganic and organic fillers. It was used in this study to modify the surface of some of the composites containing hBN. As previously discussed, high thermal interfacial resistance exists when filler materials are added into a polymer matrix. One suggested method of improving the interfacial adhesion was through the chemical functionalization of both the polymer and filler. In this particular study, PPS was used as a matrix material and mixed with 33.3 vol.\% and 74 vol.\% of treated hBN.
5.4.1.1 Methodology

The silane-based coupling agent, Struktol SCA 1100, was combined with a 50-50 water to ethanol mixture to form a homogeneous solution. Once the silane was dispersed within the mixture, hBN was added to the solution and mixed for 10 minutes using a magnetic stirrer. The powder was then filtered and dried for over 12 hours at approximately 60 °C. For all of the surface modifications, a ratio of 8 parts of silane to 100 parts of hBN was used, as suggested by the supplier of the amino silane.

Upon evaluating preliminary data regarding the thermal conductivity of treated polymer composites, the results were not as expected. As seen in Figure 5.16, the addition of amino silane to the hBN\textsubscript{PTX60} did not yield favourable results.

Silane-based coupling agents are not only used to improve the adhesion between
polymer matrix and filler, but also to promote uniform dispersion of particles. A homogeneous distribution of hBN within the matrix results in a reduction of filler-filler interactions [95]. Therefore, fewer random continuous conductive paths through the material form, decreasing thermal conductivity. Due to the difficult nature of differentiating between hBN and PPS at high filler loading, SEM micrographs do not aid in the confirmation of this hypothesis.

Studies have also shown decreases in thermal conductivity with excessive amounts of silane [3]. If the coating of silane on the surface of the particle is too large, then it may act as a thermal barrier and decrease the thermal conductivity. In a study by Yung et al, they found 1% coupling agent sufficient to enhance thermal conductivity, but 2% was counterproductive causing decreased thermal conductivities [3]. The converse may also be true, where hBN was not coated enough to improve the properties of the composite.

A thermogravimetric analyzer (TGA), from TA Instruments model Q50, was used to investigate the efficiency of the process used to coat amino silane on the surface of hBN. This analysis was performed on both PPS-hBN<sub>PT110</sub> platelets and PPS-hBN<sub>PTX60</sub> spherical agglomerates. Both types of hBN were tested with and without surface modifiers present by heating the material to 900 °C at 20 °C/min in a controlled nitrogen-gas environment.

The results of the TGA analysis show minimal losses in weight for both the treated and as-received hBN, as seen in Table 5.3. The organic coupling agent is volatile in comparison to hBN, therefore any weight loss found by heating the material to 900 °C would be equivalent to the amount of amino silane coating the surface of the treated hBN. For the as-received, untreated hBN, the results were as expected and negligible weight loss was seen. An increased loss was seen for hBN<sub>PTX60</sub> spherical agglomerates when compared to PPS-hBN<sub>PT110</sub>. These results suggest that the silane treatment was successful in coating hBN<sub>PTX60</sub>, but did not coat the PPS-hBN<sub>PT110</sub> platelets.
Figure 5.16: Effect of using a silane-based coupling agent on PPS-hBN composites.

The TGA thermographs also indicated the onset of degradation for the surface modifier was around 70 °C, and continued to 650 °C. These results suggest the processing techniques used for fabricating the polymer composite materials would degrade the surface modifier, rendering the coupling agent ineffective.
Table 5.3: TGA analysis of hBN weight loss upon heating to 900 °C

<table>
<thead>
<tr>
<th>hBN Filler</th>
<th>Weight Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTX60, as-received</td>
<td>&lt;0.05%</td>
</tr>
<tr>
<td>PTX60, surface modified</td>
<td>1.13%</td>
</tr>
<tr>
<td>PT110, as-received</td>
<td>&lt;0.05%</td>
</tr>
<tr>
<td>PT110, surface modified</td>
<td>&lt;0.05%</td>
</tr>
</tbody>
</table>
Chapter 6

Conclusions and Recommendations

6.1 Conclusions

The miniaturization of electronics is heavily dependent on the ability of electronic packaging to dissipate heat. As devices decrease in size and increase in power density, the need for multifunctional materials with high thermal conductivities and electrical resistivity grows. Polymer-matrix composites have been evaluated as an alternative to the current standards, such as embedded heat sinks. These materials are desirable because of their low cost, ease of processing, chemical stability, and electrical resistivity. Polymers are typically thermal insulators, and as such need the addition of thermally conductive fillers to improve their \( k_{eff} \). For this research thesis, PMCs were fabricated and characterized in terms of their thermal, electrical, mechanical properties, as well as their morphological characteristics. In the first study, LLDPE was used as the matrix, and was combined with hBN and SiC to determine the effects of different fillers, content, and porosity on the composite’s properties. Then PPS was used as a high temperature matrix material and was combined with various types of hBN to discover the effects of size, shape, and aspect ratio on the material, as well as the effect of hybrid ceramic fillers.
In the first parametric study, LLDPE was combined with SiC, hBN, and a hybrid of the both. The thermal conductivity was found to increase along with filler content, as did the electrical conductivity and compressive modulus. hBN was found to be more effective in promoting the thermal conductivity of the material when compared to SiC. Hexagonal boron nitride is also a much softer material, which also has a graphite-layer structure providing a lubricative effect, and therefore is more desirable for manufacturing. The combination of hybrid filler materials, of both SiC and hBN, was found to have the best $k_{\text{eff}}$. It is believed that the improvement of $k_{\text{eff}}$ was not only a result of increased filler content, but also a synergistic effect. Dielectric analysis determined that the addition of ceramic fillers into the polymer matrix did not compromise the electrical resistivity, regardless of the amount of filler placed in the composite. In general the compressive modulus and strength increased with filler content. Different types of mixing methods, dry-blending and melt-blending, were also contrasted. After comparing the effective thermal conductivity values, dry-blending was deemed the best alternative with respect to $k_{\text{eff}}$. The random agglomerates of fillers scattered in the material aid in the formation of continuous conductive pathways, in turn increasing the $k_{\text{eff}}$ of the composite, which is desirable for this particular application.

