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THE USE OF PLASMA ASHERS AND MONTE CARLO MODELING FOR THE PROJECTION OF ATOMIC OXYGEN DURABILITY OF PROTECTED POLYMERS IN LOW EARTH ORBIT

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ABSTRACT

The results of ground laboratory and in-space exposure of polymeric materials to atomic oxygen has enabled the development of a Monte Carlo computational model which simulates the oxidation processes of both environments. The cost effective projection of long-term low-Earth-orbital durability of protected polymeric materials such as SiO_X-coated polyimide Kapton photovoltaic array blankets will require ground-based testing to assure power system reliability. Although silicon dioxide thin film protective coatings can greatly extend the useful life of polymeric materials in ground-based testing, the projection of in-space durability based on these results can be made more reliable through the use of modeling which simulates the mechanistic properties of atomic oxygen interaction, and replicates test results in both environments. Techniques to project long-term performance of protected materials, such as the Space Station Freedom solar array blankets, are developed based on ground laboratory experiments, in-space experiments, and computational modeling.

INTRODUCTION

Low-Earth-orbital (LEO) atomic oxygen interacts with exposed polymers, resulting in loss of material due to oxidation. Long-term LEO missions, such as Space Station Freedom, will require the use of materials which are inherently durable to atomic oxygen or are provided with protective coatings to prevent exposure of underlying materials which would be subject to oxidation. In-space evaluation of the durability of protected polymers is neither cost effective nor timely when considering requirements for high fluence atomic oxygen exposures such as required for Space Station Freedom. Evaluation of the atomic oxygen durability of protected polymers in LEO may be possible through a combination of ground laboratory experiments, in-space LEO exposure data, and computational modeling (ref. 1 and 2). Ground-based, accelerated atomic oxygen exposure of protected polymers in RF plasma ashers can provide valuable insight into the atomic oxygen undercutting processes and the ultimate fate of protected polymers such as those required for the Space Station Freedom photovoltaic array blanket. The projection of in-space durability based on ground laboratory testing requires an understanding of the differences between the two exposure environments and quantified modeling to enable credible durability projections. Recent LDEF results (ref. 2), coupled with Monte Carlo modeling, have provided great assistance in quantifying durability projections for Space Station Freedom (SSF) solar array blanket materials based on ground-based plasma asher testing. Although previous in-space durability projections have been made using asher data from single sheets of protected Kapton and Monte Carlo modeling, new asher data with laminated solar array blanket materials in a more flight-like configuration and results of undercutting of protected polymers from LDEF allow a fresh perspective on durability projections.

APPARATUS AND PROCEDURE

Experimental Data

Samples of 1300Å-thick SiO_X ($1.9<X<2.0$) protected Kapton H on both surfaces were laminated to an unprotected sheet of Kapton H by means of a silicone fiberglass scrimcloth. The SiO_X protective coatings were magnetron sputter deposited by Sheldahl, Inc. and laminated by McGhan-NuSil, Inc. Kapton polyimide was provided by DuPont De Nemours. Two identical pieces of the flexible laminant (each constitute the SSF solar array blanket) were then clad to each other by bonding with an acrylic adhesive, as shown in figure 1, to allow atomic oxygen durability evaluation of the protected side of the laminant in an RF plasma asher. The clad laminant sample was exposed to atomic oxygen by laying the sample on a glass rack in an SPI Plasma Prep II plasma asher, with air as the working gas. Periodic documentation of the mass of the test sample, as well as the Kapton HN witness coupon ashed with the sample, was made to calculate mass loss and Kapton atomic oxygen effective fluence. The assumed erosion yield for Kapton H and Kapton HN was 3×10^{-24} cm^3/atom (ref. 3).

To assess the effects of atomic oxygen on the fiberglass scrim cloth in a silicone matrix, a sample of just this portion of the solar array laminant was also exposed in a plasma asher. This sample was exposed to atomic oxygen on both sides at the same time by also laying it on a glass rack in the plasma asher.

LDEF data from reference 2 were used to estimate atomic oxygen reaction probabilities for thermally accommodated atomic oxygen in undercut cavities beneath defects in protective coatings. The protected polymers exposed on LDEF consisted of a T-300 carbon fiber 934 epoxy composite sample, which was coated with 400Å of aluminum over 800Å of chromium. The sample was exposed to an atomic oxygen fluence of 8.72×10^{21} atoms/cm^2 on row 9 of the LDEF spacecraft (ref. 4).

Procedure

Atomic oxygen erosion modeling relations derived from reference 2 were used as a basis to convert plasma asher mass loss data from solar array blanket laminant specimens (shown in figure 1), along with Monte Carlo modeling to predict in-space mass loss. The Monte Carlo computational model is designed to replicate the atomic oxygen interaction with SiO_X-protected polyimide Kapton at defect sites in the protective coating. Kapton is modeled as an array of square cells which can be removed (oxidized) by atomic oxygen which interacts in accordance with a prescribed series of assumptions listed below:

