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THE EFFECT OF ATOMIC OXYGEN ON POLYSILOXANE-POLYIMIDE FOR SPACECRAFT APPLICATIONS IN LOW EARTH ORBIT

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ABSTRACT

Polysiloxane-polyimide films are of interest as a replacement for polyimide Kapton in the Space Station Freedom solar array blanket. The blanket provides the structural support for the solar cells as well as providing transport of heat away from the back of the cells. Polyimide Kapton would be an ideal material to use, however, its high rate of degradation due to attack by atomic oxygen in low Earth orbit, at the altitudes Space Station Freedom will fly, is of such magnitude that if left unprotected, the blanket will undergo structural failure in much less than the desired 15 year operating life. Polysiloxane-polyimide is of interest as a replacement material because it should form its own protective silicon dioxide coating upon exposure to atomic oxygen. This paper presents mass, optical and photomicrographic data obtained in the evaluation of the durability of polysiloxane-polyimide to an atomic oxygen environment.

INTRODUCTION

The Space Station Freedom solar array is being designed to provide the primary power for the first phase of the station (1). Polyimide Kapton (DuPont) was the material originally selected for the structural support of the solar cells for the flexible array. Its light weight, flexibility, strength and IR transparency made it an ideal material for this application. However, it is readily oxidized by atomic oxygen in the low Earth orbital (LEO) environment (2,3,4).

Single, neutral oxygen atoms in the ground state are the most predominant species in LEO between altitudes of 180 and 650 km (5). As spacecraft pass through the atmosphere at these altitudes, they collide with the oxygen atoms with an equivalent energy ranging from 3.3 to 5.5 eV (6). This is energetic enough to break many chemical bonds and allow the highly reactive atomic oxygen to oxidize many organic and some metallic materials (3). When atomic oxygen reacts with polymers it forms gaseous oxidation products (primarily CO) which results in material losses that can hinder system performance (7). The Space Station Freedom solar array is designed for a 15 year operating life in LEO, however, the oxidation rate of this material is great enough that structural failure of the blanket would occur in much less than 15 years. The current Space Station Freedom design utilizes a sputter deposited SiO_x (where x=1.9 to 2.0) for atomic oxygen protection.

A modified Kapton manufactured by DuPont designated as AOR (atomic oxygen resistant) Kapton has been proposed as a back up material for the Space Station Freedom solar array design. It is a polysiloxane-polyimide solid solution. Results of the testing of this material for atomic oxygen resistance is presented in this paper.

APPARATUS AND PROCEDURE

AOR Kapton

The AOR Kapton was manufactured by DuPont in an experimental batch process. It is a homogeneous dimethylpolysiloxane-polyimide film cast from a solution mixture. The dimethylpolysiloxane is added to the polyimide in an attempt to make the material resistant to attack by atomic oxygen since polysiloxane is a metal oxide former. Metal oxides are highly resistant to attack by atomic oxygen (3). The material lot # was RM449AAA. The material was received in 5 sheets from different portions of the processed roll. Four 2.54 x 2.54 cm atomic oxygen

exposure samples were taken from each sheet in order to test for process uniformity. Since past testing of a different version of AOR Kapton (93-1) exhibited non-uniformity between the air and roll processing sides of the sheet, the four samples tested were sandwich samples with identical surfaces exposed to atomic oxygen (8). Acrylic adhesive from 3M was used to bond two adjacent sections of the sheet together that the samples were cut from. Two samples were prepared with the air sides out, and 2 with the roll side out on each sheet. In this manner, the durability to atomic oxygen could be determined separately for each side. Additional atomic oxygen exposure samples were prepared from sheet #3 as well as scanning electron microscope (SEM) samples (1.27 x 1.27 cm) and single thickness optical specimens. The optical specimens could not be sandwiched because the adhesive in the center would interfere with the measurement. Therefore, during atomic oxygen exposure only one side of the sample was exposed (air side) by placing the sample on top of a glass slide with the edges held down in close contact to the slide with a thick glass ring.

