

## Effect of LEO Exposure on Aromatic Polymers Containing Phenylphosphine Oxide Groups

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### Introduction

Aromatic polymers containing phenylphosphine oxide groups have been under investigation for over a decade [1-4]. This functional group has been incorporated into a variety of aromatic polymers as a means of providing both solubility and high glass transition temperature (T<sub>g</sub>) without sacrificing mechanical properties. It was also discovered that this group can improve the resistance of the polymer to oxygen plasma and atomic oxygen (AO) by a self passivating effect in which a phosphate enriched surface layer is formed which protects the underlying material from further reaction. A variety of experiments relating to the effects of oxygen plasma and AO exposure on these types of polymers have been performed over the years in both ground-based simulations and short term space flight exposure experiments [5-9]. Until now, there has been no data available regarding the long term (> 1 year) performance of these types of polymers in low Earth orbit (LEO).

The push to develop AO resistant polymers dates back to pre-space station days and since that time a variety of approaches have been investigated. Some of the early work involved polyphosphazenes [10,11]. In addition, a large variety of silicon (Si) containing polymers were investigated in which the Si was typically incorporated in the form of an organic species such as a siloxane unit [12-21]. In both cases, the formation of an oxide rich surface layer by the reaction of phosphorus (P) or Si with atomic oxygen was observed. This oxide surface layer reduced the subsequent reaction efficiency with AO and protected the underlying polymeric material. Other approaches involved highly fluorinated polymers [13,22-23] or coatings such as aluminum oxide [24], silicon oxide [24], chromium oxide [23], and indium tin oxide [25]. Certain disadvantages exist with coatings such as the formation of defects during application, difficulty in coating large or complex shapes, cracking and spalling due to thermal cycling caused by differences in thermal expansion between coating and substrate, micrometeoroid and debris impacts, and poor adhesion to the substrate.

More recent work has focused on the incorporation of polyhedral oligomeric silsesquioxanes (POSS) molecules into polymers as a means of achieving AO resistance. POSS molecules are caged silicates typically represented by the formula Si<sub>8</sub>O<sub>12</sub> wherein organic

functional groups can be attached to one or more of the Si atoms. The functional groups are designed so that they can react with specific monomers such that POSS molecules become incorporated into the polymer backbone at a molecular level. A polyimide containing 31 weight percent POSS exhibited excellent performance in ground-based simulated AO exposure tests [26-28]. As with other Si containing polymers, the AO resistance is attributed to the reaction of AO with the Si in the material leading to the formation of a silicon oxide enriched surface layer which subsequently decreases the reaction rate with AO thereby protecting the underlying polymer.

The Materials on The International Space Station Experiment (MISSE) program is a combined effort primarily between NASA, The Air Force Research Laboratory, and Boeing Phantom Works. The MISSE 1 and 2 flight experiments consisted of two passive experiment carriers (PECs) of material specimens that were attached to the International Space Station (ISS) and passively exposed to the LEO space environment [i.e., AO, ultraviolet (UV) radiation, particulate radiation, thermal cycling, and the induced environment of the space station]. The materials were deployed and attached to the exterior of the ISS in August 2001 and were intended to experience a one year exposure. Due to the Space Shuttle Columbia accident in February 2003 and subsequent delays in returning to flight, the PECs were not retrieved until August 2005. Consequently, many polymer samples were completely eroded by AO including Kapton® HN film [127 microns (μm) or 5 mils thick]. One suitcase was intended to experience exposure in the flight (RAM) direction and the other in the WAKE direction. However, due to the orbital configuration of the ISS, the WAKE exposed samples experienced more AO fluence than expected. A report is available detailing the exposure conditions experienced by the hardware and material specimens during the MISSE flight experiment [29].

