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The Effects of Electron Radiation on the Glass Transition Temperature of a Polyetherimide

Kristen Tulloch Kern
Old Dominion University

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THE EFFECTS OF ELECTRON RADIATION ON THE GLASS TRANSITION TEMPERATURE OF A POLYETHERIMIDE

by

Kristen Tulloch Kern
B.S. December 1986, Clarion University of Pennsylvania
M.S. May 1990, Old Dominion University

A Dissertation Submitted to the Faculty of Old Dominion University in Partial Fulfillment of the Requirement for the Degree of

DOCTOR OF PHILOSOPHY
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Approved by:

Wynford L. Harries (Director)
ABSTRACT
THE EFFECTS OF ELECTRON RADIATION ON THE GLASS TRANSITION TEMPERATURE OF A POLYETHERIMIDE

Kristen Tulloch Kern
Old Dominion University, 1993
Director: Dr. Wynford L. Harries

The effects of electron radiation on a polyetherimide (PEI), Ultem®, were investigated. In particular, the changes in the glass transition temperature \( T_g \) with absorbed radiation dose were studied. The polymer was exposed to mono-energetic beams of 100-keV electrons and 1.0-MeV electrons for doses up to 100 megagram (MGy). Dosimetry for the exposures was based on Monte-Carlo simulations of the transfer of energy from an energetic electron to the polymer and on comparison to Nylon standards. Dynamic mechanical analysis was used to determine the \( T_g \) for non-exposed PEI and the changes in \( T_g \) resulting from irradiation. The \( T_g \) did not change significantly for doses up to and including 75 MGy, while a significant increase in \( T_g \) occurred for a dose of 100 MGy. The cross-link and chain scission densities in the irradiated PEI were determined using infrared spectroscopy. The cross-link density increased with dose for all doses investigated. The chain scission density increased with dose for doses up to 75 MGy, but was lower for a dose of 100 MGy than for a dose of 75 MGy. Radical population kinetics, based in part on data from an electron paramagnetic resonance study, were correlated with the cross-link density and chain scission density to investigate the
mechanism for the observed density variations with dose. The radical population simulations suggest that chain scissioning occurs less readily when the average radical separation during the exposure is less than three molecular radii. Finally, a model for the combined effects of cross-linking and chain scissioning is proposed which combines a statistical-mechanical model for the change in $T_g$ with cross-link density and a free-volume model for the change in $T_g$ with chain scission density.
Dedication

This work is dedicated to my family for their encouragement and support. In particular, to Jane whose contributions to my success are too great to be expressed here.
Acknowledgements

I would like to express my appreciation to my advisor, Dr. Wynford L. Harries, for his guidance throughout this effort and to Dr. Edward R. Long, Jr. for his support during and after this research project. I would also like to acknowledge Dr. Sheila Ann Thibeault for her guidance in the early stages of my research and the staff of NASA Langley Research Center for their support.

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| $\alpha$ | Timoshenko's shear correction factor (Ch. 3)  
|        | Coefficient of thermal expansion (Ch. 6) |
| $\Delta \alpha$ | Difference in coefficient of thermal expansion for polymer above and below $T_g$ |
| $\beta$ | $\nu/c$ for electrons in coulomb collisions |
| $\gamma$ | Number of rotatable bonds per repeat unit |
| $\delta$ | Phase angle between stress and strain in a sample |
| $\Delta H$ | Activation energy for a reaction or transition |
| $\varepsilon$ | Sinusoidal strain in a sample during DMA |
| $\varepsilon_0$ | Amplitude of strain in a sample during DMA |
| $\varepsilon_1$ | Energy of chain segment in gauche conformation |
| $\varepsilon_2$ | Energy of chain segment in trans conformation |
| $\Delta \varepsilon$ | Difference in energy between trans and gauche conformations |
| $\varepsilon_n$ | Energy of interaction between adjacent chain segments |
| $\theta$ | Angle between two segments of a polymer chain (Ch. 1)  
|        | Angle of scattered electron (Ch. 5) |
| $\kappa$ | Radius of gyration of a beam |
| $\nu$ | Wavenumber of light in IR spectroscopy |
| $\rho$ | Density of a material |
| $\sigma$ | Sinusoidal stress in a sample during DMA (Section 3.2.1)  
|        | Poisson's Ratio (Section 3.2.2)  
|        | Cross section for a coulomb collision (Ch. 5) |
σ₀  Amplitude of stress in a sample during DMA
Φ  Angle of rotation between adjacent bonds in a polymer chain
ϕ  Arm deflection angle
ω  Frequency of a kinetic reaction (Section 3.1)
    Frequency of oscillation for DMA (Section 3.2.1)
A  Absorptivity of a chemical group absorbing IR light
a₀  Cross sectional area of Faraday cup used to monitor electron beam current
A  Atomic number of atoms exposed to a beam of electrons (Ch. 2)
    Cross sectional area of a bending beam (Ch. 3)
    Absorbance of a sample in IR spectroscopy (Ch. 4)
A(E)  Energy absorbed by a material per incident electron
b  Thickness of sample for IR spectroscopy (Ch. 4)
    Impact parameter for coulomb collision (Ch. 5)
B  Distance between DMA arms
c  Concentration of groups absorbing an IR beam (Ch. 4)
    Speed of light (Ch. 5)
C  Rate of radical formation
Cᵢ  Constant for Tₙ as a function of cross-link density
d  Damping coefficient for DMA
dᵢ  Contribution to damping coefficient of the DMA system from instrument
dₛ  Contribution to damping coefficient of the DMA system from sample
D  Dose absorbed by a sample (Ch. 2)
    Width of DMA arm (Ch. 3)
    Diffusion constant for hydrogen radicals in PEI (Ch. 5)
E  Energy of a free electron in a beam of electrons (Ch. 2)
    Tensile modulus (Ch. 3)
$E_1$ Component of tensile modulus in phase with the strain

$E_2$ Component of tensile modulus 90° out of phase with strain

$E_h$ Energy associated with a hole in a polymer

$\Delta E$ Energy transferred in a coulomb collision

$f$ Frequency of intensity variation for reference laser (Ch. 4)

Fraction of chain segments in upper energy state (Ch. 6)

$F$ Flux of electrons in an electron beam

$F(t)$ Time-depandant force applied to a beam

$G$ Shear modulus

$G(x)$ G-value for cross-linking, cross-links per gram per 100 eV of energy absorbed

$I$ Intensity of IR beam transmitted by a sample (Ch. 4)

Ionization potential for an element (Ch. 5)

$I_0$ Intensity of IR beam incident on a sample

$I_f$ Current measured by a Faraday cup

$J$ Moment of inertia of DMA arm

$k$ Stiffness of system in DMA (Ch. 3)

Coulomb force constant (Ch. 5)

Boltzmann constant (Ch. 6)

$k_1$ Rate constant for first-order radical decay

$k_2$ Rate constant for second-order radical decay

$k_i$ Contribution to stiffness of DMA system from instrument

$k_s$ Contribution to stiffness of DMA system from sample

$K$ Stiffness of beam in DMA (Ch. 3)

Constant for $T_g$ as a function of cross-link density (Ch. 6)

$K'$ Constant of proportionality for $T_g$ as a function of molecular weight

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\( l_j \) Length of the jth segment in a polymer chain

\( L \) Length of beam in DMA (Ch. 3)
Effective segment length (Ch. 6)

\( m_e \) Mass of electron

\( M \) Effective mass of DMA sample (Ch. 3)
Molecular weight of a repeat unit (Ch. 6)

\( M_0 \) Molecular weight before chain scissioning

\( M(t) \) Torque applied to DMA arm

\( n \) Number of repeat units in a polymer

\( n_0 \) Number of vacancies in a lattice

\( N \) Number of electrons incident on a material per unit surface area (Ch. 2)
Number density of elements (Section 5.2)
Number density of radicals (Section 5.3)

\( N_a \) Avagadro’s number

\( N_0 \) Initial number density of radicals

\( N_x \) Number of polymer chains in a system that are made up of \( x \) segments

\( Q \) Partition function for ensemble of polymer chains

\( r \) End to end distance for a polymer chain

\( r_j \) Position vector for end of the jth segment of a polymer chain

\( R \) Range of an electron passing through matter (Ch. 2)
Universal gas constant (Ch 3)

\( s \) Fraction of lattice sites that are not occupied

\( S \) Stopping power for electron passing through PEI (Ch. 5)
Number of chain scissions per original molecule (Ch. 6)

\( S_0 \) Configurational entropy for a polymer chain
$S_c$  Configurational entropy for a polymer chain with cross-links

$\Delta S$  Change in configurational entropy resulting from the formation of cross-links

$t$  Duration of exposure (Ch. 2)
Time for hydrogen radicals to travel through PEI (Ch. 5)

$t_0$  Global relaxation time

$T$  Thickness of a sample (Ch. 2)
Temperature (Ch. 3, 6)
Transmittance of sample in IR spectroscopy (Ch. 4)

$T(x)$  $T_g$ for polymer as a function of cross-link density $x$

$T_g$  Glass transition temperature of a polymer

$T_n$  Melting temperature of a thermosetting polymer

$\Delta T_g$  Change in $T_g$

$v$  Velocity of electron (Ch. 5)
Free volume associated with a chain end (Section 6.2)

$V$  Velocity of moving arm in IR spectrometer

$V_e$  Total free volume associated with chain ends

$W$  Work done in a cycle of sample deformation (Section 3.2.1)
Width of DMA sample (Section 3.2.2)

$W(f,n_o)$  Number of ways to arrange $N_s$ chains on a lattice

$x$  Number of segments in a polymer chain (Ch. 1)
Deflection of elastic beam (Ch. 3)

$x_f$  Flexural deformation of a beam

$X$  Distance travelled by Hydrogen radical (Ch. 5)
Number of moles of chains per mole of cross-links (Ch. 6)

$z$  Valence of main-chain atoms

$Z$  Atomic weight of atoms exposed to a beam of electrons

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CHAPTER 1
INTRODUCTION

The properties of polymers\(^1\) differ greatly from the properties of low molecular weight substances and from the properties of crystalline materials. Polymers are materials which consist of molecules with very high molecular weight and generally form amorphous structures rather than crystalline structures. As a result, the properties of polymers vary widely with molecular features. The thermal behavior of polymers is among the least understood of these properties. In particular, the thermal properties of polymers include a transition, called the glass transition, which is particularly sensitive to molecular structure. Studies in which changes in the transition are related to structural features created by chemical modification of the polymer are common. However, separation of the effects of the structural changes and the effects of the chemical additives is not always possible. Ionizing radiation is also known to cause structural changes to polymers. These changes occur without the addition of chemical agents, and thus can be used to investigate the effects of the structural changes. The purpose of this study is to identify the physical processes which occur at the glass transition of a polymer and to develop a quantitative model for the effects of electron radiation on the glass transition.

\(^1\) For the benefit of the reader, a glossary of specialized terms is included as Appendix A.
As the glass transition is often used to characterize the effects of radiation on polymers, the results of this study are critical to the understanding of the glass transition for the study of polymeric materials for applications in which they may be exposed to radiation. It is useful to review the properties of polymers and the theories that are used to model them as an introduction to the current study.

1.1 DESCRIPTION OF POLYMERS

The physical structure of polymer molecules, or macromolecules, may be described under three headings: the structure, or configuration of the atoms in the chain, the shape, or conformation of each single chain without consideration for its neighbors, and finally the arrangement of the molecules with respect to one another. These topics will be discussed in turn.

1.1.1 STRUCTURE OF POLYMERS

A macromolecule may be viewed as consisting of many components, referred to as repeat units, all of which are chemically identical, with the exception of the ends of the molecule, or end caps. A molecule may consist of as many as $10^6$ repeat units [1]. Thus, the structure of the molecule, excluding the end caps, is described by specifying the structure of the repeat unit and the number of repeat units in the molecule, called the degree of polymerization. The chemical structure of the repeat unit may be described in
two parts: the main chain, which forms the backbone of the molecule, and side or pendant groups, which are smaller chemical structures attached to the main chain. In Fig. 1a, the repeat unit of polypropylene is shown, in which the carbon atoms form the main chain and the hydrogen atoms and the methyl group form side groups. The main chain of repeat units in common polymers is primarily carbon atoms, which have a valence of four, linked together by single or double covalent bonds. The main chain may also consist of nitrogen, oxygen, or sulfur linking the carbon atoms. The backbone may be a linear chain of atoms, with or without branches, or may have segments in which the atoms form rings. The linear chain structures are referred to as aliphatic structures, and feature single and double covalent bonds between atoms. The ring structures are called aromatic structures, and also feature single and double covalent bonds between atoms. Pendant groups are structures typically made of carbon, hydrogen, nitrogen and oxygen atoms, and are connected to the main chain by single or double covalent bonds. Although they are much shorter structures than the main chain, side groups may contribute greatly to the properties of polymers.

The repeat unit structure may be linear and connect to one repeat unit at each end, or it may be branched, in which case it may connect to three or more repeat units. Linear repeat units are the components of long chain molecules, while branched repeat units form networks which extend in more than two directions from each repeat unit. The molecule may contain isomeric forms of the repeat unit (see Fig. 1). Isomeric forms have chemical structures which are identical to the regular form, but have a different
Figure 1. Chemical structures for polypropylene (X=CH₃). a) Repeat unit structure. b) Polymer structure. c) Chemically isomeric repeat unit. d) Rotationally isomeric repeat unit.

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orientation in the polymer chain [2]. For example, for a molecule in which the repeat units are connected in a head-to-head fashion, Fig. 1b, repeat units which are connected in a head-to-tail fashion, Fig. 1c, are chemically isomeric forms. Another isomeric form involves rotations about single bonds in the main chain, as shown in Fig. 1d. This type of variation is called steric, or rotational, isomerism. Note that a segment of the molecule may achieve a rotationally isomeric form through thermal motion while chemically isomeric forms are permanent after the formation of the molecule.

For chains featuring carbon-carbon single bonds, the rotational potential is such that three rotationally-isomeric states are normally possible and are separated by a potential barrier. An example of such a rotational potential is shown in Fig. 2. Two of these states are called gauche conformations and are rotations in opposite directions from each other. The third state is called the trans conformation and has a lower energy than the gauche conformations. A single chain can achieve many arrangements, called conformations, which are sets of rotationally isomeric states of the molecule. The conformations available to a molecule depend on its thermal energy and any applied strain which may perturb the potential well. In addition, the presence of neighboring molecules may restrict the conformations available to each polymer. These restrictions result in the overall shape of the molecule. Amorphous polymers are considered to be a random tangle of long molecules, or in the case of molecules formed from branched repeat units, a random network of connected short chains. Crystalline structures, in which the molecules are arranged in a regular fashion, are possible in polymers.
Figure 2. Rotational isomerism in polyethylene \((\text{CH}_2)_n\). Three possible rotational states exist. The trans conformation, center, has the lowest energy, while the two gauche conformations, left and right, are formed by rotating the bond between the carbon atoms (shaded). A diagram of the potential between the states is shown at the bottom. Here, the angle \(\Phi\) is the angle of rotation for the second segment with respect to the first segment.
However, the formation of crystalline structures requires highly regular repeat unit structures and rarely occurs without special processing techniques. These considerations describe how the segments are arranged with respect to adjacent segments. A model for an entire molecule must incorporate these ideas.

1.1.2 MODELS OF POLYMER MOLECULES

Polymer molecules may be modeled as a collection of segments joined end-to-end to form a chain. The properties of the chain depend on the number of segments, \( x \), the length of each segment, \( l \), and the angles at which the segments are joined. The geometry of such a chain is shown in Fig. 3. To further approximate the properties of an actual molecule, the lengths of the segments are kept constant, and, with specification of \( x \), the conformations depend only on the angles. The bond angle, \( \Theta \), is usually restricted while the angle of rotation, \( \Phi \), of a segment with respect to the direction of the previous segment is left as a variable. Two well known models are the freely jointed chain, in which \( \Theta \) is randomly chosen, and the freely rotating model, in which \( \Theta \) has a fixed value. More realistically, the rotation of a chain segment depends on the rotational potential energy well described above. These models may be used to calculate quantities such as the mean end-to-end distance and radius of gyration for a chain. Recent efforts have used versions of these models to study the nature of properties of polymers [3].
Figure 3. Geometry for a model of a polymer chain. The position of the beginning and end of chain segment $j$ are located by the position vectors $r_{j-1}$ and $r_j$, respectively. The length of the segment is the magnitude of the vector $l_j = r_j - r_{j-1}$. The direction of segment $j$ with respect to segment $j-1$ defines the bond angle $\Theta$. The angle of rotation, $\Phi$, is not shown in this figure.
1.1.3 MODEL OF POLYMERIC MATERIALS

The above considerations may be incorporated into a model of polymeric materials which consist of many molecules. This is done by developing a statistical-mechanical model of an assembly of many chains, using as variables such quantities as chain segment length, rotation angles, energy levels, and number of segments in the chain. The model is developed by determining the number of possible ways the chains may be placed on a lattice of arbitrary geometry. This leads to the partition function for the system which gives the number of possible arrangements of the system as a function of temperature. Using this model, the thermal behavior of polymers may be investigated. Details of this model will be presented in Chapter 6.

1.2 PROPERTIES OF POLYMERS

Polymers may display a wide range of mechanical behavior, which is, in general, described as viscoelastic; a single polymer sample may exhibit the properties of a viscous liquid or an elastic solid, depending on its temperature. Each polymer has a threshold temperature below which it is a high-modulus, glassy solid. At extreme low temperatures, polymers are very brittle. As the temperature increases, the stiffness slowly decreases. When the temperature of a polymer is raised through its threshold temperature, a transition, called the glass transition, occurs during which the polymer's modulus decreases by several orders of magnitude and the material has high damping.
characteristics. The glass transition displays behavior which is, at least in appearance, a second order transition. The threshold temperature is referred to as the glass transition temperature, $T_g$. Above the $T_g$, polymers have a low modulus and exhibit rubbery properties. The mechanical behavior of polymers at temperatures well above the $T_g$ is used to define two classes of polymers, thermoplastics and thermosets [4]. Thermoplastics melt at a temperature above the $T_g$, called the melt temperature, $T_m$, and may be reshaped prior to cooling. These polymers are made of long, entangled molecules with linear repeat unit structures and may be amorphous or crystalline. Above the $T_m$, thermoplastics act as highly viscous liquids. In contrast to the behavior of the thermoplastics, thermosets will soften at temperatures above the $T_g$, but will not melt and cannot be reshaped. Thermosets are made of branched repeat units, which form a fully linked network.

The glass transition may be interpreted in terms of molecular motion which leads to a thermodynamic interpretation. At temperatures less than $T_g$, the molecules are frozen in their positions on the lattice. Motion in side groups may be possible, but backbone motion does not occur. At temperatures above the $T_g$, chain segments may spontaneously jump to rotationally isomeric states. This motion is thermal motion in the chains and is the mechanism for motion of the molecule through the material, called reptation. Thus, for temperatures greater than the $T_g$ the molecules may be in one of many possible arrangements on the lattice, while below the $T_g$, the molecules have only one accessible arrangement. Thus, the partition function for the material becomes unity for temperatures
at and below the \( T_g \). The configurational entropy, which is proportional to the natural logarithm of the partition function, vanishes at the \( T_g \) [5]. This is the basis for applying statistical-mechanical models to the glass transition. Details of these models, including a discussion of the configurational entropy will be given in Chapter 6.

The properties of polymers and polymer-based materials, their modulus, \( T_g \), elongation to failure, etc., depend on their molecular structure, additives, and processing history. Molecular structural factors include repeat unit structure: linear or branched, aromatic or aliphatic, side group structure, chemical structure, size, and shape, polarizability of the main chain and the side groups, molecular weight of the repeat unit, degree of polymerization, intermolecular bonds, and molecular arrangement; crystalline, amorphous, or amorphous with crystalline regions [6]. Many molecular structural properties may be accounted for by specifying the free volume. The modulus and \( T_g \) of a polymer can be related to its free volume as the free volume is a measure of the mobility of each molecule. Also, when a polymer system is above its \( T_g \), the molecules tend to move toward conformations which require a minimum of energy, i.e. crystalline structures. Thus, the more time a system is above its \( T_g \), the more rearrangement of the molecules occurs, resulting in a system with conformations that may be vastly different than those of a system which is only briefly above its \( T_g \). In characterizing a polymer system, all of these parameters must be considered.
1.3 POLYETHERIMIDE

The polymer examined in this study was a polyetherimide (PEI), marketed by the General Electric Company under the trade name Ultem®. PEI is a thermoplastic, the repeat unit structure of which has a mass of 592 AMU and is shown in Fig. 4. The grade of PEI studied was Ultem 1000®, which has a density of 1.27 gm/cm³. The average molecular weight of Ultem 1000® is 42,000 gm/mol [7]. Thus, there is an average of 71 repeat units per molecule. The resin is reported to have a coefficient of thermal expansion of 47 to 56 x 10⁻⁶ °C⁻¹ [8]. Ultem 1000® has a tensile modulus of 2.96 GPa, a tensile strength of 0.103 GPa, and an elongation-to-failure of 60% [9]. PEI is resistant to many chemicals and is currently used in aerospace, transportation, electrical, computer, appliance, packaging, and specialty uses. PEI is currently being evaluated for use as the matrix material for carbon-fiber reinforced materials [10].

