

THE EFFECTS OF THE EXPOSURE OF ATOMIC OXYGEN ON  
POLYMERIC MATERIALS: I. Siloxane Modified Epoxy  
Resins. II. Polyetherimide Films with Additives.

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APPROVAL SHEET

This thesis is submitted in partial fulfillment of  
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## ABSTRACT

The lifetime of polymeric materials can be shortened when exposed to the Low Earth Orbit (LEO) environment. The materials are degraded by atomic oxygen, which is the primary constituent in the LEO environment. In this study, two methods were attempted to reduce the rate of atomic oxygen degradation. The first method employed the incorporation of a siloxane modifier in the backbone of an epoxy resin. Polydimethylsiloxane and poly(dimethyl-co-diphenyl)siloxane modifiers were synthesized and used. The resins were formed into films that made an incompatible network. These films were still tested in a commercial plasma generator (asher) and showed no increased resistance to atomic oxygen. The second method used the mixing of additives into polyetherimide (PEI). Organo-siloxane, organo-silicon, organo-lead, and organo-tin additives were tested for their solubility in PEI. Bis(triphenyltin) oxide (BTO) was the only additive to have a high solubility. Films of PEI with BTO were cast and tested in the asher. Initially, the films showed a high erosion rate, but as exposure time elapsed, the erosion rates decreased. This decrease was attributed to the formation of a protective tin oxide layer, which was confirmed by ATR-FTIR, EDAX, and SEM.

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## INTRODUCTION

### Atomic Oxygen

In considering materials for use in Low Earth Orbit (LEO) environment, the effect of atomic oxygen is very important, since it is the primary component of LEO. Atomic oxygen degrades and depletes certain materials. The degradation of material is via a free radical mechanism. It is usually seen as mass loss. Degradation by atomic oxygen is a surface effect only. The erosion of a material's surface can have a harmful effect on the performance of that material.

Several methods have been used to retard degradation by atomic oxygen. One method is the use of a thin layer of film which acts as a protective coating for the material. Another method is the modification of the backbone of the material that increases its resistance to atomic oxygen. A third method is the use of filler in the polymeric matrix.

In this study, two of the methods will be attempted. The first method incorporates a siloxane modifier into the backbone of an epoxy resin. The second method uses a filler as possible retardant to atomic oxygen attack.

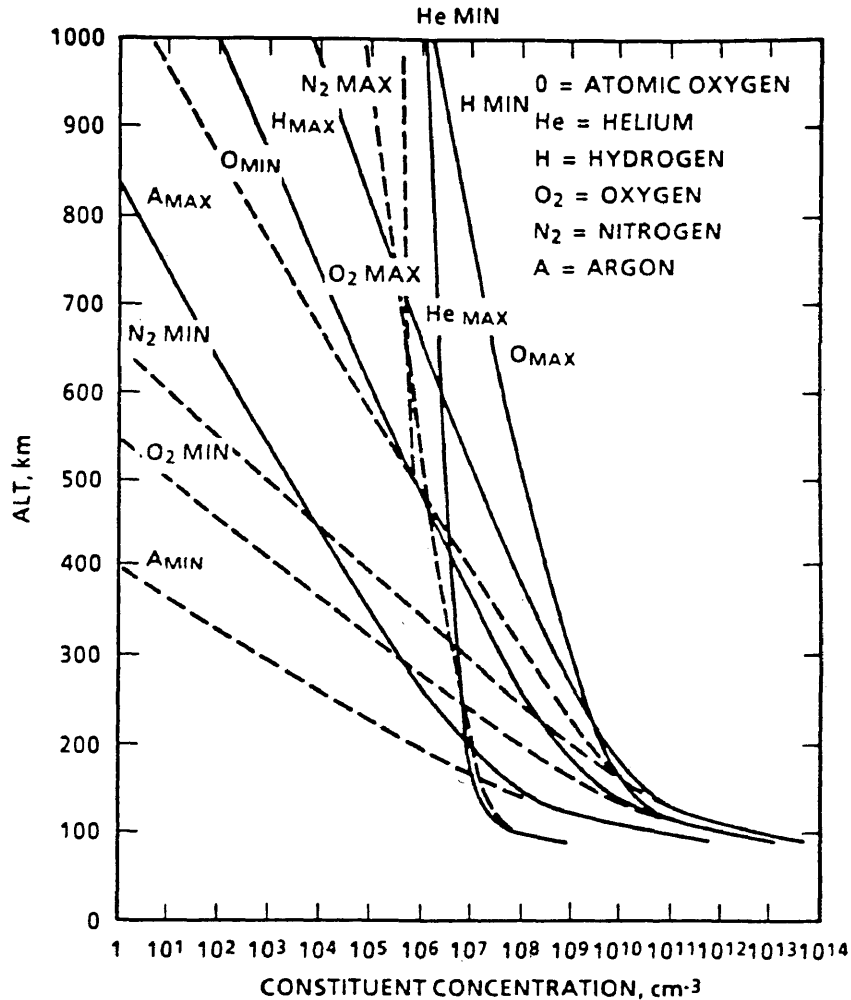
## LITERATURE REVIEW

### Atomic Oxygen

Atomic oxygen is the principal constituent of the LEO environment (Figure 1).<sup>1,2</sup> Atomic oxygen reacts readily with most organic substrates, which are important components in a spacecraft, especially the space station, placed in the low earth orbit. The attack of atomic oxygen could cause surface thickness loss for organic compounds of 6  $\mu\text{m}$ / day, which would greatly shorten the lifetime of the spacecraft.<sup>3</sup>

The concentration of atomic oxygen is between  $10^6$  and  $10^{10}$  atoms/cm<sup>3</sup> at altitudes of 150 to 650 km.<sup>1</sup> Although this concentration is quite low, the high orbital speed of about 8 km/s produces a large flux density ( $10^{13}$ - $10^{15}$  atoms/cm<sup>2</sup>-s).<sup>1</sup> The number density of the atomic oxygen decreases with increasing altitude. Fluence, or total integrated flux, determined over the exposure period is responsible for the surface recession of typical spacecraft materials, where flux equals the number density times orbital speed, and fluence is the product of flux and exposure period.<sup>1,2</sup> The composition of the atmosphere is dependent on diurnal, latitudinal, and solar activity.<sup>1-4</sup>

Atomic oxygen occurs in three states: the triplet ground

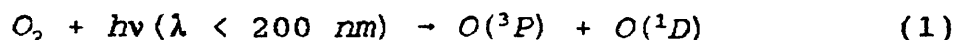


**Figure 1: Atmospheric Composition<sup>2</sup>**

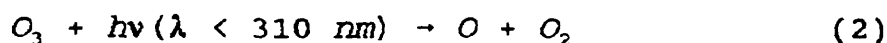
state (<sup>3</sup>P) and two singlet excited states (<sup>1</sup>D and <sup>1</sup>S). The neutral <sup>3</sup>P ground state is atomic oxygen's primary state. O(<sup>3</sup>P) is produced by the photolysis of molecular oxygen (O<sub>2</sub>), the photolysis of the triatomic ozone (O<sub>3</sub>), and the quenching of O(<sup>1</sup>D) by collisions with O<sub>2</sub> and N<sub>2</sub>.<sup>5</sup> Atomic oxygen is also produced by the photolysis of NO<sub>2</sub> and N<sub>2</sub>O in some spectral regions.<sup>5</sup>

Photodissociation of molecular oxygen is caused by solar

radiation below 200 nm producing two oxygen atoms, one in the ground state and the other in an excited state.<sup>6</sup>



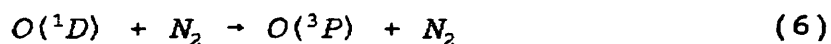
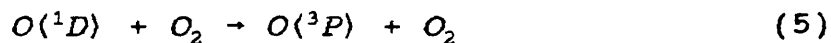
The photolysis of ozone uses Hartley continuum radiation ( $\lambda < 310 \text{ nm}$ ).<sup>7</sup> The major product is the excited atomic oxygen ( $^1D$ ).



The production of atomic oxygen by photolysis of  $NO_2$  and  $N_2O$  is very small and usually produces  $O(^1D)$ .<sup>5,8</sup>



$O(^1D)$  is quenched to  $O(^3P)$  by the following reactions:<sup>7</sup>



Recombination of atomic oxygen to form molecular oxygen involves an interaction with a third body.<sup>5,6</sup>



The probability of this reaction occurring is small in the upper atmosphere, since the density of particles is quite low.

The impact of atomic oxygen with an orbiting object occurs with high energy (4-5 eV). Several chemical and physical events on the impacted surface are affected by this energy (see Figure 2).<sup>2</sup> The first event is the simple scattering of the atomic oxygen particle. Another event is

the reaction of atomic oxygen with nitrogen to form nitrous oxide in an excited state which de-excites to produce a glow. Atomic oxygen may also react with organic material and form volatile fragments, radicals, or molecules with oxygen-containing functionality. Lastly, the oxygen may diffuse into the bulk material.

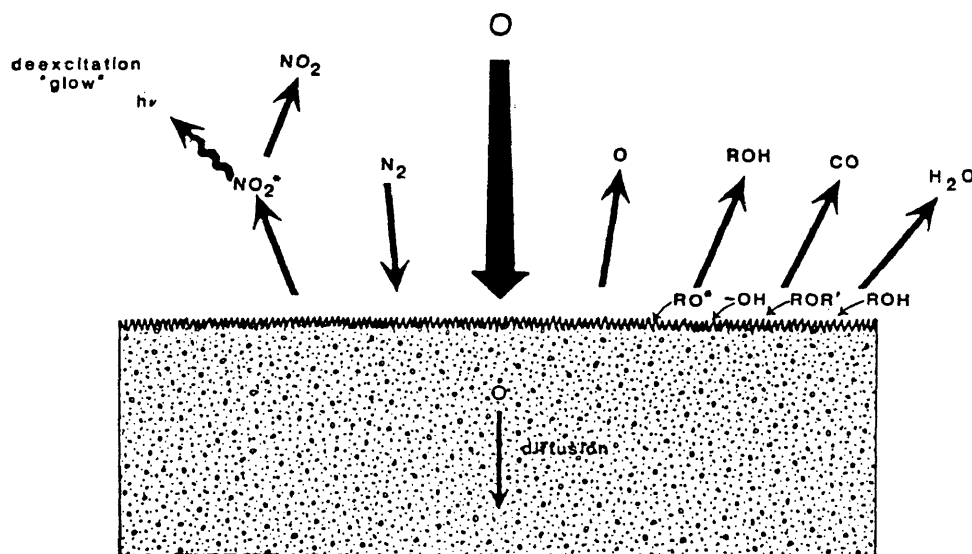


Figure 2: Atomic Oxygen Surface Interaction Processes<sup>2</sup>

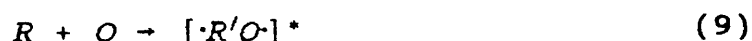
Atomic oxygen degrades polymeric materials via a free-radical process.<sup>9,10</sup> Oxidation by atomic oxygen is initiated by a direct, rapid attack on the polymer chain. The initiation reactions are described in equations 8-12. The reaction mechanism can be described by five basic processes: abstraction, addition, elimination, insertion, and replacement.<sup>2,6</sup> The three primary reactions are abstraction, addition, and replacement. Elimination and insertion are

related to the addition reaction.

In the abstraction process, the oxygen atom abstracts an atom, such as hydrogen, from the compound.



The addition reaction results when the oxygen atom attaches itself to an organic compound, especially alkenes, resulting in a vibrationally excited molecule.



This excited molecule then can undergo the elimination reaction of a hydrogen atom.



Another important form of an addition reaction is the insertion reaction in which the atomic oxygen inserts itself between two bound atoms.



An insertion between a carbon and a hydrogen usually involves the O(<sup>1</sup>D) atom, since the spin-forbidden insertion of the O(<sup>3</sup>P) atom does not occur.\* In a third variation, the replacement reaction involves the oxygen atom attaching to the molecule and part of the original molecule departs (usually as a radical). An alkoxy radical and an alkyl radical are the products formed.

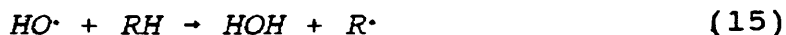


Alkyl radicals formed in the above reactions can rapidly

react with another atom of oxygen.<sup>9,10</sup>



The radical can also cause the following propagating reactions, which are rather slow and unimportant in atomic oxygen degradation.<sup>10</sup>



The formation of hydroperoxides is also a possible reaction.



The rate of degradation is dependent on total fluence which includes a dependence on sample orientation relative to ram, or normal versus sweeping impingement.<sup>3</sup> The reaction rate of the material at a high fluence is greater than the reaction rate at a low fluence. The dependence on the angle of impingement is that ram oriented surfaces receive more fluence than solar inertial surfaces; therefore, the rate of degradation is greater for surface in the ram position.

On the other hand, the rate of degradation is not dependent on the temperature, film thickness, and flux.<sup>3</sup> The attack of atomic oxygen is nontemperature dependent due to the high kinetic energy.<sup>3,11</sup> The reaction rate also seems to have no direct dependency on solar radiation and electrically charged particles.<sup>3</sup>

The degradation by atomic oxygen manifests itself as

material weight loss and changes in surface morphology.<sup>9,10,12-14</sup> Atomic oxygen only attacks the surface of the material. Erosion is usually seen as a darker colored area for exposed material versus the unexposed material. For films, the glossy finish tends to form a more diffuse appearance. The surface of the exposed material tends to have a "carpet" or "ruglike" morphology.<sup>2,13</sup> Since the reactivity of the atomic oxygen is dependent on the surface area of the material, as this "carpet" morphology is formed, the surface area increases causing the reactivity to increase.<sup>14</sup> Because the degradation is confined to the surface, the bulk properties of the exposed polymeric materials are usually unchanged.

Structures containing stronger bonds tend to exhibit greater resistance to attack by atomic oxygen relative to structures with weaker bonds.<sup>15-17</sup> These stronger bonds can be seen in the backbone or on pendant side groups. The pendant side groups can also physically block atomic oxygen from attacking the important backbone bonds (called the sheathing effect). Aromatics and polar functional groups also promote stability by enhancing radiationless deactivation of normally reactive species.<sup>17</sup>

Metals were found to be more stable and less reactive than most organic materials.<sup>1,2</sup> They usually form oxides after exposure which were less reactive. Only silver and osmium were found to be very reactive and showed substantial weight loss. In the case of silver, the oxides formed were non-

adherent and tended to spall or flake off. Osmium forms an oxide that is volatile.

Materials that were found to be more stable by at least a factor of 50 were perfluorinated and silicone polymers.<sup>1</sup> Table 1 lists the reaction efficiencies for selected compounds. The silicone polymers were less reactive due to the strong Si-O backbone. The "organic-inorganic" siloxanes were also converted to "inorganic", ceramic-like silicon dioxide and formed a protective coating. The perfluorinated polymers are relatively stable due to the possible sheathing effect of the C-F bond, which has a bond strength of 5.0 eV.

Table 1: Reaction Efficiencies for Selected Materials<sup>2</sup>

Material:	Reaction Efficiencies $\times 10^{-24}$ cm <sup>3</sup> /atom
Teflon, FEP	<0.05
Teflon, TFE	<0.05
1034 C Graphite Epoxy	2.1
5208/T3000 Graphite Epoxy	2.6
Mylar	3.4
Polycarbonate	6.0
Polyethylene	3.7
Kapton	3.0
Polymethylmethacrylate	3.1
Siloxane Polyimide (25% Sx)	0.3
Siloxane Polyimide (7% Sx)	0.6
Polystyrene	1.7
Polysulfone	2.4
Tedlar	3.2

Using the reactivity of certain materials and the fluence prediction, one can calculate the extent of degradation of components of the space station.<sup>28</sup> Table 2 lists the surface

recession predictions for space station components. As seen from these calculations, the materials to be used would not last the lifetime of the space station, if they were exposed to atomic oxygen.

