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Polymeric Materials with Additives for Durability and Radiation Shielding in Space

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Introduction

Polymeric materials are attractive for use in space structures because of their light weight and high strength   In addition, polymers are made of elements with low atomic numbers (Z), primarily carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) which provide the best shielding from galactic cosmic rays (GCR) (**ref. 1**). Galactic cosmic rays are composed primarily of nuclei (i.e., fully ionized atoms) plus a contribution of about 2% from electrons and positrons. There is a small but significant component of GCR particles with high charge (Z > 10) and high energy (E >100 GeV) (**ref. 2**). These so-called HZE particles comprise only 1 to 2% of the cosmic ray fluence but they interact with very high specific ionization and contribute 50% of the long- term dose to humans. The best shield for this radiation would be liquid hydrogen, which is not feasible. For this reason, hydrogen-containing polymers make the most effective practical shields. Moreover, neutrons are formed in the interactions of GCR particles with materials. Neutrons can only lose energy by collisions or reactions with a nucleus since they are uncharged. This is a process that is much less probable than the Coulombic interactions of charged particles. Thus, neutrons migrate far from the site of the reaction in which they were formed. This increases the probability of neutrons reaching humans or electronic equipment. Fast neutrons (> 1 MeV) can interact with silicon chips in electronic equipment resulting in the production of recoil ions which can cause single event upsets (SEU) in sensitive components (**ref. 3**). Neutrons lose energy most effectively by elastic collisions with light atoms, particularly hydrogen atoms. Therefore, hydrogen-containing polymers are not only effective in interacting with GCR particles; they are also effective in reducing the energy of the neutrons formed in the interactions.

Neutrons with very low energy can be absorbed by certain elements which have a large probability or cross section for neutron capture. Two light elements, lithium and boron each with a stable isotope (^{6}Li and ^{10}B) which has a very large neutron capture cross section have been considered for use in space. Of the two, boron is favored because it has a larger cross section and neutron capture produces only stable products. Heavier elements like cadmium (Z=48) and gadolinium (Z=64) have considerably higher neutron capture cross sections than lithium or boron and thus could be used in smaller amounts to provide the same protection.

In the Low Earth Orbit (LEO), the presence of atomic oxygen (AO) is an additional hazard for materials since AO comprises the major part of the atmosphere in this region. The AO concentration in the LEO varies from 10^{6} to 10^{9} atoms cm^{-3}

depending among other things on the distance above the earth, the latitude, and the solar cycle (**ref. 4**). Thus, a satellite in the LEO with a typical speed of 8 km s^{-1} will undergo 10^{12} to 10^{15} collisions $cm^{-2}s^{-1}$ with AO on its forward facing surfaces. Because of its high reactivity, atomic oxygen causes surface erosion on polymeric materials, although the reaction efficiency depends on the chemical structure of the polymer (**ref. 5**).

Several projects funded by the cooperative agreement are described below. A total of 9 undergraduate students from the College of William and Mary worked on these projects. Eight of them received summer research stipends provided by the cooperative agreement. The College of William and Mary has a summer research program in which students receive a stipend and free housing in a dormitory for 10 weeks. In addition, partial support was given to a graduate student for the final phase of his research. The main support for his research was provided by an earlier cooperative agreement, NCC-1-0232.

MISSE Specimens

Materials on space vehicles in the low earth orbit (LEO) are exposed to atomic oxygen (AO), UV radiation, and interactions with charged particles, primarily electrons and protons. In addition, thermal cycling between about 40 and -30 degrees Celsius occurs every 90 minutes. Thus, the durability of materials for use in space is a serious concern. Polymeric materials are attractive for space structures because of their high strength-to-weight ratios; however they are subject to degradation from the space environment. The Materials on the International Space Station Experiment (MISSE) is a series of static exposures to test the durability of materials in the space environment. Materials are attached to aluminum trays 63.5 cm by 63.5 cm. Half of the materials are exposed to atomic oxygen and space radiations (ram direction) while the other half mainly are exposed only to space radiations (wake direction). Table I lists some information about the MISSE flights in which specimens were analyzed during this project. The AO fluence was considerably smaller for MISSE 5 than for the others because the tray was oriented 90 degrees to the direction of motion of the International Space Station (ISS). The fluence varied across the tray so the values given in Table I are averages. The fluence was affected by the position of the tray on the ISS since in some positions there was shielding from AO by structural components of the ISS. Fluence of AO in the wake direction occurred because the ISS occasionally turned usually for docking of the Space Shuttle. For MISSE 2, the AO on the wake side occurred during the first 20 months of the exposure since there was little orientation change after that. MISSE 3 and 4 were flown at the same time with different trays and deployed at different locations on the International Space Station. MISSE 6A and 6B were separate trays mounted close together on the ISS. All of our specimens were flown on MISSE 6B referred to as MISSE 6 below.

Table I. Some information about the MISSE Flights

MISSE Flight	AO Fluence (atoms/cm^2) x 10^{21} Ram Direction	Wake Direction	Days in Space	Number of Specimens Ram	Wake
2	8.5	0.20	1442	2	3
3	1.2	0.20	380	3	
4	2.1	0.39	380		1
5	0.07	N/A	409	11	
6B	1.8	0.1	529	6	14

To eliminate erosion of organic polymers in space, protective coatings have been used; however, this usually requires specialized equipment and extra processing. Moreover, the coating can be breached by impact of micrometeorites or crack after many thermal cycles. In either case, erosion of the underlying polymer proceeds once the damage occurs. To avoid these problems, we added organometallic compounds or metal nanoparticles to polymers prior to processing. In this way, the metal additive is distributed throughout the polymer. When the material is exposed to AO, the metal reacts to form a metal oxide film which protects the underlying polymer (**Ref. 6**). If the surface layer of metal oxide film is damaged in any way, the polymer/additive materials will “self-heal” by forming a new protective layer.

We used two polymers with various additives to make specimens for MISSE missions. A polyimide, poly(pyromellitimide-1,4-diphenyl ether), which has the same structure as Kapton® registered with the DuPont Corporation was used because of its good thermal properties and its extensive use in space applications. A polyetherimide, Ultem®, registered with the General Electric Corporation was used because it was well characterized and our laboratory had considerable experience with it. Figures 1 and 2 show the repeat unit for the polyimide and polyetherimide respectively.

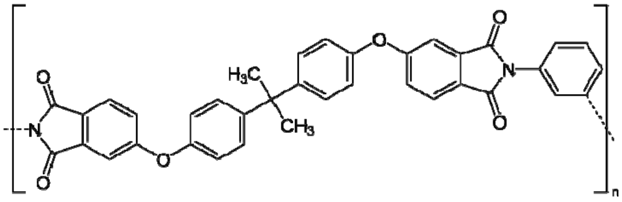

Figure 1. The repeat unit of the polyimide

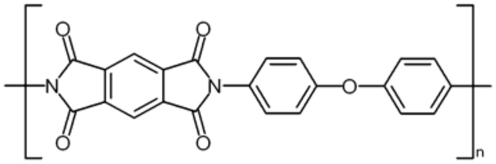

Figure 2. The repeat unit of Ultem®

We have shown in previous work that polyimide films containing aluminum acetylacetonate [$Al(C_5H_7O_2)_3$], abbreviated below as $Al(acac)_3$, showed a marked increase in surface aluminum and oxygen when exposed to atomic oxygen from a plasma generator (**Ref. 7**). This implied that a surface film of aluminum oxide formed which would impede further erosion of polymer. This hypothesis was confirmed on two MISSE missions where specimens of polyimide containing $Al(acac)_3$ survived while specimens of pure polyimide located beside it completely eroded.

