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Atomic Oxygen Erosion Yield Prediction for Spacecraft Polymers in Low Earth Orbit

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Abstract

The ability to predict the atomic oxygen erosion yield of polymers based on their chemistry and physical properties has been only partially successful because of a lack of reliable low Earth orbit (LEO) erosion yield data. Unfortunately, many of the early experiments did not utilize dehydrated mass loss measurements for erosion yield determination, and the resulting mass loss due to atomic oxygen exposure may have been compromised because samples were often not in consistent states of dehydration during the pre-flight and post-flight mass measurements. This is a particular problem for short duration mission exposures or low erosion yield materials. However, as a result of the retrieval of the Polymer Erosion and Contamination Experiment (PEACE) flown as part of the Materials International Space Station Experiment 2 (MISSE 2), the erosion yields of 38 polymers and pyrolytic graphite were accurately measured. The experiment was exposed to the LEO environment for 3.95 years from August 16, 2001 to July 30, 2005 and was successfully retrieved during a space walk on July 30, 2005 during Discovery's STS-114 Return to Flight mission. The 40 different materials tested (including Kapton H fluence witness samples) were selected specifically to represent a variety of polymers used in space as well as a wide variety of polymer chemical structures. The MISSE 2 PEACE Polymers experiment used carefully dehydrated mass measurements, as well as accurate density measurements to obtain accurate erosion yield data for high-fluence (8.43×10^{21} atoms/cm²). The resulting data was used to develop an erosion yield predictive tool with a correlation coefficient of 0.895 and uncertainty of $\pm 6.3 \times 10^{-25}$ cm³/atom. The predictive tool utilizes the chemical structures and physical properties of polymers to predict in-space atomic oxygen erosion yields. A predictive tool concept (September 2009 version) is presented which represents an improvement over an earlier (December 2008) version.

1.0 Introduction

Early Space Shuttle flight experiments found that hydrocarbon polymers exposed to the LEO environment would gradually erode as a result of atomic oxygen exposure. The atomic oxygen interacts with the polymers causing the surface to convert to volatile oxidation products. The atomic oxygen erosion rates differed from one type of polymer to another (Refs. 1 to 6). This erosion susceptibility is measured as the atomic oxygen erosion yield, which is the volume lost per incident atomic oxygen atom, given in cm^3/atom (Ref. 7). Numerous LEO flight experiments have been performed that have contributed to the available data on atomic oxygen erosion yields for a variety of materials. Many of the experiments were conducted on various short duration shuttle missions including STS-5 (Ref. 1), STS-8 (Ref. 8), and the Evaluation of Oxygen Interactions with Materials-3 (EOIM-3) experiment on STS-46 (Ref. 9). In addition, many materials were evaluated after lengthy LEO exposure (5.8 yr) on the Long Duration Exposure Facility (LDEF) (Ref. 10). Unfortunately, many of these early experiments did not utilize dehydrated mass loss measurements, and the resulting mass loss due to atomic oxygen exposure may have been obscured because samples were often not in consistent states of dehydration during the pre-flight and post-flight mass measurements. This is a particular problem for short duration mission exposures or low erosion yield materials. Inconsistent states of dehydration can cause erroneous erosion yields because polymer mass loss due to oxidation can be indistinguishable from changes in the amount of absorbed water in the polymer.

Forty different material samples, collectively called the Polymer Erosion and Contamination Experiment (PEACE) Polymers, have been exposed to the LEO space environment on the exterior of the ISS for nearly 4 years as part of Materials International Space Station Experiment 2 (MISSE 2). The purpose of the MISSE 2 PEACE Polymers experiment was to accurately determine the AO erosion yield of a wide variety of polymeric materials exposed for an extended period of time to the LEO space environment. The majority of samples were thin film polymers, flown with numerous layers stacked together (Refs. 11 and 12). Carefully obtained dehydrated pre-flight and post-flight mass measurements, as well as accurate density measurements, were used to determine accurate high-fluence (8.43×10^{21} atoms/ cm^2) erosion yield data for the MISSE 2 PEACE Polymers samples (Refs. 11 and 12). For many samples, multiple layers of the polymers were used to insure that the materials would not be oxidized all the way through.

The materials chosen for the MISSE 2 PEACE experiment were selected specifically to represent many polymers typically used in space as well as a wide variety of polymer chemical structures. The intent of choosing a variety of polymer structures was that the diversified data could assist with the development of an atomic oxygen erosion yield predictive tool. This tool could then be used to predict LEO erosion yields of new polymers based on chemical structure and simple low-cost ground laboratory test data, thus bypassing the need for actual in-space LEO testing for new polymers that are developed.

As LEO erosion yield data gradually became available, it was noticed that some polymers, such as the fluoropolymers, had low erosion yields compared to polyimide Kapton H. On the other hand, those containing significant amounts of single bonded oxygen, such as polyoxymethylene, had higher erosion yields than Kapton H. The dependence of atomic oxygen erosion yield on chemical structure has been explored based on early available LEO data (Refs. 13 to 15). A variety of approaches were considered in this paper to develop an erosion yield predictive formula based on best fit criteria to the MISSE 2 PEACE spaceflight data (Ref. 12).

2.0 Erosion Yield Modeling Concepts

The modeling information used to develop an atomic oxygen predictive tool consisted of the MISSE 2 PEACE Polymers LEO atomic oxygen erosion yield data (from Refs. 11 and 12), polymer chemical structure information concerning the number and types of chemical bonds, polymer density information (from Refs. 11 and 12), and fractional ash content data (from Ref. 16). The atomic oxygen predictive tool

was developed using these properties and assuming an unknown degree of dependence, which was tuned to the highest correlation between actual LEO results and the predictive tool. Thus, for every physical property or chemical bond type, a degree of dependence was assumed that was optimized to provide the closest match between predicted and actual erosion yields. Sequential and multiple iterations were used to gradually maximize the correlation coefficient between the predicted atomic oxygen erosion yield and the measured atomic oxygen erosion yield.

2.1 LEO Atomic Oxygen Erosion Yield Data From MISSE 2

Atomic oxygen erosion yield data was obtained from the MISSE 2 PEACE Polymers experiment, which exposed 41 one-inch diameter samples, including two Kapton H polyimide atomic oxygen fluence witness samples, to the LEO space environment. This experiment was flown in MISSE Passive Experiment Container 2 (PEC 2) Tray 1, sample tray E5, which was attached to the exterior of the International Space Station Quest Airlock, and placed in a ram facing orientation. This experiment was subjected to directed ram atomic oxygen along with solar and charged particle radiation and was exposed to the LEO environment for 3.95 years from August 16, 2001 to July 30, 2005. It was retrieved during a space walk on July 30, 2005 during Discovery's STS-114 Return to Flight mission. Figure 1 shows MISSE 2 on the International Space Station. Figures 2 and 3 show pre-flight and post-flight photos of the MISSE 2 PEACE Polymers experiment tray containing the 40 polymers and pyrolytic graphite.

