

**Enhancing Thermal Conductivity of Hexagonal Boron Nitride Filled
Thermoplastics for Thermal Interface Management**

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Abstract

Hexagonal Boron Nitride has been shown to enhance thermal conductivity in polymer composites more so than conventional ceramic fillers. However, to see a significant increase in thermal conductivity a high loading level of the advanced ceramic is often needed which can have an adverse effect on the mechanical behavior of the composite part. Applications for thermal management using thermal interface materials (TIM) continue to grow with thermoplastic injection molded parts emerging as an area for market growth. There is a growing need for published technical data in this particular area of application.

In the current study, the thermal conductivity and mechanical behavior of hexagonal Boron Nitride (hBN) loaded thermoplastic composites is investigated. The main objectives of this work is produce a novel data package which illustrates the effects of hBN, loaded at high concentrations, across several different thermoplastic resins with the ultimate goal being to find a desirable formulation for specific thermal management applications. The desired properties for such applications being high thermal conductivity and high electrical resistivity with a minimal decrease in mechanical properties. Hexagonal BN cooling filler agglomerates were compounded into polypropylene (PP), nylon-6 (PA-6), and thermoplastic elastomer (TPE) via twin-screw extruder at 3 different loading levels. Injection molded samples were produced and characterized to show varying degrees of thermal conductivity and mechanical strength. Results from this research showed that in all cases, the thermal conductivity increased with increasing levels of hBN addition. The largest increases in thermal conductivity were seen in the PA-6 and TPE systems with the possible indication of exceeding the percolation threshold in

the TPE system. This is hypothesized to occur due to the preferential migration of hBN to form conduction pathways around the elastomeric domains in the TPE matrix. Though TPE produced sizeable gains in thermal conduction it was the most negatively affected in terms mechanical strength with no increase in modulus and a drastic drop in tensile strength. The introduction of hexagonal boron nitride has the least impact on the mechanical properties in the PA-6 matrix. It is from these experimental results that a composite part comprised of a nylon-6/hBN system would be recommended as the most suitable for use thermal interface management applications due to its significant gains in thermal conductivity and minimal loss of mechanical strength, though this conclusion would only be applicable on a specific case basis.

1. Introduction

Over the last century, there has been a rapid growth in the electronics industry which has created a demand for engineered materials that can enhance the performance of newly innovated electronic products. The introduction of particle fillers to polymer parts has been around for many years, often for increases in strength or reduction of weight. Demand has grown for these composite parts to not only maintain strength but also introduce new capabilities such as thermal conductivity and electrical resistivity.

1.1. Motivation – Thermal Interface Management Applications

In electronics specifically, use of thermal interface materials (TIM) has emerged as a key focal point and their application is vital for sustaining high product performance and long product lifetimes. The use of ceramics as functional fillers has grown more prevalent in the last decade. Fillers such as Aluminum Oxide (Al_2O_3), Silicon Nitride (Si_3N_4), Silicon Carbide (SiC), and magnesium oxide (MgO) are relatively inexpensive and do offer an increase in thermal conductivity and electrical insulation. However, these ceramic fillers are abrasive and can result in wear of equipment and tooling during processing. The implementation of hexagonal boron nitride (hBN) as an alternative cooling filler has changed the market for thermal interface management. Addition of hexagonal boron nitride versus conventional fillers shows significantly higher thermal conductivity in composites with the additional characteristic of being lubricious. These properties can be utilized to not only increase product performance but also has the potential to enhance the efficiency of the manufacturing process [1].

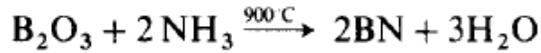
1.2. History of Hexagonal Boron Nitride

Boron Nitride was first prepared by an English chemist by the name of W.H. Balmain in the 1840s through a method that combined molten boric acid and potassium cyanide [2,3]. This particular formulation was not able to produce a stable compound. For roughly 100 years, boron nitride was formed exclusively on a laboratory scale and it wasn't until the 1950s that Union Carbide began their industrial scale production of BN composites through hot pressing techniques [2]. One of the first major uses for hBN was in cosmetics in Japan in the early 1940s. It was later re-vitalized in the 1990s for industrial application uses such as metallization, automotive, high temp furnaces, thermal management, and many more applications [3,4]. Hexagonal boron nitride can be used in powder, coating, and sintered forms and it is this versatility that further expands its range of application [3].

1.3. Hexagonal Boron Nitride Preparation

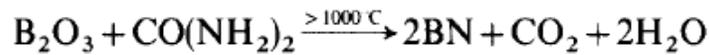
There are numerous methods of h-BN production found in the literature. Such methods include wet chemistry, precursor formation, chemical vapor deposition, as well as self-propagation. The following are three prevalent reactions for producing α -BN powder on an industrial scale:

- (1) Reaction of boric oxide with ammonia in the presence of a filler material (i.e. tricalcium orthophosphate):



A second heat treatment for purification and crystallization is performed at $>1500^\circ\text{C}$ under N_2 .

- (2) Reaction of boric oxide (or borax) with organic nitrogen compounds (i.e. urea, melamine):



- (3) Nitridation of calcium hexaboride in the presence of boric oxide:

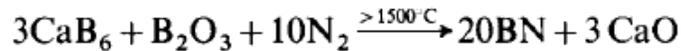


Figure 1-1. Three prevalent reactions schemes to produce hBN on an industrial scale [5].

Another significant method for fabricating hexagonal boron nitride is the direct combination of boric acid (H_3BO_3) and melamine ($\text{C}_3\text{N}_6\text{H}_6$) in a nitrogen blanket followed by a heat treatment at high temperatures reaching up to 1800°C [4,6]. The final hexagonal structure is resultant of a two stage process where it transitions from turbostratic to mesographitic. The purity, as well as the powder properties such as particle size, crystallinity, and surface area, are controlled by process parameters during the second annealing stage of formation [4].

1.4. Physical Structure of Hexagonal Boron Nitride

From a structural standpoint, hBN is very similar to graphite in that it forms sheets of closed hexagonal rings (Fig 1.2) layered on top of each other with the boron atom eclipsing the nitrogen atom from both above or below (Fig 1.3) [4]. BN is isoelectronic with the carbon atom

which is why it has been deemed “white graphite” [3,4]. Within each layer of the compound, each boron atom is covalently bonded to a nitrogen atom which is a reason for the compounds strong thermal properties. The layers of BN sheets are attracted to one another by weak van der Waals forces which allows for them to be easily sheared apart with mechanical work such as in mixing and compounding methods [4,5].

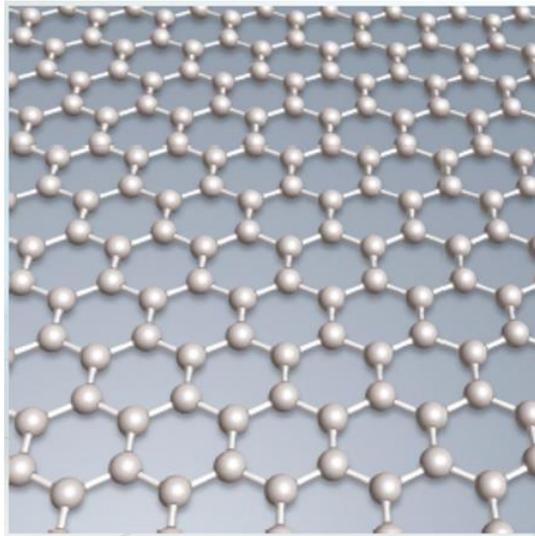


Figure 1-2. Picture of crystalline chemical structure of hexagonal boron nitride [7].

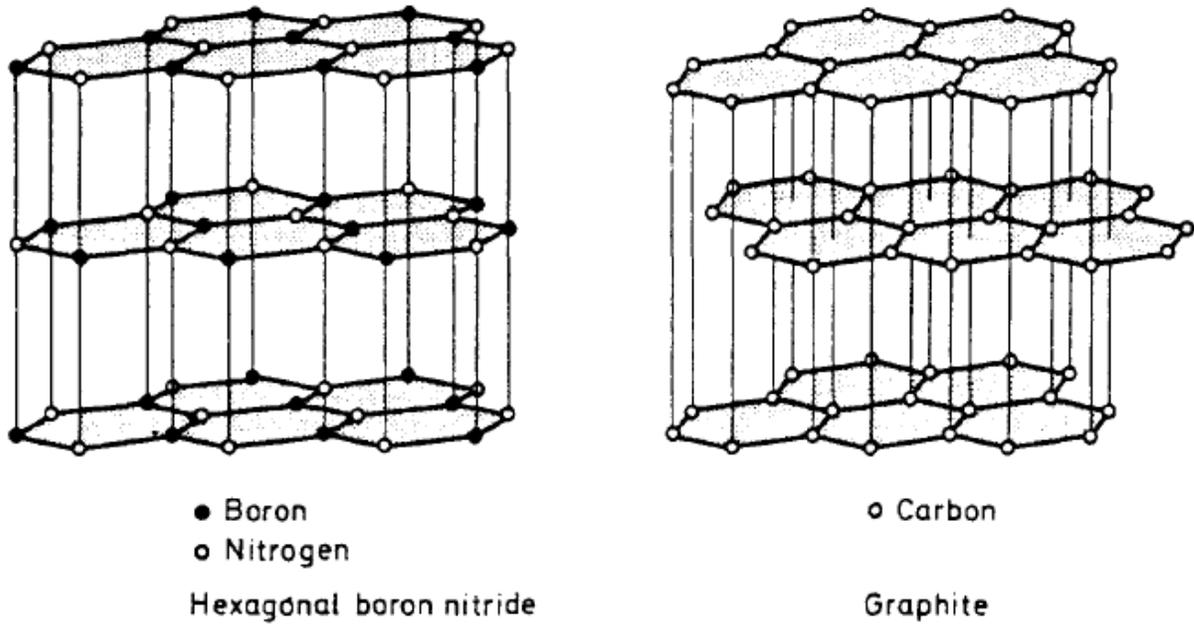


Figure 1-3. Crystalline structures of hexagonal boron nitride (alpha-BN) and graphite [5].

Due to the elements of boron and nitrogen being adjacent to carbon in the periodic table, they can mutually form 1:1 compounds. These compounds are isostructural to the polymorphs of carbon [5]. Boron nitride can be prepared in both amorphous and crystalline forms. The crystalline forms can take on 3 different structures with the first being α -BN, the most stable form, which consists of the hexagonal layered structure (Fig 1-3). Cubic, or β -BN, which is a high pressure diamond-like modification and can be used as a super abrasive [3,4]. The last crystalline structure is wurtzite, or γ -BN, which is a dense hexagonal modification. The three crystalline forms give way to distinct properties that distinguish each structure for different applications [5]. The focus of this work will be of the hexagonal structure (α -BN) as its specific properties are most suitable for application in thermal interface management and injection molding.

1.5. Inherent Properties of Hexagonal Boron Nitride

There are several inherent characteristics that make this functional ceramic so desired for composite applications. One of which is its low density of 2.27 g cm^{-3} (theoretical) and high temperature stability with a melting point of approximately 2600°C . Hexagonal α -BN is very chemically inert and shows strong resistance to acids and molten metals. Further, hBN shows good stability in air up to 1000°C , argon gas up to 2200°C , and nitrogen up to 2400°C [4,5]. Some other key properties are its low thermal expansion and good thermal shock resistance, microwave transparency, and non-toxicity [2]. However, the key properties that are a focus for TIM applications are h-BN's high thermal conductivity, high electrical resistivity, and lubricity.

1.5.1 Lubricious Properties of Hexagonal Boron Nitride

As discussed earlier, hexagonal boron nitride has a plate-like structure and the interfacial slippage between these layers of platelets permits the use of hBN as an effective dry lubricant [4,7]. Hexagonal BN has the ability to behave as a lubricant over a wide range of process temperatures due to its high thermal stability [2]. The ceramic is characteristically soft with a Mohs hardness of 1-2 [4]. It also has the ability to retain its low coefficient of friction up to 900°C whereas similar materials like molybdenum disulfide and graphite will burn off at lower temperatures. Typical hBN uses of the powder form are solid lubricants for high temperature bearings, mold release agents, as well as oil and grease additives [2].

1.5.2 Electrical Resistivity of Hexagonal Boron Nitride

Polymers alone are inherently electrically resistive. The addition of fillers can often alter the conductance of the material. Hexagonal BN shows good dielectric properties or in other words low relative permittivity. This characteristic of low dielectric constant is the basis for its use for electrical insulation which can be vital for TIM applications. Boron nitride has a dielectric constant of 4 which is half that of α -Al₂O₃, a common ceramic filler in TIM applications, making it a viable and better performing substitute [2,7]. Hexagonal boron nitride has an electrical resistivity of greater than 10^{15} ohms*cm [7]. These inherent characteristics allow for excellent electrical insulation which make it very useful for applications in the electronic industry [2].

1.5.3 Thermal Conductivity of Hexagonal Boron Nitride

Neat polymers are poor thermal conductors producing conduction rates of 0.1-0.2 W/m*K [4]. In order for their use in thermal management, a functional ceramic filler is required to boost their thermal conductive abilities. Hexagonal α -BN is known to have very high thermal conductivity with an in-plane thermal conductivity of 400 W/m*K. [7,8]. Hexagonal boron nitride at cryogenic temperatures is comparable to stainless steel and BeO above 700°C [5]. Measurement of thermal conductivity can be taken in regards to the in-plane direction which acts as a dissipation mechanism or in the through-plane direction which acts as a heat transfer mechanism (Fig 1-4).

