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Synthesis and characterization of boron-containing polymeric materials for neutron shielding applications

Michael B. Glasgow

College of William & Mary - Arts & Sciences

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SYNTHESIS AND CHARACTERIZATION OF BORON-CONTAINING POLYMERIC MATERIALS FOR NEUTRON SHIELDING APPLICATIONS

A Dissertation

Presented to

The Faculty of the Department of Applied Science

The College of William and Mary in Virginia

In Partial Fulfillment

of the Requirements for the Degree of

Doctor of Philosophy

by

Michael B. Glasgow

1996
This dissertation is submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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ABSTRACT

The development of boron-containing polymeric materials for neutron shielding applications was undertaken. Three types of materials were characterized for physical and thermal properties: boron powder-filled epoxy composites, carborane polyamides having boron chemically bonded into the polymer, and boron-loaded polyimide thin films. Addition of amorphous submicron boron powder did not affect significantly the thermal performance of the epoxy. The 17% boron loading produced a 26% increase in compressive failure strength and a 68% increase in the compressive modulus. 0.125 inch thick specimens containing 17% boron absorbed 92% of incident neutrons from a 5-Curie Pu/Be source compared with <1% for the neat epoxy. Dispersion of the boron in the epoxy was improved with the addition of larger size crystalline boron powders. Carborane polyamides containing up to 35% boron were thermally stable up to 400°C in air. The polymers had hydrogen/boron ratios from 2.0 to 3.8 and were soluble in several organic solvents. Polymer solutions were processed into clear, colored thin films. Boron-filled polyamic acid solutions of a PMDA-ODA polyimide containing up to 10% boron were processed into thin films. Neutron absorption of the opaque films measured in a 5-Curie Pu/Be neutron source was linear with boron concentration and film thickness. The fraction of neutrons absorbed varied linearly with boron concentration and film thickness. The applicability of boron-containing materials to the aerospace, nuclear power and accelerator industries was investigated.
SYNTHESIS AND CHARACTERIZATION OF BORON-CONTAINING POLYMERIC MATERIALS FOR NEUTRON SHIELDING APPLICATIONS
CHAPTER ONE: INTRODUCTION

Radiation shielding materials are vital to the development of future modes of transportation, nuclear energy sources, and nuclear safety models. In applications ranging from the exploration of planets to the containment of nuclear waste and the safe operation of nuclear reactor facilities, shielding materials will play a crucial role in the technology of tomorrow.

It is the nature of humans to reach beyond their means to attain that which was thought to be unattainable. The national space program, under the management and direction of the National Aeronautics and Space Administration, has captured the imaginations of scientists and engineers for three decades with the lunar landing in 1969. An entire generation of Americans have wondered to themselves, "What else is out there?"

A manned mission to Mars has been one of the goals of the space exploration effort. The development of new
strong, lightweight materials is a large factor in the calculation of costs of manned missions to other planets. In addition to being lighter than conventional metal structural components of spacecraft, polymers and composite materials have a greater strength per unit weight and more durability without deformation under extreme loads. However, the deep space environment beyond the van Allen radiation belts that surround and protect Earth from galactic cosmic radiation (GCR) is hazardous to most known materials. Radiation shielding materials that combine the outstanding mechanical and thermal properties of polymeric composites with protection from the deleterious effects of cosmic radiation would effectively serve a dual purpose: structure and shielding.

In order to fully understand the requirements of shielding materials in spacecraft, it is necessary to know the composition and energies associated with galactic cosmic radiation.

1.1 GALACTIC COSMIC RADIATION

There are two principal sources of radiation entering the Earth's atmosphere at any given time: solar cosmic radiation (SCR) and galactic cosmic radiation (GCR). The sun emits low-energy (<1 GeV amu⁻¹) cosmic rays which
contribute to the flux of background radiation. The 11-year cycle of solar activity modulates the amount of radiation observed. In addition, during periods of high solar flare activity, the sun emits large numbers of charged particles, which affect the total flux of radiation measured on Earth. When sun spot activity is high, the SCR flux is decreased because of the sun's increased magnetic field, which deflects low-energy particles.

Highly energetic GCR cosmic rays (1-10^5 GeV amu^{-1}) come from a variety of sources, including supernova explosions and stars in our galaxy (intragalactic GCR) and from beyond our galaxy (extragalactic GCR). Intragalactic cosmic radiation, the principal source of GCR for Earth orbit, consists of highly penetrating charged particles, creating the potential for long-term exposure risk at high altitudes and at the Earth's magnetic poles. Figure 1 summarizes flux density vs. particle energy curves of the common components of cosmic radiation.\(^1\) Although the flux of GCR is very low, the average energy per particle (10^2 to 10^4 MeV) is the highest of the background radiation types affecting Earth. Therefore, development of shielding materials for effects of GCR is important for applications that involve long-term travel at high altitudes on Earth and in Earth orbit.

Perhaps the strongest reason for radiation shielding in space is the interaction of GCR with atomic nuclei in spacecraft hull materials. GCR is composed almost
completely of protons, electrons, positrons and helium nuclei, but a small percentage (<2%) consists of larger nuclei and elements with atomic numbers up to Z=90. These energetic, highly charged heavy particles cause the most damage to materials and tissue. GCR particles impacting on materials in space cause cascade reactions which result in a flux of sub-atomic product particles, including protons and neutrons. Figure 2 shows the development of cascades caused by incident proton and alpha particle (helium nuclei) radiation. Secondary protons, being positively charged, are stopped effectively by Coulombic interactions with matter. The secondary neutrons are uncharged and have a long mean free path. Neutrons may penetrate far into the inside
Figure 2 Cascade reactions caused by GCR particles.

compartment of a spacecraft. Neutrons are slowed to thermal energies by elastic collisions with atomic nuclei. At thermal energies, neutrons are absorbed by the nuclei of target elements at a probability proportional to their respective high thermal neutron cross sections. A nucleus which absorbs thermal neutrons forms a compound nucleus/excited state atom which breaks apart into a variety of decay products, including protons and neutrons. These product particles can react with more nuclei to begin a
cascade series of reactions, as depicted in Figure 2. This series of "chain" reactions is the reason why secondary shielding materials are needed, even though the flux of heavy, energetic primary ions is such a small component of galactic cosmic radiation.

Structural materials, electronic devices, and human tissue can be damaged by the effects of the secondary particles generated by the exposure of primary shielding materials to GCR. These effects can be manifested in loss of plasticity and mechanical properties for polymer-based composites, single event upsets (SEU) of electronic devices, and possible cancer risk caused by cell damage in tissues. Theoretical study of SEUs and tissue damage in mouse cells is a topic of much research interest. The ramifications of tissue studies could possibly affect the future of manned space missions. As important as these issues are, the scope of this work will be dedicated to the effects of secondary neutrons on polymeric materials.

The effects of galactic cosmic radiation on shielding materials have not been demonstrated yet in manned spaceflight experiments. The Long Duration Exposure Facility (LDEF) was recently retrieved from low Earth orbit with the Space Shuttle, and shorter term experiments have been conducted on board the Shuttle. But to gain a true measure of the effects of GCR on polymeric structural
materials requires a mission to deep space.

Researchers at NASA-Langley Research Center and colleagues at research universities have developed computer methods and transport codes that estimate the flux of charged heavy particles and their impact effects on atoms of materials.³ In her recently published dissertation, Kim utilized a heavy ion/nucleon transport code for space radiations (HZETRN) to estimate effects of heavy ions (in particular Fe⁺26) on a variety of shielding materials.⁴ Kim's study concluded that shielding materials for GCR should have a high shielding content (polymers) and that boron-containing polymeric materials showed promise in their effectiveness to absorb secondary neutrons from cascade reactions. The exposure dose rates of various shielding materials were calculated. Kim's plot of a polyetherimide containing different percentages of boron is reproduced in Figure 3.⁵

Boron-containing polymeric materials can serve at least two purposes simultaneously in future spacecraft missions: to provide secondary neutron shielding to prevent the deterioration of materials and devices inside the spacecraft and to serve as structural support members to avoid parasitic weight and volume in spacecraft design. Another possible benefit would be reduction of costs of duplication in electronic circuits and "radiation-hardened" components.
The approach to developing polymeric materials with high boron content was essentially two-fold. The first method was to fabricate boron-filled epoxy laminates to establish the baseline mechanical and thermal properties of a boron powder-filled material. The second method was to synthesize novel boron-containing polymers with varying hydrogen content for evaluation as possible matrix resins for fiber-based composites.

The following section describes the thermal neutron
capture process for boron-10, an isotope of boron with a high neutron capture probability.

1.2 NEUTRON CAPTURE

Neutron capture processes are reactions between nuclei and neutrons. The probability of neutron capture is related to the neutron capture cross section, $\sigma$, expressed in barns or $10^{-24}$ cm$^2$. It is a measure of the "largeness" of the target nucleus as it appears to the incident neutron. Neutron capture cross section data are tabulated for nearly all isotopes of the elements in the periodic table. Cross sections for most isotopes range from 0.002 to 1.0 barns. Some nuclei, such as $^{113}$Cd, have cross sections over $10^4$ barns. The data for target nuclei are usually reported for thermal neutron capture cross section -- capture of thermal neutrons. Thermal neutrons have energies of less than 0.1 eV at standard ambient temperature. Because they are slow-moving, thermal neutrons are the most easily captured species of the neutron energy spectrum. Most of the thermal neutron capture data has been accumulated from neutron activation studies and nuclear research efforts by scientists in the United States and the Soviet Union.

In a nuclear reactor, neutrons are produced from epithermal energies (below thermal energies) to ultrafast energies of about $10^{11}$ eV. Fast neutrons (1-10 MeV) are
generally not harmful to organic tissue or electronic components since the cross section for fast neutron capture is extremely low for most elements. In addition, since neutrons do not encounter Coulombic charge interactions with matter, the mean free path of fast neutrons is extremely long, and they pass through most organic material readily. However, fast neutrons are slowed to thermal energies by elastic collisions with atomic nuclei. These collisions are more effective with decreasing nuclear size. Hydrogen-containing materials, including most organic polymers, are most effective in thermalizing neutrons. Effective neutron shielding materials can be made of hydrogen-containing materials that have 1) elements with a large neutron capture cross section for a range of neutron energies and 2) a high concentration of neutron absorbing nuclei. In addition, increasing the thickness of shielding materials provides a greater volume in which to slow neutrons to thermal energies.

In this work, neutron capture experiments focused on boron-10, an isotope of boron (19.8% natural abundance) with an unusually large thermal neutron capture cross section, about 3838 barns. The neutron capture nuclear reaction is summarized in Figure 4. Boron-10 absorbs a neutron, forming a compound nucleus excited state \(^{11}\)B atom, which
\[ ^{10}\text{B} + ^{1}\text{n} \rightarrow [^{11}\text{B}] \ 6\% \rightarrow ^{7}\text{Li} + ^{4}\text{He} + 2.79 \text{ MeV} \]

\[ 94\% \rightarrow ^{7}\text{Li}^{*} + ^{4}\text{He} + 2.31 \text{ MeV} \]

\[ \rightarrow ^{7}\text{Li} + \gamma + 2.31 \text{ MeV} \]

Figure 4. Boron\((n,a)\) nuclear reaction.

instantaneously breaks apart into an energetic lithium atom and alpha particle. The capture products, lithium and an alpha particle, are not radioactive and are easily stopped. The energy of these atomic particles, about 2.4 MeV, is dispersed over a radius of only about \(10\AA\) in tissue.\(^{10}\)

Boron-containing polymeric materials are excellent candidates for neutron shields. Polymers, composed of mostly carbon and hydrogen, can slow intermediate-to-high energy neutrons to thermal energies. Boron can stop thermal neutrons with a relatively high efficiency because of its high neutron capture cross section. Ideally, thick polymeric materials with high boron content should provide good protection from neutrons of a range of energies. In addition, the higher the boron content, the greater the neutron attenuation. For cost-sensitive applications where volume and weight savings are critical, boron-containing polymeric materials can provide a combination of good
performance with a low cost/volume ratio.

1.3 BORON-CONTAINING MATERIALS

1.3.1 CARBORANE POLYMERS

Introduction

Most of the early work on incorporating icosahedral carborane moieties into polymers can be attributed to large-scale industrial laboratory efforts in the 1960's. Reasons for the research and development of carborane polymers include improving thermal stability, resistance to oxidative degradation, and resistance to chemical attack. The rationale for these characteristics lies in the crystalline lattice of carborane which, in addition to its inherent structural stability, acts as an energy sink, absorbing thermal energy from adjacent bonds in the polymer. Several promising carborane-polymers were discovered, most notably the poly(carborane siloxanes) developed by Green and coworkers.11-13

High-temperature, stable, carborane-based polymers, such as the "PNP" and "POP" polymers which have phosphorus-nitrogen-phosphorus and phosphorus-oxygen-phosphorus groups, respectively, between carborane groups in the polymer backbone had poor processibility, were insoluble in common
organic solvents, and were prohibitively difficult to synthesize. Polymers with sidechain carborane groups were easier to synthesize, but their thermal and mechanical properties suffered. These unwanted characteristics, coupled with the advent of high-temperature aromatic polyimides such as Kapton® and the LaRC™ polymer series, resulted in declining interest in carboranes as high-temperature, high performance polymers.

Although some of the research remains in proprietary databases, the published literature of polycarboranes ("carbaboranes" in the Russian literature) is extensive. A review of the chemistry of carboranes, in particular icosahedral carboranes, with emphasis on the synthetic routes, thermal and mechanical properties, and neutron absorbing capabilities follows. Carborane polymers are typically classified into two groups: Type I -- polymers with carbon-carbon carborane linkages and Type II -- carboranes with inorganic linkages. This discussion will be restricted to the organically linked carborane polymers.

Carboranes -- General Remarks

Carboranes, named for the two primary constituent elements, have been isolated in many different forms and formulas. The three most common classifications of carboranes are the nido carboranes, the arachno carboranes, and the closo carboranes. By far the most synthetically
important carboranes of the three types are the icosahedral carboranes of the closo family. The discussion of synthetic polymer chemistry is henceforth limited to the icosahedral carboranes.

**Icosahedral carboranes**

Icosahedral carboranes are clusters of boron, carbon, and hydrogen which have the general formula, \( \text{C}_2\text{B}_{10}\text{H}_{12} \). There are three isomers of these dicarbacloso-dodecaboranes, ortho-, meta-, and para-, in which the carbon atoms occupy respectively the (1,2), (1,7), and (1,12) positions in the dodecahedron lattice (Figure 5).\(^*\)\(^*\) Their preparation from decaborane and acetylene was reported by Grimes.\(^*\)

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**Figure 5.** Structures of 1,2-, 1,7-, and 1,12-\( \text{C}_2\text{B}_{10}\text{H}_{12} \).\(^*\)

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Isomerization of \( \text{o} \)-carborane to \( \text{m} \)-carborane occurs via a high temperature rearrangement at about \( 650^\circ \text{C} \).\(^*\) Heating of carborane to \( 700^\circ \text{C} \) produces a \( 75\%/25\% \) mixture of the meta and para isomers, which are separable on columns loaded with basic alumina using a petroleum ether mobile phase. Because
of the expense involved in isomerization and purification of p-carborane, the isomer is no longer produced commercially. For this reason, discussion of the icosahedral carboranes will be limited to that of m-carborane and its extensive derivative chemistry.

Although the chemistry of the ortho isomer is best known, extensive derivative chemistry has been reported for all three isomers, including reactions to form diol, diacid chloride, diazide, dichlorosulfonate, dihydroxymethyl, dianhydride and diamine functional groups. The difunctional carborane monomers can be homo- or co-polymerized to form a variety of polymers including polyformals\textsuperscript{17}, polyesters\textsuperscript{18-20}, polyethers\textsuperscript{21}, polyamides\textsuperscript{22}, polysulfones\textsuperscript{23}, polyacrylates\textsuperscript{24}, polyurethanes\textsuperscript{25}, and polyimides\textsuperscript{26,27}. Meta- and para-carborane isomers are of greater versatility for synthesizing thermally stable polymers owing to decreased steric interactions of the bulky carborane polyhedron. In addition, Papetti and coworkers\textsuperscript{28} have reported that o-carboranes can undergo cyclization to yield exopolyhedral ring structures (Figure 6), especially when the o-carboranyl group is attached to silicon in siloxane monomers. Poly(carborane siloxanes) containing m-carborane groups in the polymer backbone have found the most utility, and their thermal and mechanical properties are best characterized.\textsuperscript{29}
Today the polymer chemistry of the icosahedral carboranes is limited to reactions involving m-carborane moieties for their synthetic utility, ability to generate long-chain linear polymers, and lower cost when compared to the para isomer.

**m-carborane-containing polymers**

Linear polymers containing m-carborane groups possess outstanding thermal stability and more synthetic facility than those with o-carborane units in the polymer backbone. Carborane polyamides and polyimides in particular are stable to over 250°C in air and are processible into thin films. Polyimides having phenylene rings display markedly higher thermal stability than their polyamide counterparts. The polymerization of carborane polyimides has been reportedly achieved starting from m-carborane-1,7-diamine and dianhydrides.
The first m-carborane-containing polyamides were synthesized by Korshak and coworkers in 1969. The reaction of m-carborane-1,7-diacid chloride with various diamines was studied extensively in the following years. The objective of this early work was to develop polymers with unusual thermo-oxidative stability and solubility in a variety of common organic solvents. Reaction conditions were studied, including the influence of solvent on the molecular weight and morphology of the polymers. Preparation of polymers in amide solvents yielded low molecular weight polymers, owing to the high activity and poor selectivity of the carborane acid chloride. Transparent m-carborane polyamide films were cast, and the increased vulnerability of the amide bonds to cleavage in the presence of water was noted.

The present study examines the synthesis and characterization of several carborane-containing polyamides not previously reported in the literature. Solubility in various solvents was investigated, as well as determination of the thermo-oxidative stability and properties of films cast from tetrahydrofuran.

An additional goal of this work was to prepare polyamides with a range of hydrogen/boron ratios. Since neutron attenuating polymers contain large amounts of hydrogen to slow fast neutrons to thermal energies,
investigation of the hydrogen content in polymer with naturally high boron content is a reasonable task. Thin films cast from concentrated solution were evaluated for creasability, brittleness, color, and transparency. Evaluation of the polyamides prepared as described in the Experimental section as neutron-shielding materials would be straightforward.

1.3.2 FILLED EPOXY RESINS

The polymer chemistry of epoxies has been known for over thirty years. The reader is referred to several excellent reviews of epoxy polymers and their history, preparation, and rich derivative chemistry.36-39

Epoxies are thermosetting polymers which have high resistance to chemicals and solvents, exhibit tack and adhesion to a variety of different materials, and possess good electrical and impact properties. The primary uses of epoxies are as surface coatings and as structures in weight-bearing applications. Coating applications include automotive and aerospace primers, pipe and floor finishes, and applications where heavy wear resistance is required. Structural applications are found in the construction and electrical industries, as well as in composite materials manufacturing. About 300 million pounds per year of epoxy polymers are produced in the United States.40 Their
relatively low cost and the breadth of the processing science of epoxies explains why epoxy resins are one of the most widely used polymeric materials today.

