ATOMIC OXYGEN EROSION RESISTANCE OF ORGANIC POLYMERS
FOR LOW EARTH ORBIT SPACECRAFT

by

Grant Rheal Cool

A Thesis submitted in conformity with the requirements
for the Degree of Doctor of Philosophy
The Institute for Aerospace Studies
University of Toronto

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1996
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ABSTRACT

Within this study, four developments are presented. First, the Atomic Oxygen Beam Facility at the University of Toronto Institute for Aerospace Studies is further characterized by measuring the charged species component of the beam (mole fraction = 4x10^-5) and the beam velocity energy spectrum (Maxwellian-like distribution with a peak at 2.1 eV).

Second, using the atomic oxygen beam facility, a series of parameters which relate the hyperthermal atomic oxygen erosion yield of a hydrocarbon polymer to its chemical content and structure is experimentally verified. Ultimately, it was determined that the erosion yield is related linearly to an effective carbon content parameter (γ). The γ-parameter accounts for the relative amount of carbon in the polymer, and the role of intramolecular oxygen in determining the reactivity of the polymer. Conclusions are reached with respect to the roles of the two driving forces in the eroding process; the chemical potential of the species involved and the kinetic energy of the atomic oxygen.

The third development, which again relates to the erosion process of hydrocarbon polymers, is an original reaction scheme proposed for the interaction of atomic oxygen with DuPont's polyimide Kapton®. This scheme is based on the well studied interaction of molecular oxygen with polyimides. The purpose of deriving this reaction scheme is to develop an applied example using the γ-parameter assumptions. The derivation process
concludes with the enumeration of the reaction products of the hyperthermal atomic oxygen interaction process with Kapton®.

Taking the knowledge gained about how and why atomic oxygen erodes polymers, and applying it to solve an important engineering problem (ie. inhibiting atomic oxygen erosion in low Earth orbit) is the goal of the final development. Two surface modification processes are explored. Plasma fluorination of Kapton® was attempted with only limited success, resulting in a maximum reduction to approximately 50% of the typical untreated sample erosion yield. A second technique, known as 3-Step Silylation or the Photosil™ Process, was demonstrated successfully with a two order-of-magnitude reduction in erosion yield for a variety of materials including: Kapton®, Mylar®, PEEK, polyethylene, graphite reinforced PEEK and epoxy composites, and the graphite fibres themselves.
ACKNOWLEDGEMENTS

I would like to thank my supervisor Professor R.C. Tennyson for his faith, advice and encouragement throughout the 4 years that it took to work through this interesting problem. In addition I would also like to thank Prof. Don Morison, Adam Mabee, Gerald Manuelpillai and all the other members of the UTIAS Aerospace Materials Group for their honest support and fine sense of humour. This work would not have been possible without the unreserved help of Prof. Z.A. Iskanderova, Prof. J.I. Kleiman, Jake Unger and my committee members, Prof. A.A. Haasz and Prof. G.M.T D’Eleuterio. Finally I would like to thank Dr. Yu. Gudimenko, a fine teacher who shared all his knowledge without asking for a single thing in return.

This work was sponsored by the Ontario Centre For Materials Research and the Institute for Space and Terrestrial Science.
DEDICATION

I dedicate this work and every day of my life to my children.
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NOTATION

\[ \Delta G^\circ \] standard change in Gibbs free energy

\[ \Delta H^\circ \] standard enthalpy change

L_f flight path

M average atomic weight of the atoms in the polymer repeat unit

N_C number of carbon atoms in the polymer repeat unit

N_O number of oxygen atoms in the polymer repeat unit

N_T total number of atoms in the polymer repeat unit

R_e reaction yield

R_e^\circ \] ultimate reaction yield

\[ \Delta S^\circ \] standard entropy change

V_a voltage applied to plates

c base length of droplet

\[ d_p \] distance between charged plates

e charge on ion

h height of droplet

l_p length of charged plates

m_i mass of ion

p_r reaction probability

r_s spherical radius of droplet

r regression coefficient

\[ t_f \] measure flight time

v_b velocity of beam

v_i velocity of ion

\[ \beta \] beta function, = N_T/N_C

\[ \gamma \] gamma function, = N_T/(N_C-N_O)

\[ \gamma' \] gamma prime function, = \gamma \bar{M}/\rho

\[ \theta \] contact angle

\[ \rho \] density
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 eV</td>
<td>1.6x10⁻¹⁹ joule, or 96.5 kJ/mol (note that the joule is per particle and must be multiplied by 6.022x10²³ to be strictly comparable)</td>
</tr>
<tr>
<td>B(DMA)DS</td>
<td>Bis (dimethylamino) dimethylsilane</td>
</tr>
<tr>
<td>B(DMA)MS</td>
<td>Bis (dimethylamino) methylsilane</td>
</tr>
<tr>
<td>HMCTS</td>
<td>1,1,3,3,5,5 - Hexamethyelotrisilazane</td>
</tr>
<tr>
<td>n</td>
<td>degree of polymerization</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-pyrrolidine</td>
</tr>
<tr>
<td>ODA</td>
<td>oxydianiline</td>
</tr>
<tr>
<td>PAA</td>
<td>polyamic acid</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PEEK</td>
<td>poly(ether ether ketone)</td>
</tr>
<tr>
<td>PEO</td>
<td>polyethylene oxide</td>
</tr>
<tr>
<td>PET</td>
<td>poly(ethylene terephthalate), Mylar®</td>
</tr>
<tr>
<td>PH</td>
<td>Polymer chain with H being the most labile or easily reacted hydrogen</td>
</tr>
<tr>
<td>PMDA</td>
<td>pyromellitic dianhydride</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl acetate)</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadrupole Mass Spectrometer</td>
</tr>
<tr>
<td>P*</td>
<td>macroradical or alkyl radical</td>
</tr>
<tr>
<td>PO*</td>
<td>macroalkoxy radical</td>
</tr>
<tr>
<td>POO*</td>
<td>macroperoxy radical</td>
</tr>
<tr>
<td>*OOH</td>
<td>hydroperoxy radical</td>
</tr>
</tbody>
</table>
•OH  hydroxide radical

\[ \text{amide} \quad \begin{array}{c}
\text{O} \\
\text{\textbullet -N-} \\
\text{H}
\end{array} \]

\[ \text{amine} \quad \begin{array}{c}
\text{N} \\
\text{H} \\
\text{H}
\end{array} \]

\[ \text{imide} \quad \begin{array}{c}
\text{C} \\
\text{\textbullet -N-} \\
\text{H}
\end{array} \]

\[ \text{cyclic imide} \quad \begin{array}{c}
\text{C} \\
\text{\textbullet -N-} \\
\text{O}
\end{array} \]

\[ \text{peroxide} \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \]

\[ \text{ketone, carbonyl group} \quad \begin{array}{c}
\text{C} \\
\text{\textbullet -} \\
\text{O}
\end{array} \]

\[ \text{alcohol, hydroxyl group} \quad \begin{array}{c}
\text{O} \\
\text{H}
\end{array} \]

\[ \text{ether} \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \]

\[ \text{ester} \quad \begin{array}{c}
\text{O} \\
\text{\textbullet -C-O-}
\end{array} \]

\[ \text{carboxylic acid} \quad \begin{array}{c}
\text{O} \\
\text{\textbullet -C-O-H}
\end{array} \]

\[ \text{phenyl, (with -OH called phenolic)} \quad \begin{array}{c}
\text{C}_6\text{H}_5
\end{array} \]
INTRODUCTION

"Space is empty!"

There is an implication, when one uses the word "Space" in referring to the region beyond the atmosphere of Earth, of an immense void in which very little exists. This perception extends well beyond "the first time you ever thought about it" circumstance for most people, because there is a grain of truth to the statement. On a human sized scale, Space really does seem empty. On a grand scale, of course, Space is as packed as a rush hour bus; but if you were to suddenly find yourself half-way between Earth and the Moon, you would be lonely indeed. Interestingly, though, if you had brought along a good mass spectrometer, quite a variety of matter could be identified nearby: residual atmosphere elements (nitrogen, oxygen etc.) in various forms (O, O₂, N, N₂, NO etc.), in both neutral and ionized states, a flux of solar wind components, hydrogen, helium and even some metals. Evidently, on the atomic/molecular scale Space can be quite crowded too.

In truth, Space isn't empty at all, especially if you happen to be near a star, or better yet, near a planet. For example, in Low Earth Orbit (LEO), 200 to 900 km or so above the Earth's surface, the environment is actually quite complex. Without even considering orbital debris, micrometeoroids or trapped high energy particles, the residual atmosphere is a veritable soup of atmospheric elements and compounds that changes in total and relative quantity, hour to hour, day to day and month to month. Figures 1 and 2 illustrate some of the neutral gaseous matter present in LEO and how their quantities vary with altitude and time.[1] It would seem, upon first glance, that the total quantity of matter in a given volume (for example, one cubic centimetre as shown in the figures) is quite low when compared to our sea level atmosphere (>10¹⁹ per cm³), and that given these small quantities of matter, one would ask: How could there possibly be any degrading effect on a relatively huge spacecraft?
Figure 1: The constituents of Earth's residual atmosphere in LEO. Atomic oxygen is the main constituent.[1]

Figure 2: Variations in the density of the residual atmospheric components in LEO.[1]
For the most part, during the early exploration of Space, this was the predominant attitude; and it was justified, because the materials that were first used (mostly aluminum) were very inert. The realities, however, of Space exploration today, particularly the effect of an ever increasing cost per kilogram of mass into orbit, dictate that lighter, stiffer materials be used. As always, there is a price to be paid for increased capability, and in this case it is Space environmental performance. If we wanted to build spacecraft that did not move, that is, a vehicle with no relative motion to the local environment, there would be no problem. Unfortunately, the mechanics of staying in orbit, or crossing the vast distances between celestial bodies, require spacecraft to move at high velocities (many kilometres per second). This means that, even though the total density of matter is fairly low, the number of particles that the spacecraft impacts, and the energy at which they hit, are both high. In LEO, the side of the spacecraft facing the direction of travel (the ram direction) can experience up to $10^{15}$ atoms/cm$^2$/second of atomic oxygen hitting the surface at a velocity of 8 km/second, which imparts a substantial amount of energy. Atomic oxygen (AO) is formed in the upper atmosphere as solar ultraviolet radiation breaks apart molecular oxygen, that is $O_2 + h\nu \rightarrow O + O$. It constitutes most of the LEO atmosphere (see figure 2). Given the significant impact energy and the high flux values encountered by orbiting spacecraft, AO erodes and degrades materials. In some cases it limits their useful lifetimes; in the worst cases, it precludes their use altogether.

In early experiments conducted in LEO, designed to examine the effects of the environment on materials for our newest generation of satellites, it became clear that certain groups of materials were going to be difficult, if not impossible, to use.[2] Anything organic, or carbon based, and some metals such as osmium and silver, erode quite rapidly. Upon examining the constituents of the environment, the most likely cause quickly became evident. Atomic oxygen is highly reactive to these materials, particularly when hitting the surface at 8 km/second because of the spacecraft's high orbital velocity. Generally AO oxidizes polymers, removing the material elements as volatile oxide compounds. Immediately this was recognized as a serious problem. Organic polymers, and composite materials containing organic polymers, were becoming the "material of choice" for many
applications. For example, polymers are used as thermal blankets and as substrates for solar arrays, and are finding use as structural materials in the form of polymer matrix composites. The impetus to use polymers is quite simple; they allow the engineer to explore new applications and reduce mass, while improving performance.

In the past, we considered Space to be relatively empty, and that the environment of Space consisted mainly of a vacuum and its associated problems. Of course, it is a gross over-simplification to say that all of Space has one environment, even more so than it is to say the Earth has only one environment in which engineered materials must work and survive. That having been said, however, it has been less than 20 years since the deleterious effects of the LEO environment on materials were seriously investigated, although almost 40 years have passed since we first started launching and recovering spacecraft. This hesitation is merely a result of the path that has been followed in our early exploration of Space.

Missions into LEO Space have been quite short — too short for severe degradation to occur. Most of our longest surviving spacecraft are working in geosynchronous earth orbit (GEO). At tens of thousands of kilometres from the Earth’s surface, GEO appears to be a more benign environment, although we have not seen the satellites since they were placed up there, and surmise their condition only from the simple fact that they are still operating.

It has only been since the mid 1980s that a serious interest in using the orbits nearest to Earth for long-term applications, such as communications and remote sensing, has existed. The key word here is long-term: use of a spacecraft for twenty years or more. Many satellites have been placed in LEO, but these were essentially disposable vehicles, not expected to last more than a few years. Today, multi-billion dollar constellations of communication satellites are being constructed for deployment before the end of the decade. The International Space Station will be in operation during that same time period, with a minimum expected lifetime of 25 to 30 years. These projects are a huge investment in money and effort that cannot be eroded away.
1.1 Motivation

Here, then, is the essence of the situation and the two opportunities it provides. It is a problem of circumstance and perception that has led to the current state of incomplete knowledge about the effects of the Space environment on spacecraft. This is particularly true with respect to the substantial effects occurring in the LEO environment. A significant level of research is currently being carried on throughout the world studying the performance of materials in the near Earth environment. In particular, much effort is being concentrated on studying the serviceability of polymer-based materials in spacecraft design.

Polymer materials are critical, as engineering materials for spacecraft design, because of their low mass, excellent strength and the fact that they can be used easily in applications where other materials could not (a flexible, durable, thin blanket for example). This fact is especially true when they are formed as fibre reinforced polymer matrix composites, which have been shown to have better specific stiffness and strength relative to metals such as aluminum. One of the limits to using polymers in LEO is the effect of atomic oxygen erosion. Unprotected polymers exposed to the atomic oxygen environment of LEO erode rapidly, limiting their long-term use capability.

In an effort to understand the mechanism of LEO atomic oxygen erosion, some important tasks still need to be accomplished. One essential task is the study of why some polymers erode faster than others, and what these facts mean in terms of the interaction between chemical oxidation and kinetic energy transfer. This is the first opportunity. In addition to the fundamental investigation of the AO erosion of polymers, one must also apply the knowledge gained toward solving the problem. Coatings and coverings are currently used to protect polymers from AO exposure with some success. However, polymers are highly adaptable materials which can be chemically modified themselves to withstand AO bombardment, so that they do not require external protection. Given the current state of knowledge in the fields of organic polymer chemistry/engineering, and physical chemistry of surfaces, it should be possible to develop new polymers or modification processes for
existing polymers that will result in materials which are highly resistant to atomic oxygen erosion. This, is the second opportunity.

1.2 Scope

Within the scope of this thesis an attempt will be made to answer some of the questions about how organic polymers erode in "LEO like" hyperthermal atomic oxygen. This will be done within a limited paradigm which states that the content and structure of the polymer has a significant effect on the reaction rate/yield when exposed to hyperthermal atomic oxygen. A number of relationships between content/structure of the polymer and reaction yield will be defined and discussed.

It is the first objective of this thesis to define a relationship or set of relationships that can predict the erosion rate of a polymer material in LEO. Ultimately the defined relationship will be used to discuss the general mechanism of AO erosion of polymers, and reveal some of the reasons why one polymer erodes faster than others. In addition it is intended that this knowledge be used to develop a more precise mechanism for AO erosion for polyimide Kapton®. Chapter 2 begins the process by characterizing more fully the University of Toronto Institute for Aerospace Studies (UTIAS) Atomic Oxygen Beam Facility in order to define the error limits of the testing program defined. In Chapter 3 a linear relationship is determined between erosion yield and a chemical content and structure parameter. In this chapter, specific conclusions are presented about the relationship between erosion yield and the chemical content and structure of hydrocarbon polymers. These conclusions are based on a consistent set of erosion yield measurements made specifically for this purpose, and a set of functions that illustrate the effect of chemical content and structure on the reaction yield under AO bombardment. Chapter 4 ends the process by:

1) reviewing the current thinking on the organic chemistry of oxidation mechanisms in thermal energy environments,
2) by proposing an original reaction scheme for the thermal oxidative degradation of Kapton®, and
3) by extending the concepts developed for thermal environments to the hyperthermal environment by suggesting and corroborating the structural origin of the reaction products of Kapton®.

In the second half of this thesis a unique methodology for suppressing atomic oxygen erosion of organic polymers is presented. Essentially, the development process is driven by the goal to make the surface of the polymer material Teflon®-like in the first case, and Silicone like in the second case. To reach this goal two surface modification processes are examined, Plasma Fluorination and 3-Step Silylation (the Photosil™ process). Both processes are surface modification techniques, rather then a coatings. With surface modification the chemical structure and content of the polymer is altered; in the one case incorporating fluorine and fluorine groups into the structure, in the other adding silicon-oxygen atoms to the structure.

Two important terms will be used routinely throughout these chapters and deserve differentiation and definition at this point because of their importance: Thermal Atomic Oxygen (TAO) and Hyperthermal Atomic Oxygen (HAO).

TAO, as used herein, is neutral atomic oxygen with thermal kinetic energy. Thermal energies (<0.1 eV) are the kinetic energies of atoms or molecules near room temperature. Spacecraft orbiting in LEO, however, represent a HAO environment. Atomic oxygen atoms impacting the surface of a material at 8 km/s, as the spacecraft moves through them, possess considerable kinetic energy (about 5 eV), and are called hyperthermal. Organic polymers exposed to the LEO environment are eroded and degraded by exposure to HAO.

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* An electron volt (eV) is a measure of energy equal to the energy acquired by an electron as it moves through a potential difference of 1 volt. It is also a measure of energy that is comparable to the energies of covalent bonds in organic polymers (eg. a C-H bond has a bonding energy of 4.3 eV).
Although the two types of atomic oxygen have much in common, there are some significant differences when they interact and degrade a material. TAO interaction and degradation is strictly a chemical process, involving only chemical bonding changes, as the covalently bonded structure is broken apart to form volatile products. The kinetic energy of the eroding species (AO) is not involved in the erosion process in a deterministic manner. HAO interaction and degradation, however, involves more than just chemical potential: an external source of energy, the kinetic energy, also drives the changes. HAO interaction is a transition state between chemical degradation and physical sputtering, exhibiting qualities of both processes. Because of the interaction of "chemical potential" and "kinetic energy transfer", there is a drastic, and not yet well-understood, increase in complexity of the process. In the chapters that follow this complexity will be explored.
CHAPTER 2

CHARACTERIZATION OF THE UTIAS ATOMIC OXYGEN BEAM FACILITY

The UTIAS AO beam facility (figure 3a,b) is a LEO simulator capable of exposing materials to AO, vacuum ultraviolet radiation, and temperature cycling simultaneously in a vacuum environment. The beam facility is made up of three main components: the plasma torch (Surfatron), the sampler-skimmer system and the vacuum chamber. In this facility, a beam of atomic oxygen is generated by heating a gaseous mixture of oxygen, helium and sometimes argon to a high temperature in the Surfatron, dissociating much of the molecular oxygen to atomic oxygen, and then supersonically expanding some of the gas into a vacuum, through small orifices in the sampler and skimmer. A carrier of light gas (helium) is used in this system since it will be accelerated the greatest amount by the available heat energy. The oxygen is "seeded" into the helium carrier and is collisionally accelerated to a greater final velocity than if it was heated and accelerated alone. The gas mixture is heated both to dissociate the oxygen molecules to atomic oxygen, and to give it heat energy that will be turned into directional kinetic motion by the expansion into vacuum.

2.1 THE UTIAS ATOMIC OXYGEN BEAM FACILITY COMPONENTS

The vacuum chamber consists of the following three sections: the sampler-skimmer interface, the test chamber, and the main chamber. The sampler-skimmer interface consists of two nickel orifice cones separated by an evacuated water cooled interface chamber. The test chamber is a 7.5 l, six-way, aluminum cross. The main chamber, to which the diffusion pump is attached, is a 15cm diameter by 25cm diameter, four-way, glass cross. Instrumentation can be mounted onto the various openings of the chambers using interchangeable aluminum plates, with o-ring seals. The instrumentation commonly mounted, includes a vacuum ultraviolet radiation assembly, a thermal cycling assembly, a Quadrupole Mass Spectrometer (QMS), a pair of Bayard-Alpert ionization gauges, and a set of six-degree-of-freedom motion manipulators.
Figure 3(a): Schematic diagram of UTIAS atomic-oxygen beam facility.

Figure 3(b): Photograph of UTIAS atomic-oxygen beam facility showing (from left) power supply, Surfatron chamber, test chamber, and main chamber.
The main pump is an Edwards 250/200M, 2300L/s, "Diffstak" oil diffusion pump connected below the main chamber. When completely sealed, the chamber can be maintained at a pressure as low as $10^{-7}$ torr. When the beam system is running the chamber pressure is in the $10^{-5}$ torr range.

2.1.1 Generating the Atomic Oxygen Beam

Atomic oxygen is generated using a microwave surface wave launcher device (Surfatron), and a sampler-skimmer system. The Surfatron device is basically a plasma torch that produces a stream of essentially neutral atomic oxygen seeded in a helium flow. The Surfatron system operates by propagating an electromagnetic surface wave along the discharge tube. A plasma column is generated inside an alumina tube through which a mixture of the appropriate gases flow. When the system is properly tuned, the energy to ionize the gas is coupled from the surface wave with high efficiency. Figure 4 illustrates the basic configuration of the Surfatron system. A transmission input line is attached to a coupler that passes through the first of two coaxial metal cylinders and nearly touches the surface of the second cylinder. A ceramic tube, the discharge tube, is held along the centre-line of the two coaxial metal tubes. The plasma is generated inside the discharge tube. The space between the coaxial tubes is filled at one end with a metal plunger, and is open at the other end. The plunger acts to close the circuit and can be used to change the length of the cavity for tuning.

The plasma discharges at atmospheric pressure toward the sampler-skimmer interface of the facility’s vacuum chamber. Atmospheric discharge, prior to entering the vacuum chamber through the sampler, allows neutralization of the ionic species produced in the plasma torch. A fraction of the neutralized plasma discharge is pulled through a small orifice into the interface chamber between the sampler and the skimmer cones. As the plasma expands in the sampler-skimmer interface, the lighter species (mostly helium) are accelerated rapidly away from the centre-line leaving the heavier species behind. The
heavier species concentrate along the flow axis, and are skimmed into the test chamber through the orifice of the skimmer cone. Most of the helium is pulled away by the interface pump, from between the sampler and skimmer cones. What results, inside the test chamber, is an energetic, slightly divergent beam consisting of helium, atomic oxygen, and molecular oxygen:

![Figure 4: Schematic diagram of the Surfatron microwave surface launcher, showing cut-away view of interior.](image)

### 2.1.2 Gas Flow and AO Flux Estimates

The standard initial gas mixture input to the Surfatron, is a metered flow of approximately 97.3% helium, 2.7% molecular oxygen, by volume. At a microwave generator power of 195 W, the excitation temperature is approximately 2800°K and the degree of molecular oxygen dissociation is approximately 64%, as determined by mass spectrometer measurements.[5] The molecular flow rate into the facility is governed by the sampler-skimmer interface pressure and the sampler-skimmer interface geometry. Since the beam is diverging, the AO flux decreases with distance away from the interface, meaning a
decrease in the acceleration factor for comparison testing to LEO (figure 5).

![Graph showing atomic oxygen flux and acceleration factor vs. distance from sampler orifice.]

Figure 5: Atomic oxygen flux and acceleration factor vs. distance from sampler orifice. [7]

The flux of AO particles also varies radially, across the beam cross-section. The effect of the radial flux distribution of the AO particles is shown in figure 6. Figure 6 displays the recession rate of a Kapton® sample exposed to the AO beam, at varying radial distances from the beam axis [7]. To make the recession rate measurements a series of samples were exposed for increasing durations at a given distance from the interface. For a given thickness of material a hole will be formed, after a certain exposure time, that will have a radius which is indicative of the flux at that distance from the centre-line.
The divergence of the atomic oxygen beam, downstream of the sampler-skimmer interface, depends on the geometry of the sampler-skimmer interface. Using the sampler-skimmer geometry as displayed in figure 7, the AO beam divergence is defined in terms of $D_2$, the maximum effective target diameter:[6]

$$D_2 = \frac{D_2 \left( L_2 + 2L_s \right)}{L_s}$$ \hspace{1cm} 2.1

Table 1 shows the results of applying the actual sampler-skimmer numbers to equation 2.1.
Figure 7: The sampler/skimmer interface geometry. $D_{sk} = 0.51$ mm, $L_s = 7.54$ mm for UTIAS system.

Table 1: Maximum effective diameter at distance.

<table>
<thead>
<tr>
<th>$L_x$ (cm)</th>
<th>$D_2$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17</td>
</tr>
<tr>
<td>4</td>
<td>0.58</td>
</tr>
<tr>
<td>7</td>
<td>0.99</td>
</tr>
<tr>
<td>10</td>
<td>1.39</td>
</tr>
<tr>
<td>13</td>
<td>1.80</td>
</tr>
<tr>
<td>16</td>
<td>2.20</td>
</tr>
<tr>
<td>19</td>
<td>2.61</td>
</tr>
<tr>
<td>22</td>
<td>3.01</td>
</tr>
<tr>
<td>25</td>
<td>3.42</td>
</tr>
</tbody>
</table>

For example, at 10 cm from the interface the maximum effective target size would have a diameter of approximately 1.4 cm.
2.2 Beam Characterization - Rationale and Requirements

Characterization of the beam generated by the Surfatron - sampler/skimmer system is required to understand the capability and limits of the UTIAS testing facility. In this thesis the AO facility is used in two main capacities. First, a set of polymer materials were tested in a consistent and repeatable manner in an effort to develop a clearer understanding of how different polymers erode. Second, the system was used to evaluate the performance of two processes developed to protect these materials. In both cases a certain degree of confidence must exist in the performance of the facility, particularly in the composition of the beam. To define the level of confidence, a standard to which comparison can be made must first be defined.

Ideally, an AO exposure simulation system would be just like LEO. The major problem is the production of large amounts of neutral atomic oxygen travelling at a uniform velocity of 8 km/sec in one direction, with very little residual ionized species or molecular oxygen present. In every system that has been developed, there have always been some compromises. In the UTIAS system the compromises are lower energy/velocity, the presence of molecular oxygen and helium in relatively large amounts, and the entrainment of some room temperature air into the system through the sampler. To deal with the effect of these compromises, their results need to be quantified. The energy/velocity spectrum of the beam must be measured, and the elemental or molecular components of the beam must be determined. Much of this work has been previously accomplished; mass spectrometer measurements have been used to determine the components of the beam, standard materials were exposed and compared to space flight samples and samples from other AO systems, and analytical characterizations of the beam were performed based on the known parameters of supersonic expansion in a sampler/skimmer system.[5][6][7] To continue this task, two other procedures were performed specifically for this thesis. First, the charged species component of the beam was measured, and second, the energy spectrum of the beam components was determined using a time-of-flight system constructed specifically for this purpose.
2.3 Measurement of the Charged Species Component of the Beam

The charged (ionized) species in the beam can dramatically change the way that the surface is eroded. The chemistry of ion interaction with polymers is quite different from the chemistry of radical interaction with polymers (AO is a radical). This is a critical fact since the oxygen ion concentration in LEO is very low. A number of effects, based on ion interaction, have been noted by researchers. Krech[8] points out that for fluorinated polymers the ion content of the bombarding species seems to have considerable effect on the erosion yield. Clearly the ion content of the UTIAS beam must be determined.

2.3.1 Charged Species Measurement System

The technique used to measure the charged species component is simple and explicit. If an electrical field is set up across the beam, at some voltage all of the ionized components will be diverted by the field onto the negative plate, causing a current to flow in the circuit. Figure 8 shows a schematic diagram of the setup.

Two aluminum flat plates, (10 cm high, 9 cm wide, 2 cm apart) were placed along the beam path, inside the test chamber, one on each side of the beam, 8 cm downstream of the skimmer orifice. A controllable voltage was applied across the plates using a DC power supply. A microampere (µA) resolution ammeter placed between ultimate ground and the negative plate measured the current generated by the ions striking the grounded plate.
When a positive voltage is applied to the plate connected to the power supply, positive ions will be deflected toward the grounded plate by the local electrical field between the plates. As the voltage increases, more and more ions will strike the grounded plate. Eventually, as the voltage reaches some high value, all of the ions in the beam will be hitting the grounded plate. When the ions strike the grounded plate a current will be generated through the ammeter to ground. This current, when accurately quantified, is an exact measure of the number of ions. Each $\mu$A is equivalent to $6.24 \times 10^{12}$ singly charged ions/sec.

