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Atomic-Oxygen Undercutting of Protected Polymers in Low Earth Orbit

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Hydrocarbon-based polymers that are exposed to atomic oxygen in low Earth orbit are slowly oxidized into volatile gases, which results in their erosion. Atomic-oxygen protective coatings that are both durable to atomic oxygen and effective in protecting underlying polymers have been developed. However, scratches, pin window defects, polymer surface roughness, and protective coating layer configuration can result in erosion and potential failure of protected thin polymer films even though the coatings are themselves atomic-oxygen durable. Issues are presented that cause protective coatings to become ineffective in some cases yet effective in others because of the details of their specific application. Observed in-space examples of failed and successfully protected materials using identical protective thin films are discussed and analyzed. Ground laboratory atomic-oxygen testing was conducted and compared with water vapor transport analyses from a previous study of protective coatings on Kapton® (polyimide), which indicates that vapor-deposited aluminized films are not as protective as sputter-deposited silicon dioxide films because of a greater number of pin window defects. Computational modeling was conducted and indicates that atomic-oxygen atoms trapped between the front and back surface aluminized films cause accelerated undercutting damage.

Introduction

THE use of atomic-oxygen protective coatings applied over conventional polymers that have traditionally been used in space has been the primary approach to date to achieve atomic-oxygen durability in space. Metal atoms or metal-oxide molecules have been used extensively for the protective coating materials. Typically thin films of silicon dioxide, fluoropolymer-filled silicon dioxide, aluminum oxide, or germanium have been sputter deposited on polymers to provide atomic-oxygen protection. For example, the large solar-array blankets on the International Space Station (ISS) have been coated with 1300 Å of SiO_2 for atomic-oxygen protection.[1] Even though protective coatings can be durable to exposure by atomic oxygen, many factors can contribute to potential inability to fully protect underlying polymers. Less than perfect atomic-oxygen protection can result from substrate surface irregularities (microscopic scratches, rills, pits, protrusions and contaminant particles), defects in the coating as a result of processing, handling, launch-vibration-induced abrasion, thermal cycling, as well as micrometeoroid and debris impact. Results of long-term in-space testing of protective coatings on the Long Duration Exposure Facility (LDEF) and analysis of micrometeoroid and debris damage to protective coatings indicate that although protection might be compromised in areas where processing, hole punching, cutting, handling, or abrasion has occurred, the protective coatings are not significantly compromised by thermal cycling or micrometeoroid and debris damage.[2,3] Instead, the dominant cause of defects in the protective coatings is the initial imperfect surface of the uncoated polymers. Extensive ground-based durability testing has been conducted on the SiO_2 coatings for ISS solar-array blanket applications using rf and microwave-generated thermal-energy plasmas.[1,4–8] Such atomic-oxygen exposure systems typically operate with the samples near room temperature in air or pure oxygen plasmas that are calibrated to enable comparison with in-space results.[2,3,9,10] Efforts to understand the erosion consequences of defects in protective coatings and to reduce their population have resulted in sufficiently low defect densities to allow such coatings to be used for ISS solar-array blanket applications.[8] Ground-based durability tests of protective coatings on solar concentrators likewise have shown the problem of defects in protective coating, allowing atomic-oxygen undercutting erosion.[11] Studies on protected polymers exposed to the low-Earth-orbit (LEO) environment on the LDEF have provided evidence of atomic-oxygen undercutting at protective coating defect sites that where exposed to only directed ram atomic oxygen exposure.[7,12] As further evidence of the importance of protective coating defects in the coatings atomic-oxygen durability, leveling coating studies have provided direct evidence of improved atomic-oxygen durability with decreased defect densities for solar concentrator applications.[13,14]

Although protective coatings can provide excellent atomic-oxygen protection of hydrocarbon or halocarbon polymers, the details of how the coatings are used and/or applied can result in widely varying protection consequences. This paper reviews various specific examples of atomic-oxygen protective coatings used on spacecraft exterior components in the LEO environment. The success of the coatings in providing protection against atomic-oxygen degradation of the specific components is discussed. Monte Carlo computational atomic-oxygen erosion studies were conducted to better understand the differences in degradation for the various degrees of atomic-oxygen protection witnessed on spacecraft. Specifically, the difference in degradation between single (front surface)-coated Kapton® and double (front and back surface)-coated Kapton films at crack or scratch and circular defect sites were compared. Mass-loss studies of ground-laboratory atomic-oxygen exposed samples were conducted to provide evidence in the difference in defect density numbers between double-SiO_2-coated Kapton and

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double-aluminized Kapton. These results were also compared with the results of prior investigations of water vapor transport studies to provide further evidence of the difference in defect densities for the type types of protective coatings.