Atomic Oxygen Durability Testing

A plasma asher (SPI Plasma Prep II) was used to evaluate the atomic oxygen durability of the AOR Kapton. It uses a 13.56 MHz RF discharge to create an air plasma of oxygen and nitrogen ions and atoms in various energy states in a glass sample chamber kept at 80-100 mTorr. The nitrogen species have been shown to be relatively unreactive with polyimide in previous experiments (9). The species in the plasma impact surfaces placed in the plasma at thermal energies which is much lower than the energy in space but still energetic enough for chemical reactions to occur. The arrival at the surface is also omnidirectional while the arrival in space is more directed but sweeping, due to the rotation of the solar array to track the sun. The arrival flux (atoms striking/cm^2 of surface every second) is much greater than that in space. The combination of directionality and higher flux make the asher a more severe environment than space, but it can provide a qualitative indication of survivability since materials which survive in the asher also survive in LEO.

The atomic oxygen testing was performed in three different plasma ashers. The samples with the roll side out were placed in a separate asher for testing than those with the air side out because of observed contamination from the roll side of DuPont 93-1 that coated the polyimide Kapton HN witness coupon. All AOR roll position uniformity tests for a particular side were performed in the same asher. Exposure of additional mass loss coupons, optical, and SEM samples from sheet #3 of the roll were exposed in the third asher. All testing was performed with a polyimide Kapton witness coupon in the asher during testing. The mass loss of polyimide Kapton is well characterized in space and was used to correlate the different ashers as well as determine the effective atomic oxygen fluence (atoms striking during exposure/cm^2 of surface) in space that the asher exposure represented.

The AOR Kapton and polyimide Kapton witness coupons were dehydrated in a vacuum (30-50 mTorr) for at least 48 hours prior to the initial mass measurement of the sample and atomic oxygen exposure. This procedure was used to eliminate any errors in mass measurement due to water vapor from the atmosphere absorbing or desorbing from the polyimide. Although the effect of humidity on polyimide Kapton is quite large, AOR Kapton did not show any noticeable mass change due to humidity; however, it was dehydrated along with the polyimide Kapton so that both would be exposed to the same conditions. After atomic oxygen exposure, the Kapton was removed from vacuum and quickly weighed on a Sartorius microbalance to achieve an accurate mass value. The AOR was also weighed on the same balance.

Since three different ashers with glass racks supporting samples at two levels were used for sample exposure, it was important to determine the effect of the power level, intensity of the plasma, and the position in the asher on the atomic oxygen arrival flux. Since the plasma intensity is difficult to quantify, a solar cell connected to a current meter was placed against the asher glass to provide a relative intensity scale. Polyimide Kapton was used as a measure of the effective flux in the asher. Figure 1 contains a plot of the effective asher flux as a function of the power level meter reading. Each level indicated represents the multiple of 20 watts with 5 representing the full power of 100 watts according to the manufacturer. Test results indicate that the flux is independent of the power level for different tuned plasma intensities. Figure 2 indicates that the flux appears to be highly dependent on the intensity of the plasma and also shows its independence from the power level. As a result of these tests, the ashers were adjusted to roughly the same visual intensity during exposure of the AOR

Kapton. In each asher, the flux can also be dependent upon the position of the material in the asher. Flux is most likely highly dependent upon the amount of material placed in the asher since it changes the path of gas flow in the asher. Samples on a double rack fully loaded in the asher exhibit the flux arrivals shown in Figure 3. To determine the difference in arrival on the top and bottom of the samples, polyimide Kapton was used which had one side coated with silicon dioxide which could act as a barrier against atomic oxygen. The duration of the exposure was kept short in order to minimize any significant losses by undercutting of defects on the coated side. In general, the flux was more uniformly distributed on the bottom rack than on the top. On the bottom rack, the direction the Kapton faced did not seem to make a significant difference, however on the top rack, the Kapton facing up had a significantly larger flux. This is believed to be due to the proximity of the glass rack on the top level with respect to the gas inlet tube. The Kapton facing down had fluxes much closer to those on the bottom rack. Flux on the bottom rack appeared to decrease the farther the samples were from the roughing pump vent. Mass loss specimens were kept on the bottom rack for testing where possible and towards the back of the asher. Kapton witness coupons were placed in close proximity to the samples with a witness on each level so that flux variations and variations between ashers could be taken into account.

