Low Earth Orbit Environmental Effects on Space Tether Materials

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Atomic oxygen (AO) and ultraviolet (UV) radiation erode and embrittle most polymeric materials. This research was designed to test several different materials and coatings under consideration for their application to space tethers, for resistance to these effects. The samples were vacuum dehydrated, weighed and then exposed to various levels of AO or UV radiation at the NASA Marshall Space Flight Center. They were then re-weighed to determine mass loss due to atomic oxygen erosion, inspected for damage and tensile tested to determine strength loss. The experiments determined that the Photosil coating process, while affording some protection, damaged the tether materials worse than the AO exposure. TOR-LM also failed to fully protect the materials, especially from UV radiation. The POSS and nickel coatings did provide some protection to the tethers, which survived the entire test regime. M5 was tested, uncoated, and survived AO exposure, though its brittleness prevented any tensile testing.

Nomenclature

F	=	fluence of atomic oxygen, atoms/cm^2
Δm	=	change in mass, g
ρ	=	density, g/cm^3
R_e	=	AO reactivity, cm^3/atom
R_e^{LEO}	=	AO reactivity in low Earth orbit, cm^3/atom
$\overline{M}$	=	average atomic weight in polymer repeat unit, a.u.
N_T	=	total number of atoms in polymeric repeat unit
N_C	=	number of carbon atoms in polymeric repeat unit
N_C^O	=	number of carbon atoms bonded with intermolecular oxygen atoms in polymer repeat unit
γ'	=	efficient carbon chemical content factor
#molecules	=	number of molecules
#atoms	=	number of atoms
t_{Ni}	=	thickness of Ni coating
l	=	length of sample (cm)

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d	=	diameter of sample (cm)
A	=	cross sectional area of sample (cm^2)
N_A	=	Avogadro's number (molecules/mole)
Mw	=	molecular weight (g/mole)
Mw_{mix}	=	molecular weight of a mixture (g/mole)

I. Introduction

A space tether is best described as a physical connection between two orbiting bodies that allows for the transfer of momentum and/or energy. Whereas the use of tethers has gotten a boost in recent years, the idea is by no means a new concept. To date, approximately sixteen tether missions have flown, beginning with the Gemini XI mission in 1966,[1] which used tethers for artificial gravity experiments to the Tether Physics and Survivability (TiPS) mission launched in 1996,[2] to study the long term dynamics and survivability of a 4 km non-conductive tether in low Earth orbit.

Currently, there are two space tether missions being considered, researched and evaluated. The first of these missions is the Multi-Application Survivable Tether (MAST) Experiment[3], proposed by Tethers Unlimited Inc., (TUI). The MAST mission consists of three one-kilogram satellites along a one kilometer Hoytether. The main goal of this mission is to gather data on the long-term survivability of a Hoytether in low Earth orbit. The second tether mission being considered is the Momentum eXchange and Electrodynamic Reboost (MXER) Mission by NASA's Marshall Space Flight Center[4]. The tether system itself can be likened to a 100-120 km bolo in a highly elliptical Earth orbit. The MXER mission employs a slingshot-like momentum exchange to launch payloads into higher orbits. MXER then regains the momentum by passing a current through the conductive portion of its tether. Both of these missions are designed to remain in low Earth orbit for an extended period of time, subjecting them to various hazards, including atomic oxygen and ultraviolet radiation.

Ultraviolet radiation poses a great hazard to polymeric materials in space. The wavelength range of solar ultraviolet radiation that is present in low Earth orbit is roughly between[5] 0.1 and 0.4 μm, which equates to 12.4 to 3.10 eV. The UV spectrum can be broken down into three main sections: vacuum-UV, below 200 nm; far UV, between 200 and 300 nm; and near UV, from 300 to 400 nm. While these are seemingly small bands that only account for about eight percent of the total solar output, they are energetic enough to break down the organic bonds found in polymeric materials, embrittling the material.

Atomic oxygen is the neutral atmospheric constituent of most concern in low Earth orbit. It is formed by the absorption of near-ultraviolet (UV) solar radiation[6] causing the photodissociation of O_2. Because of AO's dependence on vacuum-UV to form, the concentration of AO changes as sunspot activity varies over the eleven-year cycle. At solar max, concentrations of AO can reach approximately 1×10^{15} atoms/cm^3, accounting for as much as ninety percent of the atmosphere at 500 km, an average altitude for satellites and other spacecraft. As a spacecraft orbits the Earth, its velocity is around 7.8 km/sec. From the spacecraft's point of view, it is being bombarded by AO with a kinetic energy of approximately 5 eV. Because polymeric materials contain many C-H and C-C bonds, which require only 4.29 eV and 3.59 eV respectively to break, this high energy causes AO to have a devastating effect[7]. Mass loss of polymers and composite materials due to AO erosion has been well documented[8,9,10].

The AO reactivity can be calculated in one of three methods. The first method is by measuring the thickness loss of a material and comparing that value to the area over which it was eroded and the total fluence it received. The second method, consists of relating a material's mass loss, density and cross sectional area to the fluence of AO it received. The reactivity can then be calculated by this equation, taken from Ref. 11:

$$R_e = \frac{\Delta m}{\rho * F * A} \text{ (Eq. 1).}$$

This method of calculating reactivity was chosen because the exact chemical composition of each material tested was not known. In addition, since the test materials consisted of braided fibers, it would have been extremely difficult to get a measurement of thickness loss. The final method was developed by researchers at the University of Toronto in Ontario Canada as a method of predicting AO erosion[12]. It involves examining the chemical structure of the polymer repeat unit and to determine the number of C-O and C-C bonds in the material, yielding the equation

$$R_e^{LEO} \approx \frac{\overline{M}}{\rho} * \frac{N_T}{N_C - N_C^O} \text{ (Eq. 2).}$$