In-Space Protective Coating Experiences

European Retrievable Carrier

The European Retrievable Carrier (EURECA) spacecraft, which was deployed into LEO on 2 August 1992 and retrieved after 11 months on 24 June 1993, was exposed to an atomic-oxygen fluence of approximately 2.3×10^{20} atoms/cm^2 (Ref. 15). To assist in its retrieval, the spacecraft had two thin adhesively mounted acrylic optical retroreflectors for laser range finding. Prevention of atomic-oxygen attack of the retroreflector surfaces, which would have degraded the specularity of the reflectance, was accomplished by coating the surface with an $\sim$1000 Å thick film of sputter deposited SiO_2 filled with 8% fluoropolymer (by volume). The retrieved, LEO-exposed, retroreflector was inspected and optically characterized. The results indicated that the protective coating provided excellent protection and the retroreflector performed as planned except in a small 3-cm patch, where the protective coating was accidentally abraded as a result of handling during preflight ground integration.[13] Figure 1 shows a close-up picture of the retroreflectors as well as their appearance during illumination after retrieval.

ISS Retroreflectors

International Space Station retroreflectors, which serve a similar role as the EURCA retroreflectors, consist of a glass corner cube retroreflector that is housed in a 10-cm-diam Delrin® 100 polyoxymethylene mount. Polyoxymethylene is an oxygen-rich polymer and is readily attacked by atomic oxygen. To prevent atomic-oxygen attack of the Delrin, the machined polymer surfaces were coated by the same processes, in the same facility and with the same $\sim$1000 Å thin film of sputter-deposited 8% fluoropolymer-filled SiO_2 that was used for the EURECA retroreflector. Several of these retroreflectors have been mounted on the external surfaces of the ISS structures at various locations that are exposed to LEO atomic oxygen. Figure 2 shows a close-up of one of the coated retroreflectors prior to use on ISS as well as a photograph from space of one of the ISS retroreflectors after attack by atomic oxygen. It is clear from the in-space photograph that the coating was only partially attached allowing direct atomic-oxygen attack of the unprotected areas.

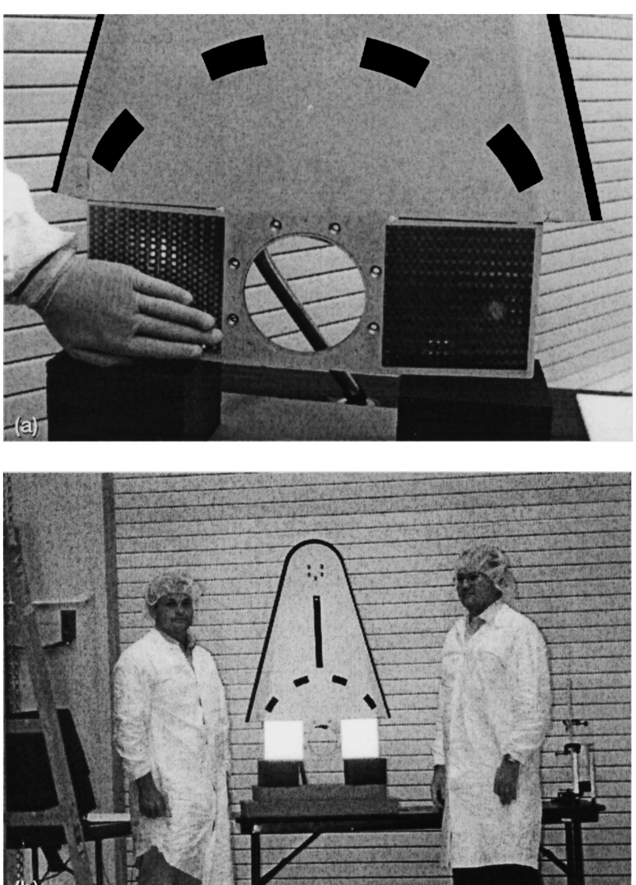


Fig. 1 EURECA retroreflectors after retrieval: a) close-up and b) during illumination.