In this study, an epoxy resin based upon the tetraglycidyl ether of methylenedianiline (TGMDA) premixed with a diaminodiphenylsulfone (DDS) crosslinking (or curing) agent will be evaluated for its basic structural and thermal properties when combined with boron powder. The repeat unit of the epoxy is shown within the dashed lines in Figure 7.

In addition to possibly improving mechanical properties, loading the epoxy with boron powder should produce a composite material with outstanding neutron shielding properties. Elemental boron powder contains almost 20% $^{10}\text{B}$, which has a high thermal neutron capture cross section, as discussed in Section 1.2 above. By combining the structural reinforcement and neutron absorbing features of boron powder with a thermally stable, chemically resistant epoxy matrix resin, load-bearing structural materials can be fabricated with a lower density than conventional metal building materials such as aluminum or steel. Several applications depend on weight and volume conservation in order to limit the cost of manufacture and functional use, including spacecraft and nuclear-powered ships. This work will investigate the attractive properties of boron-loaded epoxy composites and the possible use of the materials in several key applications.
Figure 7 Repeat unit of TGMDA epoxy resin crosslinked with DDS.
1.4 APPLICATIONS OF NEUTRON-SHIELDING MATERIALS

1.4.1 AEROSPACE

Spacecraft

The benefits of a lightweight, strong neutron shielding material in spacecraft applications are many. As discussed above, the outer hull of a spacecraft is exposed to ionizing radiation from galactic cosmic rays, which results in a cascade of neutrons, protons, and other sub-atomic particles within the hull materials. Exposure of electrical components and humans aboard manned space missions to neutrons results in damage to circuitry and tissues. Single event upsets and permanent damage to even radiation-hardened components can jeopardize missions. In addition, protection of human occupants of space vehicles from secondary particles can lower the incidence of cancer and other health problems.41

The materials used to build spacecraft must serve more than one purpose (neutron shielding) to be cost effective. Because of shrinking NASA space budgets, developing materials which can function as structural members as well as neutron shields is critical. One overriding criterion in the design of materials for spacecraft construction is that they be lightweight, yet strong. In this study, low-density, boron-containing polymeric materials with good
mechanical properties and neutron absorption are investigated.

High-altitude aircraft

Airplanes which cruise at high altitudes have a small, yet significant exposure risk to ionizing radiation from GCR. One recent Federal Aviation Administration study estimated dose equivalents for nonstop one-way flights of long duration. The results are found in Figure 8. The long, transoceanic flights from New York to Tokyo and from Athens to New York had the highest dose equivalents (99, 93 microsieverts respectively). These intercontinental flights typically fly at altitudes from 30,000 to 38,000 feet. The exposure risk of continuous service on these high-altitude flights is a factor to consider for aircrews and pregnant women, and the FAA study provides recommendations to minimize exposure to the effects of GCR.

Secondary shielding may be needed in the future for high-altitude aircraft. The NASP (National Aero-space Plane) and HSR (High Speed Research) aircraft were designed to travel at ultra-high altitudes. HSR aircraft may fly at altitudes up to 70,000 feet with more than double the exposure dose to ionizing radiation. Neutrons produced from cascade reactions of aircraft fuselage materials with GCR can be effectively shielded with materials with a high boron content. This study will examine the effectiveness of
Figure 8 Dose equivalents from galactic cosmic radiation received on air carrier flights.\textsuperscript{42}

boron-loaded epoxy samples and boron-containing polyimide films in absorbing incident thermal neutrons. (The cost considerations that apply to spacecraft also pertain to commercially-produced aircraft with shielding materials.)
1.4.2 NUCLEAR-POWERED SHIPS

Polymeric materials with excellent thermal, mechanical and chemical resistance are good candidates for service on nuclear-powered surface ships and submarines. Volume is a crucial quantity to be considered in ship design, especially in submarines. Low-density, high performance polymers can serve as replacement structural members in some noncritical applications ships. Although weight savings is not as important as volume savings, polymeric composites may eventually find use in marine environments.

Nuclear-powered ships are designed with multiple safety mechanisms in order to prevent exposure of the crew to radiation. In particular, nuclear submarines have several layers of neutron-absorbing materials which reduce the background radiation level to well below surface background levels.43

Although information on the precise volume of shielding materials currently in use is classified, it is estimated that a thickness of several inches of each type of shield exists in state-of-the-art shielding design on nuclear submarines. These layers may include but are not limited to polyethylene, borated polyethylene, hafnium-plating, and lead. A typical arrangement of these layers is shown in Figure 9. Polyethylene has a high hydrogen content, and serves to slow fast neutrons to thermal energies. The boron
in borated polyethylene absorbs the thermal neutrons, forming nonradioactive products which are trapped in the matrix. Lead is typically used for protection from gamma rays, which are produced in large, energetic amounts in nuclear reactors. Finally, hafnium coating provides strength and material integrity while absorbing slow
neutrons.

Polymeric materials with higher boron loadings than borated polyethylene can absorb neutrons more effectively with less volume. In this work, boron-containing epoxy materials will be shown to possess outstanding neutron absorption in a small material thickness.

1.4.3 ACCELERATOR FACILITIES

Electron accelerators and nuclear reactors used in boron-neutron cancer therapy (BNCT) produce a small number of neutrons from collisions of accelerated particles with the inner walls of the devices. Neutrons, having a long mean free path because of their neutral charge, can escape the matter of the accelerators and cause a small but measurable flux in the outside environment. Although the flux of neutrons that emerge from the primary shielding materials is low, the need for some shielding from the neutrons exists.

Materials developed in this work can be applied to shielding of neutrons from accelerators. Polymeric materials with a high boron content may be used to reduce the level of neutron radiation to below background levels.
2.1 BORON-EPOXY COMPOSITES

Achieving a high boron concentration in polymeric materials is not trivial. There are at least two approaches: chemically bonding boron-containing moieties into the polymer chain, and physically mixing a boron-containing compound into a polymeric matrix. The former is an ideal method to achieve a homogeneous polymer system with well-defined properties, albeit with stoichiometrically determined limits on the weight percentage of boron. The second option consists of physically mixing a high-boron material, either fibers (such as boron or boron nitride) or powders (such as elemental boron) into a polymer matrix and crosslinking or otherwise solidifying the mixture. One question that arises with physically mixing two or more different materials together is whether or not there is good consolidation of material with optimum polymer properties.

This experimental section describes the fabrication and synthesis of some boron-containing polymeric materials by each method above. Characterization of each new material by
composition, heat resistance, and mechanical properties was undertaken.

Neutron absorptive properties were investigated in an effort to determine if the materials could be effective neutron shields.

MATERIALS

Crystalline 250-micron boron powder, 99.9+%, and two grades of amorphous submicron boron powder, nominally 90% and 99% purity, were purchased from Johnson Matthey Catalog Co. (Ward Hill, MA). Crystalline, 20-44 micron boron carbide, 99.999% pure, was purchased from Noah Technologies, Inc. (San Antonio, TX). All powders were vacuum dried at 115°C for at least 24 hours before use. The purity of the 90%-labelled amorphous boron was determined from inductively coupled plasma (ICP) measurements to be 87.0% boron. The principal impurity was magnesium. The ICP method could not be used for the crystalline powders because of their insolubility in concentrated acid solutions necessary to the method.

A tetrafunctional epoxy resin, EA 934, was purchased from ICI/Fiberite, Inc. (Tempe, AZ), stored under cold conditions, and used as received. The resin contained a diaminosulfone curing agent in a pre-mixed form, therefore necessitating storage in a freezer to prolong the shelf life of the resin. Elemental analysis conducted at NASA-Langley
Research Center revealed that only carbon, hydrogen, nitrogen, oxygen, and sulfur were present.

2.1.1 FABRICATION AND PROCESSING

Hot-melt processing

Boron-containing epoxy resin materials were processed in an 8.125-inch square welded steel mold. Part thicknesses were chosen from the range of 0.375 to 0.700 inches in order 1) to minimize processing time and 2) to maximize the number of mechanical test specimens that could be cut from each plaque. Thicker plaques could be made; however, the processing time required would preclude fabrication of void-free parts, owing to the reaction rate of the epoxy resin at mixing temperatures. Boron powder was added to measured amounts of epoxy in nominal percentages from 5 to 20% by weight. Density calculations were used to determine the volume of each part, and all parts were between 0.375 and 0.700 inches thick.

A typical procedure for processing a powder-filled epoxy composite material is as follows. First, the mold was release-coated with Frekote 44N (The Dexter Corporation, Seabrook, NH), a hydrocarbon-based release agent spray, and heat-treated according to the manufacturer's specifications. The epoxy resin was then placed in the mold and heated to 57°C under vacuum until all entrapped air was eliminated, typically 0.5-1.0 hours. Boron powders were thoroughly
mixed with the resin in the mold while at 57°C, a
temperature at which the resin is fluid enough that thorough
mixing was possible. The mixture was placed in a vacuum
oven and deaerated at 57° to 62°C under vacuum until there
was no visual evidence of entrapped air. The boron-epoxy
mixture was then placed in an air convection oven under
moderate air flow and the temperature was increased to 121°C
at 2°C/min. Following a one-hour hold, the temperature was
increased to 177°C at 2°C/min and held for two hours. This
cured material was cooled overnight to ambient temperature
and removed from the oven. Both the neat epoxy and the
boron-containing epoxy materials appeared to be well-
consolidated.

Density measurements were made by weighing machined
specimens of each material in and out of water and carefully
recording the volume changes. Ultrasonic C-scan analyses
were conducted at NASA-LaRC using a computer-controlled
Panametrics, Inc. (Waltham, MA) ultrasonic scanning
instrument with software from Sonix, Inc. (Springfield, VA).
The transducer frequency was 10 MHz and C-scans indicated
that the parts were essentially void-free (See Figure 10).
Actual boron concentrations in the cured materials were
determined by a Thermo Jarrell Ash (Thermo Instruments
Systems, Inc., Franklin, MA) AtomScan 25 inductively coupled
plasma (ICP) elemental analyzer. In this spectroscopic
method, acidic solutions are prepared of each sample for
injection into the ICP instrument. Concentrations of crystalline powders in the epoxy could not be explicitly determined owing to the insolubility of the crystalline powder in strong concentrated acid solutions necessary for analysis. The actual concentrations were estimated to be close to the theoretical weight percent of crystalline boron powder combined with the actual weight percent amorphous boron powder. This approximation produced negligibly small
errors in the data.

**Powder processing**

934 Epoxy resin was ground to a fine powder using a mortar and pestle in a walk-in freezer. The freezer provided a low-humidity, cold (-18°C) environment in which to grind and mix the brittle epoxy. The powdered epoxy was sifted through a 0.0625 inch mesh and weighed. Amorphous, submicron boron powder was added to powdered epoxy in nominal weight percentages of 10 and 20%. The boron-epoxy mixture was ground in the mortar in order to achieve a smaller average particle size, and transferred to a mold prepared as above.

The mold was placed in a vacuum oven and deaerated at approximately -18°C for twenty hours under vacuum. After eliminating air from the material, the vacuum oven containing the loaded mold was removed from the freezer. The sample was warmed to ambient temperature while still under vacuum in the oven. The material was heated to 65-75°C and allowed to settle. When bubbling of the material ceased, the mold was transferred from the vacuum oven to an air convection oven and heated under atmospheric pressure according to the cure program above, i.e., 2°C/min. to 121°C, hold one hour, heat 2°C/min. to 177°C, hold for two hours, cool to ambient temperature and remove from the mold. The neat epoxy and boron-containing epoxy materials appeared to
be well-consolidated and of similar thickness as plaques described above. Ultrasonic analysis indicated that the parts were mostly void free, with pin-hole voids only on the surface of the material.

**Solution processing**

Five percent solutions of epoxy resin were made by slowly dissolving the epoxy in a suitable solvent (such as acetone) in a 1-L volumetric flask under nitrogen. The yellow-gold solutions were allowed to stand overnight. Boron powder was weighed into 300 mL beakers in 0.63, 1.25, and 2.5 gram amounts and 200 mL of epoxy/acetone solution was added carefully to each beaker. Mixing was accomplished with a mechanical stirrer equipped with a 4-blade steel rotor. Most of the solvent was evaporated in air at room temperature to a minimum volume, then the mixtures with little residual solvent were transferred to weighed, release-coated aluminum pans. Following additional solvent evaporation, the materials were placed in a vacuum oven at ambient temperature and deaerated under vacuum. The samples were heated to 65-75°C under vacuum. After deaeration at 65-75°C, the materials were heated according to the cure program described above and removed from the convection oven after cooling to ambient temperature.

The solution-processed boron-epoxy materials were generally poorly consolidated and large voids were observed,
probably owing to entrapped solvent in the cross-linked polymeric material. The rate of solvent release from the material was crucial to achieving a well-consolidated, void-free cured epoxy panel.

Acetone and acetonitrile are solvents for the epoxy. Acetonitrile has a lower polarizability (6.4 x 10^{-24} cm^3 vs. 4.4 x 10^{-24} cm^3) than acetone, and it has less ability to hydrogen-bond to the epoxy resin during cure, owing to the presence of a much weaker hydrogen-bonding substituent. In addition, acetonitrile is less volatile than acetone, as it evaporates more slowly under vacuum. As a result, evaporation of acetonitrile from the solvent-laden boron-epoxy mixture is less likely to cause bubbling of the cured composite part. For these reasons, acetonitrile proved to be the solvent of choice for the solution processing method. Small, cured epoxy samples have low void content when processed by the solution method with acetonitrile as solvent. However, voids could not be sufficiently minimized to yield composite materials with excellent consolidation. Thoroughly drying the powders, degassing the solvent, and completely deaerating the epoxy resin dramatically improve the quality of the composite.

2.1.2. THERMAL CHARACTERIZATION

Differential scanning calorimetry (DSC)

DSC scans were conducted using a Perkin-Elmer DSC 7
differential scanning calorimeter in an effort to determine the glass transition temperature \( T_g \) and thermal performance curves of the cured boron-loaded epoxy materials. A true glass transition as strictly defined by Flory\(^2\) may not be observed in crosslinked epoxy-based polymers. The term "glass transition temperature" will be understood in this section to indicate the transition known as the softening point of the boron-filled epoxy materials. The samples were heated twice from 50° to 350°C at 20°C/min.

**Dynamical mechanical analysis (DMA)**

Dynamic mechanical analyses were conducted\(^3\) using a DuPont 982 Dynamical Mechanical Analyzer connected to a DuPont 1090 Thermal Analyzer system at NASA-Langley Research Center. The DMA specimens were dried in vacuum at 80°C, and weighed to constant weight. The specimen dimensions were measured carefully with digital calipers and the initial transmitted frequency of each mounted specimen in the analyzer was noted. The specimens were heated in air from ambient to 320°C at 5°C/min. The oscillation frequency of the DMA was recorded as 18 Hz, with an oscillation amplitude of 0.2 mm. The mechanical configuration of the DMA test module is shown in Figure 11.

The glass transition temperatures of the boron-loaded samples were calculated from the tangent line drawn between the two slopes of the frequency vs. temperature curve.
Thermogravimetric analysis (TGA)

Thermogravimetric analyses of the boron-loaded epoxy materials were conducted to study the chemical stability at high temperatures. The TGA curves were determined by heating in air from ambient to 650°C at 2.5°C/min using either a Shimadzu TGA-50 or a Dupont 9900 thermogravimetric analyzer. Heat resistance of these materials was determined by measuring the temperature at which weight loss was 5, 10, and 50%.

The amount of char yield of each boron sample was calculated theoretically for complete combustion. The
amount of char, presumably boron oxide, B₂O₃, remaining might yield information about how these boron-epoxy materials degrade in a harsh thermal environment. As expected, higher boron loadings produced incrementally larger char yields. Calculations to determine whether the char was pure B₂O₃ were inconclusive. The amount of sample remaining after TGA analysis was insufficient for elemental analysis.

**Thermomechanical analysis (TMA)**

Thermomechanical analyses were conducted to determine the Tᵢ and coefficient of thermal expansion (CTE) of each sample. Samples measuring 36 mm² in area and 3 mm thick were tested using a Shimadzu TMA-80 thermomechanical analyzer in penetration mode. Three samples of each material were heated from ambient to 350°C at 5°C/min. in air and the expansion coefficients were determined in the range from 80°C to 130°C.

**Dilatometer measurements**

A high-precision, Fizeau-type laser-interferometric dilatometer system⁴ (see Figure 12-A) was used to determine the CTE of two boron-loaded epoxy materials, 10% and 20% boron by nominal weight percent. Figure 12-B shows the sample configuration in the holder used in measuring each material's coefficient of thermal expansion, with a suitable reference material present to generate the necessary
interference pattern. The reference materials used for boron-epoxy CTE determination were quartz rods, with well-defined thermal behavior. The data were collected and plotted as thermal strain vs. temperature. From these plots, the coefficients of thermal expansion were plotted vs. temperature in °F.

2.1.3. MECHANICAL PROPERTY CHARACTERIZATION

Compression tests

Specimens for compression tests were machined from the panels of cured polymer at NASA-Langley Research Center. The dimensions of the compression test specimens were 1.0" x 0.5" x 0.25". ASTM Method 695 "Compression Testing of
Plastics was rigorously followed in all tests. The specimens were instrumented with biaxial strain gauges measuring load (or stress) and strain. The instrumented samples were tested on a Baldwin-Tate-Emery 120-kip (120,000 lb. full scale) universal test plant connected to a SATEC Systems controller equipped with an Analogic ANDS 5400 series data acquisition system to record the data from the strain gages. Each boron-loaded epoxy specimen and pure epoxy was tested. Poisson's ratio was calculated for each specimen as well as ultimate compressive strength and modulus. In addition to stress and strain, a calibrated displacement transducer (from either Trans-Tek, Inc.,
Ellington, CT or Hewlett-Packard, Rockville, MD) measured the change in length of sample with respect to time (dc/dt) to supplement the strain gage data (See Figure 13). The fractured pieces of each specimen were retrieved whenever possible for fracture analysis.

**Tension tests**

Tension dogbone specimens were machined from cured boron-epoxy panels according to ASTM Method 693D "Tensile Testing of Plastics." Each dogbone was instrumented with two biaxial strain gauges mounted on each flat side at the center of the gage length. The gage length of all specimens...
was no less than four inches. The specimens were tested using a 10,000 lb. Instron test mechanical test plant equipped with an Analogic ANDS 5400 series data acquisition system to record data from the strain gauges. A few tension dogbones fractured outside the gage length and were omitted from the data. The dogbones were modified with two tabs on each end to prevent slippage when mounted in the test fixtures (See Figure 14). The fractured pieces of each specimen were retrieved for failure analysis.

