The Preparation of and Upper Atmospheric Effects on Kevlar Films

Patricia Lynne Pate

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The Preparation of and Upper Atmospheric Effects on Kevlar Films

A Thesis
Presented to
The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
of the Requirements for the Degree of
Master of Arts

by
Patricia Lynne Pate
1990
APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Arts

Patricia Lynne Pate

Approved, August 1990

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ABSTRACT

Films of Kevlar were cast from a solution obtained by dissolving Kevlar fibers in DMSO, potassium-tert-butoxide, and a small amount of methanol. These films were exposed to conditions found in the upper atmosphere, namely: ultraviolet radiation and atomic oxygen. Effects were monitored by changes in the infrared spectrum, volatile products measured by mass spectrometry, and mass loss. Also investigated were the sizing and moisture retention as well as the effects of ultraviolet radiation on the fiber.
I. INTRODUCTION

1.1 BACKGROUND OF AROMATIC POLYAMIDES

In the 1930s, W.H. Carothers initiated work on aliphatic polyamides or nylons. His work led to the production and investigation of aromatic polyamides, the general structure of which is

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\begin{array}{c}
\text{C-R_1-R_2-N} \\
\text{H-H}
\end{array}
\] (fig. 1)

where \( R_1 \) and \( R_2 \) are aromatic groups.\(^1\) "Aramid" or aromatic polyamide fibers are defined as manufactured fibers in which at least eighty-five percent of the amide (-CO-NH-) linkages are attached directly to two aromatic rings and the fiber forming substance is a long chain polyamide. The quantity of amide-aromatic linkages is the characteristic which separates aramid fibers from their nylon counter-parts which have fewer than eighty-five percent.\(^2\)

The importance of aromatic polyamides in industry is due to their high thermal stability and dimensional stability (high crystallinity or the ability to be crystallized). Either the crystalline melting point \( (T_m) \) or the polymer melt temperature \( (PMT) \) may be evidence of this stability.\(^1\) The fiber forms of these compounds have properties inclusive of these as well as medium to ultra-high tensile strength, medium to low elongation and moderately high to ultra-high modulus.\(^2\)

Increased thermal stability and flame resistance or higher degradation temperature is attributed to meta orientation of the bonds attached to the aromatic rings of the molecule as shown in figure 2. Those with principally para orientation exhibit ultra high strength and
Tenacity is increased by groups which extend the polymer chain. Polyamides which are described as "extended chain" are those in which the chain-forming groups are linked such that the chain is extended in the same direction as the amide bonds. Trans configuration is presumed to predominate in the amide bonds. However, rings which are not rigid chain extending may enhance the tensile properties of the fibers. For rod-like and para-oriented polymers, chain folding is not necessary to attain high tensile strength.

1.2 SYNTHESIS OF POLYAMIDES

Synthesis of wholly aromatic polyamides was initiated using interfacial polymerization. In interfacial polymerization, the reaction commonly occurs between a diamine and a diacid chloride in two immiscible solvents. The reaction medium is composed of a solvent for at least one of the reactants and a solvent or swelling agent for the polymer product, generally a water phase and an organic phase. Completely water miscible solvents can be used for polyamides especially if one of the reactants is a diacid chloride. Also, the medium must not initiate any side reactions. Side reactions, including low reactivity, seem to contribute to the lack of formation of wholly aromatic polyamides, while mixing of the solvents in specific ratios
apparently increases the production of certain rod-like aromatic polyamides.\textsuperscript{2}

The general reaction is as follows:

\[ \text{RNH}_2 + \text{R'COCl} \xrightarrow{\text{NaOH}} \text{RNHCO} + \text{NaCl} \quad (\text{eq. 1}) \]

Polymerization is observed at the interface between the solvents. An intermediate is formed which then penetrates the organic layer creating oligomers and growing polymer chains.\textsuperscript{6} A precipitated product which is not easily transformable into fiber form is obtained. The molecular weight of the final product obtained by this method is not high by current standards.\textsuperscript{3}

Interfacial polymerization is a valuable method for polyamide synthesis because the temperature required for efficient polymerization is much lower than that for the melt method, the reactions involved proceed at high rates, and fairly good yields are obtained. Another advantage is that an exact 1:1 ratio of reactants is not required. Reaction rates are between $10^2$ and $10^6$ L/(mol·s). These rates are directly affected by the intermediates' rate of diffusion into the reaction site.\textsuperscript{6} The melt method also does not produce products with molecular weights as high as those obtained by the interfacial method.\textsuperscript{4}

The system for interfacial polymerization may or may not be stirred. Figure 4 is an example of a non-stirred system (e.g., nylon rope trick). The stirred method is valuable for polymers which form stable or metastable solutions or rapidly precipitate.\textsuperscript{5}
For many extended chain systems, low temperature solution polymerization in amide solvents works best. It was found that in general, wholly aromatic polyamides do not remain in solution when prepared by this method unless either inorganic salts (calcium chloride or lithium chloride) or a basic solvent (dimethyl acetamide or N-methylpyrrolidinone), which forms a salt with the hydrogen chloride is present as seen in equation 2. For high melting polyamides (e.g. aramids), this method is very important because these compounds decompose or cross link if melt polycondensation is attempted.

\[
\text{RNH}_2 + \text{RCOCl} \underset{\text{NH}_3}{\overset{3}{\longrightarrow}} \text{RNHCOR} + \text{R}_3\text{NHCl}^-(\text{eq. 2})
\]

Several factors which control the efficiency of this method of synthesis are found in Table I. A factor which is at an ideal level may compensate for the lack in another.

**TABLE I**

<table>
<thead>
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<th>Reaction Rate</th>
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<tr>
<td>Purity of intermediates and solvents</td>
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Although their molecular weights are not high by today's standards, some fibers are produced from rod-like polymers with high intrinsic and inherent viscosity. For these fibers to exhibit the desired mechanical properties, the fine linear densities must be of very small cross-sectional area. They have a lower specific gravity in comparison to glass and steel as well as being stronger and stiffer.\(^2\)

Aramid fibers are generally prepared from aromatic diamines (eg. phenylene diamines, diaminotoluene, etc.) and aromatic diacids or their chloro derivatives (eg. isophthaloyl chloride, terephthaloyl chloride).\(^1\) Kevlar is one such fiber.

1.3 POLYMER STATES

Exceptionally high modulus and strength are characteristic of highly ordered molecular systems (eg. a para oriented system hydrogen bonded to form a three dimensional crystal lattice system). Materials which exhibit this quality are produced from liquid-crystalline solutions and can be in film or fiber form.\(^3\)

Linear flexible-chain polymers may adopt many states in their formation. Figures 5-8 illustrate these states. The first, random coil, is an entirely random system.\(^3\) Neither crosslinking nor stiff groups in the polymer backbone are observed. Random rod polymers, shown in figure 6, do contain stiff chain extending groups in the polymer backbone. However, there is still no crosslinking between the individual polymer chains and therefore, the arrangement of the polymer in solution is still completely random. As more and more of the rod-like molecules are introduced into the solution and if the
polymer - solvent interactions are correct, the "rods" will begin to form groups with the chains in the groups parallel to one another. This state is illustrated in figure 7. Finally, the nematic phase (fig. 8), has all of the polymer backbones extending in the same direction but the ends of the molecules are not even. This is the most ordered polymeric phase and is considered "liquid crystalline".  

In liquid crystals, a change in the position of the polymer molecules is observed at a lower temperature than a change in the orientation of bonds within the molecules unlike "normal" crystals. These changes in position give rise to three major phases: nematic, smectic, and cholesteric illustrated in figures 9-11.
The nematic phase is thread like and very much like normal solutions.\textsuperscript{8}

The smectic forms in layers, while the cholesteric is actually a subdivision of the nematic phase. In this phase, layers of nematic liquid crystals orient in different directions giving rise to an overall helical structure.\textsuperscript{7} Examples of molecules which form these structures are:

\textbf{Nematic:}

\[
\text{CH}_3\text{O}-\begin{array}{c}
\text{N}=\text{N} \vphantom{O}
\end{array}\vphantom{O}-\begin{array}{c}
\text{O}
\end{array}\text{OCH}_3
\]

\textit{p-azoxyanisole}

\textbf{Smectic:}

\[
\text{CH}_3-(\text{CH}_2)_3-O-\begin{array}{c}
\text{C}=\text{N}
\end{array}\vphantom{\text{H}}-\begin{array}{c}
\text{H}
\end{array}\vphantom{\text{O}}-\begin{array}{c}
\text{OCH}_3
\end{array}-\begin{array}{c}
\text{(CH}_2)_{7}\text{-CH}_3
\end{array}
\]

\textit{N-(p-butoxybenzylidene)-4-octylaniline}
Liquid crystal formation occurs in one of two forms - lyotropic or thermotropic. The term thermotropic identifies materials which form liquid crystals from the melt due to temperature changes. For this type of material, phase transitions occur with increasing temperature. Lyotropic describes solutions that are affected by solvent types and changes in concentration in addition to temperature changes. Here the transitions are more complex, but normally decreasing transition temperature is observed with increasing concentration. Increasing the molecular weight of these polymers decreases the critical concentration necessary for the formation of anisotropic or ordered regions. The transitions occur as follows:

\[
\text{crystalline solid} \rightleftharpoons \text{smectic} \rightleftharpoons \text{nematic} \rightleftharpoons \text{isotropic}
\]

All of the transitions are reversible as indicated and for most systems there is no definite transition from the isotropic to the nematic phase but rather coexistence as illustrated in figure 12.\textsuperscript{8}
Table II lists the requirements for the formation of liquid crystals in polyamides which are normally nematic. 