Durability Characterization

Durability to atomic oxygen was determined primarily through mass loss measurements and visual observation. Scanning electron microscopy using a JOEL 840 scanning electron microscope was used to document the visual changes occurring on the sample surface at different atomic oxygen fluence intervals. Total transmittance and reflectance measurements of the AOR Kapton representing different fluence intervals was taken with a Perkin Elmer Lambda 9 UV-VIS-NIR spectrophotometer with an integrating sphere attachment.

RESULTS AND DISCUSSION

Mass loss per area as a function of fluence was measured for AOR Kapton from each of the 5 sheets from the batch roll. Figure 4 contains the plots of this data for the air and roll sides. The data with the "*" by the number in the legend represents an adjacent piece from the same sheet which was included for improvement of test data reliability. The data indicates that the air and roll sides lose mass at very close to the same rate. The roll side may be slightly higher but is within the error of the mass measurement. The roll also shows a high degree of uniformity over the five sheets. The long term ashing test data in Figure 5 also agrees with that in Figure 4. Initially, the positional testing was to be used to determine uniformity of the roll only, with longer term ashing determining the durability. However, the AOR samples began to crack and split at a fluence of approximately $7x10^{21}$ atoms/cm^2 and fell apart completely at $9.5x10^{21}$ atoms/cm^2. One estimate for the total fluence that the SS Freedom solar array will encounter is $2x10^{22}$ atoms/cm^2 which is about twice the fluence experienced by the AOR when it structurally failed. The mass loss rate in comparison to Kapton is relatively constant for most of the exposure and is between 10 and 17 percent of that for unprotected Kapton HN. The AOR does provide an improvement over polyimide Kapton but still not enough to fulfill the SS Freedom life requirements.

Figure 6 contains a photograph of the optical samples that were exposed in the asher. Each sample represents a different atomic oxygen fluence level. The spots on the surface were believed to be caused by the remnants of a Si containing roll processing release agent which formed a thin film protective coating on the AOR Kapton. The unexposed sample has a barely visible spot of the release agent on its surface as well. The release agent coated areas offer limited protection due to the number of defects in the coating which increases with exposure. The samples which received roll side exposure were a slightly darker tan color overall in appearance with dark tan spots, while the air side was uniformly light tan with orange spots. The spots on the roll side behaved more like the overall AOR sample. In all other respects, both sides reacted the same. Eventually, the AOR begins to split and areas that were coated with release agent actually fall out as the AOR around them oxidizes through. The highest fluence sample in this photograph was too fragile to make an optical measurement on. The sample crumbled at the lower edge when trying to move it with tweezers. As exposure progressed, the once transparent surface became increasingly opaque as can be seen from the plot of transmittance as a function of wavelength at different fluence levels in Figure 7. The reflectance of the surface increased initially with fluence and then leveled off so that the net result was a slight increase in solar absorptance as shown

in Figure 8.

Scanning electron photomicrographs of the AOR Kapton as a function of fluence are shown in Figure 9. The AOR Kapton at a fluence of 1.75×10^{21} atoms/cm^2 (Figure 9a) shows two areas with release agent surrounded by AOR Kapton. Initially, there is some cracking of the AOR but the majority of the cracking is centered around the release agent coated areas. With increasing fluence, cracking of the AOR becomes widespread until finally at 9.48×10^{21} atoms/cm^2, the majority of the AOR Kapton has lifted off of the surface leaving only a thin layer of AOR Kapton sections clinging to the adhesive used to bond the two sheets together. Figure 10 contains closeups of the AOR Kapton and release agent coated areas. Overall cracking of the AOR appears to occur quickly since full cracking was observed at 5.14×10^{21} atoms/cm^2. This represented a crack length per unit area increase from approximately 50 cm/cm^2 to nearly 120 cm/cm^2. Cracking of the release agent appeared to progress more linearly. A closeup of the AOR Kapton shows that the protection is particulate in nature. The surface exposed at the maximum test fluence still has particles clinging to the adhesive in a few locations but the matrix material is noticeably absent.