Specimens Exposed on MISSE Missions

Tables 2 through 6 list the specimens flown on each MISSE mission. All polyimide and Ultem specimens were films approximately 0.025 mm thick. The Suryln specimens were about 6.4 mm thick and the space suit material was roughly 1 mm thick.

Table 2. Specimens flown on MISSE 2
Each specimen was 10.2 cm x 10.2 cm.

Ram Direction	Wake Direction
Pure polyimide	Pure polyimide
Polyimide/10% $Al(acac)_3$	Polyimide/10% $Al(acac)_3$
	Polyimide/15% $Al(acac)_3$

Table 3. Specimens flown on MISSE 3 (ram) and MISSE 4 (wake)
Each specimen was 10.2 cm x 10.2 cm.

Ram Direction	Wake Direction
Polyimide/10% $Al(acac)_3$	Surlyn 8940
Proposed material for space suit	
Surlyn 8940	

Surlyn 8940 is registered to the DuPont Corporation and consists of 94.6% polyethylene, 3.8% methacrylic acid, and 1.6% sodium methacrylate.

Table 4. Specimens flown on MISSE 5

0.953cm by 7.62 cm	**0.953 cm by 3.81 cm**	**0.953 cm by 6.35 cm**
Pure Ultem®	Ultem®/1% nanoAl	Ultem®/0.5% Al(acac)$_3$
Ultem®/5% nanoAl	Ultem®/10% borane TMA	
Pure polyimide	Ultem®/15% borane TMA	
Polyimide/5% Al(acac)$_3$	Ultem®/20% borane TMA	
Polyimide/10% Al(acac)$_3$		
Polyimide/15% Al(acac)$_3$		

Borane TMA in Table 4 stands for borane trimethylamine complex which is soluble in a solution of Ultem from which a clear boron-containing film can be made.

Table 5. Specimens from the radiation dose experiment on MISSE 6
Each specimen was about 3.6 cm by 0.8 cm.

Pure Ultem®
Ultem®/1% nanoAl
Ultem®/5% nanoAl
Ultem®/ 10% BTO
Ultem®/ 20% BTO
Ultem®/7% Al(acac)$_3$

BTO in Table 3 stands for bis(triphenyltin) oxide which is soluble in Ultem solutions from which clear tin-containing films can be made. These films each covered four small thermo-luminescent dosimeters in a passive radiation dose measurement experiment lead by the Boeing Company. No analysis was done on these films. The results of the radiation dose measurements are found in **Reference 11.**

Table 6. Larger specimens flown on MISSE 6
Each specimen was 10.2 cm x 1.3 cm.

Ram Direction	Wake Direction
Pure polyimide	Pure polyimide
Polyimide/10% Al(acac)$_3$	Polyimide/5% Al(acac)$_3$
Pure Ultem®	Polyimide/7.5% Al(acac)$_3$
Ultem®/0.5% nanoAl	Polyimide/10% Al(acac)$_3$
Ultem®/1% nanoAl	Pure Ultem®
Ultem®/5% nanoAl	Ultem®/0.5% nanoAl
	Ultem®/1% nanoAl
	Ultem®/5% nanoAl

NanoAl in Table 6 stands for nano-aluminum particles.

Analysis of MISSE Specimens

Specimens returned from space were analyzed and the results were compared with control specimens kept in the laboratory. All specimens exposed in space appeared to have a cloudy film on the space-exposed surface. The film could be easily removed with a cloth. Care was taken to not disturb the surface prior to analysis. Elemental analysis of the surface was accomplished with x-ray photoelectron spectroscopy (XPS). A visual analysis of the surface on some specimens from MISSE 6 was made with scanning electron microscopy (SEM). Both analyses were performed by the Surface Analysis Laboratory at Virginia Tech in Blacksburg, Virginia. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 in a nitrogen atmosphere with a temperature rate of 5^oC/min. Thermomechanical analyses (TMA) were made on a Shimadzu TMA-50 with a temperature rate of 5^oC/min. Some Ultem specimens were analyzed with differential scanning calorimetry (DSC) using a TA Instruments DSC 2920. The glass transition temperature of some polyimide specimens was determined by dynamic mechanical analysis (DMA) using a Thermal Analysis model 2980 analyzer with a film tension clamp, a frequency of 1 Hz, and a temperature rate of 5^oC/min from -100 to $+500^oC$.

Surface Analysis by XPS

Data from XPS analyses are found in Tables A1 through A12 in Appendix A. As a general rule, XPS analysis shows that specimens exposed to AO have a reduced percentage of carbon and an enhanced percentage of oxygen on the surface. Tables A2, A3, A6, A7, A8, and A12 show that there was serious silicon contamination on some specimens. The source of the contamination is not known but it occurred in several MISSE missions so presumably it came from the ISS. While this contamination makes the analysis more difficult, it can be seen that when aluminum is present in the specimen either as $Al(acac)_3$ or nano-aluminum particles, there is a large increase in both aluminum and oxygen on the surface after AO exposure. However, there is no corresponding increase in the percentage of surface boron in the MISSE 5 samples containing the borane TMA complex as shown in Table A8. This could result because the AO fluence on MISSE 5 was much lower than that on the other MISSE flights.

It can be seen in Tables A2 and A4 that there is a rather large amount of fluorine on the surface of some specimens after space exposure. We have seen a similar occurrence in previous work where the specimen contained aluminum (**Ref. 7**). Presumably, the fluorine combines with the aluminum though the source of the fluorine is not known. Table A4 also shows that the control specimen had silicon on the surface which mostly remained after exposure. This probably came from the glass plate when the film was made.

Thermal Analysis by TGA, TMA, DSC, and DMA

Changes in thermal properties due to exposure in space were determined by TGA, TMA, DSC, and DMA. Figure 3 shows the temperature at 10% mass loss measured by TGA for specimens exposed on MISSE 2. TGA analyses of Suryln specimens from MISSE 3 and 4 are shown in Figure 4.

