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Effects of Space Environment on Composites
An Analytical Study of Critical Experimental Parameters

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July 1, 1979

National Aeronautics and Space Administration
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California
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ABSTRACT

Uncertainty in the effect of space radiation on polymer matrix composites is a key obstacle to the cost-effective design and reliability of future large space vehicles. Development of fundamental understanding and experimental data necessary to overcome this obstacle will require a comprehensive experimental program and may require major expenditures for fabrication and/or modification of test facilities.

Laboratory duplication of the space environment within reasonable cost and time constraints is impractical. Hence, space simulation "compromises" must be made in developing test facilities and optimized test strategies. But the effect of the compromises must be accounted for in a quantifiable manner in order to achieve valid accelerations and/or extrapolations of laboratory data.

A generalized methodology, developed and currently in use at JPL, was used to develop an analytical model for effects of high-energy electrons as well as for interactions between electron and ultraviolet (UV) effects. Chemical kinetics concepts were applied in defining quantifiable parameters; the need for determining short-lived transient species and their concentration was demonstrated. Certain general conclusions regarding test facility requirements and testing strategy follow.

The results demonstrate a systematic and cost-effective means of addressing the issues and show qualitative, and in some cases, quantitative, applicable relationships between space radiation and simulation parameters. An equally important result is identification of critical initial experiments necessary to further clarify the relationships.
The issues addressed in this program and the findings are:

1) Facility and test design: Generation of the necessary information to design an effective, valid test facility is non-trivial but is a relatively small effort compared to the ultimate construction of a major new test facility.

2) Rastered vs. diffuse continuous e-beam: A rastered electron beam may be used, but: a) requires the capability to adjust raster scan rate; and b) may limit the capability for high "average" acceleration factors.

3) Valid acceleration level: The upper limit for accelerated e-beam testing of polyethylene has been calculated from available literature data. (For materials where required data are not available, they may be obtained from relatively simple experiments.)

4) Simultaneous vs. sequential exposure to different types of radiation: It is shown that, in accelerated testing involving multiple stresses, e.g., e-beam and UV radiation, synergistic effects dominate the overall degradation modes. Therefore, in order to obtain a given acceleration factor, each stress intensity has to be adjusted according to the analytical model. Equal acceleration of all stress levels does not necessarily lead to the same overall acceleration of degradation because of high synergistic effects and may in fact give rise to spurious degradation modes.

5) Interruption of test continuity: Test strategies involving interruption of radiation must consider relatively long times
(e.g., up to 100's of hours) to restore equilibrium populations of radiation-produced species.

These findings are obviously only partial answers to the issues addressed; additional experiments and analyses will be required. Several critical issues which will be addressed in subsequent reports include: 1) energy levels and spectrum of electrons; 2) other types of radiation (e.g., protons); 3) electrostatic charging effects; and 4) in-situ vs. ex-situ property measurements.
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1.0 INTRODUCTION

The operational availability of the Space Shuttle, beginning in the early 1980's, opens a whole new spectrum of opportunities for exploration and utilization of space and simultaneously raises some critical new technology issues which must be addressed in order to effectively utilize these new opportunities. One of these new issues is the determination of the effects of space radiation on the properties of polymer matrix for large, light-weight structures designed to operate for 10-30 years in the space environment. This report addresses several questions that must be answered in order to design and operate a facility to determine the long-term effects of space radiation.

Availability of the Space Shuttle makes it possible to deploy very large structures in space for purposes of communication, Earth measurement and monitoring, and measurement and monitoring of space phenomena. The structures can be implemented by deploying preassembled structures designed to be folded or otherwise compressed for launch, by assembling prefabricated structural elements in space or by fabricating structures in space from component materials.

Most spacecraft structures used to date (first 2½ decades of the space era) have been designed primarily to withstand launch loads. Such an approach has resulted in a very large (e.g., orders of magnitude) design margin for the much less severe loads encountered in space operation. Furthermore, most of these vehicles have been designed for relatively short lifetimes (e.g. < 5 years). To be technically or scientifically attractive, including practical consideration of cost-effectiveness, future large space structures must be designed for space-operational loads and designed to operate for long lifetimes (10-30 years).
One of the major uncertainties for such efficient and long-lifetime designs is the effect of space radiation on the mechanical and physical properties of polymer matrix composite materials. The body of currently available data on radiation effects is inadequate to reliably assess the effects of space radiation on these materials and thus to design structures whose function can tolerate the effects.

Generation of the data necessary for effective design will require extensive testing to determine the effects of radiation on the mechanical and physical properties of significance for engineering design. In order to develop reliable data in the time available and at reasonable cost, this engineering testing must be accompanied by and correlated with research efforts to understand both the nature and rates of the basic mechanisms which lead to the ultimate changes.

Major and costly new or modified test facilities may be required to carry out the necessary testing. The practicalities of facility construction, test execution and timely generation of data will require significant deviation from duplication of the actual space radiation environment for each expected mission orbit.

Facility design and test planning raise some critical questions related to the necessary simulation and the validity of resulting test data.

1) Rastered vs. diffuse beam. Flux uniformity over a large sample area can best be accomplished by means of a small collimated beam rastered electrically over the target plane. Such an approach produces a uniform dose over the sample area, but each area element sees a short pulse of very highly accelerated flux followed by a relatively long period of no flux. (This strategy involves both acceleration and test interruption as discussed below.)
2) Acceleration. Simulation of long-term effects of radiation on materials is frequently accomplished increasing the flux to accumulate the same amount of radiation in a shorter period of time. Such an approach is valid only if the mechanisms of degradation remain the same at the higher flux (or change only in a well characterized way so that results can be adjusted analytically). For 10-30 year mission simulation, valid acceleration of 10 X to $10^3$ X would be highly desirable. Combining this desired "average" acceleration with the inherent "instantaneous" acceleration of a rastered beam results in each area element seeing particle fluxes many (5-10) orders of magnitude higher than would be encountered in space.