**Flexure tests**

Flexural test specimens were machined from boron-epoxy plaques to 6" x 0.5" x 0.25" according to ASTM Method D790-
The specimens were not instrumented with strain gages because of the sample geometry; however, the strain was measured with a dc/dt probe. An MTS Systems model #661.23A-01 50-kip (50,000 lb. full scale) mechanical test plant was used with a 1000 lb. load cell mounted in series in order to achieve a 100 lb. full scale load at the lowest setting. An MTS Systems model 458.20 microconsole controller connected the MTS 50-kip test plant to an Analogic ANDS 5400 series data acquisition system. Careful calibration and electronics checks ensured accurate data. A four-pronged cell mount was utilized to center the breaking stress of each specimen (See Figure 15). Load was plotted vs. percent boron loading and normalized against the neat resin. The fractured pieces of each specimen were collected and analyzed for possible fracture mechanism.
2.2 BORON-CONTAINING POLYAMIDES

MATERIALS

M-carborane (99+% pure) was purchased from DEXSIL, Corp. (Hamden, CT), and used without further purification. 1,8-Diaminooctane, 1,10-diaminodecane, and 1,12-diaminododecane were purchased from Aldrich Chemical Co. (Milwaukee, WI), and vacuum fractionally distilled prior to use. 4,4'-Oxydianiline, 4,4'-methylenebis(dimethylaniline), 4,4'-methylenebis(diethylaniline), and m- and p-
phenylenediamine were purchased from Aldrich and recrystallized from ethanol prior to use. Dimethylacetamide (DMAc) and tetrahydrofuran (THF) were either HPLC grade or were distilled from calcium hydride and stored under nitrogen with molecular sieves prior to use. N-Butyllithium was purchased in a Sure-Seal® bottle from Aldrich as a 2.5 M solution in hexanes. Pyridine was purchased from Fisher Scientific, Inc. (Pittsburgh, PA) and used as received. Phosphorus pentachloride, 95%, and triethylamine, 99+%, were purchased from Aldrich and used as received.

MONOMER PREPARATION

M-carborane was functionalized to the dicarboxylic acid dichloride for polymerization with aliphatic and aromatic diamines. A typical procedure with modifications9,10 is as follows.

Preparation of m-carborane-1,7-dicarboxylic acid9 (Fig. 16)

10.0 grams (0.0694 mol) of m-carborane dissolved in 100 mL dry ether were charged into a 250-mL 3-neck round bottom (RB) flask equipped with a magnetic stirrer, nitrogen inlet/outlet, and an addition funnel capped with a rubber stopper. A large rubber stopper was inserted into one neck to facilitate addition of gaseous reagents. The flask was cooled to -10 to -5°C with an ice/acetone bath, and the solution was stirred for 0.5 hours. 56 mL (0.1387 mol) of
n-butyllithium in hexanes was added rapidly (1 mL/second) with stirring. The mixture was stirred for 1 hour, then gaseous carbon dioxide was bubbled rapidly into the solution for 0.5 hour. The mixture was acidified with dilute (10%)
hydrochloric acid, extracted with ether and separated with a separatory funnel. The extracts were dried over magnesium sulfate and the solvent evaporated to yield a yellow liquid, which was recrystallized from toluene to yield a white powder, m-carborane-dicarboxylic acid, m.p. 202-204°C. Yield: 75% of theoretical. Calculated: C 20.69%, H 5.20%, B 46.55%, O 27.56%, found: C 20.85%, H 4.63%, B 43.47%, O 31.05%. IR: O-H, 3150-2950 cm\(^{-1}\) \(\text{b, s}\), C-H 2900-2850 cm\(^{-1}\) \(\text{b, s}\), B-H 2632 cm\(^{-1}\) \(\text{m, s}\), C=O 1726 cm\(^{-1}\) \(\text{b, s}\), C-O 1418, 1277 cm\(^{-1}\) \(\text{m, s}\).

**Preparation of m-carborane-1,7-diacid chloride** (Fig. 16)

7.5 grams (0.0322 mol) of m-carborane-1,7-dicarboxylic acid were charged into a 500-mL 3-neck RB flask equipped with a magnetic stirrer, water condenser, and nitrogen inlet/outlet. 300 mL of ether were used to aid the transfer. To the stirring solution were added 14.4 grams (0.0645 mol) of phosphorus pentachloride (95% pure, 2% excess). The mixture was refluxed for 5 hours, over which time most of the solvent evaporated. The black oily residue was vacuum fractionally distilled at \(<1.0\) Torr (b.p. 103-105°C) twice to afford a white crystalline solid, m-carborane-1,7-diacid chloride, m.p. 26-28°C. Yield: 8.50 grams, 98% of theoretical.

Purification of the diacid chloride of m-carborane is difficult and tedious. It involves distilling the crude
reaction product twice via fractional distillation with a packed column under <1.0 Torr pressure vacuum. Since the diacid chloride is extremely reactive, storage under inert gas does not prevent the compound from reacting with advantageous water to form the acid. Reverse reaction of the acid chloride may not occur to both functional groups. However, if one group is converted to the carboxylic acid, functionalization of the monomer to the diamine is limited to low yields.

2.2.1 POLYAMIDE PREPARATION

All polymerizations were carried out under dry conditions in nitrogen in the presence of a HCl-acceptor such as triethylamine or pyridine. Use of pyridine as acceptor provided the simplest isolation of the resulting polymers, owing to pyridine hydrochloride's high solubility in water, the precipitating medium. A variety of aliphatic and aromatic diamines (See Figure 17) were purified and reacted with m-carborane-1,7-diacid chloride. The polyamides obtained from the polymerizations had a range of H/B mole ratios from 2.0 to 3.8. The weight percentage of boron in the polyamides was from 21 to 35%. A typical polymerization procedure with modifications is as follows (See Figure 18).
Figure 17  Diamines used in polyamide synthesis.
Polymerisation of $m$-carborane-1,7-diacid chloride and 4,4'-oxydianiline

To 1.4880 grams (7.43 x 10$^{-3}$ mol) of 4,4'-oxydianiline stirring in 80 mL of THF in a 100-mL 3-neck RB flask were added 3 mL of pyridine. 2.000 grams (7.43 x 10$^{-3}$ mol) of $m$-carborane-1,7-diacid chloride were added slowly to the solution. Stirring was increased to compensate for the increase in viscosity of the mixture. The temperature was kept at 20-25°C with a water bath. The reaction was allowed to stir for 8 hours, followed by precipitation into 1500 mL deionized water. The beige-white solids were filtered by aspiration and washed with 300 mL deionized water to remove residual salts. The polymer was collected, dried at 60°C overnight under vacuum, and weighed. Yield: 2.95 grams, 85% of theoretical.

2.2.2 STRUCTURE CONFIRMATION

The polyamides synthesized above were characterized structurally by solution $^1$H and $^{13}$C NMR with deuterated dimethyl sulfoxide using a General Electric QE-300 NMR (300 MHz for $^1$H), and by FT-IR spectroscopy using a Nicolet DX-20 FT-IR spectrometer (potassium bromide pellet). Excellent
quality KBr pellets were made from a pellet press assembly (Spectra-Tech, Inc., Stamford, CT) at 15,000 lb. of force in a hydraulic press. Typical NMR traces are found in Figures 19 and 20. FT-IR spectra for the polyamides are found in Appendix 1.
2.2.3 MOLECULAR WEIGHT CHARACTERIZATION

The weight average molecular weight, $M_w$, was found by gel permeation chromatography (GPC) using a Viscotek Model 222 HPLC pump connected to a Viscotek Model 200 viscometer and differential refractometer detector system. Two GPC columns were connected in series: column A was a Styragel divinylbenzene crosslinked polystyrene stationary phase.

Figure 19 $^1$H-NMR spectrum of MC-MDEA polyamide.
Figure 20 $^{13}$C-NMR spectrum of MC-MDEA polyamide.

(pore size 500 Å, mean particle size 10μm), manufactured by American Standards (Mentor, OH), designed to separate molecular weights from 1,000 to 80,000 g/mole. Column B, also a Styragel column (linear pore size, mean particle size 10μm), was designed to separate molecular weights from 1,000
to 1,000,000 g/mole. The carrier solvent was THF with a flow rate of 1.0 mL/min. The columns were calibrated with a series of narrow molecular weight distribution (MWD) polystyrene standards ranging from 4,075 to 184,200 g/mol. The calibration generated a Mark-Houwink plot of molecular weight vs. the constants K and a. A typical GPC trace, molecular weight calculations, and calibration curve are found in Figures 21-23.

Specific viscosity determinations were conducted at 25°C in an Ubbelohde viscometer (Thomas Scientific, Philadelphia, PA, No.1, #263) with DMAc as the solvent. DMAc was chosen as the solvent because its flow time of approx. 115 seconds was large enough to quantitate errors to less than 0.5%. Care was taken to measure the viscosities as quickly after dissolution as possible after temperature equilibration, owing to the decomposition of the polymer in DMAc over time.¹²
Figure 21: GPC Chromatogram of MC-1,12 DDA.

Concentration Chromatogram

MC-1,12 DDA

4,075 MW Std

RET VOL
Rescale HP-plot Label Print Overlay Bmove Erase
### PARAMETERS

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<td>Mp      = 1.456E 4</td>
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<tr>
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<td>Tau (V)</td>
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<tr>
<td>Threshold</td>
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### MOLECULAR WEIGHT VALUES

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<td>Mw (avQ) = 9.020E 3</td>
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<tr>
<td>Mn (no RI) = 2.715E 3</td>
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### Methods

**Method:** UCAL-BROAD

**Cal File:** mike1

**Integrated Detector Signals:**
- Baseline X Y
  - Conc (mv/mL) = 28.29 L. Visc 182 -20.89
  - Visc (mv/mL) = 31.12 R. Visc 286 -20.89

**Mark-Houwink Constants**

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<tr>
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<tr>
<td>IV (dl/g)</td>
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<tr>
<td>Viscotek Model #</td>
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<tr>
<td>R. Conc</td>
<td>301</td>
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**Polydispersity Ratios**

- \( M_z / M_n = 9.444 \)
- Skewness of Distribution = 5.737
- Skew(w) = 1.297

**VISCOTEK Model H200 Controller:**

- **Conc (mv/mL):** 28.29
- **Visc (mv/mL):** 31.12

**Integrated Detector Signals:**

- Baseline

- **Data Interval:** 3.240 sec
- **Sigma (mL):** 0.209
- **Tau (C):** 0.231
- **Tau (V):** 0.233
- **Threshold:** 0.020
Figure 23: GPC universal calibration curve.

VISCOTEX CORP.  UCAL 4.04
FILENAME: mikel

UNIVERSAL CALIBRATION PLOT

\[
\begin{align*}
A_0 &= 3.656 \times 10^1 \\
A_1 &= -3.735 \times 10^0 \\
A_2 &= 9.942 \times 10^{-2}
\end{align*}
\]
2.2.4 THERMAL CHARACTERIZATION

All polyamide powders were characterized thermally by DSC and TGA. To eliminate advantageous solvent, the powders were annealed at 150°C under vacuum for eight hours prior to analysis. The DSC scans were run over the temperature range 50-350°C at 10°C/min in a nitrogen atmosphere. Glass transition temperatures, melting temperatures, and onset of degradation were recorded. The TGA analyses were conducted in the temperature range from 100 to 650°C in air. The temperatures of five, ten, and fifty percent weight loss were recorded, as well as the temperature at which the polymer degradation began. Two polymers, MC-ODA-1 and MC-ODA-2, were analyzed a second time in argon because of a large net weight gain in air.

Characterization of polymer films

Thin films of each polyamide in THF solution were made using a doctor blade. Films were doctored onto clean, dust-free glass plates and placed in a dry-box under nitrogen at a flow rate of 50 mL/min. After drying to a firm consistency (5 days), the films were removed from the plates and evaluated for physical properties such as color, clarity, brittleness, and creasability.
2.3 BORON-CONTAINING POLYIMIDE FILMS

Kapton® is a high-performance polyimide with excellent chemical and thermal properties. Owing to its good mechanical properties, Kapton® can be fabricated into sheets, tape, and thin films. Kapton®'s low dielectric constant allows it to remain the polymeric binder of choice in the microelectronics industry. This combination of properties makes Kapton® very desirable for spacecraft applications. For these reasons, investigation of the effects of mixing boron powder into the polymer is important. The imidized polymerization product of 4,4'-oxydianiline and 1,2,4,5-benzenetetracarboxylic acid dianhydride was used as the laboratory counterpart to commercial Kapton®.

MATERIALS

4,4'-oxydianiline was purchased from Aldrich Chemical Co., recrystallized from ethanol, and vacuum dried prior to use. 1,2,4,5-benzenetetracarboxylic acid dianhydride was purchased from Aldrich, recrystallized from acetic anhydride, and vacuum sublimed immediately prior to use. Dimethylacetamide (DMAc) was purchased from Fisher Scientific, Inc., stirred with calcium hydride for 24 hours, and distilled before use.
2.3.1 SYNTHESIS

The polyamic acid precursor of the polyimide was synthesized from the room-temperature condensation of 4,4'-oxydianiline (ODA) with 1,2,4,5-benzenetetracarboxylic acid-dianhydride or pyromellitic dianhydride (PMDA). The reaction is summarized in Figure 24. The polymerization was carried out at ambient temperature with stirring in DMAc in a nitrogen atmosphere. A stoichiometric quantity of PMDA was added slowly to a stirring solution of ODA in a 500-mL round bottom flask cooled with a water bath. After addition of the monomers, the solution was stirred at RT for two hours, then stored in a freezer until film casting. The polyamic acid solution in DMAc was approximately 10 to 15% solids.

Thin films of polyamic acid in DMAc were spread onto clean glass plates with a doctor blade set to the desired thickness. The films were placed in a dry box under nitrogen (50 mL/min.) to evaporate most of the solvent. Thermal imidization was accomplished by heating the films to 100°C for 1 hour under forced nitrogen gas, 200°C for 1 hour in air, and 300°C for 1 hour in air. The polyimide films were removed from the glass plates under running water, dried under vacuum, and stored in a desiccator. PMDA-ODA polyimide films processed by this method were clear, strong, and creasable, but were of inferior quality compared to commercially available Kapton® film. Synthesized films from
0.002 to 0.006 inches thick had less strength and stiffness and were generally less homogeneous than commercial 0.003 inch thick film. One possible reason could be that the PMDA-ODA polyimide cast from polyamic acid had a lower molecular weight than commercial Kapton® film.

PMDA-ODA films containing amorphous, submicron boron powder were prepared by mixing boron powder with the polyamic acid solutions in concentrations ranging from 5 to 15% by weight. First, the boron powder was mixed with enough DMAc (about 25mL) to produce a slurry. The boron powder/DMAc slurry was added, with stirring, to known quantities of polyamic acid solution and agitated. The mixtures were spread onto clean glass plates as above and thermally imidized according to the temperature program described above. The boron powder particles were homogeneously spread throughout the cured polyimide films. Interestingly, x-ray photoelectron spectroscopic (XPS) analysis of the films revealed no boron on either glass or air surfaces of the film. This characteristic will be discussed in more detail in the Results section of this work. Boron-containing PMDA-ODA polyimide films were strong and creasable, yet were opaque owing to the brownish-black boron powder. Elemental analyses of 5% and 10% boron-loaded films are listed in Table 1.
Figure 24 Synthesis of PMDA-ODA polyimide.
Table 1. Elemental analyses of boron-loaded PMDA-ODA polypyromellitimide films.

<table>
<thead>
<tr>
<th></th>
<th>5% BORON</th>
<th></th>
<th>10% BORON</th>
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<tr>
<td></td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>Carbon</td>
<td>65.8</td>
<td>64.4</td>
<td>62.8</td>
<td>60.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.50</td>
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<td>Nitrogen</td>
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<td>Boron</td>
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<td>Oxygen *</td>
<td>19.9</td>
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<td>19.0</td>
<td>23.2</td>
</tr>
</tbody>
</table>

(* = by difference)

2.3.2 FILM CHARACTERIZATION

Fully cured neat PMDA-ODA polyimide films were characterized by FT-IR spectroscopy using a Nicolet 20DXB FT-IR spectrometer. Boron-containing polyimide films were analyzed by attenuated total reflectance (ATR) FT-IR using a 50mm x 10mm x 3mm KRS-5 thallium bromide dense crystal (International Crystal Labs, Garfield, NJ) as background. The angle of the crystal with respect to the infrared beam was 45°. The presence of the imide absorbances at 1786, 1730, 1380, and 730 cm⁻¹ and the absence of the broad amic acid -OH peak indicated that the polyamic acid was fully
imidized to the polyimide. (See Figures 25 and 26) The absence of water in the spectra was further proof that the polymer had fully reacted.
Figure 25 FT-IR spectrum of PMDA-ODA polyamic acid.
Figure 26 FT-IR spectrum of PMDA-ODA polyimide.
2.4 CARBORANE-POLYIMIDES

Synthesis of m-carborane-1,7-diamine was attempted via three pathways: direct "dry" method\textsuperscript{12}, direct "wet" method\textsuperscript{15}, and a "protected amine" synthesis (See Figures 27, 28). The direct methods utilized the Curtius rearrangement of a diazide to the diamine. The protected amine synthesis involved a Friedel-Crafts acylation mechanism followed by hydrolysis and neutralization to the free diamine. The following procedures describe the synthetic methods.

MATERIALS

Benzanilide and sodium azide were purchased from Aldrich Chemical Co. and used without further purification. Potassium hydroxide and hydrochloric acid were purchased from Fisher Scientific, Inc. and used as received. Toluene and acetone were distilled from calcium hydride and stored with molecular sieves under nitrogen.

Preparation of activated sodium azide\textsuperscript{16}

Activated sodium azide was prepared by moistening 20.0 grams of sodium azide with 1 mL 85\% hydrazine hydrate, mixing thoroughly, and letting stand for 12 hours or overnight. The solid was dissolved in a minimum amount of hot deionized water (typically about 40 mL) and precipitated into 1000 mL of cold acetone. The reconstituted white solids
Figure 27 Reaction schemes for "dry" and "wet" m-carborane(MC)-diamine synthesis.

were filtered, washed with 10 mL cold acetone and dried in air for 1 hour. The azide was active for about 24 hours.
Preparation of m-carborane-1,7-diamine via "dry" method\textsuperscript{12} (Fig. 27)

1.50 grams (0.00186 mol) of m-carborane-1,7-diacid chloride were mixed with 45 mL dry toluene and 8 grams (0.123 mol) of activated sodium azide and refluxed for 4 hours under nitrogen blanket in a 100-mL 3-neck RB flask. After cooling to room temperature, the mixture was filtered and washed with toluene. Evaporation of the solvent fraction to <5 mL and addition of 20 mL concentrated hydrochloric acid produced a black, oily residue. The mixture was heated to 65°C for 2 hours, then poured over ice/deionized water with stirring. After neutralization with potassium hydroxide, three ether extractions (500 mL total) were collected and dried over magnesium sulfate. Evaporation of solvent left a dark brown residue with light brown solids.

Preparation of m-carborane-1,7-diamine via "wet" method\textsuperscript{15} (Fig. 27)

To a stirring, nitrogen-filled 250 ml 3-neck RB flask containing 4.06 grams (0.015 mol) of m-carborane-1,7-diacid chloride in 75 ml dry acetone were added 8 mL of a 3.78 M. solution (0.030 mol) of sodium azide in water. After slow addition of the sodium azide solution, the mixture was kept below 15°C for 2 hours with vigorous stirring. The mixture was then poured into 1000 mL of deionized water. The volume of the aqueous filtrate was reduced to 300 mL with heating,
cooled in an ice bath, and clear crystals were collected.