Novel cellular composites were also successfully fabricated to determine the feasibility of maintaining high thermal conductivity while reducing the overall mass of the material. These composites were created using a technique that has not been applied to this particular problem, and as such have not been documented with respect to their effective thermal conductivities. Expancel® microspheres were found to be an effective means of aligning hBN platelets within a composite, aiding in the formation of three-dimensional thermally conductive networks throughout the material. Alignment of filler particles is a direct result of extensional flow fields during the expansion process of the microspheres. An optimal volume expansion was found to exist, through the
addition of $1.5 \times$ the theoretically-calculated amount of microspheres required to fill either a 20- or 40-vol.% void. The thermal conductivity for these unique cellular composites were measured to have significantly high thermal conductivity values when compared to neat LLDPE.

The next study focused on the use of PPS as a high temperature matrix material. Different types of hBN with varying sizes, shapes, and aspect ratios were used to determine the effect of filler geometry on the material’s properties. The composites were melt-blended, which resulted in the breakdown of the spherical and medium-density agglomerate particles. Both the thermal conductivity and mechanical properties were enhanced for the composites containing different sizes of filler particles working together to create a synergistic effect, as seen for those materials with hBN$_{PT371}$.

Hybrid fillers were also used in PPS-hBN composites. This analysis was conducted in order to determine whether a synergistic effect occurs when two ceramics varying in size, shape, and aspect ratio are combined to improve the properties of material. hBN$_{PTX60}$ and hBN$_{PT110}$ were added to PPS in ratios of PPS-hBN$_{1:0}$, PPS-hBN$_{4:1}$, PPS-hBN$_{3:1}$, PPS-hBN$_{2:1}$, and PPS-hBN$_{0:1}$. In all of the composites, SEM micrographs confirm the separation of PTX60 into small hBN crystals, and the original spherical shape was not maintained due to the aggressive processing conditions. An optimal ratio was found with respect to the thermal conductivity and mechanical properties, PPS-hBN$_{3:1}$. The smaller PTX60 particles appear to bridge gaps between the larger PT110 platelets, in turn creating a positive synergistic effect.

Comparisons between the matrix materials, LLDPE and PPS with respect to effective thermal conductivity found no significant deviation. Therefore, the matrix material can be selected based on the application and tailored to suit each individual task without having a large effect on the $k_{eff}$.

A silane coupling agent was also used in hopes of improving the interfacial thermal resistance between the filler and matrix, along with improving the dispersion of
particles within the polymer. The addition of silane to the surface of hBN did not yield the desired results, and further research in this area will have to be conducted.

Finally, data collected from micromechanical modelling was compared to the experimental results for solid, single filler composites, in regards to their effective thermal conductivities. None of the models fit the empirical data exactly. Nielsen’s was the only model used that took shape, aspect ratio, and packing factor into consideration, and as such generally fit the measured data the best. Most of the models underestimated the effective thermal conductivity of the composites at low filler concentrations, likely because they assume the particles are discrete, spherical particles. All of the models also did not take interfacial thermal resistance into account, which was a larger issue for high filler content composites.

6.2 Recommendations

The effective thermal conductivity of the composites was greatly affected by the overwhelming presence of the interfacial thermal barrier. The resistance at the surface between the matrix and filler materials provided a strong hindrance to even greater increases in \( k_{\text{eff}} \). An effective method of reducing phonon scattering, as a result of interfacial resistance, is needed to improve the heat dissipation within a composite. A possible solution to this problem could include a better coating of coupling agents on the surface of the filler materials, allowing improved bonding of the particles to the matrix. Further studies to develop a more effective method of coating the fillers could lead to a decrease in difference between calculated \( k_{\text{eff}} \) values and experimental data.

It is also recommended that a method for maintaining the shape of the PT371, PTX60 and PTX25 agglomerates be found. For a more detailed study on the effect of size, shape, and aspect ratio, the original shape of the hBN clusters must remain as close to the manufacturer’s specifications as possible. Maintaining the spherical shape
of the PTX25 and PTX60 could assist in promoting the isotropic properties of hBN, which contrasts the anisotropic thermal conductivity seen with the hBN\textsubscript{371} platelets. By employing a dry-blending technique to combine the composites, along with low pressures during the compression molding step, damage to the fillers could possibly be minimized.

Even though novel cellular structures were successfully fabricated, they provide only a preliminary foundation for the future development and characterization. The porous structure-property relationships of these materials must be further evaluated and optimized. A technique to improve the dispersion of microspheres within the composite would be beneficial. Also, the use of various sized Expancel\textsuperscript{®} could be used in order to further investigate the effects of pore size on $k_{\text{eff}}$.

There are still a number of material properties that should be evaluated in order to confirm the feasibility of these composites for use in electronic packaging. These studies include, but are not limited to: breakdown strength, shear stress behaviour, corona effect, tensile testing, environmental conditioning, and thermal cycling.

Finally, finite element models (FEM) and rapid prototypes should be employed to determine the effects of using this material within typical heat sink conditions. This process will aid in determining the feasibility of using these composites and act as validation to this experimental work. The FEM models can also be further developed and validated with the experimental data found in this research thesis, improving the predictions. This material could either be used as a compliment to the current standards or as its own independent component, and therefore should be tested within each capacity.
Bibliography