Details of the specific polymers flown, flight sample fabrication, solar and ionizing radiation environmental exposure, pre-flight and post-flight characterization techniques, and atomic oxygen fluence calculations are presented in References 11 and 12. The atomic oxygen fluence was found to be 8.43×10^{21} atoms/cm². Results of x-ray photoelectron spectroscopy (XPS) contamination analysis of two MISSE 2 sapphire witness samples in tray E6 (located on the same MISSE surface and next to tray E5) indicated the space experiment had received very little contamination. An extremely thin silica contaminant layer of 1.3 and 1.4 nm was on each slide, respectively (Ref. 16).

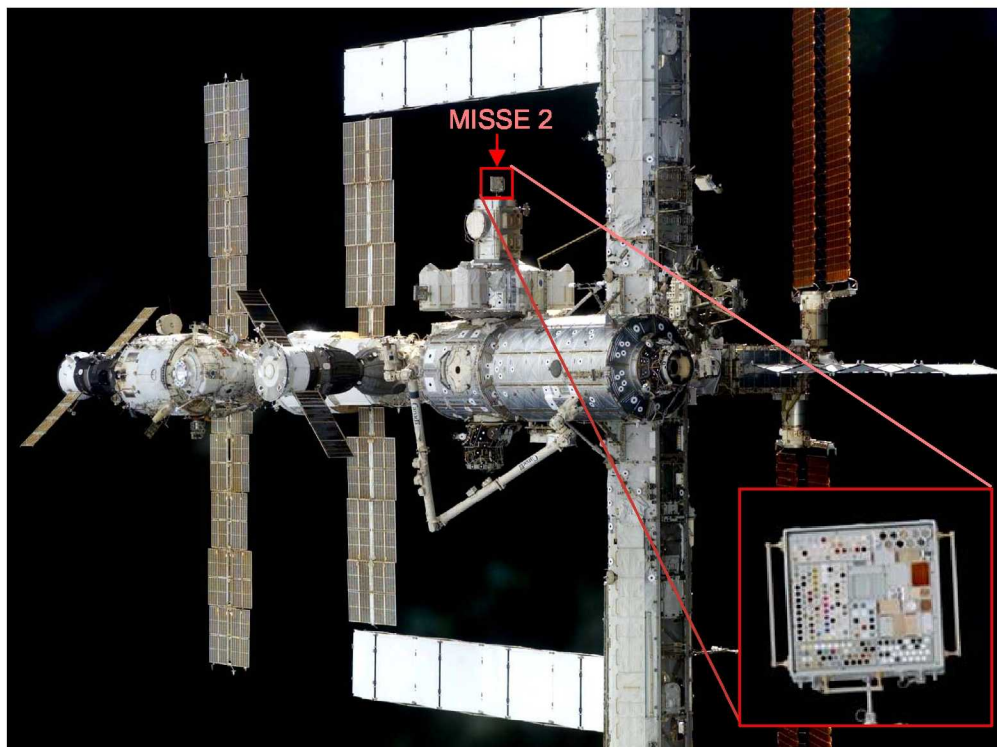


Figure 1.—MISSE 2 Passive Experiment Container Tray 1 holding the PEACE Polymers experiment attached to the International Space Station from August 16, 2001 to July 30, 2005.

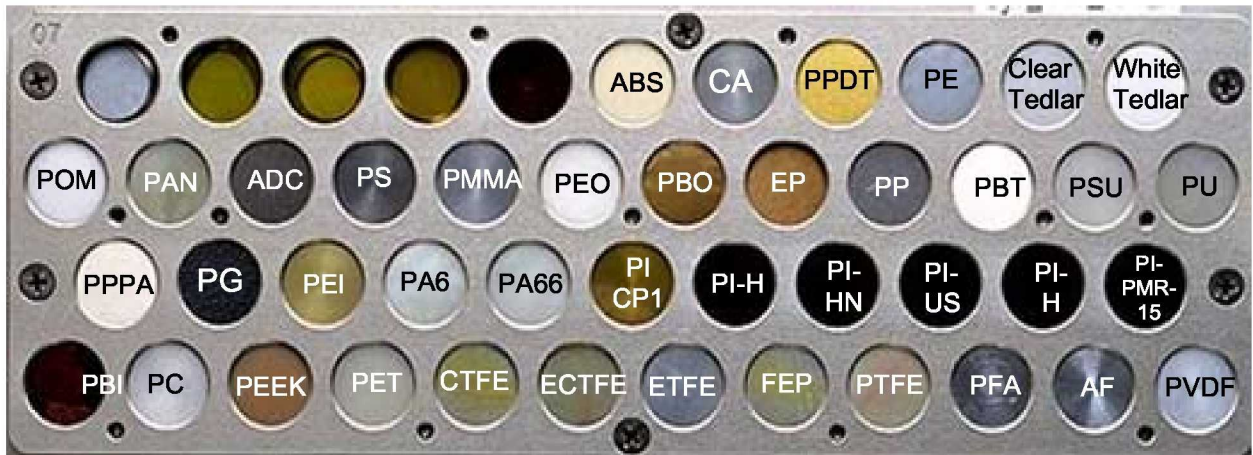


Figure 2.—Photograph of the MISSE 2 PEACE Polymers experiment prior to flight. The labels shown indicate the materials defined in Table I.



Figure 3.—Photograph of the MISSE 2 PEACE Polymers experiment post-flight.

The MISSE 2 PEACE Polymers experiment LEO atomic oxygen erosion yield data, which was used to develop the predictive tool, is given in Table I (Refs. 11 and 12). In six cases, the actual erosion yield is probably greater than the value listed because a portion or all of the exposed area of the flight sample was completely eroded away. In these cases, the measured erosion yields were also included in the data set to develop a predictive erosion yield equation because, in general, the samples appeared that they were completely eroded at a fluence level very close to the full mission fluence.