Preparation of m-carborane-1,7-diamine via Friedel-Crafts method (Fig. 28)

To a mixture of 2.516 grams (0.0189 mol) of aluminum chloride in 100 mL carbon tetrachloride in a 250-mL 3-neck RB flask were added 2.52 grams (0.094 mol) of m-carborane-1,7-diacid chloride slowly with stirring. 3.685 grams (0.0188 mol) of benzanilide were slowly added and transferred into the flask with an additional 20 mL of carbon tetrachloride. The mixture was refluxed for 2 hours at 80°C and cooled. An ice/water solution was added and the dark brown carbon tetrachloride layer separated. 80 mL of 95% ethanol was added to the flask and the mixture refluxed for 2 hours with 110 mL of a 4.06 M potassium hydroxide, leaving a brown residue. Solids were collected from three fractions of the residue by filtration and stored for later analysis.
Figure 28 Friedel-Crafts m-carborane "protected" amine synthesis.
2.5 NEUTRON EXPOSURE

Irradiation of materials

Two types of amorphous, submicron boron-containing materials were evaluated as candidate materials for neutron absorption: thick epoxy plaques and thin PMDA-ODA polyimide films. The epoxy specimens measured 1" square and 0.125" thick. The polyimide films were from 0.001 to 0.003" thick and were cut into 1" squares. The boron weight percent loading in the epoxy materials was from 0% (neat epoxy) to 17.43%. The polyimide films contained 5, 10, and 15% nominal weight percentages of boron powder evenly dispersed in the polymer. All materials were well-consolidated and had no visible voids or occlusions, owing to careful processing described above.

Neutron exposure methods were designed and exposures were conducted at William & Mary. The neutron source for the exposures was a 5-Curie alpha particle plutonium/beryllium source contained in a paraffin block inside a five gallon metal drum (See Figure 29-A). The paraffin block served two purposes: to fix the source within the container and, more importantly, to slow down the resultant neutrons from the beryllium reaction. The nuclear reactions present in the source are summarized in Figure 30.

A nylon exposure rod was fitted with a bevelled collar a few inches from one end and a screw-down sample holder at
Figure 29-A  Schematic drawing of Pu/Be source container.

Figure 30  Principal neutron reactions in Pu/Be source.

\[
\begin{align*}
\alpha & \quad ^{239}\text{Pu} \rightarrow ^{235}\text{U} \rightarrow ^{235}\text{U} \text{ decay series} \\
& \quad \text{to } ^{207}\text{Pb} \text{ (stable)} \\
\alpha & \quad ^{9}\text{Be} + ^{4}\text{He} \rightarrow ^{13}\text{C}^* \rightarrow ^{12}\text{C} \text{ (stable)}
\end{align*}
\]
the other (See Figure 29-B). The top end of the rod and the metal drum were marked so that the sample orientation within the source did not change between exposures. Minimization of orientation effects on neutron irradiation was crucial to accurate data collection. The bevelled collar facilitated placement of the shielded samples in the source, thereby forming a tight seal with the drum.

Samples of boron-containing materials were sandwiched around 0.003" thick, square indium foils. The boron-indium-boron "sandwich" was then placed into the sample holder and held in place with two nylon screws. The nylon exposure rod was then placed in the source for twenty-hour exposures. This time was necessary to completely saturate the indium foils with slow neutrons, ensuring the maximum exposure and neutron absorption. The boron-loaded materials shielded the indium foils from interaction with neutrons to form $^{116}$In, a beta-emitting radioisotope with a 54-minute half-life (See Figure 31). After irradiation, the rod was removed, quickly disassembled, and the indium foil placed inside a thick lead enclosure for counting. A Model 580 Geiger-Muller tube counter (The Nucleus, Oak Ridge, TN) was used for tabulation of counts of the radioactive foils. Beginning at approximately ten minutes after removal from the source, the number of counts was collected at five minute intervals up to two half-lives, about 110 minutes. The logarithm of the number of counts was plotted vs. exposure time and
Figure 29-B Neutron exposure rod with sample mount.
\[ ^{115}\text{In} + n \rightarrow ^{116}\text{In}^* \rightarrow ^{116}\text{Sn} \text{ (stable)} \]

\[ t_{1/2} = 54 \text{ min} \]

**Figure 31** Counting reaction of beta-emitting indium isotope.

extrapolated to time zero, removal from the source (See Appendix 2).

After counting, the nylon rod and indium foils were tested with a hand-held Geiger counter to ensure that no latent radioactivity remained. Five hours after counting two half-lives of indium, no radiation was detected.

2.6 SURFACE CHARACTERIZATION METHODS

2.6.1 X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS) were conducted on samples of boron-filled epoxy composites and boron-containing PMDA-ODA polyimide films which were exposed to atomic oxygen in low Earth orbit (LEO). The samples were placed in the ram direction of Flight STS-51 of the Space
Shuttle for forty hours exposure to the LEO environment, whose principal component is atomic oxygen. The exposed samples and the control samples were analyzed at the Brisbane Surface Analysis Facility (BSAF) at the University of Queensland in Brisbane, Queensland, Australia. XPS was performed with a Perkin-Elmer (Eden Prairie, MN) PHI Model 560 ESCA/SAM instrument (See Figure 32) using soft x-rays to probe the surface composition. Surface penetration of the Kα x-rays of magnesium (1250 eV) produced emitted electrons from elements within 100 nm of the surface according to the photoelectron effect, and the electrons were detected and counted by a PHI Multiple-technique Analytical Computer System (MACS). The XPS data were plotted as intensity (arbitrary units) vs. energy of the recoil electrons.

2.6.2 STATIC SECONDARY ION MASS SPECTROSCOPY (SSIMS)

The same instrument was utilized with an optional SSIMS module to generate 5.0 nanoampere argon ions for surface characterization. The SSIMS instrument sputtered argon ions onto each boron-containing material’s surface and evaluated the secondary molecular ions generated from surface species
with a Perkin-Elmer PHI SIMS II detector. Carbon, nitrogen, oxygen, boron, sulfur were detected from the polymeric materials, and the major contaminant species detected were silicon and fluorine. SSIMS data were plotted as intensity (arbitrary units) vs. mass number. The XPS and SSIMS data are found in Appendix 3.
3.1 BORON-LOADED EPOXY COMPOSITES

Materials processing

Amorphous submicron boron, crystalline 250μ boron, and crystalline 20-44μ boron carbide powders were mixed with an aerospace-qualified epoxy resin according to the methods described in the experimental section above. The weight percentages of amorphous boron in the parts ranged from 3.95% to 17.43% as determined from inductively coupled plasma (ICP) measurements. Panels containing 10% and 20% nominal weight percent boron were made by mixing amorphous and crystalline boron powders (50% amorphous, 50% crystalline) together into the epoxy resin. Finally, boron carbide (B₄C) was mixed with the epoxy at 20% nominal loading. All composite parts were essentially void-free and of excellent quality. Table 2 lists the nominal weight composition of boron and designation of each boron-containing epoxy material. The ICP method could not be used to determine the amount of crystalline powders present in the epoxy owing to their insolubility in concentrated acid.
solutions necessary for sample preparation. The weight

<table>
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<th>DESIGNATION</th>
<th>MATERIAL COMPOSITION</th>
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<tr>
<td>0%B-Epoxy</td>
<td>pure epoxy resin</td>
</tr>
<tr>
<td>5%B-Epoxy</td>
<td>epoxy + 5% amorphous boron powder</td>
</tr>
<tr>
<td>10%B-Epoxy</td>
<td>epoxy + 10% amorphous boron powder</td>
</tr>
<tr>
<td>15%B-Epoxy</td>
<td>epoxy + 15% amorphous boron powder</td>
</tr>
<tr>
<td>20%B-Epoxy</td>
<td>epoxy + 20% amorphous boron powder</td>
</tr>
<tr>
<td>10%B-mix</td>
<td>epoxy + 10% boron (amorph. + cryst.)</td>
</tr>
<tr>
<td>20%B-mix</td>
<td>epoxy + 20% boron (amorph. + cryst.)</td>
</tr>
<tr>
<td>20%B$_4$C-Epoxy</td>
<td>epoxy + 20% crystalline boron carbide</td>
</tr>
</tbody>
</table>

compositions of crystalline powders were assumed to be close to the nominal percentages.

The reactive epoxy resins were processed by hot-melt, powder mixing, and solution mixing methods. Of the three mixing variations, the hot-melt method produced the most well-consolidated molded plaques with the fewest voids. Ultrasonic C-scan analysis revealed only a few pinhole surface voids in the final materials. The voids were not observable to the eye, and optical micrographs showed no voids over the bulk of the material (See Figure 33). The small black pits in the micrographs are due to pull-out voids created by the specimen polishing method, and are not
evident of entrapped air or volatiles in the material. Density measurements were in good agreement, in general, with the calculated densities. The densities of the epoxy resin and boron powders used in the calculations were: 1.30 g/cm³ (934 Epoxy), 2.35 g/cm³ (amorphous submicron boron), 2.37 g/cm³ (crystalline boron), and 2.52 g/cm³ (boron carbide). Table 3 lists the calculated densities and measured specific gravities of all boron-epoxy materials.
Table 3. Theoretical and actual densities (g/cm$^3$) of boron-epoxy materials.

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<th>MATERIAL</th>
<th>THEORETICAL DENSITY</th>
<th>ACTUAL DENSITY</th>
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</tr>
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</tbody>
</table>

One difficulty with the hot-melt processing method was the persistence of boron clusters within the continuous boron powder-loaded epoxy matrix. Optical micrographs taken at 500X magnification show relatively large clusters of pure boron powder (See Figure 34) with the rest of the boron dispersed evenly in the epoxy. Powder processing and solution processing were attempts to mix the boron powder more homogeneously into the epoxy. The effects of the clustering of the boron were reflected in mechanical test data (discussed in a later section of this document).

The powder processing method seemed to mix the boron powder more intimately with the crushed epoxy powder. The small particle size of the amorphous boron (0.6 μm) aided
the grinding of the epoxy to a fine powder. The cold processing environment was produced by a cyclical refrigeration unit, which resulted in periodic levels of high humidity during mixing. Consolidation during the cure program was hindered by large amounts of entrapped air and/or water vapor. The materials processed in this fashion required much longer deaeration times, and melt flow was further slowed by the cure reaction of the epoxy. The
composite parts produced were voidy and brittle. Estimated void content of materials mixed by this method was 2-10% by weight.

The possible causes of boron clusters in the epoxy were not explicitly determined in this study. Static electricity effects, in conjunction with surface tension of the boron powder were thought to produce the clustering of boron in the epoxy. One recent study found similar behavior for carbon black-filled polypyrrole composites. In an effort to minimize these effects, the epoxy was dissolved in a suitable solvent (acetonitrile), mixed with boron powder, and poured into shallow molds for curing. Most of the solvent was removed first by air flow, then under vacuum. Some solvent remained in the material, and this contributed to the extremely high void content of the finished composites. The cured composite parts processed by this method showed somewhat less clustering of the boron. However, the large voids in the parts prevented the consideration of solution processing as a way of achieving finely dispersed boron in the epoxy. Further attempts to produce void-free cured materials were unsuccessful.

**THERMAL PROPERTIES**

The thermal history and processing of polymeric materials have a profound effect on their properties. Panels
of boron-containing epoxy and neat epoxy resin were cured for two hours, including the time specified by the manufacturer required for post-cure. Thermal measurement methods such as DSC, DMA, and TMA are sensitive to the processing methods of thermosetting polymers such as epoxies. The glass transition temperature ($T_g$), percent crystallinity, ultimate strength and modulus are several parameters that are affected by cure program. DSC, DMA, TMA, and mechanical testing were the thermal characterization methods chosen to investigate these properties.

Glass transition temperatures of crosslinkable polymers, including epoxies, are changing constantly, theoretically owing to the presence of unreacted epoxide groups in the "cured" resin. (We will again use the term "glass transition temperature" instead of "second order transition" to mean the softening point of the crosslinked polymer system.) As epoxy resins are cured, the viscosity increases dramatically until vitrification. At this point, the curing agent molecules are not sufficiently mobile to reach unreacted epoxide groups. A principle in polymer synthesis is that optimum reaction conditions occur with equal accessibility of the functional groups. When reactive groups are isolated due to gelling of the matrix, the molecular weight and thermal properties are adversely affected. The concentration of unreacted species in epoxies
is dependent on the processing program. The $T_c$'s of epoxies are also affected profoundly by the cure rate, hold time and temperature of crosslinking. Some thermosetting polymers such as epoxies and cyanate esters exhibit much higher $T_c$'s than their cure temperatures. In general, the $T_c$ is higher for polymer systems crosslinked at higher temperatures and for longer hold times at final temperature. Since the epoxy materials developed in this study were crosslinked by the same cure program, the effects of cure temperature and hold time were virtually eliminated.

**Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) measures the heat released or absorbed by the sample relative to an empty sample pan. Heat is added or removed to maintain the sample and reference pans at the same temperature. Crystallization, glass transitions, and melting phenomena are recorded as exotherms, changes in slopes, and endotherms in the DSC thermogram. $T_c$'s were measured for boron-epoxy materials, and some qualifying remarks regarding these measurements follow.

Analysis of the neat epoxy isotherm at 177°C revealed that a high degree of crosslinking (or cure) was achieved after only 25 minutes (see Figure 35). The cure reaction was almost complete after 50 minutes, as indicated by the asymptotic levelling of the heat vs. time curve. Addition
Figure 35 DSC cure isotherm at 177°C of 934 epoxy resin.
of boron to the epoxy did not significantly affect the time required to reach full cure.

Glass transition temperatures were measured for multiple samples of each specimen of boron-containing epoxy material in an effort to determine the effects of the addition of boron powder to the epoxy. DSC curves of the boron-epoxy materials were determined at 20°C/min. in nitrogen in the range of 50-350°C. A typical DSC plot is shown in Figure 36. The relatively fast heating rate was selected to accent the transitions in the brittle, composite materials. Some authors have noted that heating polymer samples at a high temperature rate may drive the $T_g$ higher than the "true" $T_g$. However, since some of the cured epoxy samples did not show measurable transitions at slower heating rates (2 to 5°C/min), the faster rate was selected in order to observe the glass transition. Table 4 lists the glass transition temperatures determined by DSC of the
Figure 36: DSC thermogram of pure epoxy.

Sample Weight: 4.800 mg

- X1: 181.800 °C
- X2: 224.800 °C
- Peak: 194.083 °C
- Area: 32.449 mJ
- ΔH: 7.054 J/g
- Height: 0.181 mV

Temperature (°C)

Heat Flow (mW)
Table 4. Glass transition temperatures for boron-epoxy materials.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>$T_g^{\circ}C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% B-Epoxy</td>
<td>194°C</td>
</tr>
<tr>
<td>5% B-Epoxy</td>
<td>215°C</td>
</tr>
<tr>
<td>10% B-Epoxy</td>
<td>238°C</td>
</tr>
<tr>
<td>15% B-Epoxy</td>
<td>227°C</td>
</tr>
<tr>
<td>20% B-Epoxy</td>
<td>237°C</td>
</tr>
<tr>
<td>10% B-mix</td>
<td>243°C</td>
</tr>
<tr>
<td>20% B-mix</td>
<td>238°C</td>
</tr>
<tr>
<td>20%B$_4$C-Epoxy</td>
<td>244°C</td>
</tr>
</tbody>
</table>

neat resin and various boron-loaded epoxy materials studied. The $T_g$'s increase from 194°C for the neat resin to 244°C of the 20%B$_4$C-Epoxy. This trend reflects the hindering of movement of the epoxy polymer network with addition of filler. Heating the boron-epoxy materials to higher temperatures is required to observe softening. No crystalline melt endotherms nor crystallization upon cooling was observed, as is typical of amorphous crosslinked networks.

**Dynamic Mechanical Analysis**

Dynamic mechanical analyses (DMA) were performed on specimens of boron-epoxy panels containing 0% (neat resin),
10% boron, 10% mixed powders, 20% boron, 20% mixed powders, and 20% boron carbide (B$_4$C). DMA utilizes a pair of mechanical arms to exert a cyclical load on the sample at a given frequency. Investigation of the glass transition is a frequency-dependent measurement and hence does not depend on heat transfer to the degree that DSC does.

Sample specifications were used in this DMA study for comparison to NASA High Speed Research (HSR) materials. The HSR program goal is to develop new composite materials for high-speed high altitude aircraft. Several aerospace companies submitted test specifications for the HSR polymeric materials development, and the DMA specimens used in this study were machined and tested according to HSR criteria.

The glass transition temperatures of the materials were determined by drawing lines tangent to the linear portions of the frequency vs. temperature curve and extrapolating the point of their intersection to the temperature axis. The initial transmitted frequency was recorded for the boron-epoxy specimens in order to compare the data with duplicate samples exposed to high energy electrons. Table 5 lists initial frequency and $T_g$ data from the DMA measurements for the boron-loaded epoxy specimens.
Table 5. Initial DMA frequencies and $T_s$ for boron-epoxy materials.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>INITIAL $\nu_0$, Hz</th>
<th>$T_s$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% B-Epoxy</td>
<td>16.35</td>
<td>191</td>
</tr>
<tr>
<td>10% B-Epoxy</td>
<td>18.59</td>
<td>218</td>
</tr>
<tr>
<td>20% B-Epoxy</td>
<td>19.43</td>
<td>228</td>
</tr>
<tr>
<td>10% B-mix</td>
<td>18.64</td>
<td>229</td>
</tr>
<tr>
<td>20% B-mix</td>
<td>19.87</td>
<td>229</td>
</tr>
<tr>
<td>20%B$_4$C-Epoxy</td>
<td>21.19</td>
<td>235</td>
</tr>
</tbody>
</table>

The initial frequency ($\nu_0$) increases with increasing boron concentration in the epoxy. The neat epoxy has a $\nu_0$ of 16.35 Hz, while the 20% B$_4$C material has a $\nu_0$ of 21.19 Hz. There is a trend of increasing frequency in the boron-epoxy materials relating to the amount of crystalline powder present:

$20\% \text{B}_4\text{C} > (20\% \text{B-mix}, 20\% \text{B}) > (10\% \text{B-mix}, 10\% \text{B}) > 0\% \text{B}.$

This implies that with increasing crystallinity and boron loading in the epoxy, the more dimensional stability the composite material retains. The shape of the DMA curve changes slightly for the crystalline boron containing...
materials. Yielding before the glass transition occurs in materials with crystalline boron-containing powders. Figure 37 shows the difference in shapes of DMA curves of 20% B-Epoxy and 20% B-mix materials. The slope of each linear portion is not as clearly defined as for the amorphous boron materials. The glass transition temperature varies from 190°C of the neat epoxy to 235°C of the 20% B₄C-filled epoxy, an increase of about 45°C. Addition of boron-containing powders does not adversely affect the glass transition temperature of the epoxy resin.