1.4 OVERVIEW OF STUDY

The purpose of this study is to investigate the effects of energetic electron radiation on the structure of PEI and to determine how these structural changes affect the $T_g$ of PEI. The effects of radiation on polymeric materials must be understood before these materials may be used in a radiation environment. Previous studies, which will be discussed below, indicated that the $T_g$ of PEI changed as a result of exposure to electron radiation. In this study, samples of PEI were exposed to mono-energetic beams of
Figure 4. Repeat unit structure of PEI. The grade of PEI in this study has $n = 71$. 

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electrons. A discussion of the use of radiation in studying polymers and the known effects of radiation on other properties of PEI is given in Chapter 2, along with the exposure methods used in this study. Chapter 3 contains a discussion of dynamic mechanical analysis, a technique which may be used to determine the \( T_g \) through the measurement of macroscopic properties, and was used to determine the \( T_g \) for non-irradiated and irradiated PEI. The microscopic effects of the radiation were also characterized. The chemical changes resulting from these exposures were investigated using infrared spectroscopy and are discussed in Chapter 4. The observed chemical changes were modeled with coulomb collisions and radical population kinetics based on electron paramagnetic resonance, and are discussed in Chapter 5. Finally, a statistical-mechanical model for the effect of radiation-induced chemical changes on the \( T_g \) of PEI is presented in Chapter 6. A summary of the results of this study appears in Chapter 7.
 CHAPTER 2
 RADIATION STUDIES

 PEI samples were exposed to electron radiation to investigate the effects of radiation-induced structural changes on the $T_g$. Radiation studies are generally performed in order to determine the survivability of a material in a radiation environment, such as the environment which exists in Earth orbit. However, the irradiation of polymers is also useful in studies conducted to develop an understanding of the nature of the properties of polymers. Radiation interacts with the atomic structure of polymers causing excitations and ionizations which may result in transformations of the chemical structure of the material. Charged particles, electrons, protons, alpha particles, etc., cause ionizations through collisions with atomic electrons, and are thus called direct ionizing particles. Indirect ionizing radiation includes photons and neutrally-charged particles which interact with the medium to form direct ionizing secondary particles. Despite the type of primary radiation, most of the energy is transferred to the medium by secondary particles, usually electrons [11]. The final effects of most types of radiation on polymers are therefore due to the interaction of energetic electrons with the electronic structure of the material. For the purposes of this study, the discussion will be limited to the case of incident electrons.

 The interaction between energetic electrons and matter has been the subject of
extensive research. Much of this work, at least from the physics aspect, has centered on the primary particles path, its rate of energy loss and penetration depth. In studying materials, it is important to view the energy loss process from the aspect of the irradiated material, in particular, to determine where the energy is deposited and what changes occur in the material as a result of this energy absorption. The final step is to understand how these changes affect the properties of the materials being studied. In this chapter, the interaction of the energetic electrons with materials will be considered from the viewpoint of the incident electron and from the viewpoint of the irradiated material. This will be followed by a review of studies of irradiated PEI. Finally, the methods used in this study to expose PEI samples to radiation will be discussed.

2.1 GENERAL CONSIDERATIONS

The interactions between electrons and matter are discussed in several texts. In particular, Charlesby [11], Makhlis [12], and Spinks and Woods [13] provide most of the general development which follows. Additionally, articles by Charlesby [14], O'Donnell [15], and Kamaratos, et. al. [16] are examples of concise reviews of the main topics covered here.

The incident, or primary, electron passing through matter loses most of its energy through collisions with atomic electrons in the material, that is electron-electron collisions. Other modes of energy loss, electron-nucleus scattering and bremsstrahlung,
are not significant for incident particle energies less than a few MeV. For example, the maximum energy that may be transferred to a carbon nucleus by an electron is 20 eV for a 0.1-MeV electron and 367 eV for a 1.0-MeV electron [17]. In addition, the cross section for electron-nucleus collisions are small, and thus, electron-nucleus collisions are not a significant mechanism for energy transfer. Bremsstrahlung is not a significant mechanism for energy transfer for electron energies less than 10 MeV, and for 1-MeV electrons passing through carbon the energy loss due to bremsstrahlung is less than one percent of the energy lost through ionization and excitation.

The primary mechanism for transfer of energy to the medium is interaction with the atomic electrons through their electromagnetic fields, resulting in scattering of the incident electron and the transfer of energy to the atomic electron, which may be great enough to cause excitation or ionization. An incident electron will be scattered in electron-electron collisions many times as it passes through matter. The scattering angle may be large, and, as the primary and secondary electrons are indistinguishable, up to one-half the energy of the primary electron may be lost in a single collision. Multiple scattering events may even result in the primary electron emerging from the same surface where it entered the material.

The penetration of the electrons, their path length, and the spatial distribution of energy transferred are subjects of investigations using cloud chambers and numerical modeling. An expression for the range, \( R \), of an electron with energy, \( E \), in the 10-
200-keV range in low atomic weight (low Z) absorbing materials is [14]

\[ R = 1.25 \frac{E^2 A}{\rho Z}, \]  

(2.1)

where \( A \) is the atomic number of the target atoms and \( \rho \) is the density of the target material. This expression gives a range of 0.2 mm for 0.1-MeV electrons incident on carbon, which has a density of 1.27 g/cm\(^3\). The range for electrons with energies greater than 200 keV increases linearly with the energy of the incident electron. The penetration for 1-MeV electrons in water is 0.5 to 0.6 cm while in aluminum it is 0.14 cm. Penetration in polymeric materials is expected to fall between these values. These considerations describe the path of the primary electron. For this study, the main concern is the effect this primary particle has on the material being irradiated.

The ionizations and excitations result in the formation of active groups, free radicals, and secondary ions within the irradiated material. The decay of these groups may result in additional transformation of the chemical structure of the material. Depending on the mobility of the active group and the presence of other active groups, one of three processes may occur: self healing, cross-linking, or chain scissioning. During self healing, the active group recombines to form a structure identical to the non-irradiated structure. The formation of a bond between adjacent molecular segments is called cross-linking, and the cleavage of the backbone of the polymer is termed chain scissioning. Each of the later two transformations may result in changes in the mechanical, electrical, and thermal properties of the polymer.
The effects of electron radiation on PEI have been reported in previous publications [7, 9, 18, 19, 20]. These studies investigated the electrical and mechanical properties of PEI and used electron paramagnetic resonance (EPR) and infrared (IR) spectroscopy to develop a model for the molecular changes which occur in irradiated PEI. Mechanical properties of irradiated fiber-reinforced PEI have also been reported [21, 22]. The electron energies used in these studies were 100 keV and 1 Mev. Doses of up to 100 MGy were studied. The results of these studies will be reviewed here.

Many bulk properties of PEI have been reported to change with radiation dose. The most dramatic change reported to date is a 96-percent decrease in the tensile elongation to failure for films which had received doses greater than 60 MGy from 100-keV electrons as compared to non-irradiated films [9]. For this same dose, the tensile strength was 22-percent lower and the modulus was 8- to 10-percent higher than the respective non-exposed values. The threshold dose for significant radiation effects was determined to be 1.0 MGy, with additional changes occurring for higher doses. These effects were determined to have no dependance on the rate at which the doses were received for dose rates between 0.01 and 1.0 MGy/hr [7]. The ac-electrical properties of PEI were found to undergo no significant changes for temperatures below the glass transition region, while the dc conductivity was found to increase slightly for a dose of 97.5 MGy from 1-MeV electrons [20]. The ac-electrical dissipation factor was used to
determine the $T_g$, which was 20 °C higher for material which had received a dose of 97.5 MGy than for non-exposed resin. In conjunction with these results, measurements of the unpaired electron density, using EPR, were made for doses up to 100 MGy. The unpaired electron (radical) density was found to increase monotonically with increasing dose. The overall decay rates for fast decaying radical species and for slow decaying radical species were determined. These radical densities and decay rates will be discussed in detail in Chapter 5.

Long and Long [9] used EPR spectra and IR spectra along with the data mentioned above to develop a model of molecular changes in irradiated PEI. Four radical species identified using the EPR spectra for irradiated PEI are shown in Fig. 5a through Fig. 5d. Also shown are two radical species, phenyl and atomic hydrogen, which are expected to form in PEI but do not appear in the EPR spectra due to their short lifetimes. The structures in PEI which contain these radicals are shown in Fig. 6. Changes in the IR spectra reported in reference 9 as a result of radiation exposure are listed in Table 1. Here, an increase indicates a higher concentration of that particular bond type for the irradiated material. Based on a comparison of the radical species identified and the changes in bond concentration, the structures shown in Fig. 7 have been proposed as a model of radiation induced cross-links in PEI [9]. This model will be discussed in greater detail in Chapter 4.
Figure 6. Radicals in irradiated PEI [9]. Here, the radicals shown in Fig. 5 have been incorporated into chain structures.
Table 1. Changes in IR spectrum of PEI resulting from radiation exposure [9].

<table>
<thead>
<tr>
<th>Infrared band</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H (phenyl)</td>
<td>Increase</td>
</tr>
<tr>
<td>C-H (methyl)</td>
<td>Decrease</td>
</tr>
<tr>
<td>C=O</td>
<td>Decrease</td>
</tr>
<tr>
<td>Ether (aromatic)</td>
<td>Decrease</td>
</tr>
<tr>
<td>C-N</td>
<td>No change</td>
</tr>
<tr>
<td>Tri- and di-substituted phenyl</td>
<td>Decrease</td>
</tr>
<tr>
<td>Mono-substituted phenyl</td>
<td>Increase</td>
</tr>
<tr>
<td>Imide ring</td>
<td>Decrease</td>
</tr>
</tbody>
</table>
Figure 7. Possible cross-linked structures in irradiated PEI [9]. The ether linkages (c) and urethane linkages (d) each have two possible forms, while peroxide linkages (e) may form three ways.
The effects of electron radiation on fiber-reinforced PEI are much less dramatic than those occurring in the resin. Small changes in the breaking strength were reported for doses of 100 MGy [21, 22]. No significant changes in other mechanical properties were reported. While the effects of radiation on the structure of the PEI in the fiber-reinforced material is expected to be identical to the effects on the resin, the changes in properties depend on the effects of radiation on the fibers as well as on the resin. It is noted that the mechanical properties of fiber-reinforced materials are also dependant on the interface between the polymer and the reinforcing fibers. The role of fibers in the glass transition of fiber-reinforced polymers will be discussed in Chapter 3.

2.3 RADIATION EXPOSURES AND DOSIMETRY FOR PRESENT STUDY

During radiation studies dosimetry serves as a means of comparing the effects of exposures involving different exposure conditions. The dose received by a sample is defined as the energy absorbed per unit mass of material, with no distinction made between sources of energy and mechanisms of energy absorption. As mentioned above, the mechanisms for the transfer of energy from energetic electrons to polymeric materials are independent of incident particle energy for energies from the keV range to tens of MeV. Also, the effects of electron radiation have been shown to be independent of dose rate for PEI [7]. Having established these, the effects on PEI for exposures of differing electron energy and dose rate will be assumed equivalent if the doses are equal.
During this study, specimens of PEI film and thick fiber-reinforced PEI were studied. The fiber-reinforced materials were required for the dynamic mechanical analysis technique and will be discussed further in Chapter 3. The film samples were irradiated with 100-keV electrons while samples of fiber-reinforced PEI were irradiated with 1-MeV electrons. The higher energy was necessary to penetrate the thick fiber-reinforced materials. Exposure to 100-keV electrons was done using a modified RCA model EMU3-H transmission electron microscope. Specimens were placed between aluminum foil and Kapton® film with the aluminum foil toward the radiation source. Windows were cut in the aluminum foil to expose the samples to the electron beam. See Fig. 8a. The Kapton® film protected the samples from contamination from the luminescent viewing screen in the microscope. Exposures to 1-MeV electrons were performed using a Radiation Dynamics, Inc., Dynamitron at NASA Langley Research Center. Exposures were done under vacuum with the samples mounted on a water cooled, aluminum exposure surface. See Fig. 8b. The effects of specimen heating during irradiation were discussed in reference 7, where it was found that the temperature of PEI would not exceed 38 °C for dose rates up to 10 MGy per hour. Other studies referred to in reference 7 give a maximum dose rate to avoid thermal effects of 30 MGy per hour. These dose-rate limits were used as a guide for the exposures performed during this study.
Figure 8. Geometry of exposure facilities. a). 100 keV exposure facility. b). 1 MeV exposure facility.
To monitor the flux of electrons during each radiation exposure, a faraday cup with cross sectional area \( a_f \) was placed at the exposure surface. The flux, \( F \), of electrons at the exposure surface is \( F = I / a_f \) where \( I \) is the current measured by the faraday cup and \( e \) is the charge of an electron. The total number, \( N \), of electrons incident per unit area during an exposure of duration \( t \) is then \( N = Ft \). If a material absorbs energy \( A(E) \) per incident electron, the total energy absorbed by a section of the material with unit surface area during an exposure is \( E_t = NA(E) \). Note that the energy absorbed, \( A(E) \), may be dependant on the energy, \( E \), of the incident electrons. The dose, \( D \), received by a sample is defined as the energy absorbed per unit mass of material, and is given by

\[
D = F_t \frac{A(E)}{\rho T} \tag{2.2}
\]

where \( \rho \) is the density of the material and \( T \) is the thickness of the sample. If \( A(E) \) is known, eq. 2.2 may be used to calculate doses for a given flux and duration. With the flux selected, this equation may also be used to find the duration of exposure required for a desired dose.

Energy absorption for the electron radiation exposures was modeled using a one-dimensional, multi-layer, electron/photon transport code entitled TIGER [23]. The TIGER code uses the thickness, density, elemental constituents and the weight fraction of each element for each layer of material to be irradiated and simulates the energy deposition by the incident radiation. The energy deposited normalized to one incident electron is simulated as a function of depth in the sample. The uncertainty in this
calculation is estimated to be less than ± 5 percent [23]. Energy absorption calculations were made for geometries representative of the samples used in each analysis technique and for the electron energies used for the respective exposures. For simulations in which the energy deposition was uniform throughout the thickness of the material, an average energy absorption per unit thickness could be calculated by dividing the total energy absorbed by the thickness of the material. Two calculations were made to simulate the energy deposition in PEI samples. The first was a simulation of the energy deposited in 12.7-μm thick PEI film by 100-keV electrons and the second was a simulation of the energy deposited in fiber-reinforced PEI by 1-MeV electrons. The simulations gave \( A(E)/T = 19.0 \pm 14.0 \text{ MeV/cm} \) for the resin and \( 3.8 \pm 0.63 \text{ MeV/cm} \) for the fiber-reinforced material. The large standard deviation associated with the simulated energy absorbed by the film is due to the lower absorption near the exposed surface of the material, and as a consequence, dosimetry for film specimens was done using the results of reference 9 for calibration with Nylon® standards.

Several electron radiation exposures were performed on samples of the above materials. Electron flux values and exposure durations for the exposures are shown in Table 2. The doses received by the samples, as calculated by eq. 2.2, are also shown in the table. The dose rate for the PEI films was 10 MGy/hr for the one-hour exposure, 12.5 MGy/hr for the 6.2-hr exposure, and 20 MGy/hr for the five-hour exposure. The dose rate for the exposure to 1.0-MeV electrons of fiber-reinforced materials was 0.5 MGy per hour for each exposure.
<table>
<thead>
<tr>
<th>Material</th>
<th>Electron Energy, MeV</th>
<th>Electron Flux, cm²s⁻¹</th>
<th>Duration, hr</th>
<th>Dose, MGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI Film</td>
<td>0.1</td>
<td>1.2 x 10¹¹</td>
<td>2.5</td>
<td>25</td>
</tr>
<tr>
<td>PEI Film</td>
<td>0.1</td>
<td>1.6 x 10¹¹</td>
<td>6.2</td>
<td>75</td>
</tr>
<tr>
<td>PEI Film</td>
<td>0.1</td>
<td>2.5 x 10¹¹</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>C6000/PEI</td>
<td>1.0</td>
<td>4.0 x 10¹¹</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>C6000/PEI</td>
<td>1.0</td>
<td>4.0 x 10¹¹</td>
<td>150</td>
<td>75</td>
</tr>
<tr>
<td>C6000/PEI</td>
<td>1.0</td>
<td>4.0 x 10¹¹</td>
<td>200</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2. Electron radiation exposures used in this study and simulated doses in PEI samples.
CHAPTER 3

GLASS TRANSITION TEMPERATURE MEASUREMENTS

The glass transition of PEI was examined through dynamic mechanical analysis (DMA), a technique which involves mechanically deforming a sample of material sinusoidally with time as the temperature is changed. In this chapter, the theory of the glass transition will be discussed, including a description of the mechanical behavior of polymers in the region of the transition. The experimental method and techniques will be described and the results of the analysis for non-irradiated PEI will be presented, followed by a discussion of the changes in $T_g$ resulting from irradiation.

3.1 THEORY OF THE GLASS TRANSITION

The glass transition will first be described in terms of the mechanical properties of a polymer. A polymer is stiff and glassy (high modulus) at temperatures below its $T_g$. As the temperature of a polymer is raised to near its $T_g$, the stiffness of the polymer decreases. As a polymer is heated through the transition, its stiffness may drop several orders of magnitude. At temperatures above the transition region, the material is soft and rubbery (low modulus), but flow does not occur until even higher temperatures. At temperatures above and below the transition region, the material has low mechanical
damping characteristics. During the transition, however, the material has high mechanical damping characteristics. Thus, a peak in the damping-temperature curve is indicative of the glass transition. The stiffness and damping of a material are commonly combined to form a complex modulus, the real part of which describes the stiffness of the material, and the imaginary part the damping of the material. The complex modulus will be discussed in detail in Section 3.2.1.

In order to illustrate the molecular theories of the glass transition, a discussion of another transition, the \( \gamma \)-transition, is useful. The mechanical behavior of a polymer during this transition is similar to that described above for the glass transition, however, the change in modulus is typically less than an order of magnitude. At temperatures above and below this transition the polymer retains its glassy characteristics and thus, the transition is called a glass-glass transition. The \( \gamma \)-transition involves motion in a segment of a molecule featuring a linear chain of at least four carbon atoms with small side groups \cite{24}. At temperatures below the \( \gamma \)-transition temperature, the segment is immobile, constrained from movement by neighboring molecules. For temperatures greater than the \( \gamma \)-transition temperature, the segment has sufficient thermal energy to make spontaneous jumps to different conformations, crossing a potential energy barrier in the process. The conformations involved are the trans and gauche conformations discussed in Chapter 1 and the motion is described as a crankshaft-like rotation. This model is illustrated in Fig. 9 for a segment of polyethylene. The application of stress to the polymer during the transition results in strain energy which may perturb the potential well in which the
Figure 9. Crankshaft-like rotation in polyethylene. The onset of this motion corresponds to the $\gamma$-transition.
molecule lies, giving the jumps a preferred direction. This jumping model of the $\gamma$-
transition has been qualitatively applied to the glass transition [25]. While determining
the segment of the molecule involved in the motion remains a difficulty, it is generally
accepted that the entire molecule is undergoing some sort of thermal motion at
temperatures above the $T_g$.

The properties of polymers at temperatures near the $T_g$ are highly dependant on
the time scale used to observe them. The simplest example of this time dependance
involves the creep response of a polymeric solid at a temperature below its $T_g$. If a
constant force is applied to the sample, the deformation increases with time in a non-
linear fashion. At some period after application of the force, the polymer will appear to
undergo a transition during which the modulus of the sample decreases rapidly. The time
at which this transition occurs is the "global relaxation" time, $t_0$, which is the average
time for the polymer chains to undergo rearrangements to conformations which minimize
their strain energy. On the other hand, as the temperature of the sample is raised, the
polymer chains acquire thermal energy, and are more likely to undergo rearrangement.
Thus, as the temperature is raised, $t_0$ decreases, and the polymer appears to have a lower
modulus. From these arguments, it can be conjectured that experiments with different
time scales, such as periodic experiments with different frequencies, will give different
values for the $T_g$. 

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The time dependance of transitions may be obtained through analogy to chemical reaction kinetics. A kinetic reaction occurs with a frequency, \( \omega \), which depends on temperature by

\[ \omega \propto \exp \left( \frac{\Delta H}{RT} \right) \]  

(3.1)

where \( \Delta H \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is the temperature. Thus, observing the reaction at \( T_1 \) and at \( T_2 \) results in a shift in the frequency of the reaction such that

\[ \ln \frac{\omega_1}{\omega_2} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right). \]  

(3.2)

This is the Arrhenius equation, which describes the temperature dependance of the rate of a system making a transition over an energy barrier of height \( \Delta H \), which is called the activation energy. According to Eyring's model for flow in solids [26], the activation energy is the energy required for a mole of molecular segments to move to the top of the potential wells in which they are contained. This frequency dependance will be used in the analysis of the DMA data to correct for frequency effects so that all \( T_g \) values will correspond to the same frequency.