1. The model is two-dimensional with atomic oxygen trajectories confined to a plane which simulates a crack or scratch defect in the protective coating.
2. Reaction probability of atomic oxygen with Kapton is proportional to:
   a. $e^{[-0.38\ eV/energy,\ eV]}$ (from reference 5) or as determined by LDEF data (to be discussed).
   b. the square root of the cosine of the angle between the surface normal and the arrival direction (ref. 2).
3. Reaction probability at normal incidence is equal to:
   a. 0.1380 for space (first impact), (ref. 2).
   b. 7.7×10^{-6} (based on thermal accommodation to 300K) or as determined by LDEF data (to be discussed) for space ($\geq$ second impact).
   c. Four times the second or later impact reaction probability for first impact in plasma ashers, (ref. 2).
   d. 7.7×10^{-6} (based on thermal accommodation to 300K) or as determined by LDEF data (to be discussed) for plasma ashers ($\geq$ second impact).
4. Atomic oxygen which thermally accommodates (i.e. leaves surfaces with a kinetic temperature equal to that of the surface) upon first impact with surfaces, results in a reduced reaction probability.
5. Atomic oxygen does not react with protective coatings, nor recombines and remains atomic after impacting protective coatings.
6. Unreacted atomic oxygen leaves surfaces in a cosine ejection distribution if it is thermally accommodated, and scatters off surfaces almost specularly if it is nonaccommodated (elastic scattering).
7. Arrival direction of space atomic oxygen is angularly distributed because of the high temperature Maxwellian distribution.
8. Arrival direction of ground laboratory plasma asher atomic oxygen is isotropically distributed.

The first step in the procedure is to establish the relationship and variables needing quantification to allow in-space performance to be predicted based on plasma asher testing.

The Kapton mass loss per unit area of protected Kapton in a plasma asher relationship to the mass loss per unit area in space as shown in equation 1, as derived in reference 1.

$$\frac{M_S}{F_S} = \frac{M_A}{F_E} \frac{Y_A}{Y_S} \qquad (1)$$

where:

F_E = Effective atomic oxygen fluence in RF plasma asher based on Kapton erosion, atoms/cm^2.

F_S = Atomic oxygen fluence in space, atoms/cm^2.

M_A = Kapton mass loss per unit area under SiO_X coating defects in RF plasma asher, gm/cm^2.

M_S = Kapton mass loss per unit area under SiO_X coating defects in sweeping space ram exposure, gm/cm^2.

Y_A = Monte Carlo predicted Kapton thickness loss for uncoated Kapton in an asher environment after the same fluence used to measure both Y_A and Y_S, cell length units.

Y_S = Monte Carlo predicted Kapton thickness loss for uncoated Kapton in a sweeping space ram environment, cell length units.

The actual fluence in a plasma asher greatly exceeds the effective fluence, F_E, because of the low erosion yield of thermal (0.04 eV) atoms compared to LEO ram atoms (4.5 eV).

Equation (1) assumes well developed undercutting where the undercut area is much greater than the protective coating defect area. Thus, additional undercutting via oxidation which would occur in an asher is identical to that which would occur in space for the same fluence for both pin window and crack defects. This is thought to be true because undercutting should become dominated by the thermally accommodated reaction probabilities which are the same for ashers and in space. The values of Y_A and Y_S for Monte Carlo predicted Kapton thickness loss for uncoated Kapton in an asher and sweeping space ram environment respectively are highly dependent upon the modeling assumptions which were determined from LDEF results.

The atomic oxygen reaction probability of thermally accommodated atomic oxygen is needed to predict the ratio of surface recession in a plasma asher, Y_A, and that which would occur in-space, Y_S, sweeping ram for atomic oxygen attack for unprotected polyimide Kapton using Monte Carlo modeling techniques. The results of LDEF atomic oxygen undercutting data (ref. 2) and ground laboratory thermal energy atomic oxygen experiments (ref. 5) are used in conjunction with Monte Carlo modeling of atomic oxygen undercutting erosion to quantify these parameters.

RESULTS AND DISCUSSION

The results of plasma ashing of the clad solar array blanket laminant indicated that atomic oxygen was able to attack, not only the most external Kapton layers, but the inner layers as well. The light areas on the sample shown in figure 2 are areas where no Kapton remains after ashing to an effective fluence of 3.98 x 10^{22} atoms/cm^2. Although some oxidation from the edges of the sample can occur, it is doubtful that a degree of loss of Kapton in the inner layers could be attributed to this effect alone. It is more probable that the defects in both the top and the bottom surface SiO_X layers, as well as bubbles in the fiberglass scrim cloth silicone matrix material allowed oxidation of the innermost Kapton layers. Because the innermost Kapton layers were clad with acrylic adhesive, which is also subject to oxidation, it is probable that regions of the acrylic adhesive were also oxidized. Figure 3 is a plot of the mass of the sample which is shown in both figure 1 and figure 2 as a function of effective fluence in the plasma asher. The plot shown in figure 3 represents 29 weight measurements at approximately equal fluence intervals. Based on figure 3, the average mass loss per area per effective fluence is 1.54 x 10^{-25} grams/atom. It is this quantity that will be used in equation 1 for the M_A/F_E term. Because erosion of both Kapton and the acrylic adhesive was possible, correction of this M_A/F_E quantity is needed if the erosion yield and density of the acrylic adhesive are significantly different than that of Kapton. The erosion yield of acrylic (polymethylmethacrylate) has been measured to be 3.1 x 10^{-24} cm^3/atom for LEO atomic oxygen (ref. 6), which is quite comparable to that of Kapton (3 x 10^{-24} cm^3/atom). The density of Kapton and acrylic adhesive are also sufficiently similar that one can consider erosion of the acrylic to be equivalent to erosion of the Kapton for the purposes of this paper. The largest uncertainty is the erosion yield of the acrylic at thermal energies compared to Kapton. Another consideration in the quantity M_A/F_E is the change in mass per unit area associated with the silicone matrix for the fiberglass scrim cloth in the solar array blanket laminant. As a result of defects in the SiO_X protective coating, as well as bubbles in the silicone matrix, atomic oxygen was available to oxidize hydrocarbon pendant groups on the Si-O silicone polymer backbone. However, weight loss of the silicone due to oxidation of hydrocarbon pendant groups is counteracted by weight gain of the Si-O backbone through oxygen attachment, causing silicone-to-silicate transformations (refs. 7-8). The net result of the weight loss and weight gain processes is a very slight gain with effective fluence. Figure 4 is a plot of the mass per unit area of fiberglass scrim cloth in a silicone matrix as a function of effective atomic oxygen fluence in the plasma asher. As can be seen in figure 4, even though oxidation of the silicone is occurring, very little net mass change occurs. For simplicity of computation and because very little mass change of the silicone occurs, all mass loss from experimental data in this paper will be assumed to be Kapton mass loss.