Tensile storage modulus, loss modulus, and tan delta data for the specimens are found in Table 6. The storage modulus, e', is calculated from the slope of the stress-strain curve plotted by the DMA instrument. Boron-epoxy materials show dramatic increases in stiffness (modulus) relative to the neat epoxy.

Thermogravimetric Analysis

High-temperature stability of the boron-epoxy composites was measured with thermogravimetric analysis (TGA). Weight loss was plotted vs. temperature in the range of 100-650°C at a heating rate of 2.5°C/min in air. The temperatures at which weight loss was 5, 10, and 50% of original weight are found in Table 7. The 5% weight loss temperatures decrease with increasing boron concentration in the materials while the 50% weight loss temperatures
increase. The 10% weight loss numbers are ambiguous, probably owing to the high weight loss rate in that portion of the curves. The amount of char remaining
Table 6. Mechanical properties of boron-epoxy materials from DMA measurements.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TENSILE STORAGE MODULUS, GPa</th>
<th>TENSILE LOSS MODULUS, GPa</th>
<th>TAN DELTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% B-Epoxy</td>
<td>3.25</td>
<td>0.03</td>
<td>0.009</td>
</tr>
<tr>
<td>10% B-Epoxy</td>
<td>4.35</td>
<td>0.06</td>
<td>0.014</td>
</tr>
<tr>
<td>20% B-Epoxy</td>
<td>5.00</td>
<td>0.07</td>
<td>0.013</td>
</tr>
<tr>
<td>10% B-mix</td>
<td>4.28</td>
<td>0.10</td>
<td>0.023</td>
</tr>
<tr>
<td>20% B-mix</td>
<td>4.84</td>
<td>0.20</td>
<td>0.040</td>
</tr>
<tr>
<td>20% B_4 C-Epoxy</td>
<td>4.40</td>
<td>0.07</td>
<td>0.016</td>
</tr>
</tbody>
</table>

after heating to 650°C (see Figure 38) also increased with weight percent boron filler, as expected. As the organic epoxy degrades, the boron powder forms boron oxides, most probably B_2 O_3. The amount of ash was not sufficient for

Table 7. Thermal stability of boron-epoxy materials from TGA.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TEMP at 5% Wt. Loss (°C)</th>
<th>TEMP at 10% Wt. Loss (°C)</th>
<th>TEMP at 50% Wt. Loss (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% B-Epoxy</td>
<td>313</td>
<td>338</td>
<td>471</td>
</tr>
<tr>
<td>10% B-Epoxy</td>
<td>309</td>
<td>345</td>
<td>488</td>
</tr>
<tr>
<td>20% B-Epoxy</td>
<td>303</td>
<td>341</td>
<td>498</td>
</tr>
<tr>
<td>10% B-mix</td>
<td>292</td>
<td>339</td>
<td>498</td>
</tr>
<tr>
<td>20% B-mix</td>
<td>287</td>
<td>341</td>
<td>502</td>
</tr>
<tr>
<td>20% B_4 C-Epoxy</td>
<td>297</td>
<td>352</td>
<td>499</td>
</tr>
</tbody>
</table>
Figure 38 Graph of char yield vs. \% boron.

Elemental analysis. The 50\% weight loss temperature increases to about 500°C at the highest boron loading. Clearly, addition of boron to the epoxy does not adversely
affect the thermal stability of the composites.

Thermomechanical Analysis

In an effort to determine coefficients of thermal expansion (CTE), thermomechanical analyses (TMA) were conducted on boron-loaded materials in penetration mode. Uncertainty in the TMA test arises from surface preparation of the specimens. The smoother the sample surface, the more accurate the test because the penetration needle distributes the load uniformly on the surface. TMA on 5%B-, 10%B-, 15%B-, 20%B-, and neat epoxy were heated from ambient to 250°C at a rate of 5°C/min under constant load. The expansivity (CTE) of the materials was measured over a large temperature range to minimize the effects of noise in the TMA signal. It should be noted that the variability in the test for three samples of each concentration of boron was high. Figures 39 and 40 show the variability between individual runs of 10% and 20% B-epoxy. Table 8 lists the values of the CTE from TMA for
Figure 39  TMA graphs of 10% B-Epoxy runs.
Figure 40  TMA plot of 20% B-Epoxy runs.
Table 8. CTE values from TMA measurements.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>CTE, ppm/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%B-Epoxy</td>
<td>70.6 ± 1.5</td>
</tr>
<tr>
<td>5%B-Epoxy</td>
<td>69.8 ± 2.3</td>
</tr>
<tr>
<td>10%B-Epoxy</td>
<td>65.3 ± 0.4</td>
</tr>
<tr>
<td>15%B-Epoxy</td>
<td>66.1 ± 0.3</td>
</tr>
<tr>
<td>20%B-Epoxy</td>
<td>65.4 ± 1.1</td>
</tr>
</tbody>
</table>

each material. Addition of boron to the epoxy lowers the CTE by approx. 5°C. From the rule of mixtures, one would expect the CTE to decrease, owing to boron’s lower CTE (approx. 6 ppm/°C).

Dilatometer measurements

A Fizeau-type interferometer-dilatometer was used to measure coefficients of thermal expansion in order to supplement the TMA measurements above and to determine coefficients for the 10%B-mix and 20%B₄C-Epoxy materials. To measure CTE accurately, a wide temperature range is necessary. In addition, several factors influenced the CTE measurements from the interferometer: sample size, reference material, sample surface preparation, and shimming...
effects. First, sample size differences between the TMA and the interferometer could have had an effect on the CTE measured. The sample size for the TMA measurement was 6 mm$^2$ x 3 mm thickness, small compared to the size of the interferometer specimen (77 mm x 25.4 mm x 6.4 mm thickness). The larger the sample, the less effect sample inhomogeneities have on the measurement. Second, the reference rods play a large role in the interferometer determination of the CTE. The interference pattern has too many bands to count when the CTE difference between the reference material and the sample is large. For experimental materials such as the boron-filled epoxy, this factor limits the range over which the CTE may be determined. Sample surface preparation is important because of the mechanics of the test. If the ends of the specimens (Figure 41) are too rough, the accuracy of the test can be compromised. Finally, shimming a sample in order for its interference pattern to be counted against the reference may change the CTE value if the shim's CTE is markedly different from the sample. The quartz glass reference rods used in this experiment have a CTE of about 0.1 ppm/°C, or about two orders of magnitude less than the sample CTE. The temperature range over which the interference pattern was able to be counted was from 25°F to 125°F. Outside this range, the number of interference lines was too great to be counted. Care was taken to machine the sample ends to
smoothness to minimize roughness effects. Owing to differences in CTE between the reference and the sample, the 20\%B_{4}C-Epoxy specimen had to be shimmed with a polymeric material whose CTE was in the same range as the sample. The effects of shimming the sample were not corrected for in the test, and the measurement was not as accurate as the 10\%B-mix epoxy specimen.

Interferometric measurements were attempted for the full temperature range of the instrument, -150°F to 150°F. Data were not recorded over the entire temperature range owing to the fact that a suitable reference material at all temperatures was not available. Plots of CTE vs. temperature in degrees°F are found in Figures 42 and 43 for

Figure 41 Schematic diagram of interferometer-dilatometer sample.
Figure 42 Graph of CTE data for 10% B-Epoxy from dilatometer measurement.
Figure 43 Graph of CTE data for 20% B-Epoxy from dilatometer measurement.
the 10%B-mix and 20%B₄C-Epoxy materials.

Table 9 lists the expansion coefficients determined

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TMA CTE, ppm/C</th>
<th>Dilatometer CTE, ppm/C **</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%B-mix</td>
<td>65.3 ± 0.4</td>
<td>43.2 ± 0.8</td>
</tr>
<tr>
<td>20%B₄C-Epoxy</td>
<td>65.4 ± 1.1</td>
<td>44.1 ± 0.9</td>
</tr>
</tbody>
</table>

(** maximum probable error)

from the interferometer measurements and from the TMA runs for comparison. Coefficients of thermal expansion determined from this method were consistently lower than the average CTE determined from TMA measurements. However, the interferometer measurements were probably more accurate, considering the larger temperature scale and lower instrument noise of the test.

Addition of boron powder to the epoxy resin lowers the CTE of the neat epoxy by up to 5 μm/m°C. A decrease in the CTE from the neat resin was expected, although the magnitude of the change is larger than anticipated, considering the relatively small weight percent of boron.

The average values of the CTE of these boron-loaded epoxy materials are useful in determining the applicability
of such materials in structural components and hybrid structures. In particular, applications in which panels of boron-filled epoxy resin are bonded to steel, concrete, wood, or other plastic materials would require precise knowledge of the expansion coefficients for structure design.

MECHANICAL PROPERTIES

To evaluate the possible structural or reinforcement properties of the boron-epoxy materials, three mechanical tests were performed according to their respective ASTM Methods: tension, compression, and flexure tests.

Structural applications of polymeric materials may require excellent behavior under both tensile and compressive loads. However, some commercial composite materials lack this versatility. The optimum polymeric composite for a particular application is dependent ultimately on the requirements for reinforcement. Asphalt, a composite of tar and stone, can withstand extremely heavy loads in compression, but its tensile strength is low. Aromatic polymer fibers have outstanding strength in the axial direction under tensile loads, but are brittle in compression. Many composites are made with woven fiber fabric reinforcement to minimize the anisotropy of
unidirectional tapes. Powder-filled composites typically have less strength when pulled in tension than when loaded in compression.

This section describes the mechanical properties of the boron-filled epoxy composites processed above, and relates these data to the structural requirements of some neutron shielding applications.

**Tensile Tests**

Specimens of boron-filled epoxy were prepared according to the procedure discussed in Section 2. The boron-epoxy specimens as machined had a smooth, hard surface. Glass fiber-epoxy composite tabs (Section 2, Figure 14) were adhesively bonded to the ends of each dogbone-shaped specimen to prevent slippage when mounting the specimens in the tester. All tensile tests involved at least five specimens of each material and concentration. The materials tested were: neat epoxy (0% boron), 5%, 10%, 15%, and 20% amorphous boron-epoxy, 10% boron(mix)-epoxy, and 20% boron carbide-epoxy. Each specimen failed within the gage length, which indicates a true tensile test result. Figure 44 lists the tensile properties determined for each material.

The ultimate tensile strength (UTS) varies from 2.97 Ksi for the 10% B-mix epoxy to 8.36 Ksi for the neat resin. A plot of UTS vs. percent boron (Figure 46) for the amorphous boron-filled epoxy materials shows the dramatic
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>STRENGTH (Ksi)</th>
<th>MODULUS (Msi)</th>
<th>STRAIN (%)</th>
<th>POISS. RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%B-Epoxy</td>
<td>8.36 ± 0.63</td>
<td>0.58 ± 0.00</td>
<td>1.67 ± 0.12</td>
<td>0.37</td>
</tr>
<tr>
<td>5%B-Epoxy</td>
<td>8.25 ± 0.71</td>
<td>0.64 ± 0.01</td>
<td>1.09 ± 0.12</td>
<td>0.36</td>
</tr>
<tr>
<td>10%B-Epoxy</td>
<td>4.35 ± 0.55</td>
<td>0.72 ± 0.01</td>
<td>0.62 ± 0.09</td>
<td>0.36</td>
</tr>
<tr>
<td>15%B-Epoxy</td>
<td>4.11 ± 1.36</td>
<td>0.82 ± 0.00</td>
<td>0.51 ± 0.18</td>
<td>0.35</td>
</tr>
<tr>
<td>20%B-Epoxy</td>
<td>5.84 ± 0.25</td>
<td>0.94 ± 0.00</td>
<td>0.65 ± 0.02</td>
<td>0.34</td>
</tr>
<tr>
<td>10%B-mix</td>
<td>2.97 ± 0.43</td>
<td>0.70 ± 0.01</td>
<td>0.41 ± 0.06</td>
<td>0.37</td>
</tr>
<tr>
<td>20%BC-Epoxy</td>
<td>3.43 ± 0.15</td>
<td>0.78 ± 0.01</td>
<td>0.44 ± 0.02</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Figure 44 Tensile data for boron-epoxy materials.

decrease in strength in the composite materials. The strength decreases from 8.36 ksi of the neat resin to 4.11 ksi of the 15% B-epoxy, then rises to 5.84 ksi for the 20% B-epoxy material. The 10% mixed amorphous/crystalline boron-filled epoxy and the 20% B₄C-epoxy had low tensile strengths of 2.97 and 3.43 ksi respectively. These results were somewhat unexpected because the optical micrographs of these materials indicated less clustering of the amorphous boron powder and more homogeneous mixing of the crystalline particles (see Figure 45). A more uniform dispersion of the boron particles throughout the epoxy matrix should result in greater strength properties for the composite.

Powder-filled composites typically display low tensile strength properties owing to the fact that the filler particles act as stress concentration points in the
material. Clusters of filler particles generally have zero strength, so the stress is greater at these non-loadbearing points. The greater the number of stress points in a material, the less strength a material has and the shorter time to failure in tension.

These boron-epoxy materials have clusters of boron particles embedded in the epoxy matrix, as well as a uniform dispersion of boron throughout the epoxy. The clusters of

![Figure 45 Optical micrograph of 20%B\textsubscript{4}C-Epoxy. [200X]]
boron are essentially stress concentration points and serve
to lower the strength of the material in tension. Various

Figure 46 Tensile strength of boron-epoxy materials.
processing methods (See Section 2) were attempted to minimize the clustering. However, each of these methods, powder processing and solution processing, resulted in a higher void content of the composite material than hot-melt processing. The effect of boron clusters on the strength of boron-epoxy materials will be discussed further in the flexural testing section.

Addition of fillers, whether in fiber or particulate form, to a polymeric matrix usually increases the modulus of the material. The stiffness, or modulus, of the boron-containing materials increases from 0.58 Msi for the neat epoxy to 0.94 Msi for the 20% B-epoxy, an increase of 62%. While not unexpected, the dramatic increase in modulus indicates that the boron powder-filled epoxy composites are more rigid than unfilled epoxy. Small (sub-micron) boron particles may occupy sites in the crosslinked epoxy network and restrict the polymer chains from translational motion under stress. The effect of filler content is also evident in the tensile strain data. The decrease in tensile strain is shown graphically in Figure 47. The more highly filled the epoxy material, the less strain to failure under tensile stress. Poisson's ratio was calculated from the slopes of the axial and transverse strain curves. Values of Poisson's ratio (0.34 to 0.37) were typical of polymeric materials.

While the tensile strength decreases rapidly for boron-filled epoxy composites, the increases in tensile modulus
Figure 47  Tensile strain for amorphous boron-epoxy materials.

and strain to failure indicate that boron-epoxy materials

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may possibly be useful in structural applications in which tensile load is present.

**Flexure tests**

Specimens of boron-epoxy materials were subjected to flexural stresses in a four-point flexure test fixture. (See Section 2, Figure 15.) Flexure testing of polymers usually involves notching the polymer sample and breaking it under three-point bend stress in order to concentrate the stress on the center line of the specimen. Because a three-point test fixture was unavailable for the mechanical test instrument used in the tests, a four-point fixture was substituted.

As pictured in Figure 15 of Section 2, the center of breaking stress in a four-point fixture is focused between the two inner rollers. However, the specimens subjected to this test actually broke into three pieces of roughly the same length. Figure 48 shows the locations of the fracture sites of the test specimens. ASTM Method D790-71 supports the use of a four-point bend test, provided that the radii of the top rollers are within the range 3.2 mm to 1.5 times the specimen depth. The four-point flexure tests conducted as above conformed to the ASTM criteria. The data for the flexure tests are listed in Table 10. Five specimens of each of five materials (neat resin, 5% B-epoxy, 10% B-epoxy, 15% B-epoxy, and 20% B-epoxy) were tested. The graph of
Figure 48  Breaking stress points in flexure specimens.

Flexure strength vs. weight percent boron are shown in Figure 49. The trend that was evident in the tensile data (see discussion above) is repeated for the flexure data. A sharp decrease in the flexural strength occurs between the neat resin and the 10% B-epoxy material. However, the flexural strength increases for the 15% and 20% B-epoxy materials. The tensile strength graphs show a pattern similar to that of the flexural strength graphs.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>STRENGTH (Ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% B-Epoxy</td>
<td>0.834 ± 0.12</td>
</tr>
<tr>
<td>5% B-Epoxy</td>
<td>0.602 ± 0.16</td>
</tr>
<tr>
<td>10% B-Epoxy</td>
<td>0.456 ± 0.03</td>
</tr>
<tr>
<td>15% B-Epoxy</td>
<td>0.472 ± 0.05</td>
</tr>
<tr>
<td>20% B-Epoxy</td>
<td>0.591 ± 0.06</td>
</tr>
</tbody>
</table>
Figure 49 Flexural strength of amorphous boron-epoxy materials.
Here a decrease in flexural strength with increased boron content is closely related to the likely cause for the sharp drop in the ultimate tensile strength data. To better understand this phenomenon, a comparison of the two mechanical tests needs to be made.

The ASTM standard tensile test described above involves pulling apart polymeric specimens by generating tensile stress along the axial direction of the tensile dogbone. The flexure test also described above can be thought of as a combination of tensile and compression tests (See Figure 50). Along the underside of the test specimen mounted in the four-point bend test fixture, the primary force the sample experiences is tension. This is created by the bending of the specimen and a "stretching" of the sample.

Figure 50 Diagram of stresses in 4-point flexure test.
plane opposite the load application point. At the same time, the top side of the specimen experiences compression, owing to deformation of the sample from the same downward force. Thus, the sample is being both pulled apart and pushed together, on opposite edges. It is not surprising that the two mechanical test modes, tensile and flexure, should yield similar data for the same materials.

It is postulated here that the reason for the similar behavior in the two is physical. At low boron concentrations in the epoxy (5-10% by weight), large clusters of pure boron powder appear infrequently in optical micrographs (See Figures 51 a-d). Large areas of almost pure epoxy are visible. Regardless of the magnification, boron clusters measuring roughly 50µm x 80µm are irregularly
Figure S1  Optical micrographs of boron clusters.
found over large areas of the microscope specimen. At 15 to 20 boron weight percent, the clusters of boron are still present (perhaps in slightly greater numbers), but the clusters are smaller relative to the ones found in 5% and 10% boron-epoxy materials. In addition, a larger fraction of the boron powder appears to be more well-mixed with the epoxy than in materials that have a lower boron content.

One possible reason for this interesting phenomenon could be that at higher boron concentrations, large clusters of boron come into contact with each other in the mixing process. The shear forces present in mixing causes clusters of boron to break apart and disperse into the material. Some of the clusters essentially annihilate each other, and the boron powder is more effectively distributed throughout the epoxy matrix. Not all the clusters are broken apart by the vigorous, if rudimentary, hand-mixing of the boron into the epoxy. However, more mixing occurs during the deaeration stage of processing, further assisting the breaking up of the clusters, therefore homogenizing the mixture to a greater extent than at low boron concentrations. At boron concentrations lower than 10-15% by weight, the clusters of boron are too far apart to destructively interfere with each other. Further experimental support for this theory is contained in the error bars surrounding the tensile and flexure data. As the concentration of boron increases in the materials, the test
data have smaller uncertainties associated with the measurements. Reproducibility of mechanical test measurements is an indication of a more uniform composition. Hence the boron-epoxy materials with higher boron concentration are more homogenous and better mixed over the large areas of the mechanical test specimens.