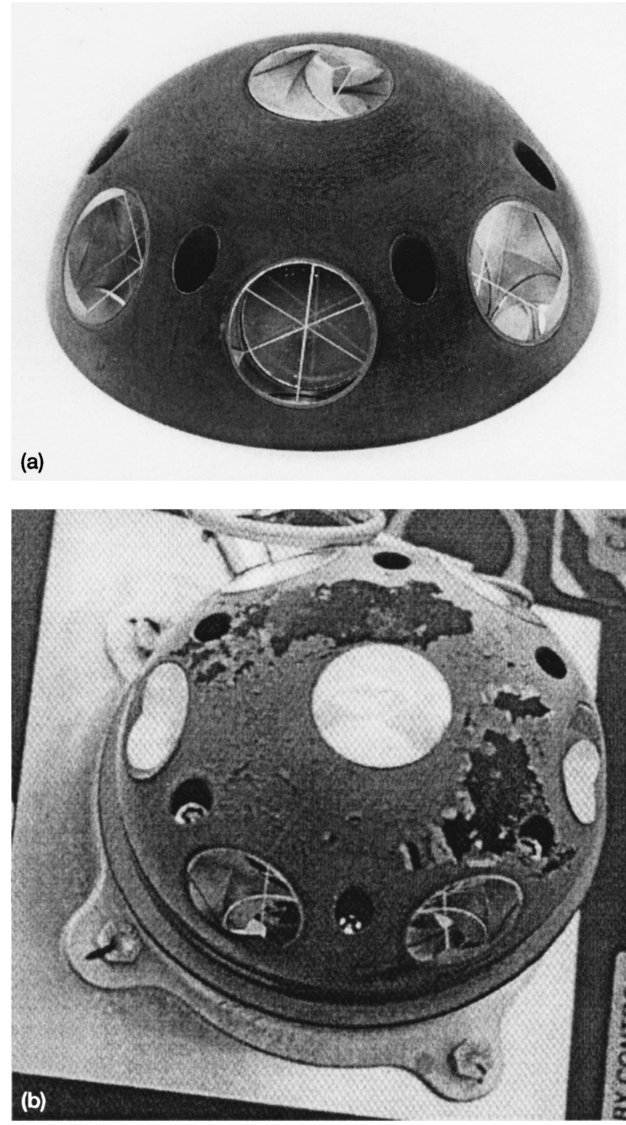
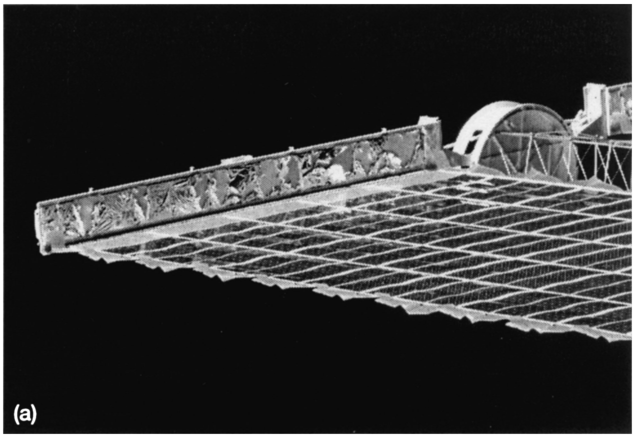


Fig. 2 ISS retroreflectors: a) prior to launch and b) during use in space on ISS after atomic-oxygen attack.

ISS Photovoltaic-Array Blanket Box Covers

Prior to deployment, the ISS photovoltaic arrays were folded into a box that allows the array to be compressed in a controlled manner against a cushion of open pore polyimide foam that was covered with a 0.0254-mm-thick aluminized Kapton blanket. The Kapton was coated on both surfaces with 1000 Å of vacuum-deposited aluminum. The array was exposed to the LEO atomic-oxygen environment from December 2000 through December 2001. Although the actual atomic-oxygen fluence on the aluminized Kapton is not accurately known, the ram atomic-oxygen fluence for that duration is approximately 3.7×10^{21} atoms/cm^2. Photographs of the array, taken in orbit, appear to indicate that the Kapton blanket had been almost completely oxidized leaving only the thin and largely torn aluminization in place, as shown in Fig. 3.