CONCLUSIONS

The experimental AOR Kapton evaluated for atomic oxygen resistance was found to exhibit a mass loss between 10 and 17% that of unprotected Kapton HN in the plasma asher. This is a significant improvement over polyimide Kapton, however the material does degrade and eventually structurally fails between 7 and 10×10^{21} atoms/cm^2 with a random atomic oxygen arrival. In space, the arrival of atomic oxygen is more directed and sweeping than in the asher so that the particulate sites of protection may provide more shielding of the matrix material allowing it to survive longer. However, this material is unlikely to meet the SS Freedom array lifetime without a thin film protective coating on the surface. A metal oxide coating would greatly improve the life of this material and the AOR Kapton underneath would add a backup safety factor to the coating since it is more durable than standard polyimide Kapton. A metal oxide coated AOR Kapton array blanket may be a viable solar array backup material for Space Station Freedom.

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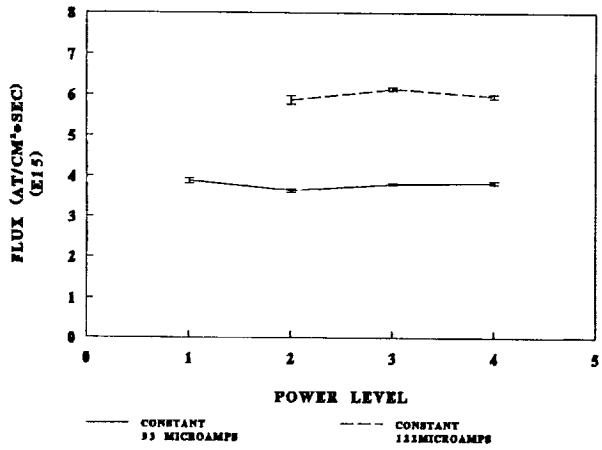


Figure 1 - Flux in the plasma asher as a function of the power level at constant plasma intensities.

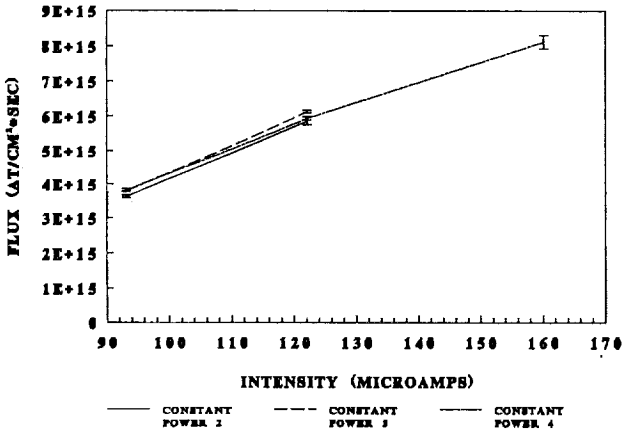
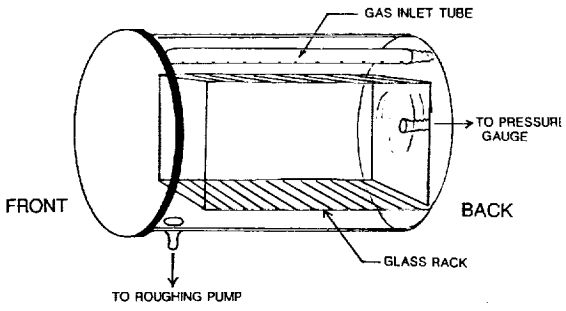
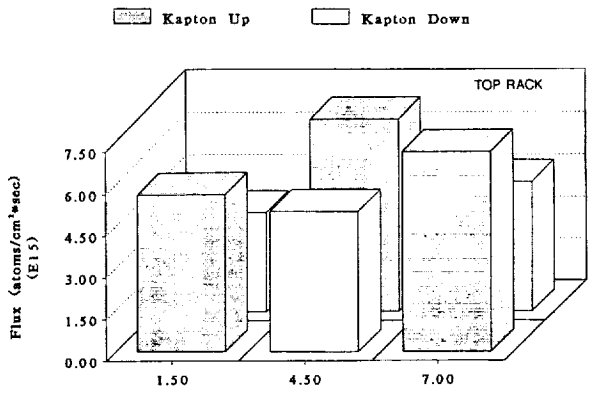