The $N_T / (N_C - N_C^O)$ term is also known as γ', the efficient carbon chemical content factor. The research assumed that $\overline{M}/\rho$ was approximately constant for all polymeric materials but noted that for better accuracy, the actual values of molecular weight and density should be used. The erosion rate of a polymeric material can then be predicted by determining its γ' and comparing it to the graph in Fig. 1.
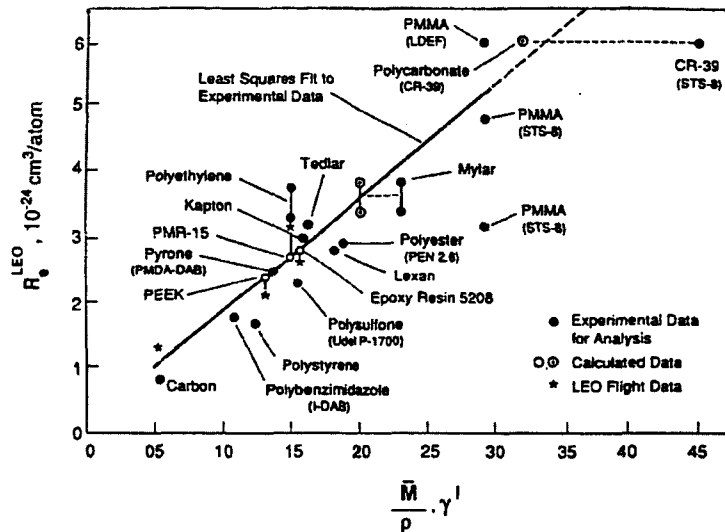
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Figure 1. Variation in Erosion Yield of Carbon, Graphite, and Polymeric Materials for LEO Exposure[12]

Due to the deleterious effects that both AO and UV have on polymeric materials, protective coatings are needed to maintain the mechanical integrity of tether materials. This is particularly true if the mission is in low Earth orbit and is long duration. There are several criteria that an AO resistant coating must meet in order to be used in orbit. These criteria include low weight penalty, high flexibility, abrasion resistance, UV radiation tolerance, and durability in thermal cycling. There are numerous possibilities for tether coating material, however, past experiments[7,12,13,14] with polymeric material and new developments in coating technology have greatly assisted in narrowing the choices for the best tether material and coating combination.

II. Tether Materials and Coatings

A number of candidate fibers and coatings were selected for AO exposure. The first sample set consisted of Spectra-2000 from the Honeywell Corporation, composed of ultra-high molecular weight polyethylene (UHMWPE), coated with Photosil. Samples of the Spectra-2000 were in the form of 130 denier strand and 4 x 130 denier braid 18.14 kg (40 lb.) test Spiderwire.

The second sample set was Zylon coated with Photosil. Zylon is composed of poly(p-phenylene-2,6-benzobisoxazole)(PBO) and is trademarked by the Toyobo Co. Ltd. The samples were in the form of 1000 denier

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strand and 3 x 1000 denier braid. Tensile data for the Spectra and Zylon strand samples coated with Photosil were previously reported in Ref. 15.

Photosil is a coating developed and trademarked by Integrity Testing Laboratories, Inc. which incorporates silicon-containing functional groups into the top micron of an organic material. This coating is applied in a three-step process such that a graded transition region is formed from the surface, allowing the material to survive the cracking caused by thermal cycling and handling of the material. It has been shown to reduce reactivity to AO with polyurethane- and epoxy-based thermal control coatings[16]. Originally, the Photosil process was designed to mask flat materials such as thermal blankets and has just recently been applied to rougher, curved objects such as braids and strands of tether materials[17].

The third sample set was 250 denier strand Zylon metallized with nickel. The nickel coating was deposited in a 1 μm thick layer onto each Zylon fiber through a multi-step process developed by Tethers Unlimited. Whereas nickel does have the ability to withstand AO attack, there are some concerns that thermal cycling may cause the nickel coating to crack because of the difference in the coefficient of thermal expansion between nickel and Zylon. Also, because nickel is a ferromagnetic material, there is concern that the interaction between the earth's magnetic field and the nickel material could produce an effect that is not yet well understood.

The fourth sample set was Zylon coated with 6% Triton Oxygen Resistant – Low Modulus (TOR-LM) polymer. TOR-LM was developed by Triton Systems, Inc. and is based on the polyarylene ether benzimidazoles class of polymers. TOR polymer films have previously been exposed[18] in the Atomic Oxygen Beam Facility (AOBF) at NASA's Marshall Space Flight Center (MSFC) and have flown on the Passive Optical Sample Assembly (POSA)-I experiment on the space station *Mir*[19]. A variant of TOR called TOR-BP was tested as a tether coating for the ProSEDS mission[20]. These samples included 3 x 2943 denier braid and a Hoytether with coated and uncoated Zylon tows.

The fifth sample set was PBO fiber coated with 10% mono-OH polyhedral oligomeric silsesquioxane (POSS). POSS is a complex copolymer that contains Si-O bonds. During an initial mass loss period, the surface-exposed organic groups are lost and silicon and AO react to form SiO_2. Previous tests of POSS on Kapton film[14] indicated the coating's viability as an AO-resistant coating. Two samples consisting of 20 fibers twisted together at 2 turns/cm were provided for this research.

The final sample set was Magellan Systems International M5 fiber, made of the polymer poly{2,6-diimidazo[4,5-b:4',5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (PIPD). PIPD was originally developed by Akzo Nobel Central Research in the Netherlands[21]. The M5 samples, similar to the PBO/POSS samples, were 20 fibers twisted together at 2 turns/cm. Only two of these samples were available for testing.

To prepare the samples for testing, each was knotted twice before cutting to prevent loss of any of the strands. Samples ranged from fifteen to twenty centimeters in length, depending on how much material was available. To ensure that none of the materials were hydroscopic, each was placed into a vacuum chamber and brought to 50 millitorr and then immediately removed and weighed with readings being taken every minute for five minutes. Regression analysis to time zero was then used to eliminate any water weight gain. Each sample was photographed before exposure to the simulated space environment.

