NASA Technical Memorandum 103711

Low Earth Orbital Atomic Oxygen and Ultraviolet Radiation Effects on Polymers

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February 1991

NASA

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ABSTRACT

Because atomic oxygen and solar ultraviolet radiation present in the low earth orbital (LEO) environment can alter the chemistry of polymers resulting in degradation, their effects and mechanisms of degradation must be determined in order to determine the long-term durability of polymeric surfaces to be exposed on missions such as Space Station Freedom (SSF). The effects of atomic oxygen on polymers which contain protective coatings must also be explored, since unique damage mechanisms can occur in areas where the protective coating has failed. Mechanisms can be determined by utilizing results from previous LEO missions, by performing ground-based LEO simulation tests and analysis, and by carrying out focussed space experiments. A survey is presented of the interactions and possible damage mechanisms for environmental atomic oxygen and ultraviolet radiation exposure of polymers commonly used in LEO.

INTRODUCTION

Many polymeric materials degrade in low earth orbit (LEO) due to the damaging environmental effects of atomic oxygen (AO), solar ultraviolet (UV) radiation, temperature cycling and micrometeoroid/debris impacts. Of these effects, atomic oxygen and ultraviolet radiation cause the most damage to the chemistry of polymeric surfaces and, therefore, have important implications on the durability of these materials.

It is necessary to have an understanding of the mechanisms of damage to polymers due to AO and UV in order to predict their long-term durability, since materials used on LEO missions such as Space Station Freedom (SSF) are required to be functional for between 15 and 30 years. Some speculations as to the damage mechanisms can be made based on results from previous LEO missions such as shuttle flights and the Long-Duration Exposure Facility (LDEF) experiments and ground-based LEO simulation tests and analysis. To further define the damage mechanisms, focussed space experiments and ground based tests should be performed utilizing the speculations from these previous tests.

Because of the reactivity of organic polymers to atomic oxygen in LEO, protective coatings are often required to minimize oxidation of polymers and to prevent them from becoming a source of contamination to other surfaces. For polymer/coating systems, it is necessary to explore the mechanisms of damage to the underlying polymer in areas where the protective coating has failed in order to predict lifetime of the component.

Polymers which are commonly considered for use on LEO missions include Kapton (polyimide) and FEP Teflon (fluorinated ethylene propylene). These will be focussed on in this paper. Kapton is used as a structural material for solar

array blankets because of its mechanical strength and suitable electrical properties. Teflon with a deposited silver backing possesses a high thermal emittance and a low solar absorptance which are desirable for thermal control materials.

LEO ENVIRONMENTAL DAMAGE TO POLYMERS

Atomic Oxygen Effects

Atomic oxygen is the most prevalent chemical species present in low earth orbit at anticipated SSF altitudes between 300 and 500 km (150-270 nautical miles). Atomic oxygen is formed by molecular bond breakage of O_2 by solar photons at wavelengths below $0.243\mu m$ [1]. Surfaces which face the direction of travel of the spacecraft (the ram direction) are impacted with a high flux of atomic oxygen (approximately 10^{14} - 10^{15} atoms/cm^2s) at collision energies of approximately 4.5eV. A result of the impact between atomic oxygen and an organic polymer surface is fragmentation of the high molecular weight polymer chains which leads to formation of a volatile condensible material (VCM) which could deposit onto nearby surfaces resulting in contamination [2]. For example, oxidation products of silicones have been shown to produce brown contamination products on adjoining surfaces on the LDEF spacecraft. Also, results from the exposures of hydrocarbons to simulated atomic oxygen environments have shown evidence that gas phase reaction products of CO and CO_2 [3, 4] are emitted which could contaminate other spacecraft surfaces. Oxidation of polymer surfaces resulting in erosion and mass loss has been observed for materials aboard shuttle missions such as STS-5 and STS-8 [5-7]. These chemical changes can lead to changes in surface morphology, strength and thermal/optical properties.