3.2 DETERMINATION OF DYNAMIC PROPERTIES

DMA is an analytical method in which a sample is subjected to a low-amplitude, sinusoidal, flexural deformation. Polymeric materials, as a result of their viscoelastic
nature, store most of the energy of the deformation, and return it to the oscillation. A fraction of the energy is dissipated each cycle and is lost from the oscillation. DMA is used to determine the stored and lost quantities and express them as the components of a complex modulus. Performed over a wide range of temperatures, DMA may be used to determine information related to transition temperatures, molecular orientation, molecular weight, relaxation spectra, cross-linking, phase separation, and chemical composition [27]. The results of DMA may also depend on testing parameters such as the frequency of oscillation, amplitude of oscillation, and rate of temperature change [28]. The effect of oscillation frequency was discussed above and its incorporation into the current study will be discussed in Section 3.2.3. The rate of temperature change was held constant throughout this study, as was the oscillation amplitude. Thus, the effects of the experimental method on the results have been accounted for.

3.2.1 THE DYNAMIC MODULUS

In dynamic mechanical analysis, a sinusoidal stress, \( \sigma \), is applied to the sample

\[
\sigma = \sigma_0 \sin(\omega t + \delta)
\]

(3.3)

where \( \omega \) is the frequency of oscillation and \( \delta \) is a phase angle. Generally, the strain in the sample, \( \varepsilon \), lags behind the stress by a phase, \( \delta \), such that

\[
\varepsilon = \varepsilon_0 \sin(\omega t).
\]

(3.4)

For a perfectly elastic material the phase angle, \( \delta \), is zero, and the stress and strain are
in phase. For a liquid, $\delta$ is $\pi/2$, so that the stress and strain are out of phase. For the case of the viscoelastic material, $\delta$ is between 0 and $\pi/2$, resulting in a more complex relationship between the stress and strain. The generalized stress can be expanded as

$$\sigma = \varepsilon_0 E_1 \sin(\omega t) + \varepsilon_0 E_2 \cos(\omega t)$$  \hspace{1cm} (3.5)$$

where

$$E_1 = \frac{\sigma_0 \cos(\delta)}{\varepsilon_0}$$  \hspace{1cm} (3.6)$$
$$E_2 = \frac{\sigma_0 \sin(\delta)}{\varepsilon_0}.$$  \hspace{1cm} (3.6)$$

Thus, the stress has a component of magnitude $\varepsilon_0 E_1$ which is in phase with the strain and a component of magnitude $\varepsilon_0 E_2$ which is 90 degrees out of phase with the strain. Again, for the case of an elastic material, $E_2 = 0$, while for a liquid, $E_1 = 0$. Alternatively, the stress and strain may be written

$$\sigma = \sigma_0 \exp(i(\omega t + \delta))$$  \hspace{1cm} (3.7)$$

and

$$\varepsilon = \varepsilon_0 \exp(i\omega t).$$  \hspace{1cm} (3.8)$$

The modulus is then

$$E = \frac{\sigma_0 \exp(i\delta)}{\varepsilon_0} = E_1 + iE_2.$$  \hspace{1cm} (3.9)$$

The real component of the modulus, $E_1$, is called the storage modulus, while the imaginary component, $E_2$, is called the loss modulus. These designations arise from
examining the work, \( W \), done in one cycle,

\[
W = \int_0^{2\pi} \sigma \varepsilon e^{i\omega t} e^{i\delta} dt.
\]

Integrating over one cycle, \( \dot{W} \) is seen to depend only on \( E_2 \) and the square of the amplitude of the strain,

\[
W = \pi E_2^2.
\]

Thus, the energy dissipated during one cycle is proportional to \( E_2 \), while the energy stored in the deformation and returned to the oscillation is proportional to \( E_1 \). Examining the cases discussed above, for an elastic material, \( E_2 = 0 \), and no energy is dissipated, while for a liquid, \( E_1 = 0 \), and no energy is stored. Dynamic mechanical analysis is usually performed by determining \( E_1 \) and either \( E_2 \) or the phase angle \( \delta \). The parameters used depend on the analysis technique involved in examining the materials.

### 3.2.2 DESCRIPTION OF DMA APPARATUS

For this study, a du Pont de Nemours 982 DMA* dynamic mechanical analyzer was used to determine storage modulus and loss modulus values as functions of time. The apparatus featured two parallel, stiff bars, which were balanced on low friction pivots. See Fig. 10. The sample was clamped between the ends of the bars. The opposite end of one bar was driven by an electromagnetic driver, while the corresponding end of the opposite arm was free. See Fig. 10a. The free arm simply supported the deformation of the sample. A sinusoidal signal was applied to the driver, resulting in
Figure 10.  a) Diagram of DMA apparatus showing the sample clamped to the ends of two stiff beams, one of which is driven while the second supports the deformation.  b) Motion of the arms of the DMA.  c) Deformation of a sample in the DMA apparatus.  The sample is flexed so that the ends are at positions A and B, and then reversed so that the ends are moved to A' and B'.  The amplitudes of motion are greatly exaggerated in this diagram.
motion of the arms, as shown in Fig. 10b, and the clamped-clamped flexural deformation of the sample illustrated in Fig. 10c. The oscillation was maintained at the frequency that required the minimum applied moment. This frequency was the resonant frequency of the arm-sample-arm system, as shown in Appendix B-1. A linear variable differential transducer (LVDT) was used to monitor the frequency and amplitude of the oscillation. The signal from the LVDT was fed into a feedback circuit which in turn applied a current to the driver to maintain a constant oscillation amplitude [29].

The standard equations used to calculate the components of the complex modulus from the frequency and damping signals may be found in reference 30 and are derived in Appendix B-2. These equations assume the validity of the equation

\[ E = 2(1 + \sigma)G \]  (3.12)

relating the tensile modulus, \( E \), to the shear modulus, \( G \). Here, \( \sigma \) is Poisson's ratio. For anisotropic materials, such as fiber-reinforced polymers, this relation is not generally valid. In most cases, an empirical relationship between \( E \) and \( G \) must be developed through extensive mechanical testing for each material configuration. In place of this empirical method, an approach may be used in which an approximate expression for the tensile modulus is determined by neglecting the shear contribution. As will be shown below, this approximation can be made for cases in which the length of the sample is much greater than its thickness. The derivation, similar to that shown in Appendix B-2, is presented here.
The equation for the flexural deformation, \( x \), of a beam of length \( L \) and cross-sectional area \( A \) is \[ x = \frac{FL^3}{12E\kappa^2A} + \alpha \frac{FL}{AG}. \] (3.13)

Here, \( F \) is the applied force, \( E \) is the modulus, \( \kappa \) is the radius of gyration, and \( \alpha \) is Timoshenko's shear correction factor. From this, the modulus is

\[
E = K\frac{L^3}{12\kappa^2A} \left[ 1 + 2\alpha(1 + \sigma)\frac{T^2}{L^2} \right]
\] (3.14)

where \( K \) is the ratio \( F/x \). The second term in the brackets is dependant on the ratio of thickness to length. If this ratio is less than 0.07, the second term is less than 0.02, where typical values for \( \alpha \) and \( \sigma \) have been used. The thickness-to-length ratios for samples in this study were typically 0.061. Thus, if the second term is disregarded, the modulus is approximated by

\[
E = K\frac{L^3}{12\kappa^2A} = K\frac{L^3}{T^3W}
\] (3.15)

which is just the tensile contribution.

The differential equation for the deflection, \( x \), of an elastic beam by a force \( F(t) \) is

\[
M \frac{\partial^2 x}{\partial t^2} + Kx = F(t)
\] (3.16)

where \( M \) is the effective mass of the beam and \( K \) is the stiffness of the beam which may
be found from eq. 3.15 to be

\[ K = \frac{F}{x} = \frac{EWT^3}{L^3} \]  

(3.17)

The effective length of the sample is taken to be the length of the sample between the grips plus one-half the length of the sample in each grip [30]. The relationship between \( x \) and the angle of arm deflection, \( \phi \), is

\[ x = \frac{1}{2}(L+D)\phi. \]  

(3.18)

as may be determined from the geometry of the system as shown in Fig. 10b. Therefore the differential equation can be written

\[ \frac{1}{2}M(L+D)\phi'' + \frac{1}{2}(L+D)EW\frac{T^3}{L^3}\phi = F(t) \]  

(3.19)

in terms of the angle \( \phi \).

The differential equation for the deflection angle, \( \phi \), of the arms of the dynamic mechanical analyzer is

\[ 2J\frac{\phi''}{\phi'} + d\frac{\phi'}{\phi'} + k\phi = M(t) \]  

(3.20)

where \( J \) is the moment of inertia for one arm, \( d \) is the damping coefficient for the system, \( k \) is the stiffness of the system, and \( M(t) \) is the torque applied by the driver. Note that \( d \) and \( k \) are coefficients for the analyzer-sample system and each has a contribution from the sample, \( d_s \) and \( k_s \), and a contribution from the instrument, \( d_i \) and \( k_i \). For a solution
to eq. 3.20 of the form

$$\phi = \phi_0 \exp(i\omega t)$$  \hspace{1cm} (3.21)$$

the differential equation can be written

$$2J \frac{\partial^2 \phi}{\partial t^2} + (k + i\omega d)\phi = M(t)$$  \hspace{1cm} (3.22)$$

by combining the frictional loss term and spring term.

The correspondence principle for viscoelastic behavior allows the viscoelastic response to be found by replacing the material parameters in the elastic case with their complex counterparts provided the stress and strain have the same frequency dependance [31]. Comparing eq. 3.19 and eq. 3.22, the following expression for the measured stiffness and damping in terms of material parameters is found to be

$$k - k_i + i(\omega d - \omega_i) = \frac{1}{2} (L + D)(E_1 + iE_2) \frac{W^3}{L^3}. \hspace{1cm} (3.23)$$

Comparing the real and imaginary parts of eq. 3.23 gives the components of the modulus

$$E_1 = \frac{L^3}{T^3} \frac{k - 2k_i}{W(L + D)} \hspace{1cm} (3.24)$$

and

$$E_2 = \frac{L^3}{T^3} \frac{\omega d - 2\omega_i}{W(L + D)} \hspace{1cm} (3.25)$$

where $k = 2J\omega^2$ when the system is at resonance. System calibration to determine the
instrument constants was performed similarly to the procedure in Appendix B-3.

For analysis of dynamic properties over a temperature range, the arms and sample were enclosed in a chamber which was lined with heating coils and surrounded by a liquid nitrogen jacket. The chamber was cooled to below -120 °C prior to the start of the experiment. Oscillation frequency and the damping signal were recorded every 2.4 seconds as the temperature inside the chamber was raised at a rate of 5 °C/min. Data were recorded until the sample passed through its glass transition.

3.2.3 ANALYSIS OF DMA RESULTS

Analyses of the frequency and damping curves were made using the basic code listed in Appendix C. At 2.4 sec between data points and analysis lasting for durations from 80 to 90 min, around 2300 data points were recorded for each sample. The number of data points was reduced to one data point per degree by averaging all damping and frequency values for temperatures within 0.5 °C of each integer degree. Storage modulus, loss modulus and loss tangent curves were then calculated from these data using the equations derived for the no-shear approximation.

After the modulus values were calculated from the frequency and damping data, the resulting modulus-temperature curves were examined to determine values which could be used to characterize the materials. In particular, the results of DMA were used to
determine the $T_g$ of the samples. The glass transition appears in the storage modulus curve as a rapid decrease with increasing temperature and as a peak in the loss modulus curve. There are several features of the modulus-temperature curves which may be used to identify the $T_g$. The temperatures at which the loss modulus curve begins to increase and the temperature at which the curve reaches its maximum value have been designated by various authors as the $T_g$ \[32\]. The beginning of the transition region is significant as it is a limiting temperature for retention of mechanical properties, while the peak position coincides with the temperature at which the damping processes occurring during the transition are at a maximum. For this study, the temperature at which the loss modulus begins to increase at the beginning of the transition will be referred to as the onset temperature to the glass transition, while the temperature at which the loss modulus reaches a peak will be referred to as the apparent $T_g$ for the sample. The temperatures at which the peaks in the loss modulus curves occurred were found by finding the temperature at which the first derivative of the curve passed through zero. The onset temperature could be determined by applying a linear least-squares fit to the curve well below the beginning of the transition and a second fit to the curve at the inflection point on the low-temperature side of the transition peak. The onset temperature was taken to occur at the intersection of these lines.

Recalling that the $T_g$ is frequency dependant, the frequency of oscillation at the temperature at which the peak occurred was determined along with the peak positions. The inverse of the $T_g$ for each sample was plotted against the natural log of the frequency.
of oscillation. A linear least-squares fit to the data points was used to determine the constants in eq. 3.2. From this fit, the $T_g$ at the reference frequency, 10 Hz, was determined and taken to be the $T_g$ for the material.

3.3 PEI SAMPLES FOR DMA

As the glass transition is the boundary between solid behavior and viscous liquid behavior, polymer samples may be permanently deformed when tested in the transition region. This may result in modes of deformation other than the simple flexural deformation on which the analysis of DMA data is based. To prevent such deformation, samples of PEI which were reinforced with carbon-fibers were used to determine the $T_g$. The fiber-reinforced PEI was 0.061 cm thick. The fibers occupied 57% of the material and were uni-directional. Samples were cut to one-half inch widths, and lengths of two inches. Before proceeding with the current study, the effect of the fibers on the observed $T_g$ of the polymer must be investigated.

Carbon fibers have mechanical properties that do not change with temperature until temperatures that are well above the $T_g$ of polymers. However, the presence of the fibers in the polymer may affect the observed $T_g$ in two ways. First, the resonant frequency of oscillation in the DMA system depends on the stiffness of the sample. See Appendix B-1. For fiber-reinforced polymers, the stiffness is a function of the fiber direction with respect to the deformation direction. For the case of flexural deformation,
if the fibers are parallel to the long axis of the sample, as shown in Fig. 11a, the sample is stiff and the frequency of oscillation is high. This will be referred to as the longitudinal fiber orientation. If the fibers are perpendicular to the long axis, the transverse orientation shown in Fig. 11b, the material may have a modulus that is an order of magnitude less than the modulus for the longitudinal case, and the frequency of oscillation will be lower than that for the longitudinal fiber orientation. As a result of their different oscillation frequencies, samples of fiber-reinforced PEI with fibers in the longitudinal orientation will have a $T_g$ that is different from that for samples with transverse fiber orientation. This effect will be used in this study through application of the Arrhenius equation (eq. 3.2) to find the $T_g$ at the reference frequency, 10 Hz.

The second effect the fibers may have on the DMA results is by restricting the motion of the polymer molecules. This filler effect has been documented for particulate fillers [33]. As an effort to quantify this effect, a thick, injection-molded bar of PEI was analyzed. The beam was permanently deformed into a horseshoe shape as a result of the testing which raises questions about the validity of the analysis in the transition region. The $T_g$ for this sample appeared to be 236 °C at a frequency of 11 Hz. As will be shown later, this $T_g$ was 19 °C lower than the $T_g$ found for the fiber-reinforced PEI for the same frequency. The current study, however, is intended to determine changes in the $T_g$ resulting from radiation exposure, rather than to find the $T_g$. As they are largely unaffected by electron radiation, the fibers are not expected to play any role in the radiation-induced changes.
Figure 11. a) Sample of a fiber-reinforced polymer with fibers in the longitudinal direction. b) Sample of fiber-reinforced polymer with fibers in the transverse direction.
3.4 $T_g$ DATA FOR PEI

The above techniques were used to determine the $T_g$ for non-irradiated and irradiated PEI samples. In addition to $T_g$ values, DMA provides modulus values, damping characteristics, and other data. This study, however, will be restricted to a discussion of the $T_g$, and other results may be found in references 21 and 22. A detailed discussion of the DMA results for non-exposed fiber-reinforced PEI will be followed by a discussion of the changes resulting from irradiation.

Fig. 12 shows the dynamic modulus curves for non-exposed PEI with longitudinal fiber orientation. As shown in Fig. 12a, the two samples had storage modulus curves which changed little for temperatures between -120 °C and 50 °C. As the temperature increased from 50 °C to 240 °C, both curves decreased slowly, the curve for the sample with the higher modulus values in this region showing a small fluctuation near 120 °C. At temperatures slightly higher than 240 °C, each curve shows a small increase in modulus followed by a sharp decrease. This sharp decrease is associated with the glass transition, while the small pre-transition increase in the storage modulus may be a result of improved fiber-polymer contact as polymer chains begin to gain segmental mobility. The curves begin to level off above the transition. In Fig. 12b, the loss modulus values for the two samples are shown. For temperatures between -120 °C and 240 °C, the loss modulus values were small. The damping peak that is characteristic of the glass transition appears for each sample at temperatures just above 240 °C. The peak positions were
Figure 12. a) Storage modulus curves for two samples of non-irradiated fiber-reinforced PEI with longitudinal fiber orientation. b) Loss modulus curves for two samples of non-irradiated fiber-reinforced PEI with longitudinal fiber orientation.
similar for the two samples, occurring at 256 °C and 255 °C.

Fig. 13a and Fig. 13b show the storage modulus and loss modulus, respectively, for the non-exposed PEI with transverse fiber orientation. As a result of the fiber direction, these modulus values are approximately an order of magnitude lower than the modulus values for the material with longitudinal orientation in Fig. 12. For each sample, the storage modulus decreases slowly with increasing temperature up to the transition region. At a temperature just below 240 °C, the storage modulus curves begin to decrease sharply. The three curves do not coincide in the transition region, but display distinct differences in transition temperature. This behavior is also reflected in the loss modulus curves, Fig. 13b, where the transition peaks occurred at a different temperature for each of the three samples, with values varying from 240 °C to 248 °C. These peak positions are lower in temperature than the positions of the peaks for the samples with longitudinal fiber orientation. This is a result of the lower oscillation frequency for the samples with transverse fiber orientation.

The data for the samples with longitudinal fiber orientation and the data for the samples with transverse orientation were combined to determine a value for $T_g$ that was characteristic of the material, rather than the individual samples. This was done by applying the Arrhenius equation, eq. 3.2, to the data for the samples with longitudinal fibers and the samples with transverse fibers. The inverse of the apparent $T_g$ for each sample in absolute temperature units is plotted against the natural logarithm of the
Figure 13. a) Storage modulus curves for three samples of non-irradiated fiber-reinforced PEI with transverse fiber orientation. b) Loss modulus curves for three samples of non-irradiated fiber-reinforced PEI with transverse fiber orientation.
frequency at the transition in Fig. 14. A linear least-squares fit to the data is included in the figure. The $R^2$ error for this fit was 0.88. The slope of the fit gives an apparent activation energy for the transition of 203 kJ/mol. From this fit, the transition temperature at a frequency of 10 Hz would be 255 °C. This value is taken to be the $T_g$ for non-irradiated, fiber-reinforced PEI. Note that the $T_g$ for the fiber-reinforced material is 19 °C higher than the $T_g$ for the injection-molded bar discussed above.

Samples of fiber-reinforced PEI exposed to 25-, 75-, and 100-MGy doses from electron radiation were analyzed in the above manner. The $T_g$'s were, as above, determined from fits to the $T_g$-frequency data for the samples. The error bars associated with each value of $T_g$ represents the spread in the data. The change in $T_g$ is plotted against radiation dose in Fig. 15. As shown in the figure, the $T_g$'s for doses of 25 MGy and 75 MGy were not significantly different from the $T_g$ for the non-irradiated PEI. However, the $T_g$ for PEI exposed to the 100 MGy dose was significantly higher than the $T_g$ for the non-exposed PEI. These results suggest several possible models for radiation effects on PEI. For one, doses of radiation less than 75 MGy may not significantly change the structure of PEI or the $T_g$ is not sensitive to the changes that do occur. On the other hand, significant cross-linking and chain scissioning may occur for doses less than 75 MGy, but the effects of one may offset the effects of the other, resulting in no net change in $T_g$. These mechanisms must be investigated by determining the changes in the structure of PEI resulting from the exposures.

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Figure 14. Plot of $1/T_g$ versus the natural logarithm of the frequency of oscillation for non-exposed fiber-reinforced PEI. The line is a linear least-squares fit to the data.