III.   Space Environmental Simulation

The atomic oxygen testing was performed in the Atomic Oxygen Beam Facility (AOBF) at NASA's MSFC. This facility is capable of producing a neutral AO beam at an energy level of 5 eV while maintaining a vacuum of about 10^{-7} torr, simulating the low Earth orbit environment. A side effect of the AO production is the production of ultraviolet radiation at a wavelength of 130 nm at a level of approximately 200 times that of the sun. The total flux produced by the AOBF is between 5×10^{15} and 10×10^{15} atoms/cm^2/s of atomic oxygen. Due to the circular geometry of the AOBF, the center of the test stand sees a slightly higher flux of AO than the outlying edges. A calibration run with Kapton strips was performed before testing began to precisely measure this effect. While the correction factors will remain constant throughout the testing period, the AO flux produced by the AOBF will change due to variations in current and AO plasma production. For this reason, a Kapton strip is always included in the center of the test section so that the exact fluence experienced by that sample set would be known. If desired, the average flux can then be calculated by dividing the fluence by the total run time of the AOBF.

Tether test samples were affixed to the AO test fixture (fig. 2) and placed in the AOBF for various amounts of time up to a maximum exposure of 3.61×10^{21} atoms/cm^2. After each exposure, the materials were photographed, removed from the testing fixture and weighed. The Kapton witness sample was first vacuum dehydrated because of

its hygroscopic nature and then weighed over a period of five minutes. From the AOBF beam current and time of exposure, corroborated with Kapton mass loss, a value for the fluence in the AOBF can be found.
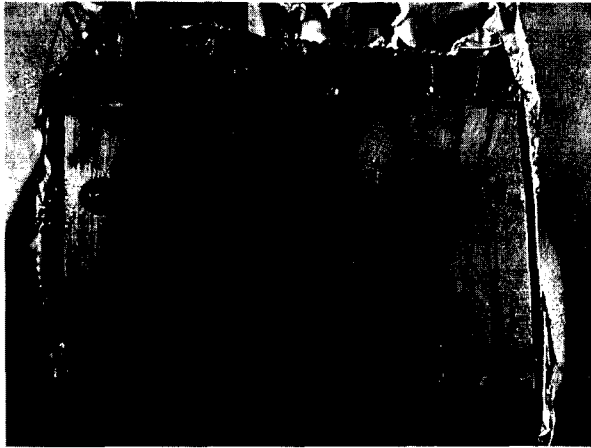
Figure 2 Tether Test Stand with Attached Tether Samples *Pictured from left to right: M5 AO-C and -D; Hoytether AO-C; Kapton; Zylon®-TOR-LM Braid AO-C and -D; and Zylon®-POSS AO-C and -D*

Tether samples were also exposed in one of MSFC's Ultraviolet Radiation Test Chambers to help separate the effects of AO and UV exposure. This was done for a minimum of 500 equivalent sun-hours (ESH) with UV radiation ranging in wavelength from 250 to 400 nm in a vacuum of 10^{-6} torr or better. A water filter was used to minimize infrared heating of the samples. More details of the AO and UV facilities may be found in Ref. 22.

After simulated space exposure, the samples were taken to the Mechanical Properties Test Lab where an Instron mechanical test machine was used to determine tensile strength. To prepare for the testing, the ends of each sample were doped with Phillystran Socketfast Blue or Adhesive Systems cyanoacrylate to allow the Instron to better grab and pull the tether sample.

IV. Results

1) Spectra-Photosil

The braided Spectra-Photosil samples consisted of forty-pound test Spiderwire coated with Photosil. It had better results than the strand samples, surviving the entire test regime, though this is not all too surprising given the greater amount of material. When a comparison between the uncoated and coated materials was made, a significant drop in tensile strength for the coated samples versus uncoated braid was noted, similar to the strand samples. Table 1 contains the mass loss and maximum tensile load data for the Spectra-Photosil braid samples.

Table 1. Test Results for Spectra-Photosil Braid

Sample	AO Fluence atoms/cm^2	% Mass Loss	Maximum Tensile Load N (lbf)
Control – Uncoated	0	0	134.66 (30.27)
Control – Photosil	0	0	90.37 (20.32)
UV	0	0	69.21 (15.56)
AO-A	2.80×10^{20}	1.41%	54.93 (12.35)
AO-B	6.06×10^{20}	3.48%	62.70 (14.09)
AO-C	1.07×10^{20}	3.69%	50.90 (11.44)
AO-D	9.70×10^{20}	4.19%	52.32 (11.76)
AO-E	2.92×10^{21}	13.84%	0.34 (0.08)

Because the exact density of the Spectra-Photosil is not known, the AO reactivity can only be approximated. The AO reactivity is calculated with Eq. 1, where the density, in this case, is that of uncoated Spectra. By performing these calculations and comparing the reactivity data to that for uncoated Spectra, it was found that the Photosil was only able to lower the AO reactivity by a factor of about five. Past experiments[7] have found the AO reactivity for uncoated Spectra to be 4.8×10^{-24} cm^3/atom. This research has found the reactivity for braided Spectra coated with the Photosil to be 0.93×10^{-24} cm^3/atom and the AO reactivity for Spectra-Photosil strand to be 1.2×10^{-24} cm^3/atom.

When the uncoated control samples for each group were pulled, a rather large discrepancy was found between the maximum tensile strength of the coated and uncoated samples as can be seen in the material data tables. Since this effect was first observed in the strand samples, the first explanation reached was the additional handling of the samples, particularly the fine Spectra strand of only 130 denier, was the culprit for the significant strength loss. As testing progressed however, evidence pointed towards UV effects as will be explained later.

2) Zylon-Photosil

The Zylon-Photosil braids were similar to the Spectra-Photosil braids in structural integrity, surviving the entire test regime. Atomic oxygen reactivity for the Zylon-Photosil braids was calculated to be 1.7×10^{-24} cm^3/atom. The samples also looked slightly bleached by the AO exposure.

Mass loss and maximum tensile load data for the Zylon-Photosil braid samples can be found in Table 2. During tensile testing, all samples failed in the gage section. Because of the shortage of testable material, assumptions had to be made about the materials themselves. Here it was assumed that the uncoated tether material would suffice for control samples and therefore the decision was made to expose all of the material to either AO or

UV rather than omit a Zylon-Photosil braid from a step in the test procedure. This assumption has since been proven wrong based upon the uncoated material testing mentioned earlier as well as the 29% drop in strength for the UV-exposed braid as compared to the unexposed sample. A conclusion was reached that Zylon is more sensitive to the UV radiation present in the AO testing, causing greater strength losses than just AO erosion alone would incur.