As mentioned in the procedures section of this paper, Equation 1 assumes that for well-developed undercutting, additional undercutting oxidation occurs at the same rate for both ashers and sweeping space ram. Figure 5 tests these assumptions by comparing Monte Carlo predicted undercutting for scratch defects in a plasma asher and sweeping space ram environments where full thermal accommodation is assumed upon first atomic oxygen impact. As can be seen from figure 5, although the initial growth of the undercut cavities appear to be dominated by the initial impact reaction probability, the rates of growth of the cavities with atomic oxygen fluence quickly become identical and independent of initial impact reaction probability after the undercutting has exposed the bottom SiO_X protective coating. Thus, except for small initial differences in the undercut cavity associated with the rapid development of undercutting in space due to its higher initial reaction probability, the rate of mature undercutting growth with atomic oxygen fluence does appear to be identical for sweeping space and plasma asher environments, as one would expect. A similar reasoning process can be made for pin window defects in both environments, thus Equation 1 should be valid for either or a mix of types of defects. The reaction probability for second or later impacts of 0.00134 shown in figure

5 is based on the results of interpolation of Monte Carlo predictions to match LDEF undercutting results based on reference 2. These results suggest thermally accommodated reaction probabilities based on LDEF results, which are lower by a factor of 7.3 than those previously predicted using reaction probabilities proportional to the 0.68 power of the oxygen kinetic energy.

The Y_A/Y_S term in Equation 1 is highly dependent upon the choice of initial atomic oxygen reaction probabilities because very few scattered atomic oxygen atoms have view factors to allow subsequent impacts with Kapton. Figure 6 compares the Monte Carlo predicted atomic oxygen undercutting of a wide defect to simulate the erosion that would occur for unprotected Kapton in both space and plasma asher environments for the same initial and subsequent impact reaction probabilities as were used in figure 5. Because Y_A/Y_S are the ratio of the Monte Carlo predicted recessions for the same actual fluence, the ratio of the recessions shown in figures 6a and 6b must be corrected to predict what they would be if they had the same fluence. The result of this correction to the profiles shown in figure 6a and 6b is $Y_A/Y_S = 0.048$. Thus, substituting the observed plasma asher mass loss data and the Monte Carlo modeling data in Equation 1 results in a projected Kapton mass loss per area per fluence in a sweeping space ram environment of 7.4×10^{-27} grams/atom as shown in Table 1. This result is based on full thermal accommodation of atomic oxygen upon its first impact with Kapton or SiO_X. In addition, a reaction probability of 1.34×10^{-3} is assumed for thermally accommodated atomic oxygen reacting with Kapton based on Monte Carlo modeling to match observed LDEF undercutting results (ref. 2). Thus, based on these assumptions, the projected Kapton mass loss per area per fluence in a sweeping space ram environment would be 0.048 of the amount which is measured in a plasma asher environment based on effective fluence. Based on the amount of Kapton initially in the Space Station Freedom photovoltaic array blanket laminant, as shown in figure 1, and a Kapton density of 1.42 grams/cm^3, the fraction of Kapton which would be remaining in an asher environment at the end of life (5.4×10^{22} atoms/cm^2) would be -0.153. Thus, the rate of mass loss of Kapton in the blanket laminant in a plasma asher environment is more than sufficiently high to result in the complete oxidation of all the Kapton in the laminant as shown in Table 1. However, based on the conversion factors to project rates of loss in a sweeping space ram environment, 94% of the solar array blanket Kapton would be remaining, as shown in Table 1.