**TABLE II**

Extended chains and trans configuration of the amide group  
Minimum molecular weight and axial values  
Solvent-polymer interaction  
High enough solubility to exceed the critical concentration  
(temperature affects solubility and liquid crystalline range)

Structural features of liquid crystalline solutions include a succession of para-oriented ring structures to give a rigid, elongated chain. (fig. 13) If X has extended side chains, the axial ratio is reduced thus suppressing liquid crystal behavior. 

Repulsions between molecules or molecular asymmetry, dominate the formation of liquid crystals. The degree of asymmetry is determined as the ratio of the equilibrium length to the diameter of the molecules. 

As long as solvent is present, for most flexible-chain
polymers, rotation about intramolecular valence bonds is possible which should allow random arrangement at any concentration.\(^9\) However, since sections in two molecules cannot occupy the same space, in rod-like polymers there is a finite number of chains which can be in a random arrangement. Therefore, restriction of rotation about single bonds increase asymmetry, thus increasing liquid crystal formation.\(^7\) The following are causes of asymmetry or a high axial ratio: 1). restrictions of free rotations, such as the inclusion of cyclic units, 2). cyclization through intramolecular hydrogen bonds, 3). quasi-conjugation and coplanarity of amide groups, 4). formation of ladder polymers.\(^9\)
II. KEVLAR

2.1 BACKGROUND

The aramid fiber, Kevlar, was originally introduced in 1970 as Fiber B - a poly p-benzamide (PPB fiber) by the DuPont company. Kevlar fiber has been identified by chemical analysis, X-ray crystallography, and infrared spectroscopy as being poly (p-phenylene terephthalamide) (PPD-T or PpPtPA). (fig. 14)

![Chemical Structure](image)

Having a weight-basis tensile modulus and strength several times that of steel, it is useful in engineering applications where high modulus, low elongation at break, and high tenacity are required. Kevlar can be found in many common places, some of which are: high quality boat sails (the fibers are used as reinforcements), high strength cables, tires, bullet proof vests, and tennis racket strings. Typical properties of Kevlar are: tenacity 1.8-2.7 GPa, modulus 44-97 GPa, and elongation at break 2-5%. Kevlar has an inherent viscosity above 4 dL/g, a number-average molecular weight of 20,000 giving a degree of polymerization of 84 and a chain repeat length of 108 nm. Its major weakness is its poor compressive properties.

There are several types and forms of Kevlar synthesized today. It may be purchased in film, pulp, or fiber form. The different fibers available are: Kevlar, Kevlar-29, Kevlar-49, and Kevlar PRD-149. All have the same chemical structure, the difference being the technique
used to process the polymer from solution, giving the fibers a variety
of properties.\textsuperscript{13}

Kevlar is utilized in mechanical rubber goods such as high
performance hydraulic, automotive, and thermoplastic hoses. It is also
found in V-belts, timing belts, and conveyor belts. In conveyor belts,
reduced belt thickness and lower weight are the result of the fiber's
high strength and modulus. As compared with steel-belt
reinforcements, Kevlar's non sparking and low heat conducting
properties are added benefits.\textsuperscript{14}

Kevlar-29 and -49 are very similar to Kevlar and one another. The
difference between these two is mainly the application of a sizing to
Kevlar-29 creating Kevlar-49. Kevlar-29 is found in electromechanical
cables, cordage, ballistic fabrics, sewing thread, parachutes, webbing,
and sailcloth. Kevlar-49 has a higher modulus and lower elongation
than both Kevlar and Kevlar-29. It was specially designed for plastics
reinforcement to replace and supplement glass and other high modulus
inorganic fibers. Because it is twice as stiff as glass with half the
weight as well as better stress fatigue and vibration damping
properties, it is found in composite laminates in interior and exterior
of aircraft. Kevlar-49 also has applications in aerospace, electrical,
marine and sporting goods.\textsuperscript{14}

Kevlar PRD-149 was first introduced in 1987. It has higher
crystallinity and a unique super-crystalline structure when compared
to the other fibers and can be fabricated with varying modulus levels
up to about thirty-five percent greater than Kevlar-49. This added
crystallinity makes PRD-149 good for optical fiber cable reinforcement
and hybrid aramid/carbon composites. Because it is not as susceptible to moisture gain, Kevlar PRD-149 is preferred for those uses where extremes, especially cyclic environmental extremes, might be encountered.\textsuperscript{13}

2.2 STRUCTURE

The polymer backbone of Kevlar exists in an extended chain form, shown in figure 15.

\begin{center}
\includegraphics[width=0.7\textwidth]{fig15.png}
\end{center}

The molecule adopts this conformation because rotation of $180^\circ$ about the amide bond would result in the structure illustrated in figure 16, thus causing a reduction in stability.

\begin{center}
\includegraphics[width=0.7\textwidth]{fig16.png}
\end{center}
The molecules of Kevlar form intermolecular hydrogen bonds which link adjacent chains together forming two dimensional sheets even though most of the material is three dimensional. This results directly from imperfect alignment of the sheets and therefore they are considered two dimensional. The structure of a sheet is thought to resemble that in figure 17. These sheets stack and then form hydrogen bonds in the fiber radial direction (fig. 18), unlike conventional fibers.
2.3 PROPERTIES

As with all compounds, the structure of Kevlar determines its properties. The extended polymer chains in the direction of the fiber axis (-C-N-) give the material a high longitudinal modulus of elasticity, while aromatic rings and the conjugation of the electrons give the material its chemical stability and mechanical stiffness. As a result of the different types of bonds extending in various directions, the lateral hydrogen bonds and the covalent bonds in the fiber axis direction, different values for mechanical measurements made in different directions are obtained.\(^{16}\)

Kevlar yarns have been found to have different initial strengths. This is thought to be caused by differences in their crystallinity, the highest strength yarn being the most crystalline. It has been shown that Kevlar filaments have a highly crystalline core with a less ordered skin. Chemical degradation always occurs more easily within disordered regions and since for Kevlar this is only a small portion of the material, surface degradation is expected to predominate.\(^{17}\)

The utility of industrial fibers is frequently determined by their resistance to the deteriorating effects of chemicals, heat, sunlight, and weather. The degree of deterioration is usually measured by the change in breaking strength. Kevlar appears to have a lower breaking strength if tested at high temperatures, but when reconditioned and retested at room temperature, normal breaking strength is observed.\(^{14}\)

The absence of free rotation about the phenylcarbon and the phenylamide bond gives Kevlar its rod-like character. Although it has a very high melting point and is heat resistant, it is not particularly
useful as a heat-resistant fiber due to the rather low elongations observed for rod-like polymers. This type of polymer exhibits rapid loss of elongation after being heated, thereby becoming too brittle to be useful. For short term exposure, retention of strength at elevated temperatures is outstanding.\textsuperscript{2} Kevlar fibers do not support combustion but will char at 427°C (800°F).\textsuperscript{8} Flame resistance may be increased by the addition of phosphorus to the polymer as long as the fiber has not been highly drawn.\textsuperscript{2}

Low thermal expansion (creep and linear coefficient) and high thermal stability are observed due to extended chain formation of the backbone, high molecular weight, and orientation- almost complete in a nearly 100% crystalline fiber. Kevlar also has low density, easy processibility, and good fatigue and abrasion resistance.\textsuperscript{13}

Crystallinity and orientation are increased after a controlled, short (1-5 s) exposure to high temperature.\textsuperscript{7} Both of these properties contribute to added chemical stability and lower rate of moisture gain. Kevlar is resistant to most ketones, alcohols, hydrocarbons, and dry cleaning solvents or oils. At excessive temperatures or concentrations, strong acids and bases will attack Kevlar.\textsuperscript{14}

Kevlar’s poor compressive properties are a direct result of its structural anisotropy. Any great amount of compression in the fiber axis direction cannot be withstood by Kevlar due to its extended chain formation which results in localization of the force in the backbone. This concentration in the backbone causes deformation in the bonds, thus decreasing the strength of the material. This is further enhanced by the weak hydrogen bonds between polymer chains.\textsuperscript{8}
Hydrolysis of the amide bond does occur under certain conditions leading to chain scission (eq. 3) and consequently to strength loss. However, this is very rare and is not seen as a serious problem.\(^7\)

\[
\begin{array}{c}
\overset{\text{O}}{\text{N}}-\overset{\text{C}}{\text{O}} - \overset{\text{N}}{\text{H}} - \overset{\text{C}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{C}}{\text{O}} - \overset{\text{N}}{\text{H}} \quad \text{+ H}_2\text{O} \quad \rightarrow \\
\overset{\text{O}}{\text{C}}-\overset{\text{H}}{\text{O}} \quad + \quad \overset{\text{N}}{\text{H}}-\overset{\text{C}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{C}}{\text{O}} - \overset{\text{N}}{\text{H}}
\end{array}
\]