3) Interruption. Practical test considerations make it desirable to be able to terminate and restart the irradiation without affecting the validity of the test results. There is an inherent short-term interruption in the use of a rastered beam, wherein each area element sees a short, high intensity pulse followed by a relatively long period of no irradiation. On a much longer time scale, it is desirable to determine rates of change as a function of radiation dose by stopping the irradiation at intervals throughout the test to measure properties. In addition, it is desirable that test validity be insensitive to unscheduled interruptions due to equipment malfunction. The reliability and redundancy necessary to assure uninterrupted operation for long times (e.g., 2 years to simulate 20 years at 10 X acceleration) would significantly increase the cost of a radiation test facility.
4) Simultaneous or sequential irradiation. A space vehicle is simultaneously irradiated by ultraviolet and higher energy electromagnetic radiation, electrons and protons. (For most missions involving large composite structures, ultraviolet and electrons are considered the major effects to be simulated.) The complexity and associated cost of radiation test facility construction and operation would be minimized if valid ultraviolet and electron irradiation could be done separately or sequentially rather than simultaneously. The interaction of the two types of radiation is further complicated in accelerated testing. For separate or sequential testing, the valid acceleration levels can be determined and used independently. If simultaneous irradiation is required, valid acceleration levels are interdependent and may not be the same for the two types of radiation.

5) Energy level. Laboratory simulation of the actual energy/flux distribution of electrons in space is impractical. The least complex and least costly facility and test program would be possible if valid results could be obtained by simulation with a single electron energy. It is likely that a number of discreet energy levels will be required; the number should be minimized to reduce testing costs.

6) In-situ vs. ex-situ measurements. The range of properties that can be made and the accuracy of such measurements will be maximized if samples can be removed from the test chamber for measurement (ex-situ) without affecting the validity of the results. If samples must be maintained under vacuum or under irradiation (see "interruption" above) for valid results, both test
facility and test plan will be more complex and costly. In-situ mechanical and physical tests are typically difficult to make. The practicality of designing and operating a facility with in-situ test capability generally results in serious limitations on both the types of measurements that can be made and in the accuracy of such measurements.

The first four of the above issues have been addressed using Performance Prediction Modeling (PPM). The results have indicated qualitative and, in some cases, quantitative applicable relationships between space radiation and simulation parameters. An equally important result is identification of critical initial experiments necessary to further clarify the relationships. Further clarification is essential before a valid test facility or test program can be designed.
2.0 APPROACH - PERFORMANCE PREDICTION MODELING

2.1 Concept

Performance Prediction Modeling (PPM), which has been defined by us and is being applied at JPL, is a systematic methodology for evaluating materials performance. In its simplest form, PPM can be used to verify the satisfactory performance of a particular material, used in a specific design and subject to a defined set of "stresses" (e.g., mechanical loads, temperature, radiation, time, atmosphere or vacuum, etc.). Conversely, it can be used to define limits of "stresses" for the materials in an available piece of hardware or design. In a more thorough form, PPM is expected to be useful (this has not been demonstrated yet) to develop the appropriate design equations for a material or class of materials exposed to a generic set of "stresses" (e.g., temperature, thermal cycling, mechanical loads and radiation in space).

In many cases, the methodology involves experimental investigations. Unlike conventional test programs, PPM leads to experiments with a clear identification of the "missing information," frequently with a quantitative definition of the accuracy to which data is needed. The tests therefore do not necessarily simulate the stress environment of concern or involve measurement of the critical engineering property.

2.2 Description

The approach to PPM for qualification of a material for a particular design and environment is illustrated in a simplified way in Fig. 1. System and component functional requirements, combined with the known properties of a material (or materials), lead to a component design. The requirements, properties and design then lead to material functional requirements (i.e., what the material must do or not do to assure satisfactory performance).
The properties and changes in properties which can affect each of the required functions are identified. The mechanisms and rates of degradation are identified for single stresses and their combinations and sequences expected in the use environment based on available data and theory. Each degradation mode is examined analytically and the resulting system performance prediction developed. This process includes, where possible, a definition of explicit reaction and rate equations with actual or estimated rate constants and, thus, prediction of performance, degradation or probability of failure. Obviously, many of the potential degradation modes can be shown, by a relatively cursory analysis, to be insignificant, allowing concentration on those which are more critical.

The predictions are then compared to the initially defined functional requirements. If predicted performance is inadequate to meet requirements, a "no" answer leads to component redesign, alternate material, constraints on the system or component function, constraints to the operating environment (including time), or relaxation of initial reliability criteria.

A "yes" answer means that the material in the design will perform satisfactorily in the specified environment. In some cases, it is possible to quantify the performance margin or probability of survival. It is important to note that, using PPM rigorously, qualification always results from comparison of a prediction to defined functional requirements, never from a "qualification test."