Mechanistically, polymers react with atomic oxygen via initial reactions of bond dissociation or oxidation, leading to reactions which form volatile, condensible species. Figure 1 summarizes the possible reactions between typical organic polymers and atomic oxygen [2, 6, 8-12]. The most probable reaction between ground state atomic oxygen $O(^3P)$ present in LEO and saturated organic molecules mechanistically occurs by means of hydrogen abstraction, while the reaction of $O(^3P)$ and C=C bonds typically proceeds by way of an addition mechanism [11]. The reaction mechanism depends upon the activation energy for the reaction of a specific polymer with atomic oxygen [13].

Differences in the atomic oxygen reactivities of Kapton and Teflon have been attributed to differing mechanisms of oxidation, and can be related to the structures of the polymer chain and dissociation energies of the various bonds present in these structures. Figure 2 shows the structures of the polymer chains for Kapton and FEP Teflon, and Table I lists the dissociation energies of various typical bonds present in organic polymers.

Teflon is known to be less reactive with atomic oxygen than Kapton [2, 6, 9] and polyethylene [6] from results of space flight experiments. Ranges of erosion yields for these materials are shown in Table II, where erosion yield is a measure of the polymer's reactivity with atomic oxygen and is expressed as the volume of material lost per incident oxygen atom. This information shows that Kapton and polyethylene have similar erosion yields, whereas the erosion yield of Teflon is lower. The lower reactivity for Teflon may be explained by atomic oxygen attack leading to bond breakage at the side-groups rather than at the backbone of the Teflon molecule [9]. Breaking of a C-C bond in Teflon

(structure shown in Figure 2) occurs at an energy of 4.3eV, and the C-C bond in polyethylene, which has the simple structure of $(CH_2-CH_2)_n$, dissociates at 3.9eV. One would expect that FEP would undergo oxidation to a similar extent as polyethylene upon exposure to LEO atomic oxygen if C-C bond breakage were the mechanism of damage for both. However, because of the lower reactivity for FEP Teflon, another mechanism of degradation may be occurring with FEP. It is suspected that C-F bond dissociation, which occurs at an energy of 5.5eV, is the primary mechanism of damage. Only about 30% of oxygen atoms possess this energy in the LEO environment. This may contribute to Teflon's relatively low reactivity in LEO [2].

For Kapton, which is highly reactive in the LEO environment, the probable cause of degradation is the breaking of the backbone structure [2]. This is due to the fact that many of the chemical bonds in Kapton, dissociate at energies below 4.5eV. ESCA analysis for Kapton exposed aboard STS-8 showed that the number of C-O bonds at the surface of the material increased, while the number of C-C bonds decreased [6]. This suggests oxidation of the aromatic rings and the imide rings of the Kapton molecule resulting in fragmentation of the backbone structure.

Besides the chemical structure of the polymer molecules, other properties which can affect susceptibility to atomic oxygen damage are degree of crystallinity, existence of amorphous regions, and permeability to oxygen. Rate of reaction is affected by surface-to-volume ratio of the polymer structure.

Knopf, et al. [9] propose a mechanism of damage to polymers which is related to the diffusion of oxygen into a polymer film. In this model, the diffusion of oxygen into the polymer film is the rate limiting step. Subsequent oxidation reactions then occur via the pathways shown in Figure 1. In materials where the diffusion of oxygen into the surface is limited (i.e. a thick polymer film), the concentration of oxygen at the surface is greater than in the bulk of the material, and the result is fast oxidation at the polymer surface with accompanying mass loss and chemical changes at the surface, but little change in bulk properties. However, for Kapton with a siloxane coating, which is resistant to oxidation, this proposed mechanism explains that a large concentration of oxygen may be prevented from building up in the surface of the material resulting in slow diffusion of oxygen into the polymer film after an induction period. This limited diffusion of oxygen results in distribution of oxygen through the bulk material and causes chemical change to occur through the bulk of the material. According to this model, cracking and crazing of the siloxane coating occurs because of the bulk chemical changes resulting from oxidation after slow diffusion of oxygen into the material [9]. Arnold and Peplinski [5] propose that gas phase reactions of atomic oxygen and consumption of atomic oxygen at the reacting polymer surface are reactions which compete with the oxygen diffusion process as the rate-limiting step in the oxidation of polymers.