Observed LDEF undercutting results can be made to agree with Monte Carlo modeling of undercutting by assuming full thermal accommodation of atomic oxygen upon its first impact, and using the Monte Carlo model to fit the observed undercut cavity by adjustment of the reaction probability of thermally accommodated atomic oxygen, as was the case for the previously described projections. One can assume that the reaction probability of thermally accommodated atomic oxygen bears an Arrhenius relation with the atomic oxygen energy as described in reference 4 with an activation energy of 0.38 eV and solve for the accommodation fraction, again using Monte Carlo modeling to fit the LDEF undercut cavity profiles. Using an activation energy of 0.38 eV, and assuming 300 Kelvin atoms, a reaction probability for thermally accommodated atomic oxygen of 7.7×10^{-6} is predicted. Based on Monte Carlo modeling to fit the observed LDEF undercut profile (ref. 2), an accommodation fraction of 0.9 is predicted.

An accommodation fraction of 0.9 for the model used means that nine out of ten atoms fully thermally accommodate upon first impact with Kapton or SiO_X, and that one out of ten atoms leaves those surfaces with the same energy that they initially arrive at, and with a near specular ejection angle. This process would continue for additional impact until all the atomic oxygen has become fully thermally accommodated. Based on this set of assumptions, a projected Kapton mass loss per area per fluence of 4.3 x 10^{-29} grams/atom is predicted for a sweeping space ram environment (Table 1). Because the reaction probability for thermally accommodated atomic oxygen is much lower (7.7 x 10^{-6} compared to 1.34 x 10^{-3}) for this set of assumptions, the ratio of Monte Carlo predicted erosion rates of unprotected Kapton in plasma asher and space environments, Y_A/Y_S, is equal to 2.8 x 10^{-4}. Because of the lower reaction probability of thermally accommodated atomic oxygen which dominates the erosion processes, the relative Kapton mass loss per area per fluence in a sweeping space ram environment is only 2.8 x 10^{-4} of that which would be observed in a plasma asher environment as shown in Table 1. The fraction of initial Kapton remaining in the Space Station Freedom solar array blanket laminant at end of life would be 99.97% of the initial mass. Thus a negligible mass loss is predicted in spite of the fact that in the plasma asher more than all the Kapton would be lost for the same effective fluence. For both columns in Table 1, initial impact atomic oxygen reaction probabilities are assumed to be four times that of thermally accommodated reaction probabilities as a result of the presence of excited state species which are more reactive. The factor of four was determined by fitting Monte Carlo results to match observed plasma asher undercut profiles as described in reference 9. Although it is not clear what fraction of atomic oxygen thermally accommodates upon first impact, and what the reaction probability of thermally accommodated atomic oxygen actually is, one would be perhaps optimistic to choose the lowest thermally accommodated reaction probabilities without good cause. Based on the results shown in Table 1, it appears that observed Space Station Freedom photovoltaic array blanket laminant will lose mass at a very acceptable rate (only 4.83% that observed in plasma ashers) in a sweeping space ram environment. Clarification or verification of the previous or other durability projections would be greatly assisted through experiments which are able to quantify erosion yields and reaction probabilities of thermally accommodated atomic oxygen.

CONCLUSION

The results of observed LDEF atomic oxygen undercutting of protected polymers are used in conjunction with Monte Carlo modeling of both plasma asher and sweeping space ram environments to project the relationship between Kapton mass loss in plasma ashers to Kapton mass loss in a sweeping space ram environment. Two models were analyzed which replicate observed LDEF undercutting geometries. The first model, based on 100% accommodation of atomic oxygen upon first impact required a reaction probability for thermally accommodated atomic oxygen of 1.34 x 10^{-3}. This model predicts Kapton mass loss per area per fluence in space equal to 0.0483 that observed in a plasma asher environment. This model also predicts that the Space Station Freedom photovoltaic blanket laminant at end of life will have 94.4% of its Kapton remaining (5.4 x 10^{22} atoms/cm^2 fluence). A second model was based on selection of a thermally accommodated atomic oxygen reaction probability of 7.7 x 10^{-6} based on an Arrhenius erosion yield relationship with an activation energy of 0.38 eV. This model required an accommodation fraction of 0.9 to replicate observed LDEF undercutting results. The projected sweeping space ram mass loss rates were two orders of magnitude lower than that for the first case, predicting more than 99% of the Kapton remaining in the Space Station Freedom photovoltaic array blanket at end of life.

Although the results are highly encouraging, they should be regarded with cautious optimism until more definitive measurement of atomic oxygen accommodation fraction and erosion yield of thermally accommodated atomic oxygen can be made.

REFERENCES

1. B.A. Banks, S.K. Rutledge, and L. Gebauer, "SiO_x Coatings for Atomic Oxygen Protection of Polyimide Kapton in Low Earth Orbit," AIAA Paper No. 92-2151, paper presented at the Coatings Technologies for Aerospace Systems Materials Specialist Conference, Dallas, Texas, April 16-17, 1992.

2. B.A. Banks, K.K. de Groh, B.M. Auer, L. Gebauer, and J.L. Edwards, "Monte Carlo Modeling of Atomic Oxygen Attack of Polymers with Protective Coatings on LDEF," paper presented at the 2nd LDEF Post-Retrieval Symposium (NASA Conference Publication in Press), San Diego, California, June 1-5, 1992.

3. B.A. Banks, S.K. Rutledge, and J.A. Brady, "The NASA Atomic Oxygen Effects Test Program," Proceedings of the 15th Space Simulation Conference, Williamsburg, Virginia, October 31-November 3, 1988.