Frequently, as is the case for long-term space radiation effects on composites, there are significant uncertainties in the controlling mechanisms, alternate models, governing rate equations and/or rate constants. In these cases, satisfactory performance is uncertain without additional information and experiments are required. For conventional materials
Figure 1. Simplified schematic logic diagram for performance prediction modeling (PPM)
testing, all or part of the "stress" environment is typically simulated (and frequently accelerated) and changes in the applicable mechanical or physical properties are measured. In contrast, with PPM, tests are designed based on a clear definition of the "missing information" and may neither simulate the expected environment nor measure the engineering parameter of concern. Once experimentally determined, the missing information is used to make an improved prediction which is again compared. Multiple passes through the experiment loop of the diagram may be required to develop a prediction which yields a clear "yes" or "no" answer when compared. In fact, a series of cycles following a hierarchy of sequential tests rather than a single complex test is most often cost-effective and achieves the desired result in minimum time.

In the case where applicable mechanisms of change are uncertain or there are several potentially applicable mechanisms, initial tests are designed to verify or identify the applicable mechanism. In the case where mechanisms and rate equations are known, sensitivity analysis of rates based on available data and reasonable assumptions can be used to identify the dominant uncertain rate constants and to estimate the accuracy to which they must be experimentally determined. As a result, effective experiments can be designed and executed.

Rigorous application of PPM can often lead to relationships and new ways to address problems which are not obvious using conventional approaches. For example, the suggestion of different acceleration factors for simultaneous electron and ultraviolet radiation developed later in this report would not be obvious in conventional test design. An empirical test matrix to arrive at the relationship would be prohibitively long and expensive. In one case where PPM was applied to encapsulation of terrestrial
photovoltaics, photochemical changes were found to be responsible for delamination. It was possible to relate the photochemistry to surface energy and loss of adhesion. Prediction of delamination failure based on infrared transmission measurement of the changes in population of photo-produced species resulted in excellent correlation with subsequently observed failures in actual operation.

As a key tool in various phases of application of PPM, we have extended the concept of the Kelley-Williams matrix (Ref. 8). Two versions of this extension are illustrated in Figures 2 and 3. In both cases, engineering behavior, molecular properties and "stress" (in the general dictionary definition) define a 3-dimensional space of potential interactions or relationships.

The first version (Fig. 2) is most useful in identifying potential degradation and/or failure modes, in identifying potential interactions and in identifying experimental and analytical approaches to estimating and quantifying the key problem areas. In this version, one coordinate is a series of physical or mechanical properties. In some cases, it is useful to use "functional requirements" (e.g., protect, adhere, transmit) on this coordinate or to relate these requirements to specific properties. The second coordinate is a series of molecular parameters (e.g., polymer backbone structure, molecular weight, cross-link density, etc.). The third coordinate is a series of individual stresses (mechanical, thermal, radiation, time, etc.) and simultaneous and sequential combinations of stresses. When identifying potential degradation modes initially (or subsequently as the modeling process proceeds), known modes can be traced to other potential modes that should be examined. For an obvious example, if radiation is known to affect cross-link density, then modulus is changed.
Figure 2. Interaction matrix-multiple parameter
and response to thermal cycling and shock (stresses) should be examined. Similarly, crosslink density affects coefficient of thermal expansion and stability of dimensional tolerances might be affected. In a less obvious case, an adhesive failure, caused directly by thermal cycling mechanical stress, was traced to (ultraviolet) photo-produced changes in the polymer chemistry which changed surface energy states at the material interface. Further examination showed that the photoreactions also caused a change in water mobility in the film which might allow increased rate of corrosion of the substrate. In fact, in the extreme, the photo-produced species may themselves contribute to corrosion. In the same case, evaluation of the corrosion problem led to identification of an additional "stress," in this case, a sequence. The corrosion product ions can diffuse into the polymer, absorb incident ultraviolet photons, transfer the energy to the polymer structure, and thus radically modify the basic polymer response to ultraviolet "stress." These potential modes are currently being "modeled" to determine their probability and possible magnitude and to define the critical initial experiments if tests are required.

In the second version of the matrix (Fig. 3), the coordinates are quantitative representations of single engineering, molecular and stress parameters. This form is most useful to identify effective or optimum experimental or analytical approaches and to ultimately determine the quantitative relationships between stress and engineering performance. In the case of the delamination described above, it was possible to quantitatively relate the delamination to surface energy and, via surface energy, to chemistry. As a result, it was possible to measure photochemical reaction rates (accurately and simply) by infrared transmission and accurately predict thermal stress-induced delamination without thermal cycling or peel
Figure 3. Interaction matrix-scalar parameter
tests. (The same understanding and experimental approach led to the recommendation, verification and subsequent implementation of an approach to eliminate the problem.)

Alternate versions are useful in developing prediction models and in planning test program strategies. One can examine the molecular and/or engineering response to a group of related stresses or a group of responses to a single stress. To the degree that validity can be verified, available data based on alternate radiation types can be used to estimate effects (e.g., gamma data for electron or ultraviolet effects), and readily available and/or easily controllable sources can be used for experiments.

As illustrated later in this report, electron radiation produces both discoloration and hydrogen generation in polyethylene, but from different molecular processes. It is possible to develop theoretical and/or experimental relationships between these and to determine the rates of each from the determination of only one. Thus, an optimum experiment could be designed, based on comparison of the ease and accuracy measuring these two.