**Compression tests**

Compressive strength and modulus are key parameters for structural applications. In addition to bearing the weight of an external load, a structural member must support its own weight. Polymeric materials such as boron-filled epoxy composites are shown in this section to perform very well under compressive loads.

Specimens of boron-epoxy materials were machined to ASTM test specifications, instrumented with strain gauges, and loaded in compression. The fracture mode was recorded, along with ultimate compressive strength, modulus, and compressive strain. In addition, Poisson's ratio was calculated from the data for each specimen. Some of the specimens fractured axially, while others failed along the horizontal midline. The test run was stopped immediately after fracture was detected.

Ultimate compressive strength, modulus and compressive strain for each boron-epoxy material are listed in Table 11.
### Table 11. Compressive properties of boron-epoxy materials.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>STRENGTH (Ksi)</th>
<th>MODULUS (Msi)</th>
<th>POISSON'S RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%B-Epoxy</td>
<td>25.6 ± 0.05</td>
<td>1.57 ± 0.00</td>
<td>0.40</td>
</tr>
<tr>
<td>5%B-Epoxy</td>
<td>25.9 ± 0.07</td>
<td>1.73 ± 0.01</td>
<td>0.39</td>
</tr>
<tr>
<td>10%B-Epoxy</td>
<td>27.2 ± 0.44</td>
<td>1.94 ± 0.01</td>
<td>0.39</td>
</tr>
<tr>
<td>15%B-Epoxy</td>
<td>29.4 ± 1.03</td>
<td>2.28 ± 0.03</td>
<td>0.38</td>
</tr>
<tr>
<td>20%B-Epoxy</td>
<td>31.7 ± 0.90</td>
<td>2.63 ± 0.04</td>
<td>0.38</td>
</tr>
<tr>
<td>10%B-mix</td>
<td>27.7 ± 0.74</td>
<td>0.80 ± 0.10</td>
<td>0.38</td>
</tr>
<tr>
<td>20%B₄C-Epoxy</td>
<td>28.4 ± 0.37</td>
<td>0.82 ± 0.19</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Addition of boron powder improved the compressive properties of the neat resin. The ultimate compressive strength increased from 25.6 to 31.7 ksi, a 24% change, for the amorphous boron-loaded materials (see Figure 52). The compressive modulus increased from 1.57 to 2.63 Msi, a change of almost 68% over the neat resin (see Figure 53). Compressive strains were not meaningful because the magnitude of the strain data exceeded the strain gage's upper limit (3.75% strain). Poisson's ratio was not significantly altered by the presence of boron powder in the matrix.

The increases in compressive strength and modulus are typical for powder-filled polymeric composites. Elemental amorphous and crystalline boron powders and boron carbide
COMPRESSIVE FAILURE STRENGTH OF BORON-LOADED EPOXY

Figure 52: Compressive strength of boron-epoxy materials.

- Maximum
- Average
- Minimum

Compressive strength, ksi

Boron loading, weight %
Figure 53

Compressive modulus of boron-loaded epoxy

Compressive modulus, Msi

<table>
<thead>
<tr>
<th>Boron loading, weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>

- Maximum
- Average
- Minimum
are hard, high-melting ceramic materials. Mixing ceramic powders with polymers improves the compressive properties by reinforcement of the polymeric matrix. In a mechanical test or in a load-bearing application, the matrix component of a composite encounters an outside stress. The force pulls on the polymer chains, thereby stretching the bonds in the polymer backbone. Assuming good adhesion to the reinforcing medium (fibers or particulates), the matrix transfers the load to the load-bearing reinforcing material. The purpose of the reinforcing material is to bear the in-plane loads. With boron-filled epoxy composites, the boron particles are the load-bearing materials, and the epoxy resin is the load-transfer medium. Carbon or boron fibers have a similar effect on fiber-reinforced composites (FRP); they act as load-bearing members in the axial direction. FRP's are typically anisotropic, with much less strength in the transverse direction. However, the properties of powder-filled composites are isotropic since the powder is randomly mixed with the polymer. The addition of boron and boron carbide to epoxy resin in this study reaffirms the utility of powder-reinforced composite materials.

NEUTRON ABSORPTION MEASUREMENTS

Thin indium foils surrounded by one-inch square
specimens of boron-filled epoxy resin were exposed to thermal neutrons in a 5-Curie plutonium/beryllium (Pu/Be) source in the Department of Physics at William & Mary. In addition, indium foils were exposed without any shielding to establish the maximum number of counts possible from the neutrons present in the source. Following a 20-hour saturation exposure in the Pu/Be source, the radioactivity induced in the indium was counted with a Geiger counter (See Appendix 2 -- Counting Data). The number of counts obtained by the counter is proportional to the number of disintegrations of indium-116 atoms decaying to atoms of the stable tin-116 isotope. Plots of the natural logarithm of the counts vs. time are linear for radioactive decay.

This experiment is very similar to neutron activation analysis (NAA), in which samples of known atomic composition are irradiated with thermal neutrons in a nuclear reactor. The flux of thermal neutrons in the reactor is typically between $10^5$ and $10^{14}$ neutrons per second. In an NAA exposure, the flux of neutrons and their energies are very precisely known in order to calculate recoil products and energies. However, in our experiments, the neutron flux is not precisely known. Calculation of neutron attenuation factors is the principal information gained from a neutron activation experiment. Because the flux of neutrons was not precisely known for our Pu/Be source, neutron attenuation factors were not expressly calculated from the data.

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Graphs of \( \ln(\text{counts}) \) vs. time were plotted for two half-lives of the radioactive indium foils, in order to present quantitative comparisons in the data. Figure 54 shows the counting data for unshielded indium foil and indium foil surrounded by neat epoxy resin. The number of counts for the indium foil alone (4,134) is less than the number of counts for indium shielded by neat resin (4,792). However, the Pu/Be source, like all neutron sources, emits neutrons in a range of energies, from epithermal to fast neutrons. The one-eighth inch thick epoxy polymer slabs slow down a portion of the more energetic neutrons to thermal energies, resulting in a higher thermal neutron flux exposure of the indium foils than when the foils alone are exposed. The greater thermal neutron flux results in a proportionally larger number of counts for the 0\% shielded foil vs. the unshielded foil. The data for the foils surrounded by 5%-20\% nominally boron-loaded epoxy are therefore normalized to the data from the foils surrounded by neat resin, not to the unshielded indium foils.

A graph of the initial activity of the shielded foils is found in Figure 55. The data show increased shielding imparted by increasing boron content in epoxy resin for samples of the same thickness. Similar graphs of PMDA-ODA polyimide in Section 3.3 confirm that
the amount of neutron absorption in boron-containing shielding materials varies linearly with both boron concentration and thickness of absorber.

Figure 56 shows a plot of the counting data for the 0%,
Figure 55: Plot of initial activity of shielded indium foils.

5%, 10%, 15%, and 20% nominal boron-containing epoxy shielded foils. As expected, the lines fit to the
regression equations in Appendix 2 are very nearly parallel. (Since the decay of indium-116 is the same regardless of the shielding material surrounding it during exposure.)

**Figure 56** Plot of ln(counts) vs. percent boron for boron-epoxy shielding materials.
A few observations can be made regarding the plots. First, the natural logarithm plot shows an order of magnitude difference between the shielding of the neat resin and the shielding of the 17.43% boron-loaded epoxy. This is a remarkable factor of "neutron attenuation" considering that it is the result of only 0.125 inch of boron-epoxy shielding surrounding the indium foil during neutron exposure. Thicker neutron shielding boron-epoxy materials, logically, result in greater neutron absorption. Second, the scatter in the data increases as the number of counts approaches the background level. In each exposure, the background was less than 17 counts/min., less than one-sixth of the number of counts at two half-lives of the 17.43% shielded foil. Finally, as the weight percentage of boron in the shielding materials increases, the fraction of neutrons absorbed increases almost exponentially toward unity. Figure 57 is a normalized graph of fraction of neutrons absorbed vs. weight percent boron in the boron-loaded epoxy materials. At 3.95% boron loading, the epoxy shielding material absorbs 75% of the incident neutrons. The maximum absorption was for the 17.43% boron-epoxy, which absorbed over 92% of the incident neutrons. For cost-sensitive applications, the nominal 5%B-Epoxy material may prove to have the best neutron absorption for the raw materials cost.

Enriched boron-10 is commercially available at over 95%
Figure 57 Normalized graph of neutrons absorbed vs. weight percent boron.
enrichment. Since the elemental boron powder used in these experiments has the natural abundance of boron-10 (approx. 20%), using enriched boron-10 should greatly increase the neutron absorption of the boron-epoxy materials.

SURFACE CHARACTERIZATION

Boron-epoxy materials were exposed to the low Earth orbit (LEO) aboard the Space Shuttle flight STS-51 in 1993. The chief component of the atmosphere in LEO is atomic oxygen. The effects of atomic oxygen on polymeric materials have been reported in the scientific literature,\(^7\) and exposure to atomic oxygen is one of the several criteria for polymeric materials use in space.

Many types of atomic oxygen-resistant materials have been developed in the past twenty years, including polymers doped with tin, silicon, and more recently, phosphorus. This section discusses the results from surface characterization of boron-loaded epoxy composite materials. Surface spectroscopy of pure PMDA-ODA polyimide films is included for completeness.

X-ray Photoelectron Spectroscopy

XPS was performed on two sets of 0.75-inch boron-epoxy discs, those exposed to LEO and the unexposed control group. Energetic K alpha x-rays of magnesium were used to expel
inner shell electrons from the atomic species on the surface of the discs according to the photoelectric effect (See Figure 58). The electrons, having a characteristic energy signature, were detected, counted, and identified by the MACS system software. The elements found in all boron-epoxy samples were carbon, nitrogen, oxygen, sulfur, silicon, and fluorine. The PMDA-ODA polypyrromellitimide samples contained only carbon, nitrogen and oxygen. Silicon and fluorine were considered contaminants because elemental analysis indicated that the 934 Epoxy resin consisted of only carbon, nitrogen, oxygen and sulfur (hydrogen is not detected in XPS). Contaminants are a major concern when evaluating the surface of specimens exposed in the LEO environment. Several experiments on board the Long Duration Exposure Facility (LDEF) were shown to be contaminated by silicon from silicone adhesives. In spite of the cleaning procedures employed by persons handling the specimens pre-flight, some contamination consisting of silicon and fluorine was present in the boron-epoxy samples.

A typical XPS spectrum plots intensity (arbitrary units) vs. the electron binding energy from highest to lowest energy. The binding energy's sign is reversed in these spectra to show the energies properly (the software program displays the peaks in reverse order of ascending binding energy).
Figure 58 Photoelectric effect in XPS.

PMDA-ODA polypyrromellitimid films

Figure A-1 of Appendix 3 shows the XPS survey spectrum of the elements on the surface of pure PMDA-ODA polyimide film. Peaks represented are oxygen, nitrogen, and carbon from left to right. The control sample is shown in bold offset. The LEO-exposed plot has some differences from the control. The carbon 1s peak is smaller in intensity while the oxygen 1s is larger than the corresponding control peaks. The reason for this is that as atomic oxygen strikes the surface of the specimen, it forms a variety of compounds of carbon and oxygen, including carbonyls, ethers, and carbonates. In addition, carbon oxides are formed which
leave the surface. These two factors account for the difference in the relative intensity of the carbon and oxygen peaks. As more atomic oxygen reacts to form carbon oxides, the intensity of the carbon ls peak diminishes while the oxygen ls peak gains intensity. Atomic oxygen also forms various oxides with nitrogen on the polymer surface. As the polymer is eroded by atomic oxygen, more nitrogen is exposed. This is the reason for the increased intensity of the nitrogen ls peak in the spectra.

Closer examination of the individual peaks reveals the chemical changes that occur when atomic oxygen reacts with carbon and nitrogen present in the polyimide. Figure A-2 shows the carbon ls peaks of the control and LEO-exposed samples, centered at a binding energy of about 285 eV, in greater detail. The peak of the exposed sample (bold line) broadens, indicating that bonding of the carbon becomes more complex than in the control. The additional peak in the exposed sample at higher binding energy indicates that the carbon is bound to more electronegative atoms, such as oxygen. The more oxygens a carbon atom is bonded to the more electropositive it becomes. The greater positive charge on carbon causes it to bind its electrons more tightly. Thus, the ls electrons that are expelled by the x-rays via the photoelectric effect have more energy. The intensity of the carbon exposed peak is almost 3.5 times less than the control, indicating a loss of carbon from the
surface of the polymer.

The nitrogen 1s peak of the polypyromellitimide (Figure A-3) centered at a binding energy of about 400 eV shows similar changes to carbon. The peak broadens, indicating a greater variety of chemical bonding states, and the peak shifts slightly towards high binding energy, indicative of a greater number of bonds to the more electronegative oxygen atoms. The small intensity of the control and exposed peaks produces the low signal to noise ratio in the graph.

In contrast, the LEO-exposed oxygen 1s peak (Figure A-4) centered at a binding energy of about 532 eV changes only slightly from the control. The peak broadens slightly, but does not shift position relative to the carbon and nitrogen shifts above. Even though the exposed peak is greater in intensity than the control, the peaks are centered at a binding energy of about 533 eV.

Boron-Epoxy materials

Comparison of the neat epoxy, 10% B-epoxy, and 20% B-epoxy XPS spectra yields several interesting phenomena. The carbon, nitrogen, oxygen, sulfur and boron peaks are roughly centered at 285, 400, 532, 169 and 187 eV respectively. However, the LEO-exposed materials show differences in peak width and peak shifts from the control samples that deserve explanation. This section will describe in detail these changes of the electron binding energy peaks, as well as
differences in relative intensities of the spectra. The spectra of the silicon and fluorine contaminants are included at the end of Appendix 3 (see Figures A-19 to A-24).

The carbon 1s peaks of the three materials are very similar (Figures A-5 to A-7). Upon exposure to atomic oxygen, all the spectra show a broadening toward higher binding energy which results from the carbon on the surface reacting with oxygen. The exposed carbon, which is more electropositive, binds its electrons more tightly which results in a higher 1s electron binding energy. As discussed above for the PMDA-ODA polyimide films, the specimens had less carbon on the surface after exposure owing to loss of carbon oxides in the atomic oxygen flux.

The spectra of the nitrogen 1s peaks (Figures A-8 to A-10) of the boron-epoxy materials indicate similarities also. There is an average of 1.7 times the amount of nitrogen on the surface for the exposed samples than for the controls. The explanation for this is the formation of nitrogen-oxygen bonds on the material's surface coupled with the loss of other surface elements such as carbon and hydrogen. As in the case of the carbon 1s spectra, the nitrogen 1s exposed peaks are shifted to higher electron binding energy owing to the nitrogen-oxygen bonds, and nitrogen becomes more electropositive in the exposed samples.

Analysis of the oxygen 1s spectra of the epoxy
materials indicates more oxygen on the surface after atomic oxygen exposure, as expected (Figures A-11 to A-13). Formation of carbon-oxygen, nitrogen-oxygen, and perhaps sulfur-oxygen bonds is the primary reason for this phenomena. However, the peaks are shifted to lower electron binding energies as the boron content in the epoxy increases. When oxygen bonds to surface elements, it becomes less negative, and hence holds its electrons less tightly, resulting in lower binding energy in XPS spectra.

The sulfur 2p spectra are almost identical for the three boron-epoxy materials (Figures A-14 to A-16). One trend evident in the data suggests that as the boron concentration in the epoxy increases, the amount of sulfur on the surface after exposure decreases. This is not unreasonable, given that more boron is present near the surface at higher loading.

The XPS spectra of the boron 1s electrons (Figures A-17, A-18) is the best evidence that there is very little boron on the surface of unexposed boron-epoxy materials. Only after exposure to atomic oxygen does the boron 1s peak show. One possible explanation for this fact could be that in forming the powder-filled composites, the powder gravitates to the bottom edge of the mold. However, the epoxy is probably too viscous to allow this process to occur. In addition, boron-loaded PMDA-ODA polymellitimides did not have any boron on either the air or glass sides of

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the film. A more probable reason for this interesting property of these epoxy materials is related to wetting of the boron powder. At sufficiently high boron concentrations, some boron powder is not completely wetted by the epoxy resin. Below this critical "solubility" of the boron in the epoxy, the resin can fully wet the powder, thereby coating the powder particles with at least a thin layer of polymer. This may explain the absence of boron on the surface of these materials.

Static Secondary Ion Mass Spectrometry

Characterization of the surface of the samples by SSIMS provides evidence of atomic oxygen's dramatic effects. In addition, mass spectrometry can determine the elemental surface composition of polymeric materials. Mass spectrometry results serve in this study to complement the results of the x-ray photoelectron spectra discussed above.

SSIMS was conducted on pure PMDA-ODA polyimide films and boron-loaded epoxy resin samples at the BSAF in Australia. Some of the boron-epoxy materials were flown on Flight STS-51 of the Space Shuttle to expose them to atomic oxygen in the LEO. Bombardment of each specimen with argon ions produced secondary molecular ions of the surface elements. The mass spectra were analyzed with a MACS data collection system, and plotted as counts vs. mass units. SSIMS spectra are divided into three graphs per specimen:
low range (0-50 mass units), medium range (51-100 mass units), and high range molecular weight ions (101-150 mass units). These plots are found in Appendix 3. LEO-exposed sample spectra appear in bold type, while control samples appear in fine type.

PMDA-ODA polypyromellitimide

The SSIMS mass spectrum for the pure PMDA-ODA polymer is found in Figures A-26 through A-28 of Appendix 3. Principal peaks are N-H (m=15), sodium (m=23), various organic groups (m=27,29,39,41,43,55,57,67, and 69), two large peaks at m=74 and its dimer at m=148. These two peaks are characteristic of common silicone contamination of the sample. The mass spectra show substantial changes between the control and LEO-exposed samples. After exposure to atomic oxygen, many of the peaks decrease substantially. Atomic oxygen reacts with elements on the surface to cause a loss of organic matter and to form oxides with a variety of elements including carbon, nitrogen, silicon, sulfur, and phosphorus. The PMDA-ODA polyimide in this study is mostly carbon and hydrogen, so weight loss by the effects of atomic oxygen is large. This is reflected in the SSIMS spectra, which shows a large reduction in almost all of the peaks. The peak at approximately 130 mass units of the LEO-exposed sample (heavy line) is probably some form of contamination which occurred while in flight in the low Earth orbit. It
is seen in several of the LEO-exposed samples, including the epoxy materials.