(eq. 3)

2.4 SYNTHESIS

Kevlar is composed of the coupling product of phenylene diamine and the chloro derivative of terephathalic acid (eq.4).\(^{16}\)

\[
\begin{array}{c}
\text{NH}_2-\overset{\text{N}}{\text{H}}-\overset{\text{C}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{C}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{C}}{\text{O}} - \overset{\text{N}}{\text{H}} \quad + \quad \text{ClC-Cl} \quad \text{amide solvent} \\
\text{NH}_2-\overset{\text{N}}{\text{H}}-\overset{\text{C}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{C}}{\text{O}}-\overset{\text{O}}{\text{N}}-\overset{\text{C}}{\text{O}} - \overset{\text{N}}{\text{H}} \quad + \quad 2 \text{HCl}
\end{array}
\]

(eq. 4)

The amide solvents used, N-methylpyrrolidone and dimethyl acetamide, may either be used alone, mixed together, or a salt added to them.\(^8\)

The product of this coupling is dissolved in sulfuric acid thus forming an oriented solution normally seen in rod-like polymers. Kevlar must be processed from a solution because it decomposes before melting and therefore cannot be prepared using a conventional melt.
method. Furthermore, since oligomers of rod-like polymers frequently form insoluble gel structures when mixed in solution, shearing action (such as that of a blender) of the solution is required in order to obtain a final product with a high molecular weight.²

The highest molecular weight obtained for poly (para-phenylene terephthalamide) resulted from a 1:2 weight ratio of hexamethylphosphoric triamide (HPT) and N-methylpyrrolidinone (NMP). Employing salts during the polymerization appears to lower the molecular weight of the final product. Presumably, this is due to the complexing of the salts with the individual solvents, thus destroying the interaction between the solvent pairs. Generally, a concentration of about .5 mol/L (about 15-20% polymer solids) is prepared in order to obtain optimum molecular weight. For Kevlar, molecular weight increases with concentration only up to about .25 mol/L or about 6-7% solids and then begins to decrease rapidly. Fiber filaments are formed from this solution by a dry-jet wet spinning process shown in figure 19.⁸
In this process, after extrusion, the polymer solution is led through a gaseous medium, and then into a polyalkylene glycol-water coagulating bath.\textsuperscript{1}

In order to remove and neutralize the sulfuric acid the filaments are washed with a solution of sodium carbonate.\textsuperscript{16} As the filaments are produced, the polymer solution forms nematic liquid crystals, like that in figure 9 (page 7). These structures are easily oriented in solution during the production of the fiber.\textsuperscript{12} From such liquid crystalline solutions, high strength can be obtained without hot drawing, a part of usual fiber spinning. If the hot drawing technique is used here, there is a two-fold increase in initial modulus without an increase in tenacity, an undesirable characteristic for Kevlar.\textsuperscript{2}
III. SPACE TETHERS

3.1 INTRODUCTION

During the 1960s, the engineers of the Apollo and Gemini space programs first employed the use of tethers in space to link the astronaut to his ship during walks in space. Since then, Guisepe Colombo of the University of Padua, introduced the "skyhook" scheme. This concept has been modified to the "Tethered Satellite System" (TSS) and is today being employed by the National Aeronautics and Space Administration (NASA). TSS will be used to conduct further studies on both the Earth's atmosphere and space.\(^1\)

3.2 TSS CONCEPT

TSS involves the deployment of a measurement device or other object- especially one which is reusable- as far as 100 km from the Space Shuttle. The payload must be deployed vertically from the Shuttle. (fig. 20) The horizontal configuration is unstable because here the tether is parallel to the Shuttles orbital velocity. The distance of the satellite from the Shuttle is influenced only by such things as the amount of tether which may be carried.\(^1\)}
TSS has many valuable scientific applications. Some which have been proposed are low altitude research, releasing chemical payloads for the study of various phenomena (e.g. ionization studies), study of the Earth’s magnetic field, and the linkage of two orbiting spacecraft creating artificial gravity. The tether will encounter what is known as LEO (low earth orbit) environment during these applications. Included in the LEO environment are atomic oxygen (AO) and ultraviolet (UV) radiation. Degradation of many materials (especially those which are organic) is encouraged by the presence of AO and UV radiation, and therefore the materials for the tethers must be chosen carefully.

3.3 PROPOSED MISSIONS

Currently, NASA is planning to conduct two tethered satellite missions. The first proposed mission will deploy a satellite upward from the Shuttle. This is an electrodynamic experiment and the tether involved will contain a core of conducting wire. Approximately twelve miles of tether will be reeled out into the Earth’s magnetic field. Measurements of the field and the induced electric current in the tether due to the field will be taken. NASA hopes that eventually the generated electric current may be used to augment the shuttle’s energy systems.

The second planned mission proposes the deployment of the tether’s entire 62-mile length down into the Earth’s atmosphere. A non-conducting tether, identical to the conducting tether minus the conducting core, will be employed in this experiment. The purpose of the mission is to study that portion of the atmosphere which is too thin
to support planes and weather balloons but too dense to allow flight of a satellite.²¹

3.4 THE TETHER

Figure 21 depicts the conducting tether which will be used in the first mission.

NASA has planned to use the materials indicated in the illustration because of their special properties. The core is surrounded by jackets of Kevlar and Nomex woven from twelve tows of 100 denier yarn. Kevlar and Nomex were chosen due to their load bearing capabilities and heat resistance. Kevlar is the stronger of the two while Nomex provides protection from atomic oxygen.²⁰
IV. EFFECTS OF ULTRAVIOLET RADIATION ON KEVLAR

4.1 ABSORPTION OF UV RADIATION

Various forms of energy including heat, radiation, light, mechanical action, etc. may break chemical bonds. Light is the most specific of these, being tuned to the cleavage of bonds. Wavelengths of approximately 280-390 nm, the near ultraviolet part of sunlight, contains enough energy to break most single carbon - carbon bonds and many between heteroatoms. The corresponding energies for these types of bonds are 400-300 kJ/mol or 95-70 kcal/mol. Cleavage of the bonds will occur only if the proper wavelength of light is absorbed. For cleavage of the amide link in aromatic polyamides, a special case of the Norrish Type-I process, wavelengths around 300 nm are required. In the case of Kevlar fibers strong absorption in the ultraviolet region around 250 nm, as well as a low broad absorption around 330 nm is observed (fig. 22).

In the presence of air, exposure to near-ultraviolet radiation (>290 nm) causes a progressive deterioration of mechanical properties (tensile strength, elongation) and a yellowing of aramid films and fibers. The yellowing observed could be attributed to crosslinking
and quinone formation and not solely to actual destruction of the material.23

PmPiPA (Nomex, fig. 23), the meta counter-part of Kevlar, has similar properties and comparisons of the two fibers are often made.

\[
\text{ figure } 23
\]

Both PpPtPA (Kevlar) and PmPiPA (Nomex) fibers were exposed to an ultraviolet lamp (120 watt, 2537 A) and then tested\textsuperscript{11} for a reduction in tensile strength, the ultimate load that the material can handle without breaking.

Figure 24 is a comparison graph of PpPtPA and PmPiPA illustrating tensile loss and elongation at break.\textsuperscript{10}

\[
\text{ figure } 24
\]

The graph demonstrates that para compounds are inherently more resistant to damage from electromagnetic radiation than meta compounds under conditions where movement in the polymer segments should be identical. This ultraviolet resistance is attributed to extended conjugation along the all-para backbone due to resonance
forms (figs. 25-26).

These resonance forms would allow delocalization of the ultraviolet energy, rather than its concentration in and subsequent destruction of the amide linkage.23

4.2 DELOCALIZATION OF UV RADIATION

If, as suggested, the ultraviolet energy is delocalized throughout the polymer backbone due to resonance, crosslinkage of the amide groups causing disruption of the bonds in the transverse direction as well as the packing in the crystal lattice due to introduced irregularities in the backbone would occur, resulting in a consequent decrease in crystallinity. This would result in a loss of tensile strength and no appreciable change in the average molecular weight.17

At the Materials Research Laboratories, Melbourne, Australia this was demonstrated17 by mounting Kevlar yarns outside during summer. After 60 days of exposure, under window glass angled at 36° to the north, the samples were tested for a change in molecular weight. Average molecular weight measurements - $M_V$, viscosity average molecular weights - were determined by dilution viscometry at 25° C in an Ubbelohde viscometer. The intrinsic viscosity, $[\eta]$, of dilute polymer solutions may be related to the molecular weight of the polymer. The equation used to relate the two is the Mark-Houwink
equation (eq. 5).

\[ [\eta] = KM^a \]  
(eq. 5)

Where K and a for Kevlar are 0.0080 cm\(^3\) g\(^{-1}\) and 1.09 respectively.\(^{17}\)

For this experiment, two types of yarns were tested, warp and weft. Warp yarns have a sizing or coating while weft yarns do not. It was noted that the warp yarn appeared to degrade faster, and therefore believed that a surface agent (eg. the sizing) might be encouraging the degradation process. However, after the removal of the sizing (a poly ethylene glycol - adipic acid ester) from the surface, no significant effect on the rate loss of mechanical properties was observed.\(^{17}\)

Viscosity average molecular weight measurements were taken before and after exposure to ultraviolet radiation (Table III). As expected, these measurements show little change in the molecular weight of the polymer thus supporting the hypothesis of delocalization of the ultraviolet radiation.