During a recent study of an advanced space system, there was serious concern for the long-term (~5 years) durability of an adhesively-bonded lap joint at moderate stress and high temperature. No applicable data was available and experimental verification of durability would have been time consuming and costly. A relationship had been developed and verified which related the time to failure of such a joint to the short-term lap shear strength and the time-dependent endurance limit of the adhesives. Since conservative estimates of both of these parameters could be made from existing data, a large positive performance margin could be demonstrated without any testing.
2.3 Application to Space Radiation Effects

The PPM methodology was used to evaluate several critical issues related to space radiation effects testing. The approach, illustrated schematically in Fig. 4, was to develop predictive models of expected mechanisms and rates for response to the space radiation environment and for response to various laboratory simulation environments. Comparison of these predictions then provides useful constraints and guidelines relevant to the test facility design and testing strategy. The most important initial result is identification of uncertainties ("missing information") which are critical to the design of an effective radiation test facility.

One of the crucial issues this methodology successfully addresses is the delineation of material-specific properties and results from those which are generic to all materials exposed to space radiation. Material-specific concerns enter into the design of an engineering test facility; thus, limiting acceleration factors and scan rates of rastered beam are different for each material. On the other hand, it would be desirable to be able to determine the range of these variables for all likely candidates for testing, so that design and construction of a facility can begin without delay. To this end, we have identified two molecular parameters which are linked to rates of radiation damage and also rates of failure, given a performance specification. These molecular parameters are generic and it can be analytically demonstrated that these parameters determine several (if not all) material-specific property degradation rates. These are: 1) lifetime of the chain radical (or radicals) generated by e-beam excitation and subsequent bond rupture; and 2) steady state concentration of these radicals. These quantities are most easily measured by transient (pulsed) excitation techniques, now being set up at JPL. In the next section, it will be
Figure 4. Simplified logic diagram — application of PPM to radiation effects testing
demonstrated how all types of degradation rates observed in a given material can be linked to these two parameters for that material. At the same time, maximum valid acceleration factors and scan rates of rastered beam are also determined by these parameters. Hence, while it will be necessary to monitor specific molecular properties for given material (surface energy, H$_2$ evolution, absorbance, carboxyl index, etc.) the transient submolecular properties mentioned above form a subset of the group of molecular parameters which is generic to all materials, the only unknowns being the identity of the chain radical(s) and their rates of formation and decay. It can also be shown that for a realistic candidate material of complex composition, the number of different types of radicals causing multistep degradation is few; hence, they can be characterized and studied specifically.

For this initial modeling effort, it was decided to use polyethylene, rather than epoxy or polyimide, since there is a substantial body of radiation effects data in the literature. Although many radiation effects are material specific, the polyethylene models demonstrate that there is an effective practical approach to understanding the key parameters relative to design and operation of a practical radiation test facility. The models further indicate the form some of these parameters will take, identify the types of additional information needed to make critical decisions, and indicate experimental approaches to obtain the information.

The approach used here examines only mechanisms and rates of the primary and secondary radiation-produced reactions. Such a simplification is valid as an initial assessment of radiation test parameters. It is theoretically possible to pursue this approach (analytically and experimentally) exclusively to determine overall chemical and physical changes and ulti-
mately to determine expected changes in engineering properties. Such an approach is not considered practical, nor is a purely simulative engineering test program. A dual-path interactive program involving basic analytical and experimental studies and concurrent engineering testing, as illustrated in Fig. 5, will be more effective.
Figure 5. Dual path to reliability prediction
3.0 AN ANALYTICAL MODEL

3.1 Introduction

Mechanistic data on polyethylene degradation have been obtained from original sources and reviews. This work consists of studies of effects of electron bombardment and γ irradiation on polyethylene at 77 K and at room temperature. Characterization of free radicals and measurement of their decay rates have been principally investigated by electron spin resonance (ESR) spectroscopy. Transient ESR and optical absorbance measurements are lacking and hence rate measurements are indirect and often imprecise. The primary degradation product is the alkyl radical (R') which is characterized by a six-line ESR spectrum. The alkyl radical is usually formed in spurs or regions of high concentration and may undergo primary recombination or may migrate along the chain or across chains through a hydrogen jump mechanism until it comes across a double bond where it forms an allyl radical (R_1').

\[
\begin{align*}
\text{CH}_2\text{CH}-\text{CH}_2 - & \rightarrow \text{CH} = \text{CH}-\text{CH}_2 - \\
R' & \rightarrow R_1'
\end{align*}
\]