2.3.2 Basic Assumptions

A few assumptions are, of course, required to allow an estimate of the number of ions to be made. First, it is assumed that the probability of forming doubly charged ions, such as $O^{++}$ or $O_2^{++}$, is very low. Second, it is assumed that He, Ar and entrained $N_2$ are not well ionized, and that they are efficiently neutralized during atmospheric discharge. Thirdly, it is assumed that the probability of forming $O^+$ and $O_2^+$ ions is the same.
Demonstrating that the probability of forming doubly charged ions is low, and that O will ionize before He, N₂, and Ar is a simple matter of examining ionization potentials. First and second ionization potentials are listed as follows:[9]

Table 2: Ionization potentials (eV) for the elements and compounds in the beam.

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>First Ionization</th>
<th>Second Ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.6</td>
<td>54.4</td>
</tr>
<tr>
<td>Ar</td>
<td>15.8</td>
<td>27.6</td>
</tr>
<tr>
<td>N₂</td>
<td>15.6</td>
<td>n/a</td>
</tr>
<tr>
<td>N</td>
<td>14.5</td>
<td>29.6</td>
</tr>
<tr>
<td>O₂</td>
<td>12.1</td>
<td>n/a</td>
</tr>
<tr>
<td>O</td>
<td>13.6</td>
<td>35.1</td>
</tr>
</tbody>
</table>

These values indicate that oxygen is preferentially ionized, since it has the lowest threshold energy in both the atomic and molecular forms. It is also quite clear that the second ionization potentials are much higher than the first ionization potentials for all of the species. The probability of producing doubly charged ions should be low, since the available energy would have to be at least two times higher, if a second electron is to be removed. In either case the assumption is a safe one, since it will result in an over-estimate of O⁺.

The final assumption, that O⁺ and O₂⁺ form equally likely, is not simple to estimate using kinetic or thermodynamic means in this case. This assumption can only be supported by relying on previous work where the assumption held true. Two cases are cited: Fite-Brackman[10], and Lam[11].

2.3.3 Results and Discussion of Charged Species Measurement

In all cases there was an initial negative current moving in the circuit. This indicates some negative potential in the chamber, to which the plates are coupling, or a grounding loop through the power supply circuitry. The exact nature of this potential was never
determined, but it appeared to be relatively constant whenever the supplied potential was set to zero, and the AO facility was operating. Therefore, all values reported were adjusted by the zero plate voltage measurement (net current) for that run. Slight variations in the zero plate voltage were noted to be coincident with natural low frequency oscillations and fluctuations in ambient conditions and the AO system parameters.

Figure 9, shows the adjusted measurements for two runs.

![Graph showing current vs. plate voltage](image)

**Figure 9:** Results of charged species measurement, current (\(\mu\)A) vs. plate voltage.

Each test run exhibits the same basic form. A rapid increase in current, to a peak in the 40 to 50 volt range, followed by a decrease of approximately 20% between 80 and 90 volts, and then a slow rise, levelling off above 250 V. The initial rise to a peak is expected as the voltage increases to a point where all of the ions are hitting the grounded plate. The relative voltages required to cause the ions to hit the plate can be predicted using the following equation (derived from the plate configuration):
Where:

- \( V_a \) is the voltage applied to the plates
- \( m_i \) is the mass of the ion
- \( d_p \) is the distance between the plates (2 cm)
- \( v_i \) is the velocity of the ion
- \( e \) is the charge on the ion
- \( l_p \) is the length of the plates (9 cm)

Using a singly charged atomic oxygen ion travelling at 5 km/s (2 eV), only 0.67 V are required for the ion to hit the furthest end of the plate, assuming that the field is uniform between the plates and does not extend beyond the edges of the plate. If the fastest atomic oxygen is assumed to be 7 m/s (4 eV), then 1.3 volts are required. A better scenario would be to have the ions hit the middle of the plate. Ions travelling 5 km/s would require 2.7 V, while those at 7 km/s require 5.2 V. Considering the voltages tested, it is fair to say that all of the atomic oxygen ions should be hitting the grounded plate. In reality, the voltages required will be higher than those calculated above since the field strength between the plates will not be uniform, and the initial ion paths will not be parallel to the plates, since the beam is diverging.

The decrease immediately after the peak was not expected. However, it can be theorized that this is caused by the fact that the field will project beyond the boundaries of the plates, causing the ions (when the voltage is very high) to miss the upstream edge of the plate. If the ions encounter the field 2 cm before the upstream edge of the plate, and the field strength remains constant outside the plates, 5 km/s ions will begin to miss the front at 16.6 V and 7 km/s ions will miss at 32.6 V. When it is realized that the field strength will be less outside the plate boundaries, the drop in current at 50 V may well be caused by this phenomenon.
The final slow rise to some stable current can be explained by the formation of an ionization region between the plates, set up by the high voltages. The system is producing new ions in the region between the plates. The value of the stable current is determined by the impedance of the ionized zone between the plates.

2.3.4 Total Number Estimates from Experiment Measurements

The total number of ions in the beam can be estimated by the current measured for each gas mixture. The average current measured at the \(~50\text{V}\) peak voltage was \(2.65\ \mu\text{A}\), which corresponds to \(1.66\times10^{13}\) singly charged ions.

2.3.5 Percent and Mole Fraction Estimates

Percentage of beam can be estimated using total molecular flow rate values derived from the gas flow analysis equations for this particular system mentioned earlier [7]. The equations give total molecular flow rate, and can be used to estimate the fraction of molecular and atomic oxygen in the beam and the flow rate of each that results. The molecular flow rates are in molecules per second. The \(\text{O}_2\) and \(\text{O}\) fractions are fractions of the total flow estimated using mass spectrometer data.[7] Flow rates are in molecules/second.

<table>
<thead>
<tr>
<th>Molecular Flow Rate</th>
<th>(\text{O}_2) Fraction</th>
<th>(\text{O}_2) Flow Rate</th>
<th>(\text{O}) Fraction</th>
<th>(\text{O}) Flow Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.498\times10^{19})</td>
<td>0.0092</td>
<td>(2.298\times10^{17})</td>
<td>0.0071</td>
<td>(1.780\times10^{17})</td>
</tr>
</tbody>
</table>

If only \(\text{O}_2\) and \(\text{O}\) are ionized, and if both are ionized to an equal extent, then the \(\text{O}^+\) flow rate can be estimated using the fractions as shown above. The mole fraction, \([\text{O}^+/(\text{O} + \text{O}^+)]\) is also shown.

<table>
<thead>
<tr>
<th>Ion Flow Rate</th>
<th>(\text{O}^+) Fraction of Ions</th>
<th>(\text{O}^+) Flow Rate</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.66\times10^{13})</td>
<td>0.436</td>
<td>(7.24\times10^{12})</td>
<td>(4.07\times10^{-5})</td>
</tr>
</tbody>
</table>
The fraction of charged species is obviously quite low. This was to be expected, considering that the design criteria for the system had this requirement, and that atmospheric expansion was employed for this purpose. It is also a strong validation of the LEO simulating capability of the system in terms of how it represents the very low charged species levels in that environment. These results also correspond well with recent results of comparison testing of FEP Teflon in various facilities and in LEO experiments. The erosion yield of FEP Teflon appears to be very sensitive to the mole fraction \( \frac{[O^+/(O^++O)]}{[O^+/(O^++O)]} \) as shown by Krech[8]. The erosion yield of FEP Teflon (5.1 to 9.3x10^-26 cm^3/atom) as measured in the UTIAS AO facility matches well with erosion yields measured in LEO (<5x10^-26 cm^3/atom)[12]. These LEO experiments reported oxygen ion mole fractions of approximately 1.0x10^-4.

2.4 TIME-OF-FLIGHT MEASUREMENT OF AO BEAM ENERGY SPECTRUM

Time-of-Flight (TOF) methods offer the best opportunity for measurement of this type of velocity/energy spectrum. The equipment required for experimentation is often quite simple and the basic method is well known and documented.[13] Time-of-flight systems in various manifestations have been used to characterize the velocity spectrum of beam sources, to characterize the inelastic and low energy reactive scattering of beam particles, and to analyze the mass distribution of particles in a beam. The UTIAS AO system was not designed with this task in mind, however. Because of the requirement for high AO flux, the system was designed for maximum pumping capability, so that high volumes of gas could be used to produce high AO fluxes. The requirements of a high pumping rate (i.e. no baffling results in some back-streaming of diffusion pump oil), and the high quality vacuum required for accurate time-of-flight mass spectrometry are not compatible. This fact required the design and development of a time-of-flight system and procedures that were quite specific to the UTIAS facility parameters. [14]
2.4.1 Time of Flight Principle

The TOF method is based on the simple principle that the velocity of individual beam particles will disperse the particles in space (distance) as time passes. That is, if a group of particles leaves one point in space at a given time, but with a range of velocities, at some time later, the positions of the particles relative to each other will be a direct function of the initial velocity conditions. In the TOF method, the flight time, \( t \), required for a beam particle to travel a predetermined flight path, \( L_f \), is measured. The velocity of this beam particle is then determined by using the simple expression \( v_b = L_f / t \). By measuring this flight time for a large number of particles, a spectrum of flight times develops. The velocity and energy distributions can be derived from the flight time distribution based on the parameters of the TOF system components.

2.4.2 System Components

Any TOF system requires a set of specific components to measure the velocity distribution for the species of a beam (figure 10). First, a system is required to modulate the incident beam. In this case a chopper wheel with two symmetric slits spins across the beam, blocking the beam except for the short interval when a slit passes across it. During this interval a short pulse of beam particles is sent in the direction of the detector. A modified quadrupole mass spectrometer head, using an electron multiplier in analog mode, is used as a detector for this system. The path length over which the particles travel is the distance between the chopper wheel and the detector. The maximum length of the flight path allowable in this chamber, is about 65 cm. The chopper was placed as close to the sampler/skimmer as possible and the detector was placed as far across the chamber as possible. This would allow the different velocities of the transmitted particles to yield a maximum spread in the arrival times at the detector.

The signal from the detector is amplified, converted to a set of pulses and directed to a multichannel scaler (MCS) device. This device collects the signal over a specific time window that is synchronized with the chopping of the beam, capturing only a signal from the particles of one pulse. The collection window can be repeated many times to build up a long
time-based picture of the pulses. In this manner, a very weak or noisy signal can be tolerated. The MCS effectively pulls the small signal out of the background, by averaging the random background noise over a long time period revealing any regular signal. This method was first used to decipher weak radio and sonar signals from background noise. The MCS outputs the time distribution, as directly collected by the detector system. Appendix A provides a more detailed description of each component and its function.

Figure 10: Schematic of the time-of-flight system component configuration.

2.4.3 Deconvolution of the Collected Data

The recorded distribution has been affected, in some way, by each of the components of the TOF system. These cumulative effects begin right from the start where the chopper wheel does not produce a perfect pulse, that is, a pulse where all of the particles leave the chopper at the exact same time. Further along, both the ionization zone of the QMS detector and the quadrupole mass filters themselves change the distribution. Once detected, the distribution is further altered by the performance characteristics of the electronic components of the detector before it is recorded by the MCS. The deconvolution of the distribution was done, for these experiments, using a FORTRAN program specifically developed for this TOF system.[14] The program and its method are outlined in Appendix A.
2.4.4 Time-of-Flight Results and Discussion

Prior to each operating session, the TOF system was aligned along the AO beam path using a laser alignment system. A laser was placed in the same position as the discharge tube of the Surfatron. The laser beam was directed through the interface orifice, past the chopper, and through the main chamber to a photodetector placed at the opening of the QMS head ionizer. The TOF system was started, and the synchronization pulse that signals the beginning of a beam pulse was adjusted to coincide with the pulse of light from the laser.

To measure a beam particle velocity spectrum, the facility was operated in its normal mode (97.3% He, 2.7% O₂, chamber pressure ~2.5x10⁻⁵ torr, microwave generator power 195 W). The facility was allowed to stabilize for about 30 minutes before any measurements were made. An aluminum flag was placed over the ionizer opening to block any flux into the QMS during this period. During the stabilization period the QMS and ionization gauges were degassed.

Once the AO facility was operating stably, the chopper wheel was set in motion at 15,000 RPM, the QMS was unflagged and set to collect ions of mass 16 for atomic oxygen, and the MCS was engaged.

During trial operations it was found that the best data sets were collected with AO beam pulse counts greater than twenty thousand, that is, twenty thousand pulses from the chopper wheel. Collecting more than twenty thousand pulses gave greater total counts but did not change the peak height to width ratio. This indicates that the back ground noise had been effectively removed from the signal. In addition it was observed, when the flag was closed, that some signal was detected. Since these particles appeared to be arriving at slower velocities than the main pulse, it is believed that scattered particles were entering the ionizer through the open sides of the ionizer structure. To compensate for this extra set of particles, which would have a different velocity spectrum from the in-line pulse, a back-ground signal was collected before each run and subtracted from the measured pulse signal. In total, 45 runs were carried out to verify the consistency of the system at various times with slightly
different conditions for all cases. A typical data collection is shown in figure 11 with the background signal already subtracted. The deconvolution program fit is also shown in the same plot.

The input system parameters to the deconvolution program were:

- Stagnation Temperature: 2800°K
- Mach Number: 3.2
- Avg. Molecular Weight: 4.2

which are reasonable values for this type of system. Figure 12 shows the corresponding energy distribution of the beam. This distribution has a maximum density at about 2.1 eV, and a significant proportion of AO atoms with an energy greater than 3 eV. This energy distribution corresponds well to the prediction by Morison et al[7] in a gas flow analysis of the UTIAS beam facility.

![Figure 11: Results of time-of-flight measurements. Number density of detected signal vs. time in μsec. Deconvolution program data fit results are superimposed.](image-url)
Figure 12: Energy distribution of AO beam determined from deconvolution of data in previous figure.

2.5 SYSTEM CHARACTERIZATION CONCLUSIONS

As tested here-in the UTIAS AO Beam Facility appears to simulate the AO degradation process that occurs in the LEO environment to a reasonable degree of accuracy. The charged species component was measured to be very low, comparable to the LEO environment as measured during Space Shuttle experiments. Although the mean energy of the beam was measured to be approximately 2.1 eV, there is a considerable fraction of AO having energies closer to the LEO value of 5 eV. In addition, comparison testing carried out previous to this work between the UTIAS facility, other facilities, and with LEO experiments, showed clearly that the erosion yields measured and the surface morphologies formed correspond well.
CHAPTER 3

CHEMICAL CONTENT AND STRUCTURE PARAMETER MODELS

When polymer materials are considered for use in LEO, the effect of hyperthermal atomic oxygen bombardment has become one of the foremost concerns. To alleviate some of this concern requires some type of comprehensive model that will allow prediction of polymer durability in the LEO environment. This model should be based on some simple characteristic parameter of the polymer that can be observed, measured or estimated. For example, it would be ideal if the erosion yield of a polymer was strictly dependent upon some unique property of the material (density for example) that can be easily measured, thus allowing one to easily determine the expected erosion yield of materials never employed before. Unfortunately, this scenario is overly simplified since no simple property has ever been defined as the primary determinant in surface interaction systems. However, the concept remains valid, even if it must be carried out using more complex property parameters. In addition to the concerns it may alleviate, this model, once defined, can also be used to expand the understanding of the HA0 interaction process that is occurring when a polymer erodes in LEO. This model has the potential to answer the all-important question of why some polymers erode faster than others.

When exposed to the LEO environment, carbon, graphite, and most hydrocarbon polymers (including graphite reinforced polymer matrix composites) have erosion yields in a range between 1x10^{-24} and 4x10^{-24} cm³/atom. Higher LEO erosion yield values for materials, such as PMMA and CR-39 [15][16], have also been published. This is an unexpected outcome, since TAO reaction yields are typically 3 to 4 orders-of-magnitude lower.[17] Clearly something other than the chemical reactive potential of the AO radical is involved in this degradation/erosion process.

At this point, some mention should be made of other types of polymer materials besides those traditionally called hydrocarbon polymers. Erosion yields for perfluorinated
polymers (DuPont's Teflon®) or silicone based polymers are generally two orders of magnitude lower than for hydrocarbons. This indicates that these polymers have significantly different erosion mechanisms: differences that may offer some insight into how the hydrocarbon degradation process works. With fluorinated polymers, oxidation of fluorine is thermodynamically difficult, which means that the side group C-F bonds act to protect the polymer chain. When silicone polymers are exposed to atomic oxygen, a passivating silica-like layer usually forms, blocking the material from further AO exposure. These fundamental differences in chemical content and structure point to a possible avenue of exploration. If chemical content and structure could be defined by some parameter, then maybe a correlation could be found. The difference in erosion yields between fluorinated/silicone polymers and hydrocarbon polymers also points to some interesting protective surface modification possibilities. The use of these two concepts (fluorine and silicon containing polymers) will be explored extensively in the second half of this thesis.

As a basic starting point for defining a relationship with reaction yield, it would be a good idea to look at the intrinsic chemical and physical structure of polymers and the differences in erosion yield that occur, as pointed out by the discussion of perfluorinated and silicone polymers above. Qualitative correlations or trends have been developed and discussed in plasma etching [18][19] and for erosion in plasma ashers [20][21]. They will be used as a foundation for the discussion that follows.

Based on an understanding of the state-of-art, it is clear that to develop such a correlation three major factors must be taken into account:

- how does the kinetic energy of the AO contribute to the process?
- what are the products (type and quantity)?
- what is the role of intramolecular oxygen* in the degradation process?

Some of the possibilities have been outlined previously with respect to AO degradation mechanisms of Kapton®.[17][15] Even with this information though, it is still difficult to

* intramolecular oxygen is the elemental oxygen that forms part of the chemical structure. For example, the oxygen in the Kapton® repeat unit (C_{22}H_{10}O_{2}N_{2}).
define which degradation processes and pathways are more likely to occur in LEO or in hyperthermal AO beams, let alone specify any commonality between polymers such as Kapton® or polyethylene, that have quite different structures. The polymers of interest have very different qualities in both a physical (structure, form etc.) and chemical sense (type of atoms, bonding strengths, etc) that could be effecting the reaction yield.

However, some facts can be stipulated; for example,

1) despite the complexity of the mechanisms of erosion, the fact remains that the basic components are the same. Hyperthermal AO hits a hydrocarbon polymer surface that is made up of carbon, hydrogen, oxygen and sometimes a few other heteroatom elements (N, S, Cl etc);

2) the bombardment causes destruction of the polymer, releasing carbon dioxide, carbon monoxide, water and sometimes methane, and heteroatom oxide products;[22]

3) since this is an oxidation process, oxygen in the structure will have some notable effect on the overall process. For example, strongly bonded groups, carbonyls (\(>\text{C}=\text{O}\)) for example, have higher bond energies (7.7 to 7.8 eV) than single carbon bonds (C-C, 3.6 to 3.9 eV), and would be more likely to survive bombardment.

With these facts in mind it should be possible to specify some relationship between reaction yield and the chemical and physical form of the polymer and at a minimum apply it to the LEO erosion yield data available. The number of experiments conducted in LEO is quite large, although the repeatability of the experimentation is low. Most of the experiments, if not all, have significant limits on the control, stability and monitoring of the environment while in orbit. For example, many experiments show significant contamination from organic materials released by the Space Shuttle and other spacecraft.[23] Because of this repeatability and comparability problem, it is clear that experimental verification of the model must also be performed. To that end, a controlled and self-consistent set of erosion yield measurements were carried out using the UTIAS Atomic Oxygen Beam Facility. This new erosion yield data will be used alongside LEO experiment data collected from recent literature to elucidate the effect of chemical content and structure in the sections that follow.
3.1 REACTION YIELD MEASUREMENTS

Testing of polymers to measure erosion rate was performed using a total mass loss method. This involves measurements before and after exposure using a single-tray balance accurate to ±10 micrograms. This measuring error translates into an erosion yield error of less than 1.3% of the measured value for Kapton®. Samples were outgassed in 10⁻⁶ Torr vacuum for two hours prior to exposure, then weighed. This eliminates most of the mass loss due to moisture outgassing. (see Appendix B) All samples were exposed to AO for a period of 5 hours, giving an average fluence of approximately 1.8x10²⁰ atoms/cm². A Kapton® control sample was exposed with each sample to estimate total fluence during the run, and to provide a consistent set of control samples to diagnose any systemic irregularities. Comparison to Kapton® is the basis for the determination of atomic oxygen flux. The fluence (atom/cm²) of the experiment is estimated from the measured mass loss of the Kapton® control, using a reaction yield of 3.0x10⁻²⁴ cm³/atom, which is the generally accepted value. The method of using Kapton® as a standard for fluence estimation and system calibration has become a standard for ground based LEO simulator operation.[24] A minimum of 3 samples were tested in each case, the reported erosion yield is an average of these. The number of samples tested was increased in some cases due to testing irregularities. Table 3 shows the results of the testing program for 10 polymers and graphite. The polymers were chosen based on their estimated reaction rate to include as wide a range as possible. Sample materials were obtained from various sources:

Graphite - Highly Oriented Pyrolytic Graphite (HOPG) from Union Carbide.
PEEK - Poly(ether ether ketone) - 10 mil sheets from Loughborough University of Technology.
Kapton® 500HN - 5 mil polyimide film sheets from DuPont
Polyethylene - 2 & 5 mil LLD film sheets from DuPont
PET - Poly(ethylene terephthalate) - 5 mil Mylar® 500EL film sheets from DuPont
Nylon 6,6 - 3 mil sheets from DuPont
PMMA - poly(methyl methacrylate) - 5 mil sheet cast from powder (Aldrich 18,224-9) using dichloromethane solvent.
PVA - Poly(vinyl acetate) - 8 mil sheet cast from beads (Aldrich 18,948-0) using toluene solvent.

PEO - Poly(ethylene oxide) - 2 mil sheet cast from powder (Aldrich 18,198-6) using chloroform solvent.

CR-39 - homopolymer from allyl diglycol carbonate monomer in 3 mm sheets from PPG Industries Inc.

Delrin - Acetal homopolymer - 3 mm Delrin 900 sheets from DuPont

PMMA, PVA and PEO film was cast by dissolving powdered polymer in an appropriate solvent, pouring a small amount of the solution into a petri dish, and allowing the solvent to evaporate. Once most of the solvent was evaporated, i.e. a relatively solid film was formed, further solvent removal was done by heating to 50°C in an oven for 2 hours. The samples were subsequently exposed to high vacuum (<10⁴ torr) for 6 hours to remove as much solvent as possible.

Table 3: AO Testing Results for Polymer Materials and Graphite (see Appendix C for data)

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction Yield (cm³/atom)x10⁻²⁴</th>
<th>Range (cm³/atom)x10⁻²⁴</th>
<th>Density (g/cm³)</th>
<th>Samples Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1.2</td>
<td>1.13 - 1.27</td>
<td>2.2</td>
<td>3</td>
</tr>
<tr>
<td>PEEK</td>
<td>2.2</td>
<td>2.10 - 2.28</td>
<td>1.32</td>
<td>4</td>
</tr>
<tr>
<td>Kapton® (Polyimide)</td>
<td>3.0</td>
<td>—</td>
<td>1.42</td>
<td>—</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3.2</td>
<td>2.87 - 3.71</td>
<td>1.10</td>
<td>4</td>
</tr>
<tr>
<td>PET (Mylar)</td>
<td>3.9</td>
<td>3.72 - 4.00</td>
<td>1.37</td>
<td>4</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>4.4</td>
<td>4.04 - 4.74</td>
<td>1.12</td>
<td>4</td>
</tr>
<tr>
<td>PMMA</td>
<td>4.8</td>
<td>4.48 - 5.15</td>
<td>1.29</td>
<td>6</td>
</tr>
<tr>
<td>PVA</td>
<td>5.2</td>
<td>4.96 - 5.38</td>
<td>1.06</td>
<td>4</td>
</tr>
<tr>
<td>PEO</td>
<td>5.7</td>
<td>5.21 - 6.22</td>
<td>1.00</td>
<td>4</td>
</tr>
<tr>
<td>CR-39</td>
<td>6.5</td>
<td>6.37 - 6.65</td>
<td>1.32</td>
<td>8</td>
</tr>
<tr>
<td>Delrin (Acetal)</td>
<td>9.5</td>
<td>9.09 - 10.13</td>
<td>1.42</td>
<td>3</td>
</tr>
</tbody>
</table>
Each sample required a total time of eight hours to complete. Since the erosion yield of Kapton® is considered to be a fixed value, no specific testing of Kapton® was carried out.

3.2 RELATIONSHIPS - CONTENT/STRUCTURE AND EROSION YIELD

To further specify a model that accounts for the differences in erosion yield, an alternative frame of reference is required. Traditionally, the direction taken has been to define the process of HAO interaction as a problem in organic chemistry, that is, akin to atmospheric oxidative degradation for example. The procedure has been to, 1) propose reaction mechanisms, and then, 2) incorporate the additional energy provided by kinetic energy exchange process into the oxidation scheme as a bonus energy or initiation source, increasing initiation probability through increased activation potential, for example. Is there anything wrong with this approach? No, it is entirely valid and very useful for individual polymers. However, when hydrocarbon polymers are viewed as a whole, it becomes difficult to provide logical extensions from one polymer to another, given the specificity of the process to that particular polymer. The initiation, propagation and termination concepts may apply; but how do they manifest themselves commonly in polymers that are so different? If, however, the problem is viewed as an enhanced-physical-sputtering-like process, other possibilities emerge.

Here is the framework. Physical sputtering is the ejection of particles (atomic or molecular) from the surface of a material due to impact from other particles. For example, a 1000 eV (22 km/sec) argon atom hits a graphite surface, knocking a carbon atom out of the structure with 100 eV of energy. In the case of low earth orbital AO bombardment, though, the kinetic energy (5 eV) of the oxygen atom is not sufficient to cause physical sputtering. However, mass loss does occur, so it must be that the thermodynamic potential of the oxygen atom to oxidize a carbon or other atom, is added to the available kinetic energy. Given this extra potential, there is enough energy in the system to cause the formation of volatile products, resulting in mass loss.
To further specify this alternate frame of reference model, one can regard the thermodynamic potential, and the kinetics that result (the chemical reactions), as a form of "black box". In other words, the energy of impact initiates the process and the result, after passing through the "black box", is the products (CO, CO₂, H₂O, etc). Remember, the goal here is to avoid dealing with for the moment, if possible, what happens inside the black box, because it may be quite different for each polymer, and non-related. The common process path for all polymers, as defined in this frame-work, is as follows:

\[ \text{HAO} \rightarrow \text{impact/interaction with surface} \rightarrow \text{chemical reactions} \rightarrow \text{volatile products} \]

Using this frame-work there are only three possible ways to define a relationship with reaction yield. Yield is related to the impact process or the chemical reaction process, or both together. To further develop the simplification, if the energy, flux and other parameters of the impacting species are kept constant (ie. control of experimental conditions), then the effects due to the impact process can be greatly simplified. What we are left with is just the energy exchange process and the black box. The only areas that offer any range of differentiation are the initial energy exchange processes themselves (ie. how is the kinetic energy of the incoming oxygen atom used), and the effects of the specific composition of the materials involved: what goes in and what comes out of the black box and how they relate to each other (phase, density, elemental composition, bonding configuration etc.) The energy exchange process and the chemical reaction "black-box" will each be examined in turn.

### 3.2.1 The Energy Exchange Process

The energy exchange process we are dealing with can be delimited, to some extent, by a reaction probability. That is, an incoming oxygen atom has a finite probability of reacting with the surface atoms to produce a volatile product. If control is exerted over variations in erosion yield due to flux, fluence, and energy, by performing a comprehensive set of tests in a common environment, any variation in reaction probability should be the result of the state of the material only. In other words, atomic oxygen will interact
differently with each polymer based on the material's intrinsic initial state, or its stable reacting state, and this difference should give each material a specific reaction probability. Taken to another extreme, if the reaction probabilities are strongly related to some factor such as particle energy, which is completely independent of material properties, then it will be found that the reaction probabilities are strongly related. Dominant non-material effects will result in similar reaction probabilities for all materials.