Traditionally, antioxidants were used to retard oxidation. Since oxidation occurs mainly on the surface for atomic oxygen attack, these antioxidants, up to 10% by weight, showed no change in the reaction rate of oxygen.<sup>9</sup> Another method to prevent atomic oxygen degradation was to use a protective coating. Although mass loss was prevented, defects in the coating could cause undercutting. Figure 3 depicts the role of undercutting on polymeric materials.

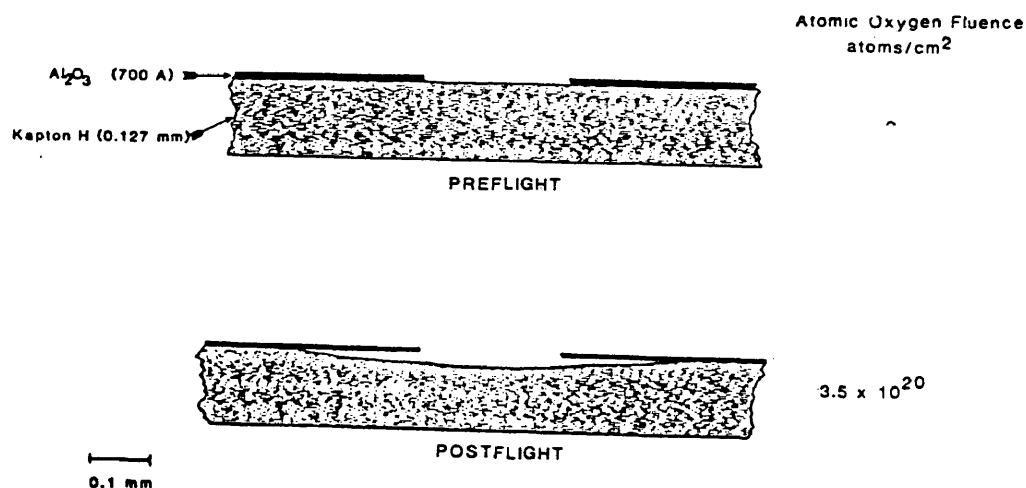


Figure 3: Undercutting in Polymeric Materials<sup>2</sup>

The use of additives is another method of protecting against oxidative attack. Additives are used to shadow incoming atomic oxygen from the organic matrix.<sup>18,19</sup> These materials are usually oxides. For example, Ueno and co-

**Table 2: Surface Recession Predictions for Space Station Components<sup>1a</sup>**

Materials:	Lifetime yr	Constant altitude (465 km)		Constant density ( $2 \times 10^8$ atoms/cm <sup>3</sup> )	
		Fluence atoms/cm <sup>2</sup>	Recession cm (mil)	Fluence* atoms/cm <sup>2</sup>	Recession cm (mil)
Graphite epoxy structural members, forward facing side	30	$3.6 \times 10^{22}$	$8.6 \times 10^{-2}$ (34)	$1.4 \times 10^{23}$	$3.2 \times 10^{-1}$ (126)
Solar power arrays front and back, exposure	20	$1.3 \times 10^{22}$	$3.8 \times 10^{-2}$ (15)	$5.5 \times 10^{22}$	$1.7 \times 10^{-1}$ (65)
Radiator surfaces front and back, exposure	20	$1.5 \times 10^{22}$	--	$6.3 \times 10^{22}$	--

\*Constant density results in approximately 4 times more fluence

workers found that polymers doped with iodine compounds and iodinated polymers were resistant to oxygen plasma.<sup>20</sup> The one drawback is that atomic oxygen only attacks the area around the filler. The area under the filler is unaffected. Thus, the filler is only partially attached to the matrix through underlying pedestal regions which may be lost in time.

Instead of using additives, the protecting substituent can be incorporated into the backbone of the polymer. Siloxane modified polyimide<sup>21</sup> and epoxy resin<sup>22</sup> were made and exposed to atomic oxygen. In the material, the siloxane was reported to migrate to the surface. The modified polyimides showed increased resistance to atomic oxygen. On the other hand, the modified epoxy resin exhibited no change in comparison to the unmodified resin.

## EXPERIMENTAL

### Atomic Oxygen

The atomic oxygen experiments were run in a commercially available radio frequency (RF) plasma generator (SPI Supplies Plasma-Prep II model 11005), which is commonly known as an asher. Figure 4 shows a schematic diagram of the apparatus. A RF oscillating field of 13.56 MHz was applied in order to dissociate the molecular oxygen. Dissociation of molecular oxygen generated a plasma of ions, electrons, and atomic oxygen (AO). A comparison of the asher and LEO constituents is given in Table 3.<sup>23</sup>

Table 3: Comparison of Asher and LEO Constituents<sup>23</sup>

<u>Constituent</u>	<u>Polymer Interaction</u>	<u>Percent Composition, %</u>	
		<u>LEO</u>	<u>Asher</u>
O( <sup>3</sup> P)	Yes	54 - 83	19 - 48
O( <sup>1</sup> D)	Yes	2x10 <sup>-6</sup> - 3x10 <sup>-4</sup>	0
O( <sup>1</sup> S)	Yes	10 <sup>-7</sup> - 7x10 <sup>-5</sup>	0
HI	Yes	4x10 <sup>-3</sup> - 1	0.9 - 2.2
O <sub>2</sub> <sup>+</sup>	Yes	5x10 <sup>-7</sup> - 7x10 <sup>-5</sup>	6x10 <sup>-5</sup> - 10 <sup>-4</sup>
O <sub>2</sub>	No	0.2 - 3	50 - 80
N <sub>2</sub>	No	1 - 50	3x10 <sup>-3</sup> - 9x10 <sup>-3</sup>
HeI	No	7x10 <sup>-2</sup> - 13	0
ArI	No	2x10 <sup>-3</sup> - 3x10 <sup>-2</sup>	0

where I corresponds to neutral atomic species

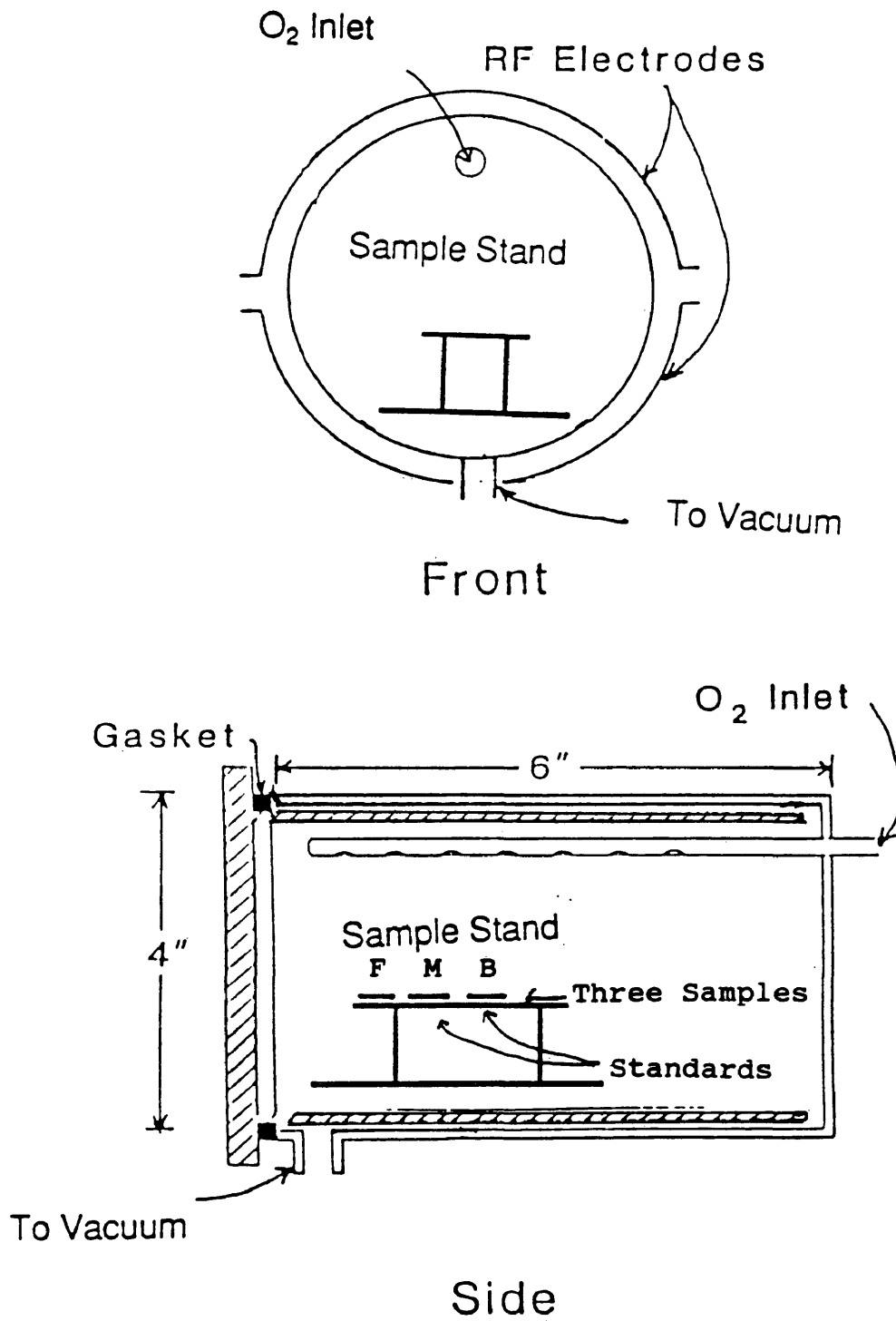


Figure 4: Reaction Chamber for Atomic Oxygen Experiments

For all atomic oxygen experiments, the film samples were cut into discs 2.22 cm (7/8 inch) in diameter, wiped clean with absolute ethanol, weighed, and then placed on a stand with the surface normal to the incident AO flux. The thickness was also measured before exposure using a micrometer. Three specimens were used in the experiments with two of the specimens being films of a standard, usually commercial polyetherimide (PEI). The third specimen was the test subject and was placed in the front position on the stand. The middle and back positions on the stand were taken up by the standard. The stand was always placed in the chamber in the same position. The chamber was then evacuated to a pressure of about 100 millitorr (about 30 min.).

Three different atomic oxygen experiments were run. The first one was run on all test samples. In this experiment, the specimens were exposed in the asher for 90 minutes four times for a total exposure of 360 minutes. After each exposure, the sample holder was taken out, and each disc was reweighed. If a sample was found to be a prime candidate for more testing, the other two experiments, continuous exposure and long-term exposure, were conducted. In the continuous exposure experiment, the specimens were exposed for 360 minutes without any breaks. In the long-term experiment, the specimens were again exposed for intervals of 90 minutes, but the total exposure time was at least 720 minutes.

## INTRODUCTION

### Siloxane Modified Epoxy Resin

Functionalized siloxane oligomers can be synthesized anionically or cationically by an equilibrium reaction. The molecular weight of the oligomers can be controlled by using a functionalized end blocker. The characteristics of the oligomers can be varied by changing the functionality of the end group and the pendant side group of the backbone chain. These oligomers can then be used to modify an epoxy resin in order to improve the properties of the network.

## LITERATURE REVIEW

### Siloxane Modified Epoxy Resins

#### Siloxane Oligomers

Polyorganosiloxanes, which are commonly known as "silicones" or "silicon elastomers", have unique properties which allow them to be utilized over a wide range of applications from biomaterials to space research. The repeat unit of a polyorganosiloxane consists of alternating silicon and oxygen atoms with two monovalent organic substituents attached to each of the silicon atoms as shown below in Figure 5. For this structure, the term "silicone" was adopted due to the similarity between the structural unit of the chain ( $R_2SiO$ ) and a ketone ( $R_2CO$ ). A more scientific term used for the Si-O bond is "siloxane". The most common substituent for the polyorganosiloxanes is the methyl group. Other important substituents are also used. Table 4 shows the substituents and the simplified terminology.

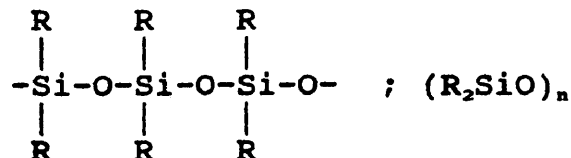


Figure 5: Repeat Unit of Polysiloxane

Table 4: Common Terminology of Linear Siloxanes

<u>Symbol:</u>	<u>Structure:</u>	<u>Name:</u>
D	$(\text{CH}_3)_2\text{SiO}$	Dimethylsiloxane
D'	$(\text{C}_6\text{H}_5)\text{CH}_2\text{SiO}$	Phenylmethylsiloxane
D''	$(\text{C}_6\text{H}_5)\text{SiO}$	Diphenylsiloxane

Many of the useful properties of the silicone elastomer are due to the molecular structure of the polymer chains. For example, an important property of a siloxane polymer is its high thermal and oxidative stability. This property stems from the Si-O bond, which is one of the most thermally stable bonds formed by silicon. A high bond energy prevents the Si-O bond from undergoing homolytic cleavage. Its bond dissociation energy of 110 kcal/mole<sup>24</sup> is higher than the C-O bond (85.5 kcal/mole), the C-C bond (82.6 kcal/mole), and the Si-C bond (76 kcal/mole).<sup>25</sup> The bond length of the Si-O bond is  $1.64 \pm 0.03 \text{ \AA}$ ,<sup>24</sup> which is smaller than that of Si-O bond length calculated from the addition of atomic radii (1.83 Å). The shortening of the bond is due to the ionic character (40-50%), the partial double bond from the  $p\pi-d\pi$  interactions, and the nature of the substituent groups.<sup>24</sup>

In polydimethylsiloxane, the ease of rotation of the methyl groups produces a large molar volume ( $75.5 \text{ cm}^3/\text{mole}$ )<sup>26</sup> and a low cohesion density<sup>27</sup> (ie., weak intermolecular forces). The low intermolecular forces and high flexibility give some very desirable properties: a low glass transition temperature ( $T_g = -123^\circ\text{C}$ ), low surface tension and energy, low solubility

parameter, and low dielectric constant.<sup>24,28</sup> The weak intermolecular forces of polysiloxanes are due to the helical structure of the chain. The helical structure consists of a coil of Si-O bonds with about 6 to 7 units per turn in its backbone structure with the organic substituents protruding.<sup>24</sup> These protruding organic substituents make the polysiloxane very hydrophobic.

Other important properties of polydimethylsiloxane are its transparency to visible and UV light, resistance to ozone and coronal discharge, and stability against atomic oxygen and oxygen plasma. Its low glass transition temperature and good thermal stability make it very useful over a wide temperature range.

All these properties can be changed to a certain degree and tailored to specific needs by replacing the substituent groups on the siloxane backbone.<sup>29,30</sup> For example, the thermal stability of the polymer can be affected by the type of substituent on the polymer backbone.<sup>31</sup> Table 5 shows the thermal life of a number of silicone polymers. Another important modification is the introduction of reactive functional groups into the siloxane chains either as pendant side groups or especially as terminal units to produce very reactive intermediates.<sup>29</sup> In this paper, the discussion will focus on these  $\alpha,\omega$ -difunctional siloxane oligomers.