$1/T_g = -4.1 \times 10^{-5} \ln(f) + 1.99 \times 10^{-3}$

$R^2 = 0.88$
Figure 15. Change in $T_g$ at 10 Hz as a function of absorbed radiation dose. Error bars represent the variation of $T_g$ values at each dose.
CHAPTER 4
CROSS-LINK AND CHAIN SCISSION DENSITIES IN IRRADIATED PEI

This chapter is concerned with the changes which occur in the structure of PEI as a result of irradiation. It is important to determine the nature of the structural changes and the number of changes which occur for an absorbed quantity of radiation. The first section of this chapter discusses a model of radiation effects on PEI that has been presented in the literature, which is followed by some additional analysis of the model. In the present study, these changes were further investigated using Infrared (IR) spectroscopy. The technique for IR spectroscopy will be described in this chapter. The objective of this investigation was to provide quantitative values for the cross-link and chain scission densities. The results of the spectroscopy will be presented along with a model which gives the cross-link and chain scission densities in irradiated PEI.

4.1 PREVIOUS STUDIES

A model proposed in reference 9 for the chemical structures which form in irradiated PEI was discussed in Chapter 2. However, the model lacks quantitative values for the cross-link density and chain scission density. Previous studies have reported cross-link densities in irradiated PEI, however, these studies involved lower doses than
those used in this study. Bradbury [34] used solubility tests for doses of up to 100 kGy, and found that cross-linking increased with dose. In addition, the same study reported that PEI was insoluble after receiving a dose of 10 MGy, suggesting cross-link densities on the order of $3 \times 10^{19} \text{ gm}^{-1}$. Basheer and Dole [35] used gel formation to determine the G-value for cross-linking, $G(x)$, in PEI. $G(x)$ is defined to be the number of cross-links formed per gram for every 100 eV/gm that is absorbed. Basheer and Dole found that $G(x) = 1.39 \times 10^{-2} \text{ gm}^{-1}$ for doses up to 40 Gy. For the maximum dose reported by Bradbury, this would predict a cross-link density of $8.7 \times 10^{18} \text{ gm}^{-1}$, which is less than 30% of the density estimated for the solubility study. This projection assumes that the results in these studies can be extrapolated to doses that are orders of magnitude larger than the doses of the original studies. No values for the chain-scission density in irradiated PEI have been reported.

4.2 CROSS-LINK FORMATION IN PEI

A model for the changes in the chemical structure of PEI was proposed in reference 9 and reviewed in Chapter 2. It is noted that the structures in Fig. 7 are not all strictly cross-links. The bonds shown in Fig. 7 are incorporated into chain structures in Fig. 16 through Fig. 18. The peroxide linkages, Fig. 16, do not form cross-links, but rather appear as repeat units in the chain which have chemical structures that are different from that of PEI. For the purposes of this study, these structures will be referred to as altered repeat units. The ether linkages and urethane linkages, Fig. 17, also are not
Figure 16. Altered repeat units in irradiated PEI. a) General structure of molecule containing defects (A - normal repeat unit, B, C - modified repeat units.) b), c), and d) Chemical structure of modified repeat units featuring peroxide linkages (C-O-O-C).
Figure 17. Branched structures in irradiated PEI. a) General structure of branched molecule (A - normal repeat unit, B,C - modified repeat units). b) Branched structures featuring ether linkages. c) Branched structures featuring urethane linkages.
cross-links, but rather are branch points in the chains. True cross-links are formed by
the ethylene linkages, amide linkages, and ketone-ketone linkages, shown in Fig. 18. In
order to understand the nature of the changes in the $T_g$, it must be determined which of
these structures form in irradiated PEI and in what quantities they appear. IR
spectroscopy is a technique which may provide quantitative values for the bond densities.

4.3 THEORY OF INFRARED SPECTROSCOPY

Changes in bond densities in irradiated PEI were determined using IR
spectroscopy. IR spectroscopy is an extremely useful tool when studying the chemical
structure of organic materials. Its usefulness comes from the fact that bonds which are
typical of organic molecules have vibrational modes with characteristic frequencies that
lie in the 400 cm$^{-1}$ to 4000 cm$^{-1}$ frequency range. Thus, absorption bands that are
characteristic of chemical bonds in organic molecules may be observed in this frequency
range. In addition, the amount of absorption is proportional to the concentration of the
absorbing bonds. IR spectroscopy therefore may provide a quantitative determination of
structural feature concentrations.
Figure 18. Cross-linked structures in irradiated PEI. a) General structure of cross-linked molecule (A - normal repeat unit, B,C - modified repeat units). b) Ethylene linkage. c) Amide linkage. d) Ketone-ketone linkage.
Absorption in the IR region occurs when a vibrational mode of a chemical group is excited. Rotational modes also exist in the IR region, but generally result in widening of vibrational absorption bands. For a molecule with \( n \) atoms, there are \( 3n-6 \) modes of vibration. However, not all of these vibrational modes result in absorption bands. The selection rules for IR absorption eliminate those vibrations which do not result in a periodic change in the dipole moment of a chemical group. These vibrations typically involve symmetric vibrations in chemical groups with high degrees of symmetry. Overtones and combination tone absorption bands also may appear in an absorption spectrum. Overtones are absorption bands which occur at a frequency that is a multiple of the frequency of a vibration, while combination tones occur at a frequency that is the sum or difference of the frequency of two different vibrational modes.

As an illustration, the modes of vibration for methyl and methylene groups are shown in Fig. 19. A methyl group is situated at the center of the repeat unit for PEI and a methylene group is one of the possible cross-link structures in the model for irradiated PEI. As shown in Fig. 19a, there are symmetric and asymmetric stretching vibrations in each chemical group. Fig. 19b shows the bending vibrations of the groups. Bending vibrations are classified as bending, rocking, scissoring, twisting, and wagging. Note that the bending vibrations do not all exist for each group.
Figure 19. Modes of vibration in methyl (CH$_3$) and methylene (CH$_2$) groups. a) Stretching vibrations. b) Bending vibrations [36].
Generally, absorption spectra are created by sending monochromatic light in the IR range through a sample and measuring the transmitted intensity. If the intensity of the beam entering the sample is $I_o$ and the intensity of the transmitted beam is $I$, then the transmittance of the sample is defined as $T = I/I_o$. The absorbance, $A$, of a sample of thickness $b$ is given by Beer's law,

$$A = \ln(1/T) = abc$$

where $a$ is the absorptivity of the absorbing groups and $c$ is the concentration of the absorbing groups. Maximum absorption, and therefore minimum transmittance, occurs when the frequency of the incident light matches the vibrational frequency of a chemical group. The absorptivity of absorbing groups is usually not known, thus preventing quantitative determination of bond densities. However, relative differences in bond densities can be determined by finding the ratio of absorbance for a given absorption band in different spectra.

4.3.2 MEASUREMENT TECHNIQUES

Typically, an absorption spectrum is produced by selecting a narrow band of frequencies from a broad-band source and passing this narrow band through the sample. Stepping through successive bands then produces the absorption spectrum for the complete frequency range. For this study, Fourier Transform Infrared (FTIR) spectroscopy was used. FTIR spectroscopy uses a two-arm interferometer with one moving arm and one stationary arm to prepare the source beam. This type of spectrometer is faster and
provides better resolution than diffraction grating systems [37].

The IR absorption spectra for this study were obtained using a Nicolet model 3600A FTIR® spectrometer [38]. A diagram of the components of the system is shown in Fig. 20. A Helium-Neon laser is used to locate the position of the moving arm as it travels through a scan. An elementary analysis of a signal with wavenumber \(v\) which passes through the system reveals that the intensity of the beam that reaches the detector varies in time with a frequency [39]

\[ f = 2vV \]  \hspace{1cm} (4.2)

where \(V\) is the velocity of the moving arm. At the same time, the broad band IR source, whose spectrum is shown in Fig. 21a, is passed through the same interferometer. The source signal now varies with time as different components will interfere constructively as the mirror moves creating the interferogram such as the one shown in Fig. 21b. The amplitude of this signal is further modified as it passes through the sample. The Fourier transform of this signal converts the spectrum into frequency domain (see Fig. 21c). Finally, the spectrum obtained with the sample in the beam path is ratioed to the spectrum obtained with no sample in the beam path.
Figure 20. Components of the FTIR spectrometer.
Figure 21. Infrared signal passing through FTIR optical system. a) Spectrum of source. b) Variation with time of signal emitted from interferometer. c) Fourier transform of signal from interferometer.
IR absorption spectra for non-exposed and irradiated PEI films were analyzed. The spectrum for the non-exposed material will be discussed in detail, including identification of the absorption bands in the spectrum. The changes in the absorption band intensities in the spectra for the irradiated material will then be discussed.

4.4.1 IR ABSORPTION SPECTRUM FOR NON-EXPOSED PEI

The absorption spectrum for non-exposed PEI is shown in Fig. 22. The most intense absorption peaks occur in the 1800 cm$^{-1}$ to 600 cm$^{-1}$ region. In addition, a group of low peaks appear near 3000 cm$^{-1}$. As shown in the figure, the peaks are labeled numerically from 1 to 23 according to wavenumber starting with the peak with the highest wavenumber. The chemical bonds and vibration modes which cause each absorption peak have been identified through use of standard references. These are summarized in Table 3, and will be discussed in this section.

The group of peaks which occur in the region around 3000 cm$^{-1}$ are due to vibrations in C-H bonds. Three peaks may be identified in this region. Peak 1 is due to C-H stretching in aromatic rings, but also has a contribution from C-H stretching in methylene groups (CH$_2$). Peaks 2 and 3, respectively, are due to asymmetric and symmetric C-H stretching in methyl groups (CH$_3$). The absorption bands for these
Figure 22. FTIR absorption spectrum for non-irradiated PEI. Absorption peaks are identified by numbers beginning with highest wavenumber.
<table>
<thead>
<tr>
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<th>$\nu$, cm$^{-1}$</th>
<th>Vibration Mode and Group</th>
<th>Reference (Page)</th>
</tr>
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<td>3067</td>
<td>C-H Stretch - Aromatic</td>
<td>34 (114-6), 40 (59)</td>
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<tr>
<td></td>
<td></td>
<td>C-H Stretch - Methylene</td>
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<td>1601</td>
<td>C=C In-Plane Vibration - Aromatic</td>
<td>34 (116), 40 (59)</td>
</tr>
<tr>
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<td>CH$_2$ Scissoring</td>
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<td>-CH$_2$, Asymmetric Bending</td>
<td>34 (99), 40 (57)</td>
</tr>
<tr>
<td>11</td>
<td>1358</td>
<td>C-N</td>
<td>40 (65)</td>
</tr>
<tr>
<td>12</td>
<td>1275</td>
<td>C-O-C Asymmetric Stretch - Ether Linkage</td>
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<tr>
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<td>1237</td>
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<td>14</td>
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<td>C-H In-Plane Vibration - Aromatic Sub.</td>
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<td>34 (102), 40 (57)</td>
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<td></td>
<td>C-N-C Out of Plane - Imide</td>
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<td>40 (59)</td>
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<td>23</td>
<td>626</td>
<td>C-C-C In-Plane Bend - Aromatic</td>
<td>42 (F211)</td>
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</tbody>
</table>

Table 3. Peaks in the absorption spectrum of PEI.
vibrations are normally moderate to intense. However, for PEI, the aromatic C-H vibrations are tempered by substitutions in the aromatic rings and the methyl and methylene groups are not present in large concentrations.

The most intense peak in the spectrum occurs at 1725 cm\(^{-1}\) and is labeled peak 5. This peak and peak 4, which lies at slightly higher wavenumbers, are due to coupled vibrations in the C=O groups on the imide ring. Peak 4 is due to asymmetric stretching while peak 5 is due to the symmetric mode. C=O groups are known to be strong absorbers, and some of the spectra in this study will show peak 5 to be saturated, or completely absorbing. Note that absorbance greater than 2.5 means that less than 10\% of the light from the source was transmitted by the sample.

Peaks 6, 7, and 8 are due to vibrations in the C=C bonds in the aromatic rings. These particular absorptions bands are due to in-plane vibrations and are reported to have intensities which vary with substitutions on the aromatic ring. Peak 9 is due to C=C in-plane vibrations in the aromatic rings as well. However, it also has a contribution from C-H scissoring deformation in the methylene groups. Peak 10 is due to a vibration of the methyl group and has a contribution from C=C in-plane vibration in the aromatic rings. This methyl vibration is the asymmetric bending shown in Fig. 19. Peak 11 is due to C-N stretching vibrations.

Peaks 12 and 13 are the result of stretching vibrations in the ether linkage. Peaks
at these frequencies are characteristic of C-O-C asymmetric stretching vibrations when at least one of the carbon atoms is part of an aromatic ring. As shown in reference 33 the intensities of the two peaks tend to increase with the mass associated with the second carbon atom. The fairly intense peaks in the spectrum for PEI is a good indication of the ether linkage between two aromatic rings.

The remainder of the spectrum is due mostly to C-H vibrations in the aromatic rings. Peak 14 is due to C-H vibration in di-substituted and tri-substituted aromatic rings and also has a contribution from C(CH₃)₂ skeletal vibrations and C-H vibrations in methylene. Peak 15 is also due to C-H vibrations in di- and tri-substituted aromatic rings, and also has a contribution from C-N-C stretching vibrations in the imide rings. Peaks 16 and 17 are also due to the C-H vibrations in the aromatic rings, however, peak 17 has a contribution from vibration in urethane linkages (C-O-O-C) and methylene skeletal vibrations. Peaks 18 through 22 are due to the C-H vibrations in substituted aromatic rings. Peak 19 has a peroxide contribution and peak 21 has an imide ring contribution. Finally, peak 23 is due to C-C-C bending vibrations in the aromatic rings.

4.4.2 IR ABSORPTION SPECTRA OF IRRADIATED PEI

Beer’s Law, eq. 4.1, relates the intensity of an absorption band to the concentration of the absorbing bonds in the sample. Thus, if a change in the intensity of an absorption band occurs when a sample is irradiated, the relative change in bond
concentration can be determined. It must be noted that a change in sample thickness due to irradiation could also result in a change in absorption band intensity. In this study, however, sample thickness was determined prior to irradiation and after irradiation, and no changes in sample thickness were observed.

A standard method of analysis in IR spectroscopy is to form difference spectra. The difference spectra in this study were created by subtracting the spectrum for a non-exposed sample from the spectrum for the same sample after it was exposed. Difference spectra for PEI after three absorbed doses are shown in Fig. 23. These spectra clearly show a general decrease in the absorption band intensities with increasing dose, indicating a decrease in bond concentrations. In each of these difference spectra, however, a large increase in absorption band intensity appears near 1700 cm⁻¹. This difference suggests an increase in bond concentration which did not occur. This change instead is an example of how difference spectra may be misleading. This positive change in absorption is accompanied by a decrease in absorption at slightly higher wavenumbers. This increase and decrease pair is the result of the difference between the irradiated and non-exposed absorption bands for the C=O symmetric coupled imide ring vibration (Peak 5, above). In the spectrum for the irradiated PEI, the peak was shifted slightly (on the order of 0.1 cm⁻¹) resulting in the pair of difference peaks. The actual intensities of the peaks were not drastically different. This effect can be seen throughout each difference spectrum, and thus difference spectra must be used with caution. For a more accurate investigation of the changes in the spectra, the actual changes in the peak intensities will be used.
Figure 23. Difference spectra for PEI. Difference spectra are absorption spectrum for non-irradiated PEI subtracted from spectrum for irradiated (a) 25 MGy, b) 75 MGy, and c) 100 MGy) PEI.
Rather than discussing the change in intensity of each peak, the peaks will be grouped by the chemical group that cause the absorption band. For instance, Peaks 6-8 have all been identified as C=C vibrations in the aromatic rings. It is expected that these peaks change by the same amount, although some may be sensitive to substitution on the aromatic ring. Also, peaks 16, 18, 20, and 22 are due to C-H vibrations in the aromatic rings. These peaks are expected to be sensitive to substitution. There are additional peaks which are characteristic of aromatic ring vibrations, but in the PEI spectrum these peaks may also have contributions from vibrations in other chemical groups. Groups of peaks can be identified which are due to the ether linkage (C-O-C), C=O on the imide ring, and the methyl group (CH₃). Averaging the fractional changes in the intensities of the peaks corresponding to each of these groups gives the changes in the concentration of the respective chemical groups. These changes are shown as functions of dose in Fig. 24.

None of the proposed chemical structures feature opening of the aromatic ring. The change in the C=C aromatic absorption band may be due to substitution on the aromatic rings. However, the changes in the C-H (aromatic) absorption bands are significant. These bands are sensitive to substitutions on the aromatic ring, which includes the ether linkage. The changes in the ether linkage absorption bands agree well with the changes in the C-H (aromatic) absorption bands. These results suggest cleavage of the ether linkage, resulting in phenyl and phenoxy radicals. The decay of phenyl and phenoxy radicals may result in several chemical structures. All three altered repeat units
Figure 24. Changes in IR bands for irradiated PEI.
result from combinations of phenoxyl radicals. In addition, all four branch structures involve phenoxyl radicals. It is noted that cleavage of the ether linkage is the only mechanism proposed which may lead to chain scissioning. In order for the altered repeat units to be identified, decreases in the ether linkage and aromatic substitution absorption bands must be coupled to an increase in peroxide linkage absorption bands. The peroxide linkage appears in peaks 17 and 18 of the PEI spectrum. Both of these peaks have contributions from C-H (aromatic) absorption and peak 17 has a contribution from CH$_2$ skeletal vibrations. As the change in CH$_2$ density has not yet been determined, peak 17 does not contribute to the estimate of peroxide linkage density. Peak 19 decreased in amplitude by an amount that was slightly greater than the change in the C-H aromatic bands. This suggests that there is no significant formation of peroxide linkages.

The opening of the imide ring, which is indicated by the decrease in the C=O imide absorption band, leads to carbonyl radicals. The urethane branch structures are formed through combinations of phenoxyl radicals with carbonyl radicals. While the formation of significant quantities of these radical species is evident from the decrease in the respective absorption bands, there is no absorption peak which indicates the formation of these particular branch structures. Carbonyl radicals may also form cross-link structures through combination of two carbonyl radicals to form a ketone-ketone cross-link or through combination of a carbonyl with a gem-dimethyl radical to form an amide cross-link.

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Gem-dimethyl radicals are the result of the removal of a hydrogen atom from a methyl group. The decrease in methyl vibrations is responsible for the largest decrease in absorption band, as shown in Fig. 24. The gem-dimethyl radicals may be incorporated into several structures. The ether branch structures are formed through the combination of a gem-dimethyl radical with phenoxy radicals. The amide cross-link structure is formed through reaction of gem-dimethyl radicals with carbonyl radicals. The remaining cross-link structure, the ethylene structure, is formed through the combination of two gem-dimethyl radicals.

Determining changes in the concentration of methylene groups, which are part of two of the branch structures and two of the cross-link structures, requires analysis of absorption peaks which are due to more than one chemical group. Peaks 1, 9, 14, and 17 have contributions from methylene vibrations. Peak 1 is of little use due to its low amplitude. Peak 9 has a contribution from \( \text{C} = \text{C} \) aromatic vibrations, and shows decreases in amplitude slightly greater than those for the \( \text{C} = \text{C} \) aromatic bands as shown in Fig. 24. Peak 17 has a contribution from \( \text{C} - \text{H} \) aromatic vibrations, which can be compared to the absorption band changes in Fig. 24, but also has a contribution from peroxide linkage vibrations, the changes in which are not yet determined, as discussed above. This leaves peak 14, which is due to \( \text{C} - \text{H} \) aromatic vibrations and skeletal vibrations in methyl groups in addition to the methylene vibrations. This peak increased in amplitude for each absorbed dose. As the \( \text{C} - \text{H} \) aromatic and methyl absorption bands both decreased with dose, the change in peak 14 must be indicative of an increase in
methylene concentration.

4.5 CROSS-LINK AND CHAIN SCISSION DENSITIES IN IRRADIATED PEI

In the above discussion, the chemical groups involved in the formation of cross-links and chain scissions in PEI were identified. The changes in the IR spectrum suggest that chemical modifications involving methylene groups occur as a result of irradiation. While the concentrations for the specific chemical structures of the four involving methylene cannot be determined, an upper bound on the number of cross-links formed can be determined. As the formation of a cross-link involving methylene requires the loss of at least one methyl group, the number of methyl groups lost may be used as an upper bound to the number of cross-links formed. It is noted that the greatest source of error in this estimate is that two of the possible structures formed are branch structures while the remaining two are true cross-links.

At the same time, the only mechanism for chain scissioning identified above is cleavage of the ether linkage. Therefore, the number of ether linkages lost may be used as an upper bound to the chain scission density. This estimate is expected to be accurate. Several chemical structures may result from cleavage of the ether linkage. These include altered repeat units and branch structures. However, the formation of altered repeat units and branch structures involve the phenoxy radical and not the accompanying phenyl radical. The phenyl radicals are expected to decay through capture of hydrogen radicals.
thus forming a chain end. Thus, each ether linkage broken results in at least one chain end.