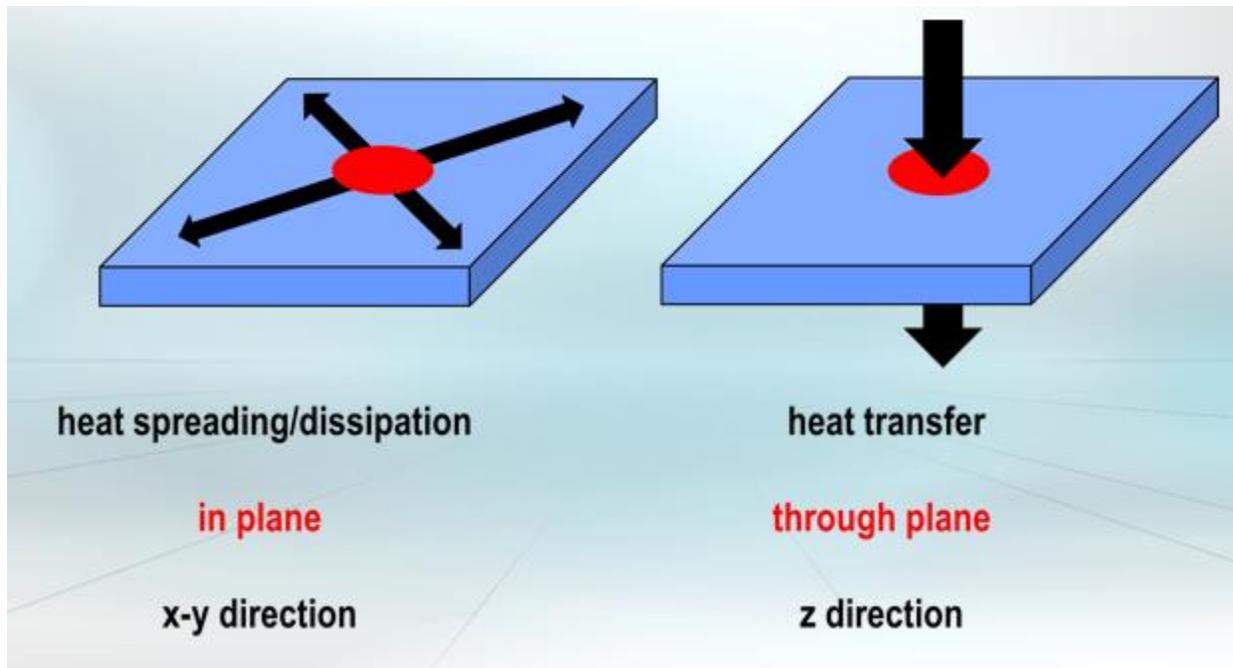


Figure 1-4. Schematic for in-plane and through-plane conduction [7].

1.5.3A Mechanism of Thermal Conductivity

Thermal conductivity, k ($\text{W}/(\text{m}\cdot\text{K})$), can be expressed by the following equation:

$$K = \alpha\rho C_p \quad (1)$$

Where α is the thermal diffusivity (mm^2/s), ρ is the density (g/cm^3), and C_p is the specific heat capacity ($\text{J}/(\text{g}\cdot\text{K})$) under constant pressure [1]. It can be defined as the rate at which heat passes through a specified material, expressed as the amount of heat that flows per unit time through a unit area with a temperature gradient of one degree per unit distance. The thermal diffusivity of a material can be directly measured and from this value one can calculate the thermal conductivity.

Many of the functional properties of composite materials such as conduction and diffusion can be linked to the geometrical arrangement of the constitutive phase and the

interfaces within. Percolation theory is used to characterize the connectivity properties in random geometries and can be used to frame the conduction behavior of random composites [9]. In percolation theory, the principle of universality can be applied to this model and specific details of the system can be disregarded and normal scaling laws can be deduced. A square lattice can be used to model static site percolation with the probability (p) that a site is occupied and probability ($1-p$) that a site is empty (Fig 1-5). If a nearest neighbor is occupied with another conducting species a cluster can form. At large enough p -values, there are enough clusters to form a connection and a conductive pathway is formed. This is accomplished when a flow of energy can travel from one side of the lattice to the other. This also marks the formation of an infinite cluster. There is a specific concentration called the percolation threshold (p_c) or critical concentration where the first instance of the percolation is observed [9].

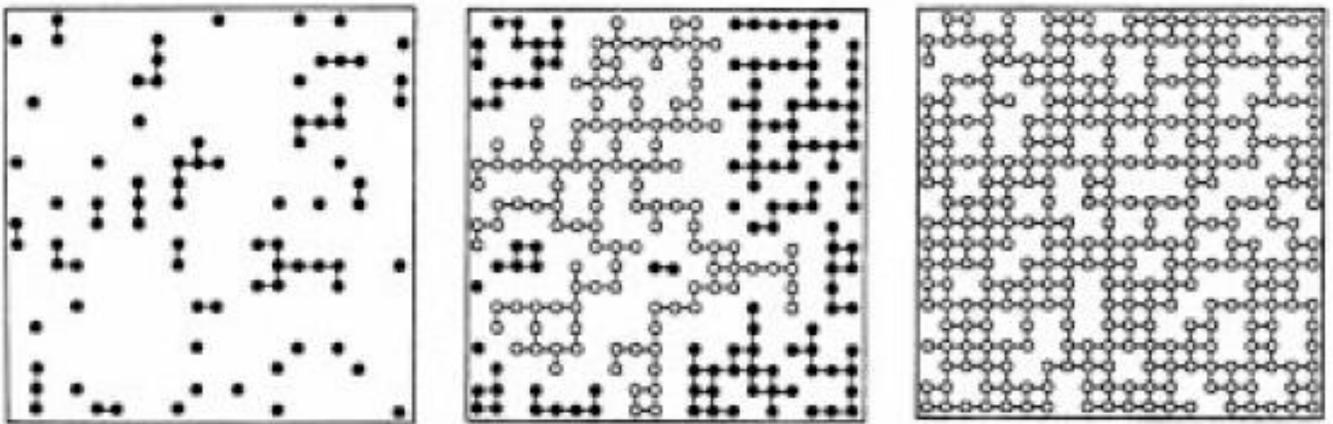


Figure 1-5. Diagram of site percolation on a square lattice: The small circles represent the occupied sites for three different concentration: $p=0.2$ (left), $p=0.59$ (middle), $p=0.80$ (right). Nearest-neighbor cluster sites are connected by lines representing the bonds. Filled circles are used for finite clusters, while open circles mark the large infinite cluster [9].

When all the sites of the sites of lattice are now occupied, bond percolation dominates the conductive dynamic (Fig 1-6). The random orientation of the occupied bonds becomes crucial for separating the infinite clusters from the finite clusters and the eventual formation of the conduction pathway (Fig 1- 6a). When the location of the conductive species is no longer restricted to lattice coordinates and a random orientation is adopted, a continuum percolation is formed (Fig 1-6b) [9]. Percolation theory can be used to describe the formation of conductive pathways with hBN particles in composites.

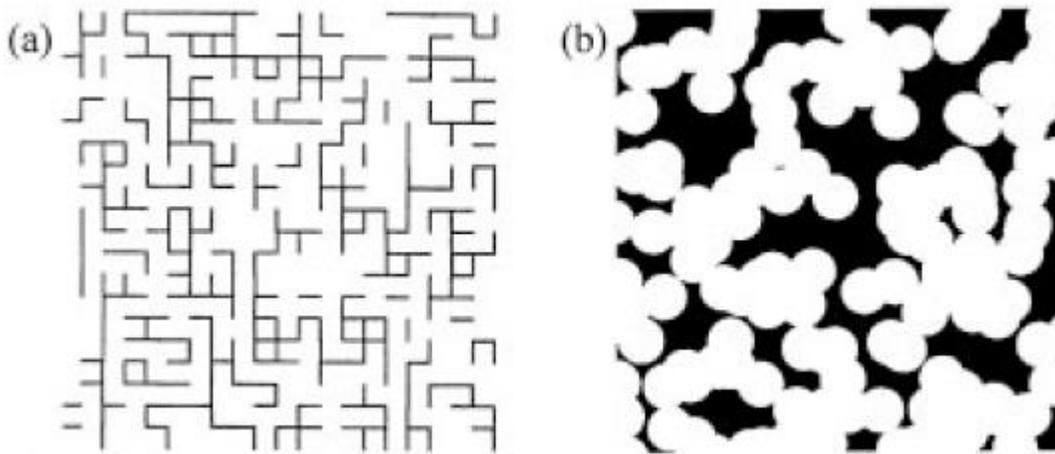


Figure 1-6. Further Percolation systems: (a) Bond percolation cluster on a square lattice and (b) continuum percolation of circular discs with fixed radius at the percolation threshold. [9]

1.5.3B Enhancing Thermal Conductivity

The maximization of thermal conductivity is highlighted by the presence of two main factors, the particle density of heat-flow paths and the number of conducting pathways. This is the basis for establishing successful percolation networks. The transport of heat in non-metals

occurs through lattice vibrational energy known as phonons [10]. There are various types of phonon scattering processes that can disrupt the energy flow such as phonon-phonon scattering, boundary scattering, and defect or impurity scattering [10,11]. In order to maximize thermal conductivity these phonon scattering processes must be minimized or even suppressed. It has been theorized that phonons travel through matter at the speed of sound and that any scattering can be attributed to an interfacial thermal barrier due to acoustic mismatch [12,13]. The energy flow pathways are dissipated when the surface layer between the filler and the matrix is damaged or incomplete. This process can be compared to the scattering of light when it travels through media of different refractive index. These percolation theories were evidenced by the work of Ishida et al.[1]. In their study, they were able to produce exceptionally high thermal conductivity in hBN-polybenzoxazine composites by reaching the maximum filler loading with a matrix resin whose viscosity allows for a high degree of wetting with the hBN particles. Through the high degree of wetting, the interfacial thermal barrier was minimized; and in combination with a bimodal particle size of BN, they were able to reach a larger particle packing density in the composite which resulted in forming a highly conductive network [14].

1.6. Use of hexagonal Boron Nitride for Thermal Interface Management

Applications

The increasing miniaturization of electronics requires materials with the capacity to distribute, transfer, and dissipate energy [4]. Thermal interface management primarily focuses on dissipating heat through thermal conduction while maintaining electrical insulation. This can

often include creating heat sinks (Fig 1-6) to transport heat away from the electrical flow and allow for the thermal energy to be dissipated by convection with the surrounding environment. This type of functionality is common for LED lighting applications, high capacity battery technologies, as well as consumer and automotive electronic applications.

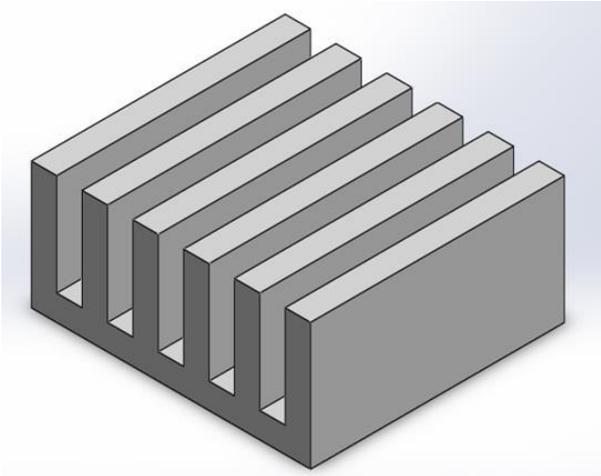


Figure 1-7. Picture of a heat sink used in thermal interface management [8].

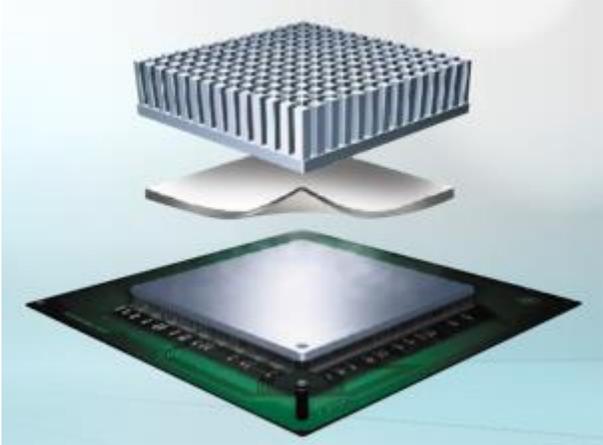


Figure 1-8. Depiction of the use of a heat sink for micro-electronic circuit boards [7].

The capacity for a heat sink to dissipate heat decreases due to interfacial thermal resistance which arises from a mismatch of surface morphology between the device and the heat sink. These gaps result in inadequate thermal contact. Selection of the thermal interface materials, both matrix and filler, is crucial for facilitating the heat conduction process. These materials must possess certain characteristics such as high thermal conductivity, low dielectric constant, and low CTE [15]. The inherent properties of hexagonal boron nitride, as discussed above, meet the requirements for a successful TIM material but also extends to provide advantages in other areas of interest to manufacturers.

1.6.1 Effect of Boron Nitride on Mechanical Properties

As thermal conductivity and electrical resistivity are the main desired properties, the composite part still needs to have acceptable physical properties such as modulus and impact strength. Typically when hBN is used in this capacity, the matrix is that of a thermoset polymer such as epoxies or polybenzoxazine [1]. Thermosets are polymer matrices that crosslink when heated in a process that is non-reversible. These types of matrix materials are prevalent in miniaturized transistor and other microelectronic applications. These parts work under high frequency which leads to an increased heat flux and power dissipation making thermal management critical [16,17]. Epoxies are a commonly used matrix because of good mechanical properties, low water uptake, and low coefficient of thermal expansion (CTE). The work of Zhou et al. [17] in a 2013 study investigated the effect of silane coupled hBN in epoxy composites with a focus on the mechanical properties. Table 1-1, seen below, summarizes their mechanical testing data. Some major results worth noting are that the tensile and flexural modulus were

both increased as hBN filler concentration was increased. This is to be expected as the rigidity of the inorganic filler is higher than that of the neat epoxy. Conversely, the tensile, flexural, and impact strength were all decreased with an increased filler content. This was attributed to the potential to form voids or interfacial defects in the composites resulting in loss of mechanical strength.

Table 1-1. Mechanical Properties of neat epoxy and its h-BN composites [17].

