Fabrications and Characterizations of Boron Containing Polyimides for Radiation Shielding

Christopher Scott Pugh

College of William & Mary - Arts & Sciences

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Fabrication and Characterization of Boron Containing Polyimides for Radiation Shielding

A Thesis
Presented to
The Faculty of the Department of Chemistry
The College of William and Mary

In Partial Fulfillment
of the Requirements for the Degree of
Master of Arts

By
Christopher Scott Pugh
1999
Approval Sheet

This thesis is submitted in partial fulfillment of

the requirements for the degree of

Master of Arts

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Approved, July 1999

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Abstract

In the era of supersonic flight and space travel, the development of radiation shielding materials has become an active area of research. The development of high-performance polymers has provided a useful lightweight alternative to metals for structural applications. This study explores the use of boron loaded polymers for use as neutron shields in space and high-altitude aerospace applications. Two types of boron, amorphous boron powder and boron carbide whiskers, were loaded into two polyimides to study the thermal and mechanical effects on the polymer matrix. The first polyimide, PETI-5, is a thermoset developed by the NASA-Langley Research Center. The second polyimide is a thermoplastic developed by DuPont called K3B. Neutron shielding tests were performed showing that the addition of 15% amorphous boron to K3B absorbed over 90% of the incident neutrons. Dynamic Mechanical Analysis showed that the boron additives may actually increase the glass transition temperature of the pure polymers. Compression, tensile, and flexural testing also proved that boron can actually enhance the properties of the pure polymers studied. In general, the boron carbide whiskers loaded in PETI-5 showed the greatest promise of the materials in this study.
Chapter 1

Background

1. A Introduction

With the advent of space stations, long duration space flights, and high-altitude flight, new emphasis has been placed on durable and lightweight materials with radiation-shielding capabilities. High-performance polymers have been the focus of much research for this specific purpose. Increased exposure to solar (<1 GeV) and galactic (up to $10^{10}$ GeV) cosmic rays in high-altitude aerospace (~70,000 ft.) and space environments can provide potential health hazards to humans.\textsuperscript{1} Fortunately, interactions of high energy particles with light nuclei produce fewer secondary particles than comparable interactions with heavy nuclei. Hydrogen-containing polymers thus provide good protection against these high-energy particles. Interactions between hydrogen and the larger nuclei produce neutrons that can be reduced in energy by interaction with H atoms. These neutrons can interact with the human body to produce harmful radioactive products. Therefore, a material that can provide a high thermal neutron capture cross-section and produce stable, non-radioactive products is needed. Boron, has an isotope, $^{10}$B, with a natural abundance of 19.9%, a neutron capture cross-section of 3838 barns, and non-radioactive product nuclei, $^7$Li and $^4$He.\textsuperscript{2,3}
However, the prudent question involved in loading polymers with boron is the effect it has on the thermal and mechanical properties of the neat resin. Boron in two forms has been loaded into high-performance polyimides, amorphous boron powder and 300 micron boron carbide whiskers. Mechanical tests will show how these two forms of boron effect the properties of the polymer. The boron carbide whiskers are of particular interest because their size could allow for a type of micro-composite to be formed. These small fibers could add stability since any additive runs the risk of interrupting the primary bonding of the polymer, thus decreasing its mechanical properties. This is an important concern in high performance polymers. The goal of this paper is to analyze the effectiveness of boron powder and boron carbide whiskers as a neutron shield and the effects they have on the mechanical and thermal properties of high-performance polyimides.

1.B Radiation

The primary form of radiation encountered in space and high altitude airplane flights results from primary and secondary cosmic rays. The cosmic ray flux at the earth’s surface is modified by both the interplanetary plasma, which is dependent on the solar cycle, and the earth’s geomagnetic field. With both of these barriers in place, only the most energetic ions enter the earth’s atmosphere, which usually takes place near the poles. The two primary forms of cosmic rays are solar cosmic rays and galactic cosmic rays (GCR). Solar cosmic rays result from solar flares and typically consist of protons
and alpha particles with relative low energies of less than 1 GeV. Since they are lightweight, and possess low energies, the major concern in dealing with harmful radiation effects are galactic cosmic rays.

Galactic cosmic rays are high-energy particles (up to $10^{10}$ GeV) that originate in outer space and primarily consist of protons and alpha particles (90%). More importantly, the other 10% consists of higher atomic number nuclei ranging from $Z = 5$ to 83. Concern for this small population of particles exists since ionization is proportional to $Z^2/v^2$, and velocity ($v$) is assumed constant. Particles with $Z > 60$ are rare since carbon, nitrogen, and oxygen comprise most of the high $Z$ and high-energy (HZE) particles. However, there is a reasonable abundance of particles with atomic numbers near iron ($Z = 26$) which interact with a large amount of ionization.

These HZE particles result from both primary and secondary galactic cosmic rays. Primary GCR are a major concern in outer space where there are few molecules for interaction before they reach objects such as space vehicles. However, for high-altitude flight in the earth's atmosphere, secondary GCR are more problematic due to high ionization from the high $Z$ particles. These large particles possess a high probability of interactions with particles in the atmosphere creating a large amount of smaller product particles. This is called a cascade reaction and can result in the formation of billions of particles per square mile falling from the upper atmosphere to the earth's surface.

Cascade reactions can also result from a primary GCR interacting with spacecraft or the fuselage of a plane at 70,000 ft. The creation of a large number of protons and neutrons is the result of the cascade reaction. Charged particles such as the proton can be stopped through Coulombic interactions with matter while uncharged particles like the
neutron can only be stopped by elastic collisions with atomic nuclei. Neutrons have a long mean free path and can travel great distances before they lose enough energy to stop. Neutrons can therefore pose potential risks to electronic equipment and humans due to their high mean free paths.

The overall result of this radiation at high altitudes is a concern in high-altitude airplane and space environments. At high-altitudes, radiation becomes a problem for persons spending large amounts of time in this environment such as the crew. These exposures are especially increased when traveling close to the geomagnetic poles since most radiation enters through these points in the atmosphere. Figure 1.A shows how flight crews can be affected by high-altitude flight compared to lower-altitude domestic flights. With a maximum possible increase of 25 mSv/yr in radiation exposure, crews in
Exposure condition | Exposure, mSv
--- | ---
**Occupational:** |  
Fuel cycle workers | 6
All workers | 2
Astronaut | 4

**Air crew (500 hr):**
Mach 0.85 | ≈7
Mach 2.4 | ≈10
Mach 3.2 | ≈13
Mach 5.0 | ≈15

**Passengers (Mach 2.4):**
1 round trip/yr | ≈0.16
1 round trip/wk | ≈8

| Exposure condition | Annual | Exceptional<sup>a</sup> | (February 1956) |
--- | --- | --- | ---
Occupational: | 6 | 1000 |
Fuel cycle workers | 2 |
All workers | 4 |
Astronaut | |

---

<sup>a</sup>No attempt made to evade exposure.
<sup>b</sup>With 5-yr career assumed.

Figure 1.B. Occupational and high latitude estimates for radiation exposure.<sup>10</sup>

A high-altitude environment could see higher radiation levels than those working in the nuclear fuel industry. The Sievert (Sv) is the SI unit for dose equivalent radiation where 1 Sv = 1000 mSv. One Sv is the amount of radiation which deposits 1 Joule per kg of absorbing material multiplied by a factor to account for the level of ionization. HZE particles have high (>20) values for the factor. Figure 1.B shows a predicted Occupational Exposure Estimate for a high-altitude crew and passengers compared to other occupations. This table shows that an air crew would experience a marked increase in radiation exposure, especially in exceptional years such as 1956 in which an exceptional solar flare occurred. Furthermore, frequent flyers would also be at risk while astronauts can potentially be exposed to high radiation levels as well. These figures show that radiation is a concern especially for supersonic flight.
1C Neutron Capture Theory

As we have seen, neutrons are a product of cosmic ray interactions with any object. These interactions produce fast neutrons which can be slowed down by both elastic and inelastic collisions with nuclei. These slower, or thermal, neutrons can present a hazard to electronic equipment or humans because they have higher capture cross sections than fast neutrons. Nuclei in a shielding material that can absorb or capture these thermalized neutrons are needed. An isotope with three of the following properties can provide the solution: high isotopic abundance, large capture cross section, and stable, non-radioactive products. It will be shown in this section how $^{10}\text{B}$ can fulfill this role.

First, a nucleus with a high isotopic abundance is important so there is a high density of capturing nuclei. For example, the attractive feature of $^{10}\text{B}$ is its 19.9% abundance in natural boron. Therefore, only a small amount of boron needs to be added for a large amount of shielding.