The cross-link density and chain scission density are shown in Fig. 25. The values plotted are the upper bounds as discussed above. It is of interest that the cross-link density is greater than the chain scission density for all doses. However, the effect of each product on the $T_g$ has not yet been investigated. The figure shows that the cross-link density increases with dose for all doses investigated. The chain scission density, however, increases with dose for doses up to 75 MGy, and decreases for doses greater than 75 MGy. The difference in the densities will be investigated in the following chapter.
Figure 25. Cross-link density and chain scission density in PEI as a function of dose.
CHAPTER 5
RADICAL FORMATION AND DECAY

In the previous chapter, the cross-link density and chain scission density were determined as functions of dose. The cross-link density increased with increasing dose, while the chain scission density increased for low doses, reaching a maximum in the 75-MGy dose region, and decreased for higher doses. See Fig. 25. This behavior is the subject of the present chapter, in which radical population kinetics in irradiated PEI will be correlated with the observed cross-link density and chain scission density.

5.1 RADICAL FORMATION AND DISTRIBUTION

Radicals are formed in polymers when chemical bonds are broken, leaving atoms with unpaired electrons. Energetic electrons passing through a polymer undergo coulomb collisions with atomic electrons resulting in excitation and ionization of the atom. These excitations and ionizations may result in the formation of radicals. The energy transferred from an incident electron to a bound electron during a coulomb collision is

\[
\Delta E = \frac{2k^2e^4}{mv^2} \frac{1}{b^2}
\]  

(5.1)

where \( k \) is the coulomb force constant, \( m \) and \( e \) are the mass and charge, respectively,
of an electron, \( v \) is the velocity of the incident electron, and \( b \) is the impact parameter for the collision. This can be used to find the cross section for a collision of a given energy transfer,

\[
\sigma = \pi b^2 = 2\pi \frac{k^2 e^4}{\beta^2 m c^2} \frac{1}{\Delta E}
\]

(5.2)

where \( \beta = v/c \) has been used. Also, the angle of deflection of the incident electron is

\[
\Theta \approx \sqrt{\frac{\Delta E}{E}}.
\]

(5.3)

If the energy transferred is just enough to ionize the atom, then eq. 5.2 gives the maximum cross section for ionization. The mean ionization potentials for the elements in PEI are given in Table 4. Note that the ionization potentials depend on the chemical state of the element. In this table, "saturated" indicates that the ionization potential is for atoms in chemical groups with no double bonds while "unsaturated" indicates that the chemical group features double bonds. It is noted immediately that for transfers of energy on the order of the ionization potential the angle of deflection of the incident electron, as calculated by eq. 5.3, is on the order of one degree. Therefore, it is expected that the primary electron passes through the material with little deviation from a straight trajectory. Also shown in Table 4 are the concentrations of each element and the maximum cross sections for ionization as calculated by eq. 5.2. These data can be used to calculate the mean cross section for ionization in PEI. The mean cross section for ionization in PEI by a 0.1 MeV electron is \( 5.60 \times 10^{-20} \text{ cm}^2 \), which would suggest a mean free path for an incident electron of \( 2.00 \times 10^{-4} \text{ cm} \). This analysis does not account
<table>
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<tr>
<th>Element</th>
<th>Z</th>
<th>Chemical State</th>
<th>$I$ (eV)</th>
<th>$N$ ($10^{21}$ cm$^{-3}$)</th>
<th>$\sigma$ ($10^{20}$ cm$^2$)</th>
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<tr>
<td>H</td>
<td>1</td>
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<td>7.76</td>
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<td></td>
<td></td>
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<td>13.0</td>
<td>23.3</td>
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<td>46.5</td>
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<td></td>
<td></td>
<td>=O</td>
<td>79.8</td>
<td>5.17</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 4. Ionization potentials, $I$, number densities, $N$, and maximum cross sections, $\sigma$, for ionization of elements in PEI.
for collisions in which the energy transfer is greater than the ionization potential, which may result in free electrons, nor does it account for collisions resulting in excitation. Each of these types of collisions may also lead to radical formation.

To account for the total loss of energy to ionization and excitation the stopping power must be considered. Bethe's expression for the stopping power (relativistic form) for an electron with energy $E$ and velocity $v$ is

$$S = \frac{2\pi Ne^4Z}{m_e v^2} \left[ \ln \frac{m_e v^2 E}{2l(1-\beta^2)} - \frac{(2\sqrt{1-\beta^2} - 1 + \beta^2)\ln2 + 1 - \beta^2 + \frac{1}{8}(1 - \sqrt{1 - \beta^2})^2}{2} \right]$$  \hspace{1cm} (5.4)$$

where $S$ is the energy lost per unit path length [43]. Here, $N$ is the number of atoms per unit volume, $e$ is the electron charge, $Z$ is the average atomic number of the absorbing material, $m_e$ is the rest mass of the electron, and $l$ is the mean excitation potential for the absorbing atoms. The stopping power includes losses to ionization as well as excitation. For a 0.1 MeV electron passing through PEI the stopping power is 5.83 MeV/cm. In Chapter 2, a Monte Carlo simulation was used for dosimetry purposes. It is noted that the simulation found that the energy deposited by a 0.1 MeV electron in PEI was 5.33 MeV/cm, which agrees well with the result using eq. 5.4. If it were assumed that the average energy transferred is on the order of the mean excitation potential for the atoms in the material, the stopping power gives a mean free path of $1.2 \times 10^5$ cm, or approximately $8.3 \times 10^4$ collisions per cm.

To estimate how many of these collisions result in radical formation, the track of
the electron must be investigated. As the incident electron loses energy, it creates a path of excited and ionized atoms and molecules in the irradiated material. See Fig. 26. Excited states are produced when bound electrons absorb energy and are raised to a higher energy level. Ionization occurs when an electron absorbs sufficient energy to be expelled from the parent atom or molecule. Ionization may also occur subsequent to excitation. The ejected electrons, called secondary electrons, may have sufficient energy to cause additional atoms to become excited and ionized. For low secondary electron energy, less than 100 eV, a small cluster of 4 to 6 excited and ionized atoms, called a spur, may be formed near the path of the primary electron. Spurs result from approximately 50% of all collisions. Approximately 2 to 4% of secondary electrons will have enough energy to travel significant distances from their origins, creating their own tracks. These secondary electrons are called δ-rays and are responsible for producing about one-half of all ionizations resulting from each primary electron [44]. The tracks of these δ-rays are described as blobs, short tracks, and branch tracks for secondary electrons of energy 100 to 500 eV, 500 eV to 5 keV, and greater than 5 keV, respectively. The neutralization of the ionized atoms and the de-excitation of the excited atoms may result in the formation of radicals. Using the number of collisions per electron, calculated above, the description of the track suggests that $4.16 \times 10^5$ radicals/cm are created as a 0.1 MeV electron passes through PEI.
Figure 26. Diagram of track of an energetic electron through matter. Radicals are formed in spurs, blobs, short tracks or along branch tracks depending on the energy transferred to the secondary electron [44].
This result can be used to find the rate at which radicals are created in PEI. For an incident flux of $2.0 \times 10^{11} \text{ cm}^2\text{s}^{-1}$, the rate of radical formation is $8.32 \times 10^{16} \text{ g m}^{-1}\text{s}^{-1}$. Cross-links are formed when these radicals react to form new bonds, and thus the rate at which these radicals decay must be determined.

5.2 RADICAL DECAY RATES

The rates for radical decay may be obtained from the literature. As mentioned in Chapter 2, EPR was used to identify the radical species in irradiated PEI. EPR was also used in reference 9 to determine the total number of radicals per gram of material. This density, determined as a function of time was used to determine decay rates for radicals in PEI. The decay kinetics determined in this manner are the overall radical decay kinetics, not the kinetics for each radical species. For example, a Gem-dimethyl radical may decay four ways; hydrogen capture to form a methylene pendant group, reacting with another Gem-dimethyl radical to form a cross-link, reacting with a ketone radical to form a cross-link, or reacting with a phenoxy to form a branch. Each mode is expected to have a separate rate of reaction. The decay rates for each mode of Gem-dimethyl decay along with those for each other radical species combine to give the overall rate for radical decay in the material, which is the rate determined from the EPR results.

Radicals generally decay following first-order or second-order reaction kinetics, although higher-order kinetics are possible. First-order kinetics are such that the rate of
radical decay is proportional to the density of radicals, \( N \), such that

\[
\frac{dN}{dt} = -k_1 N
\]  (5.5)

where \( k_1 \) is a constant. This can be integrated to give the radical density as a function of time,

\[
N = N_0 \exp(-k_1 t)
\]  (5.6)

where \( N_0 \) is the radical density at \( t = 0 \). Second-order reaction kinetics are such that the rate of radical decay is proportional to the square of the radical density,

\[
\frac{dN}{dt} = -k_2 N^2
\]  (5.7)

where \( k_2 \) is a constant. For second-order reaction kinetics, the radical density is given by

\[
\frac{1}{N} = \frac{1}{N_0} + 2k_2 t.
\]  (5.8)

For small molecules, the first-order kinetics and second-order kinetics are for reactions between like molecules and reactions between different species of radicals, respectively. However, for the case of a radical attached to a polymer chain, the radical can only migrate through the material to react with another radical if the entire molecule diffuses through the material. It was shown by de Gennes that the reaction constant for radicals attached to polymer chains in a melt depends on \( N^2 \) [45]. Thus, second-order reaction kinetics may be expected for radicals which involve chain diffusion.
The hydrogen radicals formed in irradiated PEI in conjunction with the formation of Gem-dimethyl radicals demand special consideration as these radicals are not attached to molecular chains and may travel through the material. Treating the motion of the hydrogen radical as a random walk, the mean square distance travelled in a time $t$ is

$$X^2 \approx Dt$$

(5.9)

where the diffusion coefficient, $D$, may be calculated from the thermal energy and is approximately $6 \times 10^{-7}$ m$^2$/sec at 300 K. EPR studies give a radical density on the order of $10^{18}$ gm$^{-1}$ at the conclusion of an exposure giving a 100-MGy dose [47]. Thus, the mean distance between radicals is on the order of $10^8$ m. The time for a hydrogen radical to cross this distance by random walk is on the order of $10^{-10}$ sec, much less than the time between exposure and radical density measurement. Even with a radical density as low as $10^{15}$ gm$^{-1}$, the time for migration is on the order of $10^8$ sec. Thus, hydrogen radicals are expected to decay prior to radical density measurements and, in fact, were not observed in the EPR spectrum.

The overall decay constants for radicals may be determined by examining the radical density as a function of time. The radical density in PEI after exposure to a 2.5-MGy dose of electron radiation as determined by Long, et. al., is shown in Fig. 27 [9]. Here, the rapid decrease in radical density immediately following the exposure may be modeled with second-order kinetics with $k_2 = 1.02 \times 10^{17}$ gm/hr. The long-term decay follows first-order decay kinetics with constant $k_1 = 0.086$ hr$^{-1}$. Again, these decay rates apply only to those radical species that appear in the EPR spectrum.

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Figure 27. Radical density in PEI as a function of time after exposure as measured by EPR. Exposure was to 0.1 MeV electrons for a dose of 2.5 MGy at 10 MGy/hr [9].
5.3 RADICAL DENSITY CALCULATIONS

The rates of radical density and decay may be used to simulate the radical population in PEI during and after irradiation. The change in the radical population in a time $\delta t$ is

$$\delta N = C_0 t - k_1 N \delta t - k_2 N^2 \delta t$$

(5.10)

where $C$ is the rate of radical formation, which becomes zero at the end of the exposure, $k_1 N$ is the first-order decay rate, and $k_2 N^2$ is the second-order decay rate. These decay rates were discussed above, but more consideration must be taken when interpreting their meaning. The rate found above is calculated from the stopping power which includes interactions with all atoms in the material. The radical decay rates were determined through EPR and only apply to those radicals which appear in the EPR spectrum. This excludes radical species which decay quickly, such as hydrogen radicals, and can not distinguish between the modes of decay for radicals that were identified. While it is feasible to estimate the missing decay rates, for this study the rate of radical formation will be reduced, thus giving a lower bound to the actual radical population.

A simulation of the radical density based on eq. 5.10 for an exposure to a dose of 2.5 MGy at 10 MGy/hr is shown in Fig. 28. The initial radical population was taken to be $7 \times 10^{14} \text{ gm}^{-1}$, as reported in reference 9. The conditions of this simulated exposure were the same as the exposure which resulted in the data of Fig. 27. The rate of radical formation for the simulation was chosen so that the simulated radical density 3 minutes
Figure 28. Simulation of radical density during and after exposure to 0.1-MeV electron radiation for a dose of 2.5 MGy.
after the end of the exposure matched the radical density reported from EPR measurements taken 3 minutes after the exposure.

Simulations of radical densities for doses up to 100 MGy were performed using the same formation and decay constants. Of interest from these simulations was the number of radicals created and the number of radicals which decayed. These quantities were summed during the simulations from the beginning of the exposure until 10 hr after the exposure. From these results, the total number of radicals which were created and which decayed can be determined as a function of dose, which is shown in Fig. 29. It can be determined from the figure that the number of radicals decaying through second-order decay is approximately 10 times greater than the number decaying through first-order decay. In fact, about 90 percent of all radicals created decayed through second-order decay processes. Once again, the radical densities in Fig. 29 are lower bounds to the actual radical densities.

An upper bound to the radical density may be found by considering the production of radicals. It was determined above that a 0.1 MeV electron passing through PEI creates $4.16 \times 10^5$ radicals/cm. The maximum number of radicals created during each exposure is the product of the number of radicals created per electron and the number of incident electrons. This estimate does not take into consideration the number of radicals which decay or the decay modes. This estimate gives an upper bound to the radical density.
Figure 29. From radical population simulations, total radicals created and total radicals decayed through first-order and second-order decay modes for doses up to 100 MGy.
5.4 RADICAL DENSITY AND IRRADIATION PRODUCTS DENSITIES

Radicals created through irradiation decay to form the structures discussed in Chapter 4. Cross-links are formed when two radicals which are on pendant groups react to form a bond, while chain scissions form when radicals react to form a terminal group. The results of Chapter 4 showed that in PEI, the cross-link density increased with dose, while the chain scission density increased to a maximum near 75 MGy and decreased for higher doses.

From the radical density, the mean separation of the radicals can be calculated. The upper bound to the radical density gives the lower bound to the radical separation, while the lower bound to the radical density gives the upper bound to the radical separation. It is of interest to compare these distances to the dimensions of the molecules. The repeat unit density for PEI is $1.29 \times 10^{21}$ cm$^{-3}$. Using a typical free volume fraction of 0.025 [48], each repeat unit occupies $7.6 \times 10^{-22}$ cm$^3$. The repeat unit volume can be modeled by a cylinder with a diameter-to-length ratio of 5 to 23. This analysis gives a mean radial separation between repeat units of 9 Å. In Fig. 30, the ratio of the average radical separation to the repeat unit separation is plotted as a function of dose. In the figure, the ratio of average radical separation to repeat unit separation decreases with dose. The lower bound is clearly a low estimate, as the radical separation can not be less than the repeat unit spacing. A simple approach is to discuss the average of these 2 values, which is also shown in Fig. 30. The turning point in the chain scission density-
Figure 30. Ratio of average radical separation to radial repeat unit separation as a function of dose. Shown are the upper bound, lower bound, and average values.

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dose curve corresponds to an average radical separation of slightly less than three times the molecular spacing. This suggests that reactions between radicals occurs more readily for radicals that are separated by less than three molecular diameters.
CHAPTER 6
MODEL FOR RADIATION EFFECTS ON THE $T_g$ OF PEI

In this chapter, a model for the change in the $T_g$ of PEI with radiation dose is presented. Separate theoretical models for the dependence of the $T_g$ of polymers on cross-linking and on chain scissioning have been proposed in the literature [49]. In the model presented below, these theories are combined to give the change in the $T_g$ which results from simultaneous changes in cross-link density and chain scission density which may occur as a result of irradiation. The model treats the formation of cross-links and chain scissions as separate and independent, which is expected for the dose levels investigated. The models for each effect will be presented followed by the considerations for combining the models.

6.1 EFFECT OF CROSS-LINKING ON $T_g$

Cross-links alter the $T_g$ of a polymer by restricting the ability of the molecules to move to different conformations. To develop a model for the effect of cross-links on the mobility of a molecule, a statistical-mechanical model for a system of many chains must be developed. The basis for these models is known as the Meyer-Flory-Huggins lattice model [50]. The model features $N_z$ chains, each with $x$ segments, which are placed on
a lattice such that at most one segment occupies a lattice site. The segments may be in one of the two energy states described in Chapter 1, the high-energy gauche conformation, or the low-energy trans conformation. A fraction, $f$, of the segments are in the upper energy state and the remainder are in the lower energy state. The rotational state of a segment is defined with respect to the previous two segments, and the end segments are always in the lower energy state. Therefore, the statistics must be applied to $x-3$ segments per chain [51]. In addition, sites are permitted to be unoccupied, appearing as holes in the material. Thus, the lattice contains $fN_x(x-3)$ gauche bonds with energy $e_2$, $(1-f)N_x(x-3)$ trans segments each with energy $e_1$, and $n_0$ holes. The holes each have energy $E_h = z e_h s/2$, which is the energy required to overcome the Van der Waals interaction energy between segments in adjacent chains to form a vacancy [52]. Here, $z$ is the valence of the atoms which form the main chain bonds, $e_h$ is the energy of interaction between two segments, and $s$ is the fraction of occupied sites.

The partition function for such a system is

$$Q = \sum_{W} W(f,n_0) \exp\left[ -\frac{f(x-3)N_x e_2 + (1-f)(x-3)N_x e_1 + z e_h n_0 s/2}{kT} \right]$$

(6.1)

where $W(f,n_0)$ is the number of ways the $N_x$ chains can be placed on a lattice of $xN_x+n_0$ sites when $f(x-3)N_x$ segments are flexed and there are $n_0$ holes. The summation is over all possible values of $W(f,n_0)$, so that that the partition function is a summation over all possible configurations of the system.
The function $W(f, n_0)$ was evaluated by Flory [53] and is

$$W(f, n_0) = \frac{(xN_x + n_0)z^{2N_x + zN_0}[(z-2)x+2]N_x + zn_0!(z-1)^N_x(2x-3)N_x}{(n_0)!(xN_x + n_0)2^{2N_x}(N_x)!(1-f)(x-3)N_x!/[f(x-3)N_x]!}.$$ (6.2)

While this model makes many approximations of the details of the structure of polymers, it may be used to predict features of the thermal behavior of polymers. In particular, the glass transition occurs when the configurational entropy, $S_c$, vanishes. The configurational entropy is the entropy associated with the possible arrangements of the system, and is proportional to the natural logarithm of the partition function. While the statistical model of polymers predicts a second order transition when $S_c$ vanishes, it does not accurately predict the temperature at which the transition occurs. However, the model accurately relates changes in the $T_g$ to changes in the chemical structure of polymers, such as cross-linking.

As it is the configurational entropy which vanishes at the $T_g$, the effect of cross-linking on $S_c$ must be determined. If the addition of cross-links causes a change, $\Delta S$, in the configurational entropy, then the $T_g$ occurs when

$$S_c = S_0 + \Delta S = 0$$ (6.3)

where $S_0$ is the configurational entropy for the chain prior to the addition of cross-links.
Gibbs and DiMarzio [54] found the entropy for a polymer with no cross-links to be

\[ S_0 = kxN_s \left[ \ln(1+2\exp(-\Delta \varepsilon/kT)) + \frac{\Delta \varepsilon}{kT} - 1 + \frac{T\Delta \alpha}{1 + 2T\Delta \alpha} \right] \]  

(6.4)

where \( k \) is the Boltzmann constant, \( \Delta \varepsilon \) is the energy difference between the two conformational states, and \( \Delta \alpha \) is the difference in thermal expansion coefficient for the polymer above and below the \( T_g \).

The change in entropy, \( \Delta S \), due to cross-linking is found by counting the number of ways to arrange a chain when the ends of the chain are fixed to lattice sites. DiMarzio [54] found that fixing the ends of a chain modifies the number of arrangements possible by a factor of

\[ \frac{b^3}{\pi^{3/2}} \exp(-b^2 r^2) dr \]  

(6.5)

where

\[ b^2 = \frac{3}{2} \frac{1}{nL^2} \]  

(6.6)

Here, \( r \) is the end to end distance for the chain, \( L \) is a multiple of the segment length, the multiplication factor accounting for the effect of flexing bonds, and \( n \) is the number of effective lengths. The volume of a lattice site is \( d \tau \). This factor modifies the possible
arrangements for each chain, so that for the system

\[ \exp\left(\frac{S}{k}\right) = \exp\left(\frac{S_0}{k}\right) \prod_i b_i^3 \exp\left(-b_i r_i^2\right) d\tau \sqrt{\frac{V(N_p)}{d^3}} \]  

(6.7)

where \( N_p \) is the number of chains between cross-links. The factor under the radical is a correction to the volume of the lattice site that accounts for limited motion of the cross-link sites.