Mechanical properties	hBN concentration/wt%				
	0	20	30	40	50
Tensile strength/MPa	68.2 ± 5.6	63.6 ± 4.2	58.2 ± 4.5	51.2 ± 3.9	45.1 ± 3.7
Tensile modulus/GPa	2.68 ± 0.21	2.82 ± 0.30	2.93 ± 0.24	3.12 ± 0.29	3.14 ± 0.31
Elongation at break/%	5.40 ± 0.26	5.21 ± 0.22	4.74 ± 0.18	4.1 ± 0.19	2.84 ± 0.11
Flexural strength/MPa	112 ± 9	108 ± 8	95 ± 7	86 ± 6	81 ± 6
Flexural modulus/GPa	2.71 ± 0.13	2.79 ± 0.15	2.88 ± 0.16	3.05 ± 0.14	3.07 ± 0.18
Flexural strain at break/%	4.64 ± 0.35	4.04 ± 0.25	3.51 ± 0.21	2.63 ± 0.14	1.62 ± 0.08
Impact strength/kj/m ²	16.2 ± 0.9	14.5 ± 0.8	12.3 ± 0.7	10.3 ± 0.5	8.2 ± 0.4

hBN: hexagonal boron nitride.

An additional study by Kemaloglu et al. [15] investigated the effect of hexagonal boron nitride on the thermal and mechanical properties of silicon rubber. They also compared the effect of hBN particle size with both micro and nano-sized fillers. Similar finding to the work of Zhou et al were seen in this study with hBN input decreasing the CTE, tensile strength, and strain at break while increasing modulus, hardness, and thermal conductivity. They were also able to conclude that nano-sized hBN particles had the more profound effect on tensile strength, modulus, and CTE while the largest aspect ratio produced the largest gains in thermal conductivity.

1.6.2 Effect of Boron Nitride on Thermal Conductivity in Thermoplastics

Thermosets offer strong physical properties but they require more intensive and complicated compounding methods, make batch manufacturing more difficult and costly, and also lack the ability to be recycled for remolding. Thermoplastics are a more favorable material for applications that require compounding and injection molding as processing methods.

Hexagonal boron nitride has excellent compatibility with thermoplastics. Due to its softness and lubricious properties, hBN is ideal for injection molding applications as it shows a reduction in tool wear compared to more abrasive ceramic fillers such as Al_2O_3 [4]. It has even been shown that the introduction of hBN in comparison to other ceramic fillers results in a reduction of cycle times, wall thickness reduction, and reduced shrinkage and warpage in injection molding applications [7]. It is for these reasons that the use of hBN in thermoplastic resins is of great appeal to potential composite manufacturers. Previously, the work of Hsiao et al. [1] investigated the thermal conductivity of boron nitride filled polybutylene terephthalate with an emphasis on the particle morphology, concentration, and compounding conditions. Their work found that larger hBN particles provided composites with higher thermal conductivity because smaller particles have larger interfacial areas which can form thermally resistant junctions that result in phonon scattering, as discussed in the work of Berman [10]. Further work by Zhou et al. [16] investigated the thermal conductivity of boron nitride filled polyethylene composites while also investigating the effect of hBN dispersion through either melt mixing or powder mixing. As a secondary investigation, they also aimed to determine the effect of HDPE particle on the overall thermal conductivity of the composite. They were able to conclude that increasing the filler content does indeed improve the thermal conductivity of the composite,

which is to be expected. But it was also found that the effect of mixing (powder vs melt) was not significant until higher loading levels where the powder mixing was found to improve the formation of conductive networks. Further, they found that the larger the HDPE particle size, the higher the thermal conductivity in the powder mixing because the large HDPE particles form more concentrated hBN conducting channels. This result validates the conclusions of Zhou et al. [17] And lastly, Cheewawuttipong et al. [18] further supports the research previously discussed when their team investigated the effect of hBN on the thermal and mechanical properties in two grades of polypropylene each having different viscosities. They also tested the effect of hBN particle size on the composite's thermodynamic behavior. Their work found, as in the other two studies previously discussed, that increasing the particle size also increases the thermal conductivity and the addition of the ceramic filler increased the storage and loss modulus. Also, the viscosity of the two different grades of PP did not significantly influence the thermal and mechanical properties of the composite specimens.

This aim of this work will be to expand upon the previously discussed literature to a larger range of thermoplastic systems. A comparison of both thermal and mechanical properties is investigated across three thermoplastics resins. Polypropylene, nylon-6, and thermoplastic elastomer (TPE) were chosen as the three matrix resins due to their different properties as well as their specific interest for emerging TIM applications.

1.7. Objectives

The objectives of this research were the following:

- 1.) Provide a data package that illustrates the effect of hexagonal boron nitride addition on both the thermal conductivity and mechanical properties across a spectrum of inherently different thermoplastic resins.
- 2.) Propose an optimal loading of hexagonal boron nitride for each thermoplastic resin that maximizes thermal conductivity while still maintaining mechanical feasibility for specific thermal management applications.

2. Experimental Approach

2.1 Materials

Three separate loadings of h-BN were targeted for each of the resin systems. The objective for this experiment was to load the hBN filler to a low level (~30 wt.%), medium level (~45 wt.%), and a high concentration (~60 wt.%) while keeping the number of passes constant between the resin systems (1,2,and 3 passes respectively) to show equivalence in specific energy input (SEI). Specific energy input has units of torque*RPM/throughput and is a measurement of how much work is inflicted on the resin. Excessive SEI could result in degradation of the polymer matrix. Due to the challenging compounding conditions of PA-6 with hBN there was a limited supply of masterbatch for this resin system. We were only able to

obtain approximately 35 and 60 wt. % hBN loading in the PA-6 which proved to be sufficient to draw conclusions from the testing.

2.1.1 3M Hexagonal Boron Nitride Cooling Filler Agglomerates

The 3M™ Boron Nitride Cooling Filler Agglomerates (Agglomerates 100) were obtained from 3M™ Technical Ceramics in Kempten, Germany. The powder has a Scott bulk density of 0.3-.45 g/cm³. The particle size distribution yields 90% with a diameter of 85-110 microns. The agglomerates (Fig 2-1) are composed of smaller 50 micron diameter primary particles. Agglomerates were chosen for use in this study because the 15 micron long, 0.5 micron thick primary platelet particle is difficult to feed due to bridging and poor dry flow properties. For thermoplastic compounding, the agglomerates were used due to the ease of feed through a side stuffing feeder. As stated in the Agglomerate 100 technical data sheet, this product line is designed, via particle geometry modification, to a semi-spherical particle for isotropic thermal conductivity in thermosets [19]. However, their use was adapted for thermoplastic application in this study. Preliminary experiments were done to determine that the agglomerates would be broken-up by shear to the primary particle size and shape.

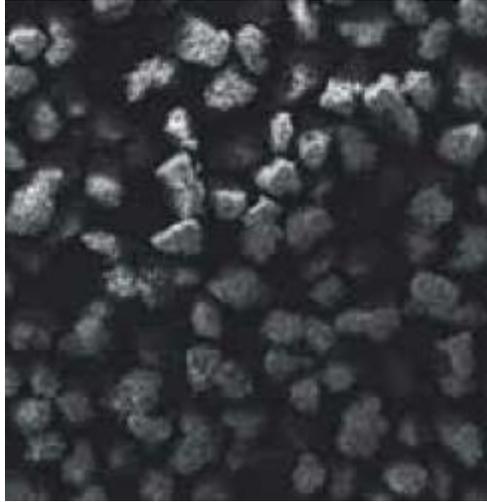


Figure 2-1. SEM micrograph of 3M Boron Nitride Cooling Filler Agglomerates [19]

2.1.2 Thermoplastic Resins

The three thermoplastic resins used for the matrix in this experiment are polypropylene (PP), nylon-6 (PA-6) and thermoplastic elastomer (TPE). Please view Table 2-1 below for the vital resin technical information.

Table 2-1. Table of polymer resin technical data. [20,21,22]

Resin	Density	Melt Temp	MFI or Melt Viscosity	Supplier	Comments
SG802 PP	0.90	165°C	35	Lyondell Basell	Injection molding grade
Schulamid NV12 PA-6	1.15 g/cm ³	219°C	130	A. Shulman	Low viscosity injection molding grade
Santoprene 8221 TPE/TPV	0.92 g/cm ³	NA	NA	Exxon	Injection molding grade

These particular thermoplastic resin were chosen because of their use in specific thermal management applications. Polyamide-6 (Fig 2-2) is used in injection molded heat sinks and automotive under the hood applications (e-motor housing) [23]. Polyamide-6 is a semi-crystalline engineering thermoplastic that is known for its balance of strength, stiffness, and chemical resistance. This material has low viscosity when molten but rapidly solidifies when exiting the die.

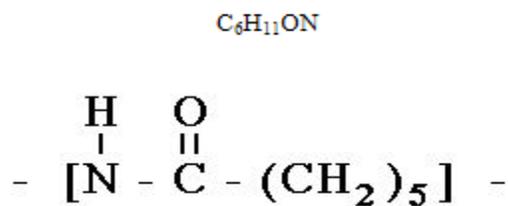


Figure 2-2. Chemical structure of Nylon-6 [24].

Polypropylene (Fig 2-3) and TPE are used for the matrix for profile extruded sheets for TIM pads in Li ion battery applications. The specific thermoplastic elastomer used in this study consists of elastomeric domains of ethylene propylene diene monomer or EPDM (Fig 2-4) that are encapsulated by a polypropylene matrix. The elastic rubber domains of TPE (Fig 2-5) provide added impact strength and elongation to the already tough and lower density polypropylene [27].

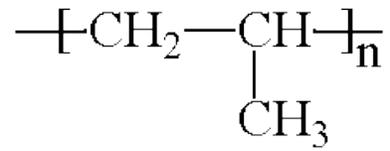


Figure 2-3. Chemical structure of Polypropylene [25].

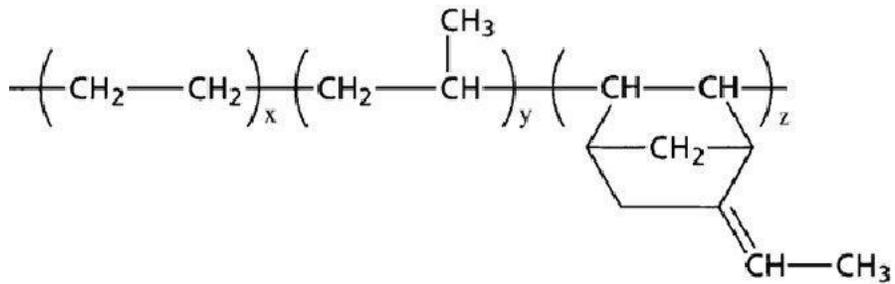


Figure 2-4. Chemical Structure of EPDM [26].

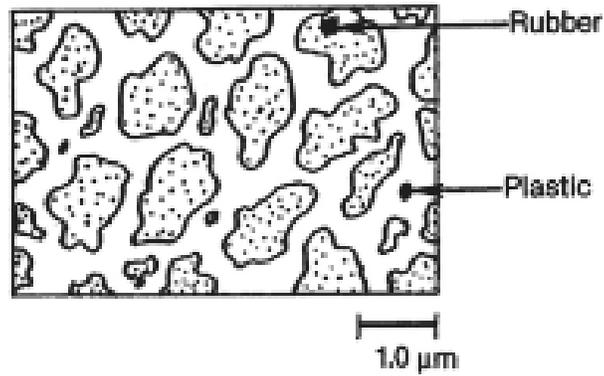


Figure 2-5. Morphology of thermoplastic vulcanizate [26].

2.2 Sample Preparation

2.2.1 Masterbatch Compounding

The boron nitride cooling filler agglomerates were compounded at varying loadings via Thermo Scientific co-rotating fully intermeshing twin screw extruder system (prism TSE 24 mc-L/D 28:1) equipped with 7 heating zones (Fig 2-6). Each commercial resin was starve-fed in zone 1 via a resin feeder and passed through a set of kneading blocks to ensure its complete melting before hBN was side fed downstream in zone 4. High channel depth conveying elements (OD/ID: 1.75) were used at the point of hBN side feeding as well as for the rest of the downstream processing. Please see Table 2-2 below for the various compounding temperature profiles for the 3 resins.



Figure 2-6. Picture of Thermo Electron TSE. Picture courtesy of Thermo Scientific [27].

Table 2-2. Table of twin screw extruder temperature profiles for each resin system.

Resin	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7
PP	170°C	230°C	210°C	210°C	190°C	190°C	190°C
PA-6	190°C	235°C	245°C	245°C	245°C	245°C	245°C
TPE	150°C	190°C	190°C	200°C	200°C	200°C	200°C

2.2.2 Burn-off Measurement

In order to attain accurate hBN loading values, all masterbatch formulations were placed in an oven and subjected to a burn off procedure which removes the organic polymer compound and leaves only the inorganic additive. The final mass of the remaining ash was recorded for the weight percent values used throughout experiment. In the instance of the TPE, roughly 8 wt. % of CaCO₃ was accounted for in virgin commercial resin.

2.2.3 Injection Molding Procedure

All samples were molded using a BOY22D injection molding machine (Fig 2-7) with a 28mm general purpose barrel and screw manufactured by Boy Machines Inc. A standard ASTM mold with cavities for tensile, impact, and flex bars was used for all molded parts. Barrel zone 1 through 4, as well as the mold was set to varying temperatures depending on the material used. The cooling time was set to 16 seconds. Additional molds were used to generate plaque specimens to be used for thermal conductivity testing. All masterbatch formulations were dried

overnight at 170°F to ensure no residual moisture would be present to affect the injection molding process. Please see Table (2-3) for a listing of the injection molding temperatures.



Figure 2-7. Picture of BoyD22 injection molder. Picture courtesy of Boy machines [28].

Table 2-3. Temperature profile of each resin system for injection molding.