<table>
<thead>
<tr>
<th>Yarn</th>
<th>(M_V \times 10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td></td>
</tr>
<tr>
<td>warp</td>
<td>33.5</td>
</tr>
<tr>
<td>weft</td>
<td>33.4</td>
</tr>
<tr>
<td>Photochemically aged</td>
<td></td>
</tr>
<tr>
<td>warp</td>
<td>31.6</td>
</tr>
<tr>
<td>weft</td>
<td>30.7</td>
</tr>
</tbody>
</table>

Under the assumption that the weights obtained are taken as
averages and the distribution of molecular weights is normal, the average number of chain scissions per molecule is estimated as being approximately 0.06. The appreciable strength loss (fig. 24) and the small number of chain scissions can be rationalized when it is taken into account that only the outer layer of the filament is degraded as suggested earlier.\textsuperscript{17}

4.3 THE PHOTO-FRIES REACTION

Concentration of ultraviolet energy in the amide link is expected to result in a classical photo-Fries rearrangement, with the predominate products being 2- and 4- aminobenzophenone units along the backbone (eqs. 6-7).\textsuperscript{23}

\[
\begin{align*}
\text{h} & \quad \text{N-C-O} \\
\text{+} & \quad \text{N-H} \\
\xrightarrow{\text{CO}_2} & \quad \text{H-N} \\
\text{2-aminobenzophenone} & \quad \text{4-aminobenzophenone}
\end{align*}
\]

However, the suggested scheme for PpPtPA photo degradation in air is oxygen interception during amide bond cleavage (the formation of
radicals initiating the process) producing -COOH groups, as well as the formation of 2-aminobenzophenone via a photo-Fries rearrangement. This would result in a small decrease in molecular weight and a more extensive decrease in mechanical properties by disruption of the highly oriented para structure. It was demonstrated that aramids in the form of thin films and fibers do show only formation of 2-aminobenzophenone during exposure to ultraviolet radiation. The proposed mechanism for this result is the following photo oxidation (eqs. 8-10).24

Moreover, it seems unlikely that peroxy radicals are formed in this reaction because the irradiations were carried out at approximately
290 nm and wavelengths less than 220 nm are required for the production of peroxy radicals from peroxides. The proposed mechanism then becomes (eqs. 11-12):

\[
\text{hv} \\
\text{N} - \text{O} \cdot \text{O} - \text{C} \rightarrow \\
\text{H} \\
\text{N} - \text{O} + \cdot \text{O} - \text{C} \quad (\text{eq. 11})
\]

\[
\text{eq. 12}
\]

Infrared spectra of irradiated fibers support this mechanism showing an increase in the broad absorption at approximately 3250 cm\(^{-1}\) consistent with -COOH formation as well as a proportional decrease in the amide absorption at 1530 cm\(^{-1}\). The products produced in the photo-Fries rearrangement (2-aminobenzophenone and 4-aminobenzophenone) are ultraviolet absorbers. Low yields in these products, however, indicate that recombination of the primary radicals to reform the amide links in the polymer cage is preferred over rearrangement or separation into scission products. This is further illustrated by the small reduction in molecular weight and chain scission products reported by J.R. Brown et al. Therefore, one concludes that the reduction in strength
observed in Kevlar as a result of exposure to ultraviolet radiation is a consequence of a reduction in crystallinity in the polymer backbone rather than its complete destruction.
V. ATOMIC OXYGEN

5.1 INTRODUCTION

The Earth's atmosphere varies in composition, density, and temperature. Figure 27 is a graphical representation of the elements composition present in Low Earth Orbit (LEO) as a function of altitude.

This composition is further affected by solar activity, variations in magnetic field, latitude, local time, and season. A specific concern is the density of atomic oxygen in low Earth orbit and its affects on particular polymeric materials. Solar activity (UV radiation) has been shown to have the largest influence on the atomic oxygen density and figure 28 illustrates the variations in this density with changes in solar activity.25
The cycle between the low and high densities appears to follow an eleven year period. As seen from the graph, the atomic oxygen density in LEO is not particularly high. However, the velocity of the object in LEO (satellite or shuttle) causes the flux (atoms cm\(^{-2}\) sec\(^{-1}\)) of the oxygen atoms to be high.\(^{25}\)

The interest in the amount and reactions of atomic oxygen with certain polymeric materials arises from the need to accurately predict changes in structure and strength in these materials. Of special interest to those working on the Tethered Satellite Project, is the resistance of Kevlar and Nomex to AO. There has been no published research in this area. Our own experiments on Kevlar shall be reported later. Therefore, general information on the effects of atomic oxygen on polymeric materials will be presented in this chapter.

The mechanism discussed in the next section may be only part of the actual reaction which causes the oxidation and subsequent degradation of polymers. There are however, only two basic results which may occur. The oxygen may react on the surface of the material in such a way that it becomes a part of the material, altering the functional properties by the formation of new stable compounds, or it may simply produce volatile products which escape causing reductions in mass and therefore loss of mechanical, optical, and/or electrical properties.\(^{25}\)

5.2 PROPOSED REACTIONS

The initiating reactions for ordinary oxidation which are believed to occur are shown below (eqs. 13-15):
There is a possibility that oxygen ions may also be produced, however, this is not believed to be true because the formation of ozone was not observed under the experimental conditions used by Hansen et al.\textsuperscript{25}

The proposed mechanism for simple thermal oxidation begins with the formation of hydrocarbon radicals (eq. 16).

\[ \text{RH} \xrightarrow{\text{slow}} \text{R}^- + \text{H}^- \text{ or } \text{R}'^- + \text{R}''^- \]  \hspace{1cm} (eq. 16)

Heat or other energy causes cleavage of the chemical link between either a carbon and hydrogen or two carbons. This is fairly slow as compared to the reaction of these radicals with oxygen (eq. 17) to give peroxy radicals:\textsuperscript{25}

\[ \text{R}^- + \text{O}_2 \xrightarrow{\text{fast}} \text{ROO}^- \] \hspace{1cm} (eq. 17)

Initiation of the oxidation of polymers by atomic oxygen differs because the atomic oxygen directly attacks the polymer as in equation 18.

\[ \text{RH} + \text{O}^- \xrightarrow{\text{fast}} \text{R}^- + \text{R}''\text{O}^- \text{ or } \text{R}^- + \text{OH}^- \] \hspace{1cm} (eq. 18)

The alkyl radicals produced by this reaction may then react with additional oxygen radicals or molecular oxygen (eqs. 17 and 19).

\[ \text{R}^- + \text{O}^- \xrightarrow{\text{fast}} \text{RO}^- \] \hspace{1cm} (eq. 19)

Rapid reaction of the alkyl radicals with both molecular and atomic oxygen is the cause of speedy surface oxidation of polymers.\textsuperscript{25}

Continuation of both types of oxidations depend on the further reaction of the radicals formed with the polymer resulting in
hydroperoxides and new alkyl radicals followed by the subsequent
de decomposition of the hydroperoxides (eqs. 20-21).  

\[
\text{ROO}^\cdot + 
\text{R}''\text{H} \rightarrow \text{ROOH} + \text{R}^\cdot \quad \text{(eq. 20)}
\]

\[
\text{ROOH} \quad \text{slow} \rightarrow \text{RO}^\cdot + \text{OH}^\cdot \quad \text{(eq. 21)}
\]

Equation 21 is the rate determining step for the thermal oxidation
process. These two propagation reaction (eqs. 20-21) can be repeated
many times before return of the polymer to a non-radical species.  

These reactions are much slower than those discussed previously
and are fairly unimportant in oxidation by atomic oxygen. Evidence
supporting this comes from the inability of antioxidants to protect the
polymer from AO attack or to affect the rate of oxidation.  

Antioxidants are employed to protect polymers from exposure to
atmospheric oxygen. Common antioxidants are those which are
hydrogen donating, for example, hindered phenols and secondary
aromatic amines.  