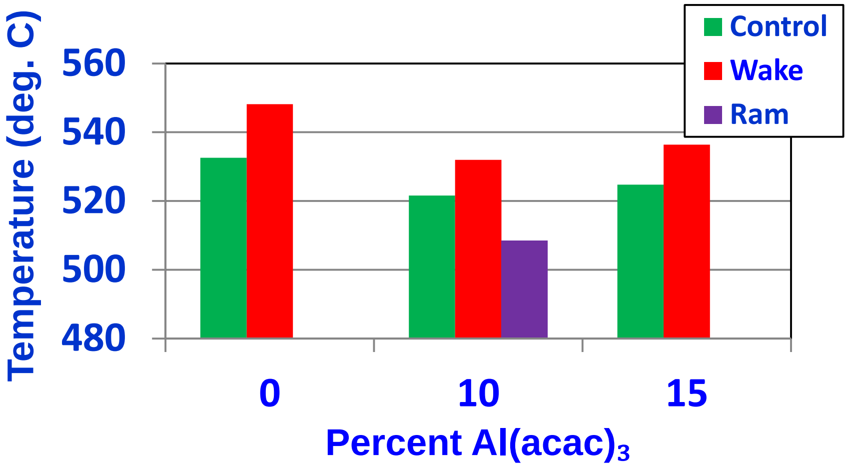

Figure 3. TGA measurement of the temperature of 10% mass loss for polyimide specimens exposed on MISSE 2.

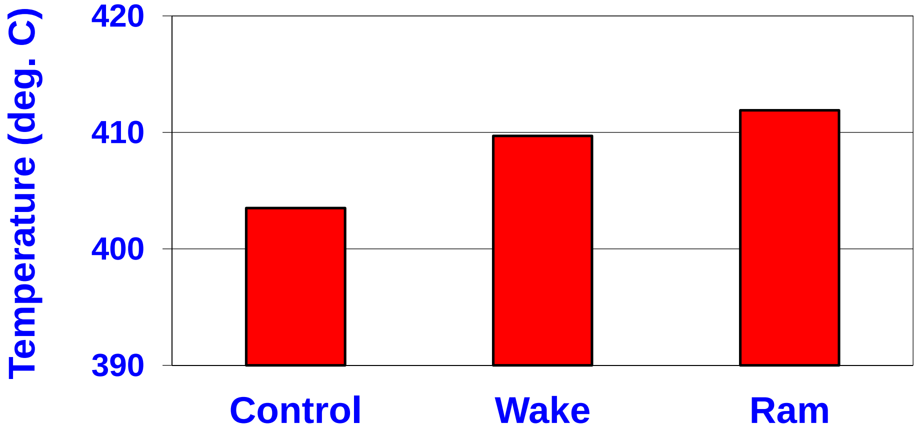

Figure 4. TGA measurement of the temperature of 10% mass loss for Surlyn specimens exposed on MISSE (ram) and MISSE 4 (wake).

Analysis by TGA of the MISSE 5 Ultem® specimens containing nano-aluminum particles showed only minor effects of space exposure as shown in Figure 5. The most significant change was for a specimen containing 5% by mass of nano-aluminum particles where the temperature for 10% mass loss increased by 5^{o} C over that of the control.

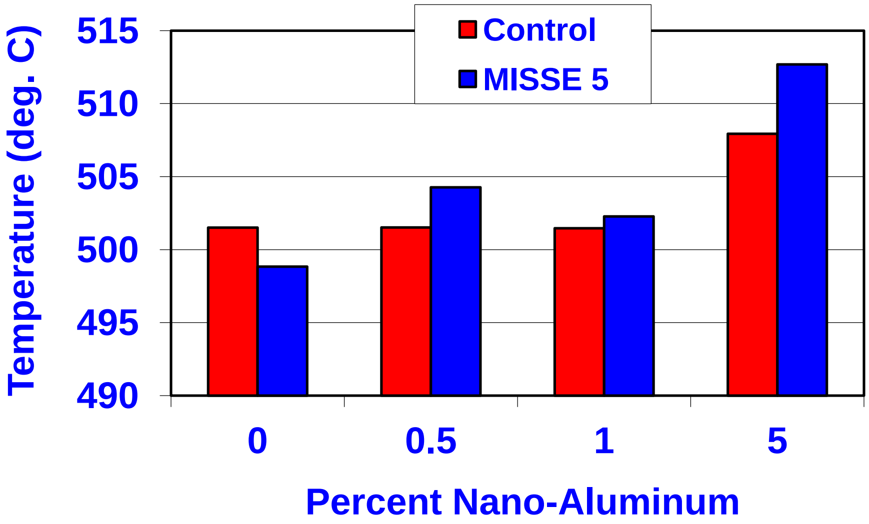

Figure 5. TGA measurement of the temperature of 10% mass loss for Ultem® films with nano-aluminum exposed on MISSE 5.

A much larger effect of space exposure is seen for Ultem® specimens containing the borane trimethylamine complex. As shown in Figure 6, the temperature of 10% mass loss decreases with increasing percent of borane TMA and is most pronounced (over 8^{o} C) in the specimen containing 20% additive. This suggests that the additive is not effective especially since XPS analysis showed no increase in surface boron after exposure. For MISSE 5, space radiation rather than AO is the major cause of changes in the specimens.

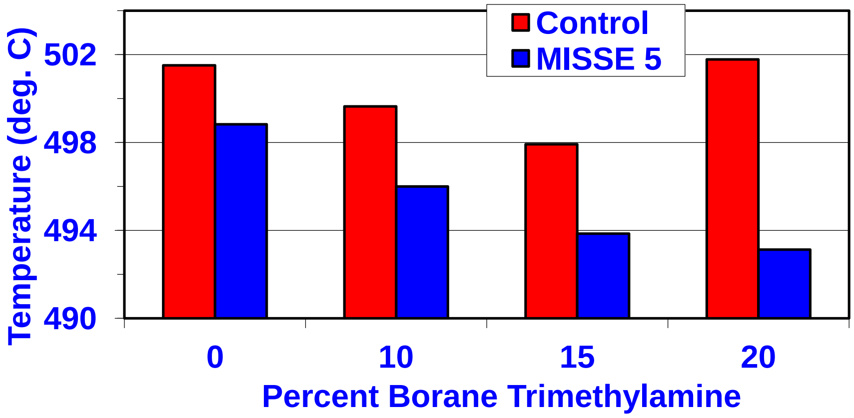

Figure 6. TGA measurement of the temperature of 10% mass loss for the Ultem® films with borane trimethylamine exposed on MISSE 5.

Analyses by TGA on specimens exposed on MISSE 6 are shown in Figure 7 for the polyimide containing Al(acac)$_3$ and Figure 8 for Ultem containing nano-aluminum. The wake direction is labeled UV in these figures. The pure polyimide specimen exposed in the wake direction showed a 6 degree decrease in 10% mass loss temperature compared to the control. On the other hand, the specimen containing 10% Al(acac)$_3$ exposed in the ram direction had a 10% mass loss temperature about 5 degrees higher than the control. The Ultem specimen containing 5% nano-aluminum showed the opposite effect when exposed in the ram direction. Its 10% mass loss temperature was almost 20 degrees lower than that of the control.