Material	Zone 1 Temp	Zone 2 Temp	Zone 3 Temp	Sprue Temp	Mold Temp
PP	420°F	420°F	450°F	450°F	90°F
Nylon	482°F	482°F	482°F	482°F	176°F
TPE	340°F	400°F	400°F	400°F	170°F

2.3 Characterization

2.3.1 SEM of hBN Agglomerates

Burn off samples from the TPE loaded masterbatch were analyzed by SEM at 1350X magnification to determine the effect of compounding on the hBN agglomerates. It was seen

that the twin screw compounding resulted in the agglomerates being sheared down to produce a primary particle form. This assumption was made throughout all resin systems testing in this study. Please see Fig 2-8 below for the micrograph of the multi-passed masterbatch.

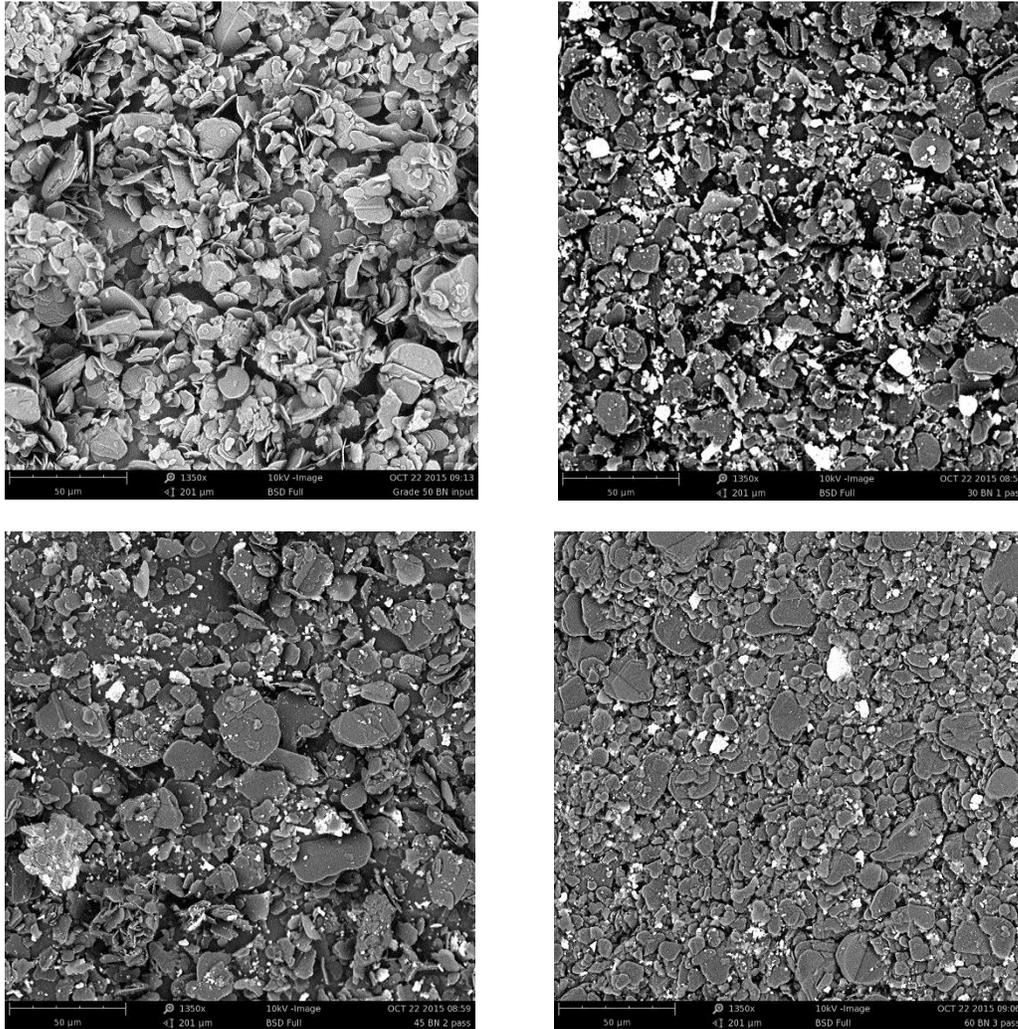


Figure 2-8. SEM micrographs of h-BN and h-BN/TPE masterbatch. Top left: h-BN agglomerate, Top right: burn off ash for 30 wt. % hBN in TPE (1 pass), Bottom left: burn off ash of 45 wt. % hBN in TPE (2 pass), bottom right: burn off ash of 57 wt. % hBN in TPE (3 pass).

2.3.2 Mechanical Behavior of h-BN Loaded Specimens

Mechanical properties of the injection-molded composites were measured using the ASTM standard test methods listed in Table 2-4 seen below. A MTS frame (Fig 2-9) with a 5kN load cell along with tensile and 3 point bending grips were used for tensile and flexural properties, respectively. Tinius Olsen model IT503 impact tester (Fig 2-10) and its specimen notcher were used to measure room temperature notched Izod and notched Charpy impact strength of the molded composites.



Figure 2-9. Picture of MTS Tensile Machine. Picture Courtesy of MTS Systems Corporation [19].



Figure 2-10. Picture of Tinus Olson Impact tester. Picture Courtesy of Tinus Olson [30].

Table 2-4. Table of ASTM test methods for measuring the mechanical properties of the specimens.

Test (Unit)	Abbr.	ASTM #
Tensile Modulus (MPa)	TM	D-638
Tensile Strength at yield (MPa)	TS	D-638
Elongation at break (%)	EL	D-638
Notched Izod Impact (J/m)	NI-I	D-256
Notched Charpy Impact (J/m)	NI-C	D-256
Flexural Strength at yield (MPa)	FS	D-790
Flexural Modulus (MPa)	FM	D-790

2.3.3 Thermal Conductivity Measurement

Thermal conductivity was tested using a Netzsch LFA 467 Hyperflash [Fig 2-11]. A short energy light pulse is used to heat the front surface of a plane-parallel sample. An infrared detector is used to measure the energy flow (temperature excursion) from the rear face of the sample specimen [Fig 2-12]. This process measures the thermal conductivity in the through-plane direction. Liquid nitrogen is used to control the temperature of the furnace for a broader range of the sample collection. The apparatus can obtain an accurate reading for the thermal diffusivity of the sample. By inputting the dimensions and density of each specimen, the thermal conductivity and the specific heat can be calculated using the analysis software. Sample density was taken using the Archimedes method [Fig 2-13] which measures the weight of sample both dry and submerged in water. Based on the known density of water one can calculate the density of the sample. In the case of PP, a pycnometer was used as PP is less dense than water and floats on the surface. Both methods were cross-calibrated to verify the accuracy of the density measurement.



Figure 2-11. Picture of Netzsch LFA Flash apparatus. Picture Courtesy of Netzsch Instruments [31].

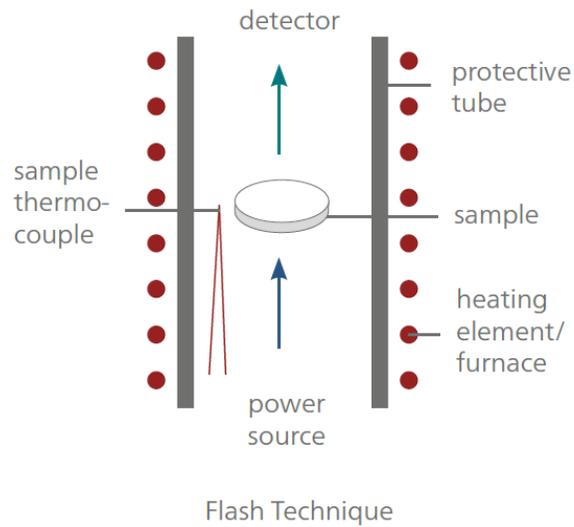


Figure 2-12. Schematic of LFA Flash Technique used to measure sample thermal conductivity [31]



Figure 2-13. Archimedes density measurement set-up. Picture courtesy of A&D Weighing [32].

Three specimens were taken from each loading concentration at different positions of the plaque mold to reduce the nuisance factor of hBN flow variance during the injection molding process. Samples were 2mm thick and either punched from a plaque to create a 13mm diameter disk or a 10mm long square cut using a table saw. All sample were coated with a black carbon graphite spray used in an attempt to prevent the laser beam from penetrating the samples. The carbon coating ensures equal and maximal absorbance as well as emittance of energy. By standardizing the amount of energy absorbance and emittance, accurate measurement of the thermal diffusivity within the sample can be taken which gave better differentiation for the resulting data. In some cases, the control samples that were free of any hBN loading were too opaque to get an accurate reading on the LFA. To combat this issue, a several nanometer thick gold-palladium layer was sputtered onto the surface. The LFA was

programmed to record data on each specimen for 5 “shots” or replicates. The laser was specified to have 230V for .01 m. The temperature program consists of 25°C start temp over a range ending at 100°C with a delta of 25°C. The results were analyzed using the Proteus 90 software and can be seen in the analysis section below.

3. Results and Discussion

3.1 Effect of h-BN on Mechanical Properties

3.1.1 Tensile Testing

Tensile elongation (Fig 3.1) was tested on all hBN resin formulations. The TPE formulation was found to have the highest strain to fracture at all hBN loading levels. At the low filler loadings, the TPE/hBN system showed a significantly higher strain to failure which would be expected due to the EPDM domains of the matrix providing an elastomeric response. Please note that the control TPE tensile specimens did not fracture in the crosshead test range of 10 inches so there is no value at the 0 wt. % loading level. All hBN resin systems showed an inverse relationship of strain to failure versus increasing hBN loading. The TPE/hBN systems showed filler input to have the most detrimental effect. This is explained by the fact that since the TPE is comprised of both EPDM and PP as the matrix materials, the input of hBN will displace the volume of the PP in the matrix. At some point there will not be enough of PP to hold together the EPDM domains and void growth will be the overwhelming dynamic in the system up on elongation. There was very little difference between the PP and PA-6

formulations at low levels of hBN input for strain to failure. At the highest hBN loadings, the difference in strain to failure between all three resins composite systems was negligible.

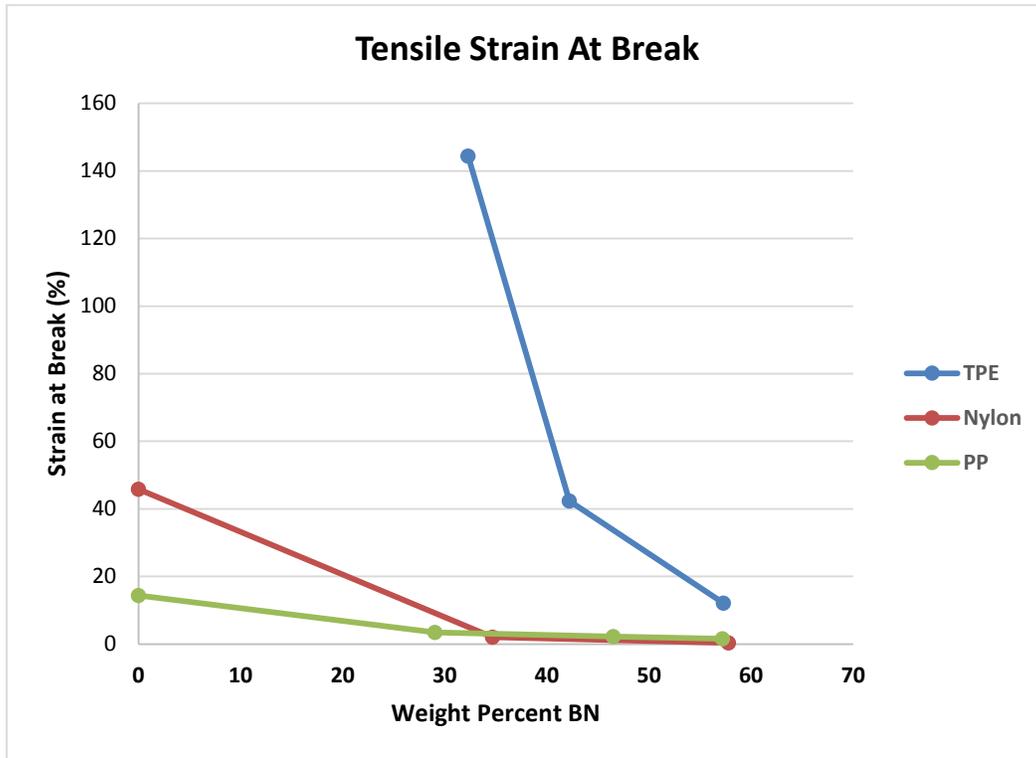


Figure 3-1. Graph of experimental measurements of tensile strain at break of hBN loaded specimens.

The effect of hBN loading on modulus (Fig 3.2) was greatest for the PA-6/hBN formulation and resulted in a dramatic increase in modulus for each loading level. This is to be expected due to the high level of stiffness which is characteristic of PA-6. The high inherent modulus can be attributed to the polarity of the polyamide chains and the resulting chain interaction which results in a pseudo-crosslinking mechanism. The PP/hBN system showed a slight increase tensile modulus with increasing hBN loading while TPE showed the filler had very

little effect on modulus. The highly flexible properties of the TPE could have skewed the results for the modulus measurement. In this case, perhaps the 5kN load cell of the tensile testing apparatus could not register an accurate modulus reading due to the relative ease of elongation. As was seen from the work of Cheewawuttipong et al. [18] and Zhou et al. [17] discussed during chapter 1, when a stiff ceramic filler is added to a soft polymer matrix, the matrix will gain certain aspects of the filler. In this case, the hBN filler is stiffer than the polymer matrix and will thus increase the overall stiffness of the composite.