Table 2. Test Results for Zylon-Photosil Braid

Sample	AO Fluence atoms/cm^2	% Mass Loss	Maximum Tensile Load N (lbf)
Control – Uncoated	0	0	385.9 (86.75)
UV	0	0	274.3 (61.66)
AO-A	3.17×10^{20}	0.82%	312.9 (70.35)
AO-B	5.58×10^{20}	1.55%	262.5 (59.02)
AO-C	1.00×10^{21}	2.28%	229.4 (51.57)
AO-D	1.16×10^{21}	2.58%	249.92 (56.18)
AO-E	3.04×10^{21}	7.11%	156.30 (35.14)

Since no previous data were available for untreated Zylon PBO, it was necessary to test this material so that a comparison could be made between it and the various coated samples. This provided valuable AO reactivity data and helped determine its susceptibility to the low Earth orbit environment. Two samples of uncoated Zylon braided material were exposed to AO at various levels, while two more samples were exposed to UV radiation for 518 ESH, the results of which can be seen in Table 3.

Table 3. Test Results for Uncoated Zylon PBO

Sample	AO Fluence atoms/cm^2	% Mass Loss	Maximum Tensile Load N (lbf)
Control	0	0	385.88 (86.75)
UV-1	0	0	330.06 (74.20)
UV-2	0	0	305.71 (68.73)
AO - D	5.410×10^{20}	1.64%	300.557 (67.57)
AO - E	5.410×10^{20}	1.44%	273.75 (61.54)

3) Zylon-Nickel

The Zylon-Nickel samples had only small changes in mass, with several samples gaining weight as can be seen in Table 4. The subscripts denote intermediate measurements of the sample.

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Table 4. Test Results for Zylon-Nickel

Sample	AO Fluence (atoms/cm^2)	% Mass Loss	Maximum Tensile Load N (lbf)
Control	0	0	42.47 (9.55)
UV	0	0	16.04 (3.61)
AO-A	6.120×10^{20}	6.39%	6.38 (1.43)
AO-B	7.319×10^{20}	1.29%	14.26 (3.21)
AO-C	1.275×10^{21}	1.62%	9.08 (2.04)
AO-D$_1$	4.68×10^{20}	0.64%	
AO-D$_2$	7.18×10^{20}	-9.51%	6.39 (1.44)
AO-E	2.461×10^{21}	-2.96%	19.18 (4.31)

The weight gains were of particular interest because this was the first material to exhibit such a change after exposure to AO. This weight gain may have been due to the formation of nickel oxide or slight inaccuracies in the scale.

For samples that lost weight, the average AO reactivity was calculated to be 8.95×10^{-26} cm^3/atom. This average was reached by considering the data from Zylon-Ni AO-A to be an outlier. Because these samples consisted of individual strands, it was very likely that some were lost in the AO-A sample during handling. Further reasoning for the exclusion of AO-A is explained later. This value also takes into account the intermediate measurement of AO-D$_1$, which recorded a mass loss of 0.00013 g.

The other point that needs to be addressed is the strength "gain" between samples AO-D and AO-E. Several things can easily explain this "gain" as no more than an anomaly. The first possible cause is that this sample simply received better coating than the other ones. This cause is unlikely because the samples were all cut from the same spool and therefore came from the same treatment batch. The second, and more likely cause, is that the samples were damaged slightly during handling. While the greatest care was taken while handling the samples, there exists the definite possibility that individual strands were inadvertently broken or lost from the sample, even though the ends were tied to prevent just that.

4) Zylon-POSS

The test regime for the Zylon-POSS samples differed from the earlier tests because of the small amount of available material. Research into the POSS coating revealed that this material was able to reduce AO erosion in Kapton-like material by an order of magnitude[14]. Due to the small number of fibers per sample, the materials were tested by exposing them to several sessions at an AO fluence of approximately 4.37×10^{20} atoms/cm^2. After each

round, the samples were removed from the chamber and weighed, allowing the AO reactivity to be calculated. The fluence and mass and strength changes were recorded in Table 5. The subscripts refer to the session number for each sample.

Table 5. Test Results for Zylon-POSS

Sample	AO Fluence (atoms/cm^2)	% Mass Loss
AO-C$_1$	4.37x10^{20}	2.22%
AO-C$_2$	3.89x10^{20}	0.85%
AO-D$_1$	4.37x10^{20}	9.44%
AO-D$_2$	3.89x10^{20}	0.29%
AO-D$_3$	6.12x10^{20}	5.56%

After the first round of exposure, significant mass loss was recorded in both samples. AO-C$_1$ realized a mass loss of 2.22% while AO-D$_1$ suffered a 9.44% mass loss. Based upon past research[14], it was known that there would be an initial mass loss while the coating began to build its protective layer, however, a mass loss of 9.44% was a matter of concern. A visual inspection of the samples showed no noticeable fraying or color change, therefore, the materials were placed back in the chamber for another round of AO exposure.

After the second round of exposure, both samples had received a total of 8.26x10^{20} atoms/cm^2 atomic oxygen. They were taken out of the chamber and weighed with much more auspicious results. After this round of AO bombardment, AO-C lost only 0.85% of its mass while the AO-D sample lost only 0.29% of its mass. These results reaffirm the earlier assumptions of initial mass loss during the formation of the protective SiO$_2$ layer. At this point, it was decided to remove AO-C from the test cycle. AO-D was placed back in the AOBF for a final round of AO bombardment.

By the third round of AO exposure, the AO-D sample had received 1.438x10^{21} atoms/cm^2 of atomic oxygen. Upon weighing the material it was found that there had been a mass decrease of 5.56%. Due to the small amount of fiber in each sample, twenty strands, it was decided that a tensile test would not give any useful data, especially since there was no POSS coated control sample to compare the data against. AO reactivities were then calculated for the samples. The reactivities for the AO-C and -D samples were found to be 5.69x10^{-24} cm^3/atom and 12.28x10^{-24} cm^3/atom respectively. While this is a very high reactivity, the material held together extremely well over the entire test regime. In comparison, the AO-C Zylon-Photosil strand sample had an AO reactivity of 9.35x10^{-24} cm^3/atom and it failed while being prepared for tensile testing after receiving 9.83x10^{20} atoms/cm^2 of AO.