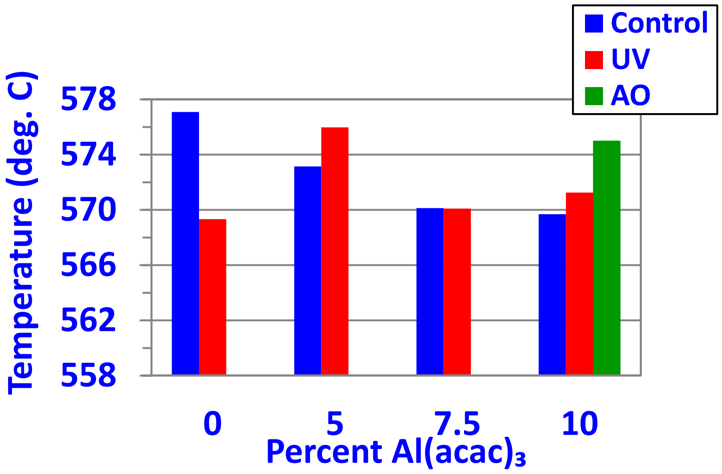

Figure 7. TGA measurement of the temperature of 10% mass loss for polyimide specimens exposed on MISSE 6.

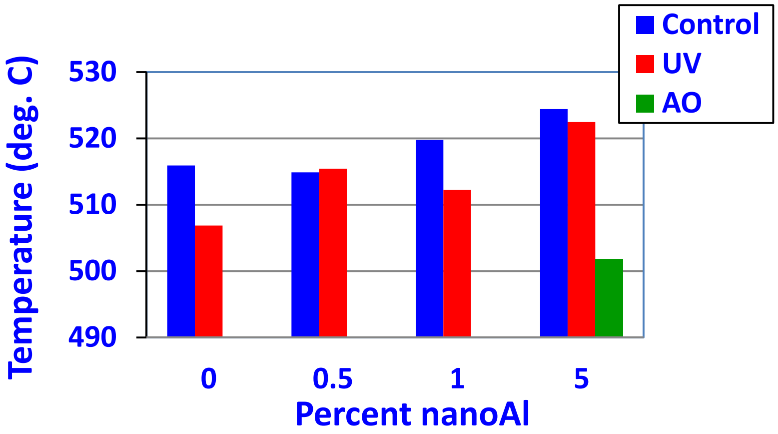

Figure 8. TGA measurement of the temperature of 10% mass loss for Ultem specimens with nano-aluminun exposed on MISSE 6.

TMA measurements were made on the Suryln specimens exposed on MISSE 3 and 4, and on the Ultem specimens containing borane trimethylamine exposed on MISSE 5. The results are shown in Figures 9 and 10. TMA measures the temperature at which the material begins to soften. The polyimide did not soften so no TMA data were taken. Suryln shows a small increase (about 3 degrees C) in softening temperature after exposure to the space environment while the Ultem with borane trimethylamine showed little change from the control after space exposure.

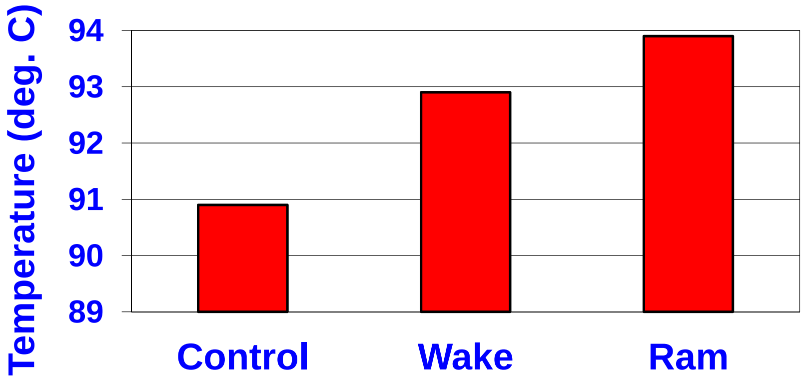

Figure 9. TMA measurement of the softening temperature of Suryln specimens exposed on MISSE 3 (ram) and MISSE 4 (wake).

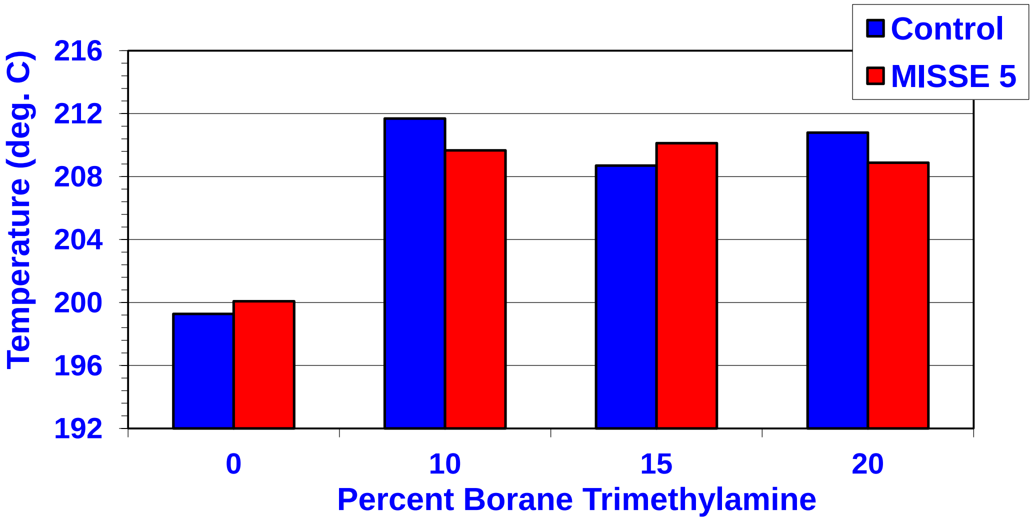

Figure 10. TMA measurement of the softening temperature for Ultem specimens with borane trimethylamine exposed on MISSE 5.

Differential scanning calorimetry (DSC) measures the temperature of both primary phase changes, such as melting point, and secondary phase changes such as glass transition temperature. The glass transition temperatures of the Ultem specimens containing nano-aluminum were measured and are shown in Figure 11. No measurements could be taken for the polyimide specimens with our instrument.

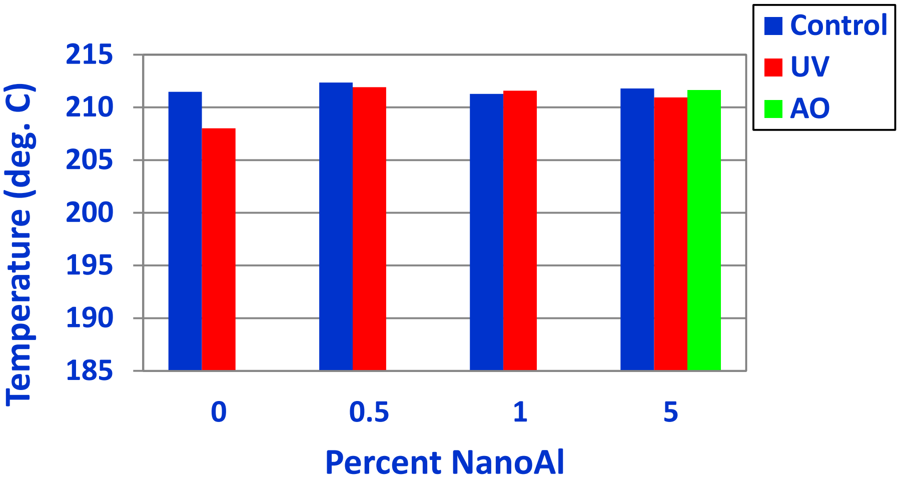

Figure 11. Glass transition temperatures from DSC analysis of Ultem specimens with nano-aluminum exposed on MISSE 6.