Another polymer which merits discussion is silicone rubber. Silicones showed low erosion yields in LEO (Table II). This can be explained by the reaction of silicone rubber with atomic oxygen at its surface leading to the formation of a thin layer of SiO_2 which is atomic oxygen resistant [2]:

$$SiOR_2 + O \ -----> \ SiO_{(1+x)}R_{2(1-x)} =====> \ SiO_2.$$
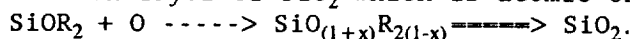
It should be noted, however, that the very reaction which makes silicone durable to atomic oxygen, makes it a source of contamination to neighboring surfaces, since the organic side groups lost are volatile condensible materials.

Certainly these simple models cannot explain all the intricacies of

reactivity of polymers with atomic oxygen in low earth orbit. For example, it is valuable to determine the oxidation dependencies upon atomic oxygen energy, flux or fluence, and, to date, there have not been focussed flight experiments to address these issues [5, 10].

One of the important reasons for understanding the atomic oxygen reaction mechanisms is that ground-based facilities are needed to accurately simulate the LEO environmental degradation effects. Because of the need for materials to last 15-30 years for the Space Station Freedom, it will be necessary to conduct ground-based tests which reliably predict the long-term durability of materials. In addition, the results of well-defined flight experiments will provide results to be used in modelling to extrapolate the long-term environmental effects. Utilization of ground-based experiments correlated with in-space mechanistic modelling could allow credible predictions of long-term durability to be made.

Solar Ultraviolet Radiation Effects

The wavelength range of solar ultraviolet radiation present in LEO is between approximately 0.1 and $0.4\mu m$ which is a small portion of the solar irradiance curve shown in Figure 3. The total energy provided by radiation in this wavelength range is approximately 8% of the solar constant, where the solar constant is defined as the total energy provided by the sun over all wavelengths up $1000\mu m$ and is equal to 136.7 mW/cm^2 [15]. This ultraviolet radiation is energetic enough to cause the breaking of organic bonds as shown in Table I and Figure 4. Although the solar radiation below 0.2 μm represents less than 0.001% of the solar constant [15], its presence may promote breakage of important organic structural bonds, such as C-C and C-O, and fuctional groups.

Absorption of a photon of ultraviolet radiation by an organic molecule causes the molecule to be raised to an excited state. If the molecule has enough energy in this excited state, bond dissociation could occur. These dissociated radical species are reactive intermediates and can diffuse within several atomic distances from their origination point, depending upon the temperature and physical properties of the polymer [16], and participate in further reactions. Figure 5 shows a generic representation of the reactions of a typical organic polymer molecule with ultraviolet radiation. Besides bond dissociation, other mechanisms of returning the excited molecule to the ground state could occur. For example, the excited species could return to its original chemical state accompanied by a release of light or heat. Another possible mechanism occurring with an excited state molecule is the electronic transfer of energy from one functional group on a molecule to another before a relaxation event occurs. This significantly increases the possibilities for reactions of molecules with multiple functional groups.

Solar ultraviolet irradiation can lead to crosslinking of polymer surfaces which may lead to embrittlement and possibly to surface cracking. UV radiation has also been shown to degrade mechanical properties of polymeric materials as is shown in the degradation in the tensile strength of Mylar [17]. Because atomic oxygen is present in LEO, it is expected that the reaction intermediates from the photon absorption will react with reaction intermediates from the oxidation process. This photo-oxidation can lead to discoloration and reduced transparency of some polymers. Chemical changes in the molecule as a result of these reactions may also lead to the formation of polar groups which may affect electrical properties [18].