The general structure of an  $\alpha,\omega$ -difunctional siloxane oligomer is shown in Figure 6. Variations can be achieved by

Table 5: Thermal Life as a Function of Alkyl or Aryl Substituent on Silicon<sup>30</sup>

<u>Group Bonded to Silicon</u>	<u>Approximate Half-life at 250°C<sup>a</sup> (h)</u>
Phenyl	>100,000
Methyl	>100,000
Ethyl	6
Propyl	2
Butyl	2
Pentyl	4
Decyl	12
Octadecyl	26
Vinyl	101

(<sup>a</sup>Time at which half of the groups are replaced by oxygen)

changing the X, R, and Y groups as shown in Table 6.<sup>32-37</sup> The reactivity of these siloxane oligomers toward other reactants is dependent on the terminal functional groups. Also, the composition of the backbone of the oligomers can be varied in order to change the glass transition temperature, solubility parameter, thermal stability, and surface behavior.<sup>35</sup> The molecular weight of the oligomer can also affect these properties.<sup>30</sup>

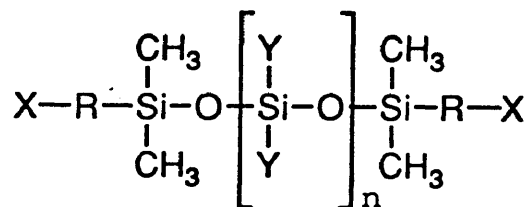
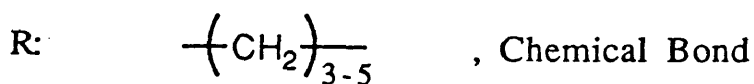
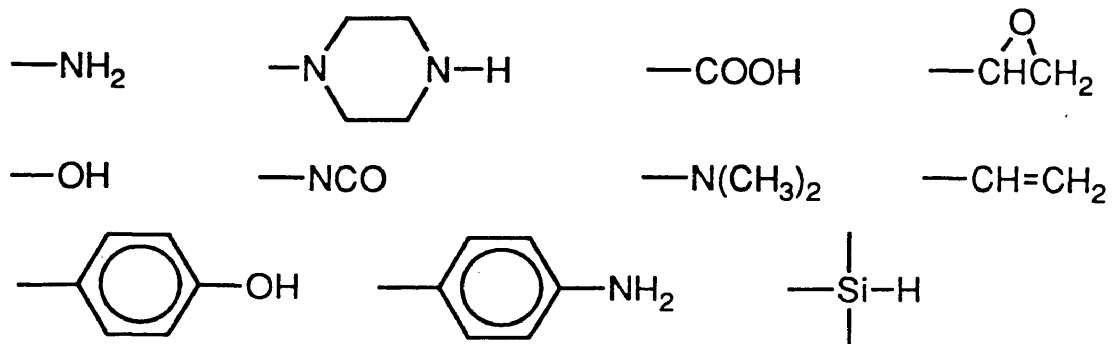


Figure 6: General Structure of an  $\alpha,\omega$ -Difunctional Siloxane Oligomer

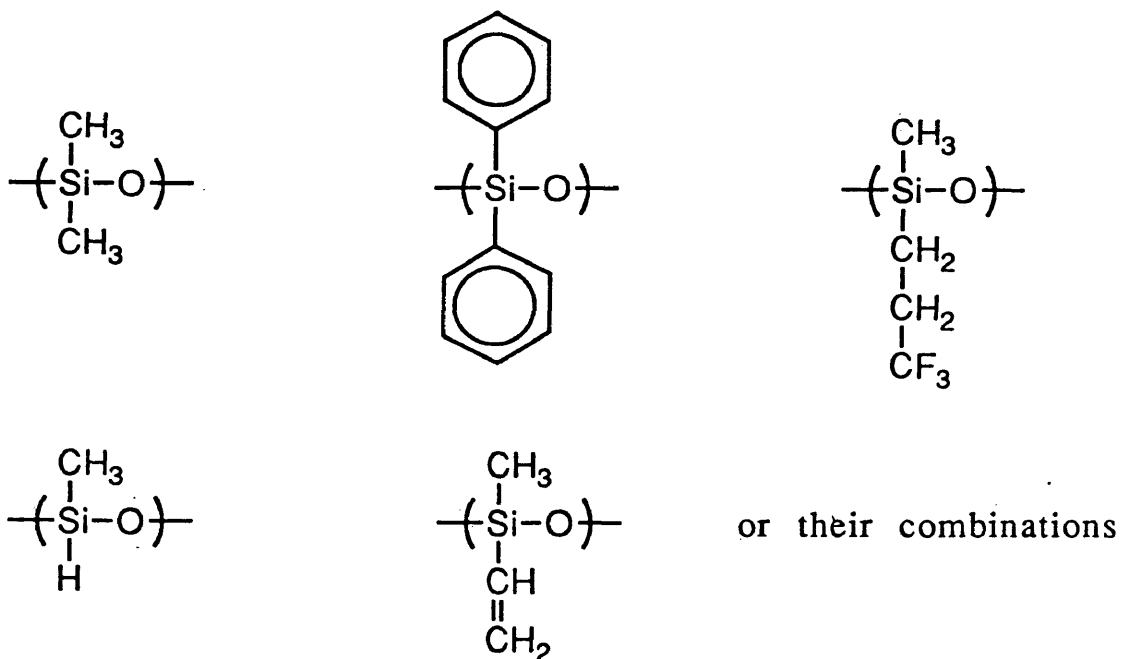
Increased thermal radiation and oxidative stability are achieved through the use of phenyl groups as the substituent. Aromatic rings offer higher stability, raise glass transition

Table 6: Variations of X, R, and Y Groups

## X: Functional End Groups



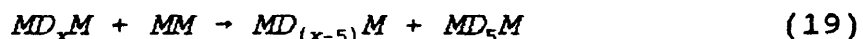
## Y: Backbone Composition



temperatures, and cause an increase in viscosity. A higher solubility parameter is also accomplished because of the increased polarizability.

Linear polysiloxanes can be synthesized by both anionic and cationic polymerizations of cyclic siloxanes.<sup>32-37</sup>

Controlled amounts of monofunctional end blockers are used to control the molecular weight of the polymer. In the reaction, both the rings and the chains are attacked by the anionic or cationic catalyst because of the similarity of the siloxane bonds between linear and cyclic species. This reaction is known as the redistribution or equilibrium polymerization. Different reactions are shown below (equation 17-20).<sup>32,34</sup> In siloxane nomenclature, M equals a monofunctional siloxane unit, and D equals a difunctional siloxane unit. Therefore, D<sub>4</sub> equals the cyclic siloxane tetramer, and MM equals the linear dimer.



The reactivity of the catalyst toward the reactants is very important to these equations. For a base catalyzed reaction (the method used in these studies), the reactivity of the siloxane toward the base is  $D_3 > D_4 > MD_2M > MDM > MM$ , where  $D=(CH_3)_2Si$  and  $M=(CH_3)_3Si$ .<sup>38</sup> Because the cyclic species react before the end blocked reactants, equations 17 and 18 proceed rapidly with equation 17 dominating. During this initial stage, the viscosity is increasing rapidly. As the concentration of D<sub>4</sub> is depleted, equation 18 starts to

dominate. As soon as the viscosity reaches its maximum and starts to decrease, equations 19 and 20 begin to govern the reaction. The equilibrium state is dependent on ratio of M to D units.

For the acid catalyzed equilibrium, no maximum viscosity is achieved. Again, the reason is the reactivity of the reactants. The reactivity of the siloxane toward the acid catalyst is  $D_3 > MM > MDM > MD_2M > D_4$ .<sup>36</sup>

A Gaussian distribution of molecular weights among the chain molecules along with an approximately monotonically decreasing distribution of cyclic species as ring size increases is observed from these reactions at thermodynamic equilibrium.<sup>32,34</sup> The rates of these various processes can be controlled by changing some factors on which the processes are dependent. These factors are catalyst type and concentration, temperature, pressure, and the type and amounts of promoters.<sup>32,34</sup>

Figure 7 shows the general scheme for the synthesis of reactive  $\alpha, \omega$ -difunctional siloxane oligomers.<sup>32,34</sup> The catalyst cleaves only the silicon-oxygen bond in the cyclic and the linear species. It does not attack the silicon-alkyl (or -aryl) bond due to its covalent nature. The cyclic species when cleaved has active ends that can be incorporated into the linear species. The cyclic species present at the end of the reaction can be removed by vacuum distillation at elevated temperature. The catalyst also has to be removed. Its

removal is dependent on the type of catalyst. For example, if the catalyst is a "transient", it is removed by raising the temperature of the reaction mixture so that it decomposes.<sup>39</sup>

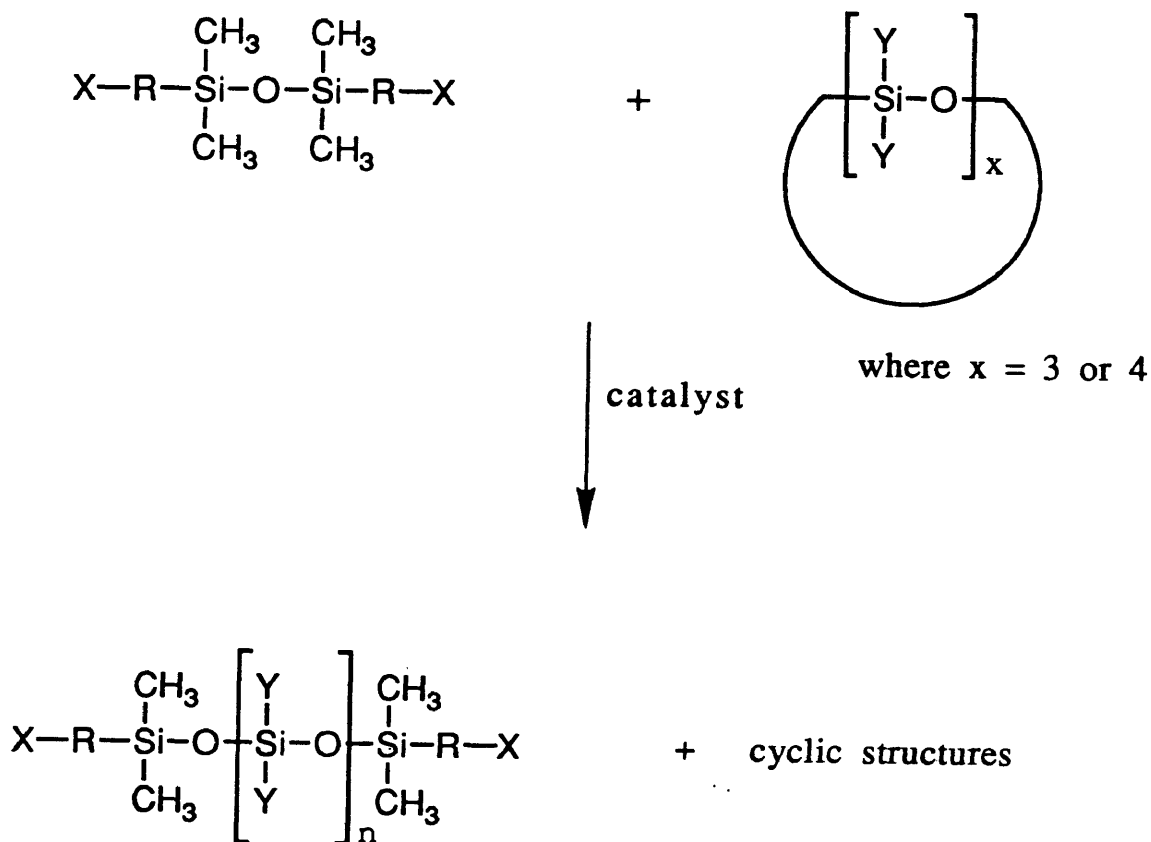


Figure 7: Synthesis of Functionally Terminated Siloxane Oligomer

For the anionically catalyzed reaction, the different bases that can affect the polymerization of cyclosiloxane include alkali metal hydroxides and their siloxanes, quaternary ammonium and phosphonium hydroxides and their siloxanates, alcoholates, phenolates and many others.<sup>40</sup> Quaternary ammonium and phosphonium bases have been found to

be very effective for the equilibration reactions and are known as "transient" catalysts.<sup>39</sup> The main advantage is their ability to decompose at high temperatures to yield easily removable inert products.

The mechanism for the base catalyzed polymerization of cyclosiloxanes is illustrated in Figure 8.<sup>38,41</sup> The base attacks the electropositive silicon atom of cyclic or linear siloxane species. The rates of polymerization are proportional to the square root of the catalyst concentration because of the tendency of the active centers to form ion pairs.<sup>28,32</sup> The rate is also dependent on the electronegativity of the substituents on the silicon atoms. An electron-withdrawing substituent increases the effective positive charge on the silicon atom and facilitates nucleophilic attack. Also, polar aprotic solvents increase the rates of anionic polymerization.<sup>42</sup>

The acid-catalyzed, or cationic, polymerization is used when the end-blockers are susceptible to base attack. An example of these types of end groups is the alkyl linked carboxylic acid. The acids generally used are sulfuric acid, sulfonic acids, Lewis acids, mineral acids, and trifluoroacetic acid.<sup>32</sup> The acid polymerized reaction is less studied than the anionic polymerization because it is less industrially important.

The cationic polymerization mechanism is shown in Figure 9.<sup>32,38</sup> The initiation step involves the protonation of the

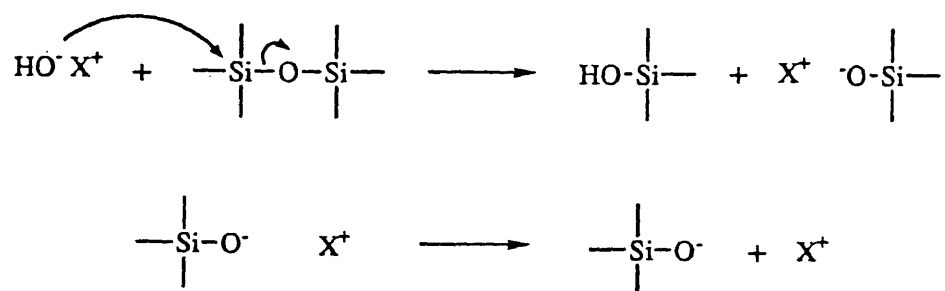
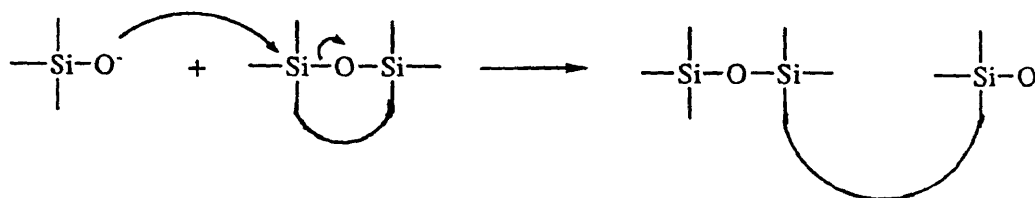
InitiationPropagation

Figure 8: Mechanism for the Anionic Polymerization of Cyclosiloxanes

oxygen atom in the cyclosiloxane followed by the cleavage of the Si-O bond. The species formed is a silanol and a siliconium cation which may be the active center and the propagating species. The rate of cationic polymerization is decreased when the cyclosiloxanes contain electron-withdrawing substituents and increased when the substituents are electron-donating groups attached to the silicon atoms.

$\alpha,\omega$ -Difunctional siloxane oligomers are important starting materials or intermediates for the synthesis of various block, segmented and graft copolymers and network structures.<sup>29</sup> The most widely used reactive end groups are hydroxyl, amine, epoxy, and carboxyl. McGrath and co-workers have synthesized different  $\alpha,\omega$ -difunctional siloxane oligomers and used them to modify different polymer systems.