TABLE I.—MISSE 2 PEACE POLYMERS EROSION YIELD DATA

Material	Polymer abbreviation	LEO MISSE 2 Erosion Yield (cm ³ /atom)
Acrylonitrile butadiene styrene	ABS	1.09×10^{-24}
Cellulose acetate	CA	5.05×10^{-24}
Poly-(p-phenylene terephthalamide)	PPDT (Kevlar)	6.28×10^{-25}
Polyethylene	PE	$> 3.74 \times 10^{-24}$
Polyvinyl fluoride	PVF (clear Tedlar)	3.19×10^{-24}
Crystalline polyvinyl fluoride with white pigment	PVF (white Tedlar)	1.01×10^{-25}
Polyoxymethylene; acetal; polyformaldehyde	POM (Delrin)	9.14×10^{-24}
Polyacrylonitrile	PAN	1.41×10^{-24}
Allyl diglycol carbonate	ADC (CR-39)	$> 6.80 \times 10^{-24}$

Material	Polymer abbreviation	LEO MISSE 2 Erosion Yield (cm ³ /atom)
Polystyrene	PS	3.74×10 ⁻²⁴
Polymethyl methacrylate	PMMA	> 5.60×10 ⁻²⁴
Polyethylene oxide	PEO	1.93×10 ⁻²⁴
Poly(p-phenylene-2,6-benzobisoxazole)	PBO (Zylon)	1.36×10 ⁻²⁴
Epoxide or epoxy	EP	4.21×10 ⁻²⁴
Polypropylene	PP	2.68×10 ⁻²⁴
Polybutylene terephthalate	PBT	9.11×10 ⁻²⁵
Polysulphone	PSU	2.94×10 ⁻²⁴
Polyurethane	PU	1.56×10 ⁻²⁴
Polyphenylene isophthalate	PPPA (Nomex)	1.41×10 ⁻²⁴
Pyrolytic graphite	PG	4.15×10 ⁻²⁵
Polyetherimide	PEI	> 3.31×10 ⁻²⁴
Polyamide 6 or nylon 6	PA 6	3.51×10 ⁻²⁴
Polyamide 66 or nylon 66	PA 66	1.80×10 ⁻²⁴
Polyimide	PI (CP1)	1.91×10 ⁻²⁴
Polyimide (PMDA)	PI (Kapton H)	3.00×10 ⁻²⁴
Polyimide (PMDA)	PI (Kapton HN)	2.81×10 ⁻²⁴
Polyimide (BPDA)	PI (Upilex-S or US)	9.22×10 ⁻²⁴
High temperature polyimide resin	PI (PMR-15)	> 3.02×10 ⁻²⁴
Polybenzimidazole	PBI	> 2.21×10 ⁻²⁴
Polycarbonate	PC	4.29×10 ⁻²⁴
Polyetheretherketone	PEEK	2.99×10 ⁻²⁴
Polyethylene terephthalate	PET (Mylar)	3.01×10 ⁻²⁴
Chlorotrifluoroethylene	CTFE (Kel-f)	8.31×10 ⁻²⁵
Ethylene-chlorotrifluoroethylene	ECTFE (Halar)	1.79×10 ⁻²⁴
Tetrafluoroethylene-ethylene copolymer	ETFE (Tefzel)	9.61×10 ⁻²⁵
Fluorinated ethylene propylene	FEP	2.00×10 ⁻²⁵
Polytetrafluoroethylene	PTFE	1.42×10 ⁻²⁵
Perfluoroalkoxy copolymer resin	PFA	1.73×10 ⁻²⁵
Amorphous Fluoropolymer	AF	1.98×10 ⁻²⁵
Polyvinylidene fluoride	PVDF (Kynar)	1.29×10 ⁻²⁴

2.2 Modeling Variable Considerations

Upon a cursory inspection of the atomic oxygen erosion yields from the MISSE 2 PEACE Polymers data, as well as previous LEO flight experiments, it was clear that polymers with a significant abundance of pendent fluorine and/or chlorine atoms (such as fluorinated ethylene propylene and chlorotrifluoroethylene) have low atomic oxygen erosion yields relative to Kapton H polyimide in LEO. Conversely, polymers with significant oxygen in their backbone (such as polyoxymethylene) had much higher atomic oxygen erosion yields. It is far less clear as to what degree the erosion yield depends upon mixes of in-the-chain or pendent oxygen, nitrogen, and benzyl rings and/or whether the bonding is single, double or triple. Thus, many approaches were explored to correlate chemical structure, the number atoms of each type in a polymer repeat unit, and number of bonds of each type (single, double, or triple as well as carbon bonding to what atoms) in the polymer repeat unit.

Polymer density was also considered as a potential erosion yield dependent variable because densely packed atoms should have lower erosion yields than loosely packed atoms because it would take more atoms to remove the same amount of volume. Data on polymer density was either obtained from supplier information or density gradient column testing.

Most polymers contain some fraction of inorganic material that does not become volatile upon reaction with atomic oxygen. The post-atomic oxygen exposure nonoxidizable residue is called ash. The presence of resulting fragile remaining ash may be a portion of the debris shown on or above some of the samples in the MISSE 2 PEACE Polymers experiment postflight photo shown in Figure 3. As atomic oxygen erodes a polymer that contains inorganic material in LEO, the resulting nonvolatile ash begins to

accumulate on the eroded surface of the polymer, tending to shield the underlying polymer from oxidation. As a result, the ash content of polymers reduces the polymer's erosion yield by shielding the polymer from atomic oxygen. If one compares the erosion yield of clear polyvinyl fluoride (clear Tedlar) with that of white Tedlar, it becomes evident that the titanium dioxide pigment particles in white Tedlar shield its surface, resulting in a very low erosion yield of $0.101 \times 10^{-24} \text{ cm}^3/\text{atom}$ compared to a much higher erosion yield, $3.19 \times 10^{-24} \text{ cm}^3/\text{atom}$, for clear Tedlar. Although the ash content expressed as a fractional volume of ash would be more correct when considering erosion yield effects, it is much easier to use the mass fraction of ash because the densities of the ash are difficult to measure.

Ash content used to develop the predictive tool described in this paper was determined experimentally for each of the 39 PEACE polymers (including Kapton H) and pyrolytic graphite. It was determined as the fraction of the initial dehydrated polymer mass that is nonvolatile and remains after the polymer has been completely oxidized in an RF plasma asher. This was accomplished by placing pieces of each polymer in thin aluminum foil cups that were previously exposed to atomic oxygen to remove organic coatings that typically reside on aluminum foil as a result of foil processing. The samples in the aluminum cups were then ashed for several hundred hours in a RF plasma asher operated on air (Ref. 16) until only ash remained. Figure 4 shows scanning electron microscope (SEM) images of the ash remaining from white Tedlar and polyethylene oxide. Using energy dispersive spectroscopy the white Tedlar ash indicated the presence of titanium as expected for the titanium dioxide pigment particles and the ash from polyethylene oxide indicated a mix of metal elements.