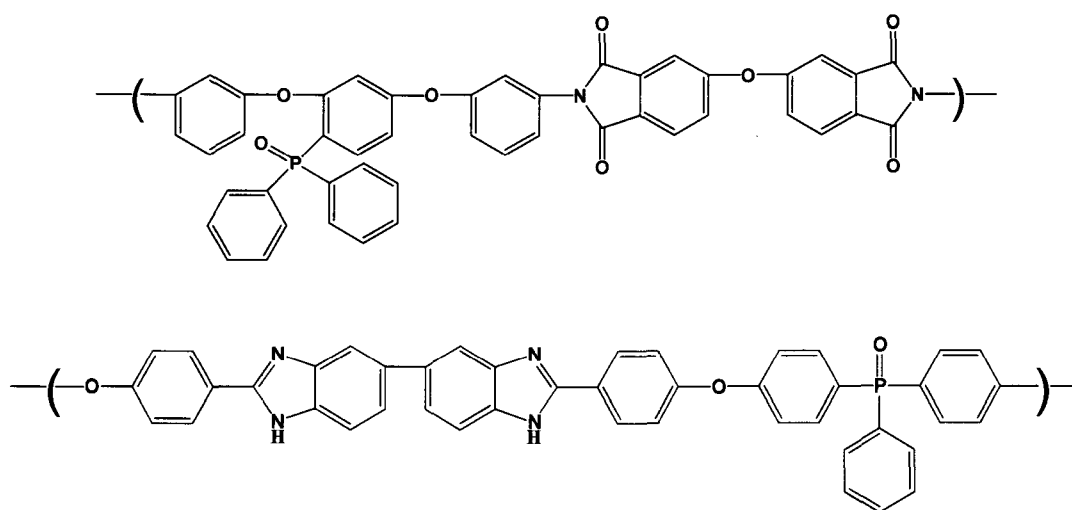


Figure 1. Chemical structure of CP (top) and TOR (bottom). TOR-LM is a 1:1 random copolymer of TOR with 4,4'-biphenol.

## Experimental

**Materials:** The polymers consisted of a colorless polyimide (CP) film and a poly(arylene ether benzimidazole) (TOR) film and thread (Figure 1). The polyimide film was prepared at NASA Langley Research Center following a procedure previously reported [30]. The poly(arylene ether benzimidazole) film (TOR-LM) was metallized with a 100 nm thick coating of vapor deposited aluminum (VDA). The film (38  $\mu\text{m}$ , 1.5 mil thick) was mounted such that the polymer surface faced the RAM direction. Both the TOR-LM film [9] and thread [6] were obtained from Triton Systems, Inc. in 2000.

**Flight Exposure Conditions [29]:** The film samples were 10.2 cm x 10.2 cm (4 in x 4 in) and 25 to 40  $\mu\text{m}$  thick and were mounted on an aluminum plate and held in place with metal strips. The conditions experienced during exposure for this set of samples (RAM facing side) were as follows: AO fluence from 6.5 to 9.1 x 10<sup>21</sup> atoms/cm<sup>2</sup>; equivalent solar hours 5870 to 6134 depending on exact sample location; thermal cycling, minimum temperature ~ -55 °C, maximum temperature ~ 66 °C, average temperature -13 °C. The normal orbital period was ~90 minutes. The polymer samples were mounted in the exposure tray (PEC) as shown in Figure 2.

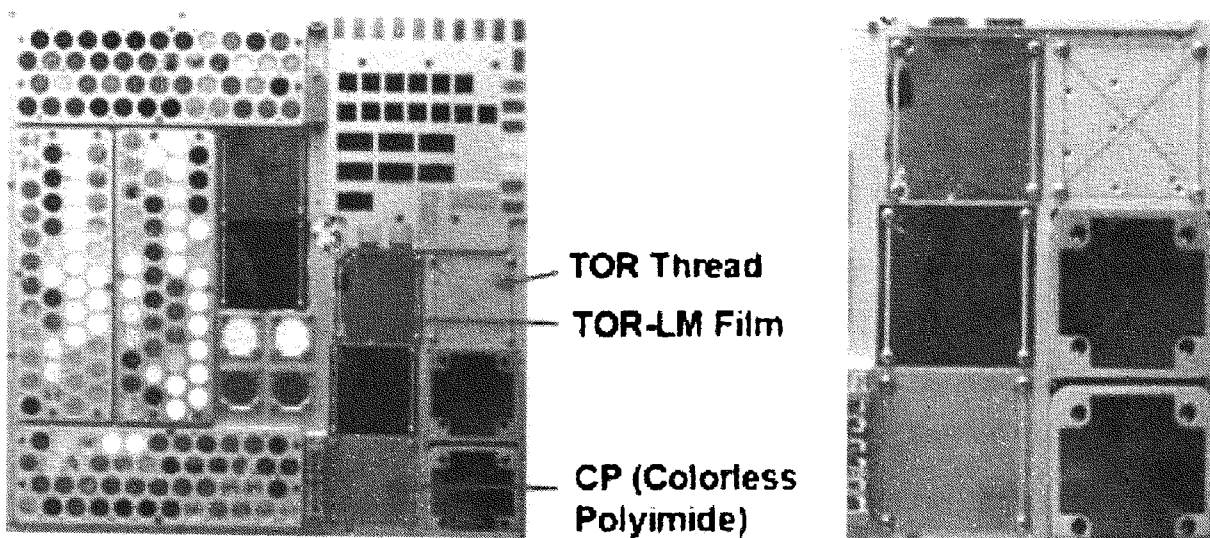


Figure 2. Samples mounted on exposure tray. A close-up is shown on the right.