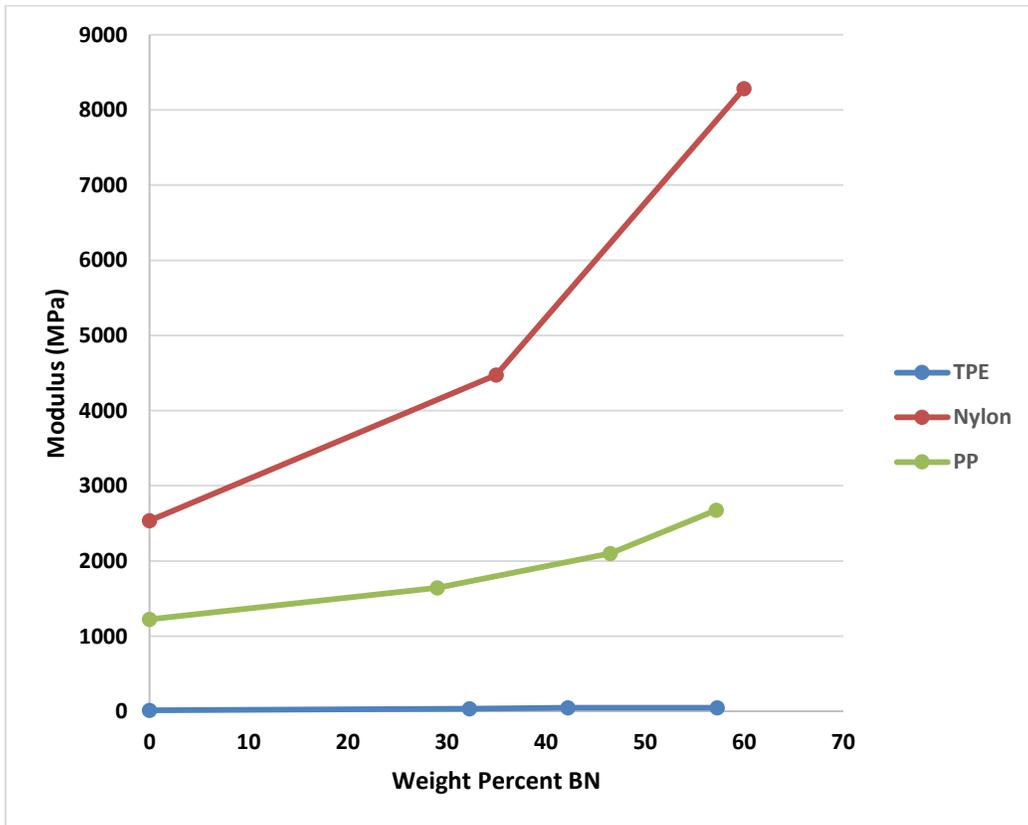


Figure 3-2. Graph of experimental measurements of tensile modulus of h-BN loaded specimens.

The experimental data from the tensile modulus testing can be compared the theoretical Halpin-Tsai model which predicts the tensile and longitudinal modulus of unidirectional fiber-reinforced composites. The classic Halpin-Tsai equation, seen below, can be modified for non-fiber fillers by altering a parameter that compensates for the particle aspect ratio and morphology [33].

$$E = E_M \frac{1 + \eta \xi V_f}{1 - \eta V_f} \quad (2)$$

$$\eta = \frac{\frac{E_f}{E_M} - 1}{\frac{E_f}{E_M} + \xi} \quad (3)$$

If we assume the agglomerate is broken down into a primary particle that most resembles a sphere with an aspect ratio of 1, we can then adjust the shape parameter (ξ). If we know the modulus of the matrix (E_m), the modulus of the filler ($E_f=3.65$ GPa) [8], and the volume fraction of each component of the composite we can then predict the modulus of the overall composite. It can be seen from Fig 3-3 that the experimental tensile modulus data follows very closely to predicted values given by the Halpin-Tsai model. There is some deviation at the high loading levels of the nylon/hBN system with the experimental modulus being larger than the predicted values.

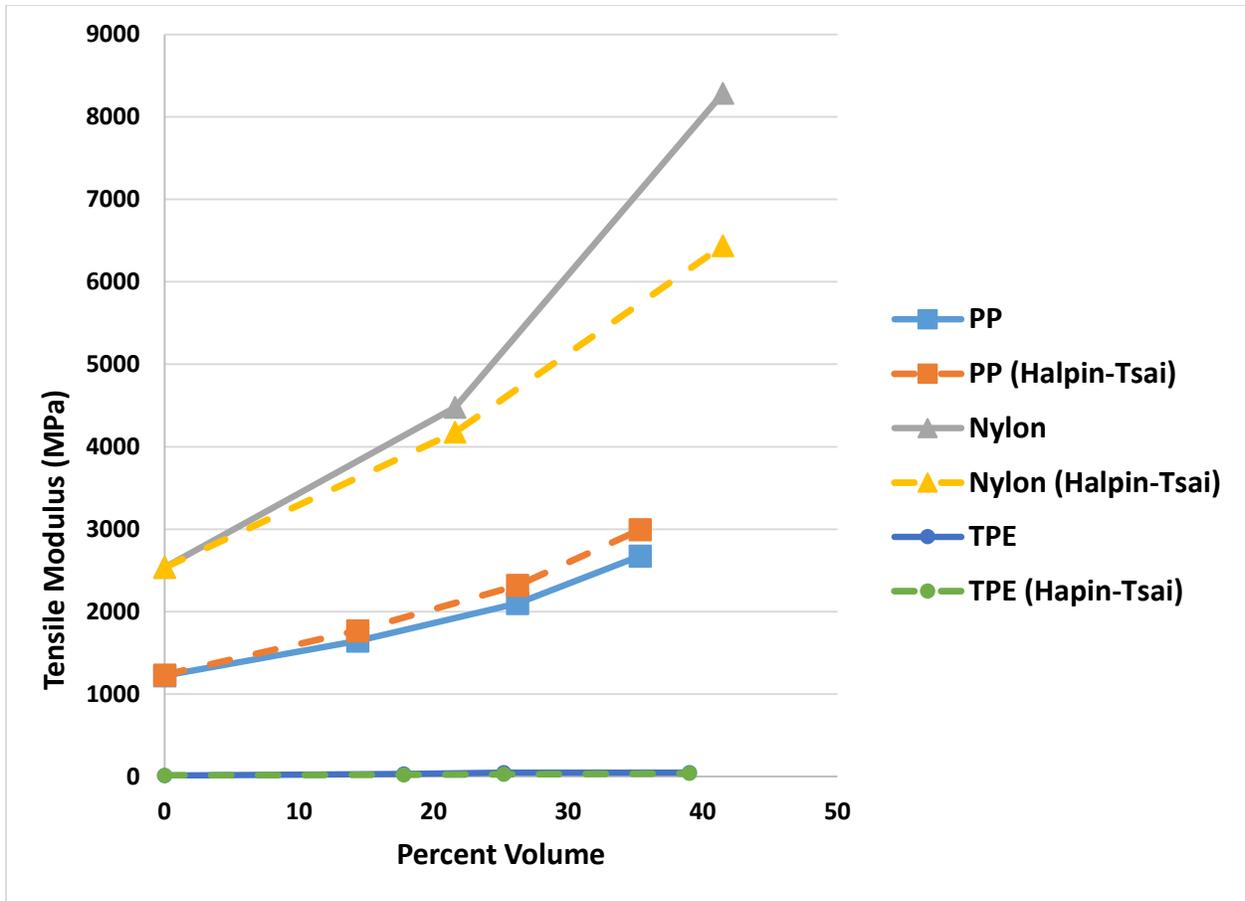


Figure 3-3. Tensile Modulus: Comparison of experimental data to Halpin-Tsai theoretical model.

The significant drop-off in mechanical strength, as seen in the peak load measurements of TPE with introduction of hBN particles can be attributed to a starved polymer matrix. Even before the introduction of hBN, the resin was soft and elastic due to the EPDM domains. By adding the hBN, we are essentially adding more defects and voids into the polymer system. This is compounded with 8 wt. % calcium carbonate already present in the commercial neat resin. At the higher loading levels, the matrix is displaced by hBN particles and the composite strength is sacrificed.

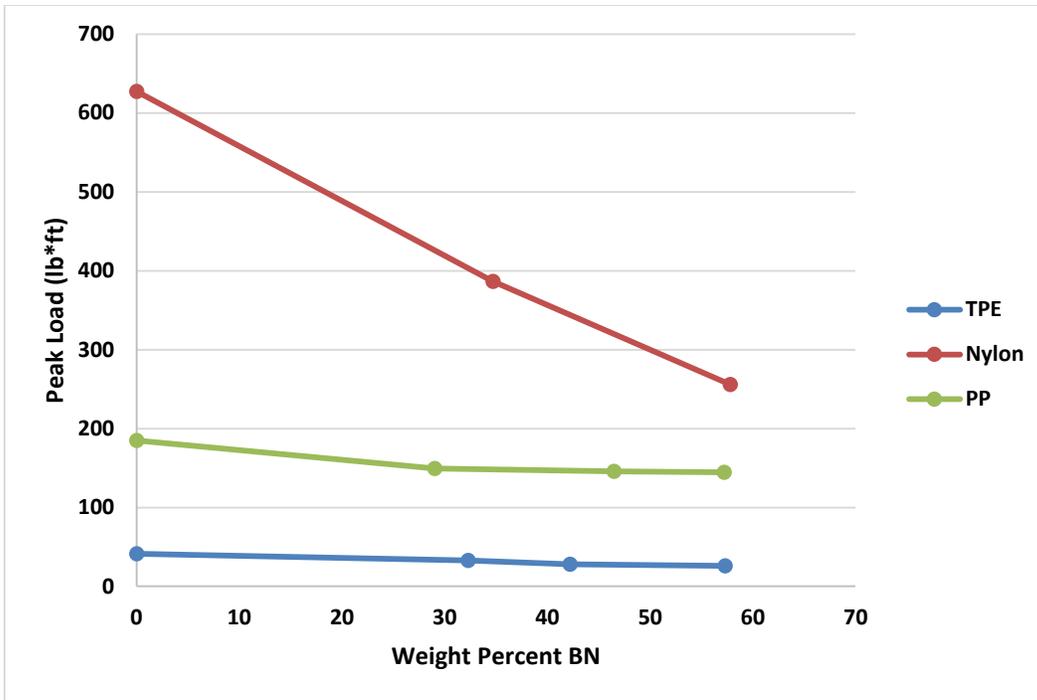


Figure 3-4. Graph of experimental measurements of tensile peak load of hBN loaded specimens.

3.1.2 Impact Testing

Notched impact testing using both the Charpy and Izod methods was conducted on both the PP and nylon-6 test specimens. TPE was excluded from this mechanical testing protocol as the test specimens were far too elastic and flexible to gain relevant data with this test method. In the resin systems that were tested, it was found that impact strength was decreased with increased loading of hBN cooling fillers. This can be attributed to a lack of mobility in the matrix deform caused by mechanical restraint of the rigid filler. Further, decreases in impact strength can also be caused by lack of stress transfer from the matrix to the filler. This weak stress transfer can result from poor interfacial interaction between the filler and the matrix as evidenced by an interphase region surrounding the particulate [34]. The PP/hBN produced

higher values for impact strength at all loading levels of hBN and compared to the nylon-6/hBN system. This is expected as polypropylene is more ductile and thus will have better shock absorbing capabilities in comparison to more rigid PA-6. This result of decreased impact strength was seen in both the Charpy and Izod test methods.

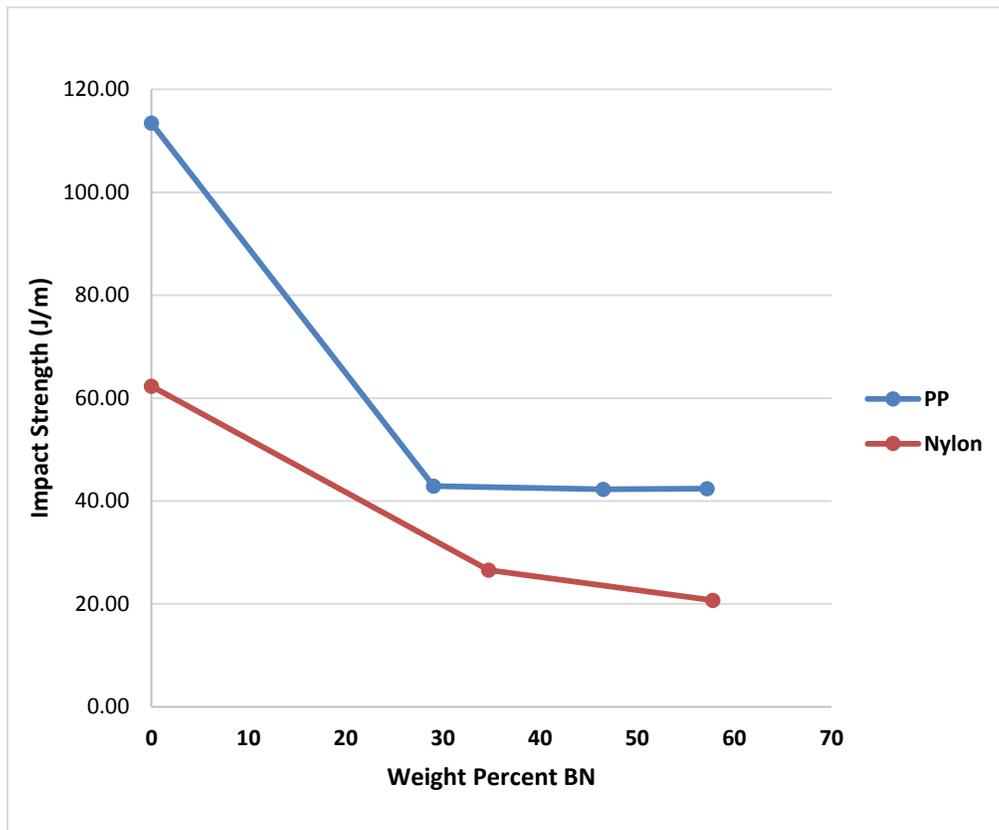


Figure 3-5. Graph of experimental measurements of notched Charpy impact strength of hBN loaded specimens.