Next, large thermal neutron capture cross sections are important properties for potential capturing nuclei. Neutrons, like all other particles, have de Broglie wavelengths according to the wave-particle duality theory. Thermalized neutrons have a relatively large de Broglie wavelength due to their low velocities. The capture cross section is then estimated by the following equation:

$$\sigma = \pi(R + \lambda/2\pi)^2$$

where $\pi R^2$ is equal to the geometric cross section of the nucleus and $\lambda$ is the neutron wavelength. The geometric cross section of a typical nucleus is about $10^{-24}$ cm$^2$. Since
the de Broglie wavelength decreases as neutron energy increases, the cross section approaches $\pi R^2$ with increasing neutron energy. Slow neutrons therefore have a large $\sigma$. Many nuclei have high resonance capture regions near the thermal region for neutrons. One such nucleus is $^{10}$B which has a capture cross section of 3838 barns (1 barn = $10^{-24}$ cm$^2$). This high resonance cross section makes $^{10}$B exceptionally good at capturing thermal neutrons.

Finally, the third concern for neutron capturing nuclei is the formation of non-radioactive products. This helps prevent the buildup of excess radiation within the shielding material that can produce harmful effects to equipment and/or humans. One such nucleus is $^{10}$B which forms a $^7$Li and $^4$He particle upon reaction with a neutron. This mechanism is shown in Figure 1.C. This property of $^{10}$B is important because many potential neutron capturing nuclei can produce radioactive products. One example of this is $^6$Li which produces $^4$He and radioactive $^3$H in its neutron absorbing reaction. Tritium is certainly not a desired product.

Therefore, a capturing nucleus with a high isotopic abundance, large capturing cross section, and one that produces non-radioactive products is the goal. Fortunately $^{10}$B possesses all of these qualities which makes it an exceptional neutron capturing nucleus.

$^{10}$B Neutron Capturing Mechanism

$^{10}$B + $^1$n $\Rightarrow$ $^{11}$B $\Rightarrow$ $^7$Li + $^4$He + 2.4 MeV
1.D Boron Carbide Whiskers/Whisker Technology

Since boron provides a remarkable increase in the neutron shielding ability of polymers, its inclusion is extremely beneficial in high-altitude and space environments. However, the inclusion of any additive can potentially decrease the mechanical and thermal properties of the polymer resin. Therefore, an additive that will either enhance or not significantly decrease the properties of the pure polymer is needed. Boron carbide whiskers (B₄C) can provide an alternative to normal amorphous or submicron boron powder. Boron carbide whiskers typically are 300 microns in length and 5-6 microns in diameter, thus giving an aspect ratio of 50. Since there are four boron molecules per carbon, the percent boron content is 77-78 per molecule. Since the normal abundance of \(^{10}\text{B}\) is 19%, the amount of \(^{10}\text{B}\) in boron carbide is around 16%. In addition, boron carbide whiskers have a high melting point of 2350 °C.

The reason for the possible increase in mechanical properties of a polymer containing boron carbide vs. amorphous boron powder can be attributed to the size of the whisker. In general, a smaller fiber such as a whisker will have better properties than a powder because it has a smaller surface area that makes it much easier to wet. Furthermore, a smaller fiber has advantages over a larger fiber due to increased crystalline perfection. Therefore, a whisker with an aspect ratio of 30-50 is sufficient to achieve high crystalline perfection while being large enough to ameliorate the wetting problem.\(^{13}\)
1.E Polymers for Radiation Shielding

The development of high-performance engineering polymers has provided a new alternative for radiation shielding. Metals have typically been used in the past to provide protection for humans and electronics against the deleterious effects of cosmic rays in high-altitude and space environments. However, metals have proved to be too heavy for the new era of supersonic transports since large fuel and passenger capacities are needed. Polymers have provided a lightweight solution to the problem without sacrificing mechanical strength. More importantly, polymers have provided a useful alternative in radiation shielding for reasons which will be explained in the following section.

Polymers are molecules mainly composed of light elements, especially carbon and hydrogen. The high content of hydrogen in many polymers helps to improve radiation shielding for two reasons. First, studies have shown that light nuclei have the
propensity to fragment incident ions into smaller fragments. Specifically, hydrogen has a large nuclear cross-section due to its large electron density and a small mean excitation energy. The radiation shielding capability of liquid hydrogen versus metals can be seen in Figure 1.D. Although liquid hydrogen is not a practical shield, it illustrates the remarkable ability of hydrogen as a shield for cosmic radiation.¹⁵

The second advantage of using hydrogen-containing materials for shielding is their ability to thermalize neutrons. Small particles such as protons, neutrons, and electrons are produced when larger HZE particles strike any shielding material. Unlike protons and electrons which can be stopped by Coulombic interactions, neutrons have to be stopped through elastic and inelastic collisions. Neutrons therefore have a longer mean free path and can potentially cause problems. Fortunately, hydrogen is very effective in undergoing elastic collisions with neutrons and can effectively thermalize the neutrons. Boron can then easily be included into the polymer matrix to capture the thermal neutrons. Recent studies have shown that boron carbide-loaded polymers can absorb at least 90% of the thermalized neutrons.¹⁶ In conclusion, hydrogen-containing materials clearly outperform metals in shielding radiation since light nuclei possess a higher nuclear cross-section and have the ability to effectively thermalize neutrons.
Polyimides

Polyimides were first developed in the 1950s and have been the subject of much research due to their high thermal stability, mechanical stability, adhesive properties, and ease of fabrication. Since polyimides are condensation polymers, classical synthesis is performed using a tetracarboxylic acid dianhydride and a diamine in polar aprotic solvents. This produces a polyamic acid which is then dehydrated to the final product. Kapton film, marketed by DuPont in the 1960s, is probably the most recognized polymide. Much research in the area of polyimides has been pursued by companies such as DuPont and Mitsubishi as well as government agencies such as NASA.

PETI-5

PETI-5 is a thermosetting polyimide developed by the NASA-Langley Research Center and stands for Phenyl Ethynyl Terminated Imide. The synthesis of PETI-5 can be seen in Figure 1.E. A slurry of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4-phenylethynylphthalic acid (PEPA) is added to a solution of 3,4'-oxydianiline (3,4'-ODA) and 1,3-bis(3-aminophenoxy)benzene (APB) in N-methylpyrrolidinone (NMP) at 23°C under nitrogen. A 30/30% w/w solution is obtained and stored under nitrogen at -40°C. A mixture of toluene and NMP is added to the solution and refluxed. The toluene is removed and the slurry is poured into water to obtain the yellow PETI powder. The powder is then washed with warm methanol and vacuum dried at 225°C to obtain the product. The PETI-5 used in this study had a molecular weight of 5,000 g/mol. PETI-5 is an amorphous polymer with a $T_g$ of 270°C and a thermal cure of 371°C for 1 hr.
Figure 1.E. Synthesis of PETI.\textsuperscript{19}

Figure 1.F. Proposed cross-linking mechanism for PETI-5.\textsuperscript{20}
cross-linking ability of the phenyl-ethynyl endcaps enhances both the mechanical and thermal strength of the polyimide. Figure 1.F shows the mechanism for cross-linking via the phenyl-ethynyl endcaps.\textsuperscript{21} This cross-linking ability of PETI-5 accounts for the high mechanical strength and \( T_g \).

\textit{K3B}

K3B is a polyimide thermoplastic developed by DuPont. Since K3B is proprietary, its exact chemical structure is not known. However, some information obtained from DuPont, shows that K3B has a \( T_g \) of 237°C and a density of 1.336 g/cm\(^3\).

\textit{1.G Mechanical Testing}

Three types of mechanical testing were performed on the PETI-5 and K3B specimens. These include compression, tensile, and flexural testing. All three of these tests are useful for determining the effects of adding different types of boron. Information from each of these tests can provide knowledge of a material's strength, stiffness, and toughness. Figure 1.G shows typical information obtained from these tests.

First, three types of stresses can be obtained from the stress-strain plot. The ultimate strength is the maximum stress obtained during the course of the test where there is no increase in stress with a given increase in strain. Next, the fracture stress is the stress value that corresponds to the breaking of the material. Finally, the yield stress is the point where the curve begins to deviate from linearity. From the beginning of the test
to the yield point, elastic deformation occurs. In other words, an applied load can be taken off the material and it would return to its original dimensions. However, after the yield point is reached, plastic deformation occurs and the material is permanently deformed.

Second, the modulus, or stiffness, of the material can be obtained from the plot of a stress-strain curve. In the initial linear section of the plot up to the yield strength, the slope of the line can be computed. This slope is equal to the stress divided by the strain \( E = \sigma / \varepsilon \). The quantity \( E \) is equal to the modulus of the material where the higher the modulus, the stiffer the material. Therefore, a steep initial slope indicates a stiff material.