From this analysis, the second-order transition for the cross-linked material occurs when

\[ \frac{S_c}{k x N_x} = \ln(1 + 2 \exp(-\frac{\Delta \varepsilon}{kT})) + \frac{\Delta \varepsilon}{kT} - 1 + \frac{T \Delta \alpha}{1 + 2 T \Delta \alpha} - \frac{3}{2} X + \frac{3}{4} X \ln(f) + \frac{3}{4} X \ln(A f X) \]

(6.8)

The cross-link density, \( X \), is defined as the number of moles of chains per mole of segments.

Eq. 6.8 can be simplified by several approximations (see reference 54) to give

\[ \frac{T(x) - T(0)}{T(0)} = \frac{K M x / \gamma}{1 - K M x / \gamma} \]

(6.9)

where \( x \) is the number of cross-links per gm, and \( T(x) \) and \( T(0) \) are the \( T_g \)'s for the material with cross-links and the material with no cross-links, respectively. Also, \( M \) is the molecular weight of a repeat unit, \( \gamma \) is the number of rotatable bonds per repeat unit, and \( K = 1.3 \times 10^{-23} \) is a constant that is independent of material. For PEI a new
constant,

\[ C_1 = KM/\gamma = 4.81 \times 10^{-22} \text{gm} \quad (6.10) \]

is defined. This model was originally proposed as a model for cross-linking through the addition of chemical agents. However, there is no basis for excluding its application to systems in which the cross-links result from reactions between radiation-induced radicals.

Also an issue for radiation studies is the effect of chain scissioning. It is noted that the parameters which describe the length of the chain, \( x \) and \( N_x \), always appear as a product in the statistical model. The same product appears if the chains are subdivided without losing any segments. Thus, this model is not sensitive to the effects of chain scissioning, and a separate model must be found for the effects of chain scissioning on \( T_g \).

6.2 EFFECT OF CHAIN SCISSIONING ON \( T_g \)

Chain scissioning causes changes in the \( T_g \) as a result of the greater free volume associated with a chain end. If a chain end has an associated free volume, \( v \), then the free volume contribution from all chain ends is

\[ V_c = v \frac{2\rho N_u}{M} \quad (6.11) \]

where \( \rho \) is the density of the material and \( M \) is the molecular weight. This is the increase in free volume created when a material of infinite molecular weight is scissioned to form...
a material of molecular weight, $M$. The $T_g$ occurs when there is sufficient free volume for molecular motion to occur. For the $T_g$ to occur for the scissioned material and for the material with infinite molecular weight at the same free volume [55], the $T_g$ must shift an amount

$$T_{gI} - T_g = \frac{\nu 2pN_a}{\alpha M} = \frac{K'}{M}$$

(6.12)

where $T_{gI}$ is the transition temperature for the non-scissioned material and $\alpha$ is the coefficient of thermal expansion for the material above the transition. Thus, if the molecular weight is changed through scissioning from $M_0$ to $M$, the shift in $T_g$ is

$$\Delta T_g = K' \left( \frac{1}{M} - \frac{1}{M_0} \right) = -\frac{K'S}{M_0}$$

(6.13)

where

$$S = \frac{M_0}{M} - 1$$

(6.14)

is the number of chain scissions per original molecule. For a liquid polymer, $\alpha \approx 5 \times 10^{-4} \, ^\circ C^{-1}$. The volume of a chain end in PEI can be approximated as the volume occupied by the groups near the chain scissions and is approximately $150 \, \text{Å}^3$. Thus, for PEI, $K' \approx 4.6 \times 10^5 \, \text{g}^{\circ} \text{Cmol}^{-1}$.

6.3 COMBINED EFFECTS

In order to determine the combined effects of cross-linking and chain scissioning
on the $T_g$ of PEI, these two models must be combined. The two structural features are
different in nature. Therefore, their effects on the $T_g$, to a first approximation, should
be independent. To be treated as independent, the models require that the cross-link
density and chain scission density be low enough that the length of the chains between
cross-links is much greater than the cross-link itself. Also, the cross-links and chain
scissions must be sufficiently separated that the site of the scission appears as a chain end
rather than a side group. This should hold for the present study, as the number of cross­
links and chain-scissions per molecule are less than the number of repeat units per
molecule.

If these criteria hold, than the net change in $T_g$ is

$$\Delta T_g = \frac{C_1x}{1-C_1x}T(0) - \frac{K'S}{M_0}.$$  
(6.15)

This function is plotted in Fig. 31, along with the observed values. For the theoretical
curves, the functions for the cross-link density, $x$, and chain scission density, $S$, were the
experimental results from Chapter 4. The calculated values agree well with the observed
changes for the 25-MGy and 100-MGy doses. At 75 MGy, however, the calculation
indicated a substantial decrease in $T_g$ while no change was observed experimentally.
Figure 31. Change in $T_g$ as a function of dose. Theoretical curve was calculated using experimental values for the cross-link and chain scission densities.
CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

This objective of this study was to determine the effects of electron radiation on the $T_g$ of PEI. The results include a characterization of the changes in the $T_g$ as a function of absorbed dose which showed that the change in $T_g$ is not linear with dose, but rather indicate that there is a threshold dose, approximately 75 MGy, above which significant change occurs. Measurements of the cross-link density and chain scission density also revealed that cross-links are created in amounts which increase linearly with dose, while it is the chain scission density which behaves differently above the threshold dose. These results show that detailed investigation should be conducted prior to using the $T_g$ as a diagnostic tool for the determination of radiation effects on a polymer.

The understanding of the mechanisms for cross-linking and chain scissioning have been advanced through this study as well. The results herein suggest that cleavage of the ether linkage leads to chain scissioning, while dehydrogenation of the methyl pendant group followed by formation of an ethylene bridge through reaction of two gem-dimethyl groups is the dominant mode for cross-link formation. Once an understanding of these mechanisms is achieved, simplified models of the molecules may be used to model properties of the polymer.
The changes in $T_g$ were modeled using quantitative models for the separate effects of cross-linking and chain scissioning. The effects of cross-links were modeled using a statistical-mechanical model of a chain with two rotational potential energy states, while the effects of chain scissioning could be understood using a free volume model. Combining the two models yielded changes for the empirically determined levels of cross-linking and chain scissioning which agreed with the measured changes of $T_g$ with dose. This model, although in agreement with the measurements, predicted changes which had associated with them large uncertainties, which stemmed from the spread in the data for the cross-link and chain scission densities.

Further study of the cross-link density and chain scission density in irradiated PEI should be conducted to reduce the uncertainty in the theoretical values for the change in $T_g$. Additional measurement of these densities and of the $T_g$ should be made at intermediate doses in order to accurately determine the threshold dose. Additional measurements of the same quantities for doses greater than 100 MGy should be made to determine if the trends indicated for doses greater than the threshold dose continue. Also, studies which include higher doses may determine the cross-link and chain scission densities at which the statistical model and the free volume model cannot be treated independently.

Finally, this study should be extended to polymers other than PEI in order to determine if the three-molecular-radii radical separation is indeed significant in the
formation of chain scissions in other polymers. Investigation of this result may, in addition, provide information as to the influence of polymer chain dynamics on radical reactions.
LIST OF REFERENCES


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## APPENDIX A

### GLOSSARY

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-transition</td>
<td>A transition which occurs in polymers and involves the crankshaft-like rotation of a segment of the chain.</td>
</tr>
<tr>
<td>Additive</td>
<td>A substance added to another substance usually to modify it’s properties: Filler.</td>
</tr>
<tr>
<td>Aliphatic</td>
<td>Backbone structures which feature atoms in a single chain.</td>
</tr>
<tr>
<td>Altered structures</td>
<td>Repeat units which have been altered by the radiation without forming a cross-link or chain scission.</td>
</tr>
<tr>
<td>Amorphous Polymer</td>
<td>A polymer with molecules that are randomly entangled.</td>
</tr>
<tr>
<td>Anisotropic materials</td>
<td>Materials which have properties which depend on the orientation of the sample.</td>
</tr>
<tr>
<td>Aromatic</td>
<td>Backbone structures which feature Benzene ring structures.</td>
</tr>
<tr>
<td>Backbone</td>
<td>The chain of atoms in a polymer which are connected to form a continuous chain.</td>
</tr>
<tr>
<td>Branch track</td>
<td>The track of an electron ejected from its parent atom.</td>
</tr>
<tr>
<td>Branched repeat unit</td>
<td>A repeat unit which connects to more than two other repeat units.</td>
</tr>
<tr>
<td>Chain Scissioning</td>
<td>Permanent cleavage of a bond in the backbone of a polymer.</td>
</tr>
<tr>
<td>Chemical isomer</td>
<td>A repeat unit which is oriented in a different configuration from others by virtue of a chemical bond.</td>
</tr>
<tr>
<td>Configuration</td>
<td>The arrangement of atoms in a molecule.</td>
</tr>
<tr>
<td>Configurational entropy</td>
<td>The entropy associated with the number of possible arrangements of the molecules in a polymer.</td>
</tr>
<tr>
<td>Conformation</td>
<td>A shape which a single polymer molecule may achieve without being modified chemically.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
</tr>
<tr>
<td>Consolidation</td>
<td>In thermoplastic composites, a process in which fiber and matrix are compressed to reduce voids and achieve desired density.</td>
</tr>
<tr>
<td>Covalent Bond</td>
<td>A chemical bond formed when one or more pairs of valence electrons are shared between two atoms, resulting in stable electron shells.</td>
</tr>
<tr>
<td>Creep</td>
<td>The change in dimension of a material under a constant load and temperature over a period of time, not to include the initial instantaneous deformation.</td>
</tr>
<tr>
<td>Cross-linking</td>
<td>Formation of a bond between adjacent segments of separate molecules.</td>
</tr>
<tr>
<td>Crystalline Polymer</td>
<td>A polymer with molecules which are arranged in a regular lattice structure.</td>
</tr>
<tr>
<td>Degree of Polymerization</td>
<td>Number of structural units, or repeat units, in a polymer molecule.</td>
</tr>
<tr>
<td>Direct Ionizing Radiation</td>
<td>Radiation which causes ionization by itself, that is, it does not require the formation of secondary particles to cause ionization.</td>
</tr>
<tr>
<td>Double Covalent Bond</td>
<td>Covalent bond in which two pairs of valence electrons are shared.</td>
</tr>
<tr>
<td>Dynamic Mechanical Analysis (DMA)</td>
<td>A characterization method which involves sinusoidally deforming a sample and measuring the energy dissipated.</td>
</tr>
<tr>
<td>End Cap</td>
<td>The chemical group which terminates a polymer chain.</td>
</tr>
<tr>
<td>Fiber Reinforcement</td>
<td>A fibrous material used to reinforce a plastic material.</td>
</tr>
<tr>
<td>Filler</td>
<td>A substance added to another substance usually to modify its properties; Additive.</td>
</tr>
<tr>
<td>Free Volume</td>
<td>That volume within the bulk of a material not specifically occupied by the molecules.</td>
</tr>
<tr>
<td>Freely jointed chain</td>
<td>A model of a polymer chain in which the bond angle is randomly chosen.</td>
</tr>
<tr>
<td>Freely rotating chain</td>
<td>A model of a polymer chain in which the rotation angle is chosen randomly.</td>
</tr>
<tr>
<td>Functionality</td>
<td>The number of reactive functional groups in a molecule.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Glass Transition</td>
<td>The reversible change in an amorphous polymer from a hard condition to a rubbery condition or from a rubbery condition to a hard condition.</td>
</tr>
<tr>
<td>Glass Transition Temperature ($T_g$)</td>
<td>The temperature at which the glass transition occurs.</td>
</tr>
<tr>
<td>Glassy Solid</td>
<td>A material below its glass transition temperature; has the characteristics of being hard and relatively brittle.</td>
</tr>
<tr>
<td>Hole</td>
<td>An unoccupied lattice site.</td>
</tr>
<tr>
<td>Indirect Ionizing Radiation</td>
<td>Radiation which causes the formation of secondary particles which cause ionization.</td>
</tr>
<tr>
<td>Injection molding</td>
<td>A processing technique which involves forcing a polymer into a mold using high pressure.</td>
</tr>
<tr>
<td>Ionizing Radiation</td>
<td>Radiation which results in the ionization of the target medium.</td>
</tr>
<tr>
<td>Isomeric Repeat Unit</td>
<td>Repeat units which have the same chemical structure as others in a polymer chain, but have different orientation on the chain (chemical isomerism), or differ by a rotation about a bond (stereo isomerization).</td>
</tr>
<tr>
<td>Kapton</td>
<td>A polyimide with excellent high temperature and radiation resistance.</td>
</tr>
<tr>
<td>Lamina</td>
<td>A single layer which may be part of a series of lamina, forming a Laminate.</td>
</tr>
<tr>
<td>Lattice</td>
<td>In polymer physics, a region of space which may contain, at most, one segment if a polymer chain.</td>
</tr>
<tr>
<td>Macromolecule</td>
<td>A molecule with a very high molecular weight; Polymer.</td>
</tr>
<tr>
<td>Main Chain</td>
<td>The primary chain of atoms in a polymer molecule; Backbone.</td>
</tr>
<tr>
<td>Matrix</td>
<td>The resin material in which fibers are imbedded to form a composite.</td>
</tr>
<tr>
<td>Melt Temperature</td>
<td>The temperature at which a polymer changes from a solid to a liquid.</td>
</tr>
<tr>
<td>Methyl group</td>
<td>CH$_3$.</td>
</tr>
<tr>
<td>Network</td>
<td>The interconnecting branches formed by a polymer made of repeat units with functionalities greater than 2.</td>
</tr>
<tr>
<td>Pendant Group</td>
<td>Side group.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Ply</td>
<td>A single layer in a multi layer material; Lamina.</td>
</tr>
<tr>
<td>Polyetherimide (PEI)</td>
<td>An amorphous polymer with good thermal properties for a thermoplastic.</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>A polymer with repeat unit CH₂.</td>
</tr>
<tr>
<td>Polymer</td>
<td>An organic compound with a high molecular weight and with a structure that can be represented by a small repeat unit.</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>A polymer with the chemical structure shown in Fig. 1.</td>
</tr>
<tr>
<td>Prepreg</td>
<td>Material in sheet form which consists of unidirectional fibers impregnated with resin.</td>
</tr>
<tr>
<td>Pyrolyze</td>
<td>Change chemically due to heat. Specifically to remove side groups from the backbone structure. With high pressure and a neutral atmosphere, carbon fibers may be formed.</td>
</tr>
<tr>
<td>Radical</td>
<td>An atom or molecule with an unpaired electron.</td>
</tr>
<tr>
<td>Range of electron</td>
<td>The decrease in stress under sustained, constant strain.</td>
</tr>
<tr>
<td>Terminal group</td>
<td>Chemical group which constitutes the end of the polymer chain.</td>
</tr>
<tr>
<td>Thermoplastic</td>
<td>A material which is capable of being repeatedly softened by an increase in temperature and hardened by a decrease in temperature, and the softening is a physical rather than a chemical change.</td>
</tr>
<tr>
<td>Thermoset</td>
<td>A material which, when cured, is changed into an infusible and insoluble material.</td>
</tr>
<tr>
<td>Time-Temperature</td>
<td>The relationship between the behavior of a polymer at one temperature and experimental time scale to the same polymer at a different temperature and experimental time scale.</td>
</tr>
<tr>
<td>Track</td>
<td>The path of an electron and the distribution of resulting radicals.</td>
</tr>
<tr>
<td>Viscoelasticity</td>
<td>A property involving the combination of elastic and viscous behavior; a combination of the properties of an elastic solid and a viscous liquid.</td>
</tr>
<tr>
<td>Viscosity</td>
<td>The property of resistance to flow exhibited within the body of a material.</td>
</tr>
</tbody>
</table>
APPENDIX B

DERIVATIONS FOR DMA

The following derivations are for the analysis of a flexural dynamic mechanical analysis instrument, in particular, the du Pont 982 DMA. An outline of these derivations may be found in the 982 DMA Operators Manual. The details of the derivation are included here for completeness. Section B-1 shows that the minimum driver current occurs when the system is at resonance frequency. Section B-2 shows the derivation of the modulus equations for DMA. Section B-3 shows the determination of calibration constants.

B-1. MINIMIZATION OF DRIVER CURRENT

The equation of motion for the arms of the DMA is found by examining the torques applied to the DMA arms and is

\[ 2J \frac{d^2 \phi}{dt^2} + \frac{F}{x} B^2 \phi + 2K \phi = M(t) = M_0 \sin(\omega t) \]  

where \( J \) is the moment of inertia of a DMA arm, \( F/x \) is the ratio of force applied to the sample to deformation of the sample, \( B \) is the length of the sample, \( K \) is the stiffness of the DMA arms, and \( M(t) \) is the sinusoidal torque applied by the driver. A solution of the form

\[ \phi = \phi_0 \exp[i(\omega t - \delta)] \]  

is assumed.

---

Substituting this solution into the differential equation and comparing coefficients of the sine and cosine functions gives two equations:

\[ (-\omega^2 + \omega d + k^2)\exp(-i\delta) = 0 \]  \hspace{1cm} (B.3)

and

\[ i(-\omega^2 + \omega d + k^2)\exp(-i\delta) = \frac{M_0}{2J\phi_0}. \]  \hspace{1cm} (B.4)

The first equation can be solved to give

\[ \sin(\delta) = \frac{\omega d}{\sqrt{[(k^2 - \omega^2)^2 + (\omega d)^2]^2}} \]  \hspace{1cm} (B.5)

and

\[ M_0 = 2J\phi_0[(k^2 - \omega^2)^2 + (\omega d)^2]^{\frac{1}{2}}. \]  \hspace{1cm} (B.6)

The driver moment is then

\[ M(t) = 2J\phi_0[(k^2 - \omega^2)^2 + (\omega d)^2]^{\frac{1}{2}}\sin(\omega t). \]  \hspace{1cm} (B.7)

Taking the derivative of this with respect to \( \omega \) and equating to 0, gives the frequency at the minimum driver moment to be

\[ \omega = k. \]  \hspace{1cm} (B.8)

Thus, the minimum driver moment occurs when the system is at resonance.

B-2. DERIVATION OF MODULUS EQUATIONS

The components of the complex modulus of a sample in flexural dynamic mechanical analysis may be found by considering a simplified diagram of the motion of the 982 DMA arms as shown in Figure 10. Here, \( \phi \) is the angle the arms have been displaced, \( B \) is the distance between the arm centers, and \( x \) is the distance the sample has...
been deformed in a direction parallel to the length of the arms. We take
\[ B = L + 2D \]  
(B.9)
where \( L \) is the distance between the arms, and \( D \) is half the width of one arm.\(^2\) For small oscillation amplitudes, a small angle approximation can be made, so that
\[ x = B \sin \phi = B \phi. \]  
(B.10)
The sample acts as a spring with spring constant \( K' \), and thus the restoring force equation for the sample is
\[ F_r = -K'x. \]  
(B.11)
The force on the arms is then
\[ F = K'x = K'B\phi \]  
(B.12)
and the spring constant of the sample is
\[ K' = \frac{F}{x}. \]  
(B.13)
The torque on the arms due to the deformation of the sample is\(^2\)\(^3\)
The equation of motion for the system is then
\[ 2J \frac{\partial^2 \phi}{\partial t^2} + \frac{F}{x} B^2 \phi + 2K\phi = M(t). \]  
(B.14)
Here, the first term on the left is the inertia of the system, the second term is the torque due to the deformation of the sample, the third term is torque due to the arm pivots which act as springs with constant \( K \), and the term on the right is the torque applied by the driver. For viscoelastic problems, the equation of motion may be solved for the purely elastic case. The correspondence principle allows us to then replace the elastic constants with their complex counterparts to solve the viscoelastic case. This method is valid provided the stress and strain components have the same frequency.\(^3\)


Standard beam bending mechanics gives the expression for the clamped-clamped deformation in an elastic beam as

\[
x_f = \frac{FL^3}{12E\kappa^2A} + \alpha \frac{FL}{AG}
\]

where the first term is the pure flexural deformation and the second term is the pure shear deformation. Here, \( E \) is the flexural modulus, \( G \) is the shear modulus, \( \kappa^2 \) is the radius of gyration of the beam, \( A \) is the cross sectional area, \( L \) is the length of the beam, and \( \alpha \) is Timoshenko's shear distortion factor. The shear distortion factor accounts for non-uniform shear stress over the cross section of the beam.\(^4\) An additional deformation, \( x_c \), is added to account for the deformation of the pivot mechanism. This is defined to be\(^1\)

\[
x_c = FJ_c
\]

where \( J_c \) is the instrument compliance. The total deformation is thus

\[
x = x_f + x_c.
\]

Substituting into the equation of motion gives\(^2\)

\[
2J \frac{\partial^2 \phi}{\partial t^2} + \left[ \frac{AB}{L} \frac{G}{\alpha} + \frac{L^2}{24(1+\sigma)\kappa^2} \frac{AGJ_c}{L} + 2K \right] \phi = M(t)
\]

where

\[
E = 2(1+\sigma)G
\]

has been used and \( \sigma \) is Poisson's ratio.