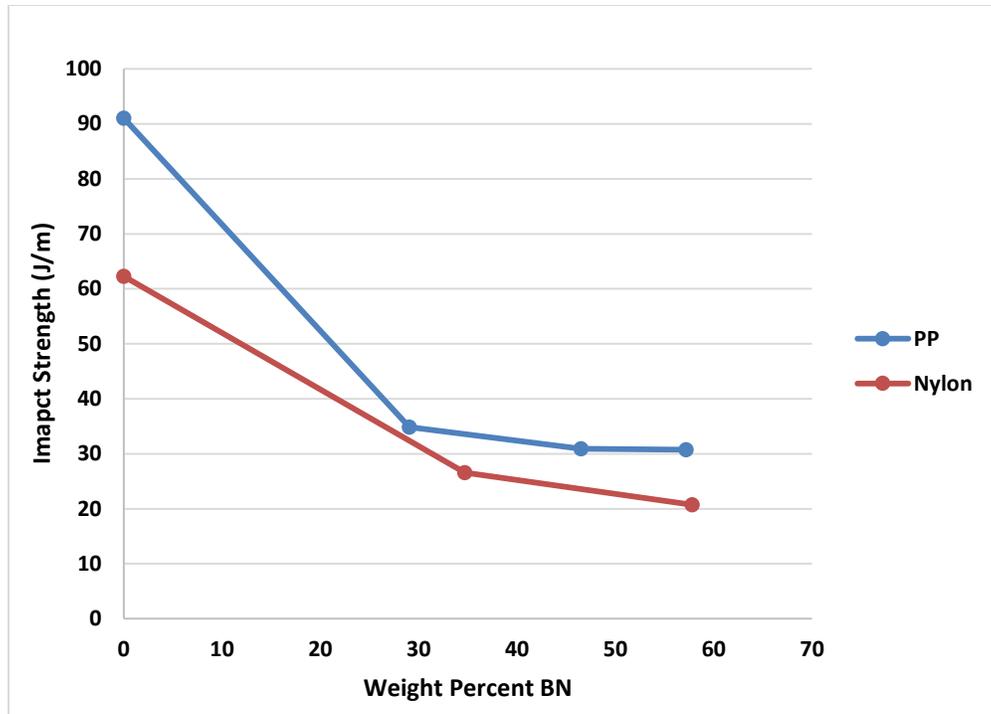


Figure 3-6. Graph of experimental measurements of notched Izod impact strength of hBN loaded specimens.

3.1.3 Three-Point Flex Testing

The results of the 3-point bend test showed PA-6/hBN specimens to have a higher ultimate tensile strength and flex modulus for the entire range of filler loadings. In regards to ultimate tensile strength, the PA-6 was negatively impacted by the addition of hBN fillers, whereas the PP appeared to be relatively unaffected. This can once again be explained by rigid filler decoupling the interaction between the polymer chains of the PA-6. This effect would be expected to be more significant for PA-6/hBN as it is more crystalline in comparison to more ductile PP matrix. The flex modulus results mirror that of the tensile modulus data with the PA-6/hBN formulations being more significantly improved by the input of the hBN filler.

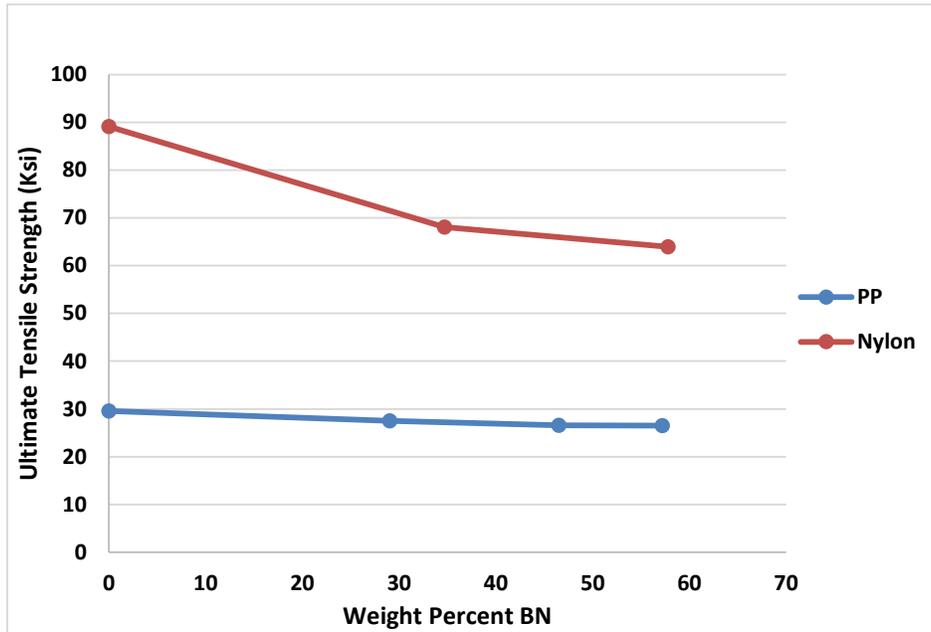


Figure 3-7. Graph of experimental measurements for ultimate tensile strength of h-BN loaded specimens.

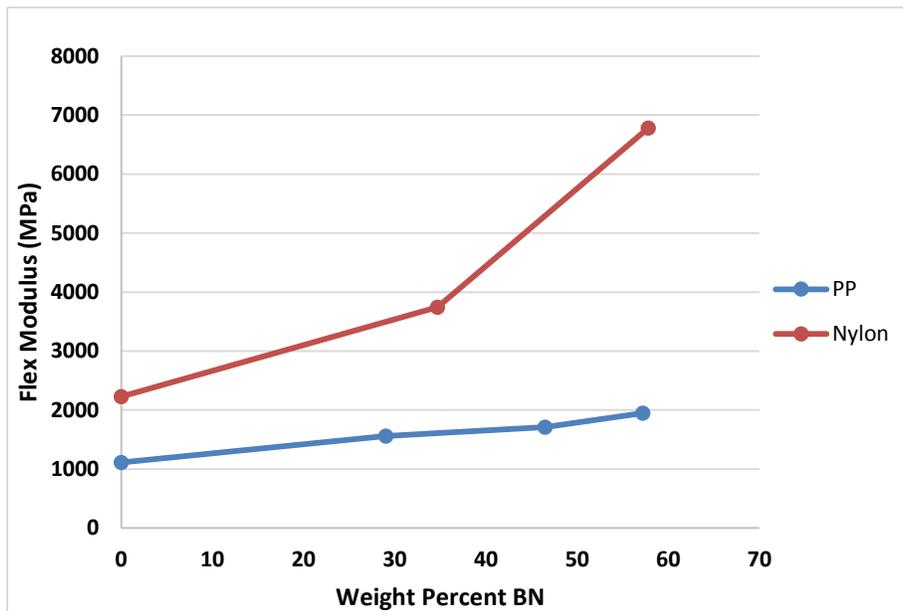


Figure3-8. Graph of experimental measurements for flex modulus of hBN specimens.

3.2 Effect of hBN on Thermal Conductivity

3.2.1 Thermal Conductivity measurement of hBN loaded PP specimens

Firstly, we can see that the trends in thermal conductivity hold regardless of the temperature in which they were tested. The PP/hBN system showed the smallest improvement in thermal conductivity compared to the other composite systems. Both the PA-6/hBN and TPE/hBN showed large gains in thermal conductivity resulting in approximately double the value for thermal conduction compared to the PP/hBN system at 2:1 W/m*K ratio, respectively. This is theorized to occur due to the higher viscosity of polypropylene matrix (compared to PA-6) which leads to less mobility of the hBN particles.

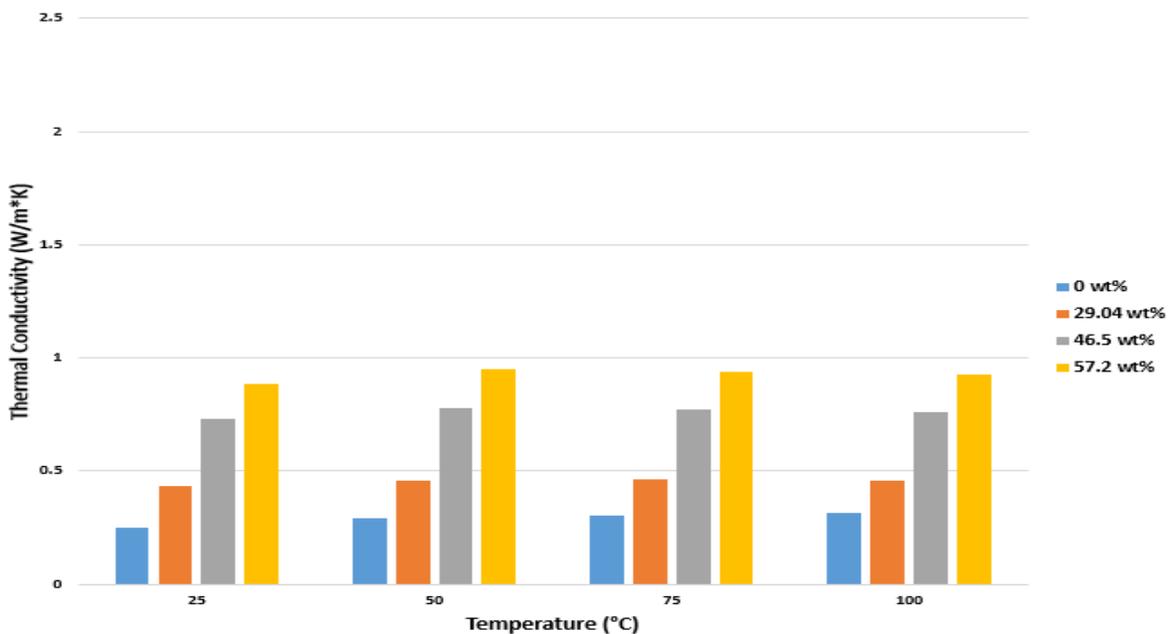


Figure 3-9. Graph of experimental thermal conductivity measurements for hBN in PP.

3.2.2 Thermal Conductivity measurement of hBN loaded PA-6 Specimens

It appears that there is a sizeable jump in the thermal conductivity with the introduction of hBN cooling fillers to the PA-6 matrix. The 35 wt. % loading of hBN in nylon-6 is comparable to 32 wt. % loading of hBN in TPE. It can be seen that the PA-6 system seems to form more robust thermal conductive networks at a lower loading level compared to TPE/hBN and PP/hBN. This could be attributed to the low viscosity of the PA-6 matrix. The hBN could have greater mobility to form conduction pathways leading to greater interaction between the primary particles. This finding can be supported through similar results seen in nylon with the work of Mosandenzadeh et al. [11] where two grades of PA-6 were used, each of different viscosity. Their results showed lower viscosity PA-6 matrix lead to higher thermal conductivity by 10%. The theory behind this result is that the lower viscosity matrix allows for greater mobility of boron nitride particles in the melt during the compounding stages. This lower viscosity also leads to a stronger interaction between polymer chains and the filler due the ability of the matrix to wet the particle which in turn reduces the void fraction in the sample. As previously discussed in chapter 1, these voids weaken the thermal conduction pathways by creating interfacial thermal barriers which disrupt the efficiency of the phonon transport and thus the heat conduction.

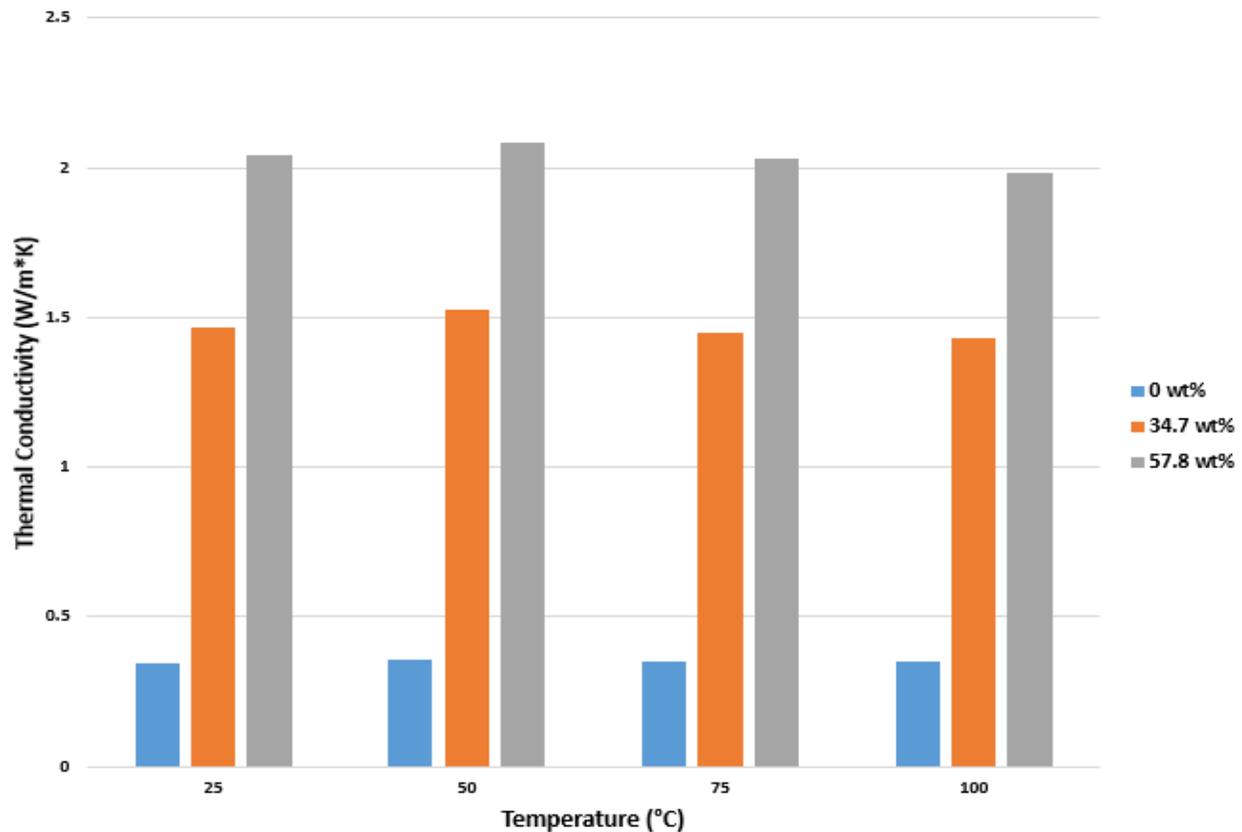


Figure 3-10. Graph of experimental thermal conductivity measurements for hBN in nylon-6.