Unfortunately, a gradual buildup of inorganic contamination from the asher itself complicates the process of determining ash content because the added mass from contaminants is observed as additional ash. This buildup is especially prevalent if the ashing is continued long after the organic portion of the polymer is completely oxidized. Additionally, materials with low erosion yields in the asher environment tend to accumulate more contamination than those with high erosion yields. The contamination is also difficult to correct for because it depends on the surface area of the ash which is difficult to measure.

The effect of ash content on erosion yield in an end Hall hyperthermal atomic oxygen facility was determined by measuring the erosion yield of five epoxy resin samples which were purposely filled with various amounts of fumed silica. Epoxy resin with no-added fumed silica was found to also contain some ash as indicated in Table II as a result of ashing samples of the cured epoxy. An additional amount of ash, in the form of fumed silica, was weighed and mixed with both parts of the uncured epoxy to achieve a total mass fraction ash indicated in Table II which was used to plot Figure 5.

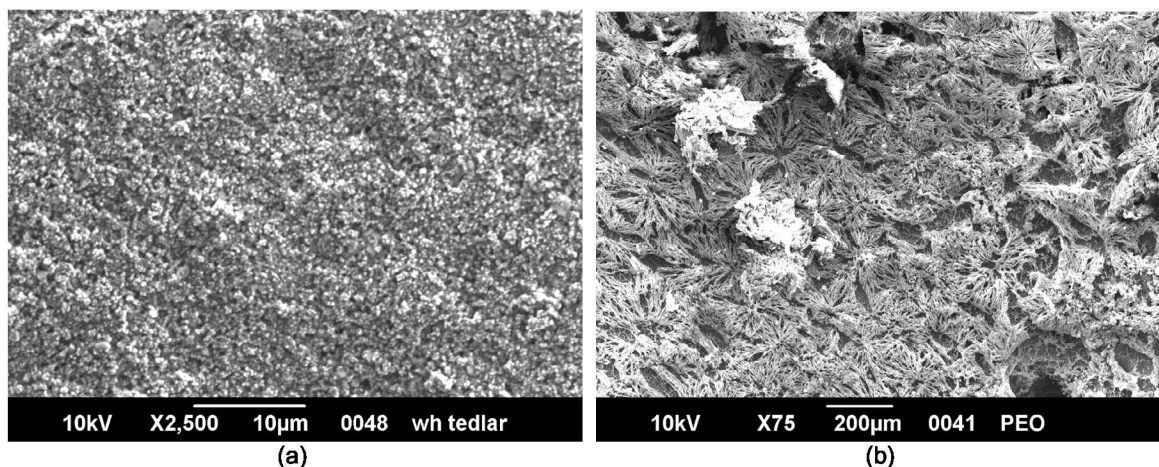


Figure 4.—Scanning electron microscope images of the ash remaining after several hundred hours of RF plasma asher air plasma exposure. (a) White Tedlar titanium dioxide ash particles. (b) Ash remaining from polyethylene oxide.

TABLE II.—ASH CONTENT OF THE FIVE SAMPLES USED TO MEASURE
EROSION YIELD DEPENDENCE ON MASS FRACTION ASH

Mass fraction of ash in as-received epoxy	Mass fraction of fumed silica added (as ash) to epoxy	Total mass fraction ash of sample	Ratio of atomic oxygen erosion yield relative to neat (no ash) polymer
0.0453	0.0000	0.0453	0.912
0.0453	0.0837	0.1252	0.758
0.0453	0.1662	0.2039	0.758
0.0453	0.3336	0.3638	0.330
0.0453	0.4167	0.4431	0.214
0.0453	0.4998	0.5225	0.120

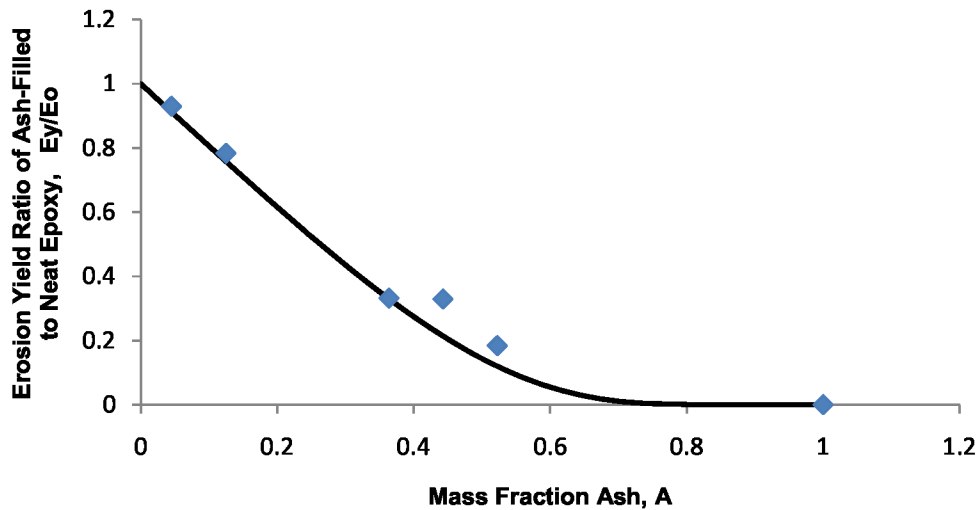


Figure 5.—Erosion yield dependence on mass fraction ash in epoxy for a Kapton H effective fluence of 1.24×10^{20} atoms/cm².

The effect of the total mass fraction ash on the erosion yield was measured using an end Hall hyperthermal atomic oxygen source operated on pure oxygen at ~70 eV. It was necessary to use hyperthermal rather than thermal energy atomic oxygen attack because thermal energy atomic oxygen is not greatly attenuated (compared to LEO hyperthermal atomic oxygen) in reaction probability as a result of impingement upon ash surfaces. Because particle-filled epoxy resins tend to have a resin rich surface all the samples were abraded prior to atomic oxygen exposure to ensure that the surfaces exposed to atomic oxygen were representative of the bulk material.