4. R.J. Bourassa and J.R. Gillis, "Atomic Oxygen Exposure of LDEF Experiment Trays," NASA CR-189627, Boeing Defense and Space Group, May, 1992.

5. S.R. Koontz, K. Albyn, and L.J. Leger, "Atomic Oxygen Testing with Thermal Atom Systems: A Critical Evaluation," Journal of Spacecraft and Rockets, Vol. 28, No. 3, May-June, 1991.

6. B.A. Banks and S.K. Rutledge, "Low Earth Orbital Atomic Oxygen Simulation for Materials Durability Evaluation," Proceedings of the Fourth European Symposium on Spacecraft Materials in a Space Environment, CERT, Toulouse, France, September 6-9, 1988.

7. A.D. Butherus, T.W. Hou, C.J. Mogab, and H. Schonhorn, "O_2 Plasma-Converted Spin-On-Glass for Planarization," Journal of Vacuum Science and Technology, Vol. 3, No. 5, September-October, 1985.

8. B.G. Bagley, W.E. Quinn, C.J. Mogab, and M.J. Vasile, "The Effect of Reactor Configuration on the Oxygen Plasma Conversion of an Organosilicone to SiO_2," Materials Letters, Vol. 4, No. 3, April, 1986.

9. B.A. Banks, B.M. Auer, S.K. Rutledge, and C.M. Hill, "Atomic Oxygen Interaction with Solar Array Blankets at Protective Coating Defect Sites," Proceedings of The Fourth Annual Workshop on Space Operations, Automation, and Robotics (SOAR '90), sponsored by the U.S. Air Force, National Aeronautics and Space Administration, and Wright State University, Albuquerque, NM, June 26-29, 1990.

TABLE I: Projection of In-Space Durability of SSF Photovoltaic Blanket Laminate Based on Plasma Asher Testing

		Environment		
		Measured in Plasma Asher	Projected in Space Sweeping Ram Based on:	
			LDEF and full accommodation $P_R = 1.34 \times 10^{-3}$ $P_A = 1$	LDEF, Activation Energy = 0.38, and partial accommodation $P_R = 7.7 \times 10^{-6}$ $P_A = 0.9$
Mass Loss / (Area)(Fluence)	Relative Comparison	1	0.048	2.8×10^{-4}
	grams/atom	1.54×10^{-25}	7.4×10^{-27}	4.3×10^{-29}
Fraction of initial Kapton remaining in SSF photovoltaic blanket laminate at End-of-Life fluence (5.4×10^{22} atoms/cm^2)		-0.153	0.94	0.9997

P_R = Probability of thermally accommodated atomic oxygen reacting with Kapton upon each impact.

P_A = Probability of energetic atomic oxygen atoms thermally accommodating upon each impact.

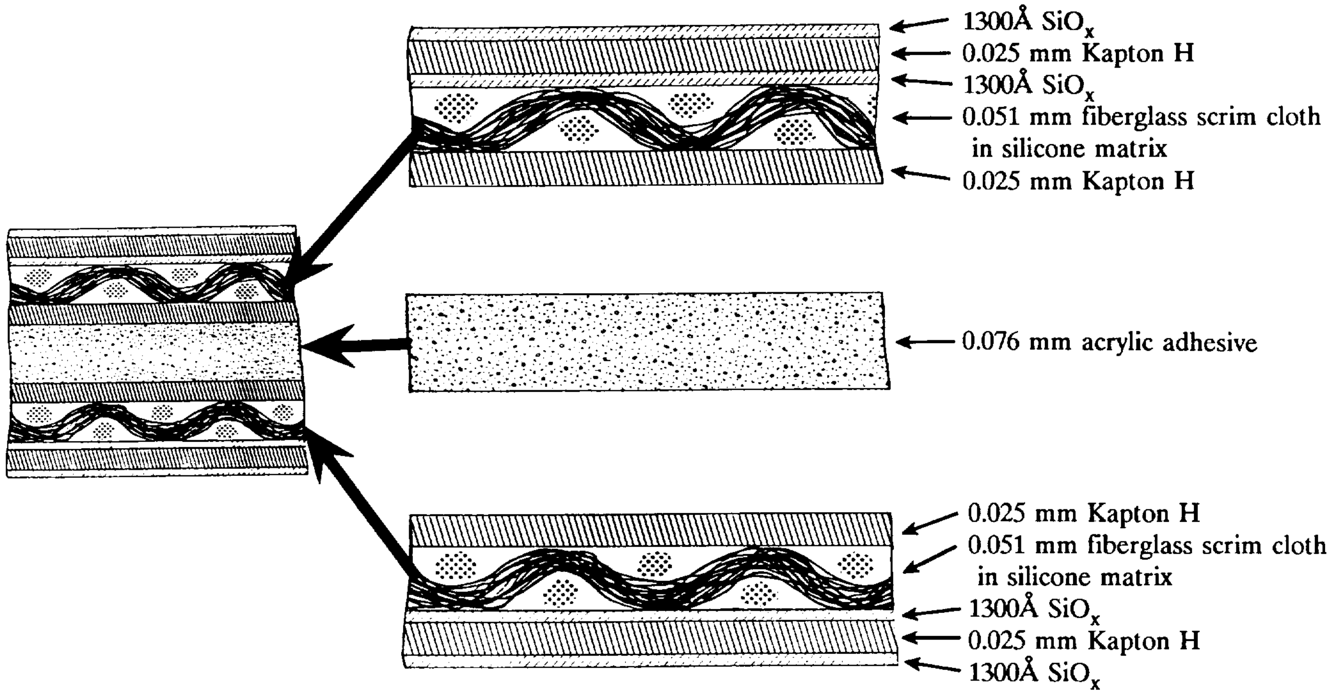


Figure 1. - Configuration of flexible solar array laminant used for atomic oxygen durability evaluation in an RF plasma asher.