3.2 Mechanism of Degradation of Polyethylene

Concordant with allyl radical formation, hydrogen radicals are also formed which either recombine with another hydrogen radical to form H_2 or abstract a hydrogen atom from the polymer backbone again forming H_2', and generating another alkyl radical (eq. 3, Scheme 1). Thus we may have two different types of alkyl radicals in the system; caged primary alkyl radical pairs or a free alkyl radical. Hydrogen is thus a principal decay product.
\[-\text{CH}_2-\text{CH}_2-\text{CH}_2- \rightarrow [-\text{CH}_2-\text{CH}_2- + '\text{CH}_2-] \quad (1)\]
\[-\text{CH}_2-\text{CH}_2-\text{CH}_2- \rightarrow [-\text{CH}_2-\text{CH}_2- + '\text{CH}_2-] \quad (2)\]
\[-\text{CH}_2-\text{CH}_2-\text{CH}_2- + \text{H}^- \rightarrow -\text{CH}_2-\text{CH}_2- + \text{H}_2 \quad (3)\]
\[-\text{CH}_2^- + '\text{CH}_2^- \rightarrow -\text{CH}_2^-\text{CH}_2^- \quad (4)\]
\[-\text{CH}_2^- + '\text{CH}_2^- \rightarrow -\text{CH}_2^- + '\text{CH}_2^- \quad (5)\]
\[-\text{CH}_2^+ - '\text{CH}_2^- \rightarrow -\text{CH}_2^-\text{CH}_2^- \quad (6)\]
\[-\text{CH}_2^-\text{CH}_2^- \rightarrow -\text{CH}_2^-\text{CH}_2^- \rightarrow -\text{CH}_2^-\text{CH}_2^- \rightarrow -\text{CH}_2^-\text{CH}_2^- \rightarrow -\text{CH}_2^-\text{CH}_2^- \rightarrow \text{etc.} \quad (7)\]
\[-\text{CH}_2^-\text{CH}_2^- + -\text{CH}=\text{CH}-\text{CH}_2^- \rightarrow -\text{CH}=\text{CH}-\text{CH}_2^- \quad (8)\]
\[-\text{CH}_2^-\text{CH}_2^- + -\text{CH}=\text{CH}-\text{CH}_2^- \rightarrow -\text{CH}_2^-\text{CH}_2^- \quad (9)\]
\[2-\text{CH}_2^-\text{CH}=\text{CH}^- \rightarrow -\text{CH}_2^-\text{CH}=\text{CH}^- \quad (10)\]
\[-\text{CH}_2^-\text{CH}=\text{CH}^- + -\text{CH}_2^-\text{CH}_2^- + -\text{CH}_2^-\text{CH}=\text{CH}^- \rightarrow \text{etc.} \quad (11)\]
\[-\text{CH}_2^-\text{CH}=\text{CH}^- + -\text{CH}_2^-\text{CH}_2^- + -\text{CH}_2^-\text{CH}=\text{CH}^- \rightarrow \text{etc.} \quad (12)\]

Scheme I.

In this scheme equations 1 and 2 represent formation of alkyl and hydrogen radicals via ion radical recombination or other primary excitation routes. There has been a proposal that allyl radicals may be directly generated from long lived ion radicals in polyethylene, but there is no experimental evidence to support this view. Crosslinking processes (eqs. 9, 10 and 12) are quite important and cause brittleness to develop in polyethylene or exposure to e-beam radiation.

Decay of free alkyl radicals, i.e., those which escape the primary cage, can take place by recombination but at realistic dose rates recombin-
ation is very inefficient. Similarly \( R_1^- \) does not efficiently combine with \( R^- \), since \([R^-]_{ss}\) the steady state concentration of \( R^- \), is expected to be small (eq. 11). Ultimately \( R^- \) starts interacting with conjugated double bonds which may be formed by recombination of \( R_1^- \) and form polyene radicals (eq. 12) which are strongly colored and diffuse very slowly, being essentially stable.

The observed failure modes of PE exposed to space radiation can be readily modeled in terms of Scheme I. Thus polyethylene becomes brittle, loses mass in the form of \( H_2 \) and becomes strongly colored. The brittleness is directly related to processes represented by eqs. 9, 10 and 11, mass loss to equations 3 and 4 and coloration by eq. 12. Hence, the rate of increase in crosslink density (related to an increase in brittleness), is proportional to the square of the steady state allyl radical concentration. These relationships illustrate the use of cubes described in the previous section. Thus, by linking modulus with crosslink density one can plot the rate of change of modulus since change in crosslink density is proportional to \( k_{10}[R_1^-]_{ss}^2 + k_{9}[V][R^-]_{ss} + k_{11}[R_1^-]_{ss}[R^+]_{ss} \), the last term being relatively unimportant. Further, we see a correlation between \( H_2 \) evolution yield and alkyl radical yield. Hence we can establish a correlation between two failure rates such as brittleness and coloration through mechanistic considerations which eliminate stress as a variable. This is of practical consideration, since it may be convenient to measure rate of coloration and predict the rate of brittleness from this analysis instead of relating these two failure modes individually to magnitude of stress. These relationships between two failure modes are expected to be independent of stress parameters up to the limit of valid acceleration. Hence this model provides us with a simple technique to measure acceleration factors, and to also
verify the model. Application of PPM thus leads to a test design in which one test would be to measure the ratio of rate of \( H_2 \) formation to that of coloration, a test which would be unlikely to be included in engineering test designs arrived at empirically.

3.3 Acceleration of e-Beam Excitation

The Literature shows that only about 3.6\% of the alkyl radicals become "force alkyl radicals" up to a dosage of 110 Mrads, which is approximately equivalent to 30 years or more exposure in an environment which deposits 6 \( \times \) 10\(^4\) MeV per second in the form of e-beam excitation.\(^2\)-\(^4\) However, the steady state concentration of allyl radicals (eq. 13) goes through a plateau at about 80 Mrad, since at these dosages\(^3\), eq. 11 becomes important.

\[
[R_1]_{ss} = \left[ \frac{k_8[V]}{k_{10}} \left( \frac{-k_8[V] + k_8^2 [V]^2 + 4k_{11} k_6 / (k_5 + k_6)}{2k_{11}} \right) \right]^{1/2} \tag{13}
\]