A high value of solar transmittance in the wavelength range between 0.3

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and 0.6 μm is necessary for polymers used as second surface reflectors for thermal control coatings. Ultraviolet radiation degradation of this transmittance may result in decreased efficiency of the thermal control surface. Laboratory experiments have been performed to determine the effects of UV radiation on the optical properties of various types of polyimides [19]. Of particular interest, in terms of ultraviolet radiation degradation mechanisms, is the fact that the most stable polyimide materials were those which contained both oxygen and $-C(CF_3)_2$ bonds, and the poorest performers were those which contained sulfur atoms within the polymer molecular structure.

Use of Polymers in the LEO Environment

Because of the degrading effects of atomic oxygen and solar ultraviolet radiation on polymeric materials, much work has gone into studying methods of protecting polymers. Laboratory experiments have been performed on candidate materials. For solar array blanket use, many methods of coating or modifying Kapton have been explored to determine whether they offer protection from atomic oxygen erosion [20-22]. Two methods of modification have been the incorporation of fluorine into Kapton and the copolymerization of silicone with Kapton (referred to as polysiloxane-polyimide). Ground-based evaluation of these materials in atomic oxygen simulation facilities have shown that these do not offer adequate protection from oxidative erosion to prevent failure of the material as a solar array structural support for its required lifetime [20, 22]. The polysiloxane-polyimide material did show durability to ultraviolet radiation, however, and a sample exposed to UV did not show an increased susceptibility to damage due to short-term atomic oxygen exposure [23].

The most promising coating to date for protection of Kapton has been a magnetron sputter deposited coating of SiO_x (where x is thought to be near 2) of approximately 1300Å. Results of atomic oxygen exposure of this coating show that it has potential to provide adequate protection to last the expected life of the Space Station Freedom solar array blanket, provided the number of defects (pinholes and scratches) in the coating can be minimized [22]. Because protective coatings of this type are not perfect in their ability to coat the substrate without defects and are subject to abrasion damage, it is necessary to coat both sides of the two layers of clad material which comprise the solar array blanket, as well as to explore the effects of atomic oxygen damage to the underlying polymer at sites where protective coating is lacking. This phenomenon of atomic oxygen erosion of the polymer at coating defect sites is referred to as undercutting. Atomic oxygen undercutting processes, which are discussed elsewhere [21, 24, 25], are related to the intrinsic stress of the protective coating, coating adherence and the angle or angular sweep of atomic oxygen attack.

Synergistic effects of atomic oxygen and ultraviolet radiation must be evaluated when determining the overall durability of a material. A study performed by Koontz, et al. [26] determined that the reaction rate for FEP Teflon with atomic oxygen in a flowing afterglow source was significantly increased by the presence of vacuum ultraviolet (VUV) radiation provided by a krypton resonance lamp. They found the reactivity of Kapton with atomic oxygen in the presence of VUV increased, but not as significantly as that of Teflon. Studies of this nature can provide insight as to mechanisms of polymer degradation due to LEO synergistic environmental effects as well as provide guidance as to requirements for proper ground based simulation facilities.

CONCLUSIONS

Because of the intricacies of the reactions of atomic oxygen and ultraviolet radiation in the LEO environment with polymers, it is difficult to make definitive predictions as to the modes of damage and the expected lifetime of materials exposed to these synergistic degradation processes.

Focussed flight experiments, well-defined laboratory tests with in situ analytical capabilities, and analytical modelling will assist in determining damage mechanisms and rates for the reactions of polymers or polymer/coating systems with atomic oxygen and solar ultraviolet radiation. These results will then enable well-informed extrapolations from short-term data as to the durability of materials to atomic oxygen and solar ultraviolet radiation.