During simple thermal oxidation, antioxidants react with the
peroxy radicals (eqs. 22-24), thus discouraging the reaction between
the hydrocarbon and the peroxy radicals and causing termination of the
polymer radicals.

\[
\text{ROO}^\cdot + \text{AH} \rightarrow \text{ROOH} + \text{A}^\cdot \quad \text{(eq. 22)}
\]

\[
\text{RO}^\cdot + \text{AH} \rightarrow \text{ROH} + \text{A}^\cdot \quad \text{(eq. 23)}
\]

\[
\text{OH}^\cdot + \text{AH} \rightarrow \text{HOH} + \text{A}^\cdot \quad \text{(eq. 24)}
\]

Torre et al. demonstrated the ineffectiveness of antioxidants
during atomic oxygen attack by adding 4,4' - butylidenebis - (3 - methyl
- 6 tert - butylphenol) to their samples. Without the addition of the
antioxidant and with .5% and 1.0%, no noticeable affect on the rate was
observed. Whereas, with a 10% addition to the sample a slight increase
in rate was seen. Further supporting the independence of AO reaction rates from equations 20 and 21, is that no indication of induction periods or auto catalysis was found as occurs in simple thermal oxidation.\(^{27}\)

Diakyl peroxides, alcohols, or carbonyl species generally result from the termination of oxidation reactions (eqs. 25-27).

\[
\begin{align*}
2R^\cdot &\rightarrow R-R \quad \text{(eq. 25)} \\
ROO^\cdot + R &\rightarrow ROOR \quad \text{(eq. 26)} \\
2ROO^\cdot &\rightarrow \text{non-radical products} \quad \text{(eq. 27)}
\end{align*}
\]

Termination yields a reduction of kinetic chain length and is significant when oxygen concentration is low.\(^{22}\)

5.3 REACTION RATE

The rate equation for the complete oxidation system is as follows:

\[
-d[O_2]/dt = (R_i)^{1/2}[C-H]k_p(2k_t)^{1/2} \quad \text{(eq. 28)}
\]

[C-H] corresponds to the number of sites which have been attacked by atomic oxygen. \(k_p\) and \(k_t\) are the rate constants for propagation and termination respectively. The rate of propagation is determined by the hydrogen which is abstracted (primary < secondary < tertiary). Termination rate depends on whether the radical is primary, secondary, or tertiary. Primary and secondary radicals react \(10^2 - 10^3\) times faster than the more stable tertiary. \(R_i\) is the rate of initiation and is determined from equation 29.

\[
R_i = 2fk_i[I] \quad \text{(eq. 29)}
\]

Here \(f\) is the efficiency of the initiating radical, \([I]\) is the concentration.
of the initiator, and $k_i$ is the rate constant. The factor 2 is required because in initiation two radicals are produced which may further the reaction.\textsuperscript{22}

For the work done by Hansen et al, the observed reaction rates were found to be constant over long periods of time as well as being independent of the thickness of the film sample. This is due to the fact that the amount of surface area which is exposed directly effects the amount of polymer that reacts.\textsuperscript{22} The absence of changes in properties of bulk polymers (low rate of oxidation) is attributed to the limitation of attack by AO to the surface layer.\textsuperscript{26}

5.4 REACTION INHIBITORS

There are several factors which appear to influence the rate of reaction (oxidation) between polymer and atomic oxygen one of which is the structure of the macromolecule. For highly branched saturated hydrocarbons, oxidation is much higher than for unbranched or highly branched sterically hindered polymers (eg. poly-vinylchloride hexane). The stability of those polymers which are both highly branched and sterically hindered is thought to result from the inability of the atomic oxygen to find adequate attack sites due to blockage of the polymer backbone by the side groups.\textsuperscript{26} Torre et al\textsuperscript{27} showed that even if the bond energies of the polymer are constant, by increasing the size of the side groups a subsequent increase of stability is observed. Ethyl groups increased stability by 24% over methyl groups while cyclohexane rings increased it by 400%.\textsuperscript{27}
Bond energies or strengths are particularly important to the stability of polymers under exposure to atomic oxygen. Table IV lists some selected bond strengths.

**TABLE IV**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Strength (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>3.58</td>
</tr>
<tr>
<td>C-H</td>
<td>4.24</td>
</tr>
<tr>
<td>C-F</td>
<td>5.02</td>
</tr>
<tr>
<td>C-O</td>
<td>3.70</td>
</tr>
<tr>
<td>C-N</td>
<td>3.16</td>
</tr>
<tr>
<td>C=C</td>
<td>6.24</td>
</tr>
<tr>
<td>C=O</td>
<td>8.27</td>
</tr>
<tr>
<td>N=O</td>
<td>6.28</td>
</tr>
<tr>
<td>Si-O</td>
<td>4.68</td>
</tr>
</tbody>
</table>

The molecules with the stronger bonds - especially in the backbone - are more resistant than those with weaker bonds. The bonds in the polymer backbone are important because cleavage of these bonds cause mass loss and thus a reduction in mechanical properties. For the same reason, bonds which result in crosslinking between polymer chains are also important. It seems that with increased crosslinking between polymer chains, acceleration of the oxidation rate is observed. The rate also appears to be controlled by the amount of stress on the material - the more stress the greater the oxidation rate. Side group bond energies are not important because they do not directly affect mechanical properties. However, as mentioned previously, the size of these groups does influence the ability and extent of attack by atomic oxygen.

It is a combination of structure and bond strengths which account for the final stability of a material. Compensation by one factor for lack in another is possible.
VI. EXPERIMENTAL

6.1 FILM PREPARATION

The first goal of the project was to dissolve Kevlar fibers and cast films from the solution. This proved to be very difficult due to the lack of previous research in this area as well as the chemical stability of the material. For all of the experimental procedures, fibers of Kevlar-29 were used per request of NASA since this is the material which will be employed in the tether.

For the first attempt at dissolving Kevlar fibers, which proved to be unsuccessful, concentrated sulfuric acid was employed as the solvent. Dry nitrogen gas was bubbled through the cut up Kevlar fibers for thirty minutes (fig. 29) in a vacuum desiccator.

\[ \text{Nitrogen was also very carefully bubbled through the acid for the same period of time. The acid was quickly added to the Kevlar fibers and replaced in the nitrogen atmosphere of the desiccator. Nitrogen continued to bubble through the apparatus for thirty minutes and then the system was closed to the air for approximately seventy-two hours. After filtration of the material it was observed that little if any Kevlar dissolved. Dissolving fibers in 6M HCl was also attempted with the same results.}

\[ \text{An attempt to synthesize Kevlar was also made using the following} \]
chemicals: 24 g of CaCl₂, 200 ml of N-methyl pyrrolidone (NMP), 7.3 g of p-phenylenediamine, and 13.9 g of terephthaloyl dichloride. The calcium chloride was first added to the NMP, placed in a beaker of ice and allowed to stir while the remaining materials were weighed out. The p-phenylenediamine was then added turning the solution a mauve color. After stirring for approximately ten minutes, the terephthaloyl dichloride was added causing the solution to become yellow in color and extremely viscous. The final product obtained resembled vanilla pudding in both color and consistency.

An infrared spectrum of the substance was taken. Comparison of the spectrum (fig. 30) with one of Kevlar fibers (fig. 31) indicated

(fig. 30)

(fig. 31)
similarities, however, the spectrum of the synthesized material seemed to be lacking the peak which corresponds to two adjacent hydrogens. The remaining peaks were identified and the synthesis did appear to have been successful but perhaps the reaction was not allowed to proceed long enough under the proper conditions and therefore complete polymerization did not occur.

An attempt to cast films from the synthesized Kevlar was made using the technique described below excluding use of the thickness gage. All films were cast by pulling a doctor blade (fig. 32) across a glass plate.

The cleaning procedure for the plates is as follows: wash with soap and water, rinse with deionized water, wash with ethanol, and finally wipe with a clean, soft, lint free cloth. Gloves were always worn when preparing the plates to avoid contact of the skin with the glass and clean plates were covered with a cloth. Before pulling a film, the plate was rinsed thoroughly with acetone and wiped dry. The doctor blade was cleaned similarly and rinsed with acetone before each use.

The thickness gage, which consists of metal pieces of varying
thicknesses, was used in order to set the doctor blade. By knowing the percent solution being pulled one can determine the approximate thickness of the resulting film, assuming that all solvents are driven off.

Two films from the synthesized "Kevlar" were pulled. The first produced a cloudy film on the glass plate. The second try resulted in a few splotches on the plate. Both plates were placed in a dry box under nitrogen gas in attempt to dry them. After five days the films still appeared wet so they were placed in an oven at 115°C overnight. The temperature was slowly increased over the next thirty-six hours to avoid blistering of the films. After a total of approximately forty-eight hours, the temperature was up to around 128°C and the films were beginning to turn black. Removal of the films from the glass plates was not achieved.