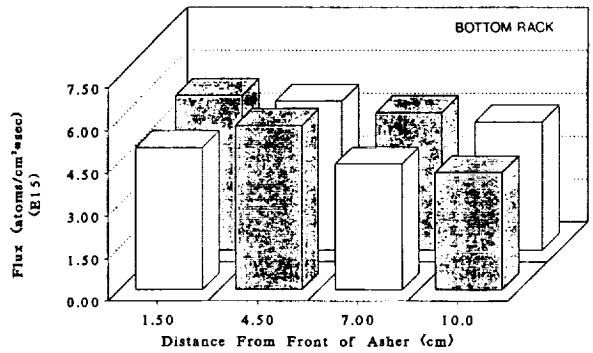
Figure 2 - Flux in the plasma asher as a function of plasma intensity at constant power levels.



ASHER GLASS CHAMBER

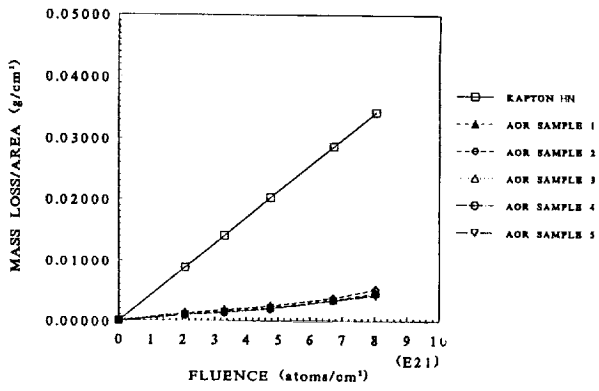


a. Asher top rack

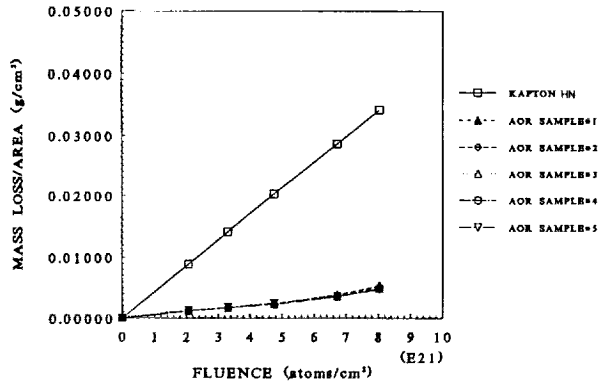


b. Asher bottom rack

Figure 3 - Flux as a function of position in the plasma asher.