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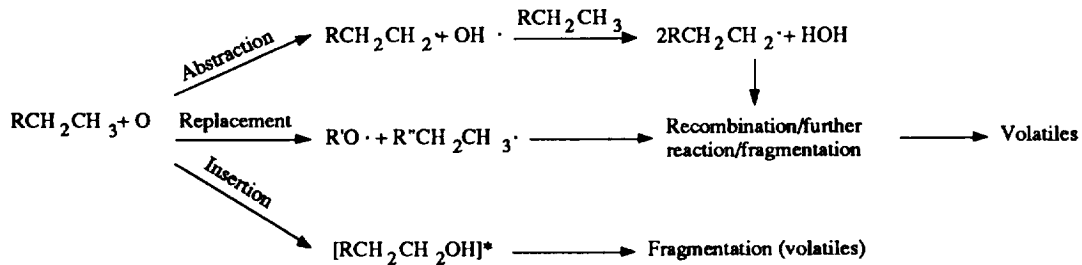
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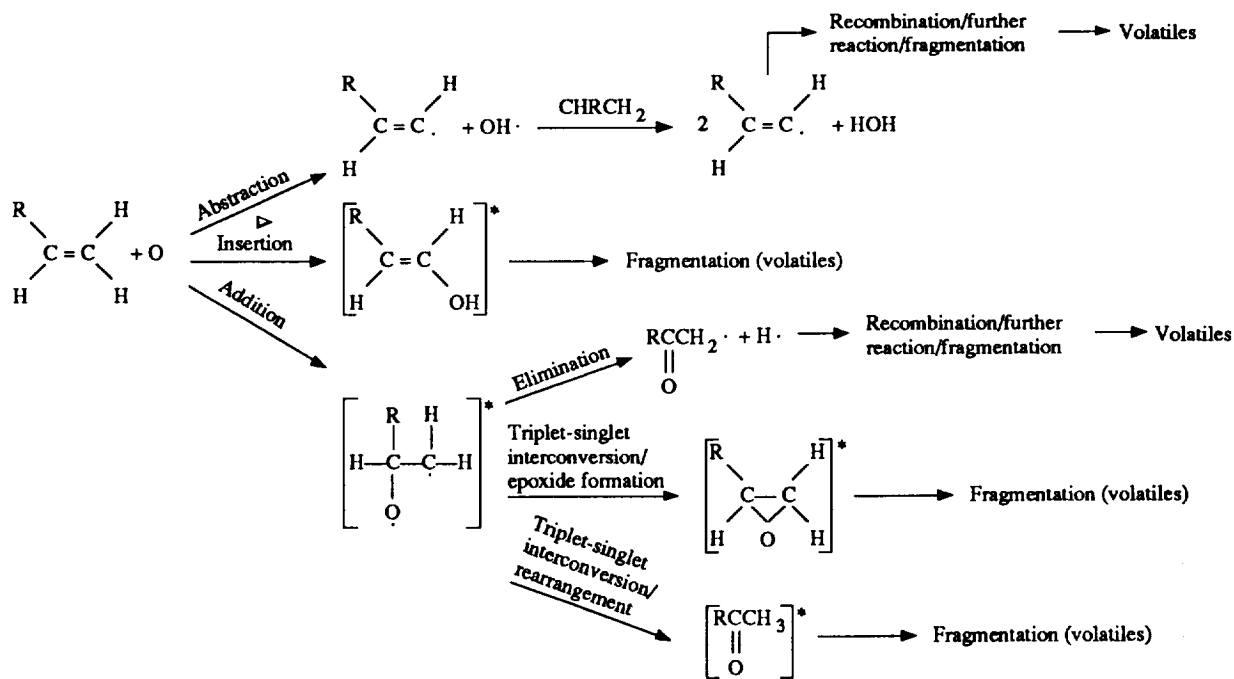# TABLE I – Dissociation Energies of Common Polymeric Bonds