Dynamic mechanical analysis is another technique to measure secondary phase transitions. Using this technique, glass transition temperatures for the polyimide specimens could be measured. The DMA instrument measures the storage modulus and the elastic modulus as a function of temperature. The ratio of the two moduli is called tan delta. A curve of tan delta peaks at a transition temperature. The results of DMA measurements for the polyimide specimens from MISSE 2, 3, and 5 are shown in Figure 12. There is an increase in the transition temperature of the polyimide specimens containing Al(acac)$_3$ when exposed in space while the pure polyimide shows little change or even a decrease for the MISSE 5 specimen. Comparing the results for the specimens containing 10% Al(acac)$_3$ shows that the glass transition temperatures were nearly the same regardless of whether the specimen was in the ram or wake direction or on which mision it flew. This would suggest that space radiation rather than atomic oxygen is responsible for the effect. There is also little difference between specimens regardless of the difference in exposure time. Possibly the mechanism causing the change achieves an equilibrium after a certain time.

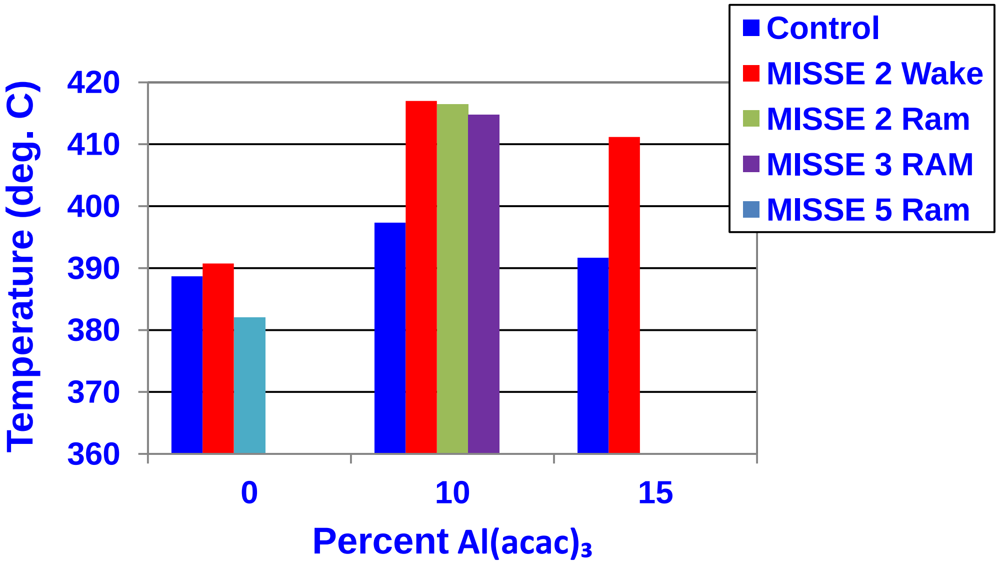

Figure 12. Glass transition temperature from DMA measurements on polyimide specimens exposed on MISSE 2, 3, and 5.

Summary of MISSE Results

The addition of aluminum acetylacetonate to polyimide films greatly enhances the resistance to erosion by atomic oxygen. While a specimen of pure polyimide eroded completely within 12 months in space, an adjacent specimen containing 10% Al(acac)$_3$ by mass remained intact with sufficient integrity to be analyzed after nearly four years of ram exposure. There was a large increase in surface aluminum and oxygen after exposure indicating that an aluminum oxide film formed on the surface and protected the underlying polymer.

There was significant silicon contamination on some specimens on MISSE 2, 5, and 6, presumably from the ISS. This made the interpretation of the XPS surface analysis difficult for these specimens. The source of the contamination is unknown. However, in all exposed specimens, there was a decrease in surface carbon and an increase in surface oxygen after space exposure. All exposed specimens had a slightly cloudy film on the surface which could be wiped off. Further study will need to be done to determine the nature of the film.

Undergraduate students William Gabler, Todd Hovey, Mark Jayanathan, and Kevin Kaurich worked on the analysis of the samples. All of the students received summer research stipends. The films used were made by former undergraduate students Richard Anderson, Eleanor Browne, and Briana Poyer. Portions of the work were reported at the 11th Pacific Polymer Conference in Cairns, Australia in December 2009. A paper based on that presentation has been published (**Ref. 8**)**.** Other parts of the work were reported at four National Space and Missile Materials Symposia (**Refs. 9, 10, 11, and 12**).

Polymers for Radiation Shielding

Gadolinium or cadmium were added to polymers because they both have high neutron capture cross sections and have high atomic numbers which enhances gamma ray absorption. Two polymers were studied, polypropylene and poly(pyromellitimide-1,4-diphenyl ether), a polyimide which has the same structure as Kapton® registered with the DuPont Corporation. Polypropylene and polyethylene have the highest hydrogen content of any polymer and thus are useful in shielding against galactic cosmic rays (GCR). Polypropylene has a higher melting temperature than polyethylene so it was chosen for study. Kapton® is used in a number of space applications and its behavior in space is well known.

Polypropylene Materials

Polypropylene (PP) is a thermoplastic material produced by polymerizing propylene monomers. It is used widely for its excellent and desirable physical, mechanical, and thermal properties at and below room temperature. There are three main types of PP, each with their own varying crystallinities. Isotactic PP (crystallizable) is composed of a carbon backbone with all methyl substituents oriented in the same direction. Atactic PP (noncrystalizable) has substituents oriented completely randomly. The other type and main focus of this investigation is syndiotactic PP (crystallizable), composed of methyl substituents oriented in alternating directions. The relative orientation of each methyl group relative to the methyl groups on neighboring monomers has a strong effect on the finished polymer's ability to form crystals, because each methyl group takes up space and constrains backbone bending.

Syndiotactic PP was used because it produced the best films. The PP was dissolved in 1, 2, 3, 4-tetrahydronaphthalene. The solution was then transferred to an aluminum pan and heated slowly up to its melting point in an oven under nitrogen. The heating lasted 5 to 7 days. Good specimens up to 2.6 mm thick were made in this manner. Gadolinium was added as gadolinium acetylacetonate (purchased from Sigma-Aldrich) and was dissolved in the solvent prior to the addition of the PP. A modifying agent, n-octadecyltriethoxysilane (purchased from Gelest), was added to enhance the dispersion of the organometallic compound in the polymer. Cadmium was added as cadmium phenyl acetate made by adding cadmium acetate hydrate to phenylacetic acid in an ammonium hydroxide solution.