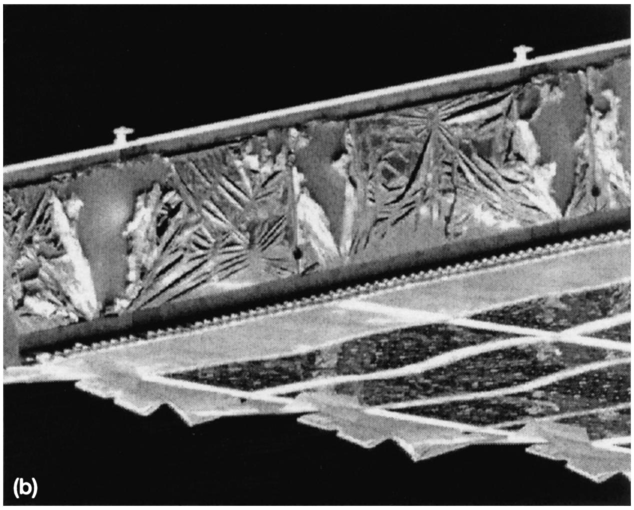


Fig. 3 ISS photovoltaic array showing effects of atomic-oxygen erosion of the double-aluminized Kapton blanket cover for the ISS photovoltaic-arrays box cushions: a) distant photo and b) close-up photo.

Analysis and Discussion

Surface Roughness and Defect Density

The drastic differences in atomic-oxygen protection provided by the same SiO_2 coating filled with 8% fluoropolymer on the EURECA retroreflectors and the ISS retroreflectors is thought to be caused by differences in the protective coating defect densities. The acrylic EURECA retroreflectors surfaces were extremely smooth as required to produce high-fidelity specular reflections. Such smooth surfaces result in low-defect-density protective coatings that have also been demonstrated, in ground laboratory testing, to perform acceptably.[13] For example, smooth surface (air-cured side) Kapton when coated with 1300 Å thick SiO_2 resulted in ~400 pin window defects/cm^2 (Ref. 1). However, the same coating on the rougher surface (drum-cured side) has been found to result in 3500 pin window defects/cm^2 (Ref. 1). Similar experiences with graphite-epoxy composite surfaces formed by casting against another smooth surface produce defect densities of ~262,300 defects/cm^2 (Ref. 13). Surface leveling polymers applied over such surfaces have been found to reduce the defect densities by an order of magnitude to ~22,000 defects/cm^2 (Ref. 13).

The machining of the Delrin 100 (polyoxymethylene) retroreflector mount surfaces produced machine marks or rills in the surface that were clearly visible to the unaided eye. The application of a protective coating onto these surface defects probably resulted in a highly defected atomic-oxygen protective coating to be produced. Such rills would allow atomic oxygen to oxidize and undercut the high erosion yield Delrin, causing the coating to gradually be left as an unattached gossamer film over the retroreflector mount, and this ultradelicate thin film could be easily torn and removed by intrinsic stresses and thruster plume loads. The use of smoother surfaces, surface-leveling coatings, over the machined Delrin or use of alternative atomic-oxygen durable materials could potentially eliminate the observed problem.

Trapping of Atomic Oxygen Between Defected Protective Surfaces

The lack of atomic-oxygen protection provided by the aluminized Kapton blanket cover for the ISS photovoltaic arrays box cushion is thought to be as a result of the trapping of atomic oxygen between the two aluminized surfaces of the 0.0254-mm-thick Kapton blanket. This hypothesis is tested in the following sections through experiment and Monte Carlo modeling. Defects in the space-exposed aluminized surface allow atomic oxygen to erode undercut cavities. If the undercut cavity extends downward to the bottom aluminized surface, then the atomic oxygen becomes significantly trapped and has multiple opportunities for reaction until it recombines, reacts, or escapes out one of the defects in the aluminization. This eventually results in a complete loss of the Kapton with only the aluminized thin film remaining. The vacuum-deposited aluminum has a slight tensile stress that would cause stress wrinkling of the unsupported aluminum films.