a. Air side out



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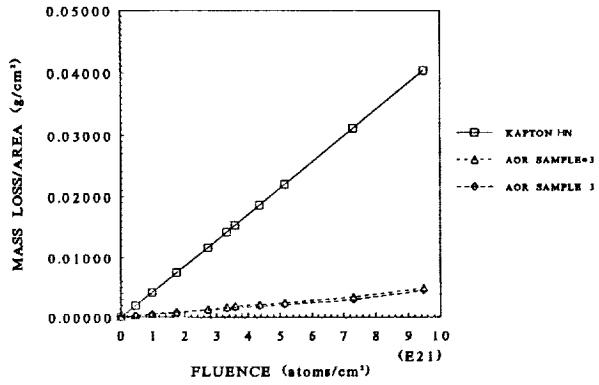
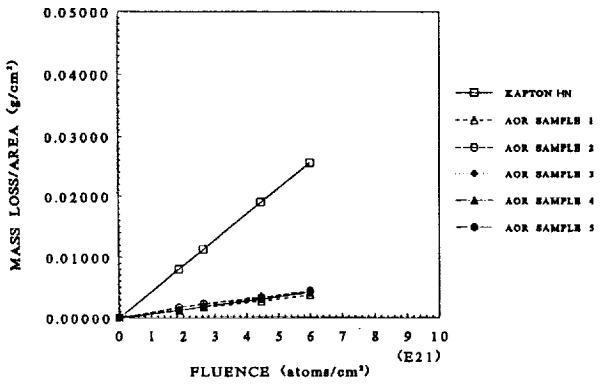
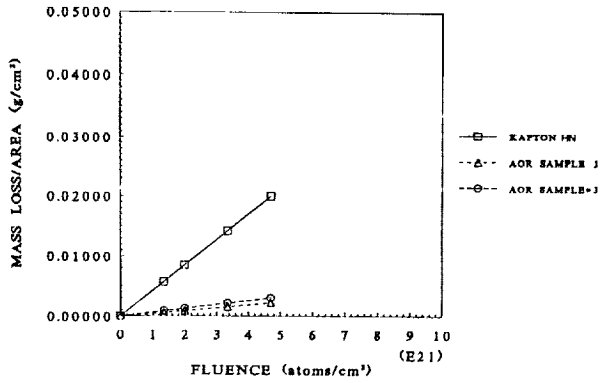


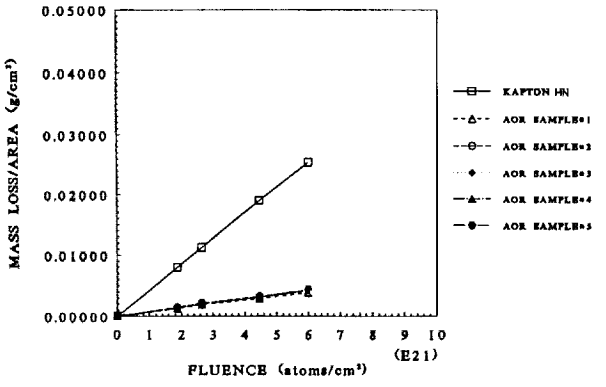
a. Air side out



c. Roll side out



b. Roll side out



d. Roll side out

Figure 4 - Mass loss per area as a function of atomic oxygen exposure for air and roll side samples from different sheets of Kapton AOR.

Figure 5 - Long term atomic oxygen exposure of AOR Kapton from sheet 3.

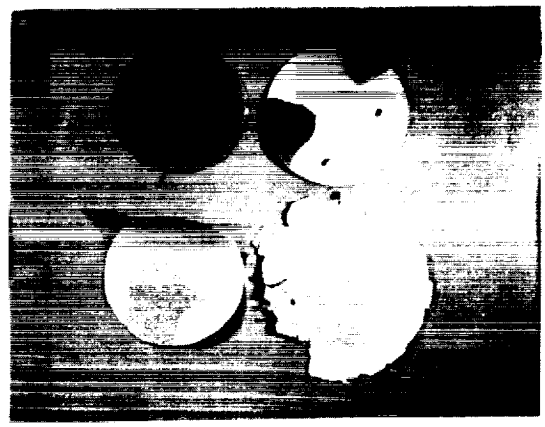


Figure 6 - Photograph of AOR Kapton optical samples exposed to various fluence levels; top left: 0 atoms/cm^2, top right: 1.75x10^{21} atoms/cm^2, bottom left: 5.14x10^{21} atoms/cm^2, and bottom right: 7.31x10^{21} atoms/cm^2.