Chemical Bond	Dissociation Energy	(μm) Wavelength of Energy	Typical Material	Ref.
C-H	3.5-4.4	0.36-0.28	Aliphatic polymers	27
C_6H_5-H	4.8	0.26	Aromatic polymers	27
$-C_6H_4$-C(=O)-	3.9	0.32	Kapton, Mylar	2
$-C_6H_3$-H	4.8	0.26	Aromatic compounds	2
C=C	6.3	0.20	Aliphatic compounds	17
C≡C	8.7	0.14	Aliphatic compounds	17
O=CO	5.5	0.23	Carboxylic acid	27
C=O	7.7-7.8	0.16	Aldehydes, ketones	17
$-CH_2-CH_2-$	3.9	0.32	Mylar, polyethylene and aliphatic compounds	2
CF_3-CF_3	4.3	0.29	FEP Teflon	2
$-CF_2$-F	5.5	0.23	FEP Teflon	2
CH_3CF_3	4.4	0.28	$-(CH_2-CF_2)_n-$	2
C-N	3.2	0.39	Kapton	17
C-S	2.8	0.44	Vulcanized rubber	17
-Si-O-	8.3	0.15	Silicones and SiO_2	2
$-Si-CH_3$	3.1	0.40	Silicones	2
-Zr-O-	8.1	0.15	Protective ctg.	2
-Al-O-	5.3	0.23	Protective ctg.	2

TABLE II - Erosion Yields for Polymers Commonly Used in LEO

Material	Erosion Yield X 10^{-24} cm³/atom	Reference
FEP Teflon	0.037 0.35	24 Preliminary LDEF Results
Kapton	3.0	24
Polyethylene	3.7 3.3	24 24
Silicone Rubber	0.05-1.5	24

RCH$_2$CH$_3$+O

Abstraction → RCH$_2$CH$_2$ + OH · $\xrightarrow{\text{RCH}_2\text{CH}_3}$ 2RCH$_2$CH$_2$· + HOH

Replacement → R'O· + R"CH$_2$CH$_3$· ────→ Recombination/further reaction/fragmentation ────→ Volatiles

Insertion → [RCH$_2$CH$_2$OH]* ────→ Fragmentation (volatiles)

(a) Alkanes

(b) Alkenes

Figure 1.—Atomic oxygen reaction mechanisms.

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(a) Kapton.

(b) Florinated ethylene propylene teflon.
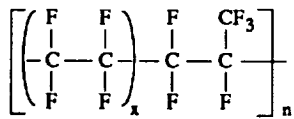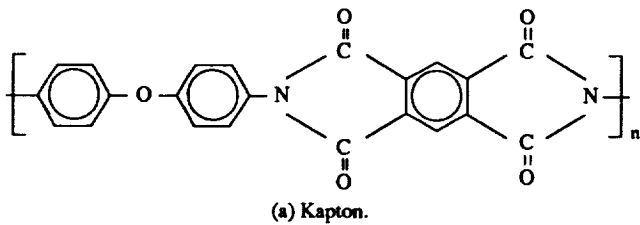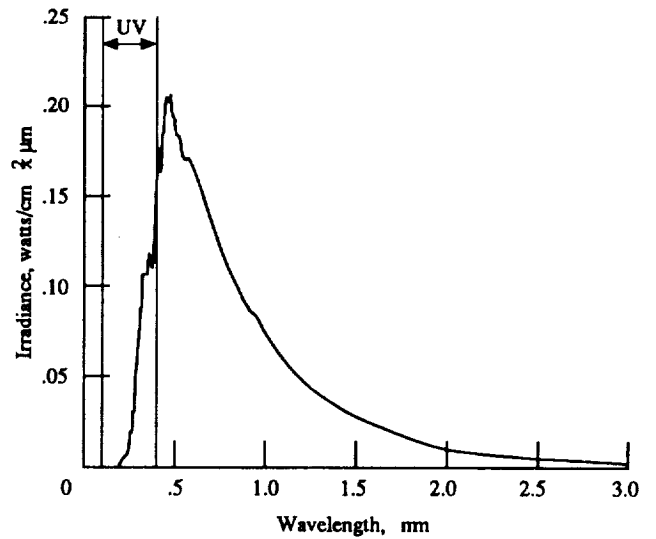
Figure 2.—Chemical structural formulas.
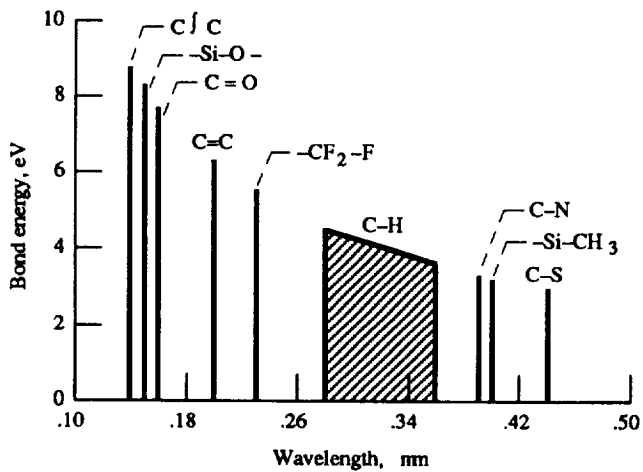