Atomic-Oxygen Plasma Ashing

Figure 4 is a photograph of a double-surface vacuum-deposited aluminized Kapton sample that was placed in a rf atomic-oxygen plasma environment to completely oxidize the Kapton over a portion of the sample (wrinkled area). As can be seen in Fig. 4b, after atomic-oxygen exposure the ~1000 Å aluminum film is left free standing, and stress wrinkles and tears have developed similar to those seen in the ISS photograph of Fig. 3.

Monte Carlo Computational Modeling

A two-dimensional Monte Carlo computational model has been developed that is capable of simulating LEO atomic-oxygen attack and undercutting at crack defects in protective coatings over hydrocarbon polymers.[15] Optimal values of the atomic-oxygen interaction parameters were identified by forcing the Monte Carlo computational predictions to match results of protected samples retrieved from the LDEF.[15] These interaction parameters and values were used to predict the consequences of atomic oxygen entering a two-dimensional crack or scratch defect in the top aluminized surface. This was accomplished using 100,000 Monte Carlo atoms entering a defect which was 20 Monte Carlo cells wide (representing a 13.4-μm-wide defect) over a 38-cell-thick (representing a 0.0254-mm-thick) Kapton blanket. The number of Monte Carlo atoms entering represents an in-space atomic-oxygen fluence of 1.5×10^{22} atoms/cm^2. Thus, the modeling represents an atomic-oxygen fluence well beyond that which the ISS solar array was exposed to when the pictures of Fig. 3 were taken. However, it allows clear illustration of the differences in behavior resulting from single and double

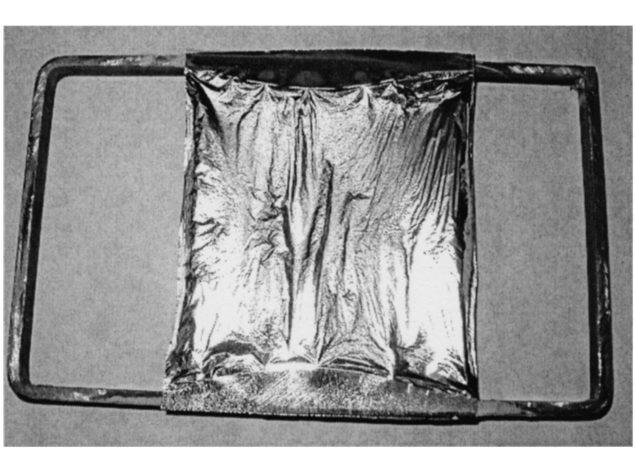


Fig. 4 Photograph of a vacuum-deposited aluminized Kapton sample bonded to a metal frame after ground laboratory oxidation of the Kapton.

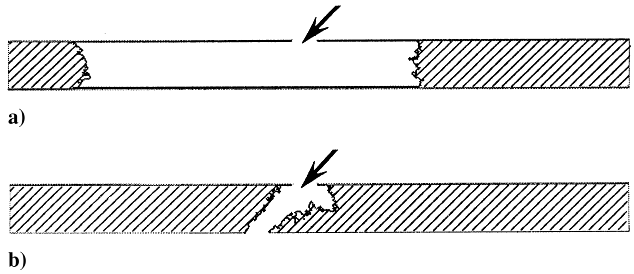


Fig. 5 Monte Carlo computational atomic-oxygen erosion predictions for a 45-deg from perpendicular angle of attack of atomic oxygen at a crack or scratch defect in the aluminized Kapton surface: a) aluminized on both sides and b) aluminized on exposed side only.

coatings. To compare the atomic-oxygen undercutting differences between single- and double-aluminized Kapton, both sweeping and fixed angle of incidence atomic-oxygen attack was simulated. Because of the ISS solar-array sun-tracking configuration, near normal angle of attack is unlikely, and a 45-deg angle of attack was chosen to be able to clearly illustrate differences in undercutting between single- and double-surface aluminized Kapton. Figure 5 compares the Monte Carlo model computational erosion results for a 45-deg angle of attack (relative to the surface normal) of the atomic oxygen for both double-surface-coated Kapton (which was the case for ISS; Fig. 5a) and single-top-surface-coated Kapton (Fig. 5b).