## Results and Discussion

**Materials:** The chemical structures of the aromatic polymers containing PPO groups are presented in Figure 1 and consist of a colorless polyimide film, a polybenzimidazole (TOR-LM) film with one side coated with VDA, and a polybenzimidazole thread (TOR). Control films and threads were cut from the same batch of material as that used in the flight experiment. The control samples were maintained in zip-lock bags under ambient conditions until the return of the flight

specimens.

Visual Inspection of Flight Specimens: Samples were returned to NASA Langley Research Center in October 2005 and placed in a clean room for observation and subsequent deintegration. Both film samples had cracks adjacent to the metal bars and near the bolt holding the sample against the plate (Figure 3). The cracks are likely due to stress build-up as a result of the thermal expansion mismatch between the metal bars and the polymer. Both the TOR-LM and CP film samples appeared diffuse as a result of AO erosion and the CP film was not visually transparent.

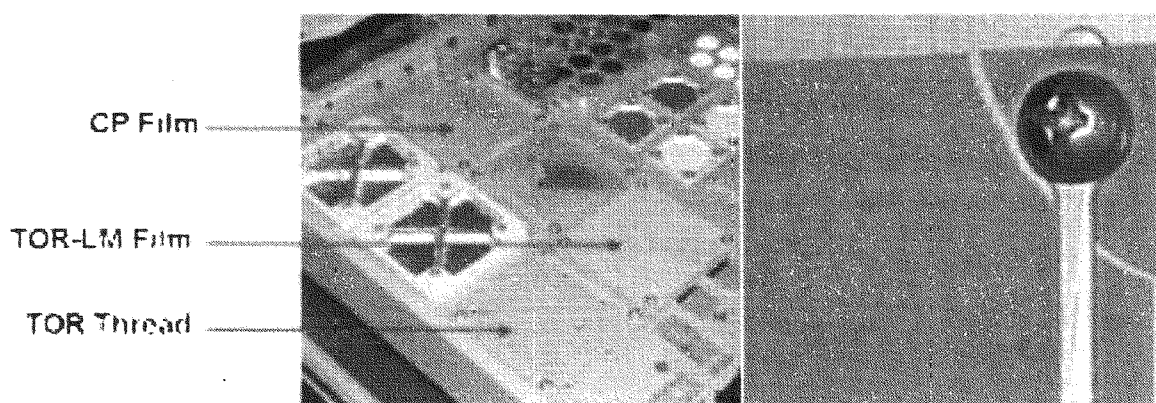


Figure 3. Samples after return from LEO (left) and a close-up of TOR-LM (right) showing a crack in the film.

Fourier transform infrared (FTIR) spectroscopy: FTIR was performed on the CP and TOR-LM films. With the CP film, the carbonyl peaks readily visible in the spectra corresponding to the control sample are significantly dampened in the spectra of the exposed film. This was the general trend for the bulk of the other significant FTIR spectral features as well as for the control and exposed TOR-LM films.

Thermo-optical properties: Solar absorptivity ( $\alpha$ ) and thermal emissivity ( $\epsilon$ ) data were collected on CP films and TOR-LM films (Table 1). Solar absorptivity increased significantly due to the AO exposure. The increase in  $\alpha$  for the CP film was the same for the RAM facing side as

Table 1. Solar Absorptivity/Thermal Emissivity

Sample	$\alpha$	$\epsilon$	$\alpha/\epsilon$
CP Control	0.07	0.67	0.11
CP Exposed Backside	0.23	0.71	0.32
CP RAM Facing Side	0.23	0.76	0.30
TOR-LM Control (polymer surface)	0.31	0.71	0.44
TOR-LM RAM Facing Side (polymer surface)	0.50	0.85	0.59

well as the backside of the film. The polymer surface of the TOR-LM film exhibited a larger increase in  $\epsilon$  than the colorless polyimide film. The exposed backside of the TOR-LM film, which had a VDA surface, did not exhibit any changes in  $\alpha$  or  $\epsilon$ .

X-ray photoelectron spectroscopy (XPS): As a means to investigate changes in surface chemistry, XPS was performed on all samples. The experiments were performed on both sides of each film. By summing the area under the photoelectron peaks corresponding to different elements, the concentrations of those elements were determined. The results for the CP film are shown in Table 2.