Finally, the third piece of information gathered from the mechanical tests is the toughness of the material. Tough materials are characterized by large areas under the
Brittle materials

Tough materials

with yield point

without yield point

Figure 1.H. Material toughness in stress-strain curves.22

stress-strain curve. An illustration of this can be seen in Figure 1.H where the stress (σ) is plotted on the y-axis and the strain (ε) is on the x-axis. Tough materials are resistant to breakage and therefore elongate a great deal before fracture. Conversely, brittle materials can be classified as having their yield, ultimate, and fracture stress at the same point. No plastic deformation occurs due to the material's inability to stretch. In conclusion, a favorable material would be one that can handle large amounts of stress, maintain a reasonable stiffness while exhibiting tough behavior.
Dynamic mechanical analysis (DMA) is a form of relaxation spectroscopy where the response of a material is measured to a sinusoidal stress over a wide range of temperatures. This technique is useful for acquiring information on changes in modulus, damping characteristics, and structural transitions of viscoelastic materials. The characterization of a material by DMA is accomplished by first applying a sinusoidal stress to a material. If the material is treated as a harmonic oscillator, elastic materials convert mechanical work into recoverable potential energy. With a solid, no heat is lost in the energy conversion and damping is not experienced. However, liquids exhibit high damping behavior since they lose heat due to their inability to store energy. Viscoelastic materials such as polymers exhibit both damping and elastic behavior.

Dynamic mechanical analysis of viscoelastic materials gives three main pieces of information. The storage modulus, loss modulus, and tan delta are the result of the DMA experiment which can be seen in a typical plot in Figure 1.I. The storage modulus \( E' \) represents the applied sinusoidal stress. The onset point of the curve defines a temperature at which mechanical strength decreases. Two tangent lines drawn at the onset point marks the glass transition temperature, or \( T_g \), of the material.

The loss modulus \( E'' \) is the strain of the material resulting from the applied sinusoidal stress. This strain has the same frequency as the applied stress but is shifted out-of-phase by some angle \( \delta \). An example of this phenomenon can be seen in Figure 1.J. The following equation of the complex modulus \( E^* \) describes the relation between...
the storage and loss moduli:

\[ E^*(\omega) = E'(\omega) + iE''(\omega) \]

The quantity \( \omega \) is the angular momentum. Loss modulus is often called the imaginary part of the complex modulus and measures the amount of dissipated energy. The peak of the loss modulus curve therefore marks the height of polymer mobility.

Finally, the third useful piece of information from the DMA experiment is the tan delta curve. The tan delta gives information on the damping characteristics of the material. It is found by the relation:

\[ \tan \delta = \frac{E''(\omega)}{E'(\omega)} \]
The tan delta is historically significant since it was the first quantified DMA property. In conclusion, DMA is a sensitive technique for measuring $T_g$ and corresponding changes in viscoelastic behavior of materials.

Figure 1.J. Difference in stress and strain under an oscillatory load.24
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8. *Ibid*, 64.


11. Ehmann, 487.

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Chapter 2
Experimental

2. A Sample Molding

Both polyimides require high heat to cure the resin powder into the black, hard, heat-resistant material used for all of the subsequent studies. Although the initial powder and final cured product of the two materials appear similar, they require different molding techniques. The cross-linking nature of the PETI-5 thermoset compared to the thermoplastic K3B accounts for this difference. Samples were molded to give five different sets of specimens for PETI-5 and K3B: Pure (control), 10% boron carbide whiskers, 20% boron carbide whiskers, 10% amorphous boron, and 20% amorphous boron. The samples were molded in a 3 x 6 in. steel mold for the tensile and flexural tests, and a 3.5 x 0.75 in. steel mold for the compression samples. The two following sections gives the preparation and cure cycle for PETI-5 and K3B respectively.

PETI-5

• Dry the resin powder and boron powder in an oven at least overnight at 120 °C.
• Mix the proper amount (10 or 20% by weight) of amorphous boron powder or boron carbide whiskers.
• Select the proper mold; clean off the mold with a razor blade; use fine grit sandpaper to lightly sand the mold.
• Apply Zyvax release agent to the mold and dry in an oven or with a heat gun.
• Cut the proper size Kapton film; coat the Kapton with Zyvax.
• In the mold, place the Kapton on the bottom and on top of the sample powder.
• Add the powder between the Kapton and attach the thermocouple to the mold.
• Heat the sample to 350°C, apply 200 psi, then continue heating to 371°C.
• Hold the temperature at 371°C with 200 psi for 1 hr.
• Cool the sample to around 100°C, release the pressure, and take out of mold.
The resulting cured polymer can then be machined for future testing.

**K3B**

The procedure for molding K3B involves a slightly more involved process since air voids can easily be introduced during the molding process. K3B requires a porous Kapton film coupled with a Teflon fabric to allow air present in the powder to be expelled during molding. Since K3B is a thermoplastic, it requires less heat to melt the powder, does not require an hour hold time to allow for cross-linking, and only requires light pressure. Since K3B is a less viscous material than PETI-5 at high temperatures, aluminum 'stops' should be used to stop the press platen from putting too much pressure on the mold since too much pressure forces the liquid out of the mold. Finally, the K3B sample must not be allowed to cool as long as PETI-5 since sample cracking can occur from the difference in coefficient of thermal expansion of the polymer and the steel mold. The exact molding procedure is as follows:

• Dry the K3B powder at least overnight in an oven set at 120°C.
• Mix the proper amount (10 or 20% by weight) of amorphous boron powder or boron carbide whiskers.
• Select the proper mold; clean off the mold with a razor blade; use fine grit sandpaper and lightly sand the mold.
• Apply the Zyvax release agent to the mold and dry in an oven or with a heat gun.
• Cut the proper size porous Kapton film and Teflon fabric; coat the Kapton with Zyvax.
• In the mold, apply the Teflon fabric, Kapton, sample powder, Kapton, and Teflon fabric in that order.
• When adding the powder, add 1/3 of the material and pack down with the top of the mold. Continue packing after 2/3 and once all the material is added. Attach the thermocouple. Add the metal stops with Kapton tape to the sides of the top of the mold.
• Heat the mold to 332°C with light kissing pressure. The sample becomes soft at 280-300°C, so if the plunger (top of the mold) drops, add pressure so it will not rise again.
• Hold at 332°C for 5-10 minutes and then cool the sample.
• Let sample cool until 170°C, release the pressure, and take the mold out of the press hot to prevent sample cracking.
The resulting sample can then be machined for future testing.

2.B Neutron Shielding Tests

The study of the neutron shielding capability of 15% amorphous boron + K3B was studied at Virginia State University. The neutron source used for the study was a \(^{239}\)Pu and \(^{9}\)Be source with an activity of three Curies. The plutonium is an alpha emitter and forms neutrons in its reaction with \(^{9}\)Be. The half-life for the source is 24,000 years.\(^1\)
The samples were prepared from two pieces of 0.75 x 0.75 x 0.15 in. squares of pure K3B (control) and 15% amorphous boron + K3B. The two pieces were clamped together with a slightly smaller piece of indium foil sandwiched between. The specimen was then inserted into the neutron source for 1.5 hr in order to produce $^{116}$In which is a $\beta^-$ emitter with a half-life of 54 min.$^2$ Counts for the background radiation of the room were taken during the activation process. Counts of the activated material were taken at one min. intervals every five min. for at least one hr. for each of the samples on an end-window Geiger counter.

2.3 Dynamic Mechanical Analysis

Dynamic mechanical testing of the five sets of PETI-5 and K3B samples was performed on a TA Instruments 2980 Dynamic Mechanical Analyzer. Testing was performed in single cantilever mode followed the guidelines set forth in ASTM E1640-94.$^3$ Samples used for the DMA testing were prepared from the clamped ends of the tensile specimens. Samples were cut to 35 mm. in length by a diamond bladed wet saw. The width and thickness dimensions were already within the range of the instrument, 15 mm. wide and 5 mm. thick.

Prior to testing, samples were dried for at least 10 days at 90°C and then weighed to the nearest 0.0001g. The PETI-5 samples were then heated at 5°C/min. to 350°C while K3B samples were heated 5°C/min. to 270°C since K3B begins to melt around 290°C. Both PETI-5 and K3B samples were run with an oscillating frequency
of 20Hz. Analysis of the resulting plot was then performed using the TA Universal Analysis program.

### 2.D Mechanical Testing

Three types of mechanical tests were performed on the 5 sets of specimens for both PETI-5 and K3B. The 5 sets of specimens for each polymer includes the following: pure, 10% boron carbide whiskers, 20% boron carbide whiskers, 10% amorphous boron, and 20% amorphous boron. All of these are weight percentages of the additive to the respective polymer.

#### K3B Compression Test Numbering System

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Numbering</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>A1K-C1K</td>
<td>PURE</td>
</tr>
<tr>
<td>K2</td>
<td>D1K-F1K</td>
<td>PURE</td>
</tr>
<tr>
<td>K3</td>
<td>A2K-C2K</td>
<td>10% B₄C</td>
</tr>
<tr>
<td>K4</td>
<td>D2K-F2K</td>
<td>10% B₄C</td>
</tr>
<tr>
<td>K5</td>
<td>A3K-C3K</td>
<td>20% B₄C</td>
</tr>
<tr>
<td>K6</td>
<td>D3K-F3K</td>
<td>20% B₄C</td>
</tr>
<tr>
<td>K7</td>
<td>A4K-C4K</td>
<td>10% AB</td>
</tr>
<tr>
<td>K8</td>
<td>D4K-F4K</td>
<td>10% AB</td>
</tr>
<tr>
<td>K9</td>
<td>A5K-C5K</td>
<td>20% AB</td>
</tr>
<tr>
<td>K10</td>
<td>D5K-F5K</td>
<td>20% AB</td>
</tr>
</tbody>
</table>

Table 2.I. Compression test numbering scheme.
Compression Testing

Compression tests were performed solely on the five sets of K3B specimens since PETI-5 had already been performed previously. Two $3.5 \times 0.75$ in. plates were molded for each set of specimens and cut for a total of six compression samples for each set. The numbering scheme for the samples can be seen in Table 2.1. The dimensions of the sample are in accordance with ASTM D695 and are shown in Figure 2.A. The samples were tested on an Instron Model 1361 universal test plant with a 25 kip (25,000 lbs.) capacity. An MTS Extensometer Model 632-26B-20 with a $\pm 0.045$ in. travel was used to measure the sample displacement. This was coupled with an Analogic ANDS 5400 data acquisition system to record the data from the extensometer.