The results of the erosion yield dependence upon mass fraction ash for a Kapton H effective fluence of 1.24×10^{20} atoms/cm² is shown in Figure 5. The erosion yield of the neat epoxy resin (if there was no ash at all in the resin) was estimated based on the slope of the curve shown in Figure 5 and the intercept at zero mass fraction ash.

The solid line in Figure 5 is an equation which models the observed dependence given by

$$E_y = E_0 e^{-KA/(1-A)} \quad (1)$$

where

E_0 Erosion yield of epoxy without any ash content in end Hall test

E_y Erosion yield of epoxy with ash content

K Erosion yield attenuation constant = 1.94 for a Kapton H effective fluence of 1.24×10^{20} atoms/cm²

A Mass fraction ash

The erosion yield dependence function in Equation (1) was designed to produce an erosion yield of zero if the ash mass fractional content is one and an erosion yield of E_0 if the ash content is zero (neat polymer). This observed erosion yield dependence on ash content was also quantifiably consistent with end Hall atomic oxygen exposure of clear and white Tedlar, thus suggesting that the equation is probably reasonably accurate for all ash containing polymers.

The solid line in Figure 6 represents the same Equation (1) erosion yield dependency constant K , 1.94, as in the Figure 5 plot.

Table III lists the density, ρ , and mass fraction of the polymer that is ash, A , measured for each of the MISSE 2 PEACE polymers.

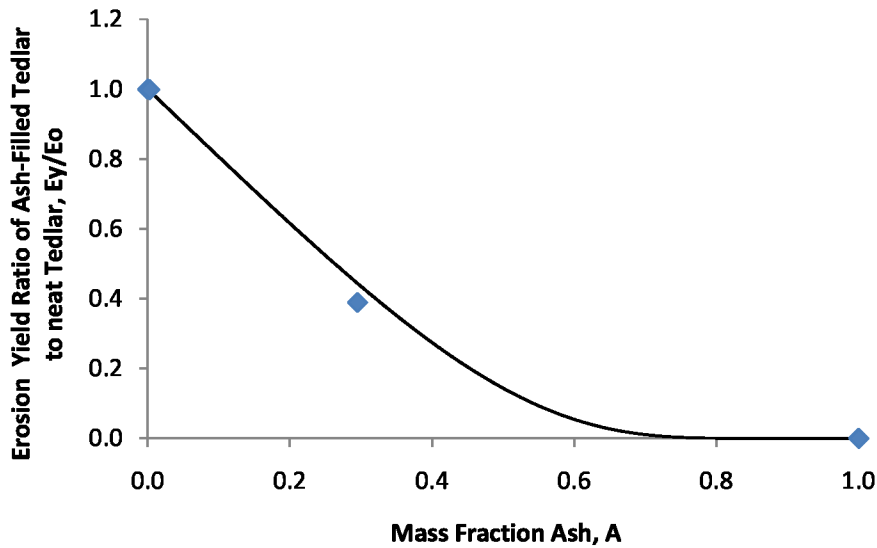


Figure 6.—Erosion yield of Tedlar relative to neat Tedlar as a function of ash.

TABLE III.—MISSE 2 PEACE POLYMERS DENSITY AND FRACTIONAL ASH CONTENT

Material	Polymer abbreviation	Density (Ref. 12) ρ (g/cm ³)	Mass fraction of polymer that is ash (Ref. 16), A
Acrylonitrile butadiene styrene	ABS	1.05	0.0458
Cellulose acetate	CA	1.2911	0.00283
Poly-(p-phenylene terephthalamide)	PPDT (Kevlar)	1.4422	0.00372
Polyethylene	PE	0.918	0.0203
Polyvinyl fluoride	PVF (Clear Tedlar)	1.3792	0.00285
Crystalline polyvinylfluoride with white pigment	PVF (White Tedlar)	1.6241	0.295
Polyoxymethylene; acetal; polyformaldehyde	POM (Delrin)	1.3984	0.00902
Polyacrylonitrile	PAN	1.1435	0.00184
Allyl diglycol carbonate	ADC (CR-39)	1.3173	0.00265
Polystyrene	PS	1.0503	0.00042
Polymethyl methacrylate	PMMA	1.1628	0.00028
Polyethylene oxide	PEO	1.1470	0.00112

Material	Polymer abbreviation	Density (Ref. 12) ρ (g/cm ³)	Mass fraction of polymer that is ash (Ref. 16), A
Poly(p-phenylene-2,6-benzobisoxazole)	PBO (Zylon)	1.3976	0.0109
Epoxide or epoxy	EP	1.1150	0.0304
Polypropylene	PP	0.9065	0.00184
Polybutylene terephthalate	PBT	1.3318	0.0629
Polysulphone	PSU	1.2199	0.00348
Polyurethane	PU	1.2345	0.00664
Polyphenylene isophthalate	PPPA (Nomex)	0.72	0.0476
Pyrolytic graphite	PG	2.22	0.00154
Polyetherimide	PEI	1.2873	0.00105
Polyamide 6 or nylon 6	PA 6	1.1233	0.00388
Polyamide 66 or nylon 66	PA 66	1.2252	0.00459
Polyimide	PI (CP1)	1.4193	0.00171
Polyimide (PMDA)	PI (Kapton H)	1.4273	0.00284
Polyimide (PMDA)	PI (Kapton HN)	1.4345	0.00441
Polyimide (BPDA)	PI (Upilex-S or US)	1.3866	0.00164
High temperature polyimide resin	PI (PMR-15)	1.3232	0.000531
Polybenzimidazole	PBI	1.2758	0.000927
Polycarbonate	PC	1.1231	0.000992
Polyetheretherketone	PEEK	1.2259	0.00177
Polyethylene terephthalate	PET (Mylar)	1.3925	0.00826
Chlorotrifluoroethylene	CTFE (Kel-f)	2.1327	0.00204
Ethylene-chlorotrifluoroethylene	ECTFE (Halar)	1.6761	0.000655
Tetrafluoroethylene-ethylene copolymer	ETFE (Tefzel)	1.7397	0.00123
Fluorinated ethylene propylene	FEP	2.1443	0.00534
Polytetrafluoroethylene	PTFE	2.1503	0.0427
Perfluoroalkoxy copolymer resin	PFA	2.1383	0.000298
Amorphous fluoropolymer	AF	2.1463	0.0362
Polyvinylidene fluoride	PVDF (Kynar)	1.7623	0.0358

It is expected that the erosion yield attenuation constant, K , increases with fluence for ash-containing polymers as the surface of the ash containing polymers becomes more covered with remaining ash with increasing atomic oxygen fluence. An approximation to this ash shielding dependence on fluence was made by modeling the erosion yield of white Tedlar in hyperthermal atomic oxygen environments for the low fluence end Hall test and the high fluence MISSE 2 LEO exposure as shown in Figure 7. In this figure the erosion yield for the end Hall test was corrected to account for the differences between the Kapton H effective fluence of the end Hall exposure and in-space exposure using the ratio between Kapton H and white Tedlar erosion yields for both environments.