Table 2. XPS Analysis Results for the CP film

Photoelectron	Control, Atomic Conc., %	RAM Exposed, Atomic Conc., %	Backside Exposed, Atomic Conc., %
O 1s	16.3	46.5	36.4
N 1s	3.2	3.4	4.1
C 1s	78.9	38.1	51.3
P2p	1.6	12.0	8.2

To summarize the results from the XPS analyses, for each sample there is a noticeable increase in the oxygen and phosphorus concentration after AO exposure. The high resolution O 1s signal from the samples could be fit with two peaks corresponding to two different bonding situations. The O 1s sub-peak at 530 eV is reduced while the sub-peak at 534 eV increases indicating that the oxygen has become more inorganic. After exposure the amount of phosphorus at the surface has increased. This is most likely in the form of an oxide (phosphate) since the binding energy of the P 2p<sub>3/2</sub> peak shifts from 132 eV to 135 eV. The changes in surface chemistry of the exposed backside followed the same trend as those on the RAM facing side indicating that AO had access to the backside of the film. Similar changes in atomic concentrations were observed for TOR and TOR-LM.

Atomic Force Microscopy (AFM): AFM analyses were performed on the samples to investigate changes in surface topography. All samples showed an increase in surface roughness upon exposure both on the exposed backside and the RAM facing side (Table 3). Samples were also examined on the exposed side in the area that was protected by the metal mounting bars. Both film samples showed a significant increase in surface roughness on the RAM facing side when compared to the control sample. The exposed backside of the colorless polyimide film showed an increase in roughness compared to both the control and the exposed backside of TOR-LM. This is consistent with the XPS results showing that the exposed backside of the colorless polyimide film

did experience exposure to AO. The exposed backside of the TOR-LM did not exhibit as much erosion (due to the VDA surface) but still had an increase in roughness compared to the control.

The exposed RAM facing surface of TOR-LM film showed what appeared to be platelet formations that seemed to serve as an etch stop (Figure 4). Even though the RAM facing surface was significantly roughened, the platelets seemed to slow the etching where they formed. It is important to note that the average surface roughness and the relative standard deviation of the roughness both increased. This indicates that the sample did not roughen in a homogeneous fashion, consistent with the theory that the sample forms platelets that are comprised of a phosphate or polyphosphate material that has a reduced AO erosion rate.

Table 3. AFM Analysis of Surface Roughness

Sample	Average $R_a$ (nm)	Standard Deviation of $R_a$ (nm)	Average $R_q$ (nm)	Standard Deviation of $R_q$ (nm)
CP Control	0.47	0.02	0.73	0.075
CP Exposed Backside	8.44	7.49	12.01	9.842
CP RAM Facing Side	419.10	371.70	517.10	452.10
CP RAM Facing Side*	80.21	80.66	99.17	95.40
TOR-LM Exposed Backside	1.76	0.70	2.36	1.435
TOR-LM Exposed RAM Facing Side	427.40	206.00	525.20	245.0
TOR-LM Exposed RAM Facing Side*	326.80	172.30	408.10	209.5

\* Denotes sample underneath the metal mounting bar

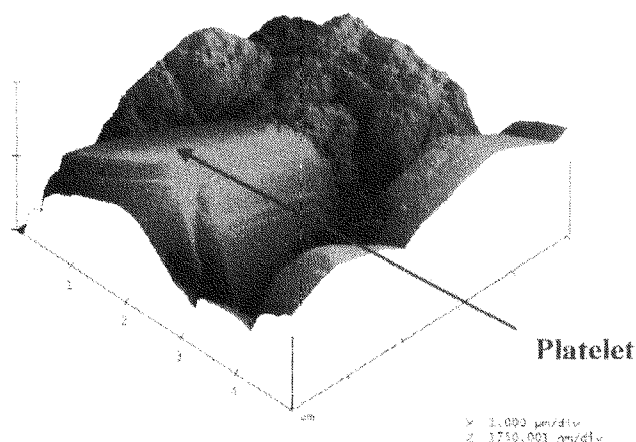


Figure 4. AFM image of the TOR-LM exposed RAM facing surface showing platelet formation (denoted by arrow). X and Y axis units are in  $\mu\text{m}$ .

The exposed thread sample (TOR) showed a decrease in overall diameter, an increase in surface roughness, and separation of the weave, however the data could not be quantified due to the uneven surface features of the thread.

### Conclusions

Aromatic polymers containing PPO groups were exposed to LEO for ~4 years. The polymers survived intact despite high AO fluence whereas other polymers such as Kapton® and metallized polyimides were completely eroded. The polymer films appeared frosted and AO erosion significantly affected optical transparency as well as solar absorptivity and thermal emissivity of the film samples. The changes in surface chemistry as determined by XPS were consistent with the formation of a phosphate surface layer. Changes in surface topography consistent with AO erosion were evident from AFM analysis. Due to the changes in properties exhibited by the films, the materials are perhaps more suitable for applications in LEO in the form of stitching thread, woven fabric, soft goods, or tethers.

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