where \( k_6 / (k_5 + k_6) \) is approximately 0.036, \( I \) is the steady state rate of generation of alkyl radicals, equaling \( PG \times 10^4 \), when \( P \) is the incident energy of electron beam in MeV/sec. \( [V] \) is the end group (double bond) concentration, which is specific to the sample, and easily measured by infrared spectroscopy. All of this modeling is based on rates measured at 293 K. The activation energy of \( k_5 \) is about 72 \( \times \) 10\(^3\) J/mol and that of \( k_3 \) is about (64-72) \( \times \) 10\(^3\) J/mol\(^5\). These experiments were performed by exposing PE to a certain dosage at 77 K and then warming up the sample in order to make rate measurements. The assumptions are that 1) no primary radical pair survives warming up and 2) no migration from initially formed spurs occurs at 77 K. The second assumption in particular is suspect. At low doses, comparable to space radiation levels,
Putting $k_6/(k_5 + k_6) = 0.036$, $k_{10} \approx 10^{-22} \text{ cm}^3/\text{sec}^4$ or $6 \times 10^{-2} \text{ It mole}^{-1} \text{ sec}^{-1}$, corresponding to a diffusion rate of $\sim 10^{-15} \text{ cm}^2/\text{sec}$ and an activation radius of $10^{4.5}$ at $293 \text{ K}$, $P = 10^4 \text{ MeV/sec}$ and $G = 3.3.1$, \[ [R_1]_{ss} = \left[ \frac{1k_6/(k_5 + k_6)}{k_{10}} \right]^{1/2} \tag{14} \]

\[ [R']_{ss} = \frac{1k_6/(k_5 + k_6)}{k_8[V]} \tag{15} \]

or $5.8 \times 10^{-6}$ moles/It. In order to determine $R'$ we need to measure $k_8$, which is actually the rate of hydrogen jump, since the rate of migration of alkyl radicals is rate determining. $k_8$ is most conveniently measured by a transient or pulsed method. Literature estimates of $k_8$ are about $1 \times 10^{-3} \text{ sec}^{-1}$. $[R']_{ss}$ is also sample dependent. In these calculations we assume 1) $G$ is independent of energy, and 2) there is a monoenergetic electron beam which is completely absorbed in $1 \text{ cm}$ of sample in a uniform manner.

Figure 6 shows a plot of $[R_1']$ as a function of $I$. This plot indicates that at a dose rate of $50 \times 10^4 \text{ MeV/sec}$, accelerated exposure rates start deviating from low (and realistic) exposure rate effects. Higher accelerations could be used by constructing a more comprehensive model which would include second order (i.e., recombination) rates and their effect on degradation (e.g. chain scission, $H_2$ evolution, coloration etc.). It may also be possible to achieve acceleration in this range by changing the relative values of rate constants in scheme I and eq. 6. Thus if we
Figure 6. Deviation from predicted degradation rate as a function of acceleration factor in polyethylene.
can increase \( k_8 \) relative to \( k_{11} \) we can accelerate exposure to a higher value. This might be done by adjusting the temperature, since \( k_8 \) and \( k_{11} \) might have different activation energies. This may also be done by increasing \([V]\), i.e., degree of unsaturation in the sample. This unsaturation traps the radicals to form allyl radicals, and prevents alkyl recombination. As exposure proceeds allyl radical recombination generates conjugated double bonds in the system which act as alkyl radical traps to yield polyene radicals which are quite stable and which are colored. This result can be dealt with as shown above for allyl radicals.

3.4 Interaction Between e-Beam and Ultraviolet

We shall now calculate the ultraviolet absorbance of alkyl radicals in our hypothetical radiation environment (e-beam at the rate of \( 10^4 \) MeV/sec cm\(^3\) of absorbed energy). This calculation will indicate whether there is any need to carry out combined UV/e-beam testing for this material, or if sequential exposure is adequate. Sequential exposure is inadequate only if it can be demonstrated that the allyl radicals at steady state concentration themselves absorb ultraviolet, since if the effect of UV is solely on the products of e-beam irradiation or on the polymer itself independent of e-beam excitation, sequential exposure is equivalent to simultaneous exposure to UV and e-beam. It is known that allyl radicals absorb UV at 238 nm and at wavelengths greater than 390 nm. Although literature data\(^2,3\) are clearly insufficient, approximate extinction coefficient values of \( 10^4 \) and \( 10^3 \) may be assigned as an upper limit at these wavelengths. Since \([R_1^+]_{ss} = 5.8 \times 10^{-6} \) moles/lit at \( 10^4 \) MeV/sec of e-beam excitation, it follows that absorbance due to \( R_1^+ \) will not exceed .058 and .0058 at these two wavelengths. This means that approximately 14% of solar irradiance at 238 nm will be absorbed by allyl radicals and 0.6% of solar irradiance in
the range 390 - 500 nm will be absorbed. It is known that the long wavelength excitation converts the allyl radicals back to alkyl radicals of the same type.

\[ -\text{CH-CH}=\text{CH-CH}_2^- + -\text{CH-CH}_2^-\text{CH-CH-CH}_2^- \]  

(17)

Hence there is some measurable effect of UV on transients generated by e-beam excitation. This effect is much more pronounced in a combined accelerated exposure, which will therefore unduly emphasize this "cross term." Thus a 10x acceleration of e-beam intensity will produce a \([R_1^-]_{ss}\) of \(\sim 2 \times 10^{-5}\) moles/Lt which will have an absorbance of 0.2 at 238 nm resulting in 40% absorption at 238 nm. Simultaneous acceleration of e-beam and UV should thus be avoided, and if acceleration of e-beam excitation is desired, UV should be attenuated relative to real time values. These absorbance values are estimated here from literature data, and may be far from real values. Transient experiments can be of great assistance here.