Several films were successfully prepared, ranging in thickness from ~0.20mm up to ~2.6mm. The thickness varied across the individual films, so a number of measurements were taken and the median was used. The thicker samples were tested for gamma ray and neutron absorption.

Neutron absorption was determined using a one-Curie americium-beryllium source available at NASA LaRC. A piece of indium foil was sandwiched between two pieces of the material to be studied. Neutrons react with ^{115}In to make ^{116}In which is radioactive and decays with a 54.2 min half-life. The neutron source was located in a cylinder of polyethylene (PE) to slow down the energetic neutrons produced by the source, allowing mostly thermal neutrons to be emitted from the PE cylinder and reach the films and the indium foil. The sample was taped to the outside of this PE cylinder and was exposed overnight so that equilibrium could be established. The activated indium foil was then counted in a standard Geiger counter with counts taken for 100 seconds, followed by a 200 second pause between counts. The foil was counted for approximately two hours to gain sufficient data to extrapolate to the initial point. The counts were recorded with a computer and exported into an Excel sheet from which the count rate at time zero was determined. Since radioactive decay is a first-order process, a plot of ln(counts) against time should yield a straight line which can be extrapolated to zero time, i.e., the time when the sample was removed from the neutron source. The results are shown in Figure 13. Neutron absorption should increase with increasing amounts of the metal (Gd or Cd) in the polymer and reduce the radioactivity induced in the indium foil. Gadolinium has a much higher cross section than cadmium and thus should be a better neutron absorber. Figure 13 shows this to be true except for the sample with 12% gadolinium. It is probable that the metal atoms agglomerate at the higher percentage.

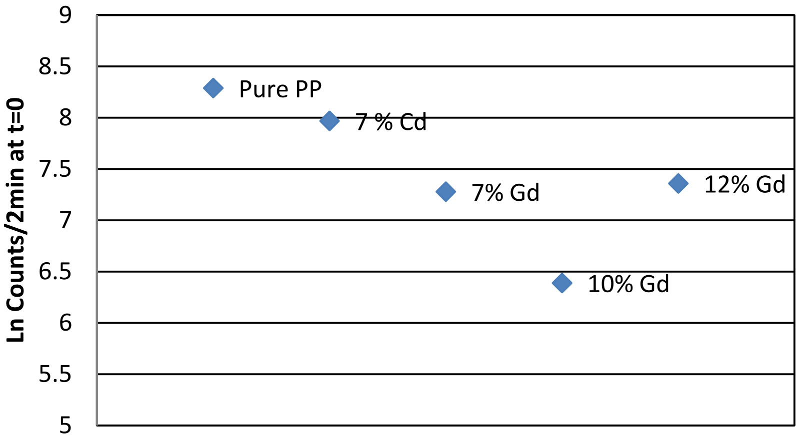

Figure 13. Neutron absorption by polypropylene films containing Cd or Gd.

The films were also tested for gamma ray absorption. Gamma rays in space arise from nuclear reactions of cosmic rays with space structures. For this study, films were placed between a ^{137}Cs source and a Geiger counter. The detector can then detect the gamma rays which did not interact with or were scattered by the polymer or filler. The source emitted 0.662MeV gamma rays as well as beta particles. A 0.4mm piece of aluminum was placed over the source to absorb the beta particles.

Gamma-ray absorption occurs best with elements which have a high atomic number (Z), however lighter elements still have some interaction. The pure polymer shows a considerable decrease in counts due to absorption or scattering. The films containing high Z elements, such as gadolinium, have much more potential for absorption, but the films composition still lies overwhelmingly towards pure polymer, so a large change in absorption should not be expected. As with neutron absorption, there exists a point where absorption decreases, even with increasing filler concentrations. As before, this is likely due to agglomeration. Figure 14 shows the results of gamma ray absorption.

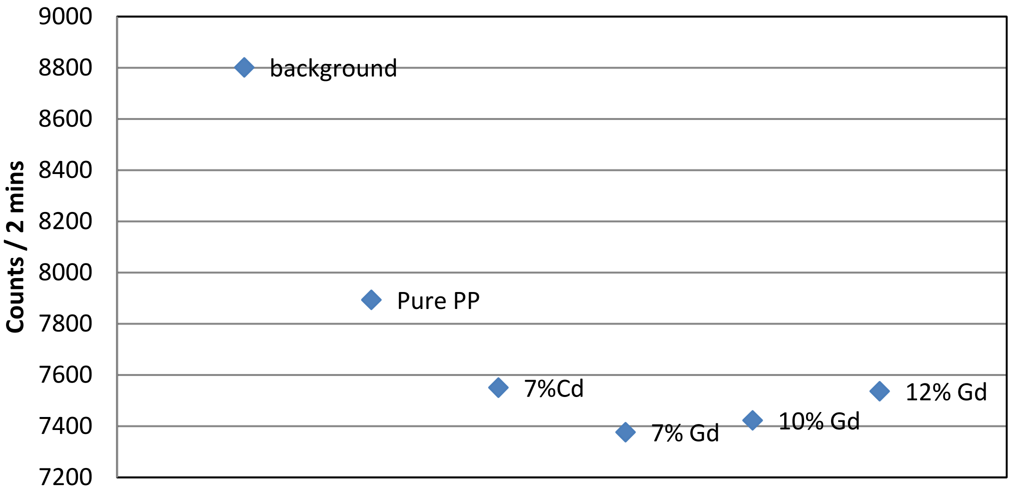

Figure 14. Absorption of ^{137}Cs gamma rays by polypropylene composites.

For greater absorption of neutrons and gamma rays, larger percentages of the absorbing metal needs to be incorporated into the polymer film. The modifier was effective in amounts up to 10% but less effective beyond that. It is possible that there is a limit for each polymer and metal combination beyond which more metal is not effective.

Recently, polypropylene samples have been made by melting PP powder in a steel mold with a heated press. The PP powder was also mixed with gadolinium oxide nano-powder. In this way, samples 4 to 5 mm thick have been made. Neutron absorption analysis on these samples has not been done yet.

Two undergraduate students, Corey Compton and Joseph Auslander worked on this project.

Polyimide Materials

We embarked on a project to incorporate gadolinium or cadmium into the high-performance polyimide, poly(pyromellitimide-1,4-diphenyl ether), which has the same structure as Kapton® registered with the DuPont Corporation. This material has superior thermal and mechanical properties to polypropylene. However, it is a thermoset material so it cannot be melted or dissolved once formed. Thus, to put additives in it, one must synthesize the polymer with the additive.