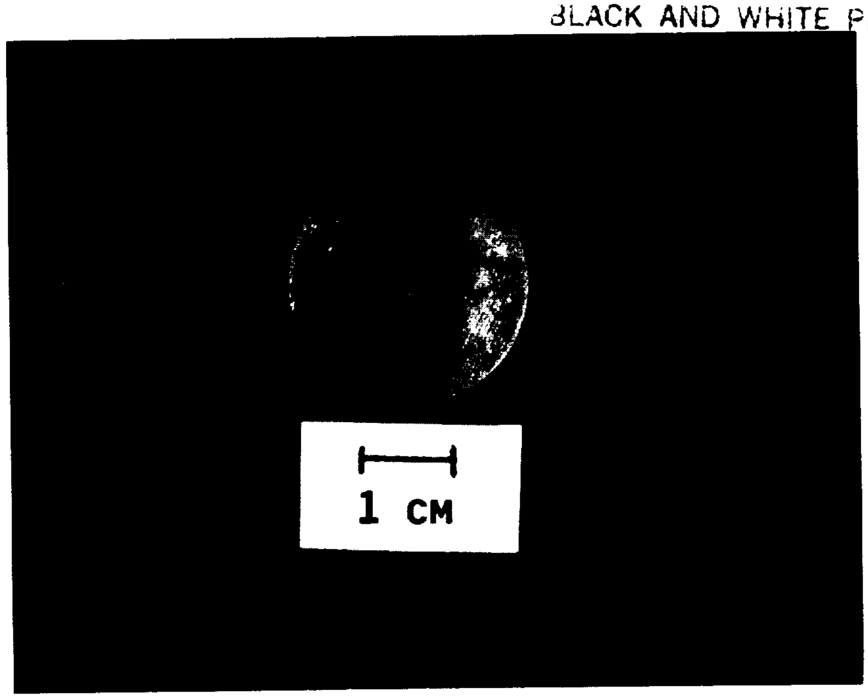


Figure 2. - Photograph of a clad flexible solar array laminant sample after atomic oxygen exposure in a plasma asher to an effective fluence of 3.98×10^{22} atoms/cm^2.