3.2.3 Thermal Conductivity measurement of hBN loaded TPE Specimens

In the case of the TPE/hBN system, there is an apparent percolation threshold between the 42 and 53 wt. % loading level corresponding with a step change in the thermal conductivity data. It is hypothesized that the spike in thermal conductivity could be attributed to the formation of conductive networks around the EPDM domains in the TPE matrix. A higher concentration of hBN particles around the EPDM domains functions similar to a continuous fiber. The preferential concentration of hBN particles gives way to higher particle interaction and thus strongly conductive pathways. The work of Zhou et al. [16] showed similar results through the use of powder coating HDPE particles with hBN. The process of powder coating

produced higher intended hBN concentrations that in turn lead to stronger conduction network formation and eventual higher thermal conductivity measurements.

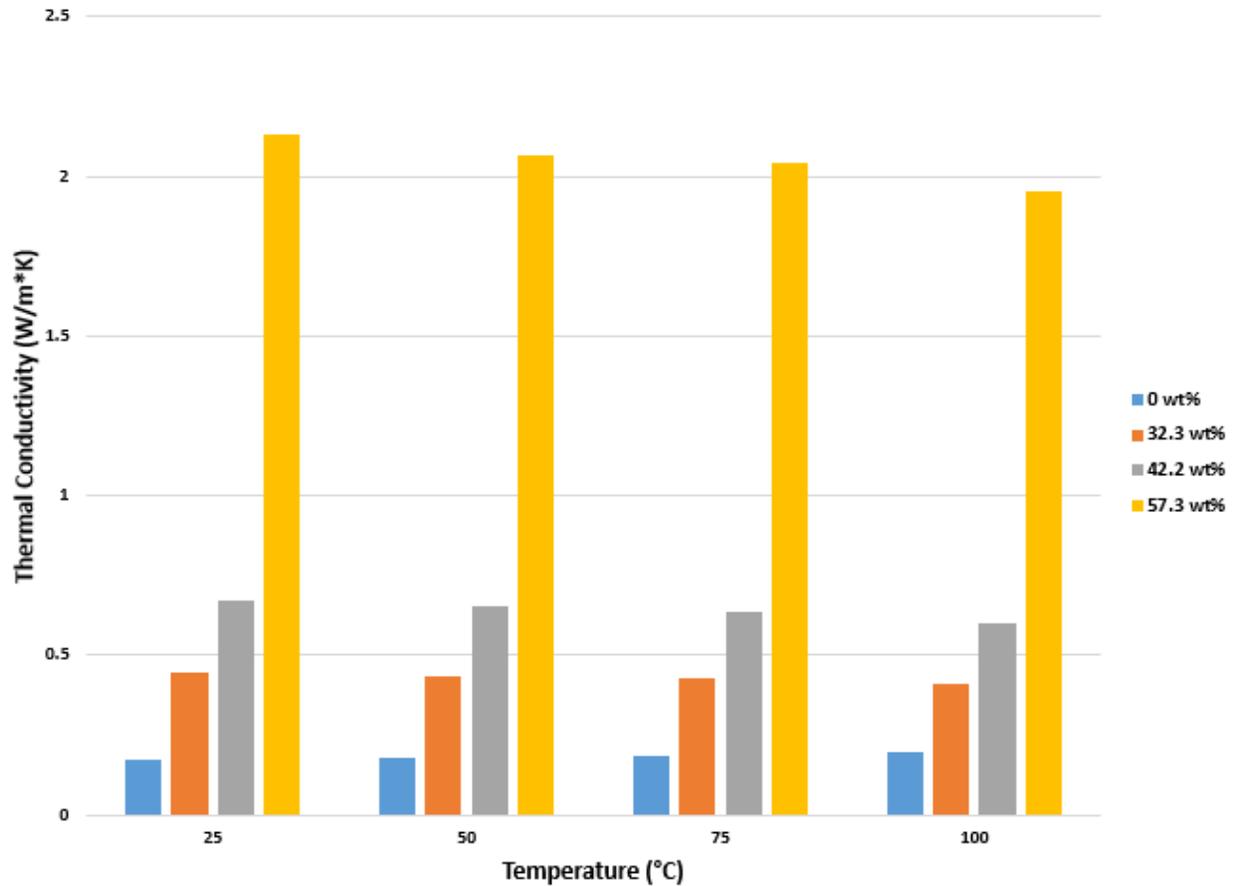


Figure 3-11. Graph of experimental thermal conductivity measurements for hBN in TPE.

A comparison of the different thermal conductivities across the different thermoplastic matrices can be seen in Fig 3-11. The graph depicts average through-plane thermal conductivity that was calculated from the measured values across the 4 test temperatures. It shows drastically different thermal conduction behavior between the three composite systems with increasing hBN loading. We can compare the experimental thermal conductivity data with theoretical values predicted with the Lewis-Nielson model [Fig 3-12].

$$K_c = K_m \left(\frac{1 + AB\phi}{1 - B\psi\phi} \right) \quad (4)$$

$$B = \frac{\lambda - 1}{\lambda + A} \quad \lambda = \frac{K_f}{K_m} \quad (4a) \text{ and } (4b)$$

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) \phi \quad (4c)$$

$$A = 2 \frac{L}{D} \quad (4d)$$

The Lewis-Nielsen model for predicting thermal conductivity was adapted from the Halpin-Tsai equation for elastic moduli of composite materials [35]. The equation uses (K_c) and (K_m) as the thermal conductivities of the overall composite and the matrix polymer, respectively. The parameter (A) is a function of aspect ratio which for this experiment we estimate to be 1 which is that of a sphere. We also estimate (ϕ_m), which is the maximum packing volume fraction of particles, to be .637 for a random close packing of spheres. And lastly, (λ) is a ratio of the thermal conductivity of the filler (K_f) to the thermal conductivity of the matrix (K_m). It can be seen that the theoretical predictions of the model drastically undershoot the experimental values for thermal conductivity (Fig 3-12). This could possibly be due to the assumption of the primary particle being spherical in morphology. However, if calculated under a platelet geometry the model overshoots the experimental values. Perhaps a median aspect ratio between spherical and platelet is needed. The PP/hBN system is the only formulation that somewhat follows the Lewis-Nielsen model theoretical predictions. The experimental data for the TPE/hBN system does produce an interesting contrast to the model. The EPDM domains clearly have an effect on the thermal conductivity of the composite. This further supports the

theory that the EPDM domains act as a barrier for the mobility of the particle filler which thus funnels the hBN into high concentrations in the PP matrix. This higher concentration of filler leads to increased particle interaction and an effective percolation network. More testing and analysis is needed to support this theory.

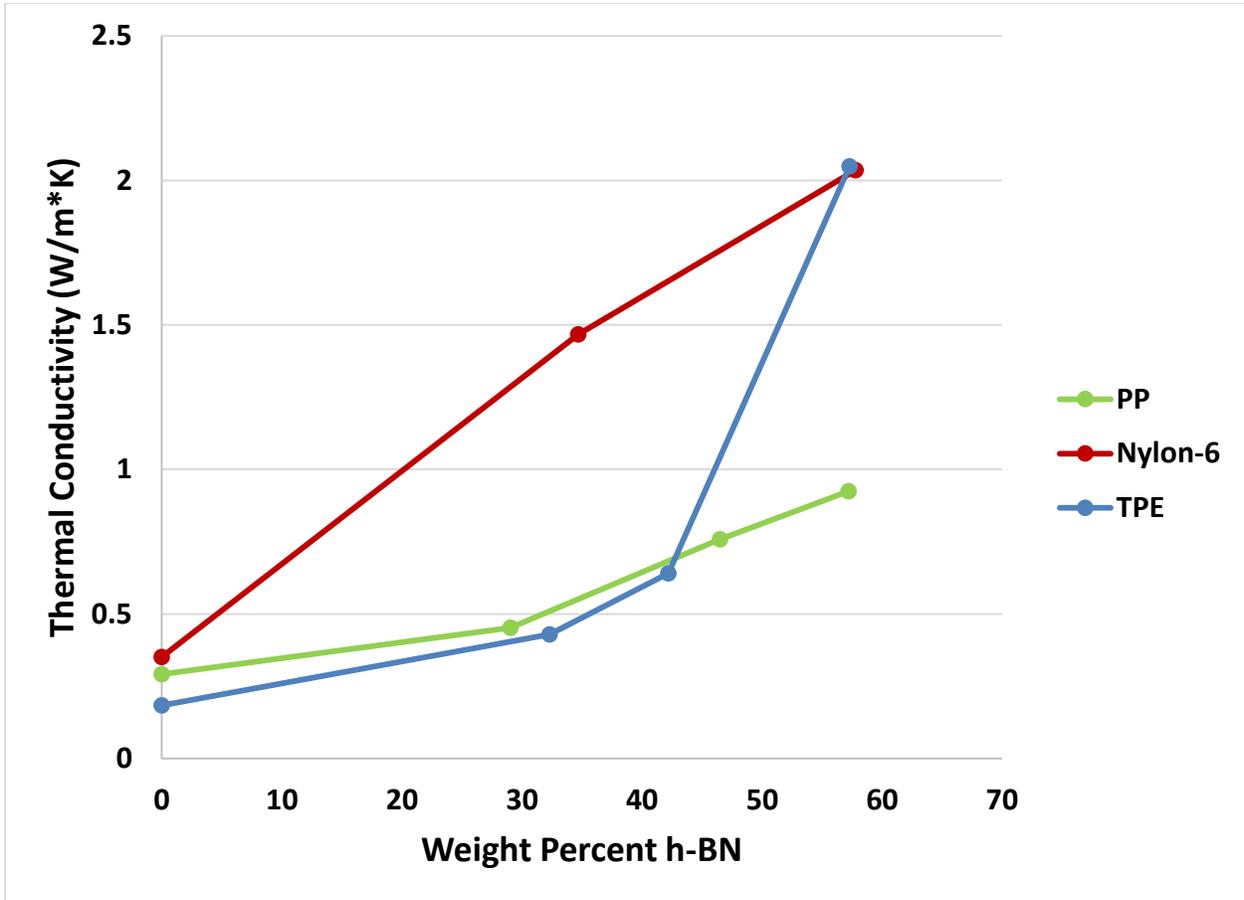


Figure 3-12. Graph of average thermal conductivity measurements for hBN loaded PP, Nylon-6, and TPE resin systems.

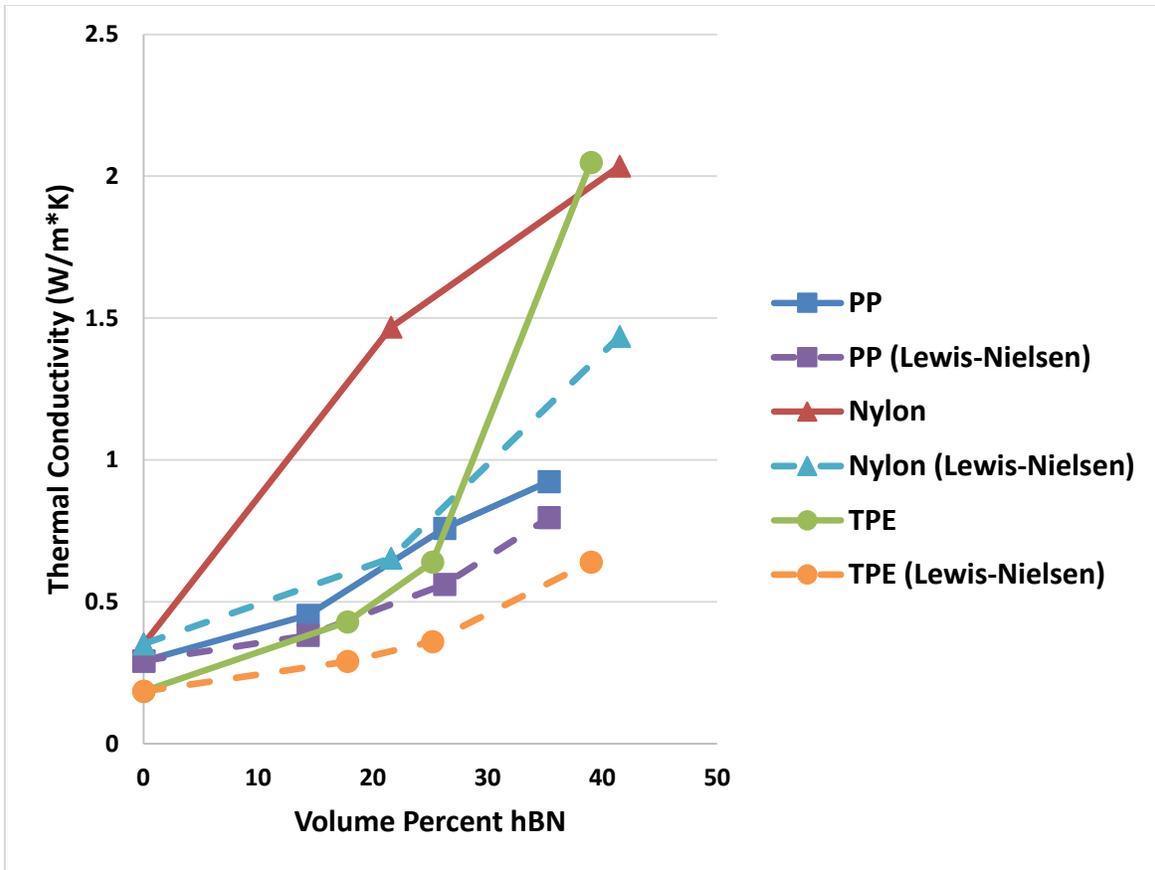


Figure 3-13. Thermal Conductivity: Comparison of experimental data to Lewis-Nielsen theoretical model.