The polyimide was made by reacting equimolar amounts of 4,4’-oxydianiline (ODA) and 1,2,4,5-benzenetetracarboxylic acid-dianhydride (PMDA) in N,N-dimethylacetamide (DMAc) (**Ref. 13**). The resulting poly(amic acid) was stirred with a predetermined amount of additive and films were cast on a glass plate and placed in a dust-free box to allow the solvent to evaporate. Dry films were thermally cured for one hour each at 100, 200, and 300^{o}C. Cadmium was added as cadmium phenylacetate made by mixing a solution of methoxy phenylacetic acid in dilute sodium hydroxide with a solution of cadmium nitrate in water and filtering the precipitated cadmium phenylacetate. Gadolinium was added as gadolinium oxide nano-powder. Gadolinium phenylacetate was also prepared but attempts to incorporate it into the polymer were unsuccessful.

Polyimide films containing cadmium or gadolinium were made with various amounts of the metal and tested for neutron absorption by the method described above. The results are shown in Figures 15, 16,and 17. Figure 15 shows neutron absorption of polyimide films containing various percentages of Gd_2O_3. While the overall trend is for lower counts with higher Gd_2O_3 percentage, it is not smooth. The variations were thought to be due to agglomeration of the Gd_2O_3 nano-particles. To minimize this, a modifier, phenethyltrimethoxysilane, was then added to the synthesis and new films were made and tested. The results are shown in Figure 16. In this case, the percentage shown is elemental gadolinium rather than the Gd_2O_3. Films containing cadmium phenylacetate were made successfully and tested in the same manner with the results shown in Figure 17. Films with more than 7% cadmium phenylacetate were too brittle to be used.

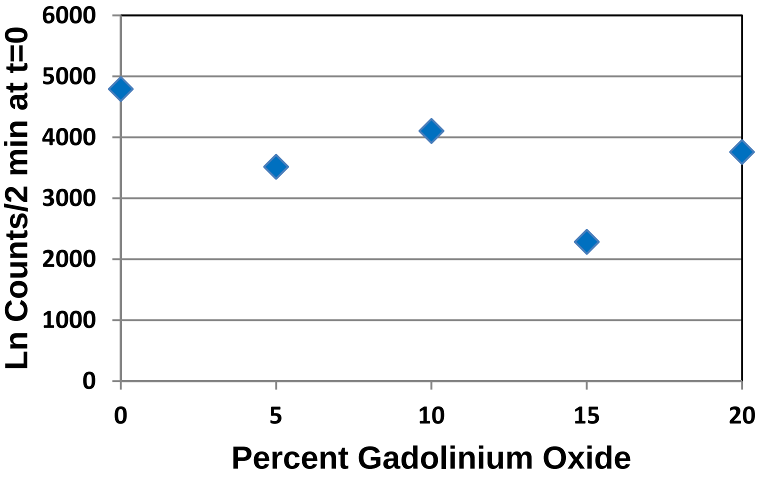

Figure 15. Neutron absorption by polyimide films containing Gd_2O_3.

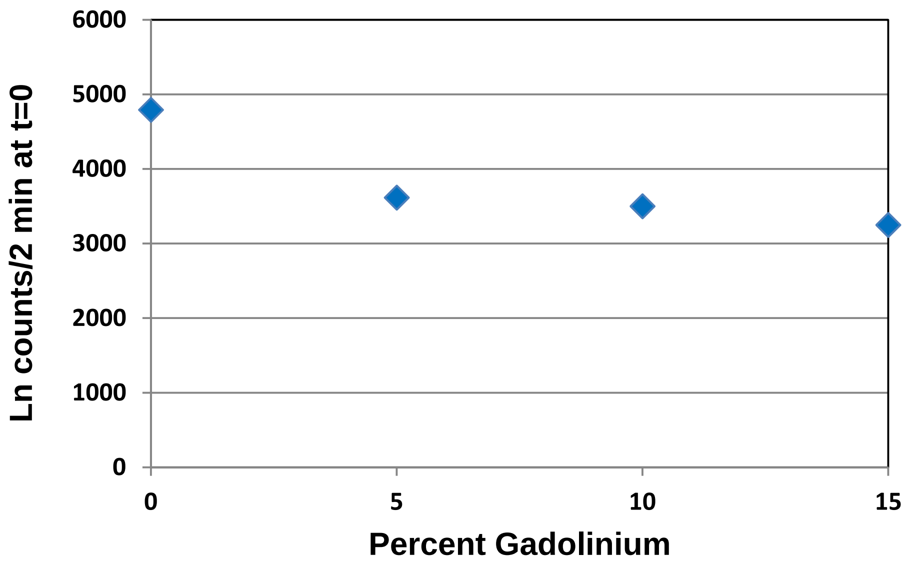

Figure 16. Neutron absorption of polyimide films containing Gd_2O_3 with a modifier.

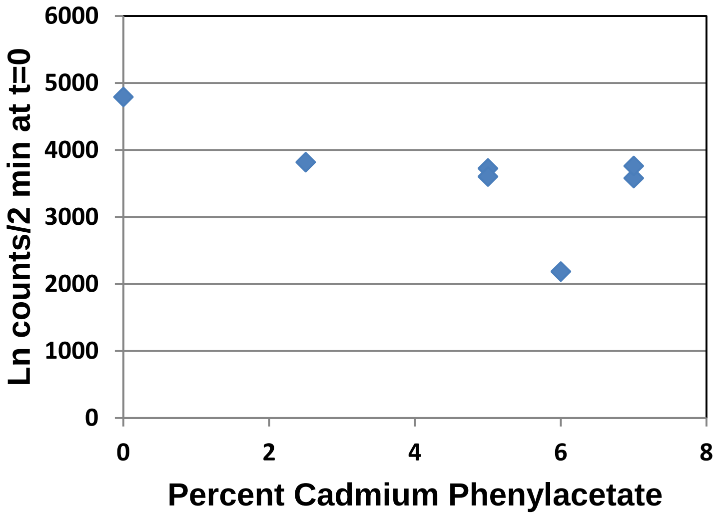

Figure 17. Neutron absorption of polyimide films containing cadmium phenylacetate.

Figure 16 shows that using a modifier to minimize agglomeration produces a much smoother trend of reduced count rate with increasing percentage of gadolinium. However, it also shows that doubling the percent gadolinium results in a relatively small decrease in count rate. For thin films, at least, there is a limit to the effectiveness of the added metal. Thicker specimens would likely show more effect of added metal.

Four undergraduate students, William Gabler, Amy Sirkis, Mark Tedesco, and Cayla Wallwork worked on this project.

Summary of Radiation Shielding Materials

Polypropylene and polyimide films containing gadolinium or cadmium showed enhanced neutron absorption over pure films even with films of 0.02 to 0.05 mm. The heavy metals in the polymer films also contributed to absorption of gamma rays. Thicker samples of polypropylene with gadolinium were made in a heated press. Analysis of these materials could not be completed because the neutron source was in use by other experimenters.

Five undergraduate students from the College of William and Mary worked on the radiation shielding projects described above. Four of them received stipends for a least one summer. The College of William and Mary has a summer research program in which students receive a stipend and free housing in a dormitory for 10 weeks.