Reaction probability has been discussed previously with respect to Kapton® in an AO environment. Banks[25] defined a simple extensive reaction probability for Kapton® based on a calculation of the number of atoms of atomic oxygen required to reduce a repeating unit of Kapton® to small volatile oxide species (CO₂, CO, H₂O, etc). He concluded that HAO has a reaction probability of approximately 13% with Kapton®. Using the same basic concept, a hypothetical ultimate reaction yield (Rₚ°), and an apparent reaction probability (p_r), can be calculated for each of the test polymers and compared to the measured reaction yields. It is assumed that only simple oxides will form, and that hydrogen becomes water. In addition the intramolecular oxygen is assumed to react with its neighbouring carbons to produce CO.

A sample calculation of Rₚ° and p_r, for a Kapton® repeat unit is shown:

Kapton®: C₂₂H₁₀O₅N₂
Reaction products: CO, H₂O, NO (simple oxides only, ie. no CO₂)
Oxidation produces: 22 CO, 5 H₂O, 2 NO

Total mass oxidized: 22(12) + 10 + 5(16) + 2(14) = 382 amu = 6.34x10⁻²² g

Oxidation requires: (using the available intramolecular oxygen)
\[ 29 - 5 = 24 \text{ atomic oxygens} \]

This gives an \( R_{p°} = \frac{6.34x10⁻²²}{24} = 2.64x10⁻²³ \text{ g/atom} \)
(\[ \text{using} \ \rho = 1.42 \] \[ \text{= 1.86x10⁻²³ cm}³/\text{atom} \]

\( p_r \) can be calculated using the measured \( R_p° \):
\[ \frac{3.0x10⁻²⁴}{1.86x10⁻²³} = 0.161 \]
$R_c^o$ is the ultimate yield because it results from using a reaction probability of one, that is, when all of the incoming atoms react with some part of the polymer. Table 4 shows the results of the calculations for the 10 polymers and graphite. Figure 13(a) presents the measured reaction yields of the 10 polymers and graphite vs. their ultimate reaction yield ($R_c^o$). Figure 13(b) shows the measured reaction yields along with the calculated reaction probabilities for each of the materials tested.

Table 4: Calculated values of ultimate erosion yield ($R_c^o$) and reaction probability ($p_r$)

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Formula of Repeat Unit</th>
<th>$R_c^o$ ($\times 10^{-24}$ atoms/cm$^3$)</th>
<th>$p_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>C</td>
<td>9.1</td>
<td>0.13</td>
</tr>
<tr>
<td>PEEK</td>
<td>C$<em>{19}$H$</em>{12}$O$_3$</td>
<td>16.5</td>
<td>0.13</td>
</tr>
<tr>
<td>Kapton$^\circ$</td>
<td>C$<em>{22}$H$</em>{10}$O$_5$N$_2$</td>
<td>18.6</td>
<td>0.16</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>CH$_2$-CH$_2$</td>
<td>11.6</td>
<td>0.28</td>
</tr>
<tr>
<td>PET (Mylar)</td>
<td>C$_{10}$H$_8$O$_4$</td>
<td>23.3</td>
<td>0.17</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>C$<em>{12}$H$</em>{22}$O$_2$N$_2$</td>
<td>14.6</td>
<td>0.30</td>
</tr>
<tr>
<td>PMMA</td>
<td>C$_3$H$_8$O$_2$</td>
<td>21.6</td>
<td>0.23</td>
</tr>
<tr>
<td>PVA</td>
<td>C$_4$H$_9$O$_3$</td>
<td>26.0</td>
<td>0.20</td>
</tr>
<tr>
<td>PEO</td>
<td>C$_2$H$_4$O</td>
<td>24.4</td>
<td>0.23</td>
</tr>
<tr>
<td>CR-39</td>
<td>C$<em>{12}$H$</em>{26}$O$_7$</td>
<td>23.2</td>
<td>0.28</td>
</tr>
<tr>
<td>Delrin</td>
<td>CH$_2$O</td>
<td>35.6</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Figure 13(a): Measured reaction yield of 10 polymers tested ($R_e$) vs. calculated ultimate reaction yield ($R_e^\circ$). Error bars indicate range of data measured for each material.

Figure 13(b): Measured reaction yield of 10 polymers tested ($R_e$) vs. calculated reaction probability.
The plot of ultimate yield \( (R_e^o) \) has a somewhat linear trend with some variation of the middle values. The linear regression line shown has an equation of \( R_e = -1.02 + 0.27R_e^o \) and a correlation coefficient of 0.89. For all of the regression plots using the 10 polymers and graphite, the null hypothesis that the population of dependent and independent variables has zero correlation has a 5% critical value of 0.553 and a 1% critical value of 0.684. A correlation coefficient value less than the critical values would indicate probabilities higher than 1% or 5% that the regression equation calculated has a zero correlation to the data.

Unfortunately, in this case, the linearity of the data appears to be skewed by the graphite and Delrin data points. The data points at the centre of the plot have a mild tendency toward an increase in \( R_e \) with increasing \( R_e^o \), but this tendency is moderated by some other unknown strong effects. These effects are illustrated by, for example, the small difference in \( R_e \) between polyethylene (PE) and Mylar (PET) despite a large difference in \( R_e^o \). The reaction probabilities further demonstrate this point.

In figure 13(b) it can be seen that all of the reaction probabilities fall between 0.13 and 0.30. Although the reaction probabilities are relatively low overall, there is a two times difference in the extrema. This means that, from the point of view of the incoming atomic oxygen, there are some substantial differences between polymers. Remember that this data was collected under consistent conditions of AO flux, fluence, energy, and direction; so, essentially, the atomic oxygen atoms were identical for all polymers. Yet, the probability of a given atomic oxygen reacting could double depending on whether it hit a PEEK surface or a Nylon surface. All that can be concluded here is that there are some strong effects that are dictated by the initial state of the material, as demonstrated by the application of the \( R_e^o \) and \( p \) parameters.

Clearly the reasons for the trend in reaction probability deserve further investigation. Unfortunately this brief discussion is the limit to which this line of exploration can be taken at this time. To explore this significant difference in reaction probability, reaction product scattering energy and angle experimentation must be employed. It would be important to look at the type of products produced and the energies they leave with, for the full range of
polymers. Using the calculated reaction probabilities as a starting point, the differences in products and energies should reveal the dominant mechanisms of interaction and energy exchange. However, it is clear that there are some considerable effects that are driving what should be similar systems, given the experimental conditions, to have quite different reaction probabilities, and that these effects appear to be related to the material state of the polymer, rather than the energy exchange factors such as energy, flux, etc..

3.2.2 The Chemical Reaction "Black-Box"

Because of the limits placed by the black box assumptions, this becomes a mass balance problem. Only the form of the incoming and outgoing components can affect the reaction yield. It can be said then, that there are a certain number of atoms in the polymer structure repeating unit (i.e. Kapton® is C25H17O3N2), and if these atoms are to be oxidized it will take a certain number of oxygen atoms to do it. The faster the oxygen atoms are delivered the faster the products will be formed, all other things being equal.

There are a number of ways in which an AO particle may interact differently, delivering the oxygen to the mass balance at different rates. For example, with one type of material, there may be a certain chemical bond that is highly susceptible to interaction with AO, while in another material all bonding sites are essentially the same (compare Kapton® to polyethylene) The reaction probability of any given AO particle will be higher if it strikes that susceptible location, resulting in more rapid initiation of the chemical processes, with respect to the number of impacts. Alternately, it may be purely a structural consideration that gives a specific yield value. This might occur if the structure has many stable side groups that physically block the AO from interacting with weaker bonds.

It may even, in fact, be the microscopic structure (surface morphology) that gives a certain erosion rate. Both Tennyson[26], and Nikiforov and Skurat[27] concluded that variations in the rate of erosion at the beginning of a ground based test in an atomic oxygen beam facility was due to the setup of surface morphology. At the beginning of an AO exposure test, the surface is smooth. In the first few minutes of a test a carpet-like surface
morphology forms. During the time that it takes to establish this morphology, the reaction rate increases. It is believed that the roughness of the surface increases the probability of interaction with the AO particles by: 1) increasing the surface area, 2) causing multiple reflective surface encounters within the valleys of the structure.

Finally, it may also be that the relative composition of the polymer effects the rate, since all elements in the molecule would not react with oxygen in the same way. C-C bonds, for example, are quite strong compared to C-N bonds. It will take more energy and, possibly, time to oxidize a C-C bond. Consequently, if the ratio of C to N atoms in the molecule is high, there will be more weak bonds compared to a molecule that has a very low C to N ratio. This could manifest itself as a higher erosion yield for the molecule with many C-N bonds. This effect is somewhat akin to the situation defined by a rate-law expression, for example, Rate = k[A]. Where, k is the rate-constant and [A] is the concentration of reactant A. As the concentration of A changes the rate of reaction will change. In the case of a liquid or gas mixture reaction, the concentration of the reactant would decrease as the reaction continues, decreasing the reaction rate proportionally as [A] approaches zero. For surface interactions the concentration of a reactant would not, in all likelihood, change during the reaction, but instead the concentration would be fixed by the initial state or stable reactive state of the material. For example, the relative concentration of carbon in a material is diluted by the presence of nitrogen in the structure, which may give that polymer a higher reaction rate than one that has no nitrogen in it. Since carbon forms the foundation of hydrocarbon polymers, it is important to first look at the effect of relative carbon concentration on the reaction yield.

3.2.3 The Beta Parameter - the effect of relative carbon content

By using the experimentally determined reaction yield data, the effect of the relative number of carbon atoms can be demonstrated. The relative number of carbon atoms is \( \beta = N_T/N_C \), where \( N_T \) is the total number of atoms in the repeating unit of the polymer and \( N_C \) is the number of carbon atoms in the repeat unit. \( \beta \) is chosen to be related to \( 1/N_C \) for convenience since we want \( R_c \propto \beta \) and the it is assumed that \( R_c \propto 1/N_C \) (higher carbon content
gives lower reaction yield). Table 5 shows the beta parameter values for all of the materials. Figure 14 illustrates the effect of carbon content quite clearly.

Table 5: Calculated beta parameter values of tested materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction Yield (cm³/atom) x 10⁴⁴</th>
<th>Chemical Formula of Repeat Unit</th>
<th>Beta (β)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1.2</td>
<td>C</td>
<td>1</td>
</tr>
<tr>
<td>PEEK</td>
<td>2.2</td>
<td>C₁₅H₁₂O₃</td>
<td>1.8</td>
</tr>
<tr>
<td>Kapton®</td>
<td>3.0</td>
<td>C₂₂H₁₀O₅N₂</td>
<td>1.8</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3.2</td>
<td>CH₂-CH₂</td>
<td>3.0</td>
</tr>
<tr>
<td>PET (Mylar)</td>
<td>3.9</td>
<td>C₁₀H₈O₄</td>
<td>2.2</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>4.4</td>
<td>C₁₂H₂₂O₂N₂</td>
<td>3.2</td>
</tr>
<tr>
<td>PMMA</td>
<td>4.8</td>
<td>C₁₂H₂O</td>
<td>3.0</td>
</tr>
<tr>
<td>PVA</td>
<td>5.2</td>
<td>C₅H₆O₂</td>
<td>3.0</td>
</tr>
<tr>
<td>PEO</td>
<td>5.7</td>
<td>C₄H₄O</td>
<td>3.5</td>
</tr>
<tr>
<td>CR-39</td>
<td>6.5</td>
<td>C₁₈H₂₀O₇</td>
<td>3.3</td>
</tr>
<tr>
<td>Delrin</td>
<td>9.5</td>
<td>CH₂O</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 14: Measured erosion yield data for 10 polymers and graphite vs. their calculated $\beta$ values. Indicates the effect of relative carbon content.

As the relative carbon content increases the reaction rate decreases. Compare Delrin® ($\text{CH}_2\text{O}$) with $\beta=3.3$, to PEEK ($\text{C}_{19}\text{H}_{20}\text{O}_3$) with $\beta=1.8$. The reaction rates vary in what appears to be a roughly linear fashion with the $\beta$ value. A linear regression fit of the data gives the equation $R_e = -1.47 + 2.22\beta$, with $r=0.88$. Considerable scatter is evident for some of the middle range values of $\beta$ where, for example, there is a large difference in measured erosion yield between polyethylene and CR-39, while the beta values are quite close, and although Kapton® and polyethylene have similar reaction yield values their beta values are quite different. Using the factors introduced at the beginning of this chapter (see page 30), and observing that the largest deviation from the beta correlation line occurred with the only polymer in the group that does not have oxygen in its structure (polyethylene), it is possible to further refine the model.
3.2.4 The Gamma Parameter - the effect of intramolecular oxygen

In the introduction to this chapter a number of facts were stipulated. One of the simplest facts observed was that this is, indeed, an oxidizing reaction that involves oxygen, and since many of the polymers of interest have oxygen in their structure, it is likely that this oxygen will play some role in defining the erosion yield. In addition to the references cited in the chapter introduction, analogies to this line of reasoning can be found in the well-studied areas of polymer combustion[18] and plasma stripping[28].

Using the beta parameter as a starting point, a refined parameter that accounts for the effect of intramolecular oxygen can be formulated. Following the logic set out by Gokan et al.[19], the number of carbon atoms in a unit volume of a polymer is given by:

\[
\frac{\# \text{ of C atoms}}{\text{unit volume}} = \frac{\rho}{M} \frac{N_C}{N_T} \frac{N_C}{N_T}
\]

where: \( \rho \) is the density of the polymer,
\( M \) is the molecular weight of the polymer repeat unit,
\( N_C \) is the number of carbon atoms in the polymer repeat unit,
\( \bar{M} \) is the average atomic weight of the atoms in the unit,
\( N_T \) is the total number of atoms in the unit.

From the arguments presented along with the beta parameter the erosion rate must be inversely proportional to the amount of carbon in the repeat unit, which means that the erosion yield can be described as:

\[
R_e \propto \frac{\bar{M}}{\rho} \frac{N_T}{N_C}
\]

To account for the role of intramolecular oxygen in the structure, some consideration must be given to what happens to it, that is, what its final form will be. Intramolecular
oxygen is already bonded to atoms in the molecule and will form the simplest volatile species it can, based on that bonding structure. Under oxygen plasma etching conditions, Gokan[19] assumed that the intramolecular oxygen was removed through decarbonylation, the formation of CO. It seems likely that this is a good first approach, so it follows then, that the number of carbons available to react with incoming AO is reduced one per one with the number of oxygens present in the structure. In other words, the erosion yield depends on the "effective" number of carbon atoms that can be oxidized in reactions with incoming oxygen flux and be "removed" as final products. Each oxygen in the structure will remove some carbon, hydrogen, or a heteroatom from the structure, increasing the yield per incoming oxygen atom.

Using Kapton® as an example, the breakup products can be examined to illustrate the intramolecular effect. The repeat unit of Kapton® has the formula C22H16O3N2. If the structure is completely oxidized the following products can be produced:

Using intramolecular oxygen: 5 CO
Using bombarding oxygen: 17 CO, 10 H2O, 2 NO

Only 4 of the 5 intramolecular COs can be predicted with any great certainty. As will be shown in the following chapter, four carbonyl groups are present in the Kapton® structure, and based on the strength of the C=O bond, it is likely that these groups will remain intact. Assuming then that intramolecular decarbonylation occurs, the effective number of carbons is reduced to Nc - No, where No is the number of oxygen atoms in the repeat unit. That is:

\[ R_e \propto \frac{M}{\rho} \cdot \frac{N_T}{N_c - N_o} \tag{3.3} \]

It has been noted that for photoresist polymers \( \frac{M}{\rho} \approx \text{constant} \)[19] If this approximation holds true for the polymers tested and typically used in spacecraft applications, then:

\[ R_e = \text{constant} \cdot \frac{N_T}{N_c - N_o} = \text{constant} \cdot \gamma \tag{3.4} \]

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giving:

\[ \gamma = \frac{N_r}{N_c - N_o} \]

What does this relationship mean in terms of the content and structure? As defined, it is the embodiment of the two stipulated assumptions and two direct corollaries:

Assumptions:
1) \( R \) is inversely proportional to the number of carbon atoms in the molecule,
2) the number of effective carbons is reduced because intramolecular oxygen reacts with other atoms in the molecule

Corollaries:
1) The reaction rate is higher when carbon atoms make up a smaller portion of the polymer repeat unit. \((\beta)\)
2) The reaction rate is higher when there are similar numbers of carbon and oxygen atoms. \((\gamma)\)

There is an implication here that it is not the weakest link in the polymer chain which is determining the erosion rate; but, that it is the strength of the carbon-carbon bond which is setting the rate, where traditionally the weakest links have made that determination. This is not true, however. The discussion above focuses on the relative quantities of carbon present, but really the driving force is the "dilution" of the quantity of carbon. This dilution of the carbon backbone in the polymer is what (essentially) differentiates one reaction rate from another; is specified by the corollaries, and is demonstrated in the first case, by applying the beta parameter. Incorporating the effect of intramolecular oxygen content should refine this broad carbon content effect. The gamma parameter is the next logical step in this refinement.
Erosion yield data from LEO experiments collected from multiple sources and plotted with reference to the gamma parameter have been reported in [29][30], and are updated and repeated in figure 15 below.

![Figure 15](image)

**Figure 15:** Reaction yield data collected from various low earth orbit experiments shown plotted against their gamma function value, illustrating the strong linear trend.

From this first application of the gamma parameter it can be seen that there is a clear linear relationship. For the materials with a gamma value less than 5, the regression line is specified by the equation: \( R_e = 0.01 + 1.1\gamma \) with a correlation coefficient, \( r = 0.94 \). The 5% critical value for the regression is 0.532 and the 1% value is 0.661. All of the materials with \( \gamma \) less than five appear to fall within \( 0.5 \times 10^{-24} \) atom/cm\(^3\) of the best fit line. At higher gamma values however, where the data is less certain; PMMA and CR-39 have erosion yield values considerably less than the predicted value.

Much of the scatter in LEO measured values is, as previously mentioned, easily attributed to the variable conditions and limited control of the experiments performed in LEO. In the ground based testing program performed for this thesis, all of the materials
were exposed to the same conditions of AO flux, temperature, pressure and possible contamination. Since the gamma parameter defines trends in erosion rate with respect to polymer characteristics, the trend should be more clearly defined when all samples are treated equally.

The results as obtained using the AO beam facility for the set of 10 polymers, plus graphite, are shown vs. their gamma parameter values in figure 16. One of the polymers tested, DuPont’s Delrin®, is not shown in the gamma parameter figures. Delrin was of specific interest since it has a gamma value of infinity: its structure has an equal number of carbon and oxygen atoms. Table 6 gives the formulas and calculated $\gamma$ values for the polymers tested.

Table 6: Measured reaction yields, formulas, and calculated gamma values of tested materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction Yield (cm$^3$/atom)x10$^{24}$</th>
<th>Chemical Formula of Repeat Unit</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1.2</td>
<td>C</td>
<td>1</td>
</tr>
<tr>
<td>PEEK</td>
<td>2.2</td>
<td>C$<em>{19}$H$</em>{13}$O$_3$</td>
<td>2.1</td>
</tr>
<tr>
<td>Kapton®</td>
<td>3.0</td>
<td>C$<em>{22}$H$</em>{10}$O$_5$N$_2$</td>
<td>2.3</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3.2</td>
<td>CH$_2$-CH$_2$</td>
<td>3</td>
</tr>
<tr>
<td>PET (Mylar)</td>
<td>3.9</td>
<td>C$_{10}$H$_8$O$_4$</td>
<td>3.7</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>4.4</td>
<td>C$<em>{12}$H$</em>{22}$O$_2$N$_2$</td>
<td>3.8</td>
</tr>
<tr>
<td>PMMA</td>
<td>4.8</td>
<td>C$_5$H$_8$O$_2$</td>
<td>5</td>
</tr>
<tr>
<td>PVA</td>
<td>5.2</td>
<td>C$_4$H$_6$O$_2$</td>
<td>6</td>
</tr>
<tr>
<td>PEO</td>
<td>5.7</td>
<td>C$_2$H$_4$O</td>
<td>7</td>
</tr>
<tr>
<td>CR-39</td>
<td>6.5</td>
<td>C$<em>{12}$H$</em>{26}$O$_7$</td>
<td>7.8</td>
</tr>
<tr>
<td>Delrin</td>
<td>9.5</td>
<td>CH$_2$O</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

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The linear regression best fit has an equation of $R_e = 1.03 + 0.72\gamma$, with a correlation coefficient of 0.98, and as shown, even the highest erosion yield values are estimated very well by this relationship.

![Graph of measured erosion yield values for 10 polymers and graphite plotted vs. their gamma function values. The consistent testing program resulted in an excellent linear correlation.](image)

**Figure 16:** Measured erosion yield values for 10 polymers and graphite plotted vs. their gamma function values. The consistent testing program resulted in an excellent linear correlation.

It is evident from figure 16 that the gamma parameter is a powerful tool for predicting erosion yields. The accuracy of the gamma parameter in predicting the erosion yields of the tested polymers also verifies some of the assumptions made in deriving it. Most importantly, the assumption that the carbonyl CO bond remains intact, is supported quite strongly by these results.
3.3 STRUCTURE/CONTENT MODEL CONCLUSIONS

The results of a materials testing program designed to explore the effects of hydrocarbon polymer chemical content and structure show good consistency with measured values in LEO experiments. At higher $\gamma$ values the trends for $R_e$ in LEO are still unclear, although the ground based testing program indicates that there may be other factors (experiment control, contamination in LEO) that give the variation in $R_e$ values, rather than some fundamental variation from the assumptions made in deriving the gamma parameter.

From an analysis of erosion of graphite and organic polymers, in LEO and in a ground based testing program, a number of useful relationships has been shown to exist between $R_e$ and parameters that describe some aspect of chemical content and structure. In particular, a relationship between $R_e$ and an "effective carbon" chemical content number ($\gamma$) has proven to be highly accurate in predicting the erosion yield of polymer materials.

Not only are these parameters useful engineering tools, but they also indicate clearly that the chemical content and structure of the polymer and the initial conditions of the material-atomic oxygen interaction are critical in determining the rate of erosion. In the next chapter the effect of intramolecular oxygen will be used to help define a reaction scheme for Kapton® degradation in LEO.

Based on the results of the reaction probabilities defined, it also seems apparent that a close look at the effects of the initial energy exchange interaction would be an ideal topic for further work. This research would help to develop a clearer picture of the processes that result in the measured erosion yield numbers, and to elucidate on the particular roles that kinetic energy exchange and thermodynamic driven chemical reactions play, individually and together in the HAO interaction process.
CHAPTER 4

ORGANIC POLYMER DEGRADATION IN LOW EARTH ORBIT

For more than a century now, organic polymers have been used in an ever expanding array of applications, but it was really not until the 1950's that the science of polymer degradation began to emerge. Since then a great deal of effort has been expended to understand and inhibit the degradation of polymers. Degradation can be defined as any undesirable change in the properties of a material. This change can take many forms, ranging from simple mechanical wear to complex chemical enhanced kinetic energy exchange erosion. Within the atmosphere of our planet many of the "elements" present contribute to the destruction of organic polymers in some way: atmospheric oxygen and moisture perform chemical attack, sunlight causes damage due to ultraviolet radiation as well as by heat build-up from infrared absorption, smog and ozone enhance atmosphere oxidation, bacteria even feed on the organic substances of the material.

Attack by oxygen is the primary reason for polymer degradation. It is often the combination of a variety of effects which causes the degradation to occur; for example, UV radiation and oxygen, or heat build-up and oxygen. For space applications near Earth (in LEO), oxygen again plays the same essential role in degrading organic polymers. Only limited work has been done to study the exact form of this surface chemical reaction system, but some analogies can be drawn to the well studied degradation of polymers by thermal energy molecular oxygen.

In the sections that follow, the work "thermal" will be used in two senses. It will continue to be used in the case of "TAO", atomic oxygen with thermal kinetic energy, and in addition it will be used when talking about "thermally induced degradation". In the second case, the word thermal refers to temperature and temperature change specifically. Thermally induced degradation occurs as the temperature of the material increases to a point where the energy input (as heat) exceeds the threshold energy requirement of the degradation reaction.
4.1 OXIDATION OF POLYMERS BY MOLECULAR OXYGEN

Thermally induced oxidation of polymers is typically a sequential process of three steps:

Initiation: The production of polymer radical sites - \( P^* \)

\[
\begin{align*}
\text{Propagation:} & \quad P^* + O_2 \rightarrow PO_2^* \\
& \quad PO_2^* + PH \rightarrow POOH + P^* \\
\text{Termination:} & \quad 2P^* \rightarrow P-P \\
& \quad PO_2^* + P^* \rightarrow POOP \\
& \quad 2PO_2^* \rightarrow \text{inactive products}
\end{align*}
\]

In all steps the process proceeds through the production and interaction of radicals. Radicals are species that contain unpaired electrons, and they are generally quite reactive. Degradation of polymers is almost exclusively a radical interaction process. The degradation can be initiated in a variety of ways. The \( P^* \) radical is often generated by heat or light energy that initiates the reaction:

\[
PH \rightarrow P^* + H^*
\]

where \( PH \) represents the polymer chain, \( H \) is the most labile hydrogen and \( P^* \) is the polymer molecule chain with a radical site. Oxygen can also produce polymer radicals, for example:

\[
PH + O_2 \rightarrow P^* + \cdot OOH
\]

During propagation, the radicals formed in the initiation step produce new radicals through reactions with oxygen (4.1) and hydrogen abstraction (4.2). Hydrogens are abstracted both from sites on new polymer chains and from other locations on a molecular chain already affected. Many new radical sites can be formed by a process such as chain branching where the hydroperoxide molecule decomposes. These new radicals can do even more damage:

\[
\begin{align*}
\text{POOH} & \rightarrow \text{PO}^* + \cdot \text{OH} \\
\text{PO}^* + PH & \rightarrow \text{POH} + P^* \\
\cdot \text{OH} + PH & \rightarrow \text{H}_2\text{O} + P^*
\end{align*}
\]
Termination occurs as an ongoing process while the polymer degrades; that is, termination and initiation compete continuously. The degradation rate will generally depend most strongly upon the efficiency of the chain branching reaction. Termination reactions depend strongly on the environment conditions; for example, $P^\ast$ radicals do not exist in large quantities when oxygen is present. This means that termination reaction 4.5 is the most common termination step for atmospheric oxidation. Termination is used as the basis for the most common method of stopping oxidation. Polymers are often doped with anti-oxidants, organic molecular compounds with a particular capacity to react with radical sites. They terminate any radical sites initiated, stopping propagation.

No mention has yet been made of the exact products formed during oxidation. In general the products and their proportions depend on the particular situation. Looking at a specific example will give the best indication of the results of oxidation, and will help to introduce the polymer of significant interest to this thesis, DuPont’s Kapton®. Kapton® is widely used in spacecraft applications. It is employed as a structural substrate onto which solar cells are bonded. It is also used, when coated with aluminum on one side, as a thermal control blanket.

4.2 Oxidation of Polyimides

Kapton® HN is a polyimide. Polyimides are organic polymers that contain cyclic imide groups in their main molecular chain. They maintain both strength and flexibility at high and low temperatures, and are well suited for use in spacecraft applications. Kapton® is prepared by reacting an aromatic tetracarboxylic acid dianhydride with an aromatic diamine. Kapton® HN is formed using pyromellitic dianhydride (PMDA) and oxydianiline (ODA).
Kapton® is usually produced in a two-step process that starts with the synthesis of a soluble precursor, poly(amic acid) (PAA). PAA is formed by combining PMDA and ODA in a polar solvent. The precursor can be cast into the required form at this stage. In the second step the polymer is imidized (the cyclic imide groups are formed) through the removal of a water product by heating:

\[
n \text{PMDA} + n \text{ODA} \rightarrow \text{Polyamic Acid}\n\]

\[
\text{H}_2\text{O} \rightarrow \text{Polyimide - Kapton}\n\]

### 4.2.1 Reaction Products - Oxidizing Polyimides

The first step in the analysis of reaction mechanisms is to look at the reaction products and the kinetics of their formation. When a polyimide thermally degrades or
thermally oxidizes, the main volatile products are \( \text{CO}_2 \), \( \text{CO} \), \( \text{H}_2\text{O} \), and \( \text{H}_2 \).\[31\][32][33][34]

A comparison of thermal degradation and thermo-oxidative degradation reveals some interesting points, particularly about the role of certain radicals.\[35\] Thermal degradation takes place at high temperature (\( >300^\circ\text{C} \)) in an inert atmosphere. Thermo-oxidation takes place at high temperature in an oxygen rich atmosphere.