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The conversion to the complex counterparts of the elastic constants is as follows:

\begin{align}
G & = G_1 + iG_2 \\
J & = J_1 + iJ_2 \\
K & = K_1 + iK_2.
\end{align}

(B.20)

Substituting these into the equation of motion gives

\begin{equation}
2J \frac{\partial^2 \phi}{\partial t^2} + \left[ \frac{AB^2}{L} \frac{G_1 + iG_2}{\alpha + \frac{L^2}{24(1+\sigma)\kappa^2} + \frac{A}{L}(G_1 + iG_2)(J_1 - iJ_2)} - 2(K_1 + iK_2) \right] \phi = M(t). \quad (B.21)
\end{equation}

Next, the real and imaginary parts of the coefficients are separated. The coefficients become

\begin{equation}
2J \frac{\partial^2 \phi}{\partial t^2} + \left[ \frac{AB^2}{L} \frac{G_1 + iG_2}{\beta^2 + \gamma^2} + 2K_2 \right] \phi + \left[ \frac{AB^2}{L} \frac{G_1 \beta + G_2 \gamma}{\beta^2 + \gamma^2} + 2K_1 \right] \phi = M(t). \quad (B.22)
\end{equation}

where we define

\begin{equation}
\beta = \alpha + \frac{L^2}{24(1+\sigma)\kappa^2} + \frac{A}{L}(G_1 J_1 + G_2 J_2) \quad (B.23)
\end{equation}

and

\begin{equation}
\gamma = \frac{A}{L}(J_1 G_2 - J_2 G_1). \quad (B.24)
\end{equation}

The real and imaginary components of the constants are now separated.

Consider the complex wave solution

\begin{equation}
\phi = \phi_0 \exp(i\omega t). \quad (B.25)
\end{equation}

Then

\begin{equation}
\frac{\partial \phi}{\partial t} = i\omega \phi = \exp(i\omega t) \phi \quad (B.26)
\end{equation}
or

\[ i \Phi = \frac{1}{\omega} \frac{\partial \Phi}{\partial t}. \]  

(B.27)

If the second term in the differential equation is combined with the first derivative term,

\[ 2J \frac{\partial^2 \Phi}{\partial t^2} + \left[ \frac{AB^2 G_2 \beta - G_1 \gamma}{L} \beta + \frac{G_2 \gamma + 2K_1}{\beta + \gamma^2} \left( \frac{1}{\omega} \frac{\partial \Phi}{\partial t} + \frac{AB^2 G_1 \beta + G_2 \gamma}{L} \beta + \frac{2K_1}{\beta + \gamma^2} \right) \right] \Phi = M(t). \]  

(B.28)

The equation of motion for a damped, driven harmonic oscillator is

\[ 2J \left[ \frac{\partial^2 \Phi}{\partial t^2} + d \frac{\partial \Phi}{\partial t} + K^2 \phi \right] = M(t). \]  

(B.29)

Comparing coefficients, we get

\[ 2J \frac{\partial^2 \Phi}{\partial t^2} + \frac{AB^2 G_2 \beta - G_1 \gamma}{L} \beta + 2K_2 = M(t). \]  

(B.30)

and

\[ 2JK^2 = \frac{AB^2 G_1 \beta + G_2 \gamma}{L} \beta + 2K_1. \]  

(B.31)

The first equation gives the damping coefficient, while the second gives the spring constant or stiffness. The instrument measures the damping of the system, \( d \), and the frequency of oscillation, \( \omega \). The sample storage modulus and loss modulus may be found by solving equations B.31 and B.32. The solution gives for the storage modulus

\[ G_1 = \frac{L}{AB^2} \left( 2JK^2 - 2K_2 \right) \frac{\beta + G_2 \gamma}{\beta} - G_2 \frac{\gamma}{\beta}. \]  

(B.32)

and for the loss modulus

\[ G_2 = \frac{L}{AB^2} \left( 2Jd\omega - 2K_2 \right) \frac{\beta + G_2 \gamma}{\beta} + G_1 \frac{\gamma}{\beta}. \]  

(B.33)
These equations may be solved for a given $d$ and $\omega$ by iteration, starting with the values:

\[
\begin{align*}
\gamma &= 0 \\
\beta &= \alpha + \frac{L}{24(1+\sigma)k^2}.
\end{align*}
\] (B.34)

Basic code for these calculations is shown in Appendix C.

B-3. DETERMINING CALIBRATION CONSTANTS

First, consider the system with no sample. Then

\[
\begin{align*}
G_1 &= 0 \\
G_2 &= 0
\end{align*}
\] (B.35)

so that equations B.33 and B.34 become

\[
\begin{align*}
2Jd\omega &= 2K_2 \\
2JK^2 &= 2K_1
\end{align*}
\] (B.36)

which give expressions for the instrument storage stiffness, $K_i$, and loss stiffness, $K_2$.

Next, consider the system with an infinitely stiff, no loss sample. For this case,

\[
\begin{align*}
G_1 &= \infty \\
G_2 &= 0
\end{align*}
\] (B.37)

so that equation 25 becomes

\[
2JK^2 = B^2 \frac{J_{c_1}}{J_c} + 2K_1
\] (B.38)
and equation 26 becomes

\[ 2Jd\omega = B^2 \frac{J_c}{J_c^2} + 2K_2 \]  \hspace{1cm} (B.39)

where

\[ J_c^2 = J_{c_2}^2 + J_{c_3}^2 \]  \hspace{1cm} (B.40)

has been used. From these, the instrument storage compliance,

\[ \frac{J_{c_2}}{J_c^2} = \frac{1}{B^2} (2JK^2 - 2K_2) \]  \hspace{1cm} (B.41)

and the instrument loss compliance

\[ \frac{J_{c_3}}{J_c^2} = \frac{1}{B^2} (2Jd\omega - 2K_2) \]  \hspace{1cm} (B.42)

are determined.
APPENDIX C

DMA ANALYSIS CODE

The following code was developed to analyze dynamic mechanical analysis data. The code is written as a main program and eight subroutines.

DECLARE SUB stat()
DECLARE SUB shift()
DECLARE SUB data.reduce()
DECLARE SUB out.put()
DECLARE SUB derivatives()
DECLARE SUB search()
DECLARE SUB modulus()
DECLARE SUB get.data()

REM
REM DMA Data Analysis Software
REM
REM Kristen T. Kern
REM Old Dominion University
REM
REM September 3, 1991
REM
REM This software is used to analyze data taken using the Du Pont
REM 1090 TA and 982 DMA. The program is written in Quick Basic
REM on an IBM PS/2 computer.
REM
REM Identify variable arrays

DIM NT(500)
DIM Freq(500), Damp(500)
DIM A$(10), b$(10), C%(10), D$(10)
DIM T(500), ti(500), F(500), D(500)
DIM E1(500), E2(500), LF(500)
DIM sl1(500), sl2(500), sl3(500)
DIM dsl1(500), dsl2(500), dsl3(500)

COMMON SHARED /variables/ DA$, D$, ver$
COMMON SHARED /variables/ A$(1), T(1), ti(1), F(1), D(1)
COMMON SHARED /variables/ E1(1), E2(1), LF(1)
COMMON SHARED /variables/ sl1(1), sl2(1), sl3(1), dsl1(1), dsl2(1), dsl3(1)
COMMON SHARED /variables/ count%, l, Wi, T
COMMON SHARED /variables/ Tmax, Fmax, Dmax, mag, mig, mlf
COMMON SHARED /variables/ TG, FG, TU, TD, TGL, FGL
COMMON SHARED /variables/ sll (), sl2(), sl3(), dsl1(), dsl2(), dsl3()

REM
REM Main Routine Directory
REM
maj.out:
CLS
PRINT "DMA Data Reduction Software"
PRINT "Version 1.0"
ver$ = "1.0"
PRINT
PRINT "Main Menu"
PRINT "1. Reduce raw data on b: \ to file on a:"
PRINT "2. Retrieve and analyze reduced file from a:"
PRINT "3. Shift data using Arhenius equation"
PRINT "4. Average curves from different samples"
PRINT "5. Quit"
PRINT

fst.out:

INPUT "Enter number of your choice ", an
IF an < 1 OR an > 5 THEN
   PRINT "Not a valid choice, choose again."

GOTO fst.out

END IF

IF an = 1 THEN
    CALL data.reduce
    GOTO maj.out
ELSEIF an = 2 THEN
    CALL get.data
    CALL modulus
    CALL derivatives
    CALL search
    CALL out.put
    GOTO maj.out
ELSEIF an = 3 THEN
    PRINT "Shift routine"
    CALL shift
    GOTO maj.out
ELSEIF an = 4 THEN
    PRINT "Average Routine"
    CALL stat
    GOTO maj.out
END IF

PRINT "Bye..."

STOP
RETURN
END

SUB data.reduce
REM
REM  This subroutine is used to reduce a raw data file on B:\ by
REM  averaging data over 1 degree intervals. Reduced file is saved
REM  on drive A:\.
REM
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PRINT "Source file assumed to be on drive B:\n"
INPUT "Enter source file name ", D$
DA$ = "B:" + D$
OPEN DA$ FOR INPUT AS #1

FOR n = 1 TO 6  'Retrieve file
    INPUT #1, A$(n)  'identification
    PRINT A$(n)
NEXT n

INPUT "Continue (y/n)? ", an$
IF an$ = "N" OR an$ = "n" THEN
    CLOSE #1
    GOTO c.out
END IF

count = 0
DO WHILE NOT EOF(1)  'Count data sets
    count = count + 1
    INPUT #1, b, c, e, g
    PRINT count, b, c, e, g
LOOP
CLOSE #1

pa$ = "A:\R" + D$ + ".ASC"
PRINT "Name of output file will be", pa$
OPEN pa$ FOR OUTPUT AS #2
OPEN DA$ FOR INPUT AS #1  'Reread file
    PRINT A$(n)  'identification
NEXT n

FOR n = 1 TO 6  'Write file
    PRINT A$(n)  'identification
    WRITE #2, A$(n)
NEXT n

PRINT
pt = 0  'Set data
Tmax = 0 'maxima to 0
Imax = 0
Fmax = 0
Dmax = 0

PRINT "Transferring Data..."
ct% = 0
cnt% = 1
T(cnt%) = -121
num% = 1
INPUT #1, b, C, e, g 'Read data
ave.start:
IF CINT(b) = T(cnt%) THEN 'Find data in
    ct% = ct% + 1 '1 degree C
    Freq(cnt%) = Freq(cnt%) + e 'intervals
    Damp(cnt%) = Damp(cnt%) + g
ELSEIF CINT(b) > T(cnt%) THEN 'Average values
    Freq(cnt%) = Freq(cnt%) / ct% 'for intervals
    Damp(cnt%) = Damp(cnt%) / ct%
    PRINT cnt%, ct%, T(cnt%), Freq(cnt%), Damp(cnt%)
    ct% = 1
    cnt% = cnt% + 1 'Increment
    T(cnt%) = T(cnt% - 1) + 1 'counters
    Freq(cnt%) = e
    Damp(cnt%) = g
END IF
num% = num% + 1

IF num% > count THEN
    GOTO count.out
END IF

INPUT #1, b, C, e, g 'Read next
goto ave.start 'data set

count.out:
FOR n% = 1 TO cnt%
    IF Freq(n%) > Fmax THEN 'Set maxima
        Fmax = Freq(n%)
    END IF
    IF Damp(n%) > Dmax THEN
        Dmax = Damp(n%)
    END IF
NEXT n%
END IF
NEXT n%

WRITE #2, "Reduced File" 'Store results
WRITE #2, cnt%
WRITE #2, T(cnt%), Fmax, Dmax
WRITE #2, "Temp", "Freq", "Damp"
FOR m = 1 TO cnt%
    WRITE #2, T(m), Freq(m), Damp(m)
NEXT m
PRINT "Done."
CLOSE #1
CLOSE #2

END SUB

SUB derivatives
REM
REM This subroutine finds the first and second derivates
REM of the loss modulus-temperature curves.
REM
REM
FOR n% = 2 TO count% 'Find first
    IF T(n%) = T(n% - 1) THEN 'derivatives
        sl1(n%) = sl1(n% - 1)
        sl2(n%) = sl2(n% - 1)
        sl3(n%) = sl3(n% - 1)
        GOTO te.out
    END IF
END IF

    sl1(n%) = (E1(n%) - E1(n% - 1)) / (T(n%) - T(n% - 1))
    sl2(n%) = (D(n%) - D(n% - 1)) / (T(n%) - T(n% - 1))
    sl3(n%) = (LF(n%) - LF(n% - 1)) / (T(n%) - T(n% - 1))

te.out:
NEXT n%

sl1(1) = sl1(2)
sl2(1) = sl2(2)

FOR n% = 2 TO count% 'Find second
    IF T(n%) = T(n% - 1) THEN 'derivatives
        sl1(n%) = sl1(n% - 1)
    END IF

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sl2(n%) = sl2(n% - 1)
sl3(n%) = sl3(n% - 1)
GOTO tf.out
END IF

dsl1(n%) = (sl1(n%) - sl1(n% - 1)) / (T(n%) - T(n% - 1))
dsl2(n%) = (sl2(n%) - sl2(n% - 1)) / (T(n%) - T(n% - 1))
dsl3(n%) = (sl3(n%) - sl3(n% - 1)) / (T(n%) - T(n% - 1))

tf.out:

NEXT n%

dsl1(1) = dsl1(2)
dsl2(1) = dsl2(2)
dsl3(1) = dsl3(2)

END SUB

SUB get.data
REM
REM This subroutine retrieves a reduced data file for
REM analysis.
REM
b.out:
CLS
PRINT "Data Analysis - File retrieval"
PRINT
PRINT "File is assumed to be reduced and have name A:\Rxxxx.ASC"
INPUT "Enter reduced data file name - xxxx ", D$
PRINT

DA$ = "A:\R" + D$ + ".ASC"
OPEN DA$ FOR INPUT AS #1

FOR n = 1 TO 7
    'Retrieve file identification
    INPUT #1, A$(n)
    PRINT A$(n)
NEXT n

INPUT "Continue (y/n)? ", an$

IF an$ = "N" OR an$ = "n" THEN
CLOSE #1
GOTO b.out
END IF

INPUT #1, count% 'Retrieve data
PRINT "The number of data points is "; count% 'parameters
INPUT #1, Tmax, Fmax, Dmax
PRINT "Max Temp", "Max Freq", "Max Damping"
PRINT Tmax, Fmax, Dmax
INPUT #1, c1$, c2$, c3$

FOR n = 1 TO count%
   INPUT #1, T(n), F(n), D(n)
NEXT n

LT$ = LEFT$(A$(4), 6) 'Convert specimen
I = VAL(LTRIM$(LT$)) 'dimensions from
WD$ = MID$(A$(4), 8, 14) 'strings to numbers
Wi = VAL(LTRIM$(WD$))
TK$ = MID$(A$(4), 16, 21)
T = VAL(LTRIM$(TK$))
I = I * .001
Wi = Wi * .001
T = T * .001

PRINT "Specimen dimensions are "; I; " X "; Wi; " X "; T; " m."
INPUT "Continue (y/n)? ", an$

CLOSE #1
END SUB

SUB modulus
REM
REM This subroutine calculates the storage modulus, loss
REM modulus, and Tan-delta from frequency and damping data
REM
REM
REM Calibration Constants - 22 JUNE 1989

pi = 3.14159
J = .0025
a1 = 1.5

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K1 = .334
K2 = .188
Fk = 19.08
J1 = 9.44E-07
J2 = 1.4E-08
Fj = 98.22
c1 = .0000269
D = .0159
o = .0002
Si = .033

PRINT "Is the data for 1. C6000/Ultem Transverse composite"
PRINT " 2. C6000/Ultem Longitudinal composite"
PRINT " 3. Other material"
PRINT
INPUT "Enter number of choice", choi

IF choi = 1 THEN 'Select length
  DL = .00094 'correction
ELSEIF choi = 2 THEN
  DL = .00171
ELSEIF choi = 3 THEN
  INPUT "Enter length correction in meters ", DL
END IF

PRINT
PRINT "Length correction is "; DL; " meters."
PRINT

REM Calculations Section

mlf = 0
mag = 0
mig = 0
l = l + DL
PRINT "Calculating modulus values"

FOR n% = 1 TO count%
  W = 2 * pi * F(n%)
  WD = 2 * J * 4 * pi * pi * c1 * D(n%) / o - K2 * F(n%) / Fk
  LT = l * l * l / (T * T * T)
  Ld = (l + D) / 2
Ld = Ld * Ld
Ca = 2 * J * W * W - 2 * K1
br = J1 * Ca
E1(n%) = LT * Ca / bl
E2(n%) = LT * WD / bl
LF(n%) = E2(n%) / E1(n%)

E1(n%) = E1(n%) * 1E-09
E2(n%) = E2(n%) * 1E-09

IF n% = count% - 1 THEN
  GOTO skip.max
END IF

IF E1(n%) > mag THEN
  mag = E1(n%)
END IF

IF E2(n%) > mig THEN
  mig = E2(n%)
END IF

IF LF(n%) > mlf THEN
  mlf = LF(n%)
END IF

skip.max:
NEXT n%
tig = T(count%)
END SUB
SUB out.put
REM
REM This subroutine saves calculated values to disk and
REM prints the results of analysis to the line printer.
REM
PRINT "Saving modulus data to a:\"; D$
pa$ = "A:\E" + D$ + ".ASC"
OPEN pa$ FOR OUTPUT AS #2

FOR n = 1 TO 6
    PRINT A$(n)
    WRITE #2, A$(n)
NEXT n

WRITE #2, "Modulus File"  'Write data
WRITE #2, count%         'headers
WRITE #2, tig, mag, mig, mlf
WRITE #2, "Temp", "freq", "E1", "E2", "Tan-d"

FOR n% = 1 TO count%
    WRITE #2, T(n%), F(n%), E1(n%), E2(n%), LF(n%)
NEXT n%

CLOSE #2

PRINT "Printing data to line printer"  'Print data
LPRINT "DMA Data reduction"
LPRINT "Software version "; ver$; " Date "; DATE$; " Time "; TIME$
LPRINT
LPRINT "Modulus and Temperature Data for file ", DA$
LPRINT
FOR n% = 1 TO 6
    LPRINT A$(n%)
NEXT n%

LPRINT
LPRINT "Number of data points in reduced file "; count%
LPRINT "Maximum value for E1 "; mag
LPRINT "Maximum value for E2 "; mig
LPRINT "Maximum value for LF "; mlf
LPRINT
LPRINT "Modulus values at selected temperatures"
LPRINT
LPRINT "Temperature"; TAB(20); "Tensile Modulus"; TAB(40); "Loss Modulus"
LPRINT ";-100"; TAB(20); Its; TAB(40); ltl
LPRINT "23"; TAB(20); rts; TAB(40); rtl
LPRINT "64"; TAB(20); hts; TAB(40); htl
LPRINT
LPRINT "Tg (E") is ", TG; TAB(40); "1/Tg = "; 1 / (TG + 273)
LPRINT "Frequency at Tg (E") is ", FG; TAB(40); "Ln(f) = "; LOG(FG)
LPRINT "Loss Modulus at Tg (E") is "; E2(tn%)
LPRINT "Tensile Modulus at Tg(E") is "; E1(tn%); " with slope "; sl1(tn%)
LPRINT
LPRINT "Tg (Tan-d) is ", TGL; TAB(40); "1/Tg = "; 1 / (TGL + 273)
LPRINT "Frequency at Tg (Tan-d) is ", FGL'; TAB(40); "Ln(f) = "; LOG(FGL)
LPRINT "Tan-d at Tg(Tan-d) is ", LF(tl%)
LPRINT
LPRINT "Increasing inflection occurs at TU = ", TU
LPRINT "Decreasing inflection occurs at TD = ", TD
LPRINT "Full width at inflections is ", TD - TU
LPRINT "E2 values at inflections are ", ue2; " and "; de2
LPRINT
LPRINT "Onset temperature (E") is ", Ton
LPRINT "Frequency at onset (E") is ", FTon
LPRINT "Least Squares Data - b0 = "; b0, " m0 = "; a0
LPRINT " b1 = "; b1, " m1 = "; a1
LPRINT " ct = "; ct, " ct1 = "; ct1
LPRINT "asl = "; asl
LPRINT
LPRINT "Onset temperature (Tan-d) is ", Lon
LPRINT "Frequency at onset (Tan-d) is ", FLon
LPRINT "Least Squares Data - b0 = "; b2, " m0 = "; a2
LPRINT " b1 = "; b3, " m1 = "; a3
LPRINT " ct = ", ct, " ct1 = ", ct1
LPRINT CHR$(12) 'Page feed
END SUB