As can be seen from Fig. 5, even though the atomic oxygen gradually becomes less energetic with the number of interactions and has approximately a 13% chance of recombination, the trapped atoms undercut far more in the ISS case of a double-aluminized Kapton film as would have occurred if the Kapton were simply aluminized on one side. Thus, contrary to intuition, the use of two atomic-oxygen protective coatings rather than a single coating appears to cause more rather than less undercutting attack.

The extent of undercutting of trapped atomic oxygen is also dependent on the opportunity for the atoms to loose energy, recombine, or escape back out the defect opening. Figure 6 compares the results of two-dimensional Monte Carlo modeling and three-dimensional pin window computational predictions for 45-deg-angle-of-attack atomic-oxygen for both single-side and double-side aluminized Kapton (Figs. 6a and 6b, respectively).[15,16] The two-dimensional modeling was of a 13.4-μm-wide crack or scratch, and the three-dimensional modeling was of a 5.1-μm-diam circular aperture.

As can be seen in Fig. 6, for both two-dimensional modeling of a crack or scratch defect and three-dimensional modeling of a circular defect the growth characteristics of the undercut cavity have similar trends with fluence. Initially, as the undercutting starts the existence or absence of the backsurface coating plays no role, and as the cavity grows the probability of atoms reacting increases because of trapping of the incoming atom. However, as the bottom surface is reached atoms begin either to escape, or in the case of no backsurface coating they recombine after collision with the SiO_2 on the backsurface. The double-surface aluminized Kapton consistently has more atomic-oxygen atoms react than the single-surface aluminized Kapton except at very low fluences, where the erosion in either case does not reach the bottom of the polymer. For both crack or scratch and circular defects cases, as the fluence increases the atomic oxygen can escape out of the bottom (in the case of the single-surface aluminized Kapton), recombine, or thermally accommodate and thus becomes less probable to react with the Kapton. Thus it appears that a single-surface aluminized Kapton would have been much more durable because the unreacted atoms passing through the bottom of the polymer would simply enter into the open pore foam and gradually react with it, without causing much damage to the aluminized Kapton.

Double-Aluminized Kapton and Double-SiO_2-Coated Kapton Ground Laboratory Comparisons

The double-SiO_2-coated ISS solar-array blankets can show similar detachment of the outer-surface SiO_2 layer with time. However, the defect density appears to be much lower than for vacuum-deposited aluminum coatings as shown in Fig. 7, which compares the experimental results of rf plasma oxidation of double-aluminized Kapton with double-SiO_2-coated Kapton. Further evidence of the greater number and/or total area of pin windows in the aluminized coatings has been shown in a separate study by comparing the water vapor transport through the two protected materials in their pristine condition, as shown in Fig. 8 (Ref. 17).

Data for the experiment shown in Fig. 8 were obtained by measuring the weight loss of water-filled petri dishes, which had covers

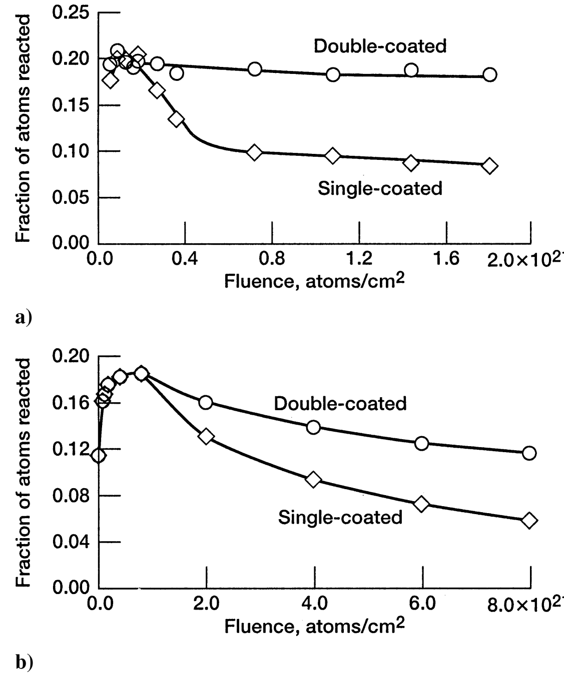


Fig. 6 Computational atomic-oxygen erosion predictions for 45-deg incident atomic-oxygen attack at defect sites in protected Kapton: a) two-dimensional model of crack or scratch defect and b) three-dimensional model of circular pin window defect.