Boron-epoxy materials

SSIMS mass spectra for neat epoxy, 10%B-Epoxy, and 20%B-Epoxy materials are found in Figures A-28 to A-41 of Appendix 3. Several important features of these spectra are compared and contrasted to the pure PMDA-ODA spectrum. First, similar hydrocarbon peaks appear at m=27,29,39,41,43, 55,57,67 and 69. Like the pure polyimide, these peaks lose intensity in the mass spectrum owing to atomic oxygen effects, however not as much material is lost. The reaction efficiency for boron-epoxy materials is much less than PMDA-ODA films in space, and the amount of weight loss due to atomic oxygen is less. Table 11 shows mass loss and reaction efficiency for PMDA-ODA and boron-epoxy materials determined from data obtained from LEO exposure on the Space Shuttle.

Next, the peaks corresponding to silicone contamination present in the polyimide films do not show up in the boron-epoxy spectra. Finally, the elemental composition of the boron-epoxy materials is not surprisingly different from the polyimide, and this is reflected in the different peak heights and positions.

To investigate the surface phenomenon of the absence of boron in the boron-epoxy materials revealed by x-ray
Table 11. Reaction efficiency of boron-epoxy materials with atomic oxygen in LEO orbit.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MASS LOSS (mg)</th>
<th>REACTION EFFICIENCY (cm³/atom x 10²⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Epoxy</td>
<td>0.89</td>
<td>4.40</td>
</tr>
<tr>
<td>10%B-Epoxy</td>
<td>0.74</td>
<td>3.59</td>
</tr>
<tr>
<td>20%B-Epoxy</td>
<td>0.53</td>
<td>2.15</td>
</tr>
</tbody>
</table>

photoelectron spectroscopy, the samples containing 20% nominal percent boron were scraped with a razor to expose the surface physically. Spectra of original, unexposed boron-epoxy and scraped boron-epoxy materials were compared. Further comparisons are made in this section between materials with different boron concentrations before and after exposure to LEO.

In the low mass unit range, the presence of boron in the 10% and 20% boron-containing epoxy materials is confirmed by the large peaks at 10 and 11 mass units. In addition, substantial peaks are recorded at mass 23 indicating the presence of sodium. The boron powder contains some impurities, including sodium. Therefore, the height of the sodium mass peak remains constant or increases due to greater exposure to boron powder in the boron-epoxy samples. The intensity of the sodium peak (also present as an impurity) in the pure epoxy spectrum decreases owing to
the effects of atomic oxygen.

The medium and high mass unit ranges (51-150 mass units) display characteristic mass losses due to atomic oxygen effects. The one interesting peak is at mass 130, which is probably present due to contamination of the samples in space.

3.2 CARBORANE POLYAMIDES

POLYMERS

Six m-carborane-containing polyamides were synthesized from the condensation polymerization reaction of m-carborane-1,7-diacid chloride with various diamines. Figures 17 and 18 of Chapter 2 show the repeat units of the polymers, including the five polyamides not found previously in the polymer literature: m-carborane-1,7-dicarbonyl-1,8-diaminoctane [MC-1,8-DDA], m-carborane-1,7-dicarbonyl-1,10-diaminododecane [MC-1,10-DDA], m-carborane-1,7-dicarbonyl-1,12-diaminododecane [MC-1,12-DDA], m-carborane-1,7-dicarbonyl-4,4'-methylenebis-(diethylaniline) [MC-MDEA], and m-carborane-1,7-dicarbonyl-4,4'-methylenebis(diethylaniline) [MC-MDMA]. The polyamide synthesized from 4,4'-oxydianiline was reported previously by Korshak and coworkers.¹⁰

The polycondensations were conducted in tetrahydrofuran (THF) at approximately 5-10°C in a nitrogen atmosphere. Isolation of the polymers was achieved by dilution of the
reaction mixture in water, followed by filtration, multiple washes with deionized water, and vacuum drying. Care was taken to minimize entrapped salts by repeating the dissolution, precipitation, and filtration steps at least twice. Typical yields were 80-100% of theoretical. Polymers obtained by this method (Reference 10 with modifications) were fine powders from dark or light brown to brownish-yellow in color. The aromatic diamines yielded the more colorful polymer powders owing to electron transfer from the more electropositive aromatic diamine to the electron deficient carborane moiety.

STRUCTURAL CHARACTERIZATION

Nuclear magnetic resonance and Fourier transform infrared spectroscopy were used to characterize the polyamides structurally. Proton and carbon-13 NMR spectra were obtained to confirm the connectivity of the carborane polyamides. The FT-IR spectra are found in Appendix 1, and FT-IR and NMR spectra are discussed in the text of this section.

Infrared Spectroscopy

FT-IR spectra for each of the six carborane polyamides confirm the presence of the carborane moiety and the amide bond. Strong absorbances present in each of the polymers
are found at 2600 cm⁻¹ (B-H stretch) and at 1430 cm⁻¹ (amide bond vibrations). The B-H stretch confirms the bonding of the carborane unit into the polymer, and the amide absorbances confirm the presence of the amide bond. In addition, the absence of the broad OH absorbance in the 3300-3000 cm⁻¹ range in the spectra indicates that the polymers were completely reacted and dry when the spectra were taken. The background interferences at 2200 cm⁻¹ are characteristic of carbon dioxide. If carbon dioxide and water vapor are not purged from the IR sample chamber completely, they can cause distortions in the spectra. Variability in the age of the background spectrum also influences the presence of carbon dioxide and water absorbances in the FT-IR spectra. However, the differences in background age do not affect the positions of the absorbances, and since the peaks were not quantitatively analyzed, no error is introduced into peak identification.

NMR Spectroscopy

Carbon-13 and proton NMR was used to characterize the polyamides. Peak identification in the aromatic polymers was complicated by the large number of resonances and lack of spectra in the literature with which to confirm absolutely the specific peaks of each substituent. Identification of the aliphatic polyamide (MC-1,8 DDA, MC-1,10 DDA, and MC-1,12 DDA) peaks was fairly straightforward,
and the peak listing appears in Table 13. NMR spectra combined with FT-IR spectra are consistent with the polyamide connectivity and structure. Boron-11 NMR has proven to be the tool of choice for verifying the structure of carborane polyamides. Given the limited utility of proton and carbon-13 NMR for carborane polymers, future studies will focus on boron-11 NMR as a diagnostic for structure elucidation.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>PEAK CENTER (ppm)</th>
<th>IDENTIFICATION</th>
<th>CENTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC-1,8 DDA</td>
<td>7.3</td>
<td>N-H [1H]</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B-H [5H]</td>
<td>1.3</td>
</tr>
<tr>
<td>MC-1,10 DDA</td>
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<td>N-H [1H]</td>
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<tr>
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<td></td>
<td>B-H [5H]</td>
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<tr>
<td>MC-1,12 DDA</td>
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<td>N-H [1H]</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>B-H [5H]</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Molecular weight characterization

The molecular weight (MW) and molecular weight distribution (MWD) of polymers influence the thermal,
mechanical, and physical properties profoundly. With increasing molecular weight, a polymer generally becomes more thermally stable, forms tough, creasable thin films, and has better mechanical properties. The utility of a synthetic polymer depends greatly on its molecular weight characteristics. For these reasons, higher average molecular weight is desired in most applications.

Investigations of the molecular weight of polymers make use of two types of methods: primary and secondary measurements. Primary measurements of polymer molecular weight include light scattering, osmometry, and ultracentrifugation. Secondary methods include gel permeation chromatography (GPC) and intrinsic viscosity. Secondary methods must have an internal standard or include a calibration curve in order to measure accurately the molecular weight. In this study, GPC and specific viscosity measurements were made on carborane polyamides to determine their molecular weight in order to characterize their physical properties. A calibration curve of narrow molecular weight polystyrene standards (Table 14) allowed calculation of the molecular weight of the polymers directly.
The molecular weights of the polyamides from GPC were lower than expected. All polymers except two, MC-1,10 DDA and MC-1,12 DDA, had peaks in the GPC that eluted at or after the lowest polystyrene standard of the calibration curve (4,075 g/mol). The molecular weights of the two polymers were $M_N = 20,500$ g/mol for MC-1,10 DDA and $M_N = 11,000$ g/mol for MC-1,12 DDA. Although these molecular weights are higher than the other four polyamides, they are not close to the molecular weights of carborane polyamides in the literature.  

The most probably reason for the low MW of the series of polymers is impurity of $m$-carborane diacid chloride monomer. The diacid chloride was meticulously vacuum fraction distilled at low pressures at least two times,
however the monomer's reactivity is very high and it reacts with advantageous water in air at a high rate. Future preparations could include a direct distillation into the reaction flask in order to prevent the reverse reaction of the functional groups to the carboxylic acid from occurring.

In an attempt to achieve higher molecular weight of the polymers, the reaction solvent was changed to dimethylacetamide. The polymerization in THF resulted in a viscosity increase, yet some solids remained during the reaction. Both monomers are completely soluble in DMAc and the change of solvent was designed to promote a higher degree of conversion because of the increased solubility (and accessibility) of the monomers. Reaction in DMAc was unsuccessful in producing high molecular weight polymers, as indicated by the solution viscosity measurements (see Table 15). The failure of the reaction to make high molecular

<table>
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<tr>
<th>POLYMER</th>
<th>SPECIFIC VISCOSITY (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC-1,8 DDA</td>
<td>0.040</td>
</tr>
<tr>
<td>MC-1,10 DDA</td>
<td>0.047</td>
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<tr>
<td>MC-1,12 DDA</td>
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<tr>
<td>MC-MDEA</td>
<td>0.035</td>
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<tr>
<td>MC-MDMA</td>
<td>0.032</td>
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</table>
weight polyamides from m-carborane diacid chloride and various diamines was not remedied by the change in reaction solvent. Further attempts to synthesize high polymer could not be conducted owing to a shortage of m-carborane.

THERMAL CHARACTERIZATION

DSC and TGA were used to characterize the thermal stability of the carborane polyamides. Analysis of the glass transition temperature and onset of degradation of the polymers were straightforward.

DSC thermograms for all the polymers are found in Appendix 4. No glass transition temperatures were observed for the polymers, in agreement with the literature.12 The information from DSC was limited to the onset of degradation. The polymers were thermally stable up to 250°C. The second heats of the polymers showed no transitions, either exothermic or endothermic. Above this temperature, degradation of the polymers was observed as large exothermic peaks in the thermograms.

The reason for the temperature stability of the polyamides is the carborane moiety in the polymer backbone. M-carborane cage units act as energy sinks, absorbing thermal energy from the environment along the polymer chain. The degradation of carborane polymers has been found to occur via formation of dicarbaundecaborate ions \([\text{C}_7\text{B}_{11}H_{10}]^+\).
which catalyze the thermo-oxidative cleavage of the polymer molecule.\textsuperscript{13}

Thermogravimetric analyses of the polyamides were conducted by heating the samples in air up to 650°C at 2.5°C/min. The relatively slow heating rate allowed the boron in the polyamides to form oxides, resulting in a net weight gain in some polymers. Figure 59 shows the graph of the TGA curves of the three linear aliphatic carborane polyamides, MC-1,8 DDA, MC-1,10 DDA, and MC-1,12 DDA. Gradual weight gain up to 400°C is followed by a steep weight loss to about 500°C, after which the curve levels off. Over 80% of these aliphatic polyamides remained after heating to 650°C. Generally, aliphatic polymers degrade quickly in air, yet these carborane-polyamides showed a much slower rate of weight loss. This stabilizing effect of m-carborane has been noted before by Korshak and coworkers\textsuperscript{14}, and its effects on degradation rate are examined here. The formation of a coating of boron oxide may insulate the polymers from further oxidation. Boron oxidation may also explain the increase in weight of the polymer samples up to the temperature of degradation.

The stabilizing effect of m-carborane on the aromatic polyamides is not as pronounced. The polymers MC-MDEA and MC-MDMA, which have aliphatic side groups on the aromatic rings, degrade at much lower temperatures than the linear aliphatic polymers. Figure 60 illustrates the onset of
Weight Loss of Aliphatic Polyamides in Air

Figure 39 TGA curves of linear aliphatic carborane polyamides.
degradation of the two polymers at about 225-250°C, followed by additional degradation above 400°C and linear weight loss up to 650°C. The stability of MC-MDEA and MC-MDMA is remarkable, given the fact that the molecular weight of these two polymers is close to 3,000 g/mol. Oligomeric species such as these usually do not display such temperature stability, instead oligomers usually degrade in the temperature range of degradation of small molecules (<225°C). The m-carborane moiety preserves the structure of the polymer until the onset of degradation.

The weight loss curve of MC-ODA shows an interesting phenomenon (see Figure 61). The polymer rapidly gains weight until it peaks at about 400°C. Subsequent weight loss is slow initially, then faster as the final temperature is approached. MC-ODA suffers a weight loss of only about 10% up to 650°C. This curious TGA behavior prompted testing the polymer again in an argon atmosphere. Figure 62 is the TGA curve for MC-ODA in argon. The polymer does not lose any appreciable mass, but gains almost 10% of its original mass up to 650°C. In the absence of air, the polymer gains weight. The reason for this weight gain is not known, but may be due to small amounts of oxygen forming oxides of boron. Further examination of this behavior is needed.

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Weight Loss of Aromatic Polyamides

Figure 60: TGA curves of MC-MDEA and MC-MDMA in air.
Figure 61 TGA curve for MC-ODA in air.
Figure 62 TGA curve of MC-ODA in argon.
FILM PROPERTIES

Thin films were cast of each polymer onto glass plates with a doctor blade. The thicknesses of the films were in the range 0.002 to 0.005 inches. All of the polymers except one, MC-1,12 DDA, formed transparent, colored films. The MC-1,8 DDA film was colorless. The MC-1,12 DDA film was transparent until the solvent was removed, then the film seemed to crystallize on the plate, forming whitened regions. The crystallization of this polymer from solution was unexpected since the m-carborane forms a kinked structure which usually prevents alignment of the polymer chains.

All of the polymer thin films were brittle and uncreasable, as expected from the low molecular weights determined by gel permeation chromatography. The oligomers do not have the chain length that permits intermingling, thus the films have almost no crease strength.
3.3 PMDA-ODA POLYIMIDE FILMS

**Film properties**

The polyamic acid from the condensation reaction of 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) was isolated as a 10-15% solid solution in DMAc. Thin films of the neat polyimide were prepared according to the procedure found in the Experimental section above. Five and ten percent boron-containing PMDA-ODA formulations were produced from a slurry of boron powder in DMAc and polyamic acid solution. Polyimide films of boron-containing PMDA-ODA polymer solutions were prepared in a similar procedure as for the neat polymer. Elemental analysis of the films (Chapter 2, Table 1) produced by the given methods indicated close agreement between the calculated and actual compositions.

Neat and boron-loaded PMDA-ODA films were strong and creasable. The boron-filled polymer produced opaque films with little surface roughness. The boron was evenly dispersed throughout the films. Surface characterization of the films is discussed in Section 3.1.3. The results of boron-loaded polyimide films exposed to atomic oxygen are described elsewhere. Neutron exposure experiments were conducted to examine the ability of the boron-loaded films to absorb neutrons.
Neutron results

Graphs of the logarithm of the counts measured by a Geiger counter vs. time were plotted and least squares regression analysis utilized to calculate the initial activity of the indium foils at time $t_0$. The counting data and linear regression results are found in Appendix 2.

Figure 63 illustrates the shielding effects of various boron-containing polyimide films. The amount of neutrons absorbed is related to the concentration of boron in the films (by Beer's Law) and film thickness. Calculations of the relative absorption of neutrons between 5% and 10% boron-containing materials are found in Appendix 2. Thicker boron-loaded shielding materials such as boron-filled epoxy resin demonstrate the dramatic neutron shielding ability of boron incorporated into a continuous matrix material. Films of boron-loaded PMDA-ODA can be cast up to 0.015 inch thickness, but in order to achieve maximum neutron shielding per volume, thicker shielding materials are the best candidate materials for neutron shielding applications. Possible uses of boron powder-loaded thin films include cloth fabrication and radiation dosimetry devices. Processing, neutron shielding effectiveness, and cost of boron-containing polymeric materials and their industrial applications are discussed in Chapter 4.
Figure 31 Neutron attenuation effects of boron loading on shielded indium foils.
CHAPTER FOUR: APPLICATIONS AND FUTURE WORK

4.1 INTRODUCTION

Neutron shielding materials have applications in several industries, including aerospace, nuclear power, and accelerators. Polymer-based shields having a high boron content effectively absorb neutrons via thermalization and neutron capture. Because of the energy dissipated by the neutron capture reaction, high temperature thermal stability of polymers used as neutron shields is required. The polymeric materials characterized in this study show promise as neutron shielding materials for their excellent thermal properties, ease of processing, good mechanical properties, and their effective removal of neutrons from a neutron-rich environment. These attractive material properties combined with the weight and volume savings of low density matrices, make these polymeric materials good candidates for neutron shielding applications in industry.
4.2 AEROSPACE

The large weight savings of polymeric composite materials over conventional metals drives the aerospace industry to develop materials with lower operational costs. Incorporation of polymeric materials not only lowers flight costs, but provides flexibility in aircraft structure design and lower tooling costs in manufacturing.

The need for neutron shielding materials has been present for years in spacecraft design. Protection of electronic circuitry and human occupants of spacecraft is vital to the success of interplanetary travel. However, the need for neutron shielding materials in the aircraft industry has been ignored because of the relatively low risk. The exposure dose of high-altitude aircraft flights is much lower than space travel beyond the Van Allen radiation belts which trap most of the galactic cosmic radiation, protecting Earth from the harmful effects of GCR. Research and development work in High Speed Research (HSR) will require some form of neutron shielding because of the ultra-high design altitudes of HSR aircraft. Design of polymeric materials that provide neutron shielding without parasitic weight and volume penalties is crucial to the HSR effort.

The boron-epoxy materials processed in this study may fulfill the neutron shielding needs of the aerospace industry while serving a structural role. The baseline mechanical
properties of these materials are good, and the thickness of material needed for complete shielding from neutrons caused by GCR cascade reactions is probably less than one inch. Shielding from the relatively low neutron flux created by ionizing radiation striking the primary structure materials is easily accomplished. However, further neutron exposures along with mechanical property testing is needed to determine the operational life of boron-epoxy structures.

Finally, the cost of polymeric materials is always a consideration in the design of aircraft. The cost of the boron powder-filled epoxy composites evaluated in this study is approximately $250/ft² for 0.5 inches of shielding. This cost can be lowered with the use of boron carbide, which is considerably cheaper than elemental boron powder. In addition the properties of boron carbide reinforcement and more complete mixing are advantages over boron powder reinforcement.
4.3 NUCLEAR POWER

Boron-containing polymeric materials are already used extensively in the nuclear power industry. Reactor shielding in nuclear-powered ships including submarines is primarily borated polyethylene for thermalization and absorption of fast neutrons. By using the boron-filled epoxy resin discussed in the above sections of this study, the volume dedicated to neutron shielding materials can be minimized aboard nuclear ships. Although the need to minimize the volume of neutron shielding in nuclear ships is an immediate concern of the U.S. Navy, budget constraints on future shipbuilding budgets may result in the examination of more effective cost/volume use of materials.
4.4 ACCELERATOR FACILITIES

Small numbers of neutrons are produced in accelerators such as the Continuous Electron Beam Accelerator Facility (CEBAF) located in Newport News, Virginia, from collisions of electrons with the walls of the beam path. While the flux of neutrons is extremely small, shielding is needed for worker safety. The neutron shielding currently used at CEBAF consists of a water barrier only, with no neutron-capturing materials.