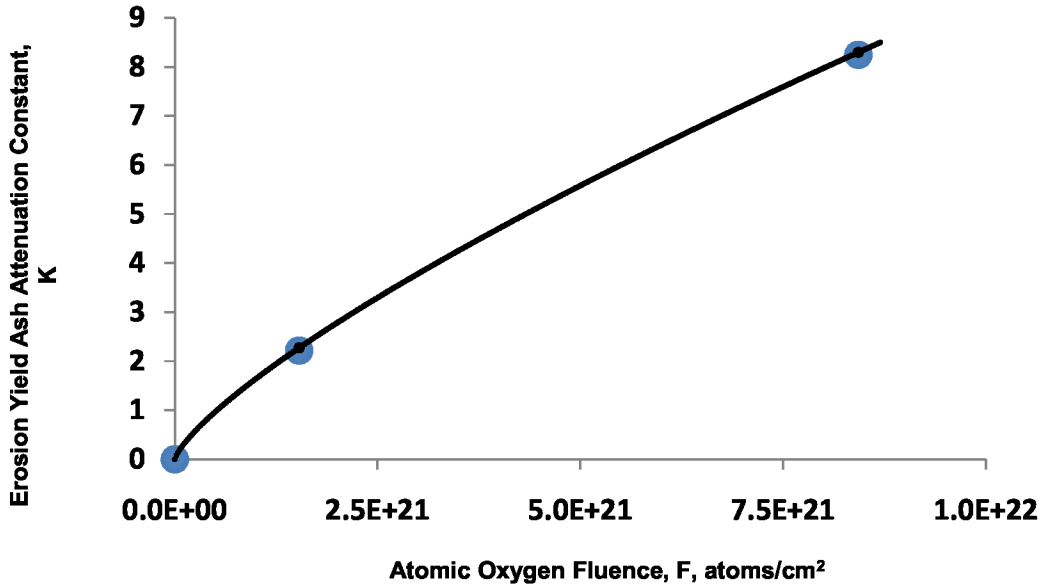


Figure 7.—Erosion yield ash attenuation constant, K , as a function of fluence, F .

A best fit curve drawn through the data is given by

$$K = (1.80 \times 10^{-16}) F^{0.76} \quad (2)$$

Additional erosion yield dependencies were considered for the predictive model including the physical density (in grams/cm³). For example, a foam polymer would have a high erosion yield compared to a fully dense polymer.

Also considered was the packing density of atoms, which relates to how densely the atoms theoretically could be packed in comparison to the actual volume of the repeat unit where larger spaces would occur between atoms due to van der Waals bonding or void spaces. Loosely packed atoms should result in a high erosion yield compared to densely packed atoms. The minimum volume of the atoms that make up a polymer repeat unit, V_{Σ} , was based on the sum of the atoms making up the polymer repeat unit assuming each atom's volume is determined by its covalent radii.

The actual volume, V_r , of each repeat unit was determined based on the chemical structure of the repeat unit as well as the molecular weight and density of the material. Thus, if the ratio of V_{Σ}/V_r was much less than one, the polymer's erosion yield would be higher than that of a similarly structured polymer with tightly packed atoms. Values of V_{Σ}/V_r are given in Reference 16.

3.0 Results and Discussion

Over 100 different types of equations were tested using the information in the previous section to determine a formula with a high correlation coefficient, R^2 , with the actual LEO erosion yield data. An initial erosion yield model (December 2009 version) which produced a correlation coefficient of 0.914 was modeled using a linear assumption of dependency relations and made extensive use of bonding information of the atoms in a repeat unit (Ref. 16). However, this equation was found to produce negative erosion yields in some cases for polymers that were not flown as part of the MISSE 2 PEACE Polymers experiment.

An alternative approach (September 2009 version) was then pursued, which used the dependency variables (such as atomic populations per repeat unit) as exponents with appropriate constants to optimize

the correlation coefficient. This prevented negative erosion yield values and enabled significant simplification of the predictive equation with very little loss in the correlation coefficient.

This simpler approach resulted in a reasonably high correlation coefficient with actual LEO MISSE 2 PEACE polymer data. The resulting equation used atomic populations in the repeat unit as well as physical density, packing density, ash content, and the number of single and double oxygen bonds in the repeat unit. The predictive LEO erosion yield equation is given by

$$E_y = C_o(V_\Sigma/V_r) C_{\Sigma/r} (\rho) C_p e^X \quad (3)$$

where

$$\begin{aligned} X = & (C_{C/t}N_C + C_{H/t}N_H + C_{sO/t}N_{sO} + C_{dO/t}N_{dO} + C_{N/t}N_N + C_{Cl/t}N_{Cl} + \\ & + C_{F/t}N_F + C_{S/t}N_S) / N_t + (C_{O/C}N_O + C_{N/C}N_N + C_{F/C}N_F + \\ & + C_{H/C}N_H + C_{Cl/C}N_{Cl} + C_{S/C}N_S) / N_C - K[(A)]/(1-A) \end{aligned}$$

and

$$K = (1.80 \times 10^{-16}) F^{0.76}$$

The coefficients C_o , $C_{\Sigma/r}$, C_p , $C_{C/t}$, $C_{H/t}$, $C_{sO/t}$, $C_{dO/t}$, $C_{N/t}$, $C_{Cl/t}$, $C_{F/t}$, $C_{S/t}$, $C_{O/C}$, $C_{N/C}$, $C_{F/C}$, $C_{H/C}$, $C_{Cl/C}$, $C_{S/C}$, and K are constants associated with the various terms relating to the number of atoms, bonds, or physical characteristics of the polymers are given by