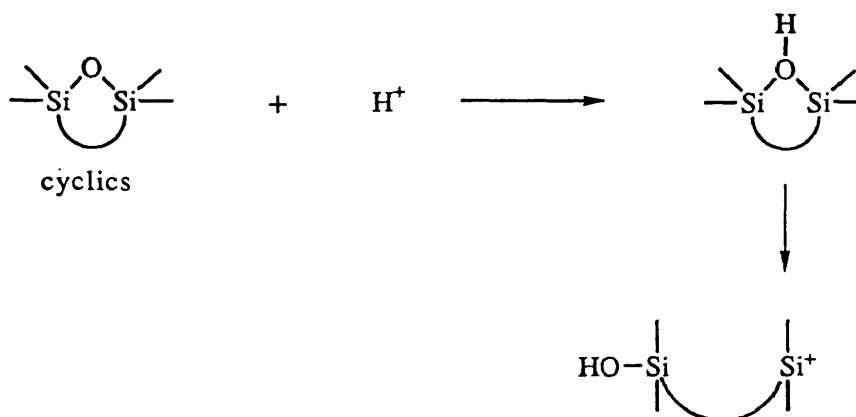
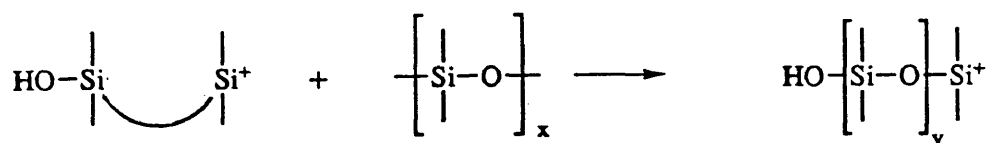
InitiationPropagation

Figure 9: Mechanism for the Cationic Polymerization of Cyclosiloxanes

Epoxy Networks

Epoxy networks are a class of thermoset polymers. They are a cross-linked, infusible three-dimensional networks. The characteristics of the epoxy network are excellent dimensional stability; high chemical and solvent resistance, excellent mechanical properties, good adhesion to many substrates, and good electrical properties.<sup>43</sup> The networks are formed by reacting an epoxy resin with a curing agent.

Epoxy resins are characterized by a three-membered ring called the epoxy, oxirane, ethoxyline, or epoxide group. The resins are reactive prepolymers of molecular weight less than 4000. The backbones of the commercial epoxy resins are made

with aliphatic, cycloaliphatic, and aromatic groups. These different background groups enable epoxy resins to exhibit excellent properties.

There are two types of epoxy resins: the glycidyl ether groups and the non-glycidylether group. The glycidyl ether groups result from a reaction of an alcohol (usually bisphenol-A) with epichlorohydrin. The non-glycidylether group are not based on epichlorohydrin. The subsequent discussion will be mainly devoted to the first group, glycidyl ether based, and those resins derived from the reaction of bisphenol-A and epichlorohydrin because this resin is the one used in the research.

The resins obtained from the reaction of bisphenol-A and epichlorohydrin are the most commercially important and widely used. The general structure of the resin is shown in Figure 10. The variable  $n$  can vary between 0 and 13, which corresponds to an average molecular weight of 340 to about 4000. Usually for most commercial resins of this type,  $n$  is equal to about 0.1.

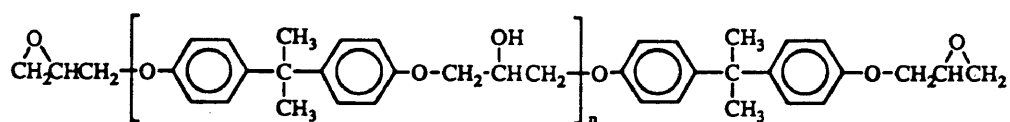


Figure 10: Structure of the Resin Based on Bisphenol-A and Epichlorohydrin

The synthesis of bisphenol-A diglycidyl ether based epoxy resin involves the condensation of bisphenol with

epichlorohydrin at temperatures of 50-60°C in the presence of alkaline catalyst which is commonly sodium hydroxide (Figure 11).<sup>44</sup> The reaction is carried out in the presence of excess epichlorohydrin. The by-products are sodium chloride and water.

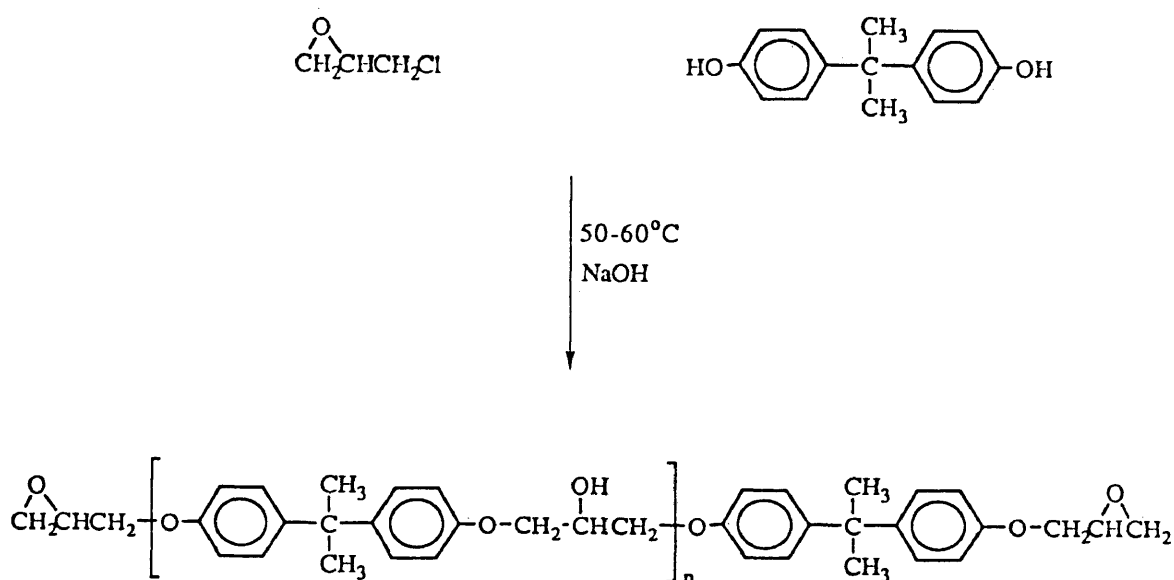


Figure 11: Synthesis of Bisphenol-A Diglycidyl Ether Based Epoxy Resin

To become a more useful material, the epoxy resins need to be reacted with other compounds, called curing agents or hardeners, in order to form a cross-linked network. The curing of the epoxy resins occurs by the reaction of the epoxide or the pendant hydroxyl group. The functionality of the epoxy resins or curing agent must be greater than 2, and the total functionality of 5 is required.<sup>45</sup> The epoxide ring

can be attacked by many compounds, which can be either acidic or basic.<sup>46</sup> The curing agents are classified into two groups: polyfunctional and catalytic.

The many different variables involved in the formation of the epoxy network make it difficult to make generalizations concerning the structure-property relationship. The nature of the network is dependent on the different properties associated with a given epoxy resin and curing agent. Some excellent properties exhibited by the epoxy network are high chemical and corrosion resistance, good mechanical and thermal properties, low shrinkage upon cure, flexibility, good electrical properties, and the ability to be processed under various conditions. Aside from these desirable properties, they are generally brittle, have low fracture energies, and may display high water absorption.<sup>44</sup> To improve on these undesired properties, the resin can include other constituents in the composition that may facilitate processing and modify the cured resin properties.<sup>44</sup> These constituents may be fillers, solvents, diluents, plasticizers, and accelerators. One such way, the modification of the epoxy network using functionalized elastomers, has been used more and more to improve the resin.

### Modified Epoxy Networks

When an epoxy network is modified with a functionalized elastomer, improvements in fracture and impact energies of the

networks can be made by changing different parameters of the modifier with little effect on the other desired properties of the epoxy resins.<sup>47,48</sup> These parameters include structure, molecular weight, solubility parameter, and concentration of elastomer. Also, the structure and reactivity of the curing agent must be carefully controlled.<sup>47,48</sup>

Previously, the majority of the research in toughening the epoxy networks has used carboxyl terminated butadiene-acrylonitrile elastomers and the amine terminated butadiene-acrylonitrile elastomers.<sup>49-51</sup> Even though the butadiene-acrylonitrile elastomers have successfully improved the toughness of epoxy networks, premature thermal and/or oxidative instability can take place due to unsaturation present in the elastomer.<sup>47,52-55</sup> Another drawback of butadiene-acrylonitrile elastomers is their comparatively high glass transition temperature which limit their low temperature flexibility.<sup>53,54</sup> Other modifiers need to be found and tested that will improve the epoxy resins toughness, without adding new undesirable characteristics to the network.

One such possible modifier is the polysiloxane with functional end groups. Siloxane structures exhibit many desirable characteristics, such as thermal and oxidative stability, low glass transition temperature, hydrophobic character, and low surface energies.<sup>47,48,52-56</sup> Because of these characteristics, polysiloxanes can be useful modifiers.

James E. McGrath and coworkers have modified epoxy resins

using different polysiloxanes.<sup>47,48,52-56</sup> The general structures of the modifiers used in one of their first studies are depicted in Figure 12.<sup>47</sup> Using these modifiers, cross-linked epoxy networks were produced. The curing reaction is conducted at 160°C for two hours.

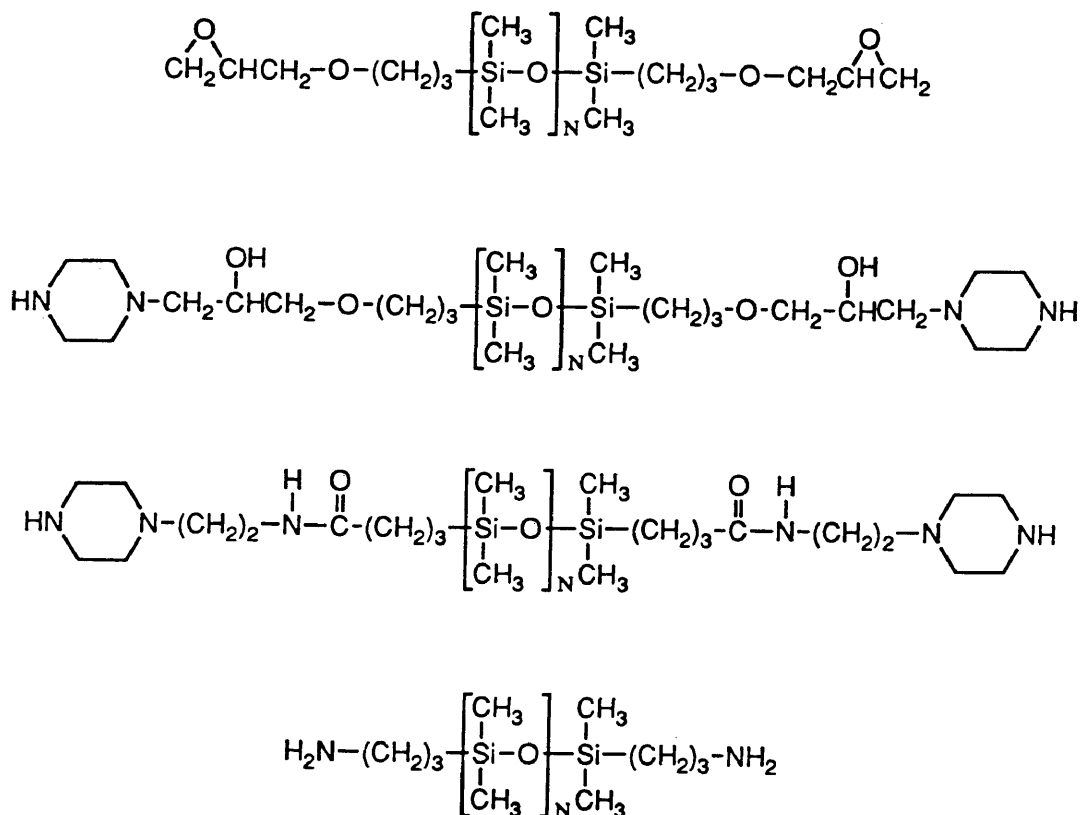


Figure 12: Structures of the Modifiers

An important aspect of the reaction is the miscibility of the modifiers with the epoxy oligomer.<sup>47,48,52,53</sup> The modifier must remain miscible before cure, and while the curing reaction takes place, it must microphase separately as small domains in the network. In the case of pure polydimethylsiloxane, the calculated solubility parameter is

7.6, which is much lower than that of the epoxy oligomer (about 9.4).<sup>53-55</sup> In order to increase the solubility parameter, a copolymer of the dimethylsiloxane with the partially aromatic diphenylsiloxane should be used.

Another important aspect is the reactivity of the functional groups, which is related to the miscibility of the modifier in the epoxy. Low miscibility can result in the product being heterogeneous in a non-controllable way. For example, undesirable, turbid, incompatible films were made from the epoxy functional siloxane. Another example is the use of a primary amine functional, or aminopropyl terminated, oligomer. The aminopropyl terminated modifiers react more slowly than the secondary amine (i.e. piperazine terminated) systems, because the modifier probably causes the epoxy system to gel prematurely.<sup>47,48</sup> Thus, the primary amine system also produced an inhomogeneous network.

Only the secondary amine terminated modifiers produce homogeneous cured networks.<sup>47,48</sup> These modifiers should only react with one epoxy group at moderate temperature. Therefore, they can be prereacted with the epoxy resin to prepare a linear soluble precursor. Then, the curing agent can be added to the precursor to form the network.

The characteristics of the epoxy networks are either improved or unaffected by the polysiloxane modifiers. In the case of the glass transition temperatures ( $T_g$ ), the length of the siloxane oligomer affects the  $T_g$  of the network.<sup>47,52</sup> A

shorter chain depresses the temperature, while on the other hand, longer chains develop a second microphase causing only nominal depression in the principal  $T_g$ .

## EXPERIMENTAL

### Siloxane Modified Epoxy Resins

#### Siloxane Oligomer

#### Materials

Octamethylcyclotetrasiloxane (or D<sub>4</sub>) and bis(3-glycidoxypropyl) tetramethyldisiloxane were received from Petrach Systems. These materials were dried over calcium hydride and vacuum distilled before use. Piperazine, 1,4-dioxane, and tetramethylammonium hydroxide pentahydrate were used as received from Aldrich. Octaphenylcyclotetrasiloxane (or D<sub>4</sub>" ) was obtained from Petrach systems and used as received.

#### Preparation of Siloxanolate Catalyst

The tetramethylammonium siloxanolate catalyst was prepared for the equilibration polymerization of siloxanes. This catalyst should be active enough for the synthesis of all the oligomers. The catalyst is also easy to deactivate, since it is a "transient" catalyst." At high temperatures (150°C), the catalyst decomposes into methanol and trimethylamine.

The apparatus was a three-neck flask equipped with an

overhead stirrer, an Argon gas inlet, a condensor fitted with a drying tube, and a heated oil bath. A 4:1 mole ratio of D<sub>4</sub> and the tetramethylammonium hydroxide pentahydrate was charged into the reaction vessel, and the reaction mixture was heated to 60°C. The reaction was allowed to run for about 48 hours at a temperature between 60 and 70°C. The argon flow should be sufficient to dehydrate the system. After a couple of hours, the solution became cloudy and very viscous. As time went on, the viscosity began to decrease, and the material became transparent. At the end of the reaction, the catalyst was stored under nitrogen and placed in a desiccating cabinet.

#### Synthesis of Epoxy Terminated Polydimethylsiloxane Oligomer

The epoxy terminated polydimethylsiloxane oligomer was prepared by equilibrium reaction of the epoxy terminated disiloxane and octamethylcyclotetrasiloxane. Figure 13 shows the chemical structure of the oligomer.