![Yield curves for the production of CO in (a) argon at 758 K, and (b) oxygen at 758 K. Adapted from [35].](image)

**Figure 17:** Yield curves for the production of CO in (a) argon at 758 K, and (b) oxygen at 758 K. Adapted from [35].

Figure 17 and Table 7, adapted from Bessonov et al. [35] and Ehlers et al.\[31\] respectively, illustrate the effect of thermally induced mass loss of a polyimide. In Figure 17 it can be seen that carbon monoxide production increases rapidly at first, but eventually plateaus. The plateauing of the reaction yield can be explained by assuming that two competitive reactions are taking place. In the early stages of the degradation a rapidly accelerating reaction develops. As time passes the second process begins to compete with the first, dampening the reaction. The accelerating process is most likely the radical chain branching process. Acceleration of the reaction rate is one key characteristic of this process type. After initiation has occurred, and as propagation becomes efficient, the number of
The page contains text discussing the expansion of radicals, their effect on product yield, and the dampening effect and its causes. It explains that as the material degrades, the most easily reactable sites are depleted, and the accumulation of products slows down the process. The text also mentions that the products of reactions deep inside the material take time to diffuse into the atmosphere, affecting the appearance and diffusion rate of the products. A table is used to show the degradation products of polyimide in an inert atmosphere at different temperatures, with mole percentages and weight loss. Two simple thermodynamic arguments are presented to explain the change in the CO-CO₂ ratio with temperature, involving reactions 4.13 and 4.14, which are plotted on an Ellingham diagram.
moles of CO are produced from one mole of oxygen and the slope of the line will be negative since the entropy change is positive. For reaction 4.14, one mole of CO₂ is produced from one mole of oxygen so the slope of the line will be virtually zero. Above Tₐ, the transition temperature, the change in Gibb's free energy (more negative) indicates that CO will be produced preferentially given the equilibrium 4.15. Tₐ has been measured to be approximately 950°K for CO₂/CO in equilibrium with graphite at 1 atm.[36] The data in table 7 exhibits this transition temperature effect somewhere before 673°K.

![Diagram](image)

**Figure 18:** Hypothetical Ellingham diagram illustrating the effect of temperature on the final products of a CO/CO₂ equilibrium.

This conclusion can be confirmed by examining the system according to Le Chatelier's principle, where an increase in temperature shifts the equilibrium away from the direction that involves the evolution of heat. Since \( \Delta H^\circ = -564.8 \text{ kJ/mole} \) for the
equilibrium reaction [36], this is an exothermic reaction, meaning that the direction of heat evolution is toward the production of CO₂. Hence, as the temperature increases, less CO₂ will be produced, or conversely, at low temperatures CO₂ production predominates.

However, there are some other considerations which imply that a much more complex system is involved, working within the general thermodynamic conditions described above. Kovarskaya et al [34] showed that when the 18 isotope of oxygen (¹⁸O) was used as the atmospheric oxygen, most of the carbon dioxide contained ¹⁸O, while only a fraction of the carbon monoxide did. This indicates that the carbon monoxide must be produced using the oxygen of the polymer structure, the intramolecular oxygen, through thermal degradation. However it is not a simple matter of atmospheric oxygen forming carbon dioxide in one reaction, while carbon monoxide is produced using the intramolecular oxygen in a separate reaction. Consider that carbon monoxide is produced at a much higher rate in an oxygen atmosphere, as compared to a similar environment without oxygen. Kovarskaya et al. also showed that unlabelled carbon monoxide was produced ten times faster at 673°C in an ¹⁸O atmosphere than in either helium or argon atmospheres. This indicates that the atmospheric oxygen is participating in the process, but not in the final product. It is possible that similar propagation mechanisms are working in both the thermal and thermo-oxidative processes, although the initiation reactions are not the same. Some discussion of possible mechanisms will illustrate the facts and concepts introduced above.

4.2.2 Reaction Mechanisms - Thermal and Thermo-Oxidative Degradation

Since carbon monoxide is the main product of the reaction mechanisms proposed for thermal degradation of polyimide, the imide ring must be the most vulnerable site.[31][32][37] Degradation, therefore, is initiated by scission of the imide ring leading to decarbonylation (loss of CO).
Once the imide ring is broken three possible paths are likely [35], producing amide groups (I), fused ladder structures (II), or through further breakdown the formation of terminal isocyanate groups (III):

\[ \text{PI} \xrightarrow{\text{CO}} \text{[chemical structure]} \]

4.16

Once the imide ring is broken three possible paths are likely [35], producing amide groups (I), fused ladder structures (II), or through further breakdown the formation of terminal isocyanate groups (III):

\[ \text{[chemical structure]} \]

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Water has also been shown to play an important role in thermal degradation.[32][38][39] Water acts to produce CO$_2$ in reaction 4.18, by first breaking the imide ring, giving a less stable configuration that degenerates to form amide groups (IV). The amide group can further react with water giving complete chain scission. Water can come from entrained moisture or from the degradation of residual polyamic acid which has been left behind in the production process.

\[
\text{PI} + \text{H}_2\text{O} \rightarrow \text{amide group} \rightarrow \text{CO}_2
\]

Thermo-oxidation of polyimides starts in a much different fashion, although the resulting products are much the same.[34][40][41] Hydrogen abstraction occurs first on a benzene ring leaving a radical site on the chain that reacts with another molecular oxygen to form a peroxide radical and producing a hydroperoxide or hydroxide free radical:
It is also obvious that cyclic peroxides may form at other sites:

At this point, it is likely that the peroxide group will interact with the cyclic imide portion of the chain. Direct decarbonylation may occur, in much the way that thermal degradation proceeds (reaction 4.17) to completion.
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UMI
movement of radicals away from the initiation sites at the surface. If the process is very rapid, that is, the radicals are initiating and propagating swiftly, the surface will be receding much faster than the diffusion of oxygen into the material. In reality, though, little can be said about AO diffusion into the bulk, since this may simply be a function of the particular environments examined so far. In LEO exposure, AO beam system testing, and also in plasma etching the atmospheric pressure is low enough that diffusion of gaseous species into the bulk would be slow.

The third difference, the lack of induction period in the reaction rate, is the clearest indicator that the kinetics of initiation and propagation must be quite rapid and may involve only a few steps, or many parallel steps. In general, for a molecular oxidation process, there is a slow increase in the rate of the reaction while the number of radical sites is increasing by propagation (figure 17 again). This does not appear to be true for HAO erosion. Mass loss measurements using a sensitive quartz crystal microbalance or aerodynamic balance systems while eroding carbon, Kapton® and poly(methyl methacrylate) (PMMA), show immediate, steady mass loss.[26][27] There is a short period of lower erosion rate that has been attributed to surface cleaning, or development of a surface morphology, but no clear early, extended period of little or no mass loss. Since there is no induction period it can be surmised that little rearrangement and slow propagation is occurring as the reaction process begins. However, since the same basic set of products is being produced from the same polymer structure, some of the reaction steps must hold true. This is the only similarity mentioned, and it is a strong one indeed.

The final difference is the kinetic energy of the incoming atomic oxygen atoms. Table 8 below, gives the bond strengths in eV of most of the common bonds in the polymer structures of interest.
Table 8: Typical Bond Strengths

<table>
<thead>
<tr>
<th>Bond</th>
<th>Strength (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N</td>
<td>3.0</td>
</tr>
<tr>
<td>C-C</td>
<td>3.6</td>
</tr>
<tr>
<td>C-O</td>
<td>3.6</td>
</tr>
<tr>
<td>C-H</td>
<td>4.3</td>
</tr>
<tr>
<td>C=C</td>
<td>6.3</td>
</tr>
<tr>
<td>C=O</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Evidently the kinetic energy of the AO atom should play a significant role in reacting with these bonds. If the energy is transmitted efficiently to the structure during collision, there will be more than enough energy available to separate the atoms. This is a critical difference, because it implies a very efficient initiation mechanism, and an efficient means to enhance propagation by encouraging the radical production process. Not only will the available energy act to produce radical sites, but energy imparted by less efficient impacts, and any leftover energy from bond breaking impacts will improve the likelihood of propagation. Because of this energy, active sites may be present that will more easily react with free radicals produced during initiation and subsequent propagation steps.

4.3.1 A Proposed Reaction Scheme

With the above comparison in mind (thermal vs. thermo-oxidative degradation) and with due consideration given to the differences outlined above, an reaction scheme can be proposed specifically for TAO erosion of Kapton®, with consideration given to the enhancing effect of the additional kinetic energy. Most importantly, it should be kept in mind that kinetic energy transfer will enhance the initiation and rate of many of the processes along the way. This reaction scheme is introduced here as an original contribution based on an understanding of the thermal energy process of molecular oxidation of Kapton®.
If, as in molecular oxidation of Kapton®, the point of first attack is on the benzene portion of the ODA segment of the molecule, a phenol structure can be formed by insertion.[47]

\[
P1 + O \rightarrow \begin{array}{c}
\text{OC} \\
\text{N} \\
\text{C} \quad \text{O} \\
\end{array} \rightarrow \begin{array}{c}
\text{OC} \\
\text{N} \\
\text{C} \quad \text{OH} \\
\end{array}
\]

(V) \hspace{2cm} 4.21

Phenol groups have not been found on the surface, however, after exposure to AO.[48] This indicates a quasi-stable configuration which can degrade quickly to other forms:

\[
(V) \rightarrow \begin{array}{c}
\text{OC} \\
\text{N} \\
\text{C} \quad \text{O} \\
\end{array} \quad \begin{array}{c}
* \quad \text{OH} \quad \text{O} \\
\end{array}
\]

(VI) \hspace{2cm} 4.22

In addition, through further interaction with atomic oxygen, molecular oxygen can also be produced, again leaving an alkyl radical, as in VI above.
From this step forward, the goal of the mechanism is to produce mostly CO, CO₂ and H₂O through the formation of alkoxy and peroxo radicals. Incoming atomic oxygen will react easily with alkyl radical sites (VI) to form the alkoxy radical:

\[(\text{V}) + \text{O} \rightarrow \text{alkoxy radical} \quad (\text{VI})\]

The formation of an alkoxy radical near the imide ring will result in fracture of the imide ring, producing CO₂ or CO, and leaving behind a new alkyl radical:

\[(\text{VII}) \rightarrow \text{CO}_2/\text{CO} + \quad (\text{IX})\]
More incoming oxygen will form a new alkoxy radical, finally breaking the chain completely as the remaining portion of the imide ring is auto-oxidized, forming more CO$_2$ or CO:

\[
\text{CO}_2/\text{CO} + \text{Polymer Fragments} \quad 4.26
\]

If any molecular oxygen is present, formed through recombination of AO at the surface, or through reactions such as 4.23, peroxy radicals can easily form from the alkyl radical VI:

\[
(\text{VI}) + \text{O}_2 \rightarrow X \quad 4.27
\]

Decomposition of the structure through hydrogen abstraction, producing a hydroxyl group would result in chain scission at the ether linkage, as CO is formed:
4.3.2 Enumerating the Reaction Products

To conclude this chapter a summary is presented of the proposed reaction possibilities by determining how each of the known products is formed, and supporting that determination with recent, specific results from HAO experimentation. Once again, the reaction products have been measured in the LEO environment, in AO beam scattering experiments, and in plasma etching, to be CO₂, CO, H₂O, H₂, N₂, and NO.

CO₂ - Formed by alkoxy formation and the resulting decomposition of imide rings (4.21 through to 4.26). The oxygen of the alkoxy radical reacts directly with the adjacent carbon of the carbonyl group to form CO₂. This pathway is supported by recent results from Minton and Moore[22], who showed using labelled carbon (¹²C in the PMDA portion and ¹³C in the ODA portion) that the majority of CO₂ produced came from the PMDA section. The PMDA section contains the cyclic imide, the ODA section contains the ether link. Carbon dioxide may also result from the combination of CO and OH:[49]  CO + 'OH → CO₂ + H'  

CO - Formed by the same reaction as above, but additionally through peroxy radical formation and decomposition of the ether linkage in the ODA portion of the polymer molecule (4.27 - 4.28). This is also indicated by the results from Minton and Moore[22] where the relative portion of ¹³C in CO is much higher than the relative portion of ¹³C in CO₂. In their results, most of the CO₂ was formed with ¹²C, but an equal amount of CO was made from both isotopes. It may be that the ODA carbons
are forming predominantly CO, and that a good portion of the $^{13}$COs formed are reacting with $^*\text{OH}$, or AO to form CO$_2$ before they are desorbed.

**H$_2$O -** Water would be formed through interaction of hydroxyl groups and abstracted hydrogens: $\text{H}^* + ^*\text{OH} \rightarrow \text{H}_2\text{O}$, or more simply and importantly through hydroxy radical abstraction of bonded hydrogens: $^*\text{OH} + \text{PH} \rightarrow \text{H}_2\text{O} + \text{P}^*$

**H$_2$ -** Molecular hydrogen would form through interactions of abstracted hydrogens or when atomic oxygen reacts with very low molecular weight products such as the methyl radical:[49] $\text{O} + ^*\text{CH}_3 \rightarrow \text{CHO} + \text{H}_2$

**N$_2$,NO -** Nitrogen compounds would be formed as the imide ring is broken apart. Destruction of the imide ring by alkoxy radical auto-oxidation would leave a vulnerable nitrogen that would either react with an incoming atomic oxygen to form NO, or it could react with another similar nitrogen to form N$_2$. 
CHAPTER 5

PROTECTION OF POLYMERS BY SURFACE MODIFICATION

When a spacecraft application requires the use of a certain polymer material, it becomes necessary to find a way to protect that material from exposure to atomic oxygen if a reasonably long lifetime is to be expected. For example, if unprotected Kapton® was placed in orbit at an altitude of 400 km it would erode at a rate of approximately 8 μm/month (0.0003"), which means that a 1 mil (one thousandth of an inch) thermal control blanket or substrate would disappear in just 90 days.

Coatings, paints, and coverings of any sort are logically the first line of defense and many different types have been used. The simplest attempts are coverings made from woven glass, the same material that is also used as a thermal/micrometeoroid shield blanket on modern spacecraft. NASA’s version is referred to as Beta Cloth: a tight weave of silica fibres, coated with a fluorinated polymer. The Russian Space Agency uses a weave of silica fibres and metal (silver, gold) strands in similar applications. In recent years, complex coatings and coating systems have been and are still being developed. The most successful coatings use oxides of silicon as their basis. Silica (SiO₂) and silica like (SiO₃) coatings deposited using chemical vapour deposition, electron beam sputtering, and other vacuum or spray processes offer considerable improvements in resistance to atomic oxygen. Erosion yield is typically reduced from greater than 10⁻²⁴ g/atom to approximately 10⁻²⁶ g/atom. The success of their short term use has led to their incorporation into most structures, such as the International Space Station. Silicon is an excellent material to use as an oxidation barrier. Once oxidized it is chemically and thermally stable, relatively tough and has good optical properties.

A good example of a commercial silicon type coating in current use is Sheldhal’s AOR SiO₂ coating applied in an RF sputtering process.[50]
Batch processing is carried out in a five thousand litre stainless steel vacuum chamber. Rolls of specially chosen and cleaned Kapton® film are passed near two magnetron cathodes which (in turn) sputter SiO₂ from SiO₂ targets onto the film. Power is supplied by five kilowatt, 13.56 MHz supplies. A coating of nominally 1300 angstroms is placed on each side of the film. Atomic oxygen erosion reactivity is reduced to 1.4% of the normal Kapton® erosion reactivity, from 4.3x10⁻²⁴ g/atom to approximately 6.0x10⁻²⁶ g/atom. Special handling of the material is required since particulate contamination is highly detrimental to the final performance.

A wide variety of other coatings have been developed in this application too. Metal oxide types include aluminum oxide[51], indium oxide [52], vapour deposited indium-tin oxide [53], and germanium oxide [54]. Thin protective layers based on silicon deposited from volatile compounds via microwave glow discharge have also been tried [55][56]. The compounds used to form the coatings include: amorphous hydrogenated silicon, inorganic silicon compounds such as silicon nitride, and organo-silicones such as hexamethyldisiloxane. Coatings of clear RTV Silicone have also been tested and used in a number of applications.[57] McGhan NuSil CV-1144-0 RTV silicone was used to protect the original Hubble Space Telescope solar arrays.[58] Fluoropolymer filled silica mixtures have also been attempted [59].

Besides coatings, it should also be mentioned that new polymers with inherently resistant chemical structures have been developed. A polysiloxane-polyimide block copolymer with a reaction rate ten times lower than Kapton® was developed recently [60]. In addition, substitutional polystyrene backbone fluorinated polymer has been shown to be more stable than the ring fluorinated polymer [54]. None of these polymers have been shown to give better resistance than coatings, however.
5.1 Problems with Coatings

For all of the examples of different coating systems, with their very low atomic oxygen erosion rates, there still remains considerable concern over the ability of any coating to protect when defects (holes, pits, cracks) are present. Defects are created during the deposition process, when the material is handled, or while in orbit by micrometeoroid and debris impact. The Sheldahl process mentioned above must be carried out in a class 10,000 cleanroom environment, because of defects created by airborne particulates.[50] Defects in the coating provide a pathway to the polymer beneath, allowing direct oxidation and undercutting to proceed unchecked in that area.[56] Extensive studies carried out at NASA’s Lewis Research Center have revealed that pin holes/windows left behind after the deposition process are the single largest contributor to failure of the coating.[61] Handling of these materials after coating is also of great concern. Bending and scratching leave cracks and crevices through the coating, exposing the polymer beneath.

Any problems due to process induced defects are further enhanced by the effects of thermal cycling and fatigue that the material experiences once in orbit. In LEO a spacecraft completes an orbit approximately every 90 minutes. During each orbit the surface temperature could change by as much as 150°C as the spacecraft moves in and out of the Earth’s shadow. The materials used in coating generally have a very low coefficient of thermal expansion (CTE), while the materials they are covering have a relatively high CTE. The constant thermal stress changes created by this situation will fatigue the coating, resulting in cracking which will lead to atomic oxygen attack and damage.

The simple problem is that, although the coating has remarkably high resistance to atomic oxygen attack, the material underneath is as reactive as it ever was. Penetrations of the coating allow atomic oxygen to erode under it, especially if the atomic oxygen flux is not unidirectional. That is, if the satellite rotates relative to its direction of travel (velocity vector) the impinging AO flux will sweep across the penetration. This undercutting destroys the integrity of the coating, causing it to separate from the polymer, crack, and spall off.
As a final negative aspect of coating cracking problems, the reaction rate of the material exposed by a hole in the coating appears to be enhanced; specifically, the erosion yield in cracks or scratches appears to increase 2.7 times, while in pin-holes the reaction rate is 7.25 times greater. It is believed that this effect is due to multiple-scattering or entrapment of the AO atoms inside the cavity of the crack or pin-hole. This multiple-scattering means that each AO atom has multiple opportunities to react with the material.

It is clear then that all coatings have some strict limitations. In the most general sense a coating is a distinctly different material from the substrate it is protecting, and sometimes, surface adhesion, especially in thermal or load fatigue conditions, can be a problem. That is, since the coating is a separate, applied layer, it naturally tends to crack, break and spall, exposing the polymer beneath. A different technique, "surface modification", can alleviate this problem by modifying the chemical content and structure of the polymer material in a thin layer at the surface, while retaining most, if not all, of the original properties. Within this layer the degree of modification varies with depth. With a graded modification it is more difficult for cracking or spalling to occur, since the degree of modification decreases gradually with depth. Specifically, this means that there is no discrete boundary where the new surface structure ends and the original substrate begins. This reduces or eliminates all of the interface problems, such as stress concentration or interlaminar diffusion of destructive elements and compounds, which may lead to loss of the coating.

The processes demonstrated in this investigation are surface modification techniques, not coatings. The surface of the material is modified at the molecular level in a manner which leaves it highly resistant to atomic oxygen erosion.

Before discussing the results of this development, a few points about methodology need to be discussed. The goal of this work is to produce a surface that is resistant to attack by hyperthermal AO. In all cases, the result of a standard test exposure to AO in the UTIAS atomic oxygen facility will be taken as proof of success, rather than elemental surface
analysis results, for example. The test used is a 5-hour exposure, resulting in a fluence of approximately $1.8 \times 10^{20}$ atom/cm$^2$. If, in this test, the treated sample weight does not change by more that $10 \ \mu g$, the sample is considered to be protected. Given the resolution of the balance used for weight measurements, this corresponds to a reduction in erosion yield to approximately 1% to 2% of the untreated value for Kapton$^\circ$.

In addition to mass loss, the change in surface morphology can be used as an indicator of the degree of protection. The initiation of change in the surface morphology (the production of a microscopic scale carpet-like surface) occurs rapidly, usually within the first few minutes of exposure to AO in the UTIAS facility. Thus, as an initial qualitative assessment of protection, the change in the surface structure, which is easily observed with the naked eye, was used as a pass/fail test. During the optimization of process factors such as activation time and exposure distance, samples were simply exposed to AO for an hour and then removed for visual inspection. If surface roughening or whitening was observed the sample was deemed to be a "failure". As final proof of this screening methodology, it will be shown that samples which were protected exhibited no surface morphology changes.

5.2 SURFACE ANALYSIS TECHNIQUES

The measurement of surface chemical (elemental, molecular) composition is still an evolving field. Sophisticated methods such as XPS (x-ray photoelectron spectroscopy), SIMS (secondary ion mass spectroscopy) or FTIR (Fourier transform infra-red spectroscopy) all have strengths and weaknesses in how they deal with the characterization of a surface. Because atomic oxygen interacts only with the surface of polymers, the correct techniques to use for surface analysis are evident, based on their depth of analysis. Of the sophisticated techniques only XPS, and to some extent SIMS, is useful. In addition, there is one technique that is easy to apply and provides a great deal of information about surface characteristics — contact angle measurement.
5.2.1 Contact Angle Measurements

The measurement of the contact angle of a liquid drop on a solid surface is one of the simplest and most widely used, surface analysis techniques. In fact, this technique is the only known true measure of surface effects. The interaction of the liquid and the surface is defined strictly by the outer surface monolayer of the solid material. For processes that are designed to affect the surface alone, this technique is the method of choice.

Most commonly, the contact angle is measured using the sessile drop method. A liquid drop is placed on the surface, and the advancing contact angle is measured. The advancing contact angle is the angle made by the liquid as it spreads over the surface. Water is particularly suited for this task since it has a relatively high surface tension in air, and measurements are readily made with simple apparatus. In its most precise application, this technique can, by using more than one liquid, determine the surface free energy and its dispersion and polar components. Figure 19 shows a typical sessile droplet with angles indicated. The angle is calculated geometrically by measuring the base (c) and height (h) of the droplet which are used to calculate the advancing contact angle:

$$\theta = \tan^{-1}(c/(c^2/4h-h))$$

which is derived using the relationship,

$$r_s = h/2 + c^2/8h$$

where $r_s$ is the spherical radius of the droplet.

All of the contact angle measurements presented here were made using a simple horizontal microscope and camera system. A 2.5 $\mu l$ droplet of water was placed on the surface using a microsyringe. The photograph was taken between 30 seconds and 1 minute after the droplet was placed. Measurements of c and h are made directly on the photograph.
In this investigation the change in contact angle is used to estimate the degree of fluorination or oxidation of the surfaces treated. In the first of the two surface modification techniques, the contact angle will be used to estimate and illustrate the change in the degree of surface fluorination. As the fluorine content of the surface layer increases the contact angle will increase (the surface will become hydrophobic). In the second surface modification method, the water contact angle will be used to illustrate changes in the oxygen content of
the surface. With oxidizing processes, the water contact angle decreases as the degree of oxidation increases, for example a silica surface (SiO₂) has a very small contact angle \( \sim 0^\circ \).

5.2.2 X-ray Photoelectron Spectroscopy (XPS)

Electron Spectroscopy for Chemical Applications (ESCA) or X-ray Photoelectron Spectroscopy (XPS) is the measurement of binding energies of core electrons ejected from atoms, by bombardment of the surface with a beam of x-rays. The binding energy of the core electrons is given by the equation 5.3[62]:

\[
E_b = h\nu - E_i - \phi - C \quad (\text{eV})
\]

where:
- \( h\nu \) = the energy of the x-ray photon
- \( E_i \) = the kinetic energy of the ejected photon
- \( \phi \) = the spectrometer work function
- \( C \) = the energy (+) associated with charging

XPS is sensitive to all elements except hydrogen and helium. It is generally thought of as a surface analysis technique since the depth of analysis extends only to approximately 100 angstroms. This is due to the fact that, although the x-rays penetrate deeper into the materials, the electrons can only be ejected from that shallow depth. In addition to the photoionization ejection of core electrons, two other processes produce electrons with various energies.[63] Both occur as a result of photoionization. When valence electrons are excited to higher unoccupied levels from their normal levels this is called "shake-up". Shake-up effects are measured as changes in the energy of core electrons due to energy loss to the shake-up process. Shake-off is the ionization of valence electrons rather than core electrons. High resolution XPS results are most often presented as a number of counts vs. an energy spectrum (see figure 20). The satellite peaks are the result of shake-up and shake-off. These extra peaks can be used both to confirm information provided by the main photoionization peak and to more precisely define the bonding environment (although they are not often used).
The most obvious problem that occurs when XPS is used to analyze polymer materials is the charging of the surface, since polymers are by their nature insulators. The effect of this charge, which may be positive or negative, is to shift the binding energy calculated. In equation 5.3, \( C \), represents this shift. The charging value is estimated using known peak values for calibration. The entire spectrum is shifted to place known peaks at their correct energy. Often the XPS system software can be used to perform this task automatically.

The interpretation of XPS data is by no means a quantitative exercise. The exact binding energy of an electron changes from atom to atom, based not only on its elemental form, but also its bonding environment. These substituent effects, which are the specific chemical structure and material phase, as well as the physical environment, can affect the energy measured. To make analysis possible, a systematic study of materials, particularly polymers, has been carried out worldwide to define the substituent effects in each material.
For polymers, certain types of core electrons are of specific interest. The substituent effects on the C₁s, N₁s, O₁s, F₂p, Si₂p, P₂p, S₂p, and Cl₂p levels of atoms in polymers have been compiled in databases, and in many journal articles referring directly to a specific form of a material. In particular, the database compiled by Beamson and Briggs [64] is most useful.

The strength of XPS analysis is its ability to quantify changes in the surface of a material. In fact, it is widely accepted as the best means for quantifying surface chemical and structure changes. In this investigation, XPS analysis was used to define the changes that occur to each material as it was modified.

Two types of XPS data are presented here. Survey scans give a quantitative measurement of all chemical elements in the material (>0.1 at%)%. The survey scan results are presented in tabular form, giving a breakdown of the composition of the material by percent of each element present. High resolution spectra are also presented. They are used primarily to define the changes in each material as it is treated. Figure 20 is an example of a high resolution XPS spectrum. Chemical bonding changes are characterized by changes in the relative height of peaks, and by the appearance or disappearance of peaks in the spectrum.

XPS testing was done by two external laboratories. At the Surface Science Laboratory (SSL), University of Western Ontario, samples were analyzed using a modified SSL model SSX-100 X-ray spectrometer with monochromatized Al Kα excitation radiation. A Gaussian-Lorentz fitting program was used at SSL to generate the appropriate spectrum from the measured data. XPS analysis was also carried out at the Centre for Biomaterials Surface Science Unit, University of Toronto, using a Leybold MAX 200 UHV Surface Analysis Unit, with a nonmonochromatized Mg Kα excitation source. Once again, a Gaussian-Lorentz fitting program was used to generate the "best-fits" to the measured data. For all high resolution spectra the binding energies were referenced (for charge correction) to the 284.7 eV hydrocarbon peak.
5.2.3 Secondary Ion Mass Spectroscopy (SIMS)

SIMS depth profiles were measured using a Cameca IMS 3F system by the Surface Science Laboratory, University of Western Ontario. A primary negative oxygen ion beam was used to bombard the sample. Positive secondary ions were monitored. This method provides the highest sensitivity for silicon (of primary interest in the Photosil™ process), and reasonable sensitivity to carbon and oxygen. Oxygen secondary ions were monitored at both mass 16 and mass 18 to account for the use of the oxygen ion beam which employed mass 16 oxygen. Charge control was accomplished by coating the sample with gold and by using the system’s auto charge compensation program. The depth of the crater made by the beam was measured using a Dektak IIA surface profilometer.