Further attempts to dissolve Kevlar resulted in the discovery that it will dissolve in concentrated sulfuric acid with the addition of heat (15 minutes) and vigorous stirring producing a brown liquid. Solutions obtained were between .1% and 3.7%. It was not possible however, to pull films from these solutions using the doctor blade method because the sulfuric acid would destroy the metal blade. The methods which could be employed using this solution (extrusion, etc.) were not available. An attempt was made to make a film by using two glass plates and a 1% solution. By pulling the solution across one plate with the edge of the other, distribution of the liquid over the surface of the plate was possible. However, this technique did not work because the viscosity of the solution was not high enough to prevent it from running
Using a more concentrated Kevlar/H₂SO₄ solution (3.7%) and the technique using the two glass plates, another attempt was made. After "pulling" the film the bottom plate was immediately placed into a cold water bath. Small pieces separated out and were dried in various manners. One was placed into an oven for ten minutes and completely destroyed, a second cracked after being placed into a vacuum desiccator, and finally those which were air dried and loosened from the plate with ethanol were so small that they could not be used.

After approximately 48 hours of exposure to the air, the solution discussed above appeared to be recrystallizing. It was found that after ten minutes of heat and stirring the material went back into solution. Benzoic acid was added to a solution obtained from sulfuric acid in hopes that it might aid in crystallization of the material. However, this was not successful.

The method which was finally employed for dissolving Kevlar and the subsequent fabrication of all of the films utilized throughout the project was supplied by Mr. Fred Sweeny of the DuPont company located in Delaware. The "recipe" calls for the addition of .5 g of Kevlar to equal amounts (.5 g) of potassium-tert-butoxide and methanol and 50 g of dimethyl sulfoxide for a one percent solution. A five percent solution may be obtained by doubling the amounts of all of the "ingredients" except the DMSO. This mixture is allowed to stir until dark redish-orange in color, approximately twelve hours for the one percent solution and at least twenty-four hours (due to the viscosity of the substance) for the five percent solution to ensure that all of the
fibers dissolved. Solutions may be frozen and kept for extended periods of time (usually one to two weeks) but those which are used immediately produce the best films.

Films from these solutions were pulled using the technique with the doctor blade described previously. After the film was cast, the glass plate is placed in a shallow bath of methylene chloride (the bath was covered with a piece of glass to keep fumes from escaping into the lab) and allowed to soak until the film became yellow. The time required for the desired color change varied from two to six hours.

The films were removed from the plates under running water and put into frames (fig. 33).

![Diagram of film and clamp](fig. 33)

Frames were necessary so that the films would retain their shape during drying. The first frame that was used had rubber bands affixed to the insides (fig 34).
It was found that the rubber "gasket" often stuck to the films causing difficulties in removing them from the frame. The solution to this problem was to use one frame with a gasket and one without.

The frames and films were then placed into a water bath to soak overnight and hung up to air dry the following morning as shown in figure 35.

Drying times varied anywhere from one to twelve hours. Use of an oven to dry the films was also tried but the air drying appeared to work best. Several attempts were made before usable films were obtained.

Kevlar pulp was also dissolved and a film was pulled from the subsequent solution. The difference in form of the starting materials did not appear to effect the efficiency of the method. Only a small amount was available, so fibers were used thereafter in making the films.
Samples of some of the films pulled (all from one percent solutions) and a fiber sample were sent to Galbraith Laboratories for elemental analysis to determine the percentage of potassium, chlorine, and sulfur in each. The results are found in Table V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Potassium</th>
<th>% Sulfur</th>
<th>%Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp Film</td>
<td>0.32</td>
<td>0.067</td>
<td>5.05</td>
</tr>
<tr>
<td>Fiber</td>
<td>0.61</td>
<td>0.021</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Fiber Film</td>
<td>0.49</td>
<td>0.13</td>
<td>0.082</td>
</tr>
<tr>
<td>Fiber Film</td>
<td>0.80</td>
<td>0.41</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table V shows a small increase in the amount of potassium and sulfur indicating that the films were possibly not soaking long enough in the methylene chloride to drive off all of the solvents. The increase in chlorine could show that the films were not soaking long enough in the water bath to ensure complete removal of the methylene chloride. Corrections in procedure were made in response to these results. A second set of samples containing films pulled from one and five percent solutions, of varying thicknesses, and with various soak times in methylene chloride, were submitted. Results are still awaited at this time.

The thickness of films produced ranged from .1 mil to 2.0 mil. Five percent solutions were used for the fabrication of the thicker films. It was noticed that the thicker films "ran" when placed in the methylene chloride and therefore after drying they would have ridges along the surface. Mr. Sweeney was contacted about this problem and suggested drying the films in an oven under nitrogen at 50°C before quenching in methylene chloride. This was tried but the solution would run off of the plate making a mess in the oven and causing inconsistencies in the
thicknesses of the films. In order to rectify the problem greater care was taken in transferring the film to methylene chloride and longer soaking times in methylene chloride were employed.

The color of the film seems to depend only on its thickness. The thinner films are colorless and almost translucent and as the thickness increases the films become more yellow and opaque.

6.2 FIBER SIZING

Nomex fibers were found by Steven C. Powell to have a sizing or coating on them which DuPont said could be removed with soap and water. It was also believed, that a sizing was present on this fiber due to the smooth finish (much like that of Nomex) of the commercial Kevlar received. DuPont confirmed this and although they would not disclose the content of the coating, said that it could be removed in the same manner. They also indicated that Kevlar could be obtained without a sizing or could be coated with anything that the customer wanted.

The first attempt to remove the sizing from the fibers involved three samples. The samples were weighed, washed in soap and water, rinsed in ethanol (to ensure complete removal of the sizing), dried in an oven, and then reweighed. The results are found in Table VI.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Weight Before (g)</th>
<th>Weight After (g)</th>
<th>Difference (g)</th>
<th>Percentage of Original Lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nomex 1</td>
<td>.0619</td>
<td>.0621</td>
<td>-.0002</td>
<td>2.35%</td>
</tr>
<tr>
<td>Nomex 2</td>
<td>.1446</td>
<td>.1412</td>
<td>.0034</td>
<td>2.35%</td>
</tr>
<tr>
<td>Kevlar</td>
<td>.0779</td>
<td>.0772</td>
<td>.0007</td>
<td>0.89%</td>
</tr>
</tbody>
</table>
The weight gain observed for Nomex 1 could be due to an accidental exposure to air at some point during the experimental process.

Several strands were then cut, measured for length, weighed, and then dried in order to determine the water content of the fibers. The data collected are found in Table VII.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Length</th>
<th>Weight Before (g)</th>
<th>Weight After (g)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 1</td>
<td>30.5 cm</td>
<td>.0357</td>
<td>.0339</td>
<td>5.04</td>
</tr>
<tr>
<td>Nomex 1</td>
<td>30.5 cm</td>
<td>.4032</td>
<td>.0423</td>
<td>2.08</td>
</tr>
<tr>
<td>Kevlar 2</td>
<td>45.5 cm</td>
<td>.0538</td>
<td>.0507</td>
<td>5.76</td>
</tr>
<tr>
<td>Nomex 2</td>
<td>45.5 cm</td>
<td>.0621</td>
<td>.0619</td>
<td>.32</td>
</tr>
<tr>
<td>Kevlar 3</td>
<td>61 cm</td>
<td>.0711</td>
<td>.0671</td>
<td>5.63</td>
</tr>
<tr>
<td>Nomex 3</td>
<td>61 cm</td>
<td>.0833</td>
<td>.0816</td>
<td>2.04</td>
</tr>
</tbody>
</table>

The difference in pre-drying weights could be attributed to either extra water retention capability for Kevlar fibers, a heavier or a larger amount of sizing on the Nomex, or just a result of the difference in tows of the two fibers. After dropping the value obtained for the 45.5 cm Nomex since it is inconsistent with the rest of the data, the calculated average percent water loss is 5.48% and 2.06% for Kevlar and Nomex respectively.

These same fibers were then washed in ethanol and dried along with four more samples (samples 4 and 5) which were washed with soap and water and then dried. Results from the ethanol wash are found in Table VIII.
### TABLE VIII

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Weight Before (g)</th>
<th>Weight After (g)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 1</td>
<td>.0339</td>
<td>.0338</td>
<td>.29</td>
</tr>
<tr>
<td>Nomex 1</td>
<td>.0423</td>
<td>.0421</td>
<td>.47</td>
</tr>
<tr>
<td>Kevlar 2</td>
<td>.0507</td>
<td>.0500</td>
<td>1.38</td>
</tr>
<tr>
<td>Nomex 2</td>
<td>.0619</td>
<td>.0610</td>
<td>1.46</td>
</tr>
<tr>
<td>Kevlar 3</td>
<td>.0671</td>
<td>.0663</td>
<td>1.19</td>
</tr>
<tr>
<td>Nomex 3</td>
<td>.0816</td>
<td>.0815</td>
<td>.12</td>
</tr>
<tr>
<td>Kevlar 4</td>
<td>.0514</td>
<td>.0507</td>
<td>1.36</td>
</tr>
<tr>
<td>Nomex 4</td>
<td>.0643</td>
<td>.0632</td>
<td>1.71</td>
</tr>
<tr>
<td>Kevlar 5</td>
<td>.0624</td>
<td>.0632</td>
<td>.16</td>
</tr>
<tr>
<td>Nomex 5</td>
<td>.0737</td>
<td>.0719</td>
<td>2.44</td>
</tr>
</tbody>
</table>

The general trend appears to be a loss of a little over one percent of the original weight and no difference between those washed solely in ethanol and those washed both with soap and water and ethanol.