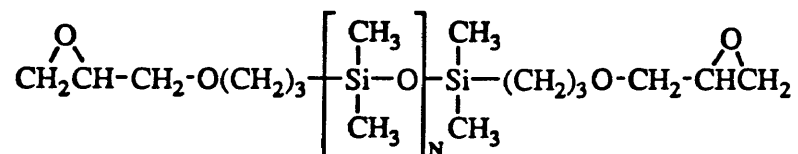


Figure 13: Structure of Epoxy Terminated Polydimethylsiloxane Oligomer

Octamethylcyclotetrasiloxane and bis(glycidoxypropyl) tetramethyldisiloxane were charged in a three-neck flask equipped with an argon inlet and a condensor with drying tube. The flask was heated in a controlled temperature bath until

the temperature of the reaction mixture stabilized (about 80°C). After stabilization, the catalyst was added. The amount of catalyst used was approximately 0.1% to 1.0% by weight. The reaction was allowed to run between 48 and 72 hours. To end the reaction, the temperature of the oil bath was raised to 150°C for about 3 hours. The oligomer was purified by vacuum stripping at 100°C. The purified oligomer was then stored under nitrogen and placed in the desiccating cabinet.

#### Synthesis of Piperazine Terminated Polydimethylsiloxane Oligomers

The piperazine terminated polydimethylsiloxane oligomers (Figure 14) were synthesized using a two-step process. First, the epoxy terminated polydimethylsiloxane oligomer was made as described previously. The second step involved the capping of the epoxy terminated oligomer with piperazine.

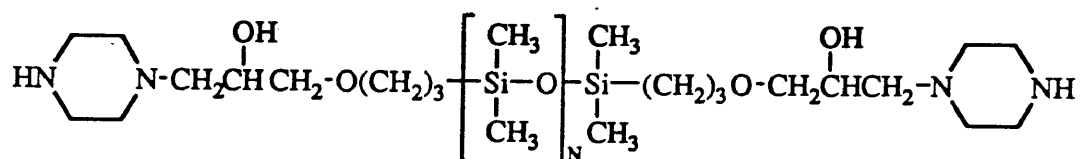


Figure 14: Structure of Piperazine Terminated Polydimethylsiloxane Oligomer

The epoxy terminated siloxane oligomer was capped with piperazine to produce an oligomer with secondary amine end groups. The molar ratio of piperazine to epoxy siloxane oligomer was 8 moles to 1 mole. The reaction was conducted in

dioxane at 60°C for about 24 hours. At the end of the reaction, the excess piperazine was removed by washing the oligomer extensively with distilled water. The final oligomer was extracted from the residue with methylene chloride. The methylene chloride was removed by rotary evaporation. The final oligomer was stored under nitrogen and placed in the desiccating cabinet.

#### Synthesis of Epoxy Terminated Poly(dimethyl-co-diphenyl) Siloxane Oligomer

The epoxy terminated poly(dimethyl-co-diphenyl) siloxane oligomer (Figure 15) was prepared by anionic equilibration. The equilibration reaction is described earlier in the epoxy terminated polydimethyldisiloxane section with the exception that the diphenyl tetramer was also used in the reaction.

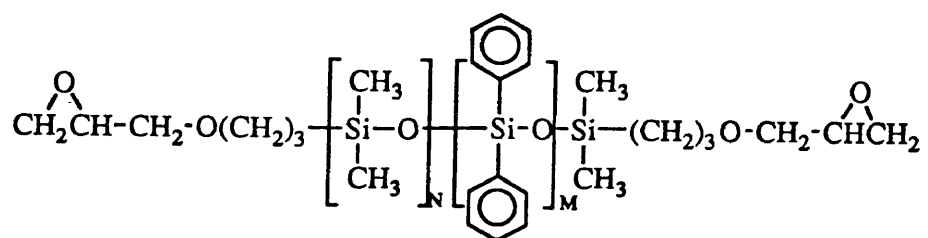


Figure 15: Structure of Epoxy Terminated Poly(dimethyl-co-diphenyl)siloxane Oligomer

D<sub>4</sub>, D<sub>4</sub>"', and the epoxy terminated disiloxane were charged to the reaction flask, and the temperature was raised between 90 and 100°C. Then, about 1.0% by weight of the catalyst was added. The reaction was carried out for 72 hours. After

about 24 hours, the reaction mixture became transparent. Upon completion of the reaction, the temperature of the oil bath was raised to 150°C for 4 hours. The volatile products were stripped off by vacuum at 100°C. Only the dimethyl cyclics and dimethyl-co-diphenyl cyclics could be stripped off under these conditions. The diphenyl cyclics could not be removed due to their high boiling points. The diphenyl cyclics were removed by dissolving the oligomer in isopropanol and filtering off the solid, if any. D<sub>n</sub> is not soluble in isopropanol. Isopropanol was removed by rotary evaporation.

#### Synthesis of Piperazine Terminated Poly(dimethyl-co-diphenyl) siloxane Oligomer

The piperazine terminated poly(dimethyl-co-diphenyl) siloxane oligomers (Figure 16) were synthesized using a two-step process similar to the one used to synthesize the polydimethylsiloxane oligomer. The first step was the synthesis of the epoxy terminated poly(dimethyl-co-diphenyl) siloxane oligomer (described previously), and the second step was the capping the epoxy terminated oligomer with piperazine (also described previously).

#### Preparation of the Epoxy Resin Films

The resin used was a bisphenol-epichlorohydrin based resin (Epon 815 from Shell). The curing agent was Curing

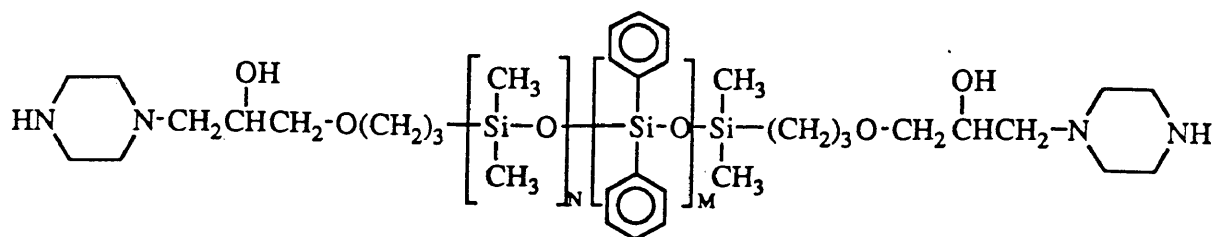


Figure 16: Structure of Piperazine Terminated Poly(dimethyl-co-diphenyl)siloxane Oligomer

Agent U also from Shell. For the modified epoxy network, the siloxane oligomers were prepared in the lab. Procedures for oligomer preparation were discussed earlier.

The epoxy network was made into a film using steel plates. For the controlled epoxy network, the ratio of Epon 815 to curing agent was about 10:1. Before placing between the plates, the mixture was degassed in a vacuum desiccator. The plates were clamped together with a C-clamp and placed into a vacuum oven at 160°C for 2 hours.

For the siloxane modified epoxy network, the network formation required two steps. First, the epoxy resin (Epon 815) was reacted with the siloxane oligomer to form a linear precursor. The reaction was run at 60°C for one hour under vacuum. The siloxane concentration ranged between 5 to 20 weight percent. The final step was the addition of the curing agent. A stoichiometric amount of the curing agent (again 10:1) was added. After mixing and degassing, the films were again made by pressing the mixture between two plates, as described previously.

### Atomic Oxygen Experiments

The procedure for the atomic oxygen experiments was described previously.

### Characterization of Siloxane Oligomers

#### Nuclear Magnetic Resonance Spectroscopy

Proton nmr spectrometry was used to verify the structure of the oligomers. The spectra were obtained using a GE-QE-300 spectrometer. The oligomers were dissolved in deuterated chloroform. From the integration of peaks, number average molecular weight and phenyl concentration could be determined.

#### Fourier Transform Infrared Spectroscopy

FTIR spectra were also obtained to confirm the chemical structure of the siloxane oligomers. The spectra are taken using a Nicolet 20DXB FTIR spectrometer. The liquid oligomers are placed between KBr salt plates.

### Characterization of Films

#### Fourier Transform Infrared Spectroscopy

The films were characterized by FTIR-ATR (Attenuated Total Reflectance) using a Nicolet 20DXB FTIR spectrometer. Spectra for both unexposed and exposed samples were obtained

and compared.

## RESULTS AND DISCUSSION

### Siloxane Modified Epoxy Resins

#### Siloxane Oligomer

Several siloxane oligomers were synthesized anionically using a siloxanolate catalyst. The synthesis of the oligomers involved two separate steps, as shown in Figure 17. An epoxy terminated siloxane oligomer was synthesized first. This reaction is the usual equilibration, or redistribution, reaction of the cyclic tetramer with a functional siloxane dimer. The functional dimer is utilized as an end blocker to control the molecular weight of the oligomer. Next, the epoxy end groups of this oligomer were capped using piperazine to produce the final piperazine terminated siloxane oligomer.

These oligomers were then used to modify an epoxy resin network. A modifier synthesized was the piperazine terminated polydimethylsiloxane oligomer, but it is known that an immiscible network is produced. An immiscible network is produced due the difference in the solubility parameters where polydimethylsiloxane and bisphenol A epoxy resin have solubility parameters of about 7.5 and 9.4, respectively. Therefore, a piperazine terminated poly(dimethyl-co-diphenyl) siloxane oligomer was synthesized to raise the solubility

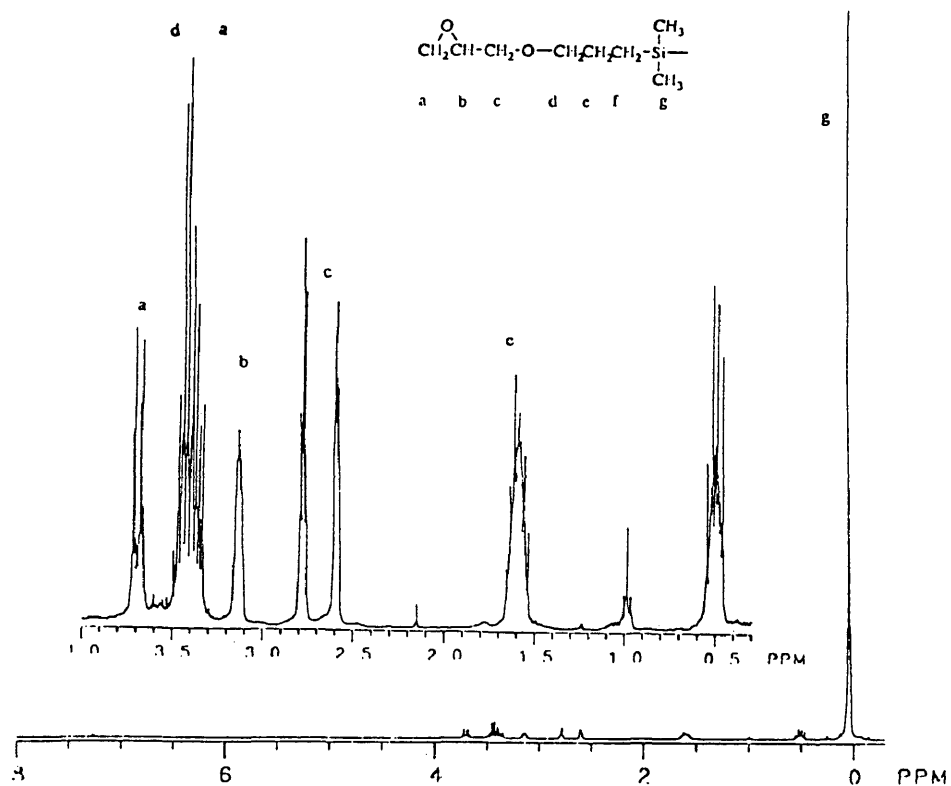


parameter of the siloxane oligomer.

The first reaction in the preparation of a piperazine terminated polydimethylsiloxane oligomer was the synthesis of the epoxy terminated oligomer. The epoxy oligomer was then capped with piperazine to form the piperazine terminated oligomer. The oligomer was characterized by  $^1\text{H}$ -nmr and FTIR spectroscopy. In all the spectra, corresponding peak assignments agreed with the expected molecular structure. The nmr spectra for both the epoxy terminated and the piperazine terminated polydimethylsiloxane oligomers are shown in Figure 18. From integration of the peaks, number average molecular weights between 1700 and 4800 were determined for several oligomers. Next, films were made in order to verify that the system was incompatible. The films showed that the epoxy and the modifier were highly incompatible, as was immediately evident when the two components were mixed.

The poly(dimethyl-co-diphenyl) siloxane modifier was then synthesized. These oligomers were also characterized by  $^1\text{H}$ -nmr and FTIR spectroscopy. The spectra obtained were similar to the spectra for the dimethyl oligomer, but with new peaks occurring due to the addition of the phenyl-siloxane repeat unit. In the nmr spectra (Figure 19), a new peak at about 7.5 ppm was obtained for the phenyl rings on the siloxane backbone. The number average molecular weight of the oligomer was again calculated by integration of the nmr peaks. The phenyl content was also calculated. These results are listed

a).



b).

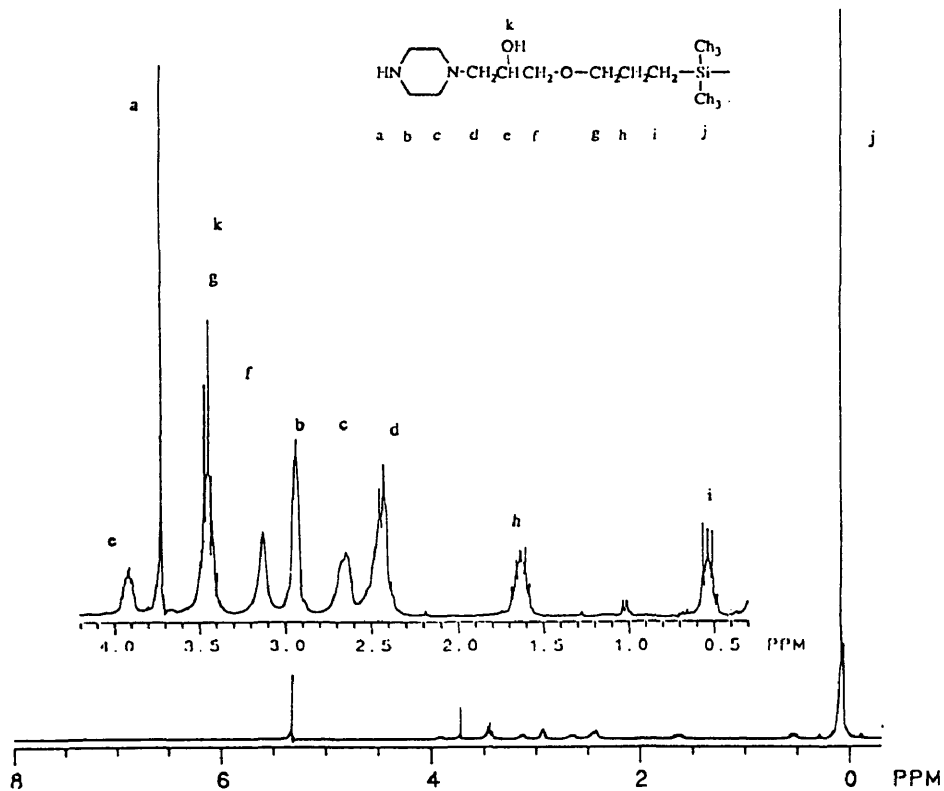
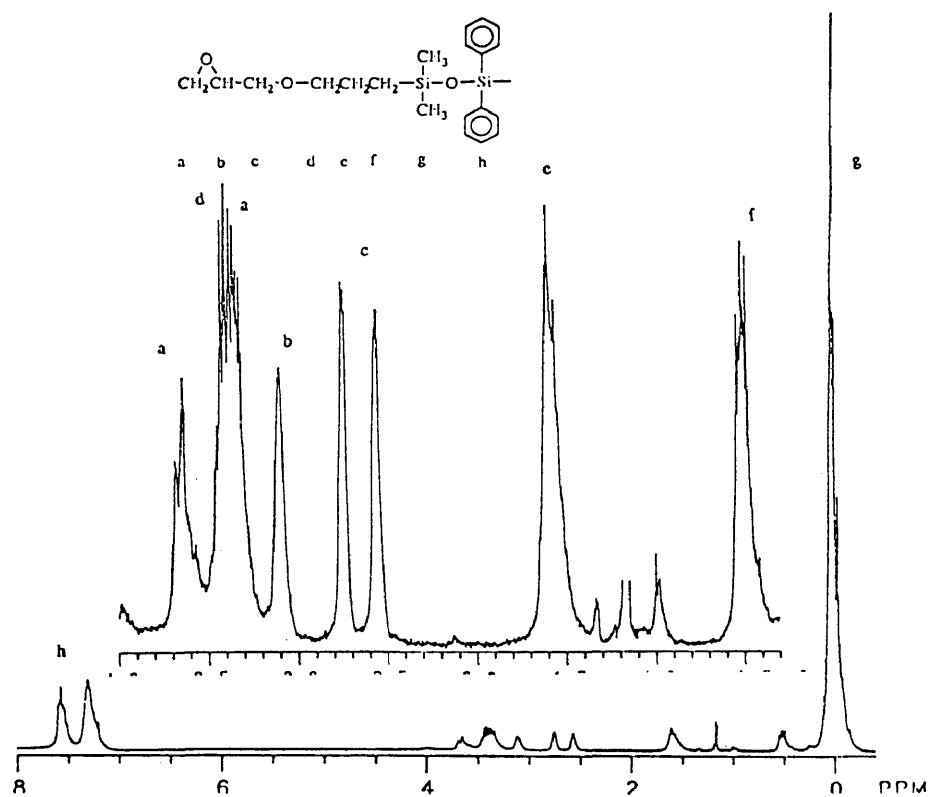