5.3 PLASMA FLUORINATION

Altering the surface chemical structure of polymer materials, in a meaningful way, is a difficult task. Their covalent bonding structure is, on the one hand, relatively strong and difficult to rearrange or combine with. On the other hand, once changes are initiated, the whole structure tends to change drastically, often catastrophically. The trick — and a vast amount of work has been done on this subject — is to choose the modification site on the polymer chain carefully and in some way limit the effect to only that particular site. Although this is sometimes a difficult accomplishment, it is important to note that there are many, many successful processes in use today that manage to accomplish this task to some extent. For example, processes have been developed to modify the surface of photoresist polymers, or so that inks will stay bonded to the surface of packaging material.

From the mechanisms proposed above for erosion by hyperthermal AO (Chapter 2 and Chapter 3), it is clear that inhibiting the erosion process can best be accomplished by blocking any initiation by the AO. Whether by replacing the labile hydrogens with stronger bonded elements or by changing the structure and composition of the materials at the surface, the degrading reactions should be prevented. This logic is hardly original, and in the most elementary sense defines the difference between polyethylene and DuPont’s FEP Teflon®.
The basic difference is obvious. FEP Teflon has fluorine side-groups instead of hydrogen side-groups, and the consequences of that difference are clear; polyethylene erodes at a rate of \(2.8 \times 10^{-24}\) cm\(^3\)/atom while Teflon\(^\circ\) erodes at a substantially lower rate of \(5.0 \times 10^{-26}\) cm\(^3\)/atom. If this concept could be applied to other materials like Kapton\(^\circ\), the results may be similar.

### 5.3.1 The Fluorination of Polymers

Fluorinating Kapton\(^\circ\) or any other polymer means replacing labile hydrogens with fluorine atoms. To replace the hydrogen atoms, an energetic process must be used. Oxygen/Fluorine plasma erosion of polymers is known to produce this result under specific conditions, characterized by the formation of aliphatic fluorine compounds (CF\(_2\)), acyl fluoride, benzoyl fluoride, acyl hypofluorite, and polyfluorinated benzene[65], the presence of which should increase the erosion resistance of the polymer. With this type of treatment the maximum depth of fluorination (500 Å) appears to occur with the use of a CF\(_4\) plasma alone, achieving a C/F ratio of 1.64. The reactive species produced in the plasma vary with gas mixture, and consist of both ions and neutrals; for example: O\(^+\), O\(_2^+\), F\(^+\), CF\(_x^+\) and O\(^*\), F\(^*\), CF\(_x^*\). The primary modification species are the neutral radicals.

### 5.3.2 Equipment and Materials

Plasma fluorination was carried out using an AC plasma etcher at NRC (National Research Council - Canada) Institute for Microstructural Studies (figure 21). In a plasma etcher, free electrons from the plasma interact with molecules and atoms in the gas phase, leading to fragmentation (dissociation) and ionization. The resulting fragments are highly reactive. Because the plasma is at higher electrical potential than the surfaces it is in contact with, positive ions will be accelerated toward the surface, attaining quite high energies.
Because of this bombardment, primary samples were treated by placing them on the bottom of a holder as shown in figure 21. These "out-of-glow" samples were not subjected to the ion bombardment, but were still exposed to the reactive fluorine species produced by the plasma. Secondary samples were also treated "in-glow" for comparison purposes. Kapton® 500HN (5 mil thick) was used for all tests. Holders were fabricated from 6061 T6 aluminum, anodized to limit any contamination possibilities.

![Figure 21: Schematic diagram of plasma "pancake" etcher used showing sample holder on cathode, with samples mounted on top and bottom of holder.]

### 5.3.3 Results and Discussion of Campaign #1

Two campaigns of experimentation were undertaken to treat samples of Kapton® using gas mixtures, treatment times and pressures determined by reference to previous published work, which reveal that CF₄ alone, or with small additions of oxygen offer the best opportunity for success.[66] In both campaigns the pressure was set at a constant (the highest operating pressure of the system), since it has been shown that fluorination is a
diffusion driven process.[65] Table 9 shows the gas-mixture and treatment time regimes tested in campaign #1. One test using SF\textsubscript{6} was done to explore the use of this gas, which has considerably different plasma species (mostly F\textsuperscript{+}).

Table 9: Gas mixtures with O\textsubscript{2} and treatment times tested during campaign #1 (out-of-glow samples).

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Gas-Mix (vol%)</th>
<th>Contact Angle</th>
<th>XPS Surface Composition (atm%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>10</td>
<td>90% CF\textsubscript{4}</td>
<td>92°</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>90% CF\textsubscript{4}</td>
<td>101°</td>
<td>25</td>
</tr>
<tr>
<td>50</td>
<td>90% CF\textsubscript{4}</td>
<td>100°</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>90% CF\textsubscript{4}</td>
<td>104°</td>
<td>35</td>
</tr>
<tr>
<td>30</td>
<td>80% CF\textsubscript{4}</td>
<td>28°</td>
<td>26</td>
</tr>
<tr>
<td>30</td>
<td>85% CF\textsubscript{4}</td>
<td>92°</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>95% CF\textsubscript{4}</td>
<td>92°</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>99.9% CF\textsubscript{4}</td>
<td>94°</td>
<td>29</td>
</tr>
<tr>
<td>30</td>
<td>99.9% SF\textsubscript{6}</td>
<td>99°</td>
<td>21</td>
</tr>
</tbody>
</table>

The two samples showing the greatest fluorine content were tested in the UTIAS AO facility, but showed no real change in erosion rate. This is not surprising, considering the low F/C ratio, as compared to the 1.64 ratio for fully fluorinated material mentioned previously, and the level of contamination. Significant aluminum contamination is evident in all of the XPS compositions. No source was clearly identified. To ensure that the source was not the holder, a much smaller holder was used for campaign #2.

Despite the contamination, the results of the XPS surface composition measurements indicate that long treatment times are required. The highest fluorine content was in the sample with the longest exposure, even though the gas mixture had 10% oxygen in it. All samples from the top of the holder (in-glow) were visibly eroded. Their normally smooth
and clear surfaces were roughened and opaque. It was clear that "in-glow" fluorination could not be used to protect the Kapton®.

### 5.3.4 Results and Discussion of Campaign #2

From the results of campaign #1 a new set of tests was determined, with the primary goals of reducing contamination, and testing different gas mixtures at longer treatment times. Table 10 outlines the regimes tested.

**Table 10: Gas mixtures with O₂ and treatment times tested during campaign #2 (out-of-glow samples).**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Gas-Mix (vol%)</th>
<th>Contact Angle</th>
<th>XPS Surface Composition (atm%)</th>
<th>New R_e (%original)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>F</td>
<td>O</td>
</tr>
<tr>
<td>30</td>
<td>80% CF₄</td>
<td>17°</td>
<td>31.8</td>
<td>11.7</td>
</tr>
<tr>
<td>30</td>
<td>85% CF₄</td>
<td>96°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>90% CF₄</td>
<td>99°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>95% CF₄</td>
<td>98°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>99.9% CF₄</td>
<td>94°</td>
<td>37</td>
<td>6.7</td>
</tr>
<tr>
<td>60</td>
<td>90% CF₄</td>
<td>115°</td>
<td>38</td>
<td>9.5</td>
</tr>
<tr>
<td>60</td>
<td>95% CF₄</td>
<td>115°</td>
<td>39.3</td>
<td>8.4</td>
</tr>
<tr>
<td>60</td>
<td>99.9% CF₄</td>
<td>109°</td>
<td>35.8</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Clearly the longer treatment times resulted in better fluorination, if the contact angle measurements are considered. Unfortunately the F/C ratio is still quite low for even the best gas mixtures at the longest times. In addition, it is also apparent that the best F/C ratios did not occur in pure CF₄ plasmas as was indicated by the literature reviewed. Testing in the UTIAS AO Facility showed that significant changes did occur in the chemical structure of the surface. The three samples given longer plasma exposures all exhibited reductions in erosion rate as shown. Although the reduction is significant, it does not reach the goal defined for the overall process.
Concurrent independent development of a fluorination process by Calius et al. reached a similar limit. They reported a maximum reduction of 50% for their process. Some chemical limit may be indicated here, based, most likely, on the fact that the fluorination process is simultaneously eroding the surface. Although the goal of <1-2% erosion was not reached at this stage, it is obvious that surface modification of the chemical structure can greatly affect the way the AO interacts with the material.

5.4 **THE PHOTOSIL PROCESS - 3 STEP SILYLATION**

Silylation is defined as the replacement of an active hydrogen of a protic group with a substituted silicon atom. The logic defined for the plasma fluorination technique is extended, using another substituent (Si instead of F). The Photosil Process replaces the labile hydrogens with a Si linkage, which can be oxidized in place, without destruction, thereby protecting the polymer. The ultimate goal of the substitution is to leave the modified material very stable in an oxidizing environment. This is accomplished by giving the surface a stable, silica-like top layer. Silylation, as a method, has existed since 1944. It has been applied routinely to produce blocked intermediates in chemical synthesis, to produce volatile derivatives for analysis by gas chromatography and to modify surface properties (eg. wettability, adhesion, or the reactivity of photoresists in semiconductor processes). Silylation has been performed on many materials, all of which however, contain functional groups in their original structure that the silylating agent can react with.

The Photosil™ Process is different from previous silylation processes because it is applied to organic polymers which could not, and have not previously been modified in this fashion. Polymers such a Kapton®, PEEK, Mylar®, or polyethylene do not contain the active hydrogen functional groups that are required for silylation modification. Using the Photosil process, a whole range of organic polymers that previously could not be silylated can now be modified.
5.4.1 Step 1 - Activation

Most polymers, especially those used in space applications, such as Kapton®, PEEK or epoxies, are quite stable and are therefore difficult to chemically modify. More specifically, as it applies here, they do not contain reactive hydrogen functional groups, and a silylating agent will not react with them. Activation, which in this case is the production of protic groups with active hydrogens, has been accomplished to some extent generally, in a number of ways. Basically, any process that oxidizes the surface will produce some functional groups. For example, UV induced oxidation, oxidizing plasmas, ion bombardment, or wet chemical processes can be used. These processes, however, have only been used in the broadest sense. In most literature and patents, the surface is considered to be either oxidized or not, with very little concern placed on the extent of oxidation. That is not to say, however, that analysis of the varying degree of oxidation has not been carried out. It is just that the fact of variable oxidation does not seem to have been applied to a specific purpose.

The end result of the activation process, when carried out in a controlled manner, will be the production of: -OH, \( =C-OOH \), -C=O, =C=O groups on the surface.

What does control mean? Control means, not over-oxidizing the surface. The idea is to replace only the most labile hydrogens of the structure, not to break apart the structure itself. When the surface is heavily oxidized, the structure will be broken apart at its weakest point. For Kapton® this would be the cyclic imide portion of the PMDA section. As shown in Chapter 3 the oxidation of Kapton® invariably involves the transformation and destruction of the cyclic imide, and therefore the whole molecule itself. Of all the processes mentioned above, UV induced oxidation appears to offer the most opportunity for control. The UV dose can be controlled easily, and the reactive atmosphere can be easily modified with simple equipment. Specifically, no vacuum system or high power/voltage equipment are required.

If the surface of Kapton® (and similar polymers) is to be successfully modified, the surface must be thoroughly functionalized. Most, if not all, of the labile hydrogen bonding
sites must be activated. Mechanisms have been proposed for the photo-oxidation of Kapton® that offer the possibility for producing large numbers of functional groups. For irradiation at 185 nm [68] and at 254 nm [69] in air, Kapton® was believed to photo-oxidize in the following manner:

\[
\begin{align*}
P + h\nu & \rightarrow R^* + R^* \quad 5.4 \\
R^* + O_2 & \rightarrow ROO^* \quad 5.5 \\
ROO^* + P & \rightarrow ROOH + R^* \quad 5.6 \\
ROOH + h\nu & \rightarrow RO^* + OH^* \quad 5.7
\end{align*}
\]

Recently Meier and Langsam [70] concluded, using modified polyimides, that with 200-300 nm irradiation in an oxygen atmosphere, intramolecular cyclization is prevented by the oxygen. This is critical, because cyclization could mean inefficient activation since chain scission can be initiated, and the rapid production of inactive groups can result. Their conclusion was that the oxygen reacts rapidly with any radical centres, producing peroxo radicals as in reaction 5.5. Through further hydrogen abstraction with neighbouring sites, hydroperoxides are produced which would decompose, with UV irradiation, to form alkoxy and hydroxy radicals (as in 5.7). Functional groups would be produced quite efficiently by these means as the alkoxy and hydroxy radicals propagate radical sites to other molecules, and to more sites on the same molecule.

In addition to the effects of UV and molecular oxygen, there will be some ozone (O₃), atomic oxygen and singlet molecular oxygen present if the sample is placed quite close to the UV source. These species are produced when UV radiation interacts with air. Singlet oxygen is an excited state of O₂, where the UV radiation has increased the electronic energy of the molecule 1.63 eV above ground state.[71] It has a relatively long half-life due to a spin-forbidden transition to ground state.

These species will react with the polymer material. Ozone has been shown to react readily with alkanes to form, in various ways, alcohols, ketones, carboxylic acids, esters and peroxides.[72] Rabek et.al. [73] believe that ozone reacts first by addition to a benzene ring,
resulting in a rapid cascade rearrangement of the structure. Although the mechanisms proposed indicate that ozone is likely to cause considerable chain scission, the production of hydroxyl and carboxyl groups are also indicated. Singlet oxygen also reacts in a similar manner. XPS analysis of polystyrene and polyethylene after exposure to singlet oxygen shows the presence of C-O, C=O, O-C-O, and O-C=O on the surface.[74] The effect of these species can be controlled by altering the distance of the sample from the UV source. In fact, as will be shown later, these species play an important role in the activation of polyethylene and polymer matrix composites, which are less susceptible to UV activation as compared to Kapton®.

With Kapton® other opportunities for activation were explored during the early studies of the activation process: wet chemical activation and oxygen plasma activation. Samples were wet-chemically activated using NaOH and acetic acid. Hydrolysis by a dilute aqueous base, followed by proton exchange conversion with weak acid, has been shown to produce a thin layer of polyamic acid on the surface.[75] Once in the acid form the surface can be silylated. Oxygen plasma activation was also attempted. Samples were exposed to a DC oxygen plasma (60-120 mtorr, 400V, 13mA) for 10 minutes prior to silylation, in an attempt to produce oxygen containing functional groups. In both cases, however, XPS analysis and AO testing showed that the activation process was not thorough enough, resulting in inconsistent protection of the surface.

5.4.2 Step 2 - Silylation

The goal of this step is to replace the reactive hydrogen from the functional groups formed in the activation process with silicon groups from the silylating agent, creating an organo-silicon molecule derived from the original organic polymer. In a final stabilization step, the surface layer will be oxidized to produce a glass-like (SiO₄) surface which cannot be oxidized further.

Silylation can be carried out in either a liquid bath or by exposure to a vapour. The activated polymer surface is exposed under controlled time, temperature and concentration
conditions to a chemical bath which includes a silylating agent, a transport solvent and if possible a diffusion enhancer.

The silylating agent is an organo-silicon molecule where a silicon-nitrogen bond exists as the central structure. During the process of silylation the Si-N bond is broken, with the Si bonding to the oxygen of the functional site on the polymer molecule, replacing the hydrogen at that site. Silylating agents can be grouped into two categories, with respect to their functionality. Monofunctional agents contain one Si-N bond, polyfunctional agents contain more than one Si-N bond. Of the many agents available, commercially, the polyfunctional agents are of most interest. Using a polyfunctional agent will increase the efficiency of the process, one molecule will be able to silylate more than one site. In addition, some cross-linking will result. Cross-linking will increase the structural strength of the layer, giving better resistance to thermal or load stress damage, and should decrease diffusion. Three polyfunctional agents are readily available:

![Chemical structures of B[DMA]MS, B[DMA]DS, and HMCTS](image)

Of the three, B[DMA]DS, offers the most advantages. The first agent listed, the methylsilane form, is unstable in air; and of the other two B[DMA]DS is the smallest in size.

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and should diffuse better into the polymer surface. It must be noted that any silylating agent will react with the functional sites, and that the selection of an agent for this process was based on the a priori estimates of the process requirements described here.

Silylation reactions with surfaces have been investigated extensively for the semiconductor industry. The production of Diffusion Enhanced Silylated Resists (DESIRE) is a well developed technique for producing patterns on novolac/diasonquinone photoresists. [76][77][78][79][80] This process is defined by the need to develop a pattern in the resist material using reactive ion etching (RIE) in an oxygen based plasma. The DESIRE process protects the patterned areas of the resist from oxygen plasma etching by incorporating silicon into the structure. The first step is to lay the pattern into the surface using UV irradiation. UV irradiation of the polymer increases the diffusion rate of the silylating agent into the material. The surface is then exposed to vapour phase hexamethyldisilazane (HMDS), which diffuses into the irradiated areas. The HMDS bonds with the -OH of the novolac structure. When the surface is exposed to an oxygen plasma the silylated areas are quickly oxidized and do not erode. The unsilylated areas are removed by the plasma, revealing the pattern. Liquid phase processes have also been used [81], showing improved Si incorporation rates and thermal stability. Liquid phase processes also require simpler equipment.

Based on the results from photoresist silylating systems mentioned above, the expected reaction with activated polymers should be of the form:

\[ \text{activated polymer} + \text{HMDS} \rightarrow \text{silylated polymer} \]

The first silylation reaction takes place in reaction 5.8. The Si-N bond breaks, the Si
containing portion of the B[DMA]DS molecule attaches to the polymer chain through the oxygen, and a H-N-(CH₃)₂ fragment is released. In 5.9 the process is repeated for the other half of the silylating agent molecule. The final result is a set of linked sites, joined by a silicone-like group.

The two other components of the silylation solution (2 solvents) are selected depending on the silylating agent used, and the material to be treated. The transport solvent must dissolve the agent, while remaining inert toward the material. The diffusion enhancer must dissolve the material’s surface slightly, increasing the silylating agent’s rate and depth of penetration.

5.4.3 Step 3 - Stabilization

As with activation, this is an oxidation step. Stabilization of the silylated surface is required to produce a highly oxidized surface layer which will, of course, be inert in an oxidizing environment. After silylation alone the new structure may still be unstable in certain types of oxidizing environments. However, in other environments, for example AO exposure in LEO, stabilization will occur in-situ. The hyperthermal AO will oxidize the organo-silicon group, removing the CH₃ pendant groups of the silicone-like structure. This capability of in-situ stabilization offers a helpful advantage. Once the surface is stabilized, any penetration through the silica like layer may result in further stabilization at the depth of the penetration. This will occur, because the depth of silylation is greater than the depth of stabilization. Only the uppermost portion of the silylated surface region is stabilized. For example, a glassy layer may form at the bottom of pits formed by small micrometeoroid or debris impact, so long as the depth of silylation is sufficient.

To stabilize the surface, UV induced oxidation can again be used. SiO and SiO₂ groups are formed in the surface layer of the silylated region, with exposure to the oxygen species present (molecular oxygen, AO, ozone, singlet oxygen).
5.5 **EQUIPMENT, CHEMICALS AND METHODS**

Activation and stabilization of the surfaces was carried out in a UV/Ozone Cleaning System (UV/OCS). The UV/OCS system produces a spectrum emission of UV irradiation in the 185 nm to 254 nm range. Intensity was measured using a Black-Ray UV intensity meter across a range of 220 to 290 nm. The meter has a peak sensitivity at approximately 254 nm. At 25 mm from the source the intensity was measured to be 28 μW/cm². The intensity increases to 31 μW/cm² at 5 mm.

To silylate the samples a heated liquid bath of silylating solution was used. The silylating solution was B[DMA]DS in p-xylene solvent. Based on the experience shown for the DESIRE process[79], a small amount of N-methyl-pyrrolidone (NMP) was added as the diffusion enhancer in some cases. The silylating solution was heated in a beaker using a temperature controlled hot plate. Rinsing of the materials after silylation was done with room temperature p-xylene. The sample was blown dried with bottled nitrogen. Before stabilization the sample was further dried in a 60°C oven for one hour to remove any remaining solvent. Annealing of some samples was done at temperatures of up to 250°C on a temperature controlled hot-plate.

5.6 **SURFACE MODIFICATION OF KAPTON® HN - METHODS AND RESULTS**

All experimentation was carried out using Kapton® 500HN and aluminized Kapton® supplied by the Aerospace Films Division of DuPont Canada. As supplied, Kapton® HN is an orange-gold coloured clear film material with a thickness of 5 mil. The aluminized Kapton® was 1 mil thick with a thin sputtered coating of aluminum on one side.

5.6.1 **UVOCS Activation**

From the beginning, it was obvious that optimizing the activation step is the key to successful silylation. Activation requires a process that functionalizes the surface as uniformly and completely as possible, while not causing unacceptable oxidation degradation. To determine the time based effects of the UV exposure, a number of tests were performed
with increasing exposure time. Contact angle measurements were made immediately after each test. Figure 22 shows the contact angle measurements made on Kapton® exposed to the UV source in air at a distance of 25 mm, for various times. The distance of 25 mm was chosen as a convenient distance that would limit the exposure of the surface to high concentrations of ozone and other active species (compared to 5 mm for example). A minimum water contact angle of 10° is reached, from the nominal pristine surface value of 72°. This indicates a considerable increase in wettability and a high degree of oxidation. The minimum is quickly reached within the first four to five minutes. Over the next six to seven minutes the contact angle increases to approximately 18° degrees then stabilizes.

![Figure 22: Contact angle measurements made on Kapton® are shown with respect to activation time. Contact angle decrease as the functional groups are formed on the polymer surface.](image)

As the surface was oxidized the initial rapid decrease in contact angle was clearly expected. The formation of oxide species on the surface increases the polar nature of the surface. This would in turn increase the surface energy, which means better wetting and a lower contact angle. The contact angle increase after six minutes or so may be related to the degradation of the surface. As reviewed in Chapter 2, at some point the population of
radical species (peroxy radicals for example) will be sufficient to initiate spontaneous propagation of radical production, chain branching and chain scission. As exposure time increases, the type of surface groups must be changing.

If the surface is left exposed to the ambient atmosphere for a day or more, the contact angle will increase to approximately 50°. This same effect has been studied extensively using XPS analysis of poly(ethylene terephthalate) PET. Briggs et al. concluded that the -OH bonds created in the corona discharge oxidation processing of PET are internally hydrogen bonded as the new surface ages, rendering them ineffective. The time lag in this process is due to the slow reorientation of the long polymer chains.

To describe the molecular level effects of the surface modification, an understanding of the initial state of Kapton® is required. Figure 23 is the measured C₁s XPS spectrum of pristine Kapton®. The main peaks, "A" and "B", represent most of the carbons bonded in the structure. "A", at 284.7 eV, is the contribution from C-C and C-H bonds in the ODA portion of the molecule. "B", at 285.8 eV, represents both C bonded to O in the ODA portion, and C bonded to N in the PMDA section. The "C" peak, at 288.6 eV, is produced by electrons from carbonyl groups in the cyclic imide. It should be noted that this measured spectrum varies significantly from theoretical [83] and ideal polyimide spectrum [84], although it does match industrial type materials.[85][86]

In the O₁s portion of the spectrum (figure 24) two peaks are evident. The larger peak at 531.8 eV, represents the imide carbonyl, while the peak at 533.2 eV is from the ether linkage in the ODA section. Surface composition analysis (Table 11) indicates the composition to be 79.6% C, 14.3% O, 5.4% N (at%) with an O/C ratio of 0.18. Hydrogen does not show up in the analysis, since the XPS system does not detect it.
Table 11: Summary of contact angle and XPS surface composition data for Kapton® HN.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle</th>
<th>%C</th>
<th>%O</th>
<th>%N</th>
<th>%Si</th>
<th>O/C</th>
<th>Si/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>72°</td>
<td>79.6</td>
<td>14.3</td>
<td>5.4</td>
<td>—</td>
<td>0.18</td>
<td>—</td>
</tr>
<tr>
<td>After Activation</td>
<td>21°</td>
<td>75.0</td>
<td>19.0</td>
<td>6.5</td>
<td>—</td>
<td>0.25</td>
<td>—</td>
</tr>
<tr>
<td>After Silylation</td>
<td>90°</td>
<td>65.0</td>
<td>16.0</td>
<td>5.2</td>
<td>14.0</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td>After Stabilization</td>
<td>~0°</td>
<td>17.0</td>
<td>50.0</td>
<td>—</td>
<td>34.0</td>
<td>2.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 23: C_{1s} spectrum of pristine Kapton® as supplied from DuPont Canada. C-C and C-H bonds in peak A, C-O and C-N in peak B, C=O in peak C.
Figure 24: O₁s spectrum of pristine Kapton® as supplied from DuPont Canada. Peak A contains the contribution from imide C=O, peak B the ether link (C-O-C).

When the surface is activated, the following changes should occur to the XPS results, if activation is to be successful. Peak "A" must decrease substantially since, hopefully, most of the C-H bonds will disappear. Peak "B" and "C" should increase proportionally as more carbons bond to oxygens. Figure 25 shows the C₁s spectrum after activation. As predicted the "A" peak has dropped substantially and the "B" and "C" peaks are much larger. The composition of the surface has changed to 75% C, 19% O, 6.5% N, with an O/C ratio of 0.25. Substantial oxidation has occurred, and such changes have been shown to indicate the formation of phenolic groups [87], which are ideal for silylation.
Figure 25: C, spectrum after activation in UVOCS system for 20 minutes. Note reduction in peak A relative to B and C indicating a large increase in carbon-oxygen bonds.

5.6.2 Silylation

In the heated (~50°C) liquid bath the functional groups produced during activation should be substituted by a Si fragment of the silylating agent, which should attach itself to the oxygen that remains at the active site (see reaction 5.8). XPS analysis of the silylated surface should show the incorporation of Si into the material, in particular Si-O bonds would appear. The contact angle of water droplets should increase as the functional groups are extinguished. Silylation conditions (temperature and concentrations) were chosen based on published experience with the DESIRE process. The temperature used (~50°C), was the maximum possible without unreasonable evaporation. At temperatures higher than 50°C the p-xylene based solution evaporated at an unreasonably fast rate. A higher temperature is desirable to increase the diffusion of the solution into the polymer surface. Times in the 5 to 15 minute range were explored with little noticeable effect on the resulting contact angle.

The concentration of silylating agent in the solution was chosen to be quite high, one third of the solution by volume, to ensure high availability of the chemical components. For Kapton® the standard solution was 2 parts of solvent (10% NMP in p-xylene) and 1 part B[DMA]DS.
Contact angle measurements made immediately after silylation show an increase to 90° from 21° for the activated surface. XPS surface composition data in table 11 shows the large increase in Si. At 14% it can be seen that a significant amount of silicon has been incorporated into the surface. Figure 26 shows the Si₂p spectrum region for an activated and silylated surface. Two peaks are evident, the larger peak at 102.3 eV corresponds to Si bonded to N, probably from silylating agent adsorbed onto the surface. The smaller peak at 102.9 eV is clearly from Si in an Si-O bond. To explore these two different ways that the silicon is being incorporated into the material, pristine Kapton® was silylated, without activation. XPS analysis of this sample (figure 27) shows a much smaller peak at 102.8 eV, demonstrating that the activation process has resulted in significant numbers of Si-O bonds, which do not appear in the non-activated case.

![Figure 26: Si₂p spectrum of Kapton® after activation and silylation. Peak A represents Si-N bonds in the adsorbed silylation agent. peak B indicates Si in a Si-O type bond.](image-url)
In an attempt to see the effects of high temperature on the adsorbed silylating agent, a sample was heated at a rate of 10° per minute up to 250°C after both activation and silylation. It was thought that this annealing of the sample between silylation and stabilization may reduce the amount of adsorbed silylating agent, giving the stabilization process a better chance of working. After annealing, the contact angle increased to 104°, the nitrogen content dropped sharply and the Si/C ratio was increased. Figure 28 shows the XPS spectrum for that sample in the Si$_2p$ region. No peak is evident for Si bonded to N, while the Si bonded to O peak is much larger. A new peak at 103.2 eV indicates the presence of SiO$_2$. These results demonstrate that most of the adsorbed silylating agent has been removed, or it has changed form.