Prior to testing, the width and thickness of each sample were measured at several points along the sample to determine its cross-sectional area. Each of the samples was then loaded into the test stand with the help of an alignment tool and the
top plate of the compression fixture was lowered to hold the sample. Once the extensometer was attached, the test was started with a speed of 0.05 in/min. Real time stress vs. strain curves were generated from the extensometer readout.

**Tensile Testing**

A total of ten 3 x 6 in. plates, five each for PETI-5 and K3B, were molded for the tensile tests. Six dogbone specimens were machined from each plate for a total of 60 samples which were 6.0 x 0.375 x 0.14 in. at the ends. The gage area of each sample was 0.375 in. long and 0.125 in. wide as seen in Figure 2.B, the dimensions prescribed by ASTM D638. Prior to testing, three width and thickness measurements were taken inside the gage area and the area was calculated. The numbering scheme can be seen in Table 2.II. The samples were then loaded into the test clamp and the MTS extensometer was mounted using two rubber bands. The tests were run using a load rate of 0.05 in/min for samples P1-P4 and 0.02 in/min for specimens P5 & K1-K7 with points taken at 4 Hz. Two channels were set up for the data where channel 1 reported load and channel 2 reported extension. Testing was discontinued after complete failure of the material.
Tensile Specimens
ASTM D638

Figure 2.B. ASTM D638.

Tensile Test Numbering System

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Numbering</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>P1A-P1F</td>
<td>Pure PETI-5</td>
</tr>
<tr>
<td>P2</td>
<td>P2A-P2E</td>
<td>10% AB + PETI-5</td>
</tr>
<tr>
<td>P3</td>
<td>P3A-P3G</td>
<td>10% B₄C + PETI-5</td>
</tr>
<tr>
<td>P4</td>
<td>P4A-P4E</td>
<td>20% B₄C + PETI-5</td>
</tr>
<tr>
<td>P5</td>
<td>P5A-P5E</td>
<td>20% AB + PETI-5</td>
</tr>
<tr>
<td>K1</td>
<td>K1A-K1E</td>
<td>Pure K3B</td>
</tr>
<tr>
<td>K3</td>
<td>K3A-K3E</td>
<td>10% AB + K3B</td>
</tr>
<tr>
<td>K4</td>
<td>K4A-K4E</td>
<td>20% AB + K3B</td>
</tr>
<tr>
<td>K6</td>
<td>K6A-K6G</td>
<td>10% B₄C + K3B</td>
</tr>
<tr>
<td>K7</td>
<td>K7A-K7G</td>
<td>20% B₄C + K3B</td>
</tr>
</tbody>
</table>

Table 2.II. Tensile test numbering scheme.
Flexural Testing

The samples were made via the processing techniques developed for PETI-5 and K3B. The samples were made in a 3 × 6 in. mold with a powder depth of around 0.33 in. Samples were cut from the 3 × 6 in. plate into the specific size obtained from ASTM D790. The standard recommends a support span-to-depth ratio of 16, while the width should not exceed \( \frac{1}{4} \) of the support span. Therefore, the length of the specimen was machined to 3 in. with a 2 in. support span. This left a 0.5 in. overhang, exceeding the recommendation of 10% by the standard. The width was determined to be 0.5 in. while the thickness was machined to 0.125 in.

The samples were conditioned in the lab at 75°F with a relative humidity around 50%. Due to the size of the original specimen plate, around 10 samples could be obtained for each data set. The numbering scheme can be found in Table 2.III.

### Flexural Test Numbering Scheme

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Numbering</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1P</td>
<td>1AP-1JP</td>
<td>Pure PETI-5</td>
</tr>
<tr>
<td>2P</td>
<td>2AP-2JP</td>
<td>10% AB + PETI-5</td>
</tr>
<tr>
<td>3P</td>
<td>3AP-3JP</td>
<td>20% AB + PETI-5</td>
</tr>
<tr>
<td>4P</td>
<td>4AP-4JP</td>
<td>10% B₄C + PETI-5</td>
</tr>
<tr>
<td>5P</td>
<td>5AP-5JP</td>
<td>20% B₄C + PETI-5</td>
</tr>
<tr>
<td>1K</td>
<td>1AK-1JK</td>
<td>Pure K3B</td>
</tr>
<tr>
<td>2K</td>
<td>2AK-2GK</td>
<td>20% AB + PETI-5</td>
</tr>
<tr>
<td>3K</td>
<td>3AK-3JK</td>
<td>10% AB + PETI-5</td>
</tr>
<tr>
<td>4K</td>
<td>4AK-4JK</td>
<td>10% B₄C + PETI-5</td>
</tr>
<tr>
<td>5K</td>
<td>5AK-5JK</td>
<td>20% B₄C + PETI-5</td>
</tr>
<tr>
<td>6K</td>
<td>6AK-6JK</td>
<td>DuPont processed</td>
</tr>
</tbody>
</table>

Table 2.III. Flexural test numbering scheme.
The samples were tested on a MTS 50 kip test stand with a three-point bend fixture. The displacement of the sample in the middle was measured using a ±0.05 in. Direct Current Displacement Transducer (DCDT). The load was measured using the corresponding MTS microconsole. The software for the readout was set up accordingly:

- Channel 1: Load y-axis
- Channel 2: DCDT x-axis
- Channel 3: Crosshead Displacement

The load rate was determined from the standard to be exactly 0.0533 in/min via the equation:

\[ R = \frac{ZL^2}{6d} \]

where \( R \) is the load rate in in/min, \( Z \) is the rate of straining of the outer fiber (which equals 0.01), \( L \) is the support span (2 in.), and \( d \) is the thickness (0.125 in.). This equation therefore gives the load rate for all of the specimens.

**Flexural Specimens**

ASTM D790

![Diagram](image)

- 3.0" length
- 0.5" height
- 2.0" support span
- Thickness equal to 0.125"

*Figure 2.C. ASTM D790.*
Literature Cited


Chapter 3

Results and Discussion

3.A Sample Molding

The result of the molding techniques described in the previous section can be seen in the microscope pictures of the tensile specimens at the failure point contained in Appendix A. The molding process for PETI-5 has been developed extensively by NASA-Langley in order to form the strongest possible polymer without defects or air voids. The lack of voids can be seen particularly in the smooth portion of the pure PETI-5 in the bottom left. The rough areas in the top of the picture are from the stress of the tensile test. The uniform consistency of PETI-5 is also maintained when boron carbide is loaded into the polymer. As the photo of the 20% boron carbide sample reveals, no major defects or voids are present. However, major defects are introduced into the polymer when amorphous boron is added. The photo of the 20% amorphous boron in PETI-5 captures the major flaw present in the sample that caused it to break under the applied tensile load. The brittleness of the 20% amorphous boron and PETI-5 is apparent from all the defects seen in the picture. The boron carbide is clearly the additive of choice for maintaining the uniform consistency of the PETI-5.

The processing of K3B is not as well developed as its PETI-5 counterpart. Air voids present in the sample were the main concern and special techniques discussed in
the experimental section were needed to improve the quality of the K3B samples. Porous Kapton film, a Teflon release cloth coupled with the packing of the powder into the mold helped to expel some of the air from the sample. Since K3B is less viscous than PETI-5, a lower processing temperature was needed to keep the sample from running out of the mold once the pressure was applied. All of these techniques helped to increase the quality of the K3B samples although voids are still present. Photos of the K3B samples at the failure point in the tensile tests can be seen in Appendix A. The photo of the pure K3B sample confirms the processing difficulties associated with the polymer. The huge void present in the middle of the sample is typical of the pure material. However, the boron carbide helps to decrease the void content of the K3B which can be seen in the photo of the 20% boron carbide sample. No major defects or voids are apparent in this sample. Porosity and defects return with the addition of amorphous boron to the K3B. The photo of 20% amorphous boron reveals the presence of both small air voids as well as large defects common to the amorphous boron samples. In the case of K3B, the presence of the boron carbide additive actually improves the quality and consistency of the polymer.