5) Zylon-6% TOR-LM

After the completion of the Photosil testing, several samples of Zylon coated with 6% TOR-LM coating were placed in the AOBF to examine their resistance to AO. Table 6 gives the mass loss and tensile strength data for this material. Because the TOR-LM samples were being tested along with the POSS and M5 samples, data for AO-C and -D samples are reported at the end of each session in the AO chamber again, denoted by subscripts. The values for AO fluence given are the total fluences that the materials had received to that point while percent mass loss is the value calculated for that individual session.

**Table 6. Test Results for TOR-LM Coated Zylon**

Sample	AO Fluence (atoms/cm^2)	% Mass Loss	Maximum Tensile Load N (lbf)
AO-A (Control)	Unexposed	0	1511.05 (339.70)
UV	0	0	584.71 (131.45)
AO-B	7.487×10^{20}	1.28%	477.49 (107.34)
AO-C$_1$	5.80×10^{20}	1.31%	
AO-C$_2$	1.10×10^{21}	0.77%	554.23 (124.60)
AO-D$_1$	5.80×10^{20}	1.23%	
AO-D$_2$	1.10×10^{21}	1.45%	
AO-D$_3$	1.676×10^{21}	3.04%	326.58 (73.42)

Constructed of 3 x 2,943 denier braid, the TOR-LM coated material naturally had a higher initial tensile strength. However, as the table illustrates, after only 518 hrs of UV exposure, the TOR-LM coated material had lost almost sixty percent of its initial strength. The other samples also lost a large portion of their initial strength after exposure to the AO and VUV. The AO-C sample decreased in strength from 1151 N to 554 N after being exposed to 1.1×10^{21} atoms/cm^2 of atomic oxygen and 768 ESH of vacuum UV radiation.

As was evidenced in the testing of the Zylon-Photosil strand samples, much of the fraying and material loss was due to AO erosion. Visual inspections of the TOR-LM AO-C and -D samples showed little to no fraying, a color change had occurred though indicating that the TOR-LM coating was active. However, when the AO reactivity measurements are taken into account, AO erosion begins to play into the overall strength loss of the material. The average AO reactivity for the TOR-LM coated samples was calculated to be 2.17×10^{-24} cm^3/atom. This value is on par with those of uncoated Zylon suggesting that the TOR-LM coating was not able to completely coat the material or that during the braiding the coating was somehow damaged.

6) PIPD/M5

Along with the TOR-LM and POSS samples, M5 was examined for its AO resistance and feasibility as a space tether. One thing that was immediately noticed about this material was its stiffness and brittleness. Excess tether material was bent around the back of the test stand and covered to allow only a fixed length to be exposed the AO beam. During the repeated testing and weighing cycles, the M5 materials began cracking and splitting, Fig. 3. It should be noted however, that none of the cracking occurred along the AO exposed portion of the material. Further visual inspection of the exposed section revealed no telltale marks that it had been exposed except for a very slight darkening which, unfortunately, is not visible in any of the pictures taken.
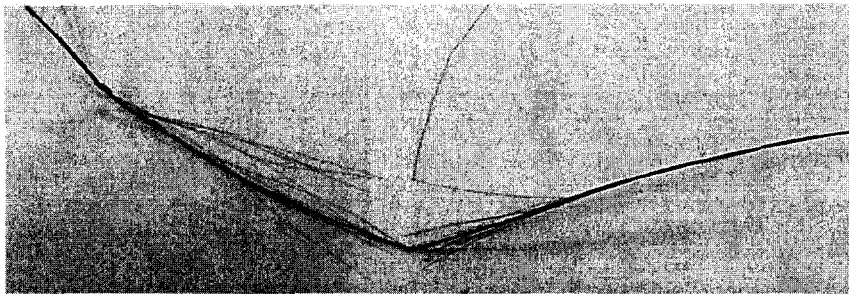
Figure 3. Cracking and Splitting of M5, AO-D

Some interesting information was garnered from this material. The M5 fiber actually experienced a weight gain over the test period, Table 7. To ensure that this was a true weight gain, the Mettler balance was calibrated and the material weighed again with similar results. As this material was also tested with the POSS samples, session numbers are denoted by subscripts.

Table 7. M5 Test Results

Sample	Total AO Fluence (atoms/cm^2)	% Mass Change
AO-C$_1$	4.74×10^{20}	2.23%
AO-C$_2$	8.96×10^{20}	0.79%
AO-D$_1$	4.74×10^{20}	6.72%
AO-D$_2$	8.96×10^{20}	-3.35%
AO-D$_3$	1.628×10^{21}	3.00%

Very little is known about this material's ability to resist atomic oxygen but judging from its numerous carbon and hydrogen bonds, it should be very susceptible to AO erosion; however, the second time AO-C and -D were placed in the chamber, AO-C experienced very little erosion and AO-D actually recorded a mass gain. With only two samples, there is no way of knowing if this is an anomaly or the pattern in which M5 reacts to AO erosion. It should be noted that the Kapton strip placed in with this session showed no anomalous measurements, neither did the 6% TOR-LM samples. The density of M5 was estimated to be 1.54 g/cm^3. The AO reactivity was calculated to be $4.71x10^{-24}$ cm^3/atom for AO-C_1, $0.862x10^{-24}$ cm^3/atom for AO-C_2, $18.24x10^{-24}$ cm^3/atom for AO-D_1, and $2.37x10^{-24}$ cm^3/atom for AO-D_3. While no fraying or cracking was evident in the exposed areas of the AO-C or AO-D samples, there is the possibility that some material did break off the end of the AO-D sample during the testing session as this would account for its nearly seven percent mass loss.