From the XPS and contact angle measurement results it can be recognized that the silylation process has added substantial silicon to the structure bonded to oxygen atoms. The annealing step appears to reduce the adsorbed silylating agent.
Figure 28: Si$_2p$ spectrum of Kapton® sample after annealing of silylated surface. Annealing has decreased the relative Si-N bonding (peak A) as adsorbed silylation agent leaves the surface.

5.6.3 Stabilization

This final step oxidizes the silylated surface, removing any reactive groups such as and producing a glass-like (high SiO$_x$ content) surface layer. Activation was carried out in the same UVOC system. The main process difference is the time involved. Standard stabilization times of 60 to 90 minutes were used for Kapton®.

After stabilization the contact angle decreases dramatically from 90° to near 0° as the surface becomes completely wetting. The surface energy is very high, indicating a highly polar surface, much like glass. The XPS results after stabilization indicate that considerable changes have occurred. Carbon content has dropped to 17% and nitrogen content has become negligible. Oxygen content has increased to 50% and silicon now makes up 34% of the surface content. The C$_1s$ spectrum (figure 29) shows a new peak at 283.2 eV which may indicate Si-C bonding. In addition, peaks at 284.7 eV, 286 eV and 287.7 eV indicates that the small amount of carbon remaining near the surface remains bonded as C-C, C-H, C=O and possibly more complex groups such as carboxylates.
The $S_{2p}$ spectrum in figure 30 has peaks at 103.8 eV, and 102.1 eV. Both can be attributed to SiO$_2$ bonding structures.[89] Peak in the region of 103.8 eV usually indicate SiO$_2$ type bonds while a peak near 102 eV represents silicon atoms bonded to single oxygens.

SIMS analysis was used to estimate the depth of silylation and stabilization. Figure 31 shows the result of measurements made on a sample that was activated, silylated and stabilized. The SIMS results are presented as a plot of signal intensity vs. depth. Signal intensity should not be taken as a direct measure of concentration, because the bonding environment will strongly effect the intensities measured. The four signals that dominate the figure are $^{28}$Si, $^{12}$C, $^{16}$O, and $^{30}$Si. The $^{16}$O signal should not be used for analysis purposes since it is the bombarding species used in the SIMS analysis. Considerable amounts of silicon are found, penetrating to a depth of at least 0.5 $\mu$m as shown by the $^{28}$Si signal. The depth of silylation is indicated by the change in slope of the $^{28}$Si and $^{12}$C signals at 0.2 $\mu$m. The silylating agent appears to have penetrated to this depth, and altered the structure therein. The stabilization zone is indicated, by the $^{18}$O signal and the $^{12}$C signal. Within the first 0.05 $\mu$m (50 nm) of the surface the carbon content increases, and then stabilizes relative to the silicon content. At the surface, the Si/C ratio is much higher than at a depth of 50 nm. The $^{18}$O signal indicates that the stabilization process has, as expected, reduced the relative carbon content at the surface, producing a silicon-oxygen rich protective region within only the first 0.1 $\mu$m (100 nm) of the surface.
Figure 29: $C_1s$ spectrum of stabilized Kapton® sample. C-H, C-C, C-O and C=O bonding dominates (peaks A, B, and D). A new peak (C) below 284.7 eV may represent Si-C bonding.

Figure 30: $Si_{2p}$ spectrum of stabilized Kapton® sample. Both peaks represent forms of Si-O bonding, SiO$_2$ in peak A, other Si-O forms in peak B.
Figure 31: SIMS depth analysis of a Kapton® sample given the full Photosil™ treatment.
5.6.4 AO Facility Testing of Treated Kapton® HN

The true test of the surface treatment is the ability to protect the polymer from mass loss under hyperthermal AO exposure. Table 12 shows the results of tests carried out to compare activation times. The effect of the optimized activation time is clear, samples 34 and 54 were activated for too long, and sample 38 was activated for too short a time. Samples 65 (5 mil) and 55 (aluminized) which were treated using optimal activation (20 min., 25 mm) show virtually no mass loss. Sample 55, which was aluminized, was activated for only 10 minutes, but proved to be well treated. This effect is not clearly understood (or well defined), but may have resulted from the presence of the reflective aluminum backing, which would have reflected some UV through the polymer again.

Table 12: Results of AO testing of treated Kapton®.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Treatment Method</th>
<th>New $R_e$ (%) Original</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>60 min. UVOCs activation</td>
<td>90</td>
</tr>
<tr>
<td>54</td>
<td>30 min. UVOCs activation</td>
<td>62</td>
</tr>
<tr>
<td>38</td>
<td>10 min. UVOCs activation</td>
<td>78</td>
</tr>
<tr>
<td>55</td>
<td>10 min. UVOCs activation</td>
<td>3</td>
</tr>
<tr>
<td>64</td>
<td>20 min. UVOCs activation</td>
<td>2</td>
</tr>
<tr>
<td>65</td>
<td>20 min. UVOCs activation</td>
<td>2</td>
</tr>
<tr>
<td>71</td>
<td>20 min. UVOCs activation</td>
<td>4</td>
</tr>
<tr>
<td>74</td>
<td>20 min. UVOCs activation</td>
<td>3</td>
</tr>
</tbody>
</table>

* aluminized Kapton®

Using the optimized treatment parameters, subsequent samples were tested for longer exposure times: 10 hours with ultraviolet irradiation, followed by 10 hours without ultraviolet exposure. No mass loss or morphology change was evident. Because of the length of this test the estimated new $R_e$ for this sample is less than 0.32% of the original $R_e$. A set of samples was also given a thermal cycling exposure and tested for 5 hours in the AO Beam Facility. After treatment, samples were sequenced ten times, alternately, in liquid...
nitrogen and then placed in a 100°C oven. No mass loss, or change in surface morphology resulted from either the thermal cycling or the AO exposure.

A special set of treatments was given to one sample (sample 56) to demonstrate the effects of the different process steps, by looking at the surface morphologies that result after AO testing. The surface of the sample was masked into four sections. Section 1 was activated and silylated, section 2 was activated, silylated and then stabilized, section 3 was silylated only, section 4 was silylated and stabilized (see figure 32).

activation - 20 minutes, UVOCS system, 25 mm from UV source
silylation - 15 minutes, 50°C
stabilization - 60 minutes, UVOCS system, 25 mm from UV source

Finally, the entire surface was exposed to AO for 5 hours before SEM micrographs were taken of the varying surface morphologies. Section 1, which was activated and silylated, and section 2, which received the full treatment, exhibited no change in surface morphology (compare figure 33a to 33b). The other two surfaces showed significant morphology changes. In figure 33a the smooth uneroded surface of treated Kapton® is shown near a contamination particle, which is required for focusing since the surface is very smooth. In contrast to the very smooth surface, figure 33b shows the surface of untreated Kapton® after exposure to HA0 in LEO. The surface is clearly eroded near a contamination particle that splattered onto the surface before AO exposure. The area around the particle was eroded away leaving a small plateau of material.
<table>
<thead>
<tr>
<th>1. activated silylated</th>
<th>2. activated silylated stabilized</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. silylated</td>
<td>4. silylated stabilized</td>
</tr>
</tbody>
</table>

**Figure 32:** Diagram of sample 56 showing four different treatment areas.
Figure 33: SEM micrographs of a) fully treated (area 2) section of sample 56 near a particle on the surface, b) an example of erosion of unprotected Kapton®. Note the height of the uneroded section underneath contaminate area. Both are 1500X.
5.7 Conclusions - Proof of Concept

The Photosil process has proven to be capable of protecting Kapton® from atomic oxygen degradation. The SEM micrographs of the fully treated regions of sample 56 demonstrate the capability of the process to strongly reduce degradation of the surface. Given this successful proof-of-concept trial of what appears to be a simple, flexible process, protection of other polymer materials can now be explored.
THE PROTECTION OF PEEK, PET AND POLYETHYLENE

Both PEEK and PET (Mylar®) exhibit many of the chemical and structural characteristics of Kapton®. Polyethylene, however, is quite different, particularly with respect to how it reacts to ultra-violet irradiation. Polyethylene does not contain groups within its structure that are photochromic (groups that can be photonically energized). Figure 34 illustrates the three structures.

![Chemical structures of PEEK, PET, and PE molecular repeating unit.](image)

Figure 34: Chemical structures of PEEK, PET, and PE molecular repeating unit.

In all three cases, it should be possible to optimize the activation process, and then apply the silylation and stabilization steps with only limited changes to the overall process.
6.1 PROTECTION OF PEEK - poly(ether ether ketone)

PEEK film, 10 mil in thickness, was obtained from Loughborough University of Technology and was used for all testing.

6.1.1 Activation of PEEK

Like Kapton®, PEEK activated quickly under UV irradiation in air (in the UVOC system). PEEK is functionalized by both the active oxygen species and, the ultra-violet light produced by the UVOC system. Figure 35 shows the contact angle vs. activation time curve for PEEK film at 25 mm from the UV source. The measured contact angles reach a minimum of 32° in approximately 4 minutes. A slight rise with longer exposure time leads to a stable contact angle of approximately 35°. Activation times in the 10 to 15 minute range were used for the processing of PEEK film.

![Figure 35: Contact angles vs. activation time for PEEK film in the UVOC system at 25 mm from the UV source.](image)
After activation the formation of considerable amounts of oxide species is confirmed by a decrease in contact angle to 22° from the original 72°, and the compositional XPS survey results show a two-fold increase in the oxygen to carbon ratio (table 13). A considerable amount of silicon was measured in the activated surface. Since the control sample did not exhibit this contamination, it is unlikely that this silicon is a processing residue. No likely source, other than airborne or handling contamination, was identified.

Table 13: Composition of PEEK at various process stages as determined by XPS analysis.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle</th>
<th>Composition (at%)</th>
<th>O/C</th>
<th>Si/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
<td>N</td>
</tr>
<tr>
<td>Control</td>
<td>72°</td>
<td>85.6</td>
<td>12.7</td>
<td>—</td>
</tr>
<tr>
<td>Activation</td>
<td>22°</td>
<td>68.0</td>
<td>26.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Silylation</td>
<td>133°</td>
<td>73</td>
<td>17</td>
<td>—</td>
</tr>
<tr>
<td>Stabilization</td>
<td>0°</td>
<td>25.5</td>
<td>48</td>
<td>1.2</td>
</tr>
</tbody>
</table>

6.1.2 Silylation of PEEK

Silylation was carried out using the same solution as for Kapton®: 2 parts of solvent (10% NMP in p-xylene) and 1 part B[DMA]DS for 20 minutes at approximately 50°C. After silylation the contact angle increased to a very high value of 133°, and the surface composition of silicon increased to 9.6%.

6.1.3 Stabilization of PEEK

As expected, the relative silicon content increased dramatically after stabilization in the UVOC system for 90 minutes at 25 mm from the UV source. Table 13 shows the silicon to oxygen ratio to be approximately 1:2 (as in SiO₂), and that the surface has become completely wetting (again as in SiO₂). The
The presence of silicon-oxygen bonding is confirmed by the large peak at 102.7 eV in the Si$_{2p}$ XPS spectrum region (figure 36).

<table>
<thead>
<tr>
<th>Description</th>
<th>P-573S1</th>
<th>Operator: NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_{2p}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy Width</td>
<td>Area</td>
<td>Z</td>
</tr>
<tr>
<td>102.85</td>
<td>2.56</td>
<td>8032</td>
</tr>
</tbody>
</table>

![Figure 36: Si$_{2p}$ spectrum of PEEK film sample after activation, silylation and stabilization. Peak at 102.7 eV represents silicon-oxygen bonding, both in Si-O and SiO$_2$ forms.](image)

6.2 PROTECTION OF PET (Mylar®) - poly(ethylene terephthalate)

Mylar® 500EL, 5 mil in thickness, obtained from the Aerospace Films Division of DuPont Canada was used for all testing.

6.2.1 Activation of PET

PET proved to be more difficult to activate than PEEK or Kapton®. Figure 37 shows the contact angle vs. activation time curve for PET film at 25 mm from the UV source. The sessile drop contact angle does not reach a minimum of $25^\circ$ until after 15 minutes of treatment in the UVOC system. An activation time of 20 minutes was used to ensure adequate functionalization.
6.2.2 Silylation and Stabilization of PET

After silylation, the silicon content of PET increased to 20%. Although the relative silicon content did not increase after stabilization, the oxygen content did increase as expected (table 14). The high resolution Si$_{2p}$ XPS spectrum analysis after full treatment is shown in figure 38.

Table 14: XPS composition of PET after silylation and stabilization.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Silylation</td>
<td>58</td>
</tr>
<tr>
<td>Stabilization</td>
<td>43</td>
</tr>
</tbody>
</table>

The peak at 102 eV is formed by Si-O bonding, and as seen before, the two peaks at 103 eV and 103.9 eV indicate the presence of SiO$_2$ bonding.
Figure 38: Si$_{2p}$ XPS spectrum of PET after activation, silylation and stabilization. Peak A and C indicate SiO$_2$ bonding, peak B represents all other Si-O bonding contributions.
6.3 PROTECTION OF PE - poly(ethylene)

Linear low density polyethylene, 2 mil in thickness, obtained from DuPont Canada was used for all testing.

6.3.1 Activation of PE

As expected PE proved to be difficult to activate using the UVOCS system. Initial attempts to activate the surface using the same basic scheme as used for Kapton®, PEEK and PET proved to be ineffective. Moving the sample to within 5 mm of the UV source, however, proved to be the key. At this close distance the concentration of active species (ozone, AO singlet oxygen) changes the mechanism of activation, by participating more strongly in the reactions. Figure 39 shows the contact angle vs. activation time curve for PE film at 5 mm from the UV source. As is typical with polyethylene, the contact angle is very high to start. The contact angle drops slowly and reaches a minimum of nearly 50° only after more than 15 minutes have passed.
6.3.2 Silviation and Stabilization of PE

The silicon content of PE increased to 16% after silylation, and then rose slightly higher to 20% after stabilization (table 15). The relative oxygen content, more than doubled bringing it to 41%, which gives a Si/O ratio of 2:1. The high resolution Si$_2$p XPS spectrum analysis after full treatment (figure 40) confirms the appearance of large quantities of SiO$_2$ type bonds with a large peak at 102.8 eV, and the smaller peak at 103.8 eV.
Table 15: XPS composition of PE after silylation and stabilization.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Silylation</td>
<td>68</td>
</tr>
<tr>
<td>Stabilization</td>
<td>39</td>
</tr>
</tbody>
</table>

6.4 AO Testing of Treated PEEK, PET and PE Films

AO testing results are summarized in table 16 below. All samples were exposed to the AO beam for 5 hours, with an average fluence of $1.8 \times 10^{20}$ atoms/cm$^2$.

Table 16: Results of AO Testing for PEEK, PET, and PE

<table>
<thead>
<tr>
<th>Material</th>
<th>New $R_e$ (%) original</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>4.7</td>
</tr>
<tr>
<td>PET (Mylar®)</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>PE</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
</tr>
</tbody>
</table>
Figure 40: Si\textsubscript{2p} XPS spectrum of PE after activation, silylation and stabilization. Peak A and C indicate SiO\textsubscript{2} bonding, peak B represents other Si-O bonds.
6.5 CONCLUSIONS - PEEK, PET AND PE FILM TREATMENTS

The Photosil™ process proved to be capable of protecting all three of the polymer film materials tested. Average AO erosion rates were lowered to below 5% for all three materials. The successful protection of PET (Mylar®) was a major accomplishment, since Mylar® is also used extensively in spacecraft applications. Although PEEK film is not used widely as a spacecraft material, it is used as a matrix for thermoplastic composite materials. Polyethylene is rarely considered as a spacecraft material because of its poor thermal performance, but the success of the treatment shown here points to a wide variety of other applications. For example, linear low density polyethylene, which is a very low cost polymer, could be used to replace other more expensive packaging materials where barrier properties and resistance to oxidation may be required.
CHAPTER 7

PROTECTION OF POLYMER MATRIX COMPOSITES

Given the success of the Photosil process to protect thin-film polymer materials, it should be possible to extend the capability to PMC (polymer matrix composite) materials, and it is in fact the ultimate goal of this thesis to do so. Unfortunately, when the method was attempted, little change resulted in the performance of the materials. Two types of PMCs were examined. A PEEK/Graphite fibre (PEEK/Gr) system (Fiberite AS4/APC-2) and an Epoxy/Graphite fibre (Ep/Gr) system (Hercules AS4/3501-6). The epoxy resin based composite in particular exhibited little change in mass loss as a result of the treatment. This material proved to be quite difficult to activate, requiring longer UVOCS irradiation times than any other material investigated. Examination of the surfaces after treatment and exposure in the AO facility showed that large areas had not been protected. It was quite clear that exposed fibres at the surface were being eroded. Thus, for composites to be protected, it would appear that the fibres themselves would also have to be protected. Fortunately, the composition of the fibres made the possibility of silylating them realistic.

One of the most popular methods for preparing graphite/carbon fibres is to use a polyacrylonitrile (PAN) polymer precursor. The Hercules AS4 fibre used in both PMCs examined herein is a high tensile strength PAN based graphite fibre. To make the graphite fibres, fine PAN fibres are pyrolysed in an inert atmosphere at high temperature. Most of the volatile components of the polymer are driven off in the process, leaving behind a carbon or graphite fibre, depending on the time and temperature conditions utilized. PAN is used because of its high degree of molecular orientation, high melting point, and very high carbon yield. The basic process involves:
- Conversion to carbon in an oxidizing atmosphere at 200-300°C under tension to stop shrinkage. The polymer is converted to a cyclic or ladder structure which resists dimensional changes that would otherwise occur during carbonization.

- Carbonization (thermal pyrolysis) in an inert atmosphere to about 1000°C. Non-carbon elements are removed as volatiles. About 50% of the original mass remains.

- Further heating of up to 3000°C to improve mechanical properties through microstructure reorganization, ultimately resulting in a highly ordered graphitic structure.

The key to silylating the PAN based fibres is the fact that the pyrolysis treatment is not perfect, some precursor material remains, especially at the surface, and it should be possible to activate this surface. Carbon fibres, as compared to graphite fibres, exhibit the highest quantities of remnant material. The higher temperature production of graphite fibres drives off more and more volatile material as the temperature goes up. The difficulty, in this case, is the fact that AS4 fibres are of the type that undergo the most heating, and as a result have the lowest amount of remnant material on their surface. To ensure activation of the fibre surfaces a process specifically aimed at producing functional groups was required. Increasing the functionality of carbon fibre surfaces is not a new concept. The idea of producing large quantities of functional groups on the surface of fibres is used to increase the interfacial bonding strength between the fibre and the matrix. The techniques used therein should be applicable.
7.1 MODIFICATION OF PAN BASED GRAPHITE FIBRE SURFACES

Considerable effort has gone into the creation and optimization of surface functional groups on graphite/carbon fibres. The result of this work is the production of oxide based groups on the fibre surface, without damaging the fibre extensively. Many methods have been explored including:

- gaseous oxidation in air, ozone, with or without UV assistance, and in plasmas or a corona discharge
- liquid phase techniques using oxidizers such as nitric acid or hydrogen peroxide.

One widely used and well studied method employs nitric acid based solutions. However a mixture of NaNO₃, H₂SO₄ and KMnO₄, called "Hummer’s reagent", has also been studied extensively, and has proven to give outstanding functionalization. Even treatments for short periods of time (3 to 10 minutes) using hummer’s reagent give large increases in functional groups, such as carboxyl and hydroxyl, concentrated on the surface.[90] To improve the chances of successful silylation of the fibres and the polymer resin, it should be possible to use a short additional treatment before UV activation that will activate any exposed fibre surfaces.

Although it was not explored in this thesis, gas phase functionalization using ozone may also be a viable means to increase the strength of the activation step. In effect, ozone, when added to the UV activation step may boost the efficiency of the process sufficiently to activate any exposed fibre surfaces.

7.1.1 Treatment of fibre bundles

To resolve the problem, AS4 fibre bundles were treated directly (oxidizer etch, activation silylation, stabilization), then exposed to AO. A short immersion
of 2 minutes in a solution of 1 part (by weight) of sodium nitrate (NaHNO₃), 1 part potassium permanganate (KMnO₄), 2 parts technical grade sulphuric acid (H₂SO₄) and 50 parts distilled water, was done. Fibre bundles were then oxidized on both sides, in the UVOCs system for 2, 5, 10 and 15 minutes at 5 mm from the source. Silylation was done in a solution of 1 part B[(UMA)]DS and 2 parts p-xylene at 50°C for 15 minutes. After a one hour drying period at 60°C the bundles were stabilized in the UVOCs system for 60 minutes at 5 mm from the source. A group of bundles was also activated, silylated and stabilized with the same conditions, but without using the acidic/oxidizer pretreatment.

After the oxidizer pretreatment the water contact angle appeared to decrease. Only qualitative estimates of contact angle could be made. The bundles of fibre do not have a smooth or continuous surface on which to place the droplet. To make the estimate, a droplet was placed on one side of the bundle while it was lying in a horizontal position. The droplet was suspended by the close lying fibres, giving it a very irregular shape, but generally discernable angle. All contact angle measurements were made at the same time so direct visual comparison could be made.

Before any treatment, the water contact angle was between 45° and 90°. After oxidizer treatment for 2 to 5 minutes the contact angle dropped to below 45°. For samples with immersion times of 10 and 15 minutes the contact angle decreased to less than 30°, but the surface of the fibres changed to a brownish colour and a dark residue could be rubbed off. The residue is most likely carbon. UVOCs treatment did not noticeably alter the contact angle. Silylation of the bundles increased the contact angle to approximately 90°. After stabilization the contact angle dropped again, to below 30°. The samples treated without the oxidizer etch showed the same contact angle measurement changes.
7.1.2 AO Testing of treated fibres

All samples were tested in the AO facility for a short one hour exposure to resolve any erosion effects. Only the samples treated with both the oxidizer etch and UV activation for greater than five minutes showed no visible degradation in the short test. A five minute oxidizer etch was chosen to be optimal, balancing reasonable functionalization against the damage indicated by the carbon residue.

The sample with a 10 minute UVOCS activation was chosen for the longer five hour qualification test. The sample, along with a control, was exposed to a fluence of $1.7 \times 10^{20}$ atom/cm$^2$. The treated sample lost 40 $\mu$g during the test, while the control lost 280 $\mu$g. Subsequent reweighing showed that any mass loss could easily be accounted for by moisture loss. The sample appeared to return to within 10 $\mu$g of its before-exposure weight when weighed the next day. It is believed that the standard two hour high vacuum de-gas was not sufficient to stabilize the moisture mass loss that occurs when a sample is first placed in the vacuum chamber. With this result it appears that successful silylation and stabilization can be carried out using the additional oxidizer etch in addition to UV activation. Table 17 summarizes the treatment and testing results.
Table 17: Summary of fibre bundle silylation and testing

<table>
<thead>
<tr>
<th>Treatment Scheme</th>
<th>Contact Angle</th>
<th>AO Testing Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min oxidizer etch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 min UV activation</td>
<td>&lt;45°</td>
<td>failed short test - visible surface degradation</td>
</tr>
<tr>
<td>15 min silylation, 50°C</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>~ 90°</td>
<td></td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>5 min oxidizer etch</td>
<td>&lt;45°</td>
<td>failed short test - visible surface degradation</td>
</tr>
<tr>
<td>5 min UV activation</td>
<td>&lt;30°</td>
<td>passed short test - no visible degradation</td>
</tr>
<tr>
<td>15 min silylation, 50°C</td>
<td>~ 90°</td>
<td>lost 40 µg in 5 hour test - mass loss accounted for by moisture loss.</td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>5 min oxidizer etch</td>
<td>&lt;30°</td>
<td>passed short test - no visible degradation</td>
</tr>
<tr>
<td>15 min UV activation</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>15 min silylation, 50°C</td>
<td>~ 90°</td>
<td></td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>2 min UV activation</td>
<td>&lt;45°</td>
<td>failed short test - visible surface degradation</td>
</tr>
<tr>
<td>15 min silylation, 50°C</td>
<td>~ 90°</td>
<td></td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>5 min UV activation</td>
<td>&lt;30°</td>
<td>failed short test - visible surface degradation</td>
</tr>
<tr>
<td>15 min silylation, 50°C</td>
<td>~ 90°</td>
<td></td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>10 min UV activation</td>
<td>&lt;30°</td>
<td>failed short test - visible surface degradation</td>
</tr>
<tr>
<td>15 min silylation, 50°C</td>
<td>~ 90°</td>
<td></td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>&lt;30°</td>
<td></td>
</tr>
<tr>
<td>15 min UV activation</td>
<td>&lt;30°</td>
<td>failed short test - visible surface degradation</td>
</tr>
<tr>
<td>15 min silylation, 50°C</td>
<td>~ 90°</td>
<td></td>
</tr>
<tr>
<td>60 min stabilization, 5 mm</td>
<td>&lt;30°</td>
<td></td>
</tr>
</tbody>
</table>
7.2 **PROTECTION OF PEEK RESIN BASED PMCs**

As mentioned above, the first attempts to extend the Photosil process to PMCs, were unsuccessful. In figure 42 exposed fibres are evident in lenticular shaped areas where the resin did not completely cover the surface. This seems to be typical of Ep/Gr composites produced at UTIAS. Five different samples, collected from random sources, were examined under an optical microscope. All exhibited the lenticular regions of fibre exposure. Figure 41, 43 is a photograph of a PEEK/Gr surface at the same magnification. The difference in surface coverage is quite evident. The Ep/Gr surface has areas where fibres can be seen clearly. It is safe to assume that most composite materials produced will exhibit, to some extent, such surface irregularities. This assumption can be considered as the "worst case scenario", and must be addressed if the protection process is to succeed for both PMC types treated here.

**7.2.1 Treatment and AO Testing of PEEK Composite**

To protect PMCs then, it is necessary to add the oxidizer etch step as demonstrated for the AS4 fibres, or some other type of process that will activate the graphite fibres. As with UV activation, the process of oxidizer treatment was studied using contact angle measurements to estimate the degree of functionalization. PEEK/Gr samples were immersed for 1, 2, 4, 8, and 12 minutes in the same Hummer's reagent solution used for the fibre treatments. Figure 43 shows the change in contact angle, as the immersion time is increased. The contact angle decreases to $90^\circ$ within the first minute of immersion. The minimum contact angle of approximately $73^\circ$ is reached by eight minutes, and does not change substantially between eight and twelve minutes. Some oxidation or functionalization has undoubtedly occurred.
Figure 41: Photograph of PEEK/Gr composite surface for comparison to Ep/Gr surface in figure 42. 43X

Figure 42: Photograph of Epoxy/Graphite composite surface showing areas of exposed fibres. 43X
Based on the results of these contact angle measurements, the 8 and 12 minute samples were treated further with a 15 minute activation in the UVOCS system at 5 mm from the source (see table 18). Activation time was chosen based on studies of contact angle. Figure 44 shows that a time of 15 minutes provides more than adequate functionalization for the PEEK composite. After activation, the water contact angle decreased to 12°. Silylation was carried out in a solution of 1 part B[DMA]DS and 2 parts p-xylene at 50°C for 15 minutes, followed by stabilization in the UVOCS system for 60 minutes at 5 mm from the source. The contact angle measurement was 79° after silylation and 22° after stabilization. Following the surface modification treatment the samples were exposed in the AO facility for a five hour qualification test. Both the 8 and 12 minute etch samples exhibited no mass loss after exposure to $1.4 \times 10^{20}$ atoms/cm$^2$.
Figure 44: Contact angle vs. activation time for PEEK composite in UVOCs system at 5 mm.