In conclusion, the PETI-5 samples are clearly more uniform than their K3B counterparts. Besides being easier to process, PETI-5 does not contain the defects and voids present in the K3B. In both of the polymers, boron carbide proved to be the additive of choice. In PETI-5, the boron carbide helped to maintain the consistency of the pure polymer while the amorphous boron tended to introduce defects. For K3B, the boron carbide actually improved the quality of the polymer by reducing the amount of voids and defects common in the pure material.
3.B Neutron Shielding Tests

The results of the neutron shielding tests can be seen in Figure 3.A with the raw data in Table 3.I. To achieve the final results, the background radiation count of 68 counts/min was subtracted from each point on the graph. The resulting ln counts/min were plotted vs. time in min. The goal of the experiment is to extrapolate the line to the y-axis, or zero time. This gives the initial activity of the indium foil.

This extrapolation can be done by first plotting the ln counts/min vs. time. Then, the slope of the line should be forced through a point equal to the half-life of the indium which is 54 min. The equation of the line can be computed as seen in the plot. For example, the line for the pure K3B sample should fit through the point (54, ln[e^{8.4166/2}]) since it represents the half-life and half of the activity. The original activity is then equal to the anti-ln of 8.4166, or 4521 cpm. The same process was repeated for 15% amorphous + K3B which yielded an activity of 426 cpm. Therefore, 90.6% of the neutron flux was absorbed by the 15% amorphous boron.

The data and the results from the neutron experiment appear reliable. The data for the 15% amorphous boron is a little scattered, but this is probably due to the high background vs. sample activity. The sample activity for this experiment was only 6 times more than the background. In conclusion, 15% amorphous boron provided a large amount of shielding for only a small amount of boron. One can then assume that smaller amounts of boron would still provide adequate shielding from thermal neutrons.
Figure 3.A. Shielding ability of 15% amorphous boron.

<table>
<thead>
<tr>
<th>Pure K3B</th>
<th>15% Amorphous Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (Min)</td>
<td>Activity (cpm)</td>
</tr>
<tr>
<td>0</td>
<td>4215</td>
</tr>
<tr>
<td>5</td>
<td>4072</td>
</tr>
<tr>
<td>10</td>
<td>3769</td>
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<tr>
<td>85</td>
<td>1438</td>
</tr>
<tr>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.I. Neutron shielding test data.
3.C Dynamic Mechanical Analysis

Dynamic mechanical analysis was performed for three specimens of each of the five sets of samples for PETI-5 and K3B. Analyses were rejected if a significant abnormality in the curve was observed. This could result from a large void or perhaps some residual moisture in the sample. Typical DMA plots can be seen in Appendix B. Since K3B had many visible voids, three consistent T<sub>g</sub> values were rarely observed. Furthermore, the tan delta peak was unable to be obtained for the K3B DMA samples since the samples melted prior to this temperature. The results of the DMA experiment can be seen in Tables 3.II. and 3.III., and in Figure 3.B.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Loss Modulus Peak (°C)</th>
<th>Tan Delta Peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1A</td>
<td>268.52</td>
<td>281.63</td>
<td></td>
</tr>
<tr>
<td>P1C</td>
<td>268.11</td>
<td>281.52</td>
<td>294.54</td>
</tr>
<tr>
<td>P1F</td>
<td>267.41</td>
<td>281.99</td>
<td>294.74</td>
</tr>
<tr>
<td>10% Amorphous Boron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2A</td>
<td>267.02</td>
<td>281.74</td>
<td>296.40</td>
</tr>
<tr>
<td>P2B</td>
<td>268.24</td>
<td>283.41</td>
<td>297.22</td>
</tr>
<tr>
<td>P2D</td>
<td>266.52</td>
<td>281.81</td>
<td>295.84</td>
</tr>
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<td>10% Boron Carbide</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P3A</td>
<td>262.23</td>
<td>276.05</td>
<td>290.31</td>
</tr>
<tr>
<td>P3B</td>
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<td>275.92</td>
<td>288.81</td>
</tr>
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<td>P3G</td>
<td>262.19</td>
<td>275.90</td>
<td>289.09</td>
</tr>
<tr>
<td>20% Boron Carbide</td>
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<td></td>
<td></td>
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<tr>
<td>P4A</td>
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<td>274.07</td>
<td>289.21</td>
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<tr>
<td>P4C</td>
<td>260.53</td>
<td>275.00</td>
<td>288.54</td>
</tr>
<tr>
<td>P4D</td>
<td>262.53</td>
<td>275.48</td>
<td>289.43</td>
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<tr>
<td>20% Amorphous Boron</td>
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<td></td>
</tr>
<tr>
<td>P5A</td>
<td>275.24</td>
<td>285.06</td>
<td>294.77</td>
</tr>
<tr>
<td>P5D</td>
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<td>284.44</td>
<td>294.62</td>
</tr>
<tr>
<td>P5E</td>
<td>269.31</td>
<td>283.98</td>
<td>295.46</td>
</tr>
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Table 3.II. PETI-5 DMA data.
### K3B DMA DATA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Loss Modulus Peak (°C)</th>
<th>Tan Delta Peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
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<td></td>
</tr>
<tr>
<td>K1A</td>
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<td>250.97</td>
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</tr>
<tr>
<td>K1D</td>
<td>229.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K1E</td>
<td>-</td>
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</tr>
<tr>
<td>10% Amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boron</td>
<td>K3A</td>
<td>236.43</td>
<td>252.03</td>
</tr>
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<td>-</td>
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<td>K3E</td>
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<td>20% Amorphous</td>
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</tr>
<tr>
<td>Boron</td>
<td>K4A</td>
<td>235.73</td>
<td>251.55</td>
</tr>
<tr>
<td>K4D</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>K4E</td>
<td>234.20</td>
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<td>-</td>
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<td>10% Boron</td>
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<td>232.57</td>
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<td>Boron</td>
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</tr>
<tr>
<td>Carbide</td>
<td>K6E</td>
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<td>-</td>
</tr>
<tr>
<td>20% Boron</td>
<td>K7B</td>
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<td>247.92</td>
</tr>
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<td>K7D</td>
<td>235.00</td>
<td>249.50</td>
</tr>
<tr>
<td>Carbide</td>
<td>K7G</td>
<td>232.85</td>
<td>247.69</td>
</tr>
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</table>

Table 3.III. K3B DMA data.

### Average Tg of PETI-5 and K3B

![Average Tg of PETI-5 and K3B](image)

Figure 3.B. Average $T_g$ of PETI-5 and K3B.
For PETI-5, the samples containing 20% amorphous boron clearly had the highest
$T_g$ of all the samples tested, an increase of 4 °C over the pure material. The samples
containing 10% amorphous boron exhibited a $T_g$ equal to that of the pure material while
the 10% boron carbide showed a 6 °C reduction in $T_g$. Finally, samples containing 20%
boron carbide reduced the $T_g$ of the pure material by 8 °C. Since the $T_g$ is based on
polymer mobility, it is not surprising why the boron carbide reduced the glass-transition
temperature. The large whiskers interrupt the cross-linking enough locally to cause
mobility between the chains at a lower temperature. Amorphous boron powder does not
have this effect because of its small size. The cross-links are not destroyed to a great
extent and the $T_g$ remains intact or increased thanks to the high melting point of the
boron.

The lack of cross-linking in K3B explains the huge difference in $T_g$ and the effect
of the additives compared with PETI-5. Despite the scattering of some of the data in
K3B due to the presence of air voids, the effect of the different additives can be seen.
The amorphous boron still enhanced the $T_g$ of the pure material with 10% amorphous
boron showing the highest values. The samples containing 10% boron carbide had
considerable deviation in $T_g$ but the loss modulus data are consistent. At the peak of
polymer mobility, the loss modulus peak, the boron carbide decreases the thermal
stability of the polymer. Even though there are no cross-links in K3B, the size of the
whisker probably inhibits the electrostatic bonds between the chains and causes them to
move at lower temperatures. The small size of the amorphous molecules does not
decrease the $T_g$, but the higher melting point of the boron increases the glass-transition
temperature.
3.D Mechanical Testing

Mechanical testing mainly showed the boron carbide whiskers to be stronger than the amorphous boron powder. When incorporated into the PETI-5, the whiskers tended to minimize the decrease in mechanical properties of the thermoset. When added to the K3B thermoplastic, the boron carbide whiskers actually improved the mechanical properties of the pure polymer. This is due in part to the high frequency of defects and voids in the K3B polymer. As seen in the pictures of the polymer samples (Appendix A), the boron carbide tends to ameliorate the void and defect problem.

Compression Testing

Results from the compression testing yielded two calculations performed in accordance with ASTM D695. All but two specimens were included in the data since they were used as test specimens for the machinery. The ultimate compressive strength was calculated by dividing the ultimate compressive load by the initial cross-sectional area of the specimen. The ultimate compressive strength was considered equal to the compressive yield strength. Second, the compressive chord modulus was calculated by determining the slope of the initial straight portion of the line in the stress vs. strain plot. All calculations were carried out to three significant digits as prescribed by the standard and standard deviations were calculated. Results of the experiment can be seen in Table 3.IV. and Appendix C.
The addition of 10% boron carbide to K3B resulted in a strength value equal to that of the pure material while the addition of 20% boron carbide only saw a 5% reduction in strength from the pure material. The addition of both percentages of amorphous boron decreased the compressive strength significantly from that of the pure material. These results are not surprising since the whiskers should add considerable amount of strength in the compression of a sample compared to the amorphous boron.