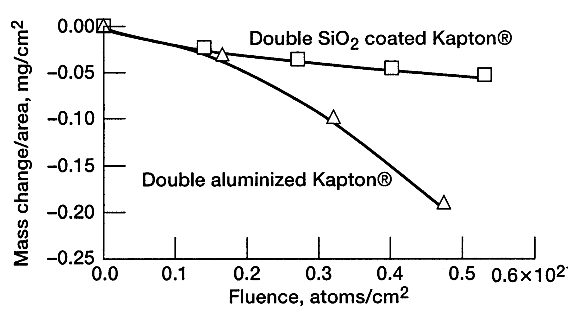


Fig. 7 Comparison of rf plasma oxidation of aluminized and SiO_2-coated Kapton.

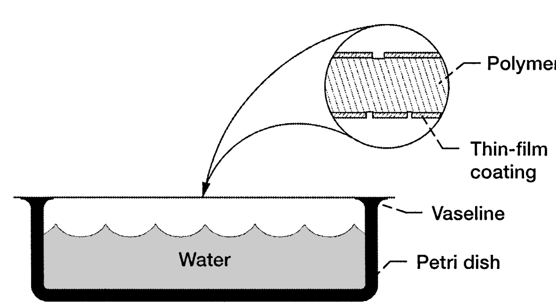


Fig. 8 Measurement of water vapor transport through protected Kapton films.

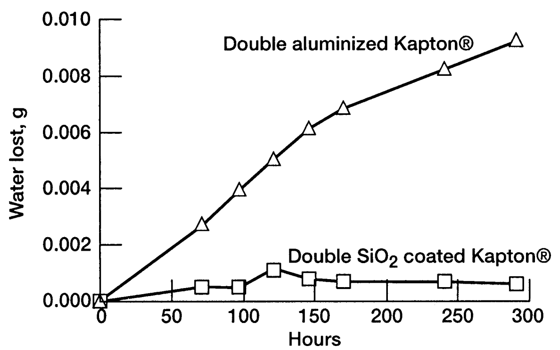


Fig. 9 Water vapor transport rate through protected Kapton.

made of the pristine ISS photovoltaic array blanket box cover (double-aluminized Kapton) and ISS PV array (double-SiO_2-coated Kapton) materials.[17] The samples were sealed to the petri dishes by means of petroleum jelly to minimize moisture loss other than from through the protected polymers. As can be seen from the resulting data in Fig. 9, there is approximately a factor of 16 greater defect area in the double-aluminized Kapton compared to the double-SiO_2-coated Kapton. When one considers the greater apparent number of defects as well as the greater area of defects, it is reasonable to believe that the aluminized Kapton has many more small defects than the SiO_2-coated Kapton.

The evidence is also supported by scanning electron microscopy comparisons of both types of protected films after ground laboratory atomic-oxygen exposure.[6] These results indicate that there are far greater number of pin window defects in the vapor-deposited aluminized films on Kapton than on the sputter-deposited SiO_2 films. Pin window defects are frequently sufficiently small that they cannot be observed by scanning electron microscopy. It is only after atomic-oxygen exposure, which causes the development of undercut cavities that the evidence for most pin window defects can be found. Thus the actual fractional are of the pin window defects might be quite small, but the long-term consequences of atomic oxygen can be devastating if their density is large.

Conclusions

Atomic-oxygen protective coatings that perform acceptably have been developed and used in space. However, rough surface substrates cause defects in the protective coatings that allow atomic oxygen to react and gradually undercut the protective coating. In the case of machined Delrin ISS retroreflector mounts, such roughness has led to detachment of portions of the protective film covering the retroreflector mount.

Atomic-oxygen undercutting of the double-aluminized Kapton blanket covers for the ISS photovoltaic-array box cushions has occurred, resulting in a highly torn and partially detached aluminum film. Ground laboratory atomic-oxygen testing, water vapor transport, and scanning-electron-microscopy analyses of protective coatings on Kapton all indicate that vapor-deposited aluminized films do not offer the level of atomic-oxygen protection that sputter-deposited silicon-dioxide protective films provide as a result of a greater number and/or area of pin window defects. Based on computational modeling, atomic-oxygen atoms that become trapped between the two aluminized films on each side of the Kapton blanket appear to cause accelerated undercutting damage in comparison to the use of a single top-surface coating.

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