7) Molecular Erosion

Previous AO erosion predictive methods[12] relied on relating AO reactivity to the number of C-O and C-C bonds in a material. This process is limited because it does not, as of the publishing of this paper, take into account materials that contain inorganic bonds. However, it is possible to look at the problem in a different light by examining the number of AO atoms it takes to erode away one molecule of a particular polymer. This value is known as the molecular erosion of a material.

The first step in calculating the molecular erosion is to calculate the number of molecules of material that was eroded from the sample. As an example, uncoated Zylon's AO-D sample will be examined which had a mass loss of 0.00129 g. Zylon has a molecular weight of 268 g/mole. The cross sectional area of the material exposed to the AO beam was 0.085 cm by 5.9 cm. Using Avogadro's number, it is possible to calculate the number of molecules eroded with the equation

$$\#molecules_{Zylon} = \frac{\Delta m}{A} * \frac{1}{Mw} * N_A = \frac{0.00129g}{0.51cm^2} * \frac{1mole}{238g} * 6.022x10^{18} \frac{molecules}{mole} \quad \text{(Eq. 3)}$$

yielding $6.40x10^{18}$ molecules of Zylon eroded. The molecular erosion can now be found by dividing the AO fluence by $\#molecules_{Zylon}$. This process was then repeated for uncoated Zylon AO-E, M5 and nickel coated Zylon. It was necessary to find the average molecular weight of the nickel coated Zylon in order to determine its molecular erosion value. Using the diameter for a single fiber of Zylon, it was possible to quickly compute the number of atoms of Zylon and nickel present in the material. This was done using the equations:

$$\#atoms_{Ni} = \rho_{Ni} * \pi * d_{Zylon} * t_{Ni} * l * N_A * \frac{1}{Mw_{Ni}} \quad \text{(Eq. 4)}$$

and

$$\#molecules_{Zylon} = \rho_{Zylon} * A_{Zylon} * l * N_A * \frac{1}{Mw_{Zylon}} \quad \text{(Eq. 5)},$$

recalling that the thickness of the nickel coating was 1 micron. When these two equations were divided, the length becomes arbitrary and the ratio of nickel atoms to Zylon was found to be 8.008. Using this value, and the molecular weight of nickel, 58 g/mole, the molecular weight of the mixture, was found to be 78 g/mole utilizing the equation

$$Mw_{mix} = \frac{8.008 Mw_{Ni} + Mw_{Zylon}}{9.008} \quad \text{(Eq. 6)}.$$

The molecular erosion of the material could then be found by following the example of uncoated Zylon.

Another interesting term to look at is the average number of atoms of AO it takes to break a single bond in the polymer repeat unit. For this value, a cue was taken from Ref. 12 where the bonds of interest in the polymer repeat unit were C-O and C-C bonds. Examining the chemical structures for Zylon and M5 gave the number of C-C and C-O bonds as seventeen for Zylon and thirteen for M5. The value for molecular erosion is then divided by this number to give an average value for the number of AO atoms it takes to sever a molecular bond in the polymer repeat unit. Exact results for the nickel coated samples could not be obtained in this fashion as it was not known exactly how the nickel and nickel-oxide bonds would interact or how many there are for a Zylon polymer repeat unit. Table 8 lists the molecular erosion values, bond severance values and AO reactivity.

Table 8. Molecular Erosion and Bond Severance Values for Selected Materials

Material	Sample	Molecular Erosion (atoms AO/molecule polymer)	Bond Severance (atoms AO/molecular bond)	Reactivity (cm^3/atom)
Zylon Uncoated	AO-D	83.12	4.88	2.01×10^{-24}
	AO-E	94.06	5.53	1.78×10^{-24}
M5	AO-C$_1$	58.98	4.54	4.71×10^{-24}
	AO-C$_2$	151.69	11.67	0.861×10^{-24}
	AO-D$_1$	15.37	1.18	18.24×10^{-24}
	AO-D$_3$	118.22	9.09	2.37×10^{-24}
Zylon-Ni	AO - A	34.27	--	51.57×10^{-26}
	AO - B	216.10	--	9.48×10^{-26}
	AO - C	276.07	--	7.42×10^{-26}
	AO - D	233.84	--	8.76×10^{-26}

Upon analysis of the data, several anomalies become readily apparent. One of these concerns the M5 material's variability in molecular erosion, which is especially apparent in M5 AO-D$_1$. As mentioned in the previous section, it is believed that these results could be tainted by a random anomaly that occurred in the AOBF or during the handling of the material a small piece could have cracked off and been lost. The low value of molecular erosion for nickel coated Zylon is also believed to be an anomaly for reasons relating to handling and fiber damage. Additional analysis of the molecular erosion values for nickel coated Zylon further supports this conclusion. Taking the mean and standard deviation of the molecular erosion values for samples AO-B through -D gives a value of 242.00 ± 38.80. If a 95% confidence interval is constructed around this average then it could be expected that the mean molecular erosion value for all similarly coated samples should fall within ± 123.46 of the mean, utilizing a sampling distribution. Even if this mean fell at the extreme edge of 118.54, AO-A's value of 34.27 would still be considered an outlier.

Further analysis of the chemical structure of uncoated Zylon and M5 allow for the determination of AO reactivity as a function of its chemical structure. This is done by following the example set forth in Ref. 12 and determining a value for γ' then using Eq. 1, and Fig. 1. The necessary values for the equation are listed in Table 9.