Boron-Containing Polypropylene Fibers

This was a project to produce fibers containing boron for neutron-absorbing fabrics. The major portion of the project was funded by a previous cooperative agreement, NNC-1-0232. Polypropylene fibers were made by the student at NASA LaRC. Two kinds of fibers were made: fibers of pure polypropylene and fibers which contained 20% boron carbide enriched to 96.77% in ^{10}B, the boron isotope with the high neutron capture cross section. Both kinds of fibers were woven into cloth fabrics at the Textile Engineering, Chemistry, and Science Department at North Carolina State University in Raleigh, North Carolina. The fibers were not thin enough to make an ideal material, but the cloth was flexible though somewhat stiff. In addition, the weave was not as tight as desired because of the thickness of the fibers.

The neutron absorbing ability of the boron-containing cloth was compared to that of the pure polypropylene cloth using the neutron source at NASA LaRC with the procedure described above. Even with the somewhat open weave, two layers of the boron-containing fabric produced a 44% attenuation of neutrons compared to the pure polypropylene material. This is shown in Figure 18 where the radioactivity of indium foil is plotted versus time of counting. It can be seen that the activity of the indium is significantly lower when two layers of the boron-containing cloth are between the foil and the neutron source compared with two layers of the pure polypropylene cloth.

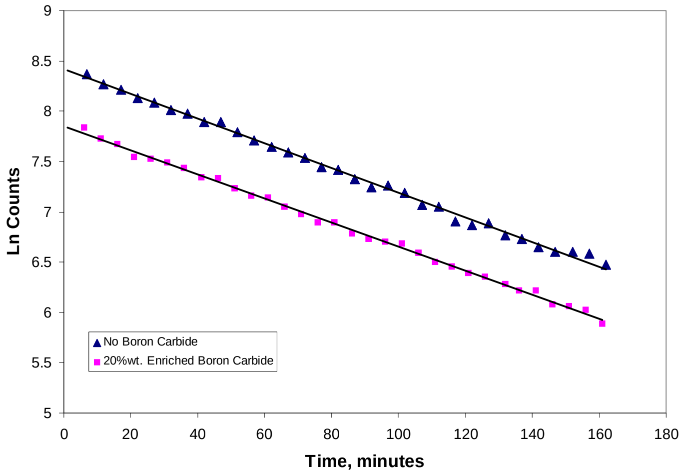

Figure 18. Effect of two layers of enriched boron-containing polypropylene fabric on neutron activation of indium.

The results of this project were reported by the student at the 48th AIAA/ASME/AHS/ASC Structures, Structural Dynamics, and Materials Conference in Honolulu, Hawaii in April, 2007 and a paper was submitted to the conference proceedings (**Ref. 14**). The project was the basis for the thesis of Derrick Manzlak for the Master of Science degree in August, 2007.

Overall Summary

Four different projects were supported either totally or partially by this cooperative agreement. A total of nine College of William and Mary undergraduate students worked on these projects. Eight of the students received summer research stipends which were enhanced by William and Mary with free housing for the ten-week summer session. In addition, seven of the students worked on the projects during the academic year for academic credit but no stipend. A graduate student received funding from this and a previous cooperative agreement. The principal investigator worked with the students throughout the entire project period.

Work from the projects was reported at six national or international conferences and two papers were published.

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Appendix A

X-ray Photoelectron Spectroscopy (XPS)

Table A1. XPS analysis of pure polyimide exposed on MISSE 2.

Sample/ Element	C	O	N	Si	Na	F	Ca
Control	76.6	17.0	5.6	0.2	0	0.6	0
Wake	67.9	23.1	6.5	1.2	1.1	0	0.2

Table A2. XPS analysis of polyimide with 10% Al(acac)$_3$ exposed on MISSE 2.

Sample/Element	C	O	N	Al	Si	Ca	F
Control	75.1	17.7	5.6	0.2	0.4	0.3	0.8
Wake	10.3	59.3	0.1	2.5	27.4	0	0.6
Ram	13.6	52.1	0.4	21.1	6.9	0	5.9

Table A3. XPS analysis of polyimide with 15% Al(acac)$_3$ exposed on MISSE 2.

Sample/Element	C	O	N	Al	Si	Ca	F
Control	72.1	20.4	6.8	0.5	0.01	0.3	0.02
Wake	10.4	59.1	0.0	2.2	27.8	0.0	0.6

Table A4. XPS analysis of polyimide with 10% Al(acac)$_3$ exposed on MISSE 3.

Sample\Element	C	O	N	Al	Si	F
Control	71.4	18.0	2.0	0	6.8	0
Ram	9.2	54.7	0	22.7	5.2	5.9

Table A5. XPS analysis of Suryln exposed on MISSE 3 (ram) and MISSE 4 (wake)

Sample/Element	C	O	F	Si	Na
Control	72.1	17.1	0.0	9.6	0.2
Ram	66.7	21.1	2.3	4.5	5.4
Wake	65.1	22.6	1.1	2.8	7.8

Table A6. XPS analysis of pure Ultem® exposed on MISSE 5

Sample\Element	C	O	N	Si	F	Na
Control	77.1	16.1	4.7	0.5	0.1	1.5
Ram	44.7	39.3	3.4	11.1	0.3	1.2

Table A7. XPS analysis of Ultem® with 5% Al nanoparticles exposed on MISSE 5.

Sample\Element	**C**	**O**	**N**	**Al**	**Si**	**F**
Control	77.6	16.4	4.6	0.1	1.2	0.1
Ram	33.7	46.4	2.1	6.9	10.7	0.2

Table A8. XPS analysis of Ultem® with 20% borane TMA exposed on MISSE 5.

Sample\Element	**C**	**O**	**N**	**B**	**Si**	**F**	**Na**
Control	80.5	14.7	3.7	0.2	0	0.9	0
Ram	50.2	37.7	4.0	0.1	6.8	0	1.2

Table A9. XPS analysis of pure Ultem® exposed on MISSE 6.

Sample\Element	**C**	**O**	**N**	**F**	**Si**
Control	81.3	13.5	2.1	0.0	2.4
Wake	56.0	32.6	3.7	0.0	7.3

Table A10. XPS analysis of Ultem® with 5% Al nanoparticles exposed on MISSE 6.

Sample\Element	**C**	**O**	**N**	**Al**	**F**	**Si**
Control	79.8	15.6	4.2	0.0	0.2	0.1
Wake	42.8	42.7	3.1	6.2	0.2	4.4
Ram	29.0	50.6	1.4	15.1	1.1	1.4

Table A11. XPS analysis of pure polyimide exposed on MISSE 6.

Sample\Element	**C**	**O**	**N**	**F**	**Si**
Control	78.7	15.1	2.7	0.0	2.2
Wake	53.7	32.8	6.0	0.4	6.7

Table A12. XPS analysis of polyimide with 10% Al(acac)$_3$ exposed on MISSE 6.

Sample\Element	**C**	**O**	**N**	**Al**	**F**	**Si**
Control	70.6	22.0	4.7	1.7	0.0	0.0
Wake	11.9	66.3	0.6	4.2	1.0	15.5
Ram	11.9	63.9	0.0	17.0	2.0	4.8