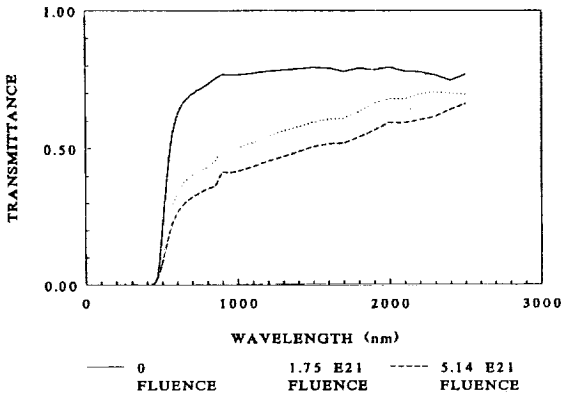


Figure 7 - Total transmittance of AOR Kapton from sheet 3 as a function of atomic oxygen exposure.

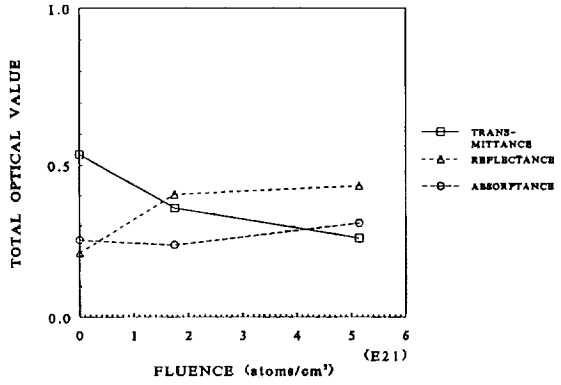
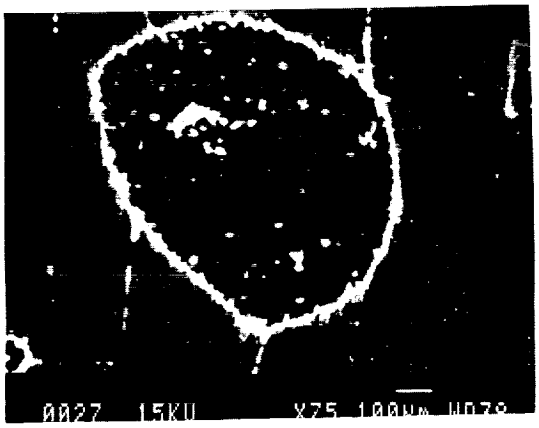


Figure 8 - Optical properties of AOR Kapton from sheet 3 as a function of atomic oxygen exposure.