E_y	Atomic oxygen erosion yield in LEO, cm^3/atom
V_Σ	The sum of the volume of the atoms making up the polymer repeat unit based on their covalent radii, cm^3
V_r	The actual volume of each repeat unit determined based on the chemical structure of the repeat unit as well as the molecular weight and density of the material
ρ	Density of the polymer, grams/cm^3
N_C	Number of carbon atoms in polymer repeat unit
N_H	Number of hydrogen atoms in polymer repeat unit
N_{sO}	Number of single bonded oxygen atoms in the polymer repeat unit
N_{dO}	Number of double bonded oxygen atoms in the polymer repeat unit
N_N	Number of nitrogen atoms in polymer repeat unit
N_{Cl}	Number of chlorine atoms in polymer repeat unit
N_F	Number of fluorine atoms in polymer repeat unit
N_S	Number of sulfur atoms in polymer repeat unit
N_t	Total number of atoms in polymer repeat unit
N_O	Number of oxygen atoms in the polymer repeat unit
A	Mass fraction of ash in the polymer
F	Atomic oxygen fluence, atoms/cm^2

With all of the C coefficients for the Equation (3) optimized, the correlation coefficient between predicted erosion yield and LEO measured erosion yield is 0.895. This correlation includes all of the MISSE 2 PEACE polymers except polyethylene oxide, which appeared to have an anomalously low erosion yield, for some unknown reason, compared to what is predicted based on the chemical and physical properties. The values of the optimized C coefficients are listed in Table IV.

TABLE IV.—DEFINITION AND VALUES OF THE OPTIMIZED COEFFICIENTS ASSOCIATED WITH EACH VARIABLE

Symbol	Definition	Value
C_O	Proportionality constant which resulted from best fit linear equation relating the measured atomic erosion yield to predicted erosion yield	$3.02 \times 10^{30} \text{ cm}^3/\text{atom}$
$C_{sO/t}$	Constant for single bonded oxygen atoms in the polymer repeat unit	-0.94
$C_{dO/t}$	Constant for double bonded oxygen atoms in the polymer repeat unit	-3.59
$C_{N/t}$	Constant for nitrogen atoms in the polymer repeat unit	4.42
$C_{S/t}$	Constant for sulfur atoms in polymer repeat unit	-22.0
$C_{Cl/t}$	Constant for chlorine atoms in polymer repeat unit	-8.60
$C_{F/t}$	Constant for fluorine atoms in polymer repeat unit	-1.54
$C_{\Sigma r}$	Constant for ratio of sum of volume of atoms in repeat unit (based on their covalent radii) to volume of the repeat unit	-2.86
$C_{S/C}$	Constant for the ratio of sulfur atoms to carbon atoms in the repeat unit	3.90
C_p	Constant for polymer density	4.87
$C_{O/C}$	Constant for the ratio of oxygen atoms to carbon atoms in the repeat unit	0.395
$C_{F/C}$	Constant for the ratio of the fluorine atoms to carbon atoms in the repeat unit	-1.70
$C_{H/C}$	Constant for the ratio of the hydrogen atoms to carbon atoms in the repeat unit	0.053
$C_{N/C}$	Constant for the ratio of the nitrogen atoms to carbon atoms in the repeat unit	-5.02
$C_{Cl/C}$	Constant for the ratio of the chlorine atoms to carbon atoms in the repeat unit	1.48
K	Erosion yield ash attenuation constant	8.30 for a fluence of $8.43 \times 10^{21} \text{ atoms/cm}^2$

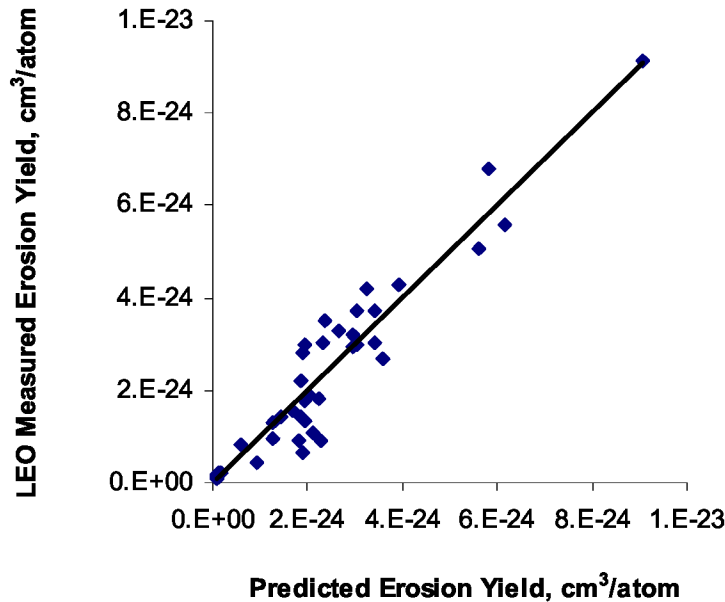


Figure 8.—Optimized linear fit between the LEO MISSE 2 PEACE atomic oxygen erosion yields and the predicted erosion yields for the MISSE 2 mission with an atomic oxygen fluence of $8.43 \times 10^{21} \text{ atoms/cm}^2$.

A plot of the optimized predicted erosion yields versus the LEO measured MISSE 2 PEACE Polymer experiment erosion yields (with the exception of PEO) using Equation 4 and the constants in Table IV is shown in Figure 8.

The resulting predicted erosion yields have a correlation coefficient of 0.895 and an uncertainty (standard deviation) of $\pm 6.3 \times 10^{-25}$ cm³/atom when comparing predicted erosion yields with actual space erosion yields (for 38 polymers and pyrolytic graphite). The predictive tool of Equations 3 and 4 allow for erosion yield prediction at any atomic oxygen fluence. This is especially relevant for polymers containing high fractional ash contents. A table listing the materials, their predicted erosion yields for the MISSE 2 fluence, and MISSE 2 measured erosion yields is given in Table V.