Those six strands (samples 1-3) which had only been washed in ethanol were next washed with soap and water and then dried. The data are found in Table IX.

### TABLE IX

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Weight Before (g)</th>
<th>Weight After (g)</th>
<th>% Difference</th>
<th>Total Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 1</td>
<td>.0338</td>
<td>.0332</td>
<td>1.479</td>
<td>1.779</td>
</tr>
<tr>
<td>Nomex 1</td>
<td>.0421</td>
<td>.0416</td>
<td>1.188</td>
<td>1.658</td>
</tr>
<tr>
<td>Kevlar 2</td>
<td>.0500</td>
<td>.0496</td>
<td>.8</td>
<td>2.18</td>
</tr>
<tr>
<td>Nomex 2</td>
<td>.610</td>
<td>.0609</td>
<td>.164</td>
<td>1.624</td>
</tr>
<tr>
<td>Kevlar 3</td>
<td>.0663</td>
<td>.0660</td>
<td>.452</td>
<td>1.164</td>
</tr>
<tr>
<td>Nomex 3</td>
<td>.0815</td>
<td>.0815</td>
<td>0</td>
<td>.12</td>
</tr>
</tbody>
</table>

This may indicate that either method of removal is usable and that the additional washings do not appear to add a significant amount to sizing removal.
6.3 EXPOSURE OF KEVLAR FIBERS TO ULTRAVIOLET RADIATION

The equipment employed to expose Kevlar films and fibers to ultraviolet radiation consists of a small vacuum chamber - 23 cm in diameter and 23 cm high, an Oriel model 6141 system, including a 1000 watt xenon-arc lamp as the source (equivalent to 1.5 suns), and a mass spectrometer to monitor the production of volatile products during irradiation.

The first exposures were carried out on Kevlar-29 fibers. Fibers were placed in the sample holder, measuring 2 x 2 inches, illustrated in figure 36.

Aluminum foil was placed between the Kevlar and the sample holder to ensure that it would remain in place. The fibers were exposed for four hours with a total of four mass spectrometer spectra taken (figs. 37-40).

Mass Spectrum of Kevlar Exposure
The last three spectra taken show an increase in size in those peaks occurring at 17, 18, 28, 29, 42, and 44. This may indicate that a period
of time is required before any products are seen. No physical changes in the fibers were noted.

Table X lists some possible combinations of the atoms present in Kevlar which correspond to peaks observed in the mass spectrometer spectra.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Mass</th>
<th>Mass</th>
<th>Atom</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>12</td>
<td>N</td>
<td>14</td>
<td>NCOH</td>
</tr>
<tr>
<td>O</td>
<td>16</td>
<td>NH</td>
<td>15</td>
<td>NC</td>
</tr>
<tr>
<td>N</td>
<td>14</td>
<td>O</td>
<td>16</td>
<td>COH</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>OH</td>
<td>17</td>
<td>NCO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO</td>
<td>30</td>
<td>NH</td>
</tr>
</tbody>
</table>

Fibers were exposed again using the same sample holder but without the aluminum foil. When the lamp was initially turned on the sample was rotated out of the light path and a spectrum taken of the background consisting of products from the sample holder itself (fig. 41). This background spectrum was stored in the instrument and subtracted from the spectra of actual fiber exposure showing an increase in peaks of mass 17 and 44 (figs. 42 - 43).

Background spectrum

(fig. 41)
The peak at mass 44 could be a result of the production of CO₂. Since however, there was no peak at 28 (CO) suggesting that this is false, the peak at 44 could be from the destruction of the phenyl-nitrogen and phenyl-carbon bonds resulting in NHCOH.

After initial exposure, when the sample was turned into the path of the lamp, an increase (4.6 x 10⁻⁷ to 5.0 x 10⁻⁷) in pressure was noted. This was believed to be caused by the production of volatile products from the sample.

The next exposure was carried out on fibers which had been dried in an oven. The temperature of the oven was set at 122°C and stayed
between 122 and 128°C. The weight after drying was .02576 g. This sample was placed on the sample holder shown in figure 44.

![Kevlar](fig.44)

The Kevlar was wrapped around the screws and positioned so that the cleanest background possible could be obtained (e.g., no ends sticking out). Water vapor was probably reabsorbed into the sample because it took sometime to secure the fiber properly in the sample holder.

After taking a background spectrum and storing it, the sample was placed in the lamp path and a spectrum taken (fig. 45).

![Mass Spectrum of Kevlar Exposure](fig.45)

The absence of peaks at mass 17 and 18 may indicate that water present in the Kevlar sample was driven off by drying. There was also no peak observed at 44. After an additional hour and twenty minutes of exposure, another spectrum was taken (fig. 46). The large peak at mass 44 leads to the conclusion that sufficient exposure to heat and UV radiation is required before reaction is initiated.
The delay in the appearance of the mass 44 peak could also be attributed to the lack of water present, indicating catalyzation of the reaction by water. The sample was then turned out of the lamp path again severely reducing the peak at 44 (fig. 47).

After allowing the background to stabilize, the sample was again placed in the light path and another spectrum obtained (fig. 48). The peak at mass 44 did not significantly increase which may indicate the production of ultraviolet absorbers (aminobenzophenones) on the surface of the fiber.
Another sample of Kevlar fibers was placed on the larger sample holder and both were placed in a vacuum oven to dry at 127°C for approximately twenty-four hours. The holder was placed in the vacuum chamber and the system evacuated. A background was taken after the UV lamp had been on for fifteen minutes and the output appeared stable (fig. 49) and then the sample was turned into the light path.

The sample was exposed for fifteen minutes and the output recorded as figure 50.
In this case the peak at mass 17 was much higher than that at 18 which was not expected. Also a peak at mass 28 was observed while the one at mass 44 was not present. Thirty minutes later another spectrum was taken (fig. 51). A significant decrease in the peak at mass 17 appears suggesting that OH groups may initially be emitted by the fiber.

A new sample holder with no backing was constructed so that the radiation could pass through the sample to test if the products observed are really coming from the Kevlar or from the sample holder. The new holder shown below as figure 52 is a hollow aluminum frame.
with two wire "bars" mounted near the top and bottom.

The Kevlar is laced around the bars making sure that none of the strands are blocked.

A sample which had been washed and dried was placed on this holder and pumped down in the vacuum chamber. A background spectrum was taken and stored and then the sample was rotated into the light path. Immediately, peaks at mass 44, 29, and 17 appeared (fig. 53) but after three minutes these peaks had almost completely disappeared (fig. 54).

Mass Spectrum of Kevlar Exposure

(fig. 53)
To verify these results, the sample was turned exposing the side which had previously not been exposed. The output showed a small peak at mass 44 and no peak at either mass 29 or 17. It was believed that this was caused by blockage of the sample from the radiation by the background shield when the sample was rotated.

Repetition of the experiment produced the same basic trend - initial peaks at mass 44, 29, 17 and an increase in pressure, decrease in the peaks accompanied by a decrease in pressure, and finally, almost complete disappearance of the peaks and a significant drop in the pressure. One thought about the appearance and quick disappearance of the peak at mass 44 is that it could be the result to a self-quenching free radical reaction.

The next fiber sample used was dried in an oven prior to exposure and the scale on the mass spectrometer was changed to scan between masses 100 and 150. This would be the area in which the peaks corresponding to the following free radicals would appear (figs. 55-56).
These would occur from cleavage of the amide bonds in Kevlar. The mass spectrum shown in figure 57 is characteristic of pump oil only, thus refuting the production of these radicals.

An identical exposure was performed on a fiber which had been dried but not washed. The same trend previously seen (peaks at masses 44, 29, 17) was observed with a weaker signal. This difference may be attributed to the possibility of the sizing interfering with the production of volatile products.

In another experiment, both sample and holder were dried prior to exposure. A spectrum was taken immediately following rotation of the sample into the light path and then one each minute for a total of ten minutes. As soon as the sample was exposed the expected peaks at masses 44, 29, and 17 were observed as shown in figure 58.
After two minutes, the peak at mass 17 disappeared, however the pressure inside the chamber appeared to remain constant. No change was observed until four minutes of exposure when the pressure dropped from $5.2 \times 10^{-7}$ to $5.1 \times 10^{-7}$ Torr. Seven minutes of exposure resulted in a decrease in peaks of masses 44 and 29 (fig. 59) and the final change monitored was a drop in pressure to $5.0 \times 10^{-7}$ after nine minutes of exposure.

All of these reports were obtained on an extremely sensitive scale which seems to indicate that there are few volatile products coming from Kevlar when it is exposed to ultraviolet radiation. Infrared
spectra were taken of the front (exposed side) and back (unexposed size) of this sample. No differences were noted.

Another sample was washed and dried then exposed for 32 hours. Figure 60 is a mass spectrum which shows the result of this exposure. No noticeable physical changes were observed.