Table 18: Summary of PEEK/Gr fibre material silylation and testing

<table>
<thead>
<tr>
<th>Treatment Scheme</th>
<th>Contact Angle</th>
<th>AO Testing Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 minute oxidizer etch</td>
<td>90°</td>
<td>—</td>
</tr>
<tr>
<td>2 minute oxidizer etch</td>
<td>90°</td>
<td>—</td>
</tr>
<tr>
<td>4 minute oxidizer etch</td>
<td>81°</td>
<td>—</td>
</tr>
<tr>
<td>8 minute oxidizer etch</td>
<td>74°</td>
<td>no mass loss in 5 hour test</td>
</tr>
<tr>
<td>15 minute UV activation</td>
<td>12°</td>
<td></td>
</tr>
<tr>
<td>15 minute silylation, 50°C</td>
<td>79°</td>
<td></td>
</tr>
<tr>
<td>60 minute stabilization, 5 mm</td>
<td>22°</td>
<td></td>
</tr>
<tr>
<td>12 minute oxidizer etch</td>
<td>72°</td>
<td>no mass loss in 5 hour test</td>
</tr>
<tr>
<td>15 minute UV activation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 minute silylation, 50°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 minute stabilization, 5 mm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.2.2 XPS Analysis of PEEK Composite Surfaces

The PEEK composite surface changed as expected based on the success of the AO testing. Table 19 contains the XPS compositional data for samples measured after each stage of processing, along with a control and theoretical composition for PEEK. The surface composition is dominated by the presence of the PEEK resin, which covers the surface. As is normally seen, some oxidation of the polymer is evident, and process based contaminants such as silicon, nitrogen and fluorine are evident. The first process step, etching, clearly oxidizes the surface, increasing the oxygen content from 18% to 25%. Activation oxidizes the material further. The silylation step incorporates substantial silicon into the surface. Stabilization clearly reduces the carbon surface content, developing a Si-O structure.

Table 19: Surface composition of treated PEEK composite samples, measured by XPS.

<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>N</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>76.1</td>
<td>18.2</td>
<td>1.5</td>
<td>3.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Oxidizer Etch</td>
<td>70.1</td>
<td>25.1</td>
<td>2.0</td>
<td>2.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Activation</td>
<td>62.5</td>
<td>32.8</td>
<td>1.8</td>
<td>2.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Silylation</td>
<td>61.9</td>
<td>24.7</td>
<td>11.5</td>
<td>1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Stabilization</td>
<td>17.9</td>
<td>52.8</td>
<td>27.4</td>
<td>1.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Once again, the changes that occur on the surface of the material will be referenced to the high resolution spectrum measured from a control sample of the material treated. Figure 45 shows the C$_{1s}$ spectrum of a PEEK composite control sample. The standard strong peak at 284.6 eV, marking the presence of C-C and C-H bonds is evident. Oxygen/carbon forms, ethers at 286 eV and carbonyls at 288.4 eV, are apparent also. A small peak at 283.1 eV may be produced by the graphite in the fibres of the composite. At 291.5 eV the $\pi-\pi^*$, shake-up/shake-off
signal from PEEK's aromatic rings is discernible.[64][91] The O$_{1s}$ spectrum (figure 46) is fit with two peaks: 531.7 eV encompasses all environments where oxygen is doubly bonded to carbon. The peak at 533.3 eV indicates all of the singly bonded states of oxygen.

The etching process resulted in a large increase in the relative amount of oxygen. The C$_{1s}$ spectrum fit (figure 47) suggests that a number of new bonding structures have been formed. A new peak at 288.9 eV can be assigned to the carbon in an ester group. The O$_{1s}$ spectrum (figure 48) shows two large new peaks in the singly bonded oxygen region above 532 eV. These peaks are formed by oxygen core electrons from hydroxide, ether and ester groups.

After activation, the C$_{1s}$ peaks at 287.2 eV and 288.8 eV (figure 49) are dramatically increased revealing the capacity of the activation process to form ester, hydroperoxide and carbonyl groups, at the expense of C-H bonds at 284.6 eV (the C-H, C-C peak dropped from 72.4% to 53.4% after activation). The peak at 289.9 eV is associated with carboxyl groups. A small $\pi-\pi^*$ peak is located at 293 eV. The O$_{1s}$ spectrum (figure 50) confirms the formation of the carbon-oxygen groups with increases in peaks at 532.9 eV, 534 eV and a new peak at 535 eV.

When silicon is added to the structure during silylation the C$_{1s}$ spectrum undergoes another substantial change (figure 51). The peak at 284.6 eV becomes clearly dominant. This is caused by the presence of C-Si bonds from the silylation process. Ether and carbonyl bonds are evident also (286.4 eV and 288.4 eV respectively). These carbon-oxygen bonds are not altered by the process, since they are the strongest part of the polymer structure. A new peak at 532 eV dominates the O$_{1s}$ spectrum (figure 52). This peak demonstrates the formation of Si-O-Si bonds, and include a contribution from the remaining carbonyl bonds (usually just below 532 eV). Hydroxyl and ether groups
contribute to the peak at 533.6 eV. The three peaks in the Si$_2p$ spectrum (figure 53) are formed by: the silylating agent at 101.7 eV, Si-O at 102.5 eV and some SiO$_2$ at 104.2 eV.

The stabilization process produces only small changes in the C$_1s$ spectrum (figure 54), with the appearance of a new peak at 283.2 eV. This peak indicates C-C bonding in a graphitic form, which may be from exposed fibre areas, or fibres near the surface. This peak is strongly evident here for the first time because the total carbon content is so low. The O$_1s$ spectrum (figure 55) now has its largest peak at 533 eV, indicating a high degree of oxidation, most likely SiO$_2$. Silicon as SiO$_2$ is now the main form of Si as shown by the dominant peak at 103.6 eV and smaller peak at 104.7 eV in the Si$_2p$ spectrum (figure 56). Si-O bonding is still evident from the peak at 102.6 eV.
Figure 45: $C_{1s}$ XPS spectrum of PEEK composite control sample. Peak A, C-C and C-H bonds, various carbon-oxygen bonding forms are represented by peaks B, C, and D. Graphite at peak E.
Figure 46: $O_{1s}$ spectrum of PEEK composite control sample. Peak A represents all doubly bonded oxygens (eg. carbonyls), peak B represents all singly bonded oxygens (eg. ethers).
Figure 47: C\textsubscript{1s} XPS spectrum of PEEK composite sample after oxidizer etching. A new peak has formed (D) which represents ester groups.
Curve-fit for region: O\textsubscript{1s}

<table>
<thead>
<tr>
<th>BE/eV</th>
<th>fwhm/eV</th>
<th>area</th>
<th>rel at.ptnt</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7.78e+004</td>
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</tr>
<tr>
<td>-531.54</td>
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</tr>
<tr>
<td>-533.95</td>
<td>1.84</td>
<td>2.56e+004</td>
<td>15.3</td>
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</tbody>
</table>

Figure 48: O\textsubscript{1s}, XPS spectrum of PEEK composite after oxidizer etching. Two peaks, A and C, in the singly bonded oxygen region are formed by hydroxide, ether, and ester groups.
Curve-fit for region: C$_{1s}$

<table>
<thead>
<tr>
<th>BE/eV</th>
<th>fwhm/eV</th>
<th>area</th>
<th>rel at. prcnt</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>-285.91</td>
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<tr>
<td>-288.77</td>
<td>1.47</td>
<td>2.29e+004</td>
<td>11.6</td>
</tr>
<tr>
<td>-287.20</td>
<td>1.39</td>
<td>2.11e+004</td>
<td>10.7</td>
</tr>
<tr>
<td>-289.85</td>
<td>1.35</td>
<td>5.35e+003</td>
<td>2.7</td>
</tr>
<tr>
<td>-293.01</td>
<td>1.30</td>
<td>7.60e+002</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Figure 49: C$_{1s}$ XPS spectrum of PEEK composite sample activated for 15 minutes. Activation has increased the number of ester, hydroperoxide and carbonyl groups (peaks D and C) and reduced the C-C, and C-H bonding shown in peak A. Peak E is from carboxyl groups.
Curve-fit for region: O₁s

<table>
<thead>
<tr>
<th>BE/eV</th>
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<th>rel at. prcnt</th>
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</thead>
<tbody>
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<td>1.18e+005</td>
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<tr>
<td>-533.96</td>
<td>1.62</td>
<td>6.13e+004</td>
<td>24.9</td>
</tr>
<tr>
<td>-531.82</td>
<td>1.70</td>
<td>5.55e+004</td>
<td>22.6</td>
</tr>
<tr>
<td>-535.06</td>
<td>1.65</td>
<td>1.12e+004</td>
<td>4.6</td>
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</table>

Figure 50: O₁s XPS spectrum of PEEK composite after activation for 15 minutes. Considerable numbers of singly bonded oxygen groups have formed, peaks A, B, D.
Figure 51: C$_{1s}$ XPS spectrum of PEEK composite after activation and silylation. Peak A dominates with the addition of numerous C-Si bonds from the silylation agent.
Figure 52: O$_{1s}$ XPS spectrum of PEEK composite after activation and silylation. Peak A is formed by Si-O-Si bonds, with some C=O contribution. Peak B comes from OH and ether groups.
Figure 53: $\text{Si}_{2p}$ XPS spectrum of PEEK composite after activation and silylation. Peak A from the silylating agent structure, peak B from Si-O bonding and peak C from SiO$_2$. 
Figure 54: \( C_{1s} \) XPS spectrum of PEEK composite after activation, silylation and stabilization. Oxygen bonding has been increased dramatically with the formation of peaks B, C, D, F. Peak E, which indicates the presence of carbon-carbon bonding in a graphitic form, is also evident.
Figure 55: O$_1$s XPS spectrum of PEEK composite after activation, silylation and stabilization. A high degree of oxidation is evident with the large single peak A.
Curve-fit for region: Si\textsubscript{2p}

<table>
<thead>
<tr>
<th>BE/eV</th>
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<th>area</th>
<th>rel at.prctnt</th>
</tr>
</thead>
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<td>-103.63</td>
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<td>8.89e+004</td>
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<td>-102.60</td>
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<td>4.07e+004</td>
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</tr>
<tr>
<td>-104.68</td>
<td>1.70</td>
<td>1.62e+004</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Figure 56: Si\textsubscript{2p} XPS spectrum of PEEK composite after activation, silylation and stabilization. Peaks A and C represent SiO\textsubscript{2} bonding, peak B indicates Si singly bonded to oxygen.
7.3 Protection of Epoxy Resin Based PMCs

The same methodology was repeated for the epoxy resin PMC. Samples of the material were etched in the same mixture of NaHNO₃, KMnO₄, H₂SO₄ and water for 1, 2, 4, 8, 12, 16 and 20 minutes. The epoxy composite took longer to functionalize than the PEEK composite based on contact angle measurements (figure 57), although damage (carbon residue) appeared quickly as the contact angle began to decrease. Brownish discoloration of the surface was noticed first on the 12 minute sample, becoming very evident on the 16 and 20 minute samples.

![Graph: Contact angle vs. etch time for Epoxy composite in Hummer's reagent.](image)

Figure 57: Contact angle vs. etch time for Epoxy composite in Hummer's reagent.

Only the 8 minute etch sample was treated further with UV activation, silylation and stabilization (see table 20). Figure 58 indicates that 15 minutes is a minimum activation time for the Epoxy composite material. During the standard 5 hour test in the AO facility, no mass loss occurred on this sample. Further
testing showed that etch treatments in the 5 to 10 minute range resulted in excellent AO resistance.

![Graph showing contact angle vs. time for Epoxy composite in UVOCS system at 5 mm.](image)

**Figure 58:** Contact angle vs. activation time for Epoxy composite in UVOCS system at 5 mm.

**Table 20:** Summary of Epoxy composite treatment and testing

<table>
<thead>
<tr>
<th>Treatment Scheme</th>
<th>Contact Angle</th>
<th>AO Testing Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 minute oxidizer etch</td>
<td>94°</td>
<td></td>
</tr>
<tr>
<td>2 minute oxidizer etch</td>
<td>95°</td>
<td></td>
</tr>
<tr>
<td>4 minute oxidizer etch</td>
<td>92°</td>
<td></td>
</tr>
<tr>
<td>8 minute oxidizer etch</td>
<td>63°</td>
<td>no mass loss in 5 hour test</td>
</tr>
<tr>
<td>15 minute UV activation</td>
<td>18°</td>
<td></td>
</tr>
<tr>
<td>15 minute silylation, 50°C</td>
<td>85°</td>
<td></td>
</tr>
<tr>
<td>60 minute stabilization, 5 mm</td>
<td>12°</td>
<td></td>
</tr>
<tr>
<td>12 minute oxidizer etch</td>
<td>51°</td>
<td></td>
</tr>
<tr>
<td>16 minute oxidizer etch</td>
<td>47°</td>
<td></td>
</tr>
<tr>
<td>20 minute oxidizer etch</td>
<td>43°</td>
<td></td>
</tr>
</tbody>
</table>
7.3.1 XPS Analysis of Epoxy Composite Surfaces

The compositional changes of the material (table 21) reflect the contact angle and AO testing results conclusively. Once again, the oxidizing steps (etch, activation) increase the oxygen content of the surface dramatically. The silylation step increases the silicon content to nearly one quarter of the surface material. Stabilization drastically reduces the carbon content and increases the Si-O content.

Table 21: Surface composition of treated Epoxy composite samples, measured by XPS analysis.

<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>Composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Control</td>
<td>72.2</td>
</tr>
<tr>
<td>Oxidizer Etch</td>
<td>73</td>
</tr>
<tr>
<td>Activation</td>
<td>54.5</td>
</tr>
<tr>
<td>Silylation</td>
<td>46.6</td>
</tr>
<tr>
<td>Stabilization</td>
<td>15.9</td>
</tr>
</tbody>
</table>

High resolution XPS spectrum reveal that the Epoxy composite surface is modified in much the same way that the PEEK material surface was. The results are summarized here for the spectra that follow (figures 59 to 70).

Oxidizer etching produced an increase in hydroxyl, ester and carbonyl groups on the surface (C$_1$s, 286.7 eV and 288.2 eV peaks in figure 61 compared to the same peaks in figure 59. In addition, the formation of the residue can be seen as two peaks (283.2 eV and 281.8 eV) which can be associated with carbon in a graphite form. The new oxide groups appear in the O$_1$s spectrum of the etched sample (figure 62) as an increase in the peak at 533.1 eV, and a new peak at 534.6 eV. Activation produces further increases in the number and type of oxygen-carbon groups, in particular carboxyl groups (289.3 eV) are now evident in the C$_1$s spectrum (figure 63). The 284.7 eV peak dominates the silylated C$_1$s.
spectrum (figure 65). The large number of Si-O bonds (102.3 eV) is evident from the \textit{Si}{p} spectrum for the silylated sample (figure 67). As with the PEEK composite, silylating agent adsorbed to the surface is shown by the peak at 102.1 eV. The large number of single bonded oxygen forms (large signals at 533.1 eV and 534 eV) is illustrated in the stabilized sample's O_{1s} spectrum in figure 69. Once stabilized the formation of SiO$_2$ is shown by the large Si$_{2p}$ peak at 103.6 eV, and smaller peak at 104.7 eV (figure 70).
Curves-fitting for region: C\textsubscript{1s}:

<table>
<thead>
<tr>
<th>BE/eV</th>
<th>fwhm/eV</th>
<th>area</th>
<th>rel at.prcnt</th>
</tr>
</thead>
<tbody>
<tr>
<td>-284.50</td>
<td>1.41</td>
<td>1.12e+005</td>
<td>52.7</td>
</tr>
<tr>
<td>-285.40</td>
<td>1.43</td>
<td>5.60e+004</td>
<td>26.2</td>
</tr>
<tr>
<td>-286.60</td>
<td>1.37</td>
<td>2.46e+004</td>
<td>11.5</td>
</tr>
<tr>
<td>-288.39</td>
<td>1.42</td>
<td>9.16e+003</td>
<td>4.3</td>
</tr>
<tr>
<td>-283.31</td>
<td>1.50</td>
<td>7.71e+003</td>
<td>3.6</td>
</tr>
<tr>
<td>-292.29</td>
<td>1.40</td>
<td>3.57e+003</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Figure 59: C\textsubscript{1s} XPS spectrum of Epoxy composite control sample. C-C, C-H bonds are shown by peak A, peaks B,C,D represent various oxygen-carbon forms. Peak E indicates graphite.
Curve-fit for region: O\textsubscript{1s}

<table>
<thead>
<tr>
<th>BE/eV</th>
<th>fwhm/eV</th>
<th>area</th>
<th>rel.at.prct</th>
</tr>
</thead>
<tbody>
<tr>
<td>-532.04</td>
<td>1.57</td>
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</tr>
<tr>
<td>-533.23</td>
<td>1.84</td>
<td>3.64e+004</td>
<td>35.2</td>
</tr>
<tr>
<td>-530.71</td>
<td>1.65</td>
<td>1.06e+004</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Figure 60: O\textsubscript{1s} spectrum of Epoxy composite control sample. The spectrum is dominated by single bonded oxygen forms, peaks A and B. Peak C is from double bonded oxygen.
**Curve-fit for region: C\textsubscript{1s}**

<table>
<thead>
<tr>
<th>BE/eV</th>
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<th>rel at. prcnt</th>
</tr>
</thead>
<tbody>
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<td>1.46</td>
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<td>-286.66</td>
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<td>-281.76</td>
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</tbody>
</table>

**Figure 61:** C\textsubscript{1s} XPS spectrum of Epoxy composite sample after oxidizer etching. Peaks B, C and D which represent hydroxyl, ether and carbonyl groups have been enhanced. Graphite/carbon residue is evident from peaks E and F.
Figure 62: O$_{1s}$ XPS spectrum of Epoxy composite after oxidizer etching. More oxide groups have been formed with a new peak (D) forming. Again, single bonded oxygens dominate the spectrum (peaks A,B,D).
Figure 63: C_1s XPS spectrum of Epoxy composite sample activated for 15 minutes. Peaks B, C and D are single bonded oxygen-carbon forms. A new peak (E) which represents the formation of carboxyl groups is evident. Graphite bonding appears again with peak G.
Curve-fit for region: O1s

<table>
<thead>
<tr>
<th>BE/eV</th>
<th>fwhm/eV</th>
<th>area</th>
<th>rel at.prctn</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>-531.65</td>
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<td>1.61</td>
<td>8.76e+003</td>
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</table>

Figure 64: O1s XPS spectrum of Epoxy composite after activation for 15 minutes. Activation caused a significant increase in double bonded oxygen forms (peak B). Single bonded forms still dominate (peaks A and C), however.
Figure 65: C$_{1s}$ XPS spectrum of Epoxy composite after activation and silylation. Once again, the silylating agent adsorbed to the surface dramatically dominates the spectrum with peak A.
Curve-fit for region: Ox

<table>
<thead>
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</tr>
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<td>74.8</td>
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<td>-533.28</td>
<td>1.77</td>
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<td>19.6</td>
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<tr>
<td>-530.65</td>
<td>1.67</td>
<td>9.36e+003</td>
<td>5.6</td>
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</tbody>
</table>

Figure 66: Ox XPS spectrum of Epoxy composite after activation and silylation. Activation has reduced the double bonded forms of oxygen to incidental amounts (peak C).
Figure 67: Si\textsubscript{p} XPS spectrum of Epoxy composite after activation and silylation. Silicon is mainly bonded as Si-O and Si-C from peaks A and B. Some SiO\textsubscript{2} is evident (peaks C and D).
Curve-fit for region: C$_{1s}$

<table>
<thead>
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<th>fwhm/eV</th>
<th>area</th>
<th>rel at. pct</th>
</tr>
</thead>
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</tr>
<tr>
<td>-285.99</td>
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<td>1.39</td>
<td>$4.46e+003$</td>
<td>6.7</td>
</tr>
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<td>-292.22</td>
<td>1.20</td>
<td>$3.43e+003$</td>
<td>5.1</td>
</tr>
<tr>
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<td>4.3</td>
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<tr>
<td>-289.56</td>
<td>1.31</td>
<td>$1.23e+003$</td>
<td>1.8</td>
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</tbody>
</table>

Figure 68: C$_{1s}$ XPS spectrum of Epoxy composite after activation, silylation and stabilization. Most of the small amount of carbon left at the surface is bonded with carbon or hydrogen atoms (peak A). Small amounts of oxygen bonding (peaks B, C and D) and graphite bonding (peak F) are also indicated.
Figure 69: $O_{1s}$ XPS spectrum of Epoxy composite after activation, silylation and stabilization. The oxygen spectrum is dominated solely by singly bonded oxygen forms.
Curve-fit for region: Si$_{2p}$

<table>
<thead>
<tr>
<th>BE/eV</th>
<th>fwhm/eV</th>
<th>area</th>
<th>rel at. prcnt</th>
</tr>
</thead>
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<td>1.81</td>
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</tr>
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</table>

![XPS Spectrum](image)

**Figure 70**: Si$_{2p}$ XPS spectrum of Epoxy composite after activation, silylation and stabilization. SiO$_2$ bonding (peaks A and C) dominate the Si spectrum. Other forms of Si-O bonds are indicated by the B peak.
CONCLUSIONS

Two developments are central to the heart of this thesis, the verification of the gamma parameter, and the demonstration of the Photosil™ process to protect polymer film and polymers resin composites. The successful experimental verification of the effective-carbon gamma parameter allows two distinct, but complementary, directions to be followed from this point. In an applied sense, the simple linear nature of the gamma correlation can be used to predict the performance of polymers that have never been used in LEO before. Or, new materials, coatings and/or surface treatments can be designed and evaluated on the basis of this performance indicator. Beyond the applied nature of the gamma parameter model, in a fundamental sense, the fact that the content and structure of the polymer has such a strong effect on the erosion yield can be used to explore new avenues of investigation, in both the areas of thermal and hyperthermal oxidation.

Clearly the Photosil™ process appears to have successfully reached the goal outlined for this thesis. Using this new surface modification technique, four polymers and two polymer matrix composites were successfully protected to the point where their reaction yield was reduced by two orders-of-magnitude. In addition, the process appears to lend itself well to other applications. The glass-like layer could protect polymers in a variety of other reactive environments, for example, oxidizing liquids such as blood or food. Polymer packaging materials often need to be treated to inhibit UV enhanced molecular oxygen degradation. The Photosil™ process appears to be capable of providing this type of protection at a reasonable cost. In addition to the decrease in reactivity provided by the silylation treatment, other surface related properties such as wettability and barrier properties to water and oxygen, can be altered.
Two secondary developments form the basis for the success of the two primary contributions. First, the information provided by the characterization of the AO beam facility allows for a fuller understanding of the performance of the AO system as both a simulator for LEO material investigation, and as a scientific tool. The performance of the UTIAS AO Beam Facility was found to correlate well with the expected values. The energy spectrum and charged species component of the beam were measured to sufficiently like LEO conditions to warrant substantial confidence in the validity of any testing performed. Secondly, the proposed reaction scheme for thermal atomic oxygen with Kapton® provides a first step to applying the concepts revealed by the success of the gamma parameter, while expanding the general understanding of the process of polymer erosion by hyperthermal atomic oxygen.

As a final note, some mention should be made of the ongoing work to verify the findings demonstrated herein using only the UTIAS AO beam facility. The entire suite of polymers tested to define the gamma function, and a set of silylated polymer film and polymer matrix composite samples are scheduled to spend six months in LEO aboard the Mir Space Station during 1996. The results from this testing campaign will hopefully verify the ground-based testing results, and in doing so confirm both the conclusions of this investigation and the capability of the UTIAS AO beam facility to simulate the LEO environment.
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APPENDIX A

Detailed Theory, Component Description and Procedures Manual
UTIAS AO Facility Time-of-Flight System

by Grant Cool and Vibhor Bageshwar

The Time-of-Flight (TOF) method is based on the principle that the velocity distribution of a pulse of particles will disperse in space and time in a manner that is representative of their average velocity across a measured distance. For each particle, of course, the average velocity is given by the expression:

\[ \nu = \frac{L_f}{t} \]  \hspace{1cm} (A.1)

In a direct beam TOF experiment, the detector signal, \( I(t) \), directly represents the flight time distribution for a beam species. However, the detector signal indirectly represents the velocity distribution of the beam species. The influence of various resolution degrading components on the transmitted beam particles, located at various stages throughout the TOF system, limits the resolution of the experiment by broadening the flight time distribution of the transmitted beam particles beyond the broadening induced by the velocities of the transmitted beam particles.

To derive a velocity distribution of a beam species from its measured flight time distribution, the velocity distribution must first be transformed to the time domain. The velocity distribution, \( f(v) \), of a beam species is transformed to the time domain, \( g(t) \), by considering a flux weighted velocity distribution \( f(v)dv \), which can be expressed as follows:

\[ g(t) \, dt = f(v) \, d\nu(t) \]  \hspace{1cm} (A.2)

\( f(v)dv \) is the intensity of the beam species per unit cross-sectional area of the beam, per unit time, with velocities in the range \( (v, v+dv) \); from A.1:

\[ d\nu = \frac{L_f}{t^2} \, dt \]  \hspace{1cm} (A.3)

Therefore, by substituting into eqn. A.2, the velocity distribution of a beam species, in the time domain, can be expressed as follows:

\[ g(t) \, dt = \frac{L_f}{t^2} \left( \frac{L_f}{t} \right) \, dt \]  \hspace{1cm} (A.4)
The measured flight time distribution is dependent on the type of detector used in the experiment. The detector signal is a function of the beam characteristic to which the detector is sensitive [12]; these characteristics include the beam particle flux and the beam particle density. The speed dependent efficiency of a density detector is proportional to the flux of the incident beam particles divided by the velocity of the incident beam particles. Therefore, using a density sensitive detector in an TOF experiment, the velocity distribution of a beam species transformed to the time domain can be expressed as follows:

\[ g(t) \sim \frac{1}{t} f \left( \frac{L_f}{t} \right) \]  
(A.5)

To derive the velocity distribution for a beam species from a measured flight time distribution, first consider an ideal TOF experiment. An ideal TOF experiment can be expressed as follows:

\[ I(t) = \int_{0}^{\tau} C(t - \tau) g(\tau) d\tau \]  
(A.6)

Where: I(t) is the time response detector output function.

The ideal TOF experiment consists of a modulation system with an impulse modulation function, and a detector with zero physical length and with an infinite response speed. Since the modulation function for an ideal TOF experiment is a delta function, eqn. A.6 can be expressed as follows:

\[ I(t) = \int_{0}^{\tau} \delta(t - \tau) g(\tau) d\tau = g(t) \]  
(A.7)

Therefore, in an ideal TOF experiment, the detector signal is equivalent to the velocity distribution, of a beam species, transformed to the time domain (eqn. A.7). However, the derivation of the velocity distribution of a beam species from the detector signal, suggested in eqn. A.5 & A.7, is only a first approximation. The resolution degrading components that limit the experimental resolution must be quantified to estimate their effects on the detector signal and to derive the actual velocity distribution of a beam species.
A.1 Time-of-Flight System Components

The components of a TOF system are designed or selected to optimize both the resolution and the intensity of the transmitted beam particles for the particular TOF experiment. The general components of TOF system used in this application are as follows:

- the modulation system
- the detector
- the signal processing electronics
- the deconvolution software

The following sections outline the function and the requirements of these components. For a more extensive theoretical and engineering description of this system see Bageshwar[1].

A.1.1 Beam Modulation

The modulation system consists of a thin disk, with slits cut along the edges in a specific configuration, driven by a high speed vacuum compatible motor, and is referred to as a chopper. The chopper disk is positioned normal to the beam axis in order to modulate the beam. Beam particles are transmitted and admitted to the flight path only while a chopper disk slit rotates through the beam cross-section.

The resolution of a TOF experiment depends on the length of the flight path and the full width at half maximum (FWHM) of the beam transmission. As the length of the flight path increases, the resolution of the experiment improves because there exist greater flight time differences between faster and slower particles travelling along the flight path. The FWHM is a figure classifying the time width of a distribution and it corresponds to the time between the two half-maximums of the distribution. A half-maximum is a point on a distribution corresponding to half of the peak value of the distribution. As the FWHM of the beam transmission approaches zero, the resolution of the experiment improves.

In addition to modulating the beam, the modulation system generates a signal coincident with the beginning of a beam transmission. This signal serves as a consistent time origin for the experiment and it is available to synchronize the remaining TOF components with the beginning of a beam transmission. The velocity of a transmitted beam particle, detected during the experiment, is determined from this time origin. Therefore, the flight time distributions of the transmitted beam particles, measured during successive sampling periods, can be averaged because every sampling period is consistently initiated with the beginning of a beam transmission. In a conventional TOF experiment, the duration of a sampling period is the time between beam transmissions.

A.1.2 Beam Particle Detection

A detector is selected for a TOF experiment by ensuring the detector has the following characteristics:

- fast response for incident beam particles
- high sensitivity to the beam species of interest
- low background sensitivity
Generally, ionization detectors are used in TOF experiments to characterize seeded beams. These detectors are equipped with mass selection capabilities to prevent undesired beam species from being detected. Quadrupole mass spectrometers (QMS) possess these characteristics and are often used as detectors in TOF experiments.