Furthermore, the boron carbide whiskers added a considerable amount of stiffness to the K3B matrix. Due to the stiffness of the whiskers compared to the soft polymer, the addition of 20% boron carbide increased the modulus by 24% while the addition of 10% boron carbide raised the modulus by 13%. In the amorphous boron samples, the addition of 10% amorphous boron slightly increased the modulus while the addition of 20% amorphous boron decreased the stiffness of the polymer.

In conclusion, the results of the compression testing clearly show that the addition of boron carbide to K3B is much better compared to the addition of amorphous boron. The superior mechanical properties of the boron carbide increase the stiffness of the polymer matrix without sacrificing compressive strength.

### Table 3.IV. K3B compression test data.

<table>
<thead>
<tr>
<th></th>
<th>Pure</th>
<th>10% Boron Carbide</th>
<th>20% Boron Carbide</th>
<th>10% Amorphous Boron</th>
<th>20% Amorphous Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Compressive</td>
<td>13.8</td>
<td>13.7</td>
<td>13.3</td>
<td>12.6</td>
<td>10.3</td>
</tr>
<tr>
<td>Strength (ksi)</td>
<td>1.22</td>
<td>0.581</td>
<td>0.667</td>
<td>0.158</td>
<td>0.919</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressive Chord</td>
<td>336</td>
<td>381</td>
<td>416</td>
<td>360</td>
<td>306</td>
</tr>
<tr>
<td>Modulus (ksi)</td>
<td>0.0386</td>
<td>0.0248</td>
<td>0.0224</td>
<td>0.0173</td>
<td>0.0562</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Tensile Testing

The tensile tests performed on both the PETI-5 and K3B were analyzed according to ASTM D638. Enough data were collected from the samples to be conclusive even though many samples were not included in the results. The reason for discarding the data for certain samples was threefold. First, the sample data were discarded if the specimen broke outside the 0.375 in. gauge area. Second, if a sample broke under a small load due to obvious air voids, the sample was not counted. Due to molding problems, many of the K3B samples were rejected for this reason. Finally, human and machine error accounted for the rejection of two samples.

Three calculations were performed for the tensile data for each of the tested samples. All values are reported to three significant figures as recommended by the standard. First, the ultimate tensile strength of the material was found by dividing the ultimate load achieved by the sample divided by the gauge area of the sample. Next, the percent elongation of the sample was calculated by dividing the elongation of the extensometer at the ultimate load by the original gauge length of the sample. Multiplying this value by 100 gave the percent elongation of the sample. Finally, the elastic modulus was found by calculating the slope of the initial linear part of the stress-strain curve.
PETI-5

Results of the tensile tests for PETI-5 can be seen in Table 3.V and in Appendix D. All samples were tested to complete failure of the material. Values for the ultimate tensile strength show that samples containing 10% boron carbide had the highest strength of the four additives with only a 10% reduction in tensile strength from the pure material. The 20% boron carbide proved to be too much additive and significantly decreased the tensile strength. The second best additive proved to be the 10% amorphous boron with a 16% reduction in tensile strength while the 20% amorphous is, not surprisingly, the worst. The 10% boron carbide is also the most consistent of the materials with a standard deviation close to that of the pure material.

Contrary to previous thought, the boron carbide did not add stiffness to the PETI-5 neat resin in the tensile test. In fact, the addition of 10% boron carbide reduced the modulus by 33% while samples with 20% boron carbide experienced a 13% decrease in stiffness. In both sample sets containing amorphous boron, the modulus increased over that of the neat resin with the 10% boron sample exhibiting the greatest stiffness. One reason for the decrease in stiffness with boron carbide could be the greater interruption of

<table>
<thead>
<tr>
<th>PETI-5</th>
<th>Pure</th>
<th>10% Boron Carbide</th>
<th>20% Boron Carbide</th>
<th>10% Amorphous Boron</th>
<th>20% Amorphous Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Tensile Strength (ksi)</td>
<td>18.9</td>
<td>17.1</td>
<td>12.5</td>
<td>15.8</td>
<td>7.61</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.217</td>
<td>0.262</td>
<td>1.03</td>
<td>0.321</td>
<td>0.870</td>
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<tr>
<td>Elastic Modulus (ksi)</td>
<td>487</td>
<td>324</td>
<td>426</td>
<td>596</td>
<td>503</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>7.83</td>
<td>41.9</td>
<td>88.1</td>
<td>8.49</td>
<td>66.5</td>
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<tr>
<td>Percent Elongation</td>
<td>8.68</td>
<td>6.22</td>
<td>3.04</td>
<td>3.41</td>
<td>1.74</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.339</td>
<td>0.519</td>
<td>0.767</td>
<td>0.424</td>
<td>0.0401</td>
</tr>
</tbody>
</table>

Table 3.V. PETI-5 tensile test data.
the cross-linking because of the large whisker size. A smaller cross-link density would decrease the stiffness of the PETI-5.

The percent elongation of the samples illustrates the ability of the sample to be stretched before yield or break. Values for the percent elongation were calculated at the ultimate strength of the material. Only the pure material had enough elasticity to extend after the ultimate strength was reached. Plots of the stress-strain curve for each of the five sets of specimens can be seen in Appendix D. For samples containing additives, the most elastic contained 10% boron carbide. All of the other samples with additives proved to be very brittle and did not experience any plastic deformation according to the stress-strain plots.

Since the main concern of the tensile test lies in the ultimate strength of the material, 10% boron carbide proves to be the best additive, although it decreases the stiffness relative to that of the pure material.

\textit{K3B}

Results for the K3B tensile testing can be seen in Table 3.VI. and in Appendix D. All samples were tested to complete failure of the material. Values for the ultimate strength show that both of the boron carbide additives significantly improved the strength of the K3B polymer. Specifically the addition of 10% boron carbide increased the tensile strength of the pure material by 55% while the addition of 20% increased the value by 29%. Both of the amorphous boron additives did not improve the mechanical properties of the pure K3B like the boron carbide whiskers. Since K3B is a thermoplastic, the
whiskers add a large amount of strength to the polymer without interrupting cross-linking. Thus, the effect of the whiskers is more pronounced in K3B as compared to PETI-5.

The pronounced effect of the boron carbide whiskers in K3B can also be seen in the modulus calculations. The addition of 10% boron carbide enhanced the stiffness of the thermoplastic by 18% while the addition of 20% boron carbide enhanced the modulus to a lesser degree. The addition of the amorphous boron powder decreases the stiffness in K3B.

Finally, the percent elongation for K3B follows the trend seen in the tensile strength calculations. The data plots for the K3B samples in Appendix D show that K3B possesses a much more brittle nature than PETI-5. As a result, none of the samples showed any extension once the ultimate strength was attained. The enhanced strength of the samples containing 10% boron carbide allows them to withstand a greater elongation before failure. Amorphous boron does not enhance the elongation ability of K3B. The

<table>
<thead>
<tr>
<th>K3B</th>
<th>Pure</th>
<th>10% Boron Carbide</th>
<th>20% Boron Carbide</th>
<th>10% Amorphous Boron</th>
<th>20% Amorphous Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Tensile Strength (ksi)</td>
<td>7.02</td>
<td>10.9</td>
<td>9.05</td>
<td>~6.85</td>
<td>5.45</td>
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<tr>
<td>Standard Deviation</td>
<td>0.277</td>
<td>0.612</td>
<td>0.533</td>
<td>0.894</td>
<td>0.371</td>
</tr>
<tr>
<td>Elastic Modulus (ksi)</td>
<td>496</td>
<td>586</td>
<td>534</td>
<td>479</td>
<td>414</td>
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<tr>
<td>Standard Deviation</td>
<td>5.32</td>
<td>15.6</td>
<td>54.8</td>
<td>28</td>
<td>18.5</td>
</tr>
<tr>
<td>Percent Elongation</td>
<td>1.53</td>
<td>2.11</td>
<td>1.96</td>
<td>1.53</td>
<td>1.45</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.0619</td>
<td>0.185</td>
<td>0.291</td>
<td>0.172</td>
<td>0.194</td>
</tr>
</tbody>
</table>

Table 3.VI. K3B tensile test data.
elongation data and the plots in Appendix D clearly show that specimens containing 10% boron carbide are the toughest of all the K3B samples tested.

**Flexural Testing**

Calculations for the flexural testing of PETI-5 and K3B followed the guidelines set forth in ASTM D790. Most specimens were used in the final calculation of the data but two reasons accounted for the exclusion of samples. First, improper machining accounted for the dismissal of some samples. Second, if the maximum load deviated significantly from the average, i.e. greater than around 10 lbs., the sample was excluded. Three important calculations can be made with the data which give information on the properties of the material. First, the maximum fiber stress was calculated using the following equation:

$$ S = \frac{3PL}{2bd^2} $$

The symbol $S$ stands for the maximum fiber stress in psi, $P$ symbolizes the load (pounds) at a given point on the load/deflection curve, $L$ is the support span (in.), $b$ stands for the width of the specimen (in.), and $d$ is the depth of the specimen (in.).