4. Summary and Conclusions

Hexagonal boron nitride agglomerates, when introduced into a thermoplastic polymer matrix, produced significant improvement in thermal conductivity but also had a negative impact on some aspects of mechanical behavior. There were several specific results from the data that are worth noting. A small improvement in thermal conduction was made when hBN was added to polypropylene but over a 500% increase in thermal conduction was seen when added to both PA-6 and TPE resins. The TPE/hBN system illustrated the presence of a step

change in the thermal conductivity which can be theorized to be resultant of the formation of a percolation network. In all cases, the modulus (either tensile or flex) of the composite specimen was either increased or unaffected. The impact strength was always weakened with the loading of hBN. The addition of hBN on TPE had the largest adverse effect on mechanical properties. The TPE/hBN specimens began to crumble at the higher loading levels and the modulus was not improved. In general, as was the case for all polymer resins, the addition of hBN weakened the strength of the composite specimen with reductions in tensile strength, strain to break, peak load, and impact strength which correlates well with results seen in previous studies by Zhou et al [17] and Kemaloglu et al. [15].

Applications in thermal interface management require advanced materials that will not only enhance the performance of the composite part but also provide manufacturers with a cost effective process. The information discussed here clearly shows the relevance as well as the advantages for the use of hBN for emerging TIM technologies and products. It can be seen from the data presented in this study that a fine balance exists between maximizing thermal conductivity and maintaining mechanical strength. Loading hBN to a concentration past the percolation threshold produces incredible gains in thermal conductivity but significantly reduces the impact strength, tensile strength, and strain at break which are very important for real world applications such as heat sinks, electric motor housing, and base pads for Li ion batteries. Care must be taken in the formulation process. In the case of the TPE/hBN, there were sizeable gains in thermal conduction; however at the highest loading (57.3 wt. %) the structural integrity of the composite was lost. In applications that require TPE as the matrix material, a lower loading level of hBN, for example 45-50wt%, would produce adequate gains in

thermal conductivity and still allow for the part to withstand a legitimate impact force. The PP/hBN system gave a moderate response to all testing. The gains for thermal conductivity in this system were mediocre resulting in a roughly 200% increase with a final value at .9 W/m*K. The mechanical properties were not as largely affected in comparison to the other systems. Though there was some decline in mechanical strength, the maximum loading of hBN (57.2 wt. %) would be adequate. Given the results from the mechanical testing, PA-6 appears to be the most robust resin system for adding hexagonal boron nitride cooling fillers. It shows steady, somewhat linear improvements in thermal conductivity and yields minimal losses in mechanical properties. Obviously, specifications for any TIM application needs to be taken on a case by case basis but the information in this work can provide a general starting point for the formulation process.

5. Recommendations for Future Work

5.1 Surface Modification

The full potential of hBN use has yet to be realized. One possible route to increasing its effectiveness for Thermal interface management applications is through exploration of surface modification. The challenge, as discussed previously in Chapter 1, lies in the inherent inertness of the hBN compound. Silane coupling has been tried however this modification depends heavily on the concentration of hydroxyl groups on the surface of the inorganic and in the case of hBN, this functional group is scarce [36]. Modification of the surface of hBN to promote the silane coupling to boron oxide has been proposed but this impact is also

somewhat limited as the presence of the B_2O_3 is greatly influenced by the processing procedure [37]. More recent work done by Jin et al. [36] shows formation of an organized hexagonal boron nitride (OhBN) through a novel 2 step method what introduces 5 times more reactive amine groups to the surface of the hBN than conventional methods. This modification method was shown to produce better particle matrix interaction. In the future, a successful and robust method for surface modification could lead to a higher degree of interaction with the matrix material which could in turn enhance the mechanical properties of the overall composite as well as minimize the interfacial thermal barrier.

5.2 Modifying Particle Geometry

In addition to enhancing the mechanical strength of the hBN composites through surface modification of the particles, another avenue for improving mechanical strength would be altering the particle geometry. This would focus on preparation methods to increase the aspect ratio with the ultimate goal being to produce continuous hBN fibers. In regards to fibers, this would be the most ideal condition as the thermal conduction network would be maximized but also impart added mechanical strength if the fiber has decent tensile strength. However, the structural integrity of the fiber is of the highest importance because any break in the structure will lead to heat concentrations inside the composite which would have an adverse effect on the thermal conduction of the overall composite as well as hinder mechanical strength. The work of Lan et al. [38] has already shown incredible improvements in thermal conductivity of hexagonal boron nitride nanoribbons. Also the work of Mosanenzadeh et al. [11] has simulated a continuous network of hBN fiber through pressing a series of PPS disks with hBN centers then fusing the disks in tandem. This continuous fiber simulation produced a

dramatic improvement in thermal conductivity in comparison to composites of dispersed hBN particles. Hexagonal boron nitride fibers have been produced on a laboratory scale however there is no robust manufacturing method known at this point [11].

5.3 hBN Platelet Orientation through Compounding

Another route for the innovation of hBN use as a TIM is through exploring compounding methods that can enhance the percolation networks by orientation of the hBN primary particles in the through-plane direction. A recent work by Yoshihara et al. [39] investigated the effect of orienting liquid crystal chains of the matrix resin in relation to the hBN platelets. The group was able to conclude that thermal conductivity was at a maximum when the liquid crystals were arranged perpendicular to the hBN platelets. They found that the oriented molecular chains of the LC polymer matrix produced effective heat paths between particles thus boosting the thermal network of the composite. Another interesting route for future research could be through the use of chaotic mixing schemes. Chaotic mixing uses flow tracers to model the mixing phenomena in fluids. In chaotic mixing, the advection of the fluid can be modeled to produce exponential growth of fluid filaments [40]. Perhaps this sort of mixing modeling could be used to enhance the dispersion of hBN in the polymer melt and predict the structure of percolation network formation. Research in these areas could perhaps be the building blocks for controlling hBN platelet orientation in all composites and further innovate the field of thermal interface management.

References

1. Hsiao YN, Soo KL. *Thermal Conductivity of Boron Nitride-Filled Thermoplastics: Effect of Filler Characteristics and Composite Processing Conditions*. Polymer Composites (2005). DOI 10.1002/pc.20151.
2. Ertug B (2013). *Powder Preparation, Properties and Industrial Applications of Hexagonal Boron Nitride, Sintering Applications*. (Ed.), ISBN: 978-953-51-0974-7, InTech, DOI: 10.5772/53325.
3. Eichler J, Lesniak C. *Boron Nitride (BN) and BN composites for high-temperature applications*. Journal of the European Ceramic Society 28 (2008) 1105-1109.
4. Engler M, Lesniak C, Damasch R, Ruisinger B, Eichler J. *Hexagonal Boron Nitride (hBN)-Applications from Metallurgy to Cosmetics*. Cfi/Ber. DKG 84 (2007) No.12 49-53.
5. Lipp A, Schwetz KA, Hunold K. *Hexagonal Boron Nitride: Properties, Fabrication, and Applications*. Journal of the European Ceramic Society 5 (1989) 3-9.
6. Zhong J, Feng Y, Wang H, Hu D. *Fabrication and characterization of hexagonal boron nitride powder by a precursor conversion method*. Journal of Ceramic Processing Research. Vol. 14, No. 2, pp. 269-273 (2013).
7. Armin Kayser. *Advanced functional fillers for thermally conductive compounds: Key technology for cost reduction in electronic thermal management*. ESK Ceramics GmbH & Co KG, Germany. Compounding World Forum (2013).
8. Raman C, Yeske A. *Innovative Thermal Management Solutions with Thermally Conductive Plastics Containing Boron Nitride*. Copyright © 2013 Momentive Performance Materials Inc.
9. Bunde A, Dieterich W. *Percolation in Composites*. Journal of Electroceramics 5:2 (2000) 81-92.
10. Berman R. *Heat Conductivity of Non-Metallic Crystals*. Contemp. Phys. 14 (1973) 101.
11. Mosanenzadeh SG, Naguib HE. *Effect of filler arrangement and networking of hexagonal boron nitride on the conductivity of new thermal management polymeric composites*. Composites Part B 85 (2016) 24-30.
12. Ruth R, Donaldson KY, Hasselman D. *Thermal conductivity of boron carbide– boron nitride composites*. J. Am. Ceram. Soc. 75 (1992) 2887.

13. Pettersson S, Mahan GD. *Theory of the thermal boundary resistance between dissimilar lattices*. Phys. Rev. B 42 (1990) 7386.
14. Ishida H, Rimdusit S. *Very high thermal conductivity obtained by boron nitride-filled polybenzoxazine*. Thermochimica Acta 320 (1998) 177-186.
15. Kemaloglu S, Ozkoc G, Aytac A. *Properties of thermally conductive micro and nano size boron nitride reinforced silicon rubber composites*. Thermochimica Acta 499 (2010) 40-47.
16. Zhou W, An Q, Zhao H, Liu N. *Thermal conductivity of boron nitride reinforced polyethylene composites*. Material Research Bulletin 42 (2007) 1863-1873.
17. Zhou W, Zuo J, Zhang X, Zhou A. *Thermal, electrical, and mechanical properties of hexagonal boron nitride-reinforced epoxy composites*. Journal of Composite Materials 0(0) 1-10 (2013).
18. Cheewawuttipong W, Fuoka D, Tanoue S, Uematsu H, Lemoto Y. *Thermal and Mechanical Properties of Polypropylene/Boron Nitride Composites*. Energy Procedia 34 (2013) 808 – 817.
19. 3M™ Boron Nitride Cooling Filler Agglomerates Technical Data Sheet. Copyright 3M 2015.
20. Lyondell Basell SG802 Polypropylene Technical Data Sheet. SG802 PP. Copyright Lyondell Basell 2015.
21. A. Schulman NV-12 Polyamide-6 Technical Data Sheet. Copyright Lyondell Basell 2015.
22. ExxonMobil Santoprene™ 8221 TPE/TPV. Technical Data sheet. Copyright ExxonMobil 2015.
23. Hassan, Mohammad M., Yuanxin Zhoua, Hassan Mahfuz, Shaik Jeelani. *Effect of SiO₂ nanoparticle on thermal and tensile behavior of nylon-6*. Materials Science and Engineering A 429 (2006) 181–188.
24. Polymer Processing: Nylon-6. <http://www.polymerprocessing.com/polymers/PA6.html>. Retrieved on 1-16-2016.
25. Society of Plastics Engineering. History of Polymers and Plastics for teachers. <http://www.4spe.org/contentnrelated.aspx?ItemNumber=22532>. Retrieved on 1-16-2016.

26. Drobny, J. G., *Handbook of Thermoplastic Elastomers*. Elsevier, 2014 2nd Edition, Oxford UK. ISSN: 978-0-323-22136.
27. Thermo Electron Product Specification Manual. © 2006 Thermo Electron Corp
http://www.masterlabsrl.it/wp-content/uploads/2012/11/TSE24_MC.pdf. Retrieved on 1-16-2016.
28. Boy Product Page: BOY 22 A injection molding machine. <http://www.dr-boy.de/en/products/boy-22-a/>. Retrieved on 1-16-2016.
29. MTS Tensile Testing Product Page. <http://www.mts.com/en/products/application/materials-testing/plastics/tensile/index.htm>. Retrieved on 1-16-2016.
30. Tinius Olsen Product Page: Impact Systems.
<http://www.tiniusolsen.com/products/impact-systems/model-it503.html>. Retrieved on 1-16-2016.
31. Netzsch LFA 467 Technical Brochure. <https://www.netzsch-thermal-analysis.com/us/products-solutions/thermal-diffusivity-conductivity/lfa-467-hyperflash/>. Retrieved on 1-16-2016.
32. A&D Weighing Product Page. <https://www.andweighing.com.au/category/market-sector/laboratory-analytical-instruments#All>. Retrieved on 1-16-2016.
33. Kalaitzidou K, Fukushima H, Miyagawa H, Drzal LT. *Flexural and Tensile Moduli of Polypropylene Nanocomposites and Comparison of Experimental Data to Halpin-Tsai and Tandon-Weng Models*. Polymer Engineering and Science (2007) 1796-1803.
34. Sharma K, Maiti SN. *Studies on Polypropylene Composites filled with Talc Particles*. Journal of Materials Science 27 (1992) 4605-4613.
35. Pal R. *On the Lewis-Nielsen model for thermal/electrical Conductivity of composites*. Composites: Part A 39 (2008) 718-726.
36. Jin W, Zhang W. *Surface Functionalization of hexagonal Boron Nitride and its effect on the structure and performance of composites*. Applied Surface Science 270 (2013) 561-571.
37. Kochetov R, Andritsch T, Lafont U, Morshuis PHF, Picken SJ, Smit JJ. Preparation and dielectric properties of epoxy-BN and epoxy-AlN nanocomposites. Electrical Insulation Conference, Montreal, Canada (2009), pp. 397-400.
38. Lan JH, Wang JS, Gan CK, Chin SK. *Thermal transport in hexagonal boron nitride nanoribbons*. Phys Rev B 79 11 (2009) 115401.

39. Yoshihara S, Sakaguchi M. *Influence of Molecular Orientation Direction on the In-plane Thermal Conductivity of Polymer/Hexagonal Boron Nitride Composites*. J. Appl. Polym. Sci. (2014) DOI: 10.1002/APP.39768.
40. Ottino, J., *Mixing, Chaotic Advection, and Turbulence*. Annu. Rev. Fluid Mech. (1990) 22:207-53.

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