Figure 18: <sup>1</sup>H NMR Spectra for Polydimethylsiloxane Oligomers: a). Epoxy Terminated and b). Piperazine Terminated

a).



b).

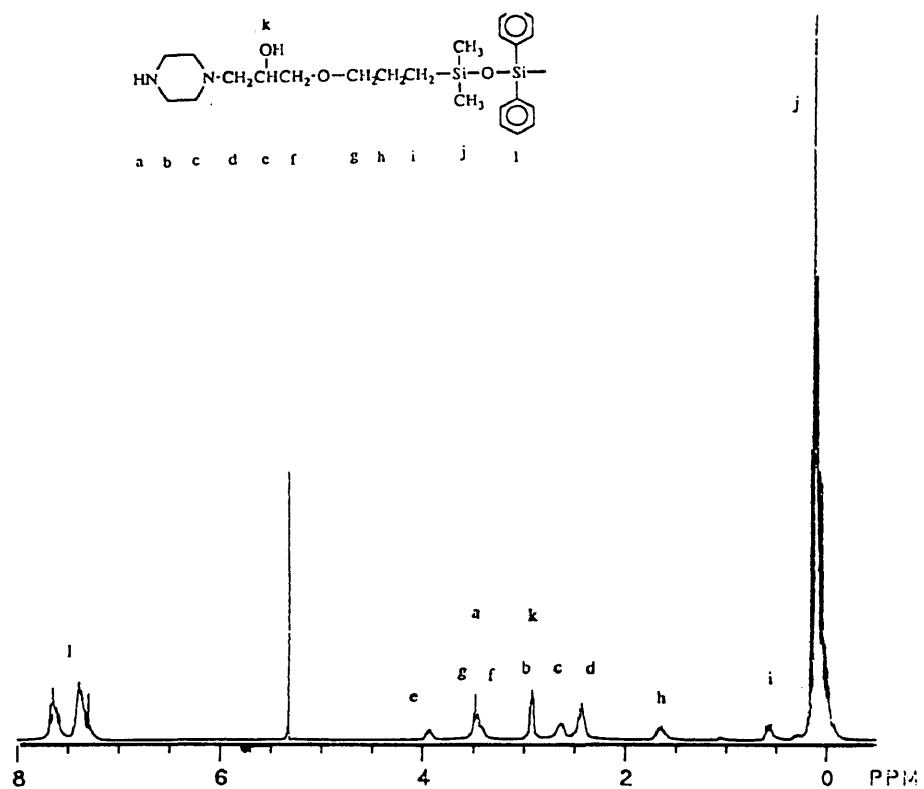


Figure 19: <sup>1</sup>H NMR Spectra of Poly(dimethyl-co-diphenyl) Siloxane Oligomers: a). Epoxy Terminated and b). Piperazine Terminated

in Table 7. A comparison of the FTIR spectra (Figure 20) of the dimethyl oligomer and dimethyl-co-diphenyl oligomers shows a new peak at about  $1425\text{ cm}^{-1}$  for the phenyl ring siloxane stretch.

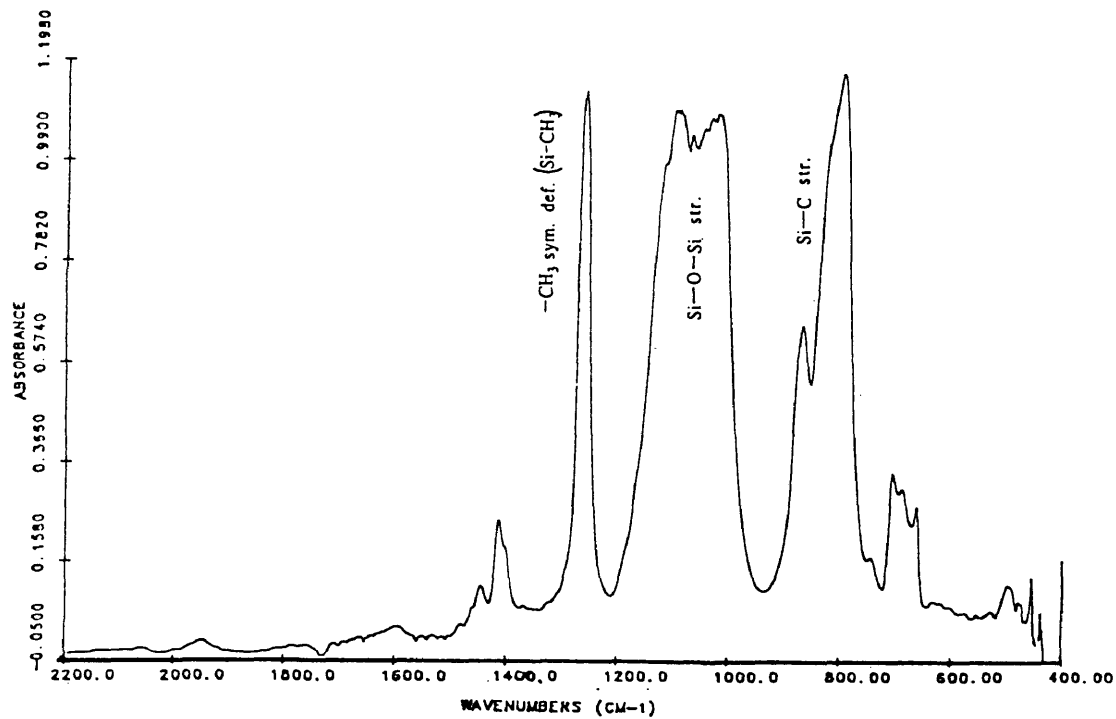
Table 7: Number Average Molecular Weight and Percent Phenyl Content of Oligomers

Oligomer	MW	% Phenyl
me/ph PIP #061590	2200	66
me/ph PIP #062790	5400	47
me/ph PIP #062990	3200	48
me/ph PIP #070490	2500	33

These oligomers were also used for films to test for their compatibility with epoxy resin. These films also formed incompatible systems. However, they showed slightly more compatibility than the dimethyl oligomer system. This increased compatibility can be seen during the formation of the linear precursor. The oligomer became slightly more soluble within the epoxy resin as the temperature was raised. Even though the solubility parameter of the modifiers was closer to the solubility parameter of the epoxy resin, the miscibility of the network is also dependent on the molecular weight of the blocks. In previous studies, McGrath and coworkers used Epon 828.<sup>53-55</sup> This study used Epon 815 resin which has a lower molecular weight than the Epon 828.

Even though the films formed an incompatible system, the films were still tested in the asher. The degradation of the films was followed by the amount of mass loss experienced by

a).



b).

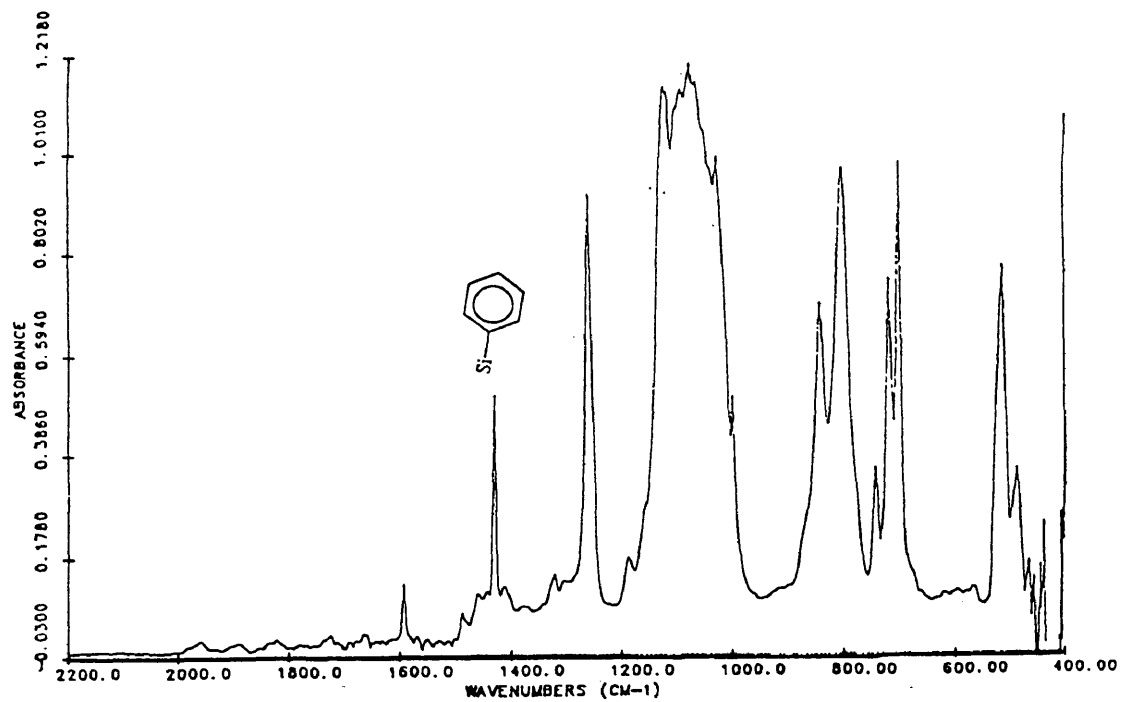


Figure 20: FTIR Spectra of Siloxane Oligomers:  
a). Polydimethyl and b). Poly(dimethyl-co-diphenyl)

the sample. The erosion rates were then calculated using the following equation:

$$\text{Erosion Rate} = \frac{\text{mass loss}}{\text{time exposed} * \text{surface area}} \quad (21)$$

The time exposed was equal to 90 minutes, and the surface area of the samples was 3.88 cm<sup>2</sup>. It was assumed that erosion took place on the upper side of the sample. (The bottom side in contact with the sample holder showed little evidence of erosion when examined by electron microscopy.) These results are shown in Table 8. The erosion rates of the modified epoxy resin are compared with the erosion rates of the unmodified epoxy resin. In an initial study, a polydimethylsiloxane oligomer was used as the modifier. As Figure 21 shows, the modified epoxy resin eroded about twice as fast as the unmodified network.

Table 8: Erosion Rates For Modified Epoxy Resins  
(mg min<sup>-1</sup> cm<sup>-2</sup>)

Sample:	Time Interval (90 min.)			
	1	2	3	4
Unmodified	0.94	0.69	0.74	0.83
PIP modified	1.9	1.8	1.8	1.7
9.1% me/ph PIP #070490	1.2	1.8	1.7	2.7
20.0% me/ph PIP #070490	0.94	0.94	1.0	1.3
18.1% me/ph PIP #062990	1.5	1.5	2.2	--

Two poly(dimethyl-co-diphenyl) siloxane modifiers of different phenyl contents were also tested and compared. The modified films still degraded faster than the unmodified film.

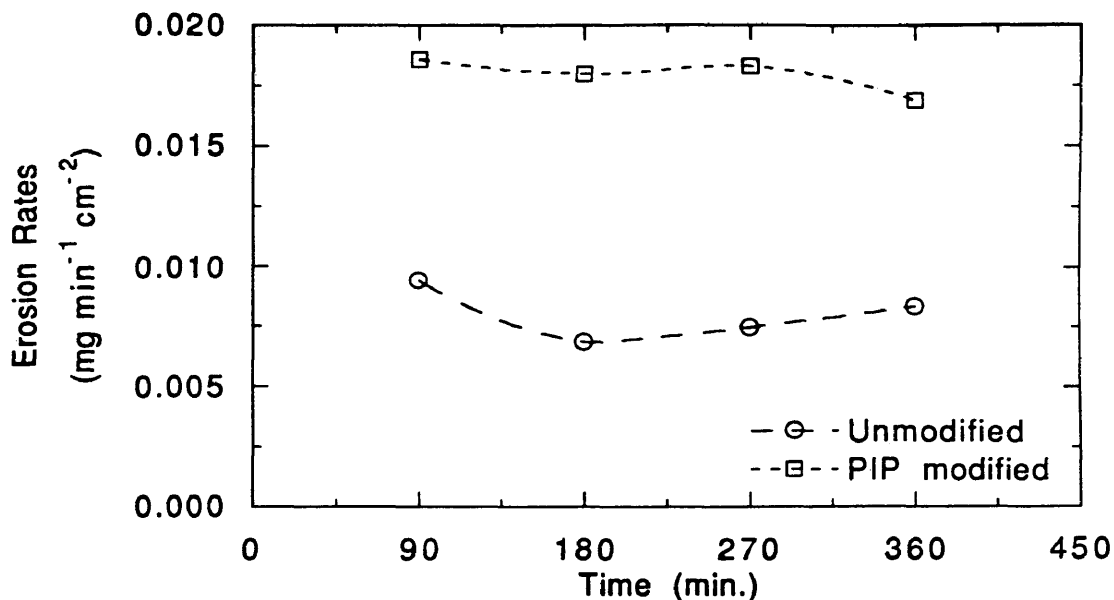


Figure 21: Plot of Erosion Rates Versus Time:  
PIP modified Epon 815

As will be seen later, the modified networks erosion rates had a tendency to increase as time increased. Figure 22 is an erosion rate versus time plot comparing the two different modifiers. It can be seen that the modifier with the lesser phenyl content erodes at a faster rate as time increases. Figure 23 shows a plot comparing a modifier at different concentration. The film with the lesser modifier content had erosion rates that increased as time increased. In comparison with the higher modifier content, its erosion rates did not increase as much.