Table 9. Summarized Data for the Reactivity Equation

Material	Average Atomic Weight (amu)	Density (g/cm^3)	N_T	N_C	N_C^0	$\dfrac{\overline{M}}{\rho} * \gamma'$
Uncoated Zylon	9.912	1.54	24	13	4	17
M5	18.57	1.54	14	13	6	24

As per Eq. 1, the reactivity for Zylon should be around 2.7×10^{-24} cm^3/atom and the reactivity of M5 should be approximately 4×10^{-24} cm^3/atom. The data points for these two samples were then plotted in Fig. 4 using the reactivity results from this research. Analysis of these results show that the values for Uncoated Zylon and M5 AO-C$_1$ fell no further from the least squares fit to the past experimental data than some values for PMMA, Polyethylene or Mylar did proving that this was a good fit. When the data for M5 AO-C$_2$ and -D$_3$ are placed on the chart an interesting trend appears. Using simple linear regression, a second line, gray, can be plotted to the right and passed through CR-39, PMMA, M5 AO-C$_2$, and M5 AO-D$_3$ with the equation:

$$R_e = 2*10^{-25}\left(\frac{\overline{M}}{\rho}\gamma'\right) - 4*10^{-24} \text{ (Eq. 7)}.$$
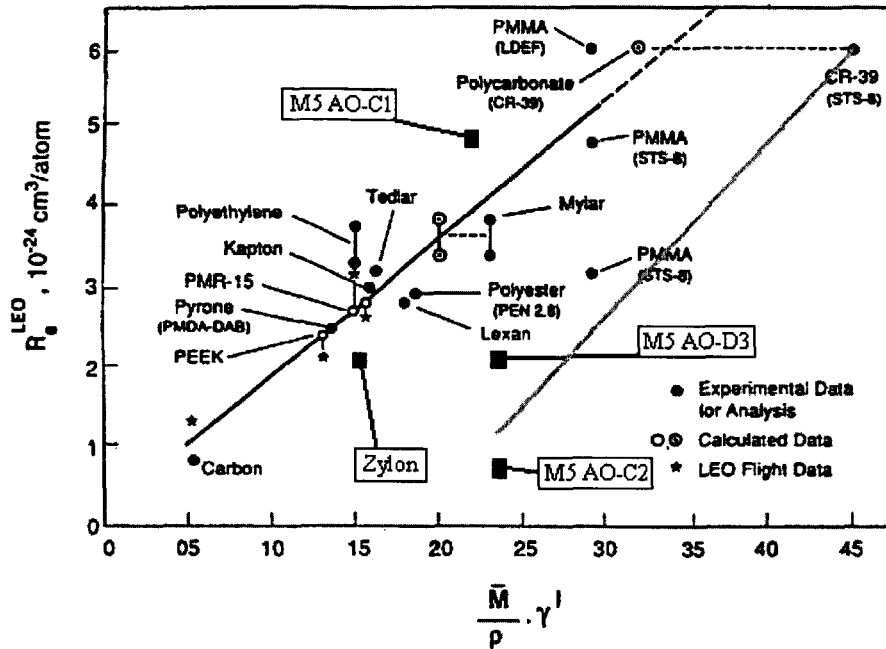

Figure 4. Variation in Erosion Yield for AO Exposure with Zylon and M5 Data

V. Conclusions and Future Work

1) Tensile and AO Reactivity Results

Each sample set carried with it its own obstacles that affected the outcome of the testing in one manner or the other. The Photosil and TOR-LM coatings did not provide the amount of protection that they had in previous experiments[12, 7, 18]. According to the reactivity calculations, nickel coated Zylon was able to resist AO's erosive effects, but due to it being a loosely grouped set of strands, the tensile test results were erroneous. Finally, it appeared as if M5 and POSS were able to survive the testing regime without any apparent fraying or other damage but this was only from a visual perspective.

The most immediate evidence that the Photosil coating did not perform to specifications is that the reactivity that was calculated for the braided Zylon-Photosil samples was around 2×10^{-24} cm^3/atom. In previous experiments[16], this reactivity was calculated around 10^{-26} cm^3/atom. The greatest finding from this portion of the

research, however, is the damage that the Photosil coating did to the tether materials before they were even exposed to atomic oxygen. As was discovered from both the Photosil patent as well as Ref. 16, the first step in the Photosil process is photo-activation of the surface by UV, corona, or oxygen plasma, the exact effects from which the Zylon material needs to be protected. A comparison was made between the uncoated AO-D Zylon sample and the AO-B Zylon-Photosil samples which received approximately the same fluence of AO. The mass losses for both materials were very similar, with the uncoated sample losing 1.55% of its mass and the Zylon-Photosil sample losing 1.64%. What was even more striking was that when tensile tested, the uncoated specimen outperformed the Photosil coated sample. The AO-D and -E uncoated Zylon samples were both exposed to 5.41×10^{20} atoms/cm^2 of AO and maintained tensile strengths of 300.56 N and 347.75 N respectively. In comparison the AO-B Zylon-Photosil sample, which received the same fluence of AO, had a maximum tensile strength of only 262.5 N. This shows that the Photosil did not adequately protect the Zylon material and furthermore, demonstrates the damage that the Photosil coating process did to the Zylon.

The TOR-LM coating is another one that was not able to perform to its desired level. The first indication of this is the reactivity calculation. The average reactivity for the TOR-LM coated samples was calculated to be 2.21×10^{-24} cm^3/atom. This value is on par with that of uncoated Zylon, which was calculated to be 1.86×10^{-24} cm^3/atom. Based on this evidence alone, the conclusion can be drawn that the TOR-LM coating did not sufficiently protect the Zylon from AO erosion. Evidence from the tensile tests points to TOR-LM not being able to protect from UV radiation. As was mentioned before, UV radiation affects Zylon in a particularly strong fashion, causing it to rapidly lose its tensile strength. An unexposed sample of TOR-LM coated Zylon had a maximum tensile load of 1511.05 N. The UV sample, which received only 518 hrs of UV radiation, had a maximum tensile strength of merely 584.71 N, a decrease of 61.3%. The AO exposed samples did not fare any better as they were exposed to 576, 768 and 1344 ESH of VUV radiation for the AO-B, -C, and -D samples respectively. After AO-D's final exposure, its mass loss amounted to a mere 5.7%, yet it retained only 21.6% of its initial tensile strength.

The nickel coated Zylon fibers were much more difficult to analyze, yet they also showed the most promise of any of the materials. The AO-D and -E nickel coated samples actually experienced mass gain by the end of their test regime suggesting that a nickel oxide had formed and was protecting the Zylon from any further damage. This finding is backed up by the reactivity calculations. The AO reactivity for the samples that did lose weight averaged to 8.55×10^{-26} cm^3/atom, several orders of magnitude lower than any other material, implying that Ni coated space

tethers could survive long duration space missions. The problem that arose from their being tested as strand samples is that the tensile tests provided dubious results at best. Because the samples were placed in the AO chamber as one group of fibers, it was necessary to pull them as such. This allowed for strands that were shadowed from the AO beam to be tested along with those that got a full dose giving an accurate comparison to what the tether would experience in orbit. However, as the materials were tested in the AOBF, various fibers would twist around the end knots, others would inadvertently be broken, others still would slip out of one of the knots and then twist around the sample. When the samples were prepared for tensile testing, every effort was taken to make sure that they would be pulled as one continuous sample but in the process, further damage was caused to the individual strands as the samples were straightened. It is believed that because of this, the AO-E sample exhibited a higher maximum tensile strength than some of the other samples.