Lastly we will calculate the time needed to reach steady state for real time and accelerated exposures. All of the above calculations assume that the test duration is long compared to this time period. This is done by integrating eq. 18.

\[
\frac{d[R^\cdot]}{dt} \approx k_8 [V][R^\cdot] - k_{11}[R^\cdot]^2 + k_5 / (k_5 + k_6)
\]  

(18)

This equation assumes that recombination within a spur (primary recombination) is extremely rapid relative to reactions of radicals outside the spur. This approximation breaks down on long exposures when concentration of traps increase to high values, or at high temperatures.
Figure 7. Energy spectrum at L = 3
Figure 8. Stopping power of polyethylene as a function of energy
\[ [R']_t \equiv [k_6^2 (V)^2 + 4k_{11} l k_6 /(k_5 + k_6)]^{-1} \log \left[ \frac{2l k_6/(k_5 + k_6)}{2l k_5/(k_5 + k_6)} \right]^{1/2} - k_{11} - \left\{ k_6^2 (V)^2 + 4k_{11} l k_6 /(k_5 + k_6) \right\}^{1/2} \]

This equation can be plotted to yield the time needed to reach stationary state equilibrium for alkyl radicals. To a first order it is apparent that this time is somewhat greater than \( 4 \times 10^{-6}/2 \times 10^{-12} \) seconds or \( 2 \times 10^6 \) seconds or 600 hours for a real time test. The time needed to reach this steady state steadily diminishes as the acceleration factor increases, i.e. for a 10x acceleration, the minimum time drops to roughly 200+ hours, and for a 100x acceleration it is 70+ hours. This time can also be shortened by raising the temperature of the sample.

3.5 Modeling of A Realistic e-Beam Spectrum

The above conclusions illustrate the application of performance prediction modeling methodology using an oversimplified model of radiation stress experienced by polyethylene. The model has been stated in the previous section in terms of two assumptions, viz; 1) radiation consists of a monoenergetic beam and 2) it is completely absorbed uniformly throughout the sample, 1 cm in thickness. We shall make the model more realistic by using a real electron energy distribution for a given orbit (\( L = 3, L \) being Earth radius) and experimental values of range of electrons in PE as a function of particle energy. Figure 7 shows the energy spectrum used in this calculation, and Figure 8 shows a plot of "stopping power" or \( \frac{dE}{dx} \) when \( E \) is energy and \( x \) is thickness of material penetrated as a function
Figure 9. Alkyl radical yield profile in polyethylene at \( L = 3 \) orbit.
Figure 10. \([R^1]_{ss}\) profile at \(L = 3\)
of energy. From this data we have calculated alkyl radical formation rate in polyethylene as function of depth of penetration. Assuming that G or the radical yield per 100 eV of radiation is independent of energy beyond 1 keV we can calculate radical yield profile in polyethylene, shown in Figure 9. These are the values of I(x) and should be used in calculation of \([R_1']\) and \([R']_{ss}\) in eqs. 14 and 15. Figure 10 is a plot of \([R_1']_{ss}\) or steady state concentration of allyl radical as a function of penetration depth in PE for a real electron energy distribution at \(L = 3\). The calculation of \(I(x)\) was carried out manually and hence is only approximate. However, it is straightforward to computerize this calculation for any orbit. This calculation will obviously be materials-specific and hence we propose to carry out a more precise calculation of \(I(x)\) for a serious candidate material for which we will also measure \(G(E)\) as a function of energy.

### 3.6 Role of Lifetime of Chain Radicals in Polyethylene

In this section analysis of data on polyethylene is summarized with emphasis on engineering test planning and construction of a test facility for this purpose. The analytical model clearly indicates that the choice of an accelerated test strategy is dependent on the material being tested and also on the failure mode being studied. The critical parameter is the lifetime of the transient radical which is uniquely determined by the material. It is the radical reactions which generate degradation products, while radical formation rate is proportional to the bond cleavage resulting from radiation damage. The rates of formation of degradation products are functions of stationary state concentration of the radical which is simply

\[
I(t,d)/\Sigma k_i \frac{[J]}{[R']} + k_m [R']^2
\]

when \(I(t,d)\) is the rate of formation of the radical \(R'\) as a function of time and thickness, \(k_i\) is the rate of rearrange-
ment, $k_j$ is the rate of reaction with impurities, end groups and other traps in the polymer and $k_m$ is the recombination rate. In particular if we have two major degradation processes as shown in Scheme II, we can write

$$P + e^- \rightarrow R_1^- + H^+ + e^-$$ \hspace{1cm} (20)

$$R_1^- + A + AR_1^-$$ \hspace{1cm} (21)

$$R_1^- + R_1^- \rightarrow R_1^- - R_1^-$$ \hspace{1cm} (22)

$$AR_1^- + AR_1^- \rightarrow AR_1^- - AR_1^-$$ \hspace{1cm} (23)

$$R_1^- + AR_1^- - AR_1^- - AR_1^-$$ \hspace{1cm} (24)

Scheme II

$$\frac{d[AR_1^-]}{dt} = k_1[R_1^-][A] - k_3[AR_1^-]^2 = 0$$ \hspace{1cm} (25)

and hence

$$\frac{d}{dt} [R_1^- - AR_1^- - AR_1^-] = k_4[R_1^-][AR_1^- - AR_1^-] \approx k_1[R_1^-][A]$$ \hspace{1cm} (26)

Here formation of $R_1^- - AR_1^- - AR_1^-$ represents coloration while formation of $R_1^- - R_1^-$ causes crosslinking in polyethylene, if $R_1^-$ is an alkyl radical, and $A$ is a vinylic end group, so that $AR_1^-$ is an allyl radical. This analysis shows that all degradation rates depend on lifetime and steady state concentration of radicals, these two quantities being inversely related to each other. If radical decay processes are slow, steady state concentration is high and time to reach steady state is long, which makes accelerated testing results deviate from real time test data at relatively low levels of acceleration. Simultaneously, multistress testing at accelerated stress levels causes undue emphasis to be placed on "cross terms," e.g. in com-
bined UV-e-beam testing the radicals absorb UV and undergo secondary reactions. In such a situation a high level of e-beam intensity may be used if the UV is attenuated by an amount calculated from transient radical lifetime and concentration measurements, or if the lifetime is reduced by operating the test at a high temperature. Thus in polyethylene it is possible to accelerate the e-beam excitation by 50 times only if the UV excitation is simultaneously attenuated by a factor of more than 7.3 from one sun (AM 0) level.