These films were characterized by attenuated total reflectance FTIR spectroscopy (ATR-FTIR). The spectra obtained for all the unexposed film showed the characteristic spectrum of Epon 815 (Figure 24). After exposure, the spectra

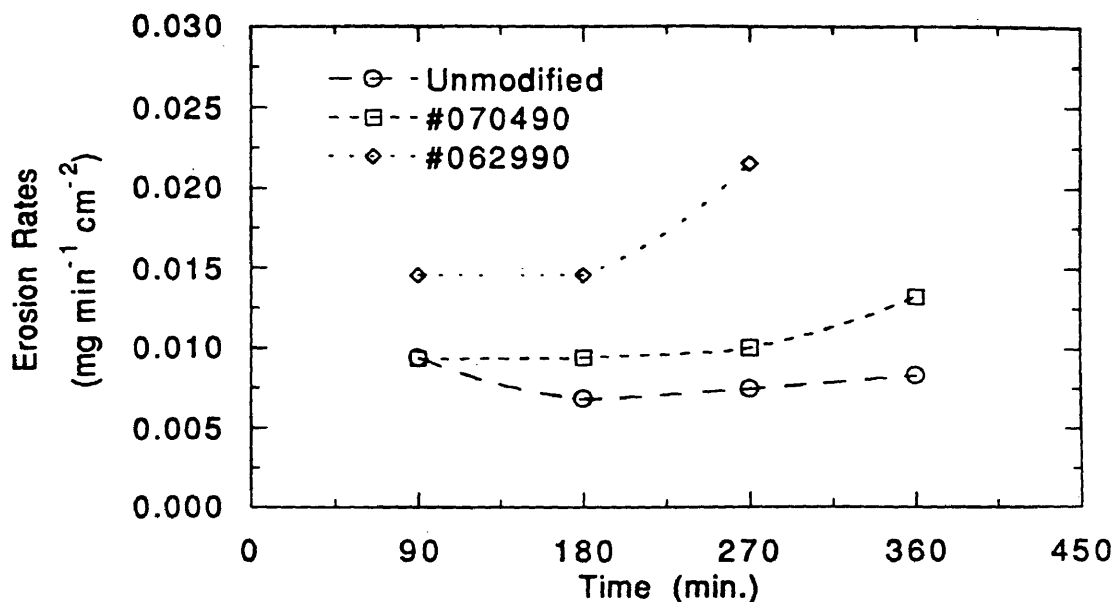


Figure 22: Plot of Erosion Rates Versus Time:  
Epon 815 Modified with 20% me/ph  
PIP Oligomers

for the modified network showed none of the original peaks while the unmodified network still showed the characteristic peaks for Epon 815 (Figure 25). The new peaks obtained correspond to the formation of a silicon oxygen network. These peaks are identified as Si-O-Si at about 1000 cm<sup>-1</sup> and Si-C at about 800 cm<sup>-1</sup>.

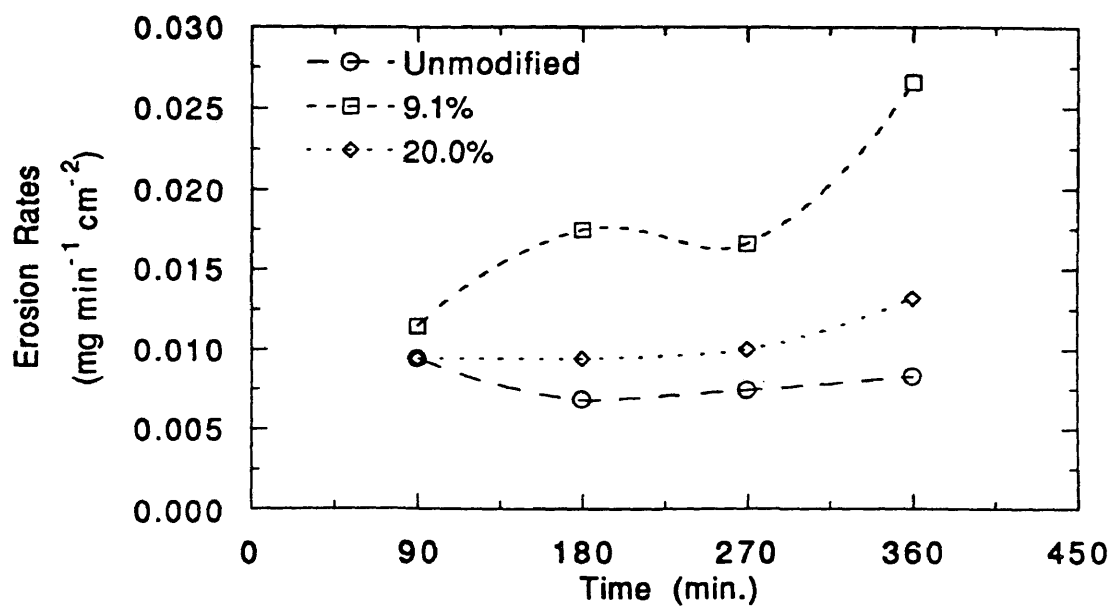
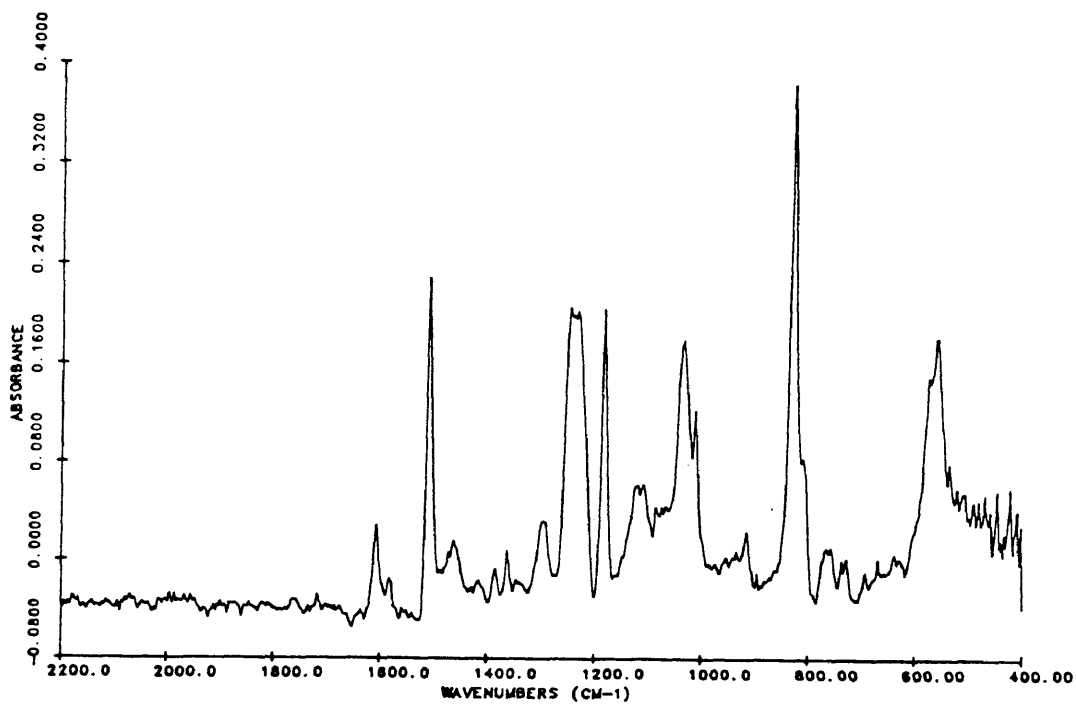


Figure 23: Plot of Erosion Rates Versus Time:  
EPON 815 modified with me/ph PIP  
#070490 Oligomer

a).



b).

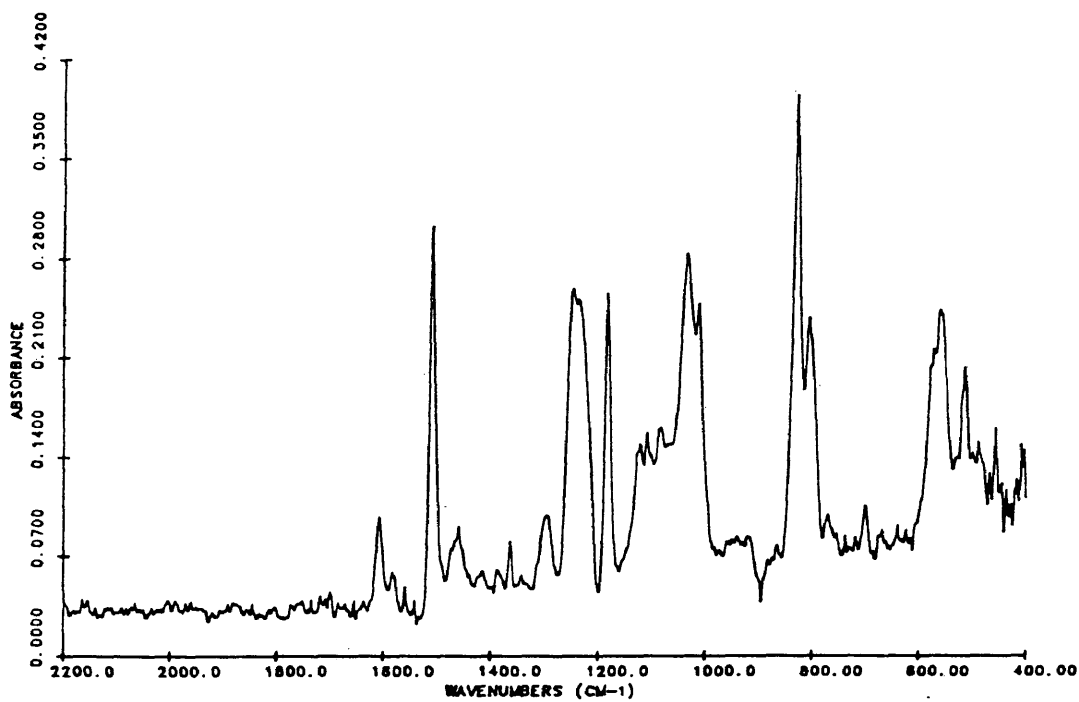
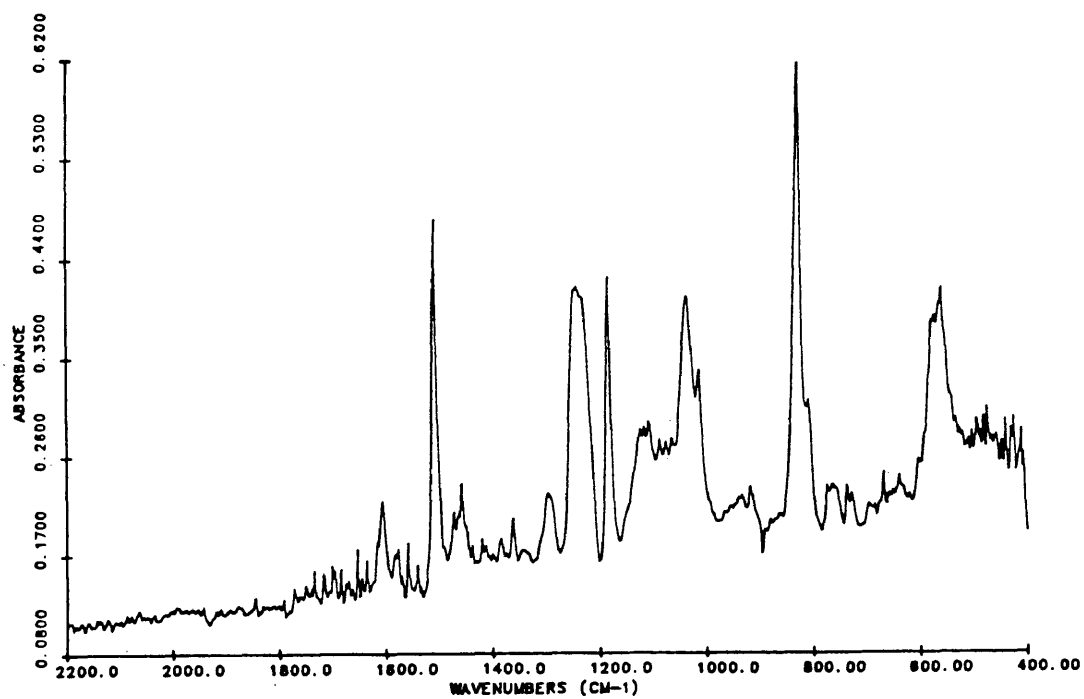


Figure 24: ATR-FTIR Spectra of Epon 815 Unexposed:  
a). Unmodified and b). Modified

a).



b).

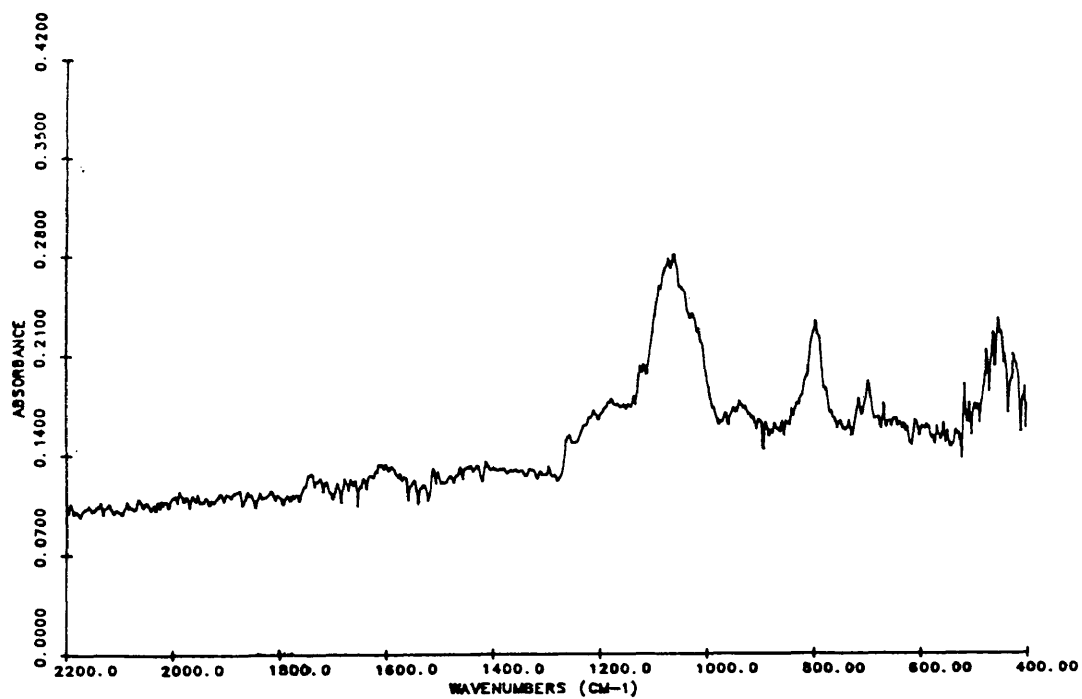


Figure 25: ATR-FTIR Spectra of Epon 815 Exposed:  
a). Unmodified and b). Modified

## INTRODUCTION

### Polyetherimide

Polyetherimide (PEI) resin is a new amorphous, high performance thermoplastic introduced in 1982 by General Electric Company under the Tradename ULTEM\*. This polyetherimide has excellent mechanical properties and outstanding electrical properties over a wide frequency and temperature range. It is resistant to aliphatic hydrocarbons, acids, and dilute bases. Another property is its high temperature stability and resistance to UV and gamma radiation. In this section, additives are mixed with PEI in hopes of increasing its resistance to atomic oxygen.