A QMS operates in either a digital or an analog mode. In its digital mode, the QMS output signal consists of pulses superimposed on the signal representing the noise detected by the QMS. One output pulse corresponds to one beam particle detected by the QMS. To measure the digital output of a QMS, each pulse has to be well-defined or there exists the possibility that successive pulses will overlap. If successive pulses overlap, it is difficult to determine the individual beam particle contribution to the QMS output signal. This pulse overlap phenomenon occurs when the incident beam particle flux causes the QMS output pulse rate to exceed $10^6$ pulses/s. If the QMS output pulse rate exceeds $10^6$ pulses/s, the QMS has to be operated in its analog mode. In its analog mode, the QMS output signal consists of a continuous voltage. The amplitude of this voltage is proportional the beam particle flux detected by the QMS superimposed on the noise detected by the QMS.[12]

A.1.3 Beam Flight Time Distribution

A TOF experiment requires an electronic device capable of transforming the detector output signal into a corresponding flight time distribution. The selection of this instrument depends on the particle fluence detected during one sampling period and the time resolution required for the measured flight time distribution. For the high beam flux measured in many TOF experiments, multichannel scalers (MCS) are used to determine the flight time distribution from the detector signal.

An MCS consists of a set of sequential memory blocks called time channels and it operates as follows. The MCS accepts two types of external periodic digital signals: a trigger signal and a data signal. One trigger signal pulse initiates one sweep through the time channels of the MCS. Each time channel is enabled for an equal sampling period. Within this period, the enabled time channel counts the number of arriving data pulses and it adds this number to the already accumulated sub-total counted by the channel during previous channel sweeps. Following the completion of the sampling period of a time channel, the channel is disabled, and the next channel is enabled, allowing the newly enabled channel to accumulate data.

The MCS operates elegantly with a chopper assembly for TOF measurements because the assembly produces both a periodic synchronization signal and a periodic beam transmission. The synchronization signal is used to initiate time channel sweeps, synchronizing the channel sweep with the beginning of the beam transmissions, indefinitely. The number of time channels that span a channel sweep is selected to correspond to the length of the beam sampling period. Therefore, following each beam transmission, the detector signal will contribute to the same sub-group of time channels. The MCS stores the detector signal as a time histogram where the time channels represent the measured flight time for the detected beam particles. The total number of counts accumulated in each time
A further advantage of using an MCS in an TOF experiment is that an MCS improves the signal-to-noise ratio of a periodic data signal that is unavoidably combined with a random background noise signal. As previously indicated, the detector signal contributes to the same sub-group of time channels during each beam sampling period. The random background noise signal contributes to every time channel, including the sub-group of channels accumulating the detector signal, because the noise signal is not synchronized with the channel sweep. Therefore, the fluctuations of the noise signal about the average accumulated noise signal determine whether the detector signal is recognizable above the noise signal during a test. During MCS operation, the detector signal accumulates linearly with time, and the average random background noise signal accumulates linearly with time: however, the noise fluctuations about the average noise signal accumulate proportionally to the square root of time.

Consider the following example of a TOF test using an MCS. During one time channel sweep, suppose the time channels each accumulate 100 counts from the noise signal and the channel counting the peak detector signal accumulates 4 counts. The fluctuation of the noise counts in the time channels is 10, the signal-to-noise ratio following one sweep is 0.4, and the data signal is indistinguishable from the noise fluctuations. However, following 1000 time channel sweeps, the channels each accumulate 10000 counts from the noise signal and the channel counting the peak data signal accumulates 4000 counts. The fluctuation of the noise counts in the time channels is 316, the signal-to-noise ratio following 1000 sweeps is 12.6, and the data signal is distinguishable from the noise fluctuations.

A.2 THE TIME-OF-FLIGHT SYSTEM CONFIGURATION

The following sections describe the components of the UTIAS TOF system, illustrated in figure A.1. This TOF system operates as follows. The incident AO beam is modulated by a rotating disk, the chopper. The angular position of the rotating chopper disk is monitored by an infrared switch. The switch emits a (synchronization) pulse coincident with the beginning of a beam particle transmission. At the end of the flight path, the transmitted beam particles are detected by a QMS, operating in an analog mode. The QMS output signal is converted to pulses by a voltage-to-frequency converter (VFC), from which a flight time distribution is developed by an MCS.

A.2.1 The Chopper Assembly

The chopper assembly is designed to maintain a chopper transmission duty cycle of approximately 2%. The chopper transmission duty cycle is a function of the axial position of the chopper disk downstream of the sampler-skimmer interface along the beam axis, the effective beam radius at the chopper disk position (EBR), the chopper disk slit width, and the chopper disk diameter. The FWHM of the beam transmission is a function of the EBR, the chopper disk slit width, and the chopper disk speed. The EBR is the most important of these
parameters and it has to be minimized to maintain a chopper transmission duty cycle of 2%. The EBR is minimized by positioning the chopper disk as close to the sampler-skimmer interface as allowed by the geometry of the vacuum test chamber.

The chopper assembly (figure A.2) consists of the conventional disk, a motor to drive the disk, the motor housing block, an infrared switch and housing, an electrical feedthrough, and a dedicated base plate for insertion into the vacuum test chamber. Within the vacuum test chamber, the chopper disk is positioned normal to the beam axis, at a fixed axial distance of 7.6 cm downstream of the sampler-skimmer interface. The horizontal position of the chopper disk is adjustable by physically moving the chopper disk housing block. The vertical position of the chopper disk is selected so that the centre of the chopper disk slits coincides with the beam axis.

The chopper disk has a diameter of 76.2mm and a thickness of 1mm. There are two diametrically opposed trapezoidal slits cut symmetrically from the edges of the chopper disk. The slits are 15mm long; their thickness varies from 1.0mm at the edge of the disk to 0.6mm towards the centre of the disk. The length of the slits exceeds the EBR to maximize the transmitted beam flux at the detector. The width of the slits decreases toward the centre of the chopper disk to prevent the FWHM of the chopper beam transmission from becoming a function of the slit angular position while the disk rotates through the beam cross-section.

The chopper disk is driven by a Globe MM DC permanent magnet motor designed for vacuum operation. The maximum rotational speed of the chopper disk using this motor is 20000RPM. The motor power supply (figure A.3) provides the capability of varying the chopper disk speed from 3000RPM to 20000RPM in either a clockwise or counterclockwise direction. The chopper disk speed is monitored by measuring the frequency of the synchronization pulses emitted by the infrared switch. These pulses are used in a feed-back system to limit the chopper disk speed fluctuations to ±0.75%. The chopper disk speed is controlled to maintain a consistent FWHM of the chopper beam transmission during an experiment. Since the maximum chopper disk speed is 20000RPM, the disk is dynamically balanced.

The synchronization pulses are generated using a Honeywell HOA2001 infrared slotted switch (figure A.4). The switch is equipped with both an emitter and a detector. The switch monitors the angular position of the slit diametrically opposite to the slit modulating the beam. The horizontal position of the switch is physically adjustable to align the emitter-detector with the slit position that initiates the beam transmission. The vertical position of the switch is selected to allow the chopper disk to rotate through the emitter-detector slot, interrupting the emitter-detector path. The positions of the chopper disk and the infrared switch are not adjustable during an experiment, therefore an electronic delay system was incorporated to allow fine tuning of the initializing pulse (figure A.5). The time required for the internal electronics of the switch to produce a pulse is 1μs, while the rise time for the leading edge of a pulse is 60ns.
A.2.2 The Detector

The transmitted beam particles are detected at the end of the flight path from the chopper disk by a Vacuum Generator Micromass PC 100D QMS. The QMS is positioned 53.0 cm downstream of the chopper disk position along the beam axis. The centre of the QMS is aligned with the beam axis which coincides with the center of the sampler-skimmer interface.

The QMS is equipped with a radial flow-through electron bombardment ionization source, a mass filter, an electron multiplier, and a Faraday Cup. Flow-through ionizers are required in TOF experiments because there exists a velocity dependence for ions extracted from cross beam ionization sources. The radius of the ionizer's entrance aperture is 3.0 mm, and the length of the ionizing region is 5.0 mm. The ions, generated by the ionizer, are mass selected by the 127 mm long, 6.3 mm diameter filter rods of the mass filter. The length of the flight path from the ionizer to the electron multiplier, through the mass filter, is 19.0 cm. The measurements are conducted in these TOF experiments using the electron multiplier as the ion detector because the electron multiplier has a superior response time and has greater sensitivity to the species of the AO beam as compared to the Faraday Cup.

The QMS is operated in its analog mode because the minimum flux of transmitted AO particles, incident to the ionizer, is approximately \(10^{10} \text{atoms/cm}^2/\text{s}\). This transmitted flux exceeds the flux that causes pulse overlap of an output signal generated by the QMS in its digital mode. The signal from the electron multiplier is normally passed through multiple stages of amplification before it is displayed on the system's CRT display. For use as a time-of-flight detector the QMS head was modified to allow the electron multiplier signal to be pulled directly off and passed directly to a voltage-to-frequency converter. The QMS output signal is proportional, at any given time, to the beam particle flux ionized by the ionizer. Over time this becomes a function of the transmitted beam particle flight times over the flight paths from the chopper disk.

A.2.3 The Voltage-to-Frequency Converter

The output analog signal of the QMS is converted to countable digital pulses by a 10 MHz VFC circuit designed and built specifically for this purpose (figure A.6). The VFC produces digital pulses whose number is proportional to the amplitude of a continuous analog voltage input. The VFC operates as follows. The analog voltage input is integrated and compared to an internal threshold voltage. When the integrated voltage exceeds this internal threshold voltage, one digital pulse is produced. The integrated voltage level is then reset, the input voltage is again integrated, and this process repeats itself. The frequency with which digital pulses are produced by the VFC depends on the speed with which the integrated voltage exceeds the threshold voltage. The maximum frequency at which this VFC is able to produce digital pulses is 10 MHz.
A.2.4 The Multichannel Scaler

The digital signal of the VFC is then directed to an EG&G Ortec ACE™-MCS to determine the flight time distribution for a species of the transmitted beam particles. The distribution developed by the MCS from the QMS output signal is referred to as the measured flight time distribution and it is proportional to the transmitted beam particle flux detected by the electron multiplier from the effective ionizing volume of the QMS as a function of the beam particle flight times over the flight paths from the chopper disk. In this application, the MCS receives two input signals: the synchronization signal from the chopper assembly and the digital signal from the VFC.

The MCS is adjusted for a specific application based on the requirements of four operating parameters. These parameters, including their operating ranges, are as follows:

- the channel dwell time: minimum - 2μs, maximum - 2147s
- the number of channels that span one sweep: minimum - 4 channels, maximum - 4096 channels
- the number of channel sweeps for the TOF test
- the channel sweep trigger type for each TOF test: external or internal

The first two parameters depend on requirements of the specific TOF test. The number of time channel sweeps that constitutes a TOF test is limited only by the memory available to store the number of data pulses counted during the sampling period of each channel. The time channel sweep trigger type selected for every TOF test is the external trigger to synchronize the channel sweeps with the beginning of the beam transmissions.

The internal electronics of the MCS require the following time delays and the MCS requires that the input signals conform to the following specifications. The MCS requires approximately 110μs to switch between successive time channel sweeps and the MCS requires approximately 20ns to switch between successive time channels. The MCS requires input data signals to have pulse widths exceeding 5ns and the

A.3 Time-of-Flight System Deconvolution

The resolution degrading components of a TOF system affect the measured flight time distribution by broadening this distribution beyond the natural broadening induced by the flight paths of the system. The resolution of a TOF experiment is affected by the following resolution degrading components:

- the finite length of the transmitted beam particle pulse (chopper transmission function)
- the finite length of the detector ionizing region
- the flight time through the QMS mass filter region
- the analog response of the QMS

These resolution degrading components are necessary compromises in an actual TOF experiment to increase the flux of the transmitted beam particles detected by the QMS at the
expense of the experimental resolution. For example, an impulse beam modulation provides insufficient transmitted beam particle flux to the QMS to determine a flight time distribution.

A deconvolution procedure is required to derive the velocity distribution of a beam species from its measured flight time distribution and to derive functions to model the actual operation of these resolution degrading components. The deconvolution procedure uses these functions to mathematically simulate the effects of the resolution degrading components on the transmitted beam particles. The following sections describe the deconvolution procedure of this TOF system and the functions that model the resolution degrading components of this TOF system. For a more extensive description of the theory and software see Bageshwar[1].

A.3.1 The Deconvolution Algorithm

Three deconvolution algorithms have been previously applied in TOF experiments to derive velocity distributions from measured flight time distributions. These algorithms require functions that model the effects of the resolution degrading components on the measured flight time distribution. These three deconvolution algorithms are as follows:

- direct numerical deconvolution [1]
- moment analysis [2]
- fitting a model flight time distribution to a measured flight time distribution

These deconvolution algorithms are methods of solving the convolution integral (eqn. A.6) using the measured flight time distribution and the functions that model the resolution degrading components. The function C(t) (eqn. A.6) is replaceable by other functions, describing the effects of the other resolution degrading components on the transmitted beam particles.

A deconvolution procedure, based on the direct numerical deconvolution algorithm, operates as follows. The convolution integral, which has the form of a Fredholm integral of the first kind, is replaced by a Fredholm integral of the second kind. An iterative algorithm is then applied to solve this integral, to derive the actual velocity distribution of the beam species. A deconvolution procedure, based on the moment analysis algorithm, operates as follows. Algebraic relationships are derived relating moments of the measured flight time distribution of a beam species, moments of the resolution degrading functions, and moments of a model velocity distribution. The moments of these distributions are then manipulated, as suggested by the algebraic relationships, to derive the actual velocity distribution of the beam species.

The deconvolution procedure used in this application is the third deconvolution algorithm previously indicated, and it operates as follows [3]. A model velocity distribution, \( f(v, \{p_i\}) \), is generated for the beam’s species where the parameters, \( \{p_i\} \), of this distribution adjust the model for the specific beam. The evolution of this model velocity distribution is followed throughout a simulation of the TOF system, based on the system’s resolution degrading components and the system’s flight paths, to generate a model flight time distribution, \( O_{\text{mod}}(t) \), for a beam species. The model flight time distribution is then compared to the flight time distribution, \( O(t) \), measured for this beam species. If deviations exist
between the model and the measured flight time distributions, the parameters of the model velocity distribution are refined, and a new model flight time distribution is generated from the evolution of the refined velocity distribution through the TOF system simulation. This iterative process is repeated until the deviations between the model and the measured flight time distributions are minimized for a set of model velocity distribution parameters. The velocity distribution and the energy distribution of the beam species are calculated using the parameters that minimized deviations between the model and measured flight time distributions. This deconvolution algorithm is applicable in any TOF experiment by appropriately defining the model velocity distribution, the functions that model the resolution degrading components of the TOF system, and the flight paths of the TOF system.

A.3.2 The Model Velocity Distribution

The selection of a model velocity distribution for the species of a beam depends on the Mach number of the beam, the radial flux distribution of the beam species, and the radial velocity distribution of the beam's species. The complexity of the model velocity distribution increases for high Mach number beams, for beam species with a varying radial flux distribution, or for beam species with a varying radial velocity distribution. For a low Mach number supersonic nozzle beam, with a constant radial flux distribution and a constant radial velocity distribution, a model velocity distribution for a beam species can be expressed as follows [4][5][6]:

\[
\begin{align*}
    f(v) &= N v^2 \exp \left( \frac{(v - v_o)^2}{\alpha^2} \right) \\
    I(v) &\sim v^3 \exp \left( \frac{(v - v_o)^2}{\alpha^2} \right)
\end{align*}
\]

(A.9)

where \( N \) is a normalization constant whose role is to make \( \int f(v)dv = 1 \). \( f(v) \) represents the number density velocity distribution of the beam's species. \( I(v) \) is based on the model number density velocity distribution function and it represents the flux of the beam species per unit volume of physical space and per unit volume of velocity space.

These velocity distribution functions are based on two refinable parameters, \( v_o \) and \( \alpha \), that adjust these velocity distributions for the specific facility. \( v_o \) represents the flow velocity of the beam's species; \( \alpha \) represents the velocity spread of the beam's species from its peak velocity. \( v_o/\alpha \) is referred to as the speed ratio, \( S \), of the beam and it is a figure classifying the quality of the supersonic expansion of the beam. This model (eqn. A.9) of the velocity distribution for a supersonic nozzle beam is derived from Maxwell's model velocity distribution functions for an effusive beam. Maxwell's velocity distribution functions for an effusive beam can be expressed as follows:[7]
The velocity distribution model, expressed in eqn. A.9, is a Maxwellian velocity distribution superimposed on the flow velocity based on the assumption of an isentropic expansion of the beam with a constant specific heat ratio, \( \gamma \). This flow velocity is lower than the peak velocity of the velocity distribution because for a distribution of the following form:

\[
f(v) \sim v^2 \exp \left( -\frac{m v^2}{2 k T_o} \right)
\]

\[
I(v) \sim v^3 \exp \left( -\frac{m v^2}{2 k T_o} \right)
\]

(A.10)

the peak velocity of the distribution can be expressed as follows:

\[
v_p = \frac{v_o}{2} + \frac{v_o}{2} \sqrt{1 + \frac{2n \alpha^2}{v_o^2}}
\]

(A.12)

**A.3.3 The Parameters of the Model Velocity Distribution**

The purpose of the deconvolution procedure in this TOF application is to determine the parameters of the model velocity distribution, \( v_o \) and \( \alpha \) (eqn. A.9). The assumptions underlying this model of the velocity distribution of the beam's species are that the beam undergoes an isentropic expansion through the discharge gap, at constant \( \gamma \) [8]. Based on these assumptions, the two parameters of the model velocity distribution can be defined in terms of the following thermodynamic relationships [4]:

\[
v_o = M \left( \frac{\gamma k T}{m} \right)^{\frac{1}{2}}
\]

\[
\alpha = \left( \frac{2 k T}{m} \right)^{\frac{1}{2}}
\]

(A.13)

In eqn. A.13, the molecular weight of the beam, \( m \), depends on the composition of the gas mixture at the beam source; the beam temperature, \( T \), defines the spread of the beam species velocity from the peak velocity.
In this TOF application, the flight time distributions of the AO beam species are measured downstream of the sampler-skimmer interface. The skimmer cone is the final downstream position of the transition region between continuum flow and free-molecular flow of the beam.[9] Therefore, the beam properties, the Mach number, $M$, and the beam temperature, $T$, exist at their freezing point values downstream of the skimmer. The relationship between the stagnation temperature and the beam temperature, assuming ideal gas behaviour and constant $\gamma$, can be expressed as follows:[4]

$$ T = T_o \left( 1 + \frac{1}{2} (\gamma - 1) M^2 \right)^{-1} \quad \text{(A.14)} $$

where $\gamma$, for this AO beam, is selected to be the specific heat ratio of a monatomic gas, 1.644.[9] By substituting for $v_o$ and $\alpha$ (eqn. A.9), using eqn. A.13 & A.14, the parameters that require refinement in the deconvolution procedure are the freezing Mach number.

The effect of increasing the Mach number of the beam, from a Mach number of 1, is to narrow the shape of the AO velocity distribution while the peak velocity of the distribution remains, essentially, constant. The effect of increasing the stagnation temperature of the beam, from a stagnation temperature of 1700K, is to increase the peak velocity of the AO distribution while the shape of the distribution remains, essentially, constant.

A.3.4 The Chopper Transmission Function

The chopper transmission function mathematically simulates the modulation of the AO beam and it is the first component in the series of resolution degrading components in this TOF system. The chopper transmission function represents the time evolution of the transmission intensity of the AO beam with respect to the effective cross-sectional area of the beam at the chopper disk position. The FWHM of the beam transmission is a function of the EBR, the chopper disk slit geometry, and the chopper disk speed, however, the FWHM is independent of the velocities of the AO beam particles. The optimal chopper transmission function approaches a delta function, but still provides sufficient flux to allow detection of the transmitted beam particles. The effect of the chopper transmission function on the QMS output signal is simulated using the convolution integral as follows:

$$ I(t) = \int_0^\tau C(t - \tau) g(\tau) \, d\tau \quad \text{(A.15)} $$

$C(t)$ is normalized with respect to its maximum transmission intensity where zero indicates zero transmitted flux and one indicates maximum transmitted flux.
A.3.5 The QMS Ionizer

The QMS ionizer is the second component in the series of resolution degrading components in this TOF system. The effect of the finite length of the QMS ionizing region is to delay the transmitted beam particles as they travel to the QMS mass filter. The QMS ionizer has an insignificant distorting effect on the shape of transmitted beam particle flight time distribution.[10] The delaying effect of the ionizing region on the QMS output signal is simulated by using the following expression:[10]

\[
I(t) = \int_0^T \int_0^L f_{L'}(v, t) - f_{L}(v, t) \frac{d v}{L_i} \, d t
\]  

(A.16)

In eqn. A.16, the functions \( f_{L'}, f_L \) represent the flight time distributions of the transmitted beam particles at either end of the QMS ionizing region. These two functions depend on the chopper transmission function and the flight path from the chopper disk to the QMS ionizer.

A.3.6 The QMS Mass Filter

The flight time of the ions, travelling from the ionizer to the electron multiplier through the QMS mass filter, is the third component in the series of resolution degrading components in this TOF system. For the spectrometers often used in other TOF experiments, the ion flight time is constant for a particular species, regardless of the particle’s velocity incident to the QMS ionizer, and this flight time is proportional to the square root of the mass of the species.[11] The proportionality constant between the ion flight time and the square root of the species mass is determined by using a seeded beam. The peak flight times for the species of this beam are measured and these times are plotted using the square root of the species mass. The proportionality constant is the slope of the line connecting these peak flight times.

However, following ionization within the QMS used in this TOF system, the ions are given a velocity component, normal to the beam axis; the axial velocity component of the ionized particles remains unaffected. This normal velocity component is proportional to the beam mass allowing the QMS to filter the undesired species from the beam path. Therefore, the effect of the QMS mass filter on the ionized particles is to add a further flight path for the beam particles. The flight time required for the ionized particles to travel through the filter region depends on their axial velocity component which is determined based on their arrival times at the filter region, measured from the beginning of a beam sampling period.

A.3.7 The QMS Analog Response

The QMS response, in its analog mode, is the final component in the series of resolution degrading components in this TOF system. The response of the signal amplifying electronics of the QMS detector head are assumed to have a linear response function, \( A(t) \), to a signal input.[12] These signal amplifying electronics significantly affect the QMS output signal by adding an exponentially decaying tail component to the output signal, and hence,
the measured flight time distribution. The effect of the QMS analog response on the output signal is simulated using the convolution integral as follows:[3][12]

\[ O(t) = \int_{0}^{\infty} A(\tau) I(t - \tau) \, d\tau \]  

\[ A(t) = \frac{1}{\lambda} \exp\left(-\frac{t}{\lambda}\right) \quad (A.17) \]

In eqn. A.17, \( \lambda \) is the linear time constant corresponding to the amplifying electronics of the QMS detector head.
Figure A.1: Block diagram of TOF system components.

Figure A.2: Diagram of chopper assembly inside test chamber.
Figure A.3: Circuit diagram of motor speed control and power supply.
Figure A.4: Circuit diagram of infrared switch/detector system on chopper mount.
Figure A.5: Circuit diagram MCS trigger circuit and time delay system.
Figure A.6: Circuit diagram of 10MHz VFC system.
REFERENCES - APPENDIX A


5. H.M. Parker et al., in Rarefied Gas Dynamics, 1st International Symposium, (1958)


APPENDIX B

Protocol for sample weighing to account for moisture loss in vacuum

Before every atomic oxygen beam exposure, samples had to be outgassed for a certain period of time to stabilize the mass changes due to moisture outgassing. The problem is, that to be weighed, samples must be removed from the vacuum chamber. While in the chamber they lose a significant amount of mass due to moisture outgassing (0.5 - 1.0% of total mass for Kapton®). In addition, this mass loss was found to be quite dependant on the relative humidity of the room during experimentation. To get reliable, and comparable mass loss data, a protocol was established for weighing samples.

1) weigh sample
2) 2 hours at <10^-4 torr vacuum
3) remove samples from vacuum, weigh within 1 minute
4) atomic oxygen test in vacuum
5) after test remove samples and weigh within 1 minute

The mass loss was taken as the difference between the weights measured in step 3 and step 5.

To validate this approach two procedures were carried out:

1) To test if one minute was a short enough period after removal. Samples of Kapton were placed in vacuum for 2 hours, removed and weighed at 1 minute intervals for 10 minutes. On average, the 3 samples tested lost 0.51% of total mass (about 100 µg), during the 2 hours in vacuum. Between 1 and 10 minutes they gained back 45 µg of that mass. One minute measurements were within 10 µg of the 2 minute measurements. This indicates an error of no greater than 10 µg if the measurements were made before 2 minutes. This error is identical to the error of the balance, which is the limit of the total experimental error.

2) To test if 2 hours of outgassing was sufficient for comparison to a 5 hour or greater AO test, 3 samples of Kapton were placed in vacuum for 1, 2 and 4 hours and weighed after each time period. On average the samples lost 0.76% of total mass after one hour, 1.2% after 2 hours, and 1.4% after 4 hours. Using these measurements as a guide, 2 hours was chosen as being the optimal time.
### APPENDIX C

**Experimental Data - Gamma Parameter**

Reaction Yields Measured in cm³/atom x 10⁻²⁴.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1.2</td>
<td>1.13</td>
</tr>
<tr>
<td>PEEK</td>
<td>2.2</td>
<td>2.10</td>
</tr>
<tr>
<td>Kapton®</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3.2</td>
<td>2.87</td>
</tr>
<tr>
<td>PET (Mylar)</td>
<td>3.9</td>
<td>3.72</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>4.4</td>
<td>4.04</td>
</tr>
<tr>
<td>PMMA</td>
<td>4.8</td>
<td>4.48</td>
</tr>
<tr>
<td>PVA</td>
<td>5.2</td>
<td>4.96</td>
</tr>
<tr>
<td>PEO</td>
<td>5.7</td>
<td>5.21</td>
</tr>
<tr>
<td>CR-39</td>
<td>6.5</td>
<td>6.37</td>
</tr>
<tr>
<td>Delrin</td>
<td>9.5</td>
<td>9.09</td>
</tr>
</tbody>
</table>

Kapton® is the standard by which all others are measured

5 unuseable samples due to system and testing irregularities
APPENDIX D

Summary Table - Erosion Yields of Photosil™ Treated Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Erosion Yield (cm³/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kapton® 500HN</td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>3.0x10⁻²⁴</td>
</tr>
<tr>
<td>After Modification</td>
<td>&lt;6.0x10⁻²⁵</td>
</tr>
<tr>
<td>PEEK</td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>2.2x10⁻²⁴</td>
</tr>
<tr>
<td>After Modification</td>
<td>9.0x10⁻²⁶</td>
</tr>
<tr>
<td>PET (Mylar®)</td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>3.9x10⁻²⁴</td>
</tr>
<tr>
<td>After Modification</td>
<td>9.6x10⁻²⁶</td>
</tr>
<tr>
<td>Polyethylene</td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>3.2x10⁻²⁴</td>
</tr>
<tr>
<td>After Modification</td>
<td>7.8x10⁻²⁶</td>
</tr>
<tr>
<td>PEEK/Gr Fibre Composite</td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>2.2x10⁻²⁴</td>
</tr>
<tr>
<td>After Modification</td>
<td>&lt;4.9x10⁻²⁶</td>
</tr>
<tr>
<td>Epoxy/Gr Fibre Composite</td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>2.8x10⁻²⁴</td>
</tr>
<tr>
<td>After Modification</td>
<td>&lt;6.22x10⁻²⁶</td>
</tr>
<tr>
<td>Graphite Fibres</td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>1.7x10⁻²⁴</td>
</tr>
<tr>
<td>After Modification</td>
<td>&lt;5.8x10⁻²⁶</td>
</tr>
</tbody>
</table>

Where values are reported as less-than (<), the treated samples did not exhibit any mass loss or surface morphology change during testing. The value reported is the resolution of the experiment, for example: the resolution of the electronic balance is 10 μg, and in a typical experiment the control sample would lose 450 μg. In this experiment the resolution is 10/450 = 2.2% of the reaction yield. Other factors, such as evidence of surface morphology change, were used to confirm that the erosion yield was indeed below the experiment threshold.