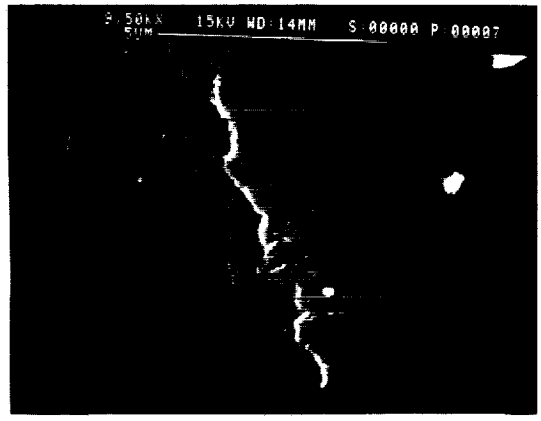


a. 1.75×10^{21} atoms/cm^2

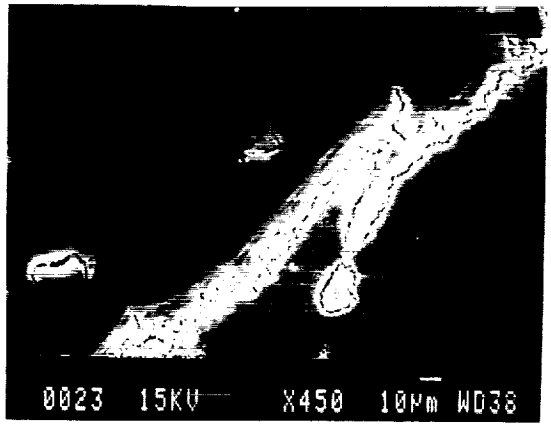
b. 5.14×10^{21} atoms/cm^2

c. 9.48×10^{21} atoms/cm^2

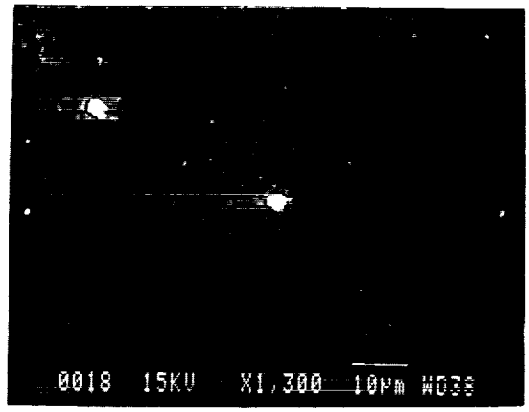
Figure 9 - Scanning electron photomicrographs of AOR Kapton from sheet 3 (air side out) as a function of atomic oxygen exposure.



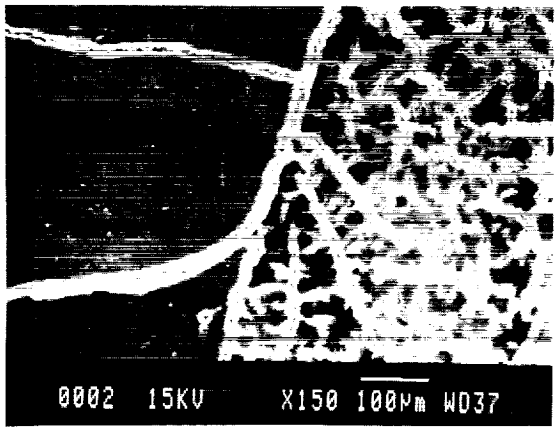
a. 0 atoms/cm^2



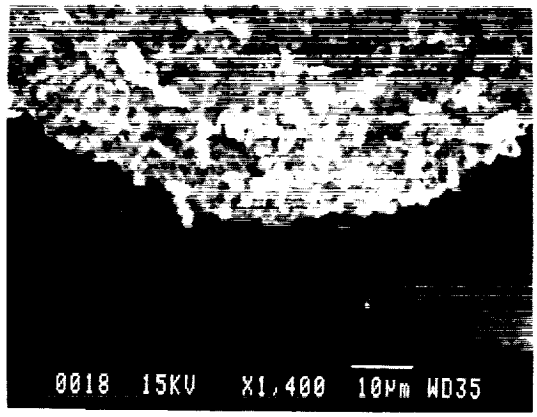
b. 1.75×10^{21} atoms/cm^2



a. 1.75×10^{21} atoms/cm^2

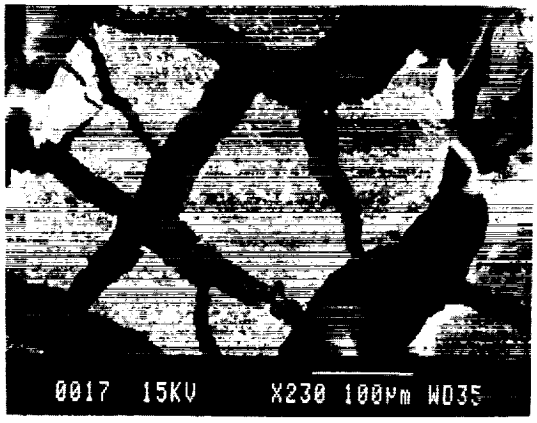


c. 5.14×10^{21} atoms/cm^2



b. 9.48×10^{21} atoms/cm^2

Figure 11 - Scanning electron photomicrographs of AOR Kapton from sheet 3 (air side out) showing particulate nature of the protection.



d. 9.48×10^{21} atoms/cm^2

Figure 10 - Scanning electron photomicrographs of AOR Kapton from sheet 3 (air side out) as a function of atomic oxygen exposure.