3.7 Use of Rastered Beam on Polyethylene

The two criteria which may be used to characterize the contribution of a radical in the decay scheme, lifetime and steady state concentration also determine if a diffused e-beam is needed for particle bombardment or if a rastered beam can be used. Figure 11 is a collection of schematic plots giving radical concentrations as a function of time for different radical decay rates, rates consisting of bimolecular and unimolecular components. It is clear that for slow decay rates (relation to repetition frequency of the e-beam) we have the situation shown in Figures 11g and h. For fast decay the system is as shown in Figures 11c and 11f. Intermediate cases are shown in Figures 11c and 11d and in Figure 11i. For slow decay and relatively low intensity raster beam, the test is approximately equivalent to real-time testing. In this case time to come to steady state equilibrium is large compared to raster frequency, and as long as the intensity (flux) of the raster beam is such that it does not exceed the limit of valid acceleration either under single stress or multistress test conditions, the test procedure is valid. Polyethylene falls in this category. At the other extreme, when the lifetime is short relative to the repeat period in the raster, the same constraints limit the validity of the
test; in other words the test is valid if the rastered beam flux does not exceed the range of valid accelerated levels of flux. However, in the intermediate cases, high radical concentration levels reached at certain times tend to favor formation of one degradation product to others and hence deviation will be observed between degradation rates measured with a diffuse beam and a rastered beam of equal time integrated fluxes, even when the intensity of the raster beam falls within the range of valid acceleration. A schematic plot of deviation vs. lifetime of a radical causing a particular type of degradation to occur is shown in Figure 12. This analysis has been carried out with one chain radical as the sole mediator in the degradation process. Its extension to more complicated systems is straightforward. It should also be noted that even in complex systems, the number of chain radicals of crucial importance to the degradation scheme is very few. Excited states may also play an important role in degradation in certain systems, and in these cases, lifetime and stationary state concentrations of excited states will have to be taken into account.
Figure 11. Schematic presentation of radical concentration obtained with a rastered beam
Figure 12. Schematic plot of deviation from real-time test data using a rastered beam.
4.0 CONCLUSIONS

In conclusion, we shall discuss issues raised in the introduction concerning facility design and test planning and demonstrate that the preliminary analytical model developed for polyethylene addresses several of these concerns and provides boundaries of design parameters which could not be otherwise obtained except by carrying out concurrent multi-year real-time and empirically designed accelerated tests.

Acceleration

On the basis of calculated steady state concentrations of alkyl and allyl radicals, it appears that the maximum permissible acceleration level is 50x or less in polyethylene at 293 K. Higher acceleration levels can be used at higher temperatures; however, more detailed testing and modeling is needed to understand the effect of raising temperature on the degradation rate.

Rastered vs. Diffused Beam

Based on the above analysis, the ratio of raster beam width to the time interval between adjacent excitation pulses (reciprocal of repetition rate) cannot be less than 5, if an acceleration of 10x is needed. Frequencies of less than 1 sec\(^{-1}\) are entirely acceptable if the temperature of the test is less than 373 K.

Energy Level

Since stopping power is a steep function of energy at low electron energies, very large concentrations of radicals are generated at the polymer surface if PE is exposed to a spectrum of electron energies corresponding to orbit \(L = 3\). This implies that the chemistry and degradation modes and rate are different at the surface from those in bulk. In practice, the surface will crosslink and become brittle much faster, causing cracking and crazing. This effect will also have a profound influence on
adhesion properties if the polymer is used as a matrix in a composite. This cannot be simulated by using a monoenergetic beam of electrons, and hence our conclusion is that we need electrons at two energy levels at least, with high energy electrons which reach into the bulk and a substantially higher dosage of low energy (0.05 - 0.2 MeV) electrons which cause surface degradation.

Simultaneous vs. Sequential Exposure

We find that in polyethylene it is probably safer to carry out sequential testing since the errors (which can be estimated from the model presented here), generated by sequential testing, are likely to be small relative to other errors in the test. If simultaneous exposure to UV and e-beam is desired, great care must be taken not to overemphasize the "cross-term." Indeed, if the e-beam is accelerated 50x, UV must be attenuated by a factor of 5.5 relative to real-time values in order to keep the UV intensity absorbed by radicals constant. If acceleration of UV is needed, e-beam intensity must be attenuated relative to real-time values.

Interrupted Testing

Calculation of the time needed to reach steady state concentration by alkyl radicals shows that 200+ hours are needed for a test at 10x acceleration level. This can be considered to be the minimum period of uninterrupted testing needed at this acceleration level. However, this period can be shortened by raising the temperature of the sample.

Other Issues

We have not addressed issues such as: 1) whether simulation of protons or other charged particles is necessary; 2) whether monitoring of degradation has to be carried out in-situ, or whether ex-situ measurements are sufficient. A more detailed mechanistic model, together with more experiments, are needed to answer these questions.
5.0 REFERENCES