The maximum strain in the outer fibers is the next calculated quantity using the test data. The equation used for this calculation is as follows:

$$ r = \frac{6Dd}{L^2} $$

where $r$ is the strain (in./in.) and $D$ is the maximum deflection (in.) at the center of the specimen.
Finally, the tangent modulus of elasticity is obtained from the slope of the straight portion of the load/deflection curve. The slope is then used in the following equation to find the modulus:

\[ E_B = \frac{L^3 m}{4bd^3} \]

Where \( E_B \) is the tangent modulus of elasticity (psi) and \( m \) is the slope of the linear portion of the curve.

**PETI-5**

Results of the flexural testing of the PETI-5 samples can be seen in Table 3.VII. and Appendix E. All samples were tested either to complete failure or to the limit of the Direct Current Displacement Transducer (DCDT) which had a 0.5 in. maximum travel. Some of the pure PETI-5 samples did not completely fail but the ultimate stress was achieved in these samples. The calculation of maximum fiber strength shows that the boron carbide clearly contributes more strength to the polymer matrix than the amorphous boron. Samples loaded with 10% boron carbide

<table>
<thead>
<tr>
<th>PETI-5</th>
<th>Pure</th>
<th>10% Boron Carbide</th>
<th>20% Boron Carbide</th>
<th>10% Amorphous Boron</th>
<th>20% Amorphous Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Fiber Strength (ksi) Standard Deviation</td>
<td>28.2</td>
<td>28.3</td>
<td>25.1</td>
<td>18.9</td>
<td>14.2</td>
</tr>
<tr>
<td>Maximum Strain (in./in.) Standard Deviation</td>
<td>0.0971</td>
<td>0.0842</td>
<td>0.0607</td>
<td>0.0493</td>
<td>0.0375</td>
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<tr>
<td>Tangent Modulus of Elasticity (ksi) Standard Deviation</td>
<td>547</td>
<td>684</td>
<td>799</td>
<td>486</td>
<td>455</td>
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</tbody>
</table>

Table 3.VII. PETI-5 flexural test data.
maintain the same flexural strength as the pure PETI-5. The larger amount of additive in
the 20% boron carbide samples begins to disrupt the polymer matrix enough to degrade
the flexural strength. However, the whiskers clearly add strength compared to the
amorphous boron samples. Ten percent amorphous boron degrades the properties of the
pure polymer by 33% while samples containing 20% only show half the strength of the
pure PETI-5.

Second, the maximum strain calculation shows that the pure polymer can
withstand more stretching than any of the other sets of samples. The samples containing
10% boron carbide, because of its rigidity, cannot stretch as much as those of the pure
material but they still outperform samples containing amorphous boron. The samples
containing 20% boron carbide also possess the ability to withstand more strain than those
containing amorphous boron. The brittleness of the samples containing amorphous boron
do not allow them to withstand the strain that the pure and boron carbide containing
samples can.

Finally, the effects of the boron carbide can be seen in the calculation of the
tangent modulus of elasticity. Both 10% and 20% boron carbide add considerable
stiffness to PETI-5. Specifically, the addition of 20% boron carbide increases the
modulus by almost 50% over that of the pure material while the 10% boron carbide
additive adds 25% stiffness over the pure PETI-5. For both of the sample sets containing
amorphous boron, the stiffness decreased by at least 11% over that of the pure polymer.
The results of the flexural testing for K3B can be seen in Table 3.VIII. and in Appendix E. Due to the brittleness of the samples, all were tested to complete failure without exceeding the limit of the DCDT. For comparison purposes, samples were cut from a plate of K3B processed by DuPont. The material processed by DuPont did not contain the voids and defects that our K3B possessed even though the molding cycles were similar. The data shows that the DuPont K3B far exceeded the values of our material. However, the standard deviations of the strength and strain show that the DuPont material is anything but consistent. There were great fluctuations in the data showing that even the DuPont material lacks uniformity. The rest of this section will deal with the material we molded for this study at NASA.

As with the compression and tensile tests, the effect of the boron carbide whiskers is significant when loaded into K3B. For the addition of both 10% and 20% boron carbide the maximum fiber strength increased significantly over that of pure K3B. For example, the addition of 10% boron carbide increased the fiber strength by 59% over that

<table>
<thead>
<tr>
<th>K3B</th>
<th>Pure</th>
<th>10% Boron Carbide</th>
<th>20% Boron Carbide</th>
<th>10% Amorphous Boron</th>
<th>20% Amorphous Boron</th>
<th>DuPont Processed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Fiber Strength (ksi)</td>
<td>9.26</td>
<td>14.7</td>
<td>13.2</td>
<td>10.5</td>
<td>6.71</td>
<td>18.6</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.41</td>
<td>1.49</td>
<td>0.698</td>
<td>0.629</td>
<td>1.08</td>
<td>2.83</td>
</tr>
<tr>
<td>Maximum Strain (in./in.)</td>
<td>0.0232</td>
<td>0.0321</td>
<td>0.0271</td>
<td>0.0221</td>
<td>0.0195</td>
<td>0.0363</td>
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<tr>
<td>Standard Deviation</td>
<td>0.00329</td>
<td>0.00304</td>
<td>0.00184</td>
<td>0.00203</td>
<td>0.00301</td>
<td>0.00718</td>
</tr>
<tr>
<td>Tangent Modulus of Elasticity (ksi)</td>
<td>407</td>
<td>537</td>
<td>619</td>
<td>501</td>
<td>373</td>
<td>558</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>12.2</td>
<td>62.3</td>
<td>36.1</td>
<td>22.6</td>
<td>36.7</td>
<td>3.48</td>
</tr>
</tbody>
</table>

Table 3.VIII. K3B flexural test data.
of the pure material. The 20% boron carbide samples showed an increase in the fiber strength but to a lesser degree. Despite the lack of favorable mechanical properties, the addition of 10% amorphous boron powder strengthened the K3B by 13%, however, the addition of 20% degraded the polymer matrix too much and significantly reduced the strength.

The results of the strain calculation follow the results from the maximum fiber strength measurement. Both of the boron carbide sample sets showed a significant increase in the stretching ability over that of the pure K3B with 10% samples having the highest strain values. As expected, both of the amorphous boron sample sets showed a decrease in the strain capability of the K3B.

Finally, the stiffness of the K3B increased significantly with the addition of the boron carbide whiskers. The addition of 20% boron carbide enhanced the stiffness of the K3B by 52% while the 10% boron carbide samples experienced a 32% increase in modulus. The addition of 10% amorphous boron improved the modulus also, but not to the degree of the boron carbide. As usual, 20% amorphous boron proved to be the worst additive with a decrease in modulus of 9% compared to the pure material.

In conclusion, the toughest of the K3B materials would be the two boron carbide-containing sets of specimens. The 10% boron carbide samples particularly showed the highest strength and strain capacity of the materials studied. Upon analysis of the curves in Appendix E, it is easy to see that the 10% boron carbide samples showed the least amount of brittleness.
Boron carbide whiskers and amorphous boron powder were loaded into two polyimides, a thermoset called PETI-5 and a DuPont thermoplastic named K3B, to improve the radiation shielding ability of the polymers. The boron acts as a neutron shield which can significantly decrease the radiation dose received by humans and electronics. The object of this research was to study the effects of the two boron additives on the processability, neutron shielding ability, thermal properties, and mechanical properties of the two polyimides. It will be shown in this section that the stability of PETI-5 is significantly higher than K3B and that boron carbide proves to be the best additive to retain or enhance the properties of the polymer.

From a molding standpoint, the PETI-5 requires less preparation and has an easier molding cycle than the K3B. Many precautions need to be taken with the K3B thermoplastic to help reduce the void content. Furthermore, the photographs in Appendix A show that PETI-5 is a much more uniform polyimide free of voids that plague K3B. The photographs also show that the addition of boron carbide reduces the number of defects and voids in both polymers compared to the addition of amorphous boron.
powder. In fact, boron carbide actually helps improve the quality of the K3B polymer matrix.

Neutron shielding tests were performed on 15% amorphous boron + K3B and pure K3B samples. The $^{10}$B nucleus proves to be effective in scavenging neutrons since greater than 90% of the radiation was shielded when only 15% boron was added to the polymer. Boron carbide should also shield a significant amount of radiation since it contains about 16% of the $^{10}$B nucleus per molecule as opposed to the natural abundance of 19.9% in pure boron.

Dynamic mechanical analysis of the PETI-5 and K3B samples gave two major pieces of information. First, the PETI-5 thermoset possessed a much higher $T_g$ than the K3B thermoplastic. The cross-linking ability of the PETI-5 is the main reason for the 35°C increase in $T_g$ over the K3B. Second, the dynamic mechanical analysis showed that the addition of amorphous boron powder increased the $T_g$ of both polymers. The addition of boron carbide only decreased the $T_g$ of PETI-5 by 6°C and did not change the $T_g$ of K3B.