Figure 3.—Solar spectrum at air mass zero [28].

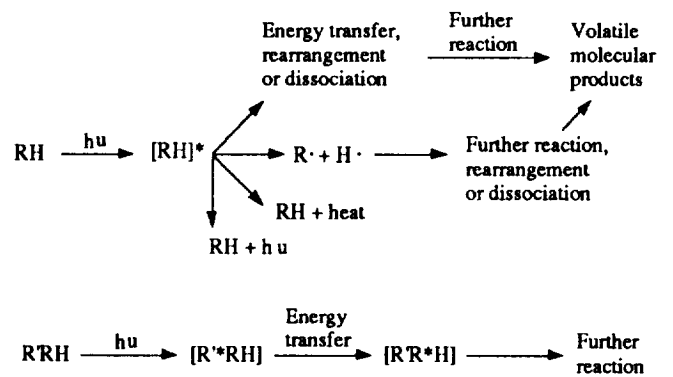Figure 4.—Wavelength requirement to break various polymeric material bonds.

Figure 5.—Ultraviolet radiation degradation of organic materials.

Report Documentation Page

1. Report No. NASA TM-103711	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Low Earth Orbital Atomic Oxygen and Ultraviolet Radiation Effects on Polymers		5. Report Date February 1991
		6. Performing Organization Code
7. Author(s) Joyce A. Dever		8. Performing Organization Report No. E-5943
		10. Work Unit No. 506-43-11
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Because atomic oxygen and solar ultraviolet radiation present in the low earth orbital (LEO) environment can alter the chemistry of polymers resulting in degradation, their effects and mechanisms of degradation must be determined in order to determine the long-term durability of polymeric surfaces to be exposed on missions such as Space Station Freedom (SSF). The effects of atomic oxygen on polymers which contain protective coatings must also be explored, since unique damage mechanisms can occur in areas where the protective coating has failed. Mechanisms can be determined by utilizing results from previous LEO missions, by performing ground-based LEO simulation tests and analysis, and by carrying out focussed space experiments. A survey is presented of the interactions and possible damage mechanisms for environmental atomic oxygen and ultraviolet radiation exposure of polymers commonly used in LEO.

17. Key Words (Suggested by Author(s)) Atomic oxygen; Ultraviolet radiation; Materials degradation; Polymers; Low earth orbital environment	18. Distribution Statement Unclassified – Unlimited Subject Category 27		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 14	22. Price* A03