SUB search
REM
REM This subroutine searches the modulus curves for points
REM of interest. These include Tg, To, Modulus values,
REM and peak widths.
REM
CLS

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'Find modulus values at selected temperatures

FOR n% = 2 TO count%
    IF T(n% - 1) < -100 AND T(n%) > -100 THEN
        Its = E1(n% - 1) + (E1(n%) - E1(n% - 1)) * (-100 - T(n% - 1)) / (T(n%) - T(n% - 1))
        Itl = E2(n% - 1) + (E2(n%) - E2(n% - 1)) * (-100 - T(n% - 1)) / (T(n%) - T(n% - 1))
    ELSEIF T(n%) = -100 THEN
        Its = E1(n%)
        Itl = E2(n%)
    END IF
    IF T(n% - 1) < 23 AND T(n%) > 23 THEN
        rts = E1(n% - 1) + (E1(n%) - E1(n% - 1)) * (23 - T(n% - 1)) / (T(n%) - T(n% - 1))
        rtl = E2(n% - 1) + (E2(n%) - E2(n% - 1)) * (23 - T(n% - 1)) / (T(n%) - T(n% - 1))
    ELSEIF T(n%) = 23 THEN
        rts = E1(n%)
        rtl = E2(n%)
    END IF
    IF T(n% - 1) < 64 AND T(n%) > 64 THEN
        hts = E1(n% - 1) + (E1(n%) - E1(n% - 1)) * (64 - T(n% - 1)) / (T(n%) - T(n% - 1))
        htl = E2(n% - 1) + (E2(n%) - E2(n% - 1)) * (64 - T(n% - 1)) / (T(n%) - T(n% - 1))
    ELSEIF T(n%) = 64 THEN
        hts = E1(n%)
        htl = E2(n%)
    END IF
NEXT n%

PRINT "Modulus data at selected temperatures"
PRINT
PRINT "Temperature"; TAB(20); "Tensile Modulus"; TAB(40); "Loss Modulus"
PRINT ";"; TAB(20); T(n%); Tab(40); Its; TAB(40); Itl
PRINT ";"; TAB(20); rts; TAB(40); rtl
PRINT ";"; TAB(20); hts; TAB(40); htl

'Find Tg

FOR n% = 1 TO count%
    IF E2(n%) > .5 * mig AND dsl2(n%) < 0 THEN
        IF sl2(n%) = 0 THEN
            139
TG = T(n%)  
FG = F(n%)  
GOTO GT.out
ELSEIF sl2(n% - 1) > 0 AND sl2(n%) < 0 THEN
  TG = T(n% - 1) + (T(n%) - T(n% - 1)) * (0 - sl2(n% - 1)) / (sl2(n%) - sl2(n% - 1))
  FG = F(n% - 1) + (F(n%) - F(n% - 1)) * (0 - sl2(n% - 1)) / (sl2(n%) - sl2(n% - 1))
  tn% = n%
  GOTO GT.out
END IF
IF sl2(n%) > 0 THEN
  IF dsl2(n%) = 0 THEN
    TU = T(n%)
    ue2 = E2(n%)
  ELSEIF dsl2(n% - 1) > 0 AND dsl2(n%) < 0 THEN
    TU = T(n% - 1) + (T(n%) - T(n% - 1)) * (0 - dsl2(n% - 1)) / (dsl2(n%) - dsl2(n% - 1))
    ue2 = E2(n%)
    asl = sl2(n%)
  END IF
END IF
END IF
NEXT n%
GT.out:

'Determine temperature of rising inflection
FOR n% = 1 TO count%
  IF LF(n%) > .5 * mlf AND dsl3(n%) < 0 THEN
    IF sl3(n%) = 0 THEN
      TGL = T(n%)
      FGL = F(n%)
      GOTO GL.out
    ELSEIF sl3(n% - 1) > 0 AND sl3(n%) < 0 THEN
      TGL = T(n% - 1) + (T(n%) - T(n% - 1)) * (0 - sl3(n% - 1)) / (sl3(n%) - sl3(n% - 1))
      FGL = F(n% - 1) + (F(n%) - F(n% - 1)) * (0 - sl3(n% - 1)) / (sl3(n%) - sl3(n% - 1))
      tl% = n%
      GOTO GL.out
    END IF
  IF sl3(n%) > 0 THEN
    140
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IF dsI3(n%) = 0 THEN
    TUL = T(n%)
    ue3 = LF(n%)
ELSEIF dsI3(n% - 1) > 0 AND dsI3(n%) < 0 THEN
    TUL = T(n% - 1) + (T(n%) - T(n% - 1)) * (0 - dsI3(n% - 1)) / (dsI3(n%) - dsI3(n% - 1))
    ue3 = LF(n%)
END IF
END IF
END IF
NEXT n%

GL.out:

'Determine temperature of falling inflection

FOR n% = tn% TO count%
    IF E2(n%) > .25 * mig AND sl2(n%) < 0 THEN
        IF dsI2(n%) = 0 THEN
            TD = T(n%)
            de2 = E2(n%)
            GOTO SGT.out
        ELSEIF dsI2(n% - 1) < 0 AND dsI2(n%) > 0 THEN
            TD = T(n% - 1) + (T(n%) - T(n% - 1)) * (0 - dsI2(n% - 1)) / (dsI2(n%) - dsI2(n% - 1))
            de2 = E2(n%)
            GOTO SGT.out
        END IF
    END IF
NEXT n%

SGT.out:

ct = 0
c1 = 0
S = 0
SS = 0
SF = 0
FX = 0
S1 = 0
ss1 = 0
SF1 = 0
FX1 = 0
SLM = 0
SLF = 0
SLM1 = 0
SLF1 = 0

'Fit to curve above and below onset temperature

FOR n% = 1 TO count%
    IF T(n%) > TG - 10 * (TG - TU) - 5 AND T(n%) < TG - 10 * (TG - TU) + 5 THEN
        ct = ct + 1
        S = S + T(n%)
        SS = SS + T(n%) * T(n%)
        SF = SF + E2(n%)
        FX = FX + E2(n%) * T(n%)
        LS = LS + T(n%)
        LSS = LSS + T(n%) * T(n%)
        SLM = SLM + LF(n%)
        SLF = SLF + LF(n%) * T(n%)
    END IF
    IF T(n%) > TU - 3 AND T(n%) < TU + 3 THEN
        ct1 = ct1 + 1
        S1 = S1 + T(n%)
        ss1 = ss1 + T(n%) * T(n%)
        SF1 = SF1 + E2(n%)
        FX1 = FX1 + E2(n%) * T(n%)
        LS1 = LS1 + T(n%)
        LSS1 = LSS1 + T(n%) * T(n%)
        SLM1 = SLM1 + LF(n%)
        SLF1 = SLF1 + LF(n%) * T(n%)
    END IF
NEXT n%

a0 = (FX - SF * S / ct) / (SS - S * S / ct)
b0 = SF / ct - a0 * S / ct
a1 = (FX1 - SF1 * S1 / ct1) / (ss1 - S1 * S1 / ct1)
b1 = SF1 / ct1 - a1 * S1 / ct1

a2 = (SLF - SLM * LS / ct) / (LSS - LS * LS / ct)
b2 = SLM / ct - a2 * LS / ct
a3 = (SLF1 - SLM1 * LS1 / ct1) / (LSS1 - LS1 * LS1 / ct1)
b3 = SLM1 / ct1 - a3 * LS1 / ct1

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Ton = (b0 - b1) / (a1 - a0)  'Use fit to determine To
Lon = (b2 - b3) / (a3 - a2)

FOR n% = 2 TO count%
  IF T(n% - 1) < Ton AND T(n%) > Ton THEN
    FTon = F(n% - 1) + (F(n%) - F(n% - 1)) * (Ton - T(n% - 1)) / (T(n%)
- T(n% - 1))
  ELSEIF T(n%) = Ton THEN
    FTon = F(n%)
  END IF
  IF T(n% - 1) < Lon AND T(n%) > Lon THEN
    FLon = F(n% - 1) + (F(n%) - F(n% - 1)) * (Lon - T(n% - 1)) / (T(n%)
- T(n% - 1))
  ELSEIF T(n%) = Lon THEN
    FLon = F(n%)
  END IF
NEXT n%

PRINT 'Print data to screen
PRINT "Glass Transition data"
PRINT
PRINT "Tg is ", TG
PRINT "Freq at Tg is ", FG
PRINT "Loss Modulus at Tg is ", E2(tn%)
PRINT "Tensile Modulus at Tg is ", E1(tn%), " with slope ", sl1(tn%)
PRINT
PRINT "Increasing inflection occurs at TU = ", TU
PRINT "Decreasing inflection occurs at TD = ", TD
PRINT "Full width at inflections is ", TD - TU
PRINT "E2 values at inflections are ", ue2; " and "; de2
PRINT
PRINT "Onset temperature (E") is ", Ton
PRINT "Frequency at onset (E") is ", FTon
PRINT "Least Squares Data - b0 = "; b0, " m0 = "; a0
PRINT " b1 = "; b1, " m1 = "; a1
PRINT " ct = ", ct, " ct1 = ", ct1
PRINT "asl = ", asl
PRINT
PRINT "Onset temperature (Tan-d) is ", Lon
PRINT "Frequency at onset (Tan-d) is ", FLon
PRINT "Least Squares Data - b0 = "; b2, " m0 = "; a2
PRINT " b1 = "; b3, " m1 = "; a3
PRINT " ct = ", ct, " ct1 = ", ct1

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INPUT "Press return when ready", dms$

END SUB

SUB shift

REM REM This subroutine uses a known activation energy and REM shifts the data in the transition region to temperatures REM corresponding to a 10 Hz deformation.
REM

CLS
PRINT "Arhenius Time-Temperature superposition shift routine"
PRINT
d.out:

PRINT "File is assumed to be modulus values and have name A:\Exxx.ASC"
INPUT "Enter reduced data file name - xxxx ", D$
DA$ = "A:\E" + D$ + ".ASC"

OPEN DA$ FOR INPUT AS #3

FOR n = 1 TO 7 'Retrieve file
   INPUT #3, A$(n) 'identification
   PRINT A$(n)
NEXT n

INPUT "Continue (y/n)? ", an$

IF an$ = "N" OR an$ = "n" THEN
   CLOSE #1
   GOTO d.out
END IF

INPUT #3, count% 'Retrieve data
PRINT count% 'limits
INPUT #3, tig, mag, mig, mlf
PRINT tig, mag, mig, mlf
INPUT #3, c1$, c2$, c3$, c4$, C5$

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FOR n% = 1 TO count%
    INPUT #3, T(n%), F(n%), E1(n%), E2(n%), LF(n%)
NEXT n%

pa$ = "A:\SE" + D$ + ".ASC"

PRINT "Output file will be ", pa$

OPEN pa$ FOR OUTPUT AS #4

FOR n = 1 TO 6
    PRINT A$(n)
    WRITE #4, A$(n)
NEXT n

WRITE #4, "Shifted Data File"
WRITE #4, count%

INPUT "Enter Tg for specimen"; TG

FOR n% = 1 TO count%
    IF T(n%) > TG - 51 AND T(n%) < TG - 49 THEN
        start% = n%
    END IF
NEXT n%

PRINT start%, T(start%)

INPUT C$

INPUT "Enter activation energy ", DH

R = 8.315
r1 = DH / R
C = 1 / r1

FOR n% = start% TO count%
    I = LOG(F(n%) / 10)
    ot = 1 / (T(n%) + 273)
    ti = ot + C * I
    NT(n%) = 1 / ti - 273
NEXT n%

WRITE #4, "Temp", "New Temp", "Freq", "E1", "WD"
FOR n% = start% TO count%
    WRITE #4, T(n%), NT(n%), F(n%), E1(n%), E2(n%)
NEXT n%

CLOSE #3
CLOSE #4

END SUB

SUB stat

REM
REM This subroutine averages the curves for up to 3 files.
REM
REM
CLS

PRINT "Curve averaging routine"
PRINT

INPUT "How many files would you like to average (1-3)? ", fs

PRINT "Files are assumed to be modulus values and have name A:\Exxx.ASC"

f1.out:

PRINT "First File"
PRINT
INPUT "Enter reduced data file name - xxxx ", D$
DA$ = "A:\E" + D$ + ".ASC"
OPEN DA$ FOR INPUT AS #5

PRINT DA$
PRINT

FOR n = 1 TO 7
    INPUT #5, A$(n)
    'Retrieve first
    PRINT A$(n)
    'file identification
NEXT n

INPUT "Continue (y/n)? ", an$

IF an$ = "N" OR an$ = "n" THEN
    CLOSE #5

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GOTO f1.out
END IF

INPUT #5, count1%
PRINT count1%
INPUT #5, tig1, eag1, eig1
INPUT #5, c1$, c2$, c3$, c4$

FOR n% = 1 TO count1%
    INPUT #5, T1(n%), F1(n%), SE1(n%), LE1(n%)
    PRINT T1(n%), SE1(n%), LE1(n%)
NEXT n%

F2.out: 'Retrieve second file identification
PRINT "Second File"
PRINT
INPUT "Enter reduced data file name - xxxx ", D2$
DA2$ = "A:\E" + D2$ + ".ASC"
OPEN DA2$ FOR INPUT AS #6

PRINT DA2$
PRINT

FOR n = 1 TO 7
    INPUT #6, a2$(n)
    PRINT a2$(n)
NEXT n

INPUT "Continue (y/n)? ", an$

IF an$ = "N" OR an$ = "n" THEN
    CLOSE #6
    GOTO F2.out
END IF

INPUT #6, count2%
PRINT count2%
INPUT #6, tig2, eag2, eig2
INPUT #6, c1$, c2$, c3$, c4$

FOR n% = 1 TO count2%
    INPUT #6, T2(n%), F2(n%), SE2(n%), LE2(n%)
    PRINT T2(n%), SE2(n%), LE2(n%)
NEXT n%
IF fs < 3 THEN
    cnt% = 1
    T = -120
    GOTO dn.inpt
END IF

'Retrieve third file identification
PRINT "Third File"
PRINT
INPUT "Enter reduced data file name - xxxx ", D3$
DA3$ = "A:\E" + D3$ + ".ASC"
OPEN DA3$ FOR INPUT AS #7

PRINT DA3$
PRINT
FOR n = 1 TO 7
    INPUT #7, a3$(n)
    PRINT a3$(n)
NEXT n

INPUT "Continue (y/n)? ", an$
IF an$ = "N" OR an$ = "n" THEN
    CLOSE #7
    GOTO F3.out
END IF

INPUT #7, count3%
PRINT count3%
INPUT #7, tig3, eag3, eig3
INPUT #7, c1$, c2$, c3$, c4$
FOR n% = 1 TO count3%
    INPUT #7, T3(n%), F3(n%), SE3(n%), LE3(n%)
    PRINT T3(n%), SE3(n%), LE3(n%)
NEXT n%

cnt% = 1
T = -120

dn.inpt:
ct% = 0
Temp(cnt%) = T
FOR n% = 2 TO count1%  
   'Select points
   IF T1(n%) = T THEN  
      'from first file
      ct% = ct% + 1
      E1(ct%) = SE1(n%)
      E2(ct%) = LE1(n%)
      GOTO ff.out
   ELSEIF T1(n%) < T AND T1(n% + 1) > T THEN
      ct% = ct% + 1
      E1(ct%) = SE1(n%) + (SE1(n% + 1) - SE1(n%)) * (T - T1(n%)) / (T1(n% + 1) - T1(n%))
      E2(ct%) = LE1(n%) + (LE1(n% + 1) - LE1(n%)) * (T - T1(n%)) / (T1(n% + 1) - T1(n%))
      GOTO ff.out
   END IF
NEXT n%
ff.out:
er1 = E1(cnt%)
err1 = E2(cnt%)

FOR o% = 2 TO count2%  
   'Add second file
   IF T2(o%) = T THEN
      ct% = ct% + 1
      E1(ct%) = E1(ct%) + SE2(o%)
      E2(ct%) = E2(ct%) + LE2(o%)
      GOTO sf.out
   ELSEIF T2(o%) < T AND T2(o% + 1) > T THEN
      ct% = ct% + 1
      E1(ct%) = E1(ct%) + SE2(o%) + (SE2(o% + 1) - SE2(o%)) * (T - T2(o%)) / (T2(o% + 1) - T2(o%))
      E2(ct%) = E2(ct%) + LE2(o%) + (LE2(o% + 1) - LE2(o%)) * (T - T2(o%)) / (T2(o% + 1) - T2(o%))
      GOTO sf.out
   END IF
NEXT o%
sf.out:
er2 = ABS(E1(cnt%) - er1)
err2 = ABS(E2(cnt%) - err1)

IF fs < 3 THEN  
   GOTO fl2.out
END IF
FOR p% = 2 TO count3%  
  IF T3(p%) = T THEN
    ct% = ct% + 1
    E1(cnt%) = E1(cnt%) + SE3(p%)
    E2(cnt%) = E2(cnt%) + LE3(p%)
    GOTO fl2.out
  ELSEIF T3(p%) < T AND T3(p% + 1) > T THEN
    ct% = ct% + 1
    E1(cnt%) = E1(cnt%) + SE3(p%) + (SE3(p% + 1) - SE3(p%)) * (T - T3(p%)) / (T3(p% + 1) - T3(p%))
    E2(cnt%) = E2(cnt%) + LE3(p%) + (LE3(p% + 1) - LE3(p%)) * (T - T3(p%)) / (T3(p% + 1) - T3(p%))
    GOTO fl2.out
  END IF
NEXT p%

fl2.out:  
  'Determine error
  err3 = ABS(E1(cnt%) - er2 - er1)  
  'bounds
  err3 = ABS(E2(cnt%) - err2 - err1)
  E1(cnt%) = E1(cnt%) / ct%  
  'Average values
  E2(cnt%) = E2(cnt%) / ct%
  IF ABS(err1 - er2) < ABS(err1 - err3) THEN
    max(cnt%) = ABS(err1 - err3) / 2
  ELSE
    max(cnt%) = ABS(err1 - er2) / 2
  END IF
  IF max(cnt%) < ABS(err2 - err3) THEN
    max(cnt%) = ABS(err2 - err3) / 2
  END IF
  IF ABS(err1 - err2) < ABS(err1 - err3) THEN
    mix(cnt%) = ABS(err1 - err3) / 2
  ELSE
    mix(cnt%) = ABS(err1 - err2) / 2
  END IF
  IF mix(cnt%) < ABS(err2 - err3) THEN
    mix(cnt%) = ABS(err2 - err3) / 2
  END IF
  PRINT cnt%, T, Temp(cnt%), ct%  
  'Print to
PRINT E1(cnt%), max(cnt%), E2(cnt%), mix(cnt%), 'screen

PRINT

CNT% = CNT% + 1
T = T + 1

IF T > Tig1 THEN
   GOTO dn.avg
END IF

IF T > Tig2 THEN
   GOTO dn.avg
END IF

IF T > Tig3 THEN
   GOTO dn.avg
END IF

GOTO dn.inpt

DN.AVG:

INPUT "Enter name of output file A:\ES", of$    'save to
np$ = "A:\ES" + of$ + "ASC"      'disk
ep$ = "A:\ER" + of$ + "ASC"
OPEN np$ FOR OUTPUT AS #8
OPEN ep$ FOR OUTPUT AS #9

PRINT "Writing to output file ", np$

FOR n% = 1 TO 6
   WRITE #8, A$(n%)
   WRITE #9, A$(n%)
NEXT n%

WRITE #8, "Averaged Data"
WRITE #9, "Error Bound"
WRITE #8, CNT%
WRITE #9, CNT%
WRITE #8, Temp(cnt%), E1(1), E2(cnt% - 20)
WRITE #8, "Temp", "E1", "WD"
WRITE #9, "Temp", "Error in E1", "Error in WD"

FOR n% = 1 TO CNT%
   WRITE #8, Temp(n%), E1(n%), E2(n%)
WRITE #9, Temp(n%), max(n%), mix(n%)
NEXT n%

CLOSE #5
CLOSE #6
CLOSE #7
CLOSE #8
CLOSE #9
END SUB
Biographical Statement

Kristen Tulloch Kern was born in Phoenixville, Pennsylvania on October 19, 1964. He is the son of Stuart G. Kern and Annesley C. Kern and has a brother, Biff, and two sisters, Sue and Margaret. He is married to Jane R. Kern.

Kris graduated from Oley Valley High School in 1982, after which he attended Clarion University of Pennsylvania. While at Clarion University, he participated in the department of the Army Scientific Exchange Program, through which he worked for the Human Factors and Infrared Branch of the Combat Systems Test Activity at Aberdeen Proving Grounds, Maryland. In December, 1986 he received a Bachelor of Science in Physics from Clarion University and an Army Reserve Commission.

Kris enrolled in the graduate program at Old Dominion University in August, 1987 and received a master of science in physics an 1990. His research was conducted with the Applied Materials Branch at NASA Langley Research Center. Kris currently teaches physics at Norfolk State University.