The compressive testing of PETI-5 and K3B data further support the conclusion that PETI-5 pure and with boron carbide whiskers comprise the best materials tested. Previous compressive testing of PETI-5 loaded with boron carbide whiskers and amorphous boron powder proved that the addition of boron carbide could increase the compressive chord modulus by as much as 75% and the compressive strength by 9% over that of the pure polymer. Amorphous boron powder, when added to the PETI-5, decreased the modulus and the strength of the pure material. All of the K3B specimens tested exhibited much lower compressive strength and modulus values compared to the
PETI-5. However, the boron carbide did help to improve both the strength and stiffness of the K3B.

The tensile testing of both polyimides also proved that PETI-5 pure and with boron carbide were the preferred materials. The PETI-5 exhibited a tensile strength almost 3 times greater than the K3B as well as a much greater ability to stretch. Although the addition of boron carbide decreased the modulus of PETI-5, it exhibited much greater strength than the with the addition of amorphous boron powder. When loaded into the K3B, the boron carbide whisker enhanced both the modulus and strength of the pure polymer.

Finally, the PETI-5 pure and with boron carbide whiskers exhibited the best properties of all the samples in the flexural tests. Not only did the boron carbide whiskers increase the modulus of the pure polymer, they also did not affect the flexural strength of the polymer to a significant degree. The amorphous boron powder degraded both the modulus and strength of the PETI-5. The flexural properties of the K3B are very poor compared to those of PETI-5 despite the reinforcing nature of the boron carbide whiskers.

In conclusion, the boron carbide whiskers are the preferred additive due to their reinforcement of the mechanical strength and modulus in both polymers. The cross-linking nature of PETI-5 provides a greater amount of strength and stiffness compared to the thermoplastic K3B. Thus, the 10% boron carbide in PETI-5 proves to be the best of all the materials tested. The addition of 20% boron carbide degrades the polymer matrix too much due to the high amount of additive while the amorphous boron powder provides no reinforcement to the polymer.
With the increased frequency of high-altitude and space flight, boron loaded polymers can provide a useful alternative to metals for the construction of high-altitude aerospace and space vehicles. High-performance polymers can decrease both the weight of the vehicle and the radiation dosage compared to commonly used metals. Although further studies of polymers for radiation shielding are required, the materials in this study could provide a useful alternative to metals in the future.
Appendix A

Microscope Photos of PETI-5 and K3B samples
Pure PETI-5

20% Boron Carbide + PETI-5
20% Amorphous Boron + PETI-5

Pure K3B
20% Boron Carbide + K3B

20% Amorphous Boron + K3B
Appendix B

DMA plots of PETI-5 and K3B samples
10% Amorphous Boron + PETI-5
Sample: P4A
Size: 17.6400 x 9.5900 x 3.7550 mm
Method: DMA Standard 5°C/min

File: C:\Data\DMA\Pugh\P4*
Operator: Pugh
Run Date: 3-Jun-99 16:29

20% Boron Carbide + PETI-5
Sample: K1A
Size: 17.5900 x 9.5750 x 4.0200 mm
Method: DMA Standard 5°C/min

File: C:\TA\Data\DMA\Pugh\K1a
Operator: Pugh
Run Date: 4-Jun-99 15:02

---

Temperature (°C) vs. Storage Modulus (MPa) and Loss Modulus (MPa)

- Pure K3B
- DMA Standard 5°C/min

Universal V2.3C TA Instruments
10% Amorphous Boron + K3B
20% Amorphous Boron + K3B

Temperature (°C)
Sample: K6A
Size: 17.5750 x 9.7100 x 3.9350 mm
Method: DMA Standard 5°C/min

File: C:\TA\Data\DMA\Pugh\K6a
Operator: Pugh
Run Date: 11-Jun-99 10:17

10% Boron Carbide + K3B

Temperature (°C)

Storage Modulus (MPa)
Loss Modulus (MPa)

Tan Delta

Universal V2.3C TA Instruments
Appendix C

Compression Test Information for K3B
K3B Ultimate Compressive Strength

![Bar Chart]

- Pure
- 10% Boron Carbide
- 20% Boron Carbide
- 10% Amorphous Boron
- 20% Amorphous Boron

Compressive Strength (ksi)
STRESS VS. STRAIN - Pure K3B
STRESS VS. STRAIN - 10% Boron Carbide + K3B
STRESS VS. STRAIN - 20% Boron Carbide + K3B
STRESS VS. STRAIN - 10% Amorphous Boron + K3B

- Graph showing the relationship between Stress (ksi) and Strain (in/in.).
- The graph indicates a typical stress-strain curve for the material.
- The curve starts at zero stress andstrain, increases until a maximum stress is reached, and then levels off.
STRESS VS. STRAIN - 20% Amorphous Boron + K3B
Appendix D

Tensile Test Information for PETI-5 and K3B
Average Tensile Strength of PETI-5 and K3B

The diagram shows the tensile strength of PETI-5 and K3B under different compositions:
- Pure
- 10% Boron Carbide
- 20% Boron Carbide
- 10% Amorphous Boron
- 20% Amorphous Boron

PETI-5 has a significantly higher tensile strength compared to K3B across all compositions.
Average Elastic Modulus of PETI-5 and K3B

Elastic Modulus (ksi)

Sample

Pure 10% Boron Carbide 20% Boron Carbide 10% Amorphous Boron 20% Amorphous Boron

PETI-5 K3B
Average Percent Elongation of PETI-5 and K3B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pure</th>
<th>10% Boron Carbide</th>
<th>20% Boron Carbide</th>
<th>10% Amorphous Boron</th>
<th>20% Amorphous Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent Elongation (%)</td>
<td>9</td>
<td>6</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>
STRESS VS. STRAIN -- Pure PETI-5

Stress (ksi.) vs. Strain (in./in.)
STRESS VS. STRAIN – 10% Amorphous + PETI-5
STRESS VS. STRAIN — 10% Boron Carbide + PETI-5
STRESS VS. STRAIN -- 20% Boron Carbide + PETI-5

![Stress vs. Strain Graph](image)

Axes:
- Stress (lbs.)
- Strain (in./in.)

Values on the graph:
- Stress ranges from 0 to 16 lbs.
- Strain ranges from 0 to 4.5E-02 in./in.

Note: The graph shows a typical stress-strain curve for a composite material with a 20% Boron Carbide content.
STRESS VS. STRAIN - 20% Amorphous + PETI-5
STRESS VS. STRAIN -- Pure K3B
STRESS VS. STRAIN -- 10% Amorphous + K3B
STRESS VS. STRAIN -- 20% Amorphous + K3B

![Stress vs. Strain Graph](graph.png)
STRESS VS. STRAIN -- 10% Boron Carbide + K3B
STRESS VS STRAIN -- 20% Boron Carbide + K3B
Appendix E

Flexural Test Information for PETI-5 and K3B
Average Maximum Fiber Stress of PETI-5 and K3B

- PETI-5
  - Pure
  - 10% Boron Carbide
  - 20% Boron Carbide
  - 10% Amorphous Boron
  - 20% Amorphous Boron
  - DuPont Processed Pure

- K3B
  - Pure
  - 10% Boron Carbide
  - 20% Boron Carbide

Fiber Stress (ksi)
Average Maximum Strain for PETI-5 and K3B

Maximum Strain (in/in)

Sample

- Pure
- 10% Boron Carbide
- 20% Boron Carbide
- 10% Amorphous Boron
- 20% Amorphous Boron
- DuPont Processed Pure
Average Tangent Modulus of Elasticity of PETI-5 and K3B

Elastic Modulus (ksi)

Sample

- Pure
- 10% Boron Carbide
- 20% Boron Carbide
- 10% Amorphous Boron
- 20% Amorphous Boron
- DuPont Processed Pure
LOAD VS. DEFLECTION - Pure PETI-5

Graph showing the relationship between force at midspan (lbs) and midspan deflection (in.).
LOAD VS. DEFLECTION - 10% Amorphous Boron + PETI-5

Midspan Deflection (in.)

Force at Midspan (lbs)
LOAD VS. DEFLECTION - 20% Amorphous Boron + PETI-5

![Graph showing the relationship between force at midspan and midspan deflection.](image-url)
LOAD VS. DEFLECTION - 10% Boron Carbide + K3B

Graph showing the relationship between force at midspan (lbs.) and midspan deflection (in.).
LOAD VS. DEFLECTION - 20% Boron Carbide + K3B
LOAD VS. DEFLECTION - 10% Amorphous Boron + K3B
LOAD VS. DEFLECTION - 20% Amorphous Boron + K3B
LOAD VS. DEFLECTION - DuPont Processed K3B
Vita

Christopher Scott Pugh


After earning a Master of Arts degree in Chemistry, the author will make his home in Richmond, Virginia. He will be employed with Carpenter Co., a polyurethane foam manufacturer.