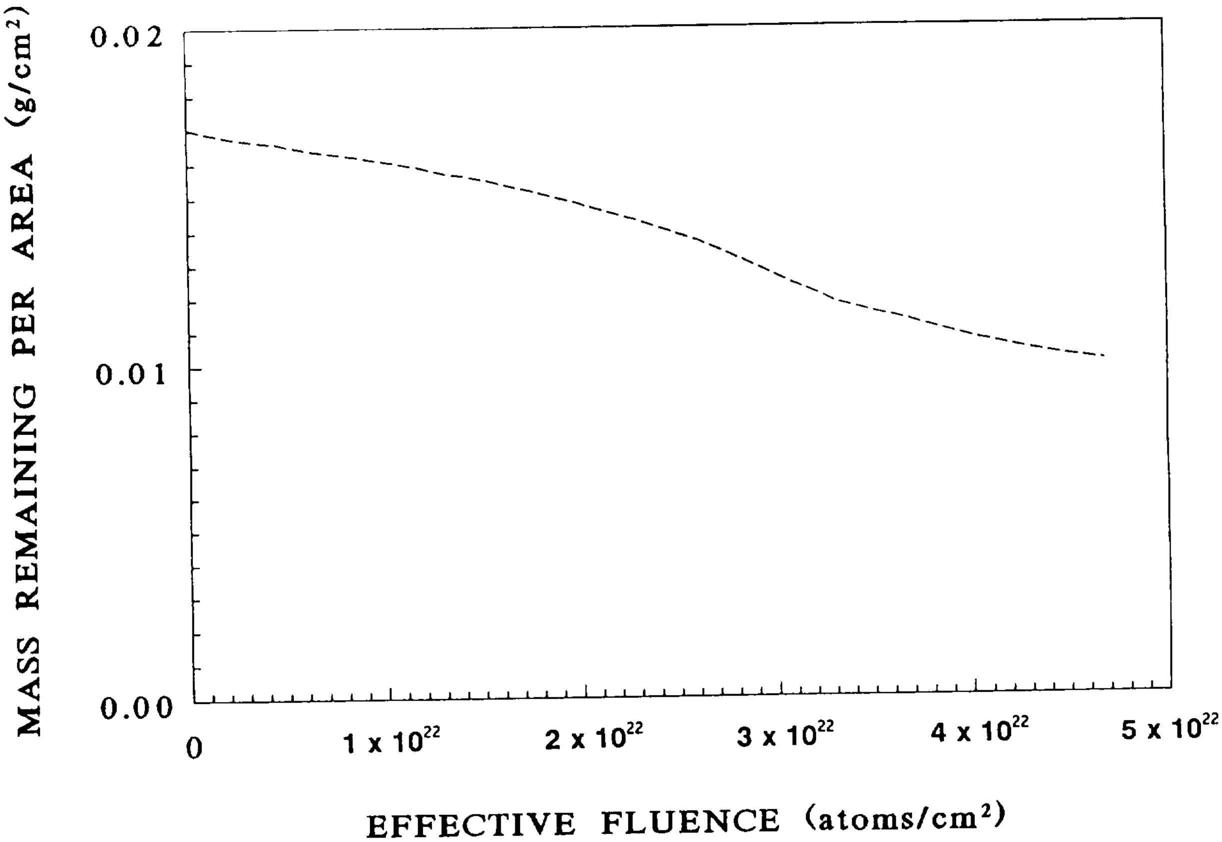


Figure 3. - Mass per unit area of clad, flexible laminant sample as a function of atomic oxygen effective fluence in a plasma asher. Based on figure 2, the average mass loss per unit area per effective fluence is 1.54×10^{-25} grams/atom.

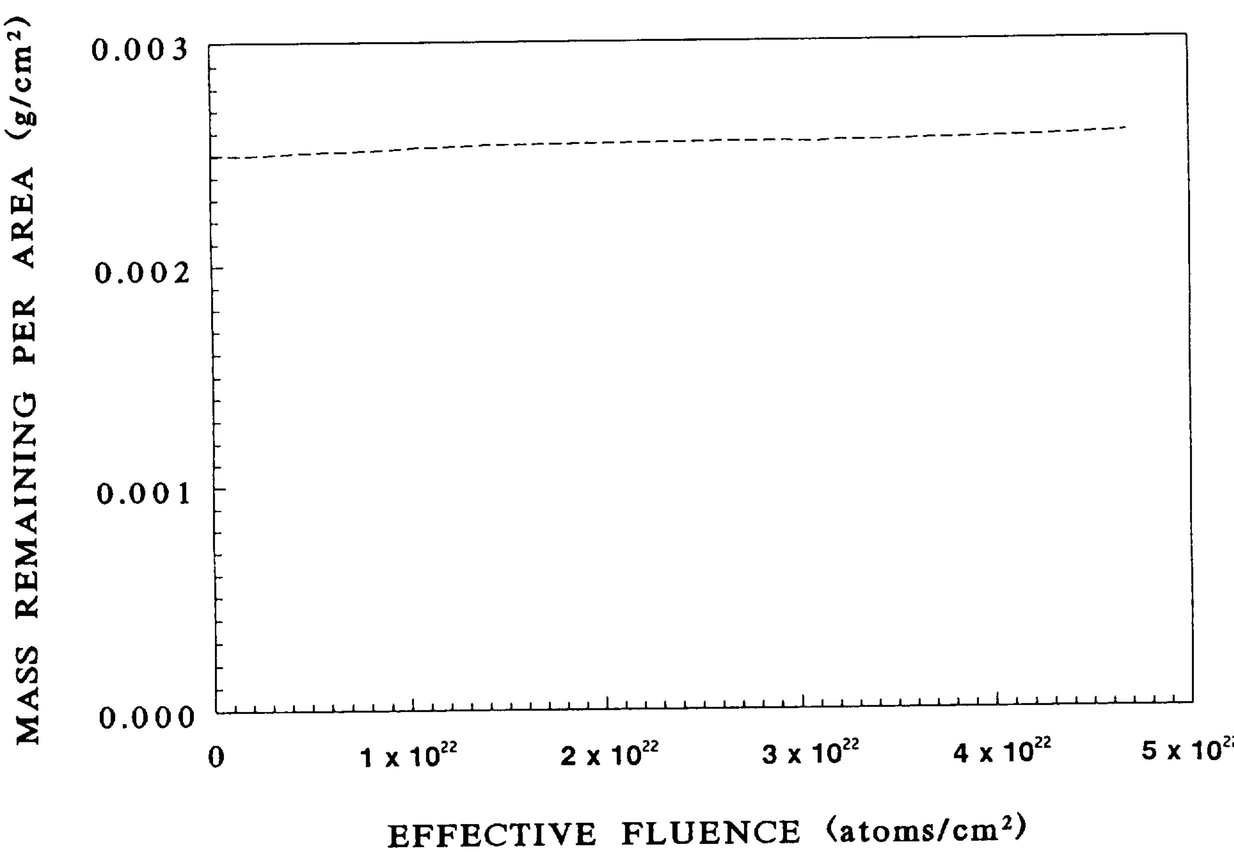


Figure 4. - Mass per unit area of fiberglass scrim cloth in a silicone matrix dependence upon effective atomic oxygen fluence.