6.4 EXPOSURE OF KEVLAR FILMS TO ULTRAVIOLET RADIATION

A .1 mil film of Kevlar, fabricated in the manner discussed previously, was prepared for exposure by placing it in the 2 x 2 inch sample holder and trimming the edges with a razor blade. The lamp was turned on, a fairly clean background obtained, and the sample turned into the light path. After five minutes, no volatile products were observed (fig. 61).
The pressure as well as the peaks at 17 and 18 slowly began increasing after a total of fifteen minutes and stabilized after three additional minutes (fig. 62).

Approximately twenty minutes later, both the pressure and the intensity of the peaks began decreasing. The behavior observed was characteristic of water being driven out of the sample and was expected due to the method used to prepare the films. Total exposure time for the film was twenty-four hours. This exposure was repeated and the same results obtained.

A new sample, approximately .3 mil, was dried in an oven for two
hours and then exposed for 79 hours. No volatile products were observed. The only physical change was a slight discoloration in the film.

Tables XI and XII contain the area of the peaks from two different samples corresponding to the IR spectra KEVB2.989 (background -1), KEVUV2.271 (front-1), KEVB4.271 (background-2), and KEVUV4.276 (front-2) respectively (figs. 63-66).

**TABLE XI**

<table>
<thead>
<tr>
<th>Wavelength (cm⁻¹)</th>
<th>Group</th>
<th>Sum Integral Back</th>
<th>Sum Integral Front</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1240</td>
<td>N-CO</td>
<td>8.668</td>
<td>8.297</td>
<td>.371</td>
</tr>
<tr>
<td>1319</td>
<td>N=N</td>
<td>14.42</td>
<td>14.00</td>
<td>.42</td>
</tr>
<tr>
<td>1408</td>
<td>C=C (ring)</td>
<td>8.533</td>
<td>8.514</td>
<td>.019</td>
</tr>
<tr>
<td>1528</td>
<td>C=C (ring)</td>
<td>53.77</td>
<td>53.03</td>
<td>.74</td>
</tr>
<tr>
<td>1649</td>
<td>C=O</td>
<td>17.56</td>
<td>17.98</td>
<td>+.42</td>
</tr>
<tr>
<td>3326</td>
<td>N-H</td>
<td>10.92</td>
<td>11.66</td>
<td>+.74</td>
</tr>
</tbody>
</table>

**TABLE XII**

<table>
<thead>
<tr>
<th>Wavelength (cm⁻¹)</th>
<th>Group</th>
<th>Sum Integral Back</th>
<th>Sum Integral Front</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1239</td>
<td>N-CO</td>
<td>10.62</td>
<td>10.35</td>
<td>.27</td>
</tr>
<tr>
<td>1321</td>
<td>N=N</td>
<td>16.46</td>
<td>16.35</td>
<td>.11</td>
</tr>
<tr>
<td>1407</td>
<td>C=C (ring)</td>
<td>9.807</td>
<td>10.02</td>
<td>.787</td>
</tr>
<tr>
<td>1527</td>
<td>C=C (ring)</td>
<td>63.01</td>
<td>63.42</td>
<td>.41</td>
</tr>
<tr>
<td>1652</td>
<td>C=O</td>
<td>18.70</td>
<td>20.49</td>
<td>+1.79</td>
</tr>
<tr>
<td>3326</td>
<td>N-H</td>
<td>9.143</td>
<td>10.67</td>
<td>+.1.527</td>
</tr>
</tbody>
</table>

The data show a slight increase in the peaks corresponding to the carbonyl stretch and the nitrogen-hydrogen stretch supporting the conclusions found in the literature¹¹ concerning the photo-Fries reaction and subsequent production of aminobenzophenones (UV absorbers). These experiments also show that there are no immediate
or long term volatile products from exposure of Kevlar to ultraviolet radiation.
6.5 EXPOSURE OF KEVLAR FILMS TO ATOMIC OXYGEN

The apparatus used for atomic oxygen exposure was a Plasma Prep II asher manufactured by Structural Probe, Inc. The samples were mounted on a glass stand (fig. 67) and placed in the vacuum chamber parallel to the oxygen flow. The conditions inside the chamber—pressure and oxygen flow rate—were kept constant throughout the study. Values for these conditions varied slightly, ranging from 200-260 milli Torr for pressure and 0.032-0.033 standard liters per minute (slpm) for the flow rate.

![Diagram of Kevlar and Ultem samples](fig. 67)

The films were cut into disks having a diameter of 7/8 inches or 2.2 centimeters giving an area of 3.88 square centimeters and arranged as shown above. For each run, one Kevlar disk and two commercial Ultem disks (used as a standard) were exposed. If there were any rips or jagged edges in the films, an increase in the erosion rate was noted due to increased surface area. Erosion rates were determined using the following formula:

\[
ER = \frac{\text{mass loss}}{\text{area} \times \text{time exposed}} = \frac{mg}{cm^2 \times min} \quad (\text{eq. 30})
\]
Numerous exposures were carried out for various lengths of time. The erosion rates obtained varied to such an extent that no determination of the exact erosion rate of Kevlar films was possible. The commercial Ultem did erode at a fairly constant rate, indicating that the plasma produced in the asher was constant.

It was noticed that the films produced from five percent solutions did not withstand atomic oxygen as well as those produced from one percent solutions. An average value for erosion rate for a five percent solution was \(0.082 \text{ mg/cm}^2 \times \text{min}\) while for a one percent solution this value was only \(0.014 \text{ mg/cm}^2 \times \text{min}\). The inconsistency in these values is thought to be related to the method of film production which may result in unevenness in the surface of the five percent films thus increasing the surface area and therefore the erosion rate.

Steven Powell performed the same type of experiment on both Nomex and Kevlar fibers. His results shown in Table XIII indicate a slightly higher erosion rate for Kevlar. These exposures were carried out at pressures between 410 and 450 milli Torr for Kevlar and 460 milli Torr for Nomex. \(m(t)\) is the mass of the fiber after time \(t\), \(m(0)\) is the initial mass, and \((m(t)/m(0))^{-5}\) is the value when plotted against time which gives a linear representation of the erosion rate assuming that the fiber is composed of very long cylinders. By extrapolating, the amount of time required for complete destruction of the fiber which turns out to be 91 minutes for Kevlar and 114 minutes for Nomex (fig. 68) may be determined. The difference between these values is rather large, however, after correcting for the difference in fiber thicknesses.
(eg. the diameter), comparative mass loss per unit area is observed.
These values are -4.7E-6 g/cm² min for Kevlar and -4.8E-6 g/cm² min for Nomex.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Init. Mass (g)</th>
<th>Final Mass (g)</th>
<th>Time (min)</th>
<th>(\frac{m(t)}{m(0)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 1</td>
<td>.0348</td>
<td>.0318</td>
<td>6</td>
<td>.956</td>
</tr>
<tr>
<td>Kevlar 2</td>
<td>.0352</td>
<td>.269</td>
<td>15</td>
<td>.874</td>
</tr>
<tr>
<td>Kevlar 3</td>
<td>.0328</td>
<td>.0167</td>
<td>25</td>
<td>.714</td>
</tr>
<tr>
<td>Kevlar 4</td>
<td>.0358</td>
<td>.0185</td>
<td>35</td>
<td>.719</td>
</tr>
<tr>
<td>Kevlar 5</td>
<td>.0359</td>
<td>.0032</td>
<td>62</td>
<td>.299</td>
</tr>
<tr>
<td>Nomex 1</td>
<td>.0410</td>
<td>.0378</td>
<td>7.5</td>
<td>.960</td>
</tr>
<tr>
<td>Nomex 2</td>
<td>.0411</td>
<td>.0310</td>
<td>15</td>
<td>.868</td>
</tr>
<tr>
<td>Nomex 3</td>
<td>.0409</td>
<td>.0227</td>
<td>30</td>
<td>.745</td>
</tr>
<tr>
<td>Nomex 4</td>
<td>.0399</td>
<td>.0147</td>
<td>45</td>
<td>.607</td>
</tr>
<tr>
<td>Nomex 5</td>
<td>.407</td>
<td>.0096</td>
<td>60</td>
<td>.486</td>
</tr>
</tbody>
</table>

MASS LOSS FROM FIBERS IN THE ASHER
6.6 CONCLUSIONS

Perhaps the most important result obtained from the study was the discovery that Kevlar could easily be dissolved and good films consistently produced from the solution in various thicknesses. The data obtained from the exposure of Kevlar to ultraviolet radiation indicates little, if any, reaction due to the exposure. This belief is supported by the lack of volatile products produced during exposure and the slight increases in the CO and NH peaks in the IR spectra. The increases observed could indicate the production of UV absorbers which would then protect the material from further degradation. The atomic oxygen data is inconclusive, but there is evidence -mass loss and physical burning of the films- that the material does erode due to atomic oxygen.

The erosion caused by the atomic oxygen may impede the production of the UV absorbers thus increasing the rate of material degradation. Therefore further study on the combined affects of the two needs to be explored.
LITERATURE CITED


VITA

Patricia Lynne Pate