A one-eighth inch thick slab of 17.43% boron-filled epoxy resin absorbs over 92% of the incident neutrons from a plutonium/beryllium source. Although more neutron exposures are needed to measure neutron attenuation factors, boron-epoxy materials clearly could be utilized as neutron shielding at accelerators. The good compressive properties of boron-epoxy materials should provide enough strength for the design of wall panels. The panels can be placed at locations where the neutron flux is greatest for reduction of exposure to background levels.
CHAPTER 5: CONCLUSIONS

The effects of galactic cosmic radiation on materials in space orbit and in the Earth's atmosphere are potentially harmful to materials and man. Secondary particles produced from collisions of heavy ions with matter (neutrons, protons, helium nuclei) may cause single event upsets in electronic devices, weakening and embrittlement of synthetic materials and composites, and possibly cancer in human tissue. The most effective radiation shielding can provide protection from all types of secondaries formed from GCR interactions, both charged and uncharged. Few materials known possess such outstanding qualities. Contemporary shielding materials are designed to shield against one type of radiation, i.e. gamma rays, charged fragments, or neutrons.

Neutrons, having no charge, can travel long distances in even the most dense materials. Neutrons with a large range of energies are produced in nuclear reactors, neutron point sources, and in cascade reactions resulting from the interaction of GCR with matter. Neutron shielding materials must accomplish two basic tasks: slow down neutrons to
thermal energies and capture the neutrons to form stable isotopes. Shielding materials with high hydrogen content are the most efficient at reducing fast neutrons to thermal energies. Polymeric materials are essentially composed of carbon and hydrogen. Therefore, polymers are good choices for thermalizing neutrons. Materials that contain large amounts of boron-10 (which has a natural abundance of about 20% in elemental boron) are very effective neutron absorbers. The large thermal neutron capture cross section of $^{10}\text{B}$ (about 4000 barns) is a factor of $10^6$ greater than that of typical elements. The products of the reaction between $^{10}\text{B}$ and a neutron ($^7\text{Li}$ and $^4\text{He}$) are energetic but stable and are easily stopped within a few angstroms in most materials. In summary, some of the most effective neutron shielding materials are polymers that contain a high concentration of boron.

Polymeric materials were synthesized and characterized for thermal stability, neutron absorption ability, and possible structural properties. Three different types of polymers were made: boron powder-filled epoxy resin, boron containing polyamides, and boron-loaded polyimide films.

Amorphous submicron boron powder and two types of crystalline boron-containing powders were mixed up to 20% nominal weight percent with an aerospace qualified epoxy resin. The epoxy was cured to manufacturer's specifications, and the dispersion of the boron in the epoxy matrix was characterized with optical micrographs. The mixing was not
homogeneous; rather, clusters of boron measuring up to 50 microns by 80 microns were observed. To improve the mixing, crystalline, 250-micron boron powder was mixed at 50% weight ratio with submicron boron. Although several batches were processed, only a small improvement in boron dispersion was observed. The thermal properties of the epoxy were not adversely affected by the addition of boron powder. The glass transition temperature increased by more than 40°C while the coefficient of thermal expansion decreased by approximately 5 ppm/°C and the thermal degradation temperature rose slightly to just over 500°C in air. Mechanical test specimens were prepared for tension, compression, and flexure tests. The boron-epoxy materials' compressive failure strengths and compressive moduli increased by 28% and 68% respectively. However, the materials performed worse in tension. Tensile and flexural strength decreased with addition of boron up to about 15% boron by weight. Above 15%, the mechanical properties increased. One rationale for this behavior is that as boron content is increased beyond a critical percentage, clusters of boron are dispersed by mechanical shear forces during mixing. Boron-epoxy materials have good mechanical strength under compressive loads, hence they could be used as construction applications in ceiling and wall panels. Neutron shielding results of boron-loaded epoxy materials were excellent. Indium foils shielded by 17.43% boron-epoxy slabs of 0.125 inch thickness absorbed over 92% of incident neutrons.
from a 5-Curie Pu/Be neutron source. The 3.95% boron-epoxy material absorbed over 70% of incident neutrons. Thicker plaques would absorb a larger percentage of neutrons. The development of neutron shielding structural materials from boron-epoxy composites would be straightforward. 10% and 20% boron-epoxy materials were exposed to atomic oxygen in the LEO aboard the Space Shuttle. Mass loss and reaction efficiency of the boron-filled epoxy specimens decreased compared to the neat epoxy owing to formation of boron oxides on the surface.

Six polyamides containing the $\text{m-carborane moiety (C}_2\text{B}_{10}\text{H}_{12})$ were synthesized from the polycondensation of $\text{m-carborane diacid chloride with aliphatic and aromatic diamines. The amorphous polymers had a hydrogen/boron ratio ranging from 2.0 to 3.8, contained from 21-35% boron, and were soluble in organic solvents. Thermal stability measurements by thermogravimetric analysis indicated that all but two of the polyamides did not degrade below 400°C in air. Transparent, colored polymer films from 0.001 to 0.005 inches thick were cast from solution onto glass plates. However, the molecular weight of the polymers was lower than expected (<25,000 g/mol) and the films were brittle. Several attempts to improve the molecular weight were unsuccessful.

Boron powder in DMAc was mixed in a slurry with the polyamic acid of PMDA-ODA. Thin films from 0.005 to 0.015 inches thick were cast and thermally imidized up to 300°C under vacuum. The opaque films were strong and creasable.
The boron was evenly dispersed in the polymer, yet no boron was observed on the polymer surface by XPS and SSIMS. Films containing up to 10% boron were exposed to neutrons in a 5-Curie Pu/Be neutron source. The fraction of neutrons absorbed increased in a Beer's Law relationship with boron content and film thickness. Boron-containing polymer films could be used for neutron shielding of areas with complex surface geometries such as electrical wiring, electronic circuitry, and cloth shielding. Aerospace applications of the boron-containing materials produced in this study include spacecraft which travel beyond the Van Allen radiation belts and high-altitude, high speed aircraft currently in research under NASA's High Speed Research program. Nuclear power applications include nuclear-powered ships and submarines, nuclear power facilities, and high level nuclear waste containers. Accelerator facilities including hospitals and electron accelerators such as CEBAF can also benefit from the neutron-shielding attributes of these boron-containing materials.
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33. Ibid, p. 634.


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17. XPS and SSIMS conducted by R.L. Kiefer and B. Wood.
CHAPTER THREE


11. Ibid, p. 2355.


APPENDIX 1.

Infrared Spectra of Carborane-Polyamides
Figure 1. FT-IR Spectrum of poly(m-carborane-1,7-dicarbonyl-1,8-diaminoctane) [MC-1,8 DAO]
Figure 2. FT-IR Spectrum of poly(m-carborane-1,7-dicarbonyl-1,10-diaminodecane) [MC-1,10 DDA]
Figure 3. FT-IR Spectrum of poly(m-carborane-1,7-dicarbonyl-1,12-diaminododecane) 
[MC-1,12 DDA]
Figure 4. FT-IR Spectrum of poly(m-carborane-1,7-dicarbonyl-4,4'-oxydianiline) [MC-ODA]
Figure 5. FT-IR Spectrum of poly(m-carborane-1,7-dicarbonyl-4,4'-methylenebis(dimethylaniline) [MC-MDMA]
Figure 6. FT-IR Spectrum of poly(m-carborane-1,7-dicarbonyl-4,4’methylenebis(diethylaniline)
[MC-MDEA]
Figure 7 (a). FT-IR spectrum of m-carborane. [MC]

Figure 7 (b). FT-IR spectrum of m-carborane-dicarboxylic acid. [MC-DA]
APPENDIX 2.

Counting Data for Boron-Containing Materials
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Note: The data represents Cts Ln readings for different compositions of Epoxy with varying percentages and dates ranging from 3/17/94 to 3/31/94.
Indium Foil Analysis
Boron-Epoxy

Linear Best-Fit Equation: $\ln (\text{Counts}) = -M \times \text{time} + B_0$

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Slope (M) and intercept ($B_0$) data from regression analysis.
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<td>57 8.888</td>
<td>56 8.638</td>
<td>57 8.915</td>
</tr>
<tr>
<td>61 8.786</td>
<td>63 8.711</td>
<td>62 8.814</td>
<td>61 8.548</td>
<td>62 8.840</td>
</tr>
<tr>
<td>71 8.664</td>
<td>73 8.597</td>
<td>72 8.709</td>
<td>71 8.449</td>
<td>72 8.728</td>
</tr>
<tr>
<td>76 8.615</td>
<td>78 8.538</td>
<td>77 8.629</td>
<td>76 8.376</td>
<td>77 8.668</td>
</tr>
<tr>
<td>81 8.561</td>
<td>83 8.491</td>
<td>82 8.588</td>
<td>81 8.297</td>
<td>82 8.649</td>
</tr>
<tr>
<td>86 8.477</td>
<td>88 8.419</td>
<td>87 8.503</td>
<td>86 8.266</td>
<td>87 8.553</td>
</tr>
<tr>
<td>91 8.420</td>
<td>93 8.344</td>
<td>92 8.436</td>
<td>91 8.168</td>
<td>92 8.485</td>
</tr>
</tbody>
</table>
Indium Foil Analysis
PMDA-ODA

Linear Best-Fit Equation: \( \ln(\text{Counts}) = -M \times \text{time} + B_0 \)

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Slope, ( M )</th>
<th>Intercept, ( B_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>no shielding</td>
<td>0.0121 ± 0.0001</td>
<td>9.60 ± 0.01</td>
</tr>
<tr>
<td>PMDA-ODA, 2 mil</td>
<td>0.0124 ± 0.0001</td>
<td>9.59 ± 0.01</td>
</tr>
<tr>
<td>5% Boron, 5 mil</td>
<td>0.0123 ± 0.0001</td>
<td>9.55 ± 0.01</td>
</tr>
<tr>
<td>5% Boron, 15 mil</td>
<td>0.0123 ± 0.0001</td>
<td>9.50 ± 0.01</td>
</tr>
<tr>
<td>10% Boron, 15 mil</td>
<td>0.0123 ± 0.0001</td>
<td>9.31 ± 0.01</td>
</tr>
</tbody>
</table>

Slope (\( M \)) and intercept (\( B_0 \)) data from regression analysis.
Boron-containing PMDA-ODA Film

Neutron Absorption Calculations

\[
\ln C(5,5) = 9.546644 - 0.01234 (t) \\
\ln C(\text{Kapton}) = 9.590223 - 0.01237 (t) \\
\ln C(10,15) = 9.305481 - 0.01232 (t) \\
\ln C(\text{foil}) = 9.604140 - 0.01206 (t)
\]

Evaluating each equation at time = 30 minutes and taking the natural log yields

\[
C(\text{foil})(30) = 10,125 \text{ counts} \\
C(\text{Kapton})(30) = 10,088 \text{ counts} \\
C(5,5)(30) = 9,667 \text{ counts} \\
C(10,15)(30) = 7,600 \text{ counts}
\]

Subtracting the counts of each boron-loaded film from the counts of pure Kapton film yields

\[
C(\text{Kapton})(30) - C(5,5)(30) = 10088 - 9667 = 421 \text{ counts} \\
C(\text{Kapton})(30) - C(10,15)(30) = 10088 - 7600 = 2488 \text{ counts}
\]

Theoretically, the 10% B-loaded film at 15 mils thick should provide six times as much protection from neutrons as the 5% film at 5 mils thick, 2 times for the percent boron loading, and 3 times for the thickness difference.

Comparing the above numbers shows

\[
\text{5\% film counts / 10\% film counts} = 2488 / 421 = 5.9
\]
APPENDIX 3.

XPS, SSIMS Spectra
XPS Spectra of Pure Polypyromellitimide Films

![Graph showing XPS Spectra of Pure Polypyromellitimide Films with peaks for O 1s, N 1s, and C 1s. The graph includes a control and an exposed in LEO comparison.](image)
XPS Spectra of Pure Polypyromellitimide Films, C 1s Peak

Intensity (Arbitrary Units)


- Binding Energy (eV)

- LEO Exposed (x3.4) — Not Exposed
XPS Spectra of Pure Polypyromellitimidide Film, N 1s Peak

Exposure in LEO vs. Not Exposed (x1.4)
XPS Spectra of Pure Polypyromellitimide Films, O 1s Peak
XPS Spectra of Cured 934 Epoxy
C1s Peak

Intensity (Arbitrary Units)

-Binding Energy (eV)


-294 -292

-282

-278

LEO Exposed (x1.7)  Not Exposed
XPS Spectra of Cured 934 Epoxy with 10% Boron Powder, C1s Peak

![Graph showing XPS Spectra of Cured 934 Epoxy with 10% Boron Powder, C1s Peak. The graph indicates two curves: one labeled "LEO Exposed (x3)" and the other labeled "Not Exposed." The x-axis represents binding energy in eV, ranging from -296 to -278, while the y-axis represents intensity in arbitrary units, ranging from 0 to 7.]
XPS Spectra of Cured 934 Epoxy with 20% Boron Powder, C1s Peak

Intensity (Arbitrary Units) vs. Binding Energy (eV)

- LEO Exposed (x1.7)
- Not Exposed
XPS Spectra of Cured 934 Epoxy with 10% Boron Powder, N1s Peak

-Binding Energy (eV)

Intensity (Arbitrary Units)

-410 -408 -406 -404 -402 -400 -398 -396 -394 -392

- LEO Exposed  Not Exposed (x1.6)
XPS Spectra of Cured 934 Epoxy with 20% Boron Powder, N1s Peak
XPS Spectra of Cured 934 Epoxy with 20% Boron Powder, O1s Peak

- Binding Energy (eV)

Intensity (Arbitrary Units)

- LEO Exposed
- Not Exposed (x 1.7)
XPS Spectra of Cured 934 Epoxy
with 10% Boron Powder, O1s Peak
XPS Spectra of Cured 934 Epoxy
O1s Peak

Intensity (Arbitrary Units)

Binding Energy (eV)

-542 -540 -538 -536 -534 -532 -530 -528 -526 -524

-530 -532 -534 -536 -538 -540 -542

LEO Exposed
Not Exposed (x1.9)
XPS Spectra of Cured 934 Epoxy with 20% Boron Powder, S2p Peak

-Intensity (Arbitrary Units)

-Binding Energy (eV)

LEO Exposed
Not Exposed (x1.6)
XPS Spectra of Cured 934 Epoxy
with 10% Boron Powder, S2p Peak

Intensity (Arbitrary Units)

-176 -174 -172 -170 -168 -166 -164 -162

- Binding Energy (eV)

LEO Exposed
Not Exposed (x2.2)
XPS Spectra of Cured 934 Epoxy
S2p Peak

Intensity (Arbitrary Units)

-176 -174 -172 -170 -168 -166 -164 -162 -160

-Binding Energy (eV)

- LEO Exposed
- Not Exposed (x3.8)
XPS Spectra of Cured 934 Epoxy with 20% Boron Powder, B1s Peak

Intensity (Arbitrary Units)

-194 -192 -190 -188 -186 -184
-180 -176 -172
-168 -164
-160
-156
-152
-148
-144
-140
-136
-132
-128
-124
-120
-116
-112
-108
-104
-100
-96
-92
-88
-84
-80
-76
-72
-68
-64
-60
-56
-52
-48
-44
-40
-36
-32
-28
-24
-20
-16
-12
-8
-4
0

-Leo Exposed

Not Exposed (x10.6)
XPS Spectra of Cured 934 Epoxy with 10% Boron Powder, B1s Peak

![Graph showing XPS Spectra of Cured 934 Epoxy with 10% Boron Powder, B1s Peak. The graph compares the intensity (arbitrary units) against binding energy (eV) for not exposed and LEO exposed samples. The peak is centered around -186 eV.]
XPS Spectra of Cured 934 Epoxy
F1s Peak

Intensity (Arbitrary Units)

-Binding Energy (eV)


--- LEO Exposed (x1.3) --- Not Exposed
XPS Spectra of Cured 934 Epoxy with 10% Boron Powder, F1s Peak
XPS Spectra of Cured 934 Epoxy with 20% Boron Powder, F1s Peak

Intensity (Arbitrary Units)

-Binding Energy (eV)


1.6 1.4 1.2

LEO Exposed (x3.9) Not Exposed
XPS Spectra of Cured 934 Epoxy
Si2p Peak

![Graph showing XPS Spectra of Cured 934 Epoxy Si2p Peak. The graph compares the LEO Exposed (x1.3) and Not Exposed spectra, with intensity on the y-axis and binding energy on the x-axis.]
XPS Spectra of Cured 934 Epoxy with 10% Boron Powder, Si2p Peak

Intensity (Arbitrary Units)


-Binding Energy (eV)

LEO Exposed
Not Exposed (x1.3)
XPS Spectra of Cured 934 Epoxy
with 20% Boron Powder, Si2p Peak

- Binding Energy (eV)

Intensity (Arbitrary Units)

LEO Exposed
Not Exposed (x2.6)
SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder

![Graph showing SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder. The graph displays counts on the y-axis against mass units on the x-axis. Two lines are shown: one for Exposed in LEO and another for Not Exposed.]
Static SIMS Spectra
Pure Polypyromellitimide Films

Mass Units

Counts

Exposed in LEO — Not Exposed
Static SIMS Spectra
Pure Polypyromellitimide Films

Counts

Mass Units

Exposed in LEO — Not Exposed
Static SIMS Spectra of Cured 934 Epoxy
SSIMS Spectra of Cured 934 Epoxy with 10% Boron Powder

Extrapolated in LEO  Not Exposed
SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder

Exposure in LEO: Not Exposed

Counts

mass Units

Exposed in LEO - Not Exposed
SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder

Counts

Mass Units

Scraped with Razor  Original
Static SIMS Spectra of Cured 934 Epoxy

Counts

Exposed in LEO  Not Exposed
SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder

Exposed in LEO — Not Exposed

Counts

mass Units

0 50 60 70 80 90 100
SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder
Static SIMS Spectra of Cured 934 Epoxy
SSIMS Spectra of Cured 934 Epoxy with 10% Boron Powder

- Exposed in LEO
- Not Exposed

Counts

Mass Units

100 110 120 130 140 150
SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder

Exposed in LEO — Not Exposed
SSIMS Spectra of Cured 934 Epoxy with 20% Boron Powder

Counts

Mass Units

Scraped with Razor -- Original
APPENDIX 4.

DSC Thermograms of Carborane Polyamides
Curve 1: DSC
File Info: mike31105 Tue Mar 12 04:52:42 1996
Sample Weight: 2.600 mg
Carborane-1,12(THF) Polyamide

Heat Flow (mW) vs. Temperature (°C)

Sample: Carborane-1,12(THF) Polyamide
Heat Flow (mW) ex 2

Temperature (°C)

Heat Flow (mW)
VITA

Michael B. Glasgow