TABLE V.—COMPARISON OF PREDICTED AND MEASURED ATOMIC OXYGEN EROSION YIELDS

Material	Polymer abbreviation	Predicted erosion yield, cm ³ /atom	MISSE 2 erosion yield, cm ³ /atom
Acrylonitrile butadiene styrene	ABS	2.12×10^{-24}	1.09×10^{-24}
Cellulose acetate	CA	5.63×10^{-24}	5.05×10^{-24}
Poly-(p-phenylene terephthalamide)	PPD-T (Kevlar)	1.92×10^{-24}	6.28×10^{-25}
Polyethylene	PE	3.04×10^{-24}	3.74×10^{-24}
Polyvinyl fluoride—clear	PVF (Clear Tedlar)	2.94×10^{-24}	3.19×10^{-24}
Polyvinyl fluoride—with white pigment	PVF (White Tedlar)	9.39×10^{-26}	1.01×10^{-25}
Polyoxymethylene; acetal; polyformaldehyde	POM (Delrin)	9.03×10^{-24}	9.14×10^{-24}
Polyacrylonitrile	PAN	1.42×10^{-24}	1.41×10^{-24}
Allyl diglycol carbonate	ADC (CR-39)	5.83×10^{-24}	6.80×10^{-24}
Polystyrene	PS	3.43×10^{-24}	3.74×10^{-24}
Polymethyl methacrylate	PMMA	6.17×10^{-24}	5.60×10^{-24}
Polyethylene oxide	PEO	7.02×10^{-24}	1.93×10^{-24}
Poly-(p-phenylene-2,6-benzobisoxazole)	PBO (Zylon)	1.91×10^{-24}	1.36×10^{-24}
Epoxide or Epoxy	EP	3.24×10^{-24}	4.21×10^{-24}
Polypropylene	PP	3.58×10^{-24}	2.68×10^{-24}
Polybutylene terephthalate	PBT	2.31×10^{-24}	9.11×10^{-25}
Pulsulphone	PSU	2.95×10^{-24}	2.94×10^{-24}
Polyurethane	PU	1.73×10^{-24}	1.56×10^{-24}
Polyphenylene isophthalate	PPPA (Nomex)	1.84×10^{-24}	1.41×10^{-24}
Pyrolytic graphite	PG	9.41×10^{-25}	4.15×10^{-25}
Polyetherimide	PEI	2.66×10^{-24}	3.31×10^{-24}
Polyamide 6 or nylon 6	PA 6	2.40×10^{-24}	3.51×10^{-24}
Polyamide 66 or nylon 66	PA 66	2.28×10^{-24}	1.80×10^{-24}
Polyimide	PI (CP1)	2.02×10^{-24}	1.91×10^{-24}
Polyimide (PMDA)	PI (Kapton HN)	1.91×10^{-24}	2.81×10^{-24}
Polyimide (BPDA)	PI (Upilex-S)	1.83×10^{-24}	9.22×10^{-25}
Polyimide (PMDA)	PI (Kapton H)	1.93×10^{-24}	3.00×10^{-24}
High temperature polyimide resin	PI (PMR-15)	2.33×10^{-24}	3.02×10^{-24}
Polybenzimidazole	PBI	1.83×10^{-24}	2.21×10^{-24}
Polycarbonate	PC	3.94×10^{-24}	4.29×10^{-24}
Polyetheretherketone	PEEK	3.03×10^{-24}	2.99×10^{-24}
Polyethylene terephthalate	PET (Mylar)	3.44×10^{-24}	3.01×10^{-24}
Chlorotrifluoroethylene	CTFE (Kel-f)	6.03×10^{-25}	8.31×10^{-25}
Ethylene-chlorotrifluoroethylene	ECTFE (Halar)	1.94×10^{-24}	1.79×10^{-24}
Tetrafluoroethylene-ethylene copolymer	ETFE (Tefzel)	1.26×10^{-24}	9.61×10^{-25}
Fluorinated ethylene propylene	FEP	9.82×10^{-26}	2.00×10^{-25}
Polytetrafluoroethylene	PTFE	7.09×10^{-26}	1.42×10^{-25}
Polyvinylidene fluoride	PVDF (Kynar)	1.26×10^{-24}	1.29×10^{-25}
Perfluoroalkoxy copolymer resin	PFA	7.54×10^{-26}	1.73×10^{-25}
Amorphous fluoropolymer	AF	1.38×10^{-25}	1.98×10^{-25}

4.0 Summary

A predictive tool was developed to estimate the LEO atomic oxygen erosion yield of polymers based on the results of the MISSE 2 PEACE Polymers experiment, which accurately measured the erosion yield of a wide variety of polymers and pyrolytic graphite. The flight experiment materials were selected specifically to represent a variety of polymers used in space as well as a wide variety of polymer chemical structures. The September 2009 version predictive tool utilizes the chemical structure, atomic populations of the polymer repeat unit, oxygen bonding information, and physical properties (such as density and ash content) that can be measured in ground laboratory tests. The prediction does not require the use of asher erosion yield information. The tool has a correlation coefficient of 0.895 and an uncertainty of $\pm 6.3 \times 10^{-25}$ cm³/atom when compared with actual MISSE 2 PEACE Polymers space data (for 38 polymers and pyrolytic graphite). One polymer, polyethylene oxide (PEO), was found to be significantly off the linear fit for some unknown reason and was not used in the predictive tool equation. The predictive tool does appear to predict reasonable atomic oxygen erosion yields, even for those polymers that yielded a negative erosion value with the previous predictive process. The tool also allows for the prediction of atomic oxygen erosion yields as a function of fluence which is relevant for polymers containing high ash contents. The intent of the predictive tool is to be able to make estimates of LEO atomic oxygen erosion yields for new polymers without requiring expensive and time consumptive in-space testing.

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14. ABSTRACT The ability to predict the atomic oxygen erosion yield of polymers based on their chemistry and physical properties has been only partially successful because of a lack of reliable low Earth orbit (LEO) erosion yield data. Unfortunately, many of the early experiments did not utilize dehydrated mass loss measurements for erosion yield determination, and the resulting mass loss due to atomic oxygen exposure may have been compromised because samples were often not in consistent states of dehydration during the pre-flight and post-flight mass measurements. This is a particular problem for short duration mission exposures or low erosion yield materials. However, as a result of the retrieval of the Polymer Erosion and Contamination Experiment (PEACE) flown as part of the Materials International Space Station Experiment 2 (MISSE 2), the erosion yields of 38 polymers and pyrolytic graphite were accurately measured. The experiment was exposed to the LEO environment for 3.95 years from August 16, 2001 to July 30, 2005 and was successfully retrieved during a space walk on July 30, 2005 during Discovery's STS-114 Return to Flight mission. The 40 different materials tested (including Kapton H fluence witness samples) were selected specifically to represent a variety of polymers used in space as well as a wide variety of polymer chemical structures. The MISSE 2 PEACE Polymers experiment used carefully dehydrated mass measurements, as well as accurate density measurements to obtain accurate erosion yield data for high-fluence (8.43×10^{21} atoms/cm ²). The resulting data was used to develop an erosion yield predictive tool with a correlation coefficient of 0.895 and uncertainty of $\pm 6.3 \times 10^{-25}$ cm ³ /atom. The predictive tool utilizes the chemical structures and physical properties of polymers to predict in-space atomic oxygen erosion yields. A predictive tool concept (September 2009 version) is presented which represents an improvement over an earlier (December 2008) version.					
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