When the POSS and M5 samples were examined, it was decided that tensile testing these materials would prove fruitless. For the POSS sample, it was because with only twenty strands per sample and no control, a strength drop might occur but the magnitude of these results would be unknown. For M5, tensile testing was not performed for the additional reason of the fiber cracking occurring and thus having very little fiber to pull. The reactivity calculations performed on the materials do however give some conclusions. The first is that M5, with its chemical structure consisting of mainly C-C bonds and high reactivity, needs to be coated with some AO resistant material to survive the LEO environment. The POSS coated material had a surprisingly high AO reactivity when compared to measurements made in Ref. 14, which either leads to the conclusion that it was not coated fully or the SiO_2 layer was unable to fully protect the material. However, with only twenty strands of material, it was difficult to draw any further conclusions.

2) Molecular Erosion and Bond Severance Results

As shown in Table 8, the materials that were unable to resist AO erosion had low molecular erosion values. The fact that the value for molecular erosion increases as AO reactivity decreases is auspicious because is proves that there is a corollary between the two values and, therefore, that the molecular erosion value is a valid way to characterize a material. Using the value of molecular erosion, it is easy to see why nickel coated Zylon was able to resist AO erosion better than other materials. For most of the samples, it took over 200 collisions with AO to erode away a single molecule of the sample. Taking this line of reasoning a step further, it should be possible to

predict the length of time in orbit it will take to erode away a significant percent of nickel coated Zylon. By graphing the molecular erosion as a function of AO fluence, simple linear regression can be performed on the data to get an equation for molecular erosion as a function of AO fluence. By taking into account the solar cycle, the change of AO flux through the Earth's shadow and a spacecraft's orbital parameters, it would be possible to arrive at a fairly accurate estimation of the total AO fluence the spacecraft would encounter while in orbit. Unfortunately, many more data points are needed than the four provided by this experimentation to arrive at a statistically viable equation that would be capable of making accurate predictions.

As previously mentioned, it was possible to formulate a second line in Fig. 4 utilizing both the data from this research as well as past experiments. It is difficult to believe that this line could have been formed nearly parallel to the original line by coincidence. This indicates that the model for predicting AO reactivity may have to be reexamined, which is especially true if other materials tested fall in this new region defined by the two lines on the chart. It suggests that the erosion prediction method set forth in Ref. 12, might not be accurate enough to predict an exact value of reactivity but is capable of giving a range of AO reactivities within which the material should fall. It also reinforces the reasoning that M5 AO-D_1 was indeed an anomaly when compared to the rest of the data.

While Eq. 1 is not designed to handle coated materials, a surprising relation occurs when the average AO reactivity of nickel coated Zylon, 8.00×10^{-26} cm^3/atom, is analyzed. Assuming that the nickel coating does not erode or erodes at a much slower rate than Zylon, then the sample can be analyzed in terms of the average atomic weight of Zylon. If this value were placed on the graph, it would fall within this newly defined region. If more testing is done on AO reactive materials and this second line becomes better defined, there is a definite possibility that the data point for nickel coated Zylon could lie along this line. If that were the case, then it could be surmised that this line reflected the AO reactivity of materials that could, at least for a time, form a protective layer. However, further research is still needed to define nickel's performance in low Earth orbit.

3) Future Work

While this research has made some discoveries and been able to draw several conclusions regarding several new space tether coatings, there are still several avenues of research that need to be followed up. One such avenue is to test braided samples of nickel and POSS coated Zylon fully. These samples should be analogous to those that would be later launched into orbit, as this would give the most accurate results. It would also be beneficial to determine what is happening with the chemistry in these samples, as that would allow a predictive model to possibly

be created. Examining each sample's chemistry can be done utilizing one of a number of methods including X-ray photoelectron spectroscopy, environmental scanning electron microscopy or atomic adsorption spectroscopy.

Research also needs to be performed as to whether or not the tether material and its respective coating can survive the thermal cycling it will have to endure in LEO. If the coating and tether material expand and contract at different rates, then cracking and splitting of the coating can occur allowing the underlying layers to be exposed to AO. This is of particular concern in the nickel-Zylon samples where the nickel is a 1 μm thick layer placed on top of the Zylon rather than a gradual coating or protective polymeric string built into the chemical structure of the material. While the results of nickel coated Zylon showed promise, this material could be completely useless if thermal cracking occurs.

Follow up also needs to be performed on the predictive measures set forth earlier in this chapter. Ideally, to prove this method is sound, upwards of twenty to thirty samples of a material must be tested at various levels of AO fluence. The equation must then be compared not only to simulated AO effects but also to actual flight data to examine its predictive abilities. This can easily be done by choosing a material that has already been AO tested in orbit on either the LDEF or MISSE experiments. It would also be interesting to compare the molecular erosion value to the Boltzmann distribution of AO energy, thereby relating it to a percent of AO that could affect the material.

Finally, if a space tether material and coating are selected, a full regime of AO, UV and thermal cycle tests needs to be performed on a set of samples that will be used for any future mission. Multiple samples need to be exposed as various levels of AO fluence to help eliminate any errors that can occur when only one sample at each level is exposed and tensile tested. Some of these samples should also be sent for chemical analysis to determine if a protective coating has formed on the surface and how well it will protect after several years in space. It is only then that any material can be truly considered for a long duration, high-risk, high-payoff mission such as MXER or any other future space tether mission.

VI.   Acknowledgements

is to develop in-space propulsion technologies that can enable or benefit near and mid-term NASA space science missions by significantly reducing cost, mass or travel times.

VII.   References

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