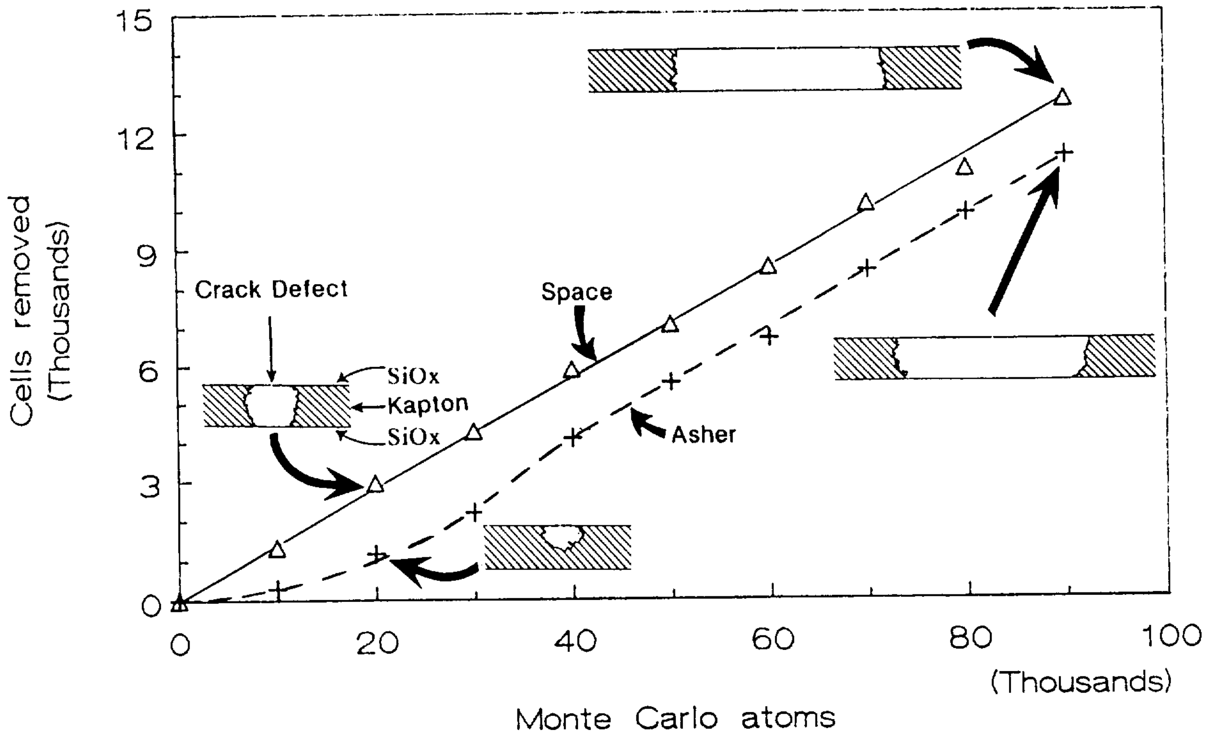
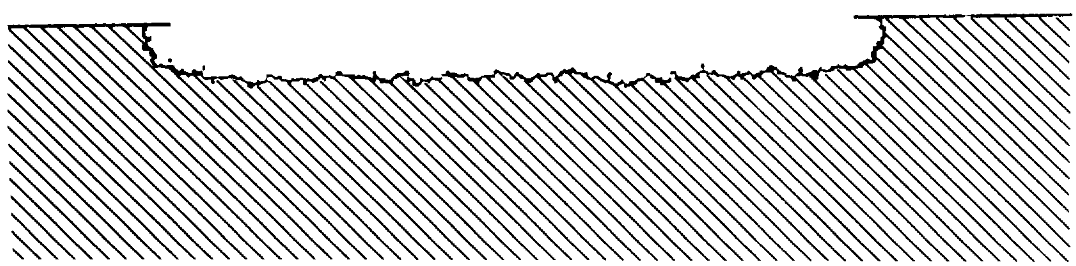
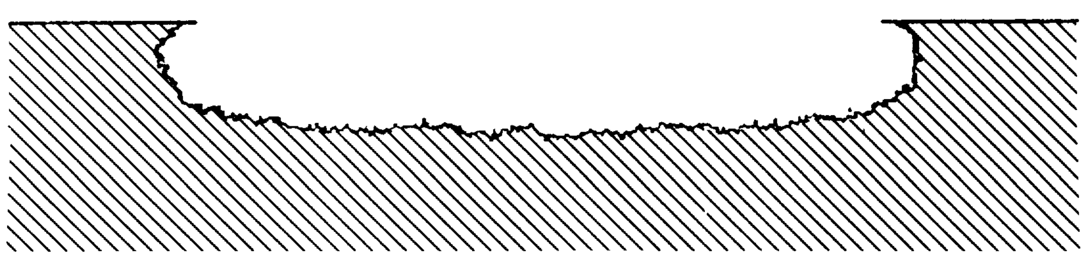


Figure 5. - Monte Carlo model predicted atomic oxygen undercutting at scratch defect sites in Kapton protected on both sides by SiO_X based on initial impact reaction probabilities of 0.138 in space, and 0.00536 in plasma ashers; and second or later impact reaction probabilities of 0.00134 for both environments.



6a. - In plasma asher environment after 2,200,000 atoms arrival.



6b. - In sweeping space ram environment after 200,000 atoms arrival.

Figure 6. - Monte Carlo model predicted atomic oxygen undercutting for wide defects in Kapton protected on its exposed surface using the identical assumptions as shown in figure 5. The defect shown is 400 Monte Carlo model cell units wide.