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\*Registered Trademark of General Electric Company

## EXPERIMENTAL

### Polyetherimide Films

#### Preparation of Films

The polymer system studied in this experiment is PEI (Tradename Ultem\*) made by General Electric Co. The structure for PEI is given in Figure 26. The solvents used are chloroform and 1,1,2,2-tetrachloroethane (TCE). Chloroform was supplied by Fisher, and TCE was obtained from Aldrich.

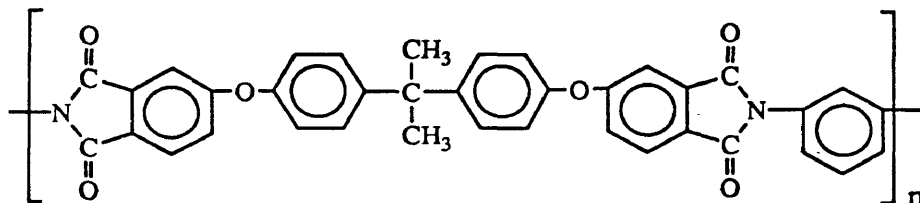


Figure 26: Structure for Polyetherimide

Films were casted from solution that were usually 15% by weight of solid in solvent. The solvent was a 60/40 mixture by weight of chloroform and TCE. The components were stirred for 24 hours to ensure that the solid has completely dissolved.

The solution was cast into a film by pouring the viscous solution onto a glass plate and drawing a film of uniform thickness using a doctor blade. The desired film thickness

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can be calculated by multiplying the percent of the solution with the blade setting. For example, a 15% solution is cast with a blade setting of 20 mils; therefore, the resulting film will be about 3 mils thick. Before casting of the film, the glass plate was cleaned with a dust free cloth. Three solvent cleaners were used: first chloroform, then acetone, and lastly absolute ethanol. The plate was then placed in a nitrogen-filled "dry-box" at room temperature on a level platform, and the film was pulled.

The "dry-box" was used to help remove the solvent while keeping the film free of dust. The film was kept in the box for at least 24 hours. To further evaporate the solvent, the glass plate was then placed in a vacuum oven. Starting at 60°C, the oven temperature is raised 10°C everyday until the temperature reached 220°C. This temperature was just above the glass transition temperature of PEI ( $T_g = 215^\circ\text{C}$ ) to allow the residual solvent to escape. After the temperature was held at 220°C for 24 hours, the oven was turned off. After cooling, the plate was taken out of the vacuum oven, and the film was removed from the plate.

In some films, a non-volatile filler was added in hopes that the film would become resistant to AO attack. A major problem, though, was the solubility of the filler in the polymer system. The different additives tried were organo-lead, organo-silicon, organo-siloxane, and organo-tin compounds. Table 9 is a list the additives, all of which were

obtained from Aldrich.

Table 9: List of Additives

Organo-lead:	
Tetraphenyllead	(M.W.=515.6; m.p.=227°)
Organo-silicon:	
Diphenylmethylsilane	(M.W.=198.3; b.p.=93°/1mm)
Diphenylsilane	(M.W.=184.3; b.p.=96°/13mm)
Organo-siloxane:	
Octamethylcyclsiloxane	(M.W.=296.6; b.p.=175°)
Octaphenylcyclsiloxane	(M.W.=793.2; m.p.=197°)
Organo-tin:	
Bis(triphenyltin) oxide	(M.W.=716.0; m.p.=121°)
Tetrabutyltin	(M.W.=347.2; b.p.=145°/10mm)
Tetraphenyltin	(M.W.=427.1; m.p.=225°)

The solubility of each additive to PEI was determined by making films. Films of different composition of additive to PEI were made and dried. If the film came out cloudy, then that amount of additive was not soluble in the polymer system.

### Atomic Oxygen Experiments

The procedure for the atomic oxygen experiments was discussed previously. Only films that had soluble additives were tested.

### Characterization of Films

#### Fourier Transform Infrared Spectroscopy

The films were characterized by FTIR-ATR (Attenuated Total Reflectance) with a Nicolet 20DXB FTIR spectrometer.

Spectra for both unexposed and exposed samples were obtained and compared.

Energy Dispersive X-ray Analysis/Scanning Electron Microscopy

Energy Dispersive X-ray Analysis (EDAX) and Scanning Electron Microscopy (SEM) are also used to characterize films. The EDAX was used to determine the composition of the surface of the film. SEM provided pictures of the surface. Again, both unexposed and exposed were tested and compared.

## RESULTS AND DISCUSSION

### Polyetherimide

The solubility of several additives was determined. The results are listed in Table 10. As can be seen, the organotin compounds showed the most solubility in polyetherimide (or PEI), especially bis(triphenyltin) oxide (or BTO). BTO had a solubility up to 40% by weight in PEI, but films above 25% were too brittle and fell apart when handled. The additive, tetrabutyltin, displayed an increase in its solubility with PEI only after annealing, but this increase might be due to the evaporation of the additive at the higher temperature.

The films of PEI using BTO as the additive were then tested in the asher. The extent of degradation was again followed by the amount of mass loss experienced by the sample. From the mass loss, the erosion rates were determined where the surface area is equal to the 3.88 cm<sup>2</sup> and time exposed was equal to 90 min.

The first experimental run was the normal exposure experiment where the samples are exposed for four successive 90 minute intervals. The rates obtained are listed in Table 11, and Figure 27 shows a plot of erosion rate versus time. As can be seen from the plot, the rate of degradation

Table 11: Solubility of Additives in Polyetherimide

Percent of Additive:	1	2	3	4	5	7	10	15	20	25	30	40
Polydimethylsiloxane	I	I		I								
Octaphenylcyclotetrasiloxane	S	S	S		I	I	I					
Octamethylcyclotetrasiloxane					I							
Diphenylsilane					I		I					
Diphenylmethylsilane							SS					
Tetraphenyltin												
Tetraphenyllead		S										
Bis(triphenyltin) oxide		S			S		S	S	S	S	S	S <sup>b</sup>
Tetrabutyltin		S <sup>a</sup>				S <sup>a</sup>	I					

where I=insoluble, S=soluble, SS=slightly soluble, and Blank=untested

<sup>a</sup> soluble only after annealing

<sup>b</sup> films too brittle

decreased as the exposure time increased for the films with BTO. On the other hand, the film with no additive stayed at a constant erosion rate.

Table 11: Erosion Rates for Polyetherimide:  
Normal Exposure Experiment  
( $\times 10^{-2}$  mg min $^{-1}$  cm $^{-2}$ )

Sample:	Time Interval (90 min.)			
	1	2	3	4
w/o BTO	0.46	0.40	0.72	0.66
w/ 10.0% BTO	1.9	1.3	0.72	0.66
w/ 19.6% BTO	1.6	0.74	0.57	0.46
w/ 20.0% BTO	1.6	0.66	0.54	0.34
w/ 25.0% BTO	1.1	0.89	0.46	0.40

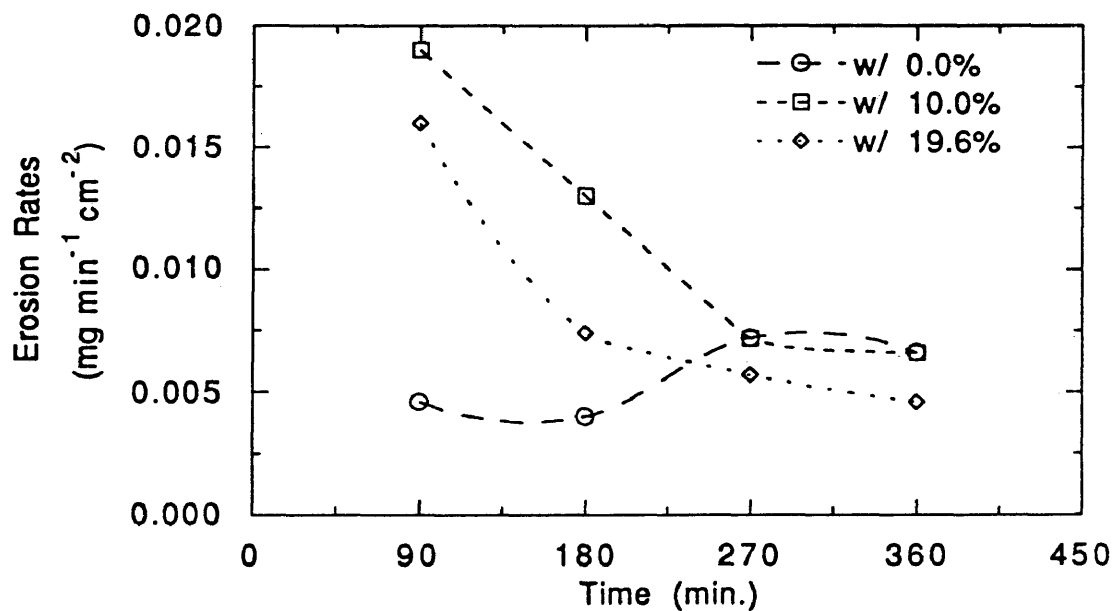


Figure 27: Plot of Erosion Rates Versus Time:  
Normal Exposure Experiment

The second experiment conducted was the continuous

experiment on the PEI with 19.6% BTO sample. This experiment showed that the extent of degradation was affected by the interruptions in the runs to weigh the sample. It was found that the total mass loss for the continuous experiment was 15.5 mg, while the mass loss for the sample with breaks was just 11.6 mg. The increase in mass loss when the sample was exposed continuously with no breaks may have been due to the fact that in the continuous experiment the concentration of the active species is allowed to stay constant. In the case of the normal exposure experiment, each time the asher was turned on the concentration of the active species must be built up again.

The final asher experiment performed was a long exposure experiment. Again, the samples are exposed in the asher for 90 minute intervals, but the number of intervals was doubled from the normal experiment. The mass loss after each interval was obtained, and the erosion rates were calculated. Table 12 gives these results. The erosion rates versus time plots were then drawn (Figure 28). Again, the plot shows that as the samples with BTO had an increase in resistance as the time exposed increased. After a while, the films with BTO leveled off to a constant erosion rate that was lower than the film without BTO.

These films were then characterized by ATR-FTIR. The spectra obtained are shown in Figures 29 through 31. For the unexposed films, the characteristic peaks for PEI were

Table 12: Erosion Rates of PEI with BTO:  
Long-term Exposure Experiment  
( $\times 10^{-2}$  mg min $^{-1}$  cm $^{-2}$ )

Time (min.)	w/o	w/ 10.0%	w/ 19.6%	w/ 25.0%
90	6.6	14	16	9.7
180	6.6	16	6.9	6.3
270	5.7	10	5.4	4.6
360	6.9	8.6	4.6	3.4
450	3.7	5.7	4.0	2.9
540	4.9		3.2	1.4
630	5.2		3.7	3.2
720	5.7		3.2	2.9

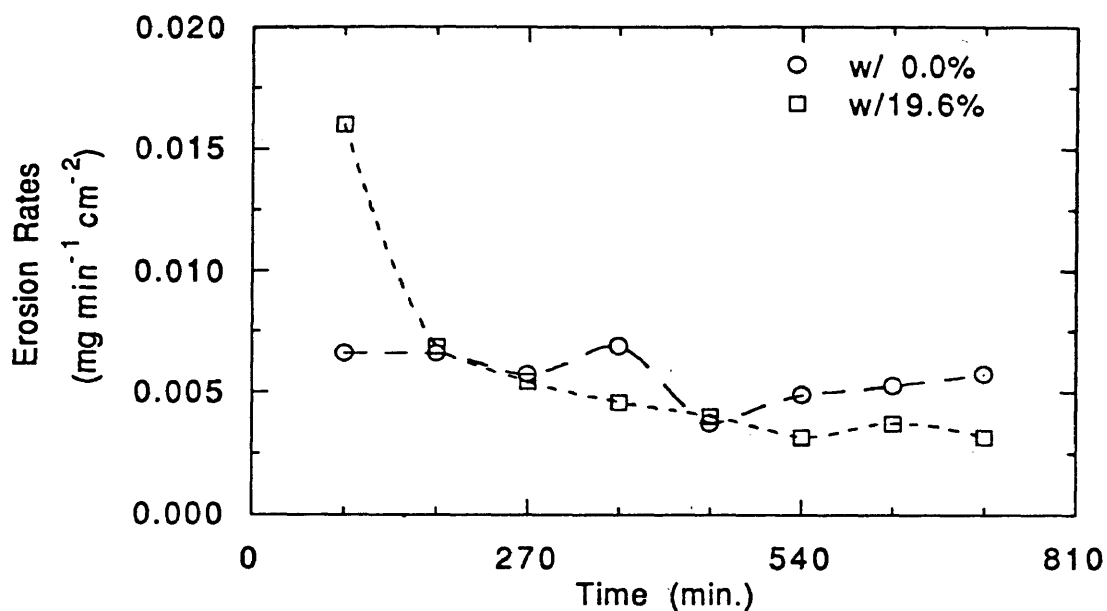


Figure 28: Plot of Erosion Rates Versus Time:  
Long Exposure Experiment

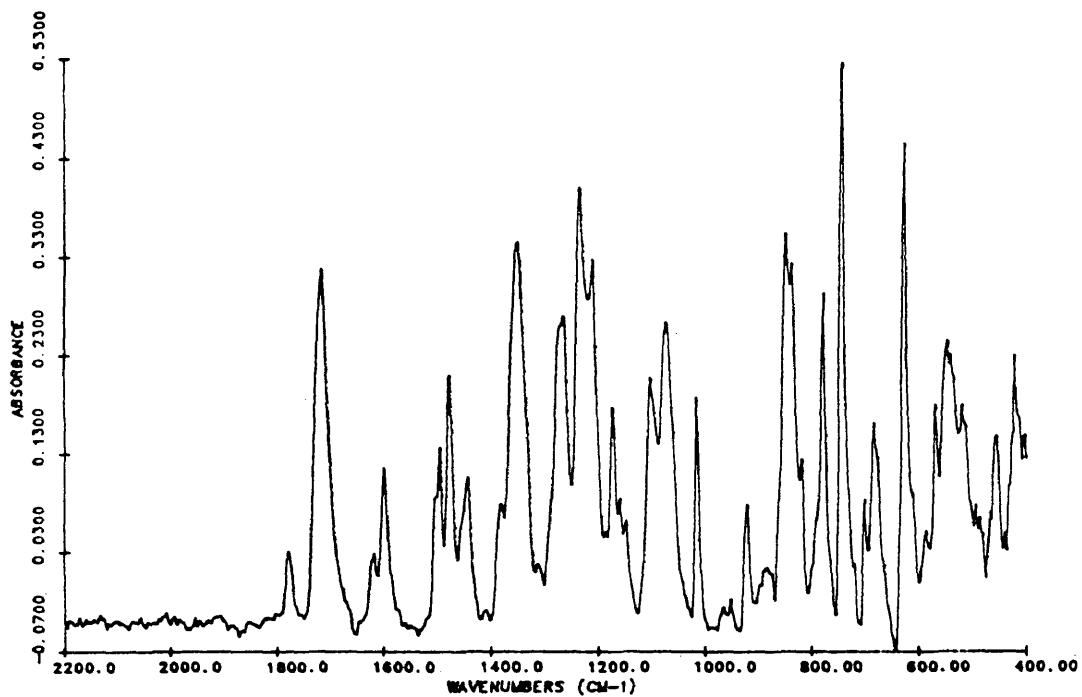
present. After exposure to atomic oxygen, the film without BTO still displayed the characteristic peaks of PEI. On the other hand, all the peaks disappeared on the spectra of the films with BTO. This disappearance of the peaks is attributed to the possibility that a tin oxide layer is being formed to

protect the material from further attack of atomic oxygen.

This formation of a protective layer is further confirmed by scanning electron microscopy (SEM) and energy dispersion analysis by X-ray (EDAX) studies. In the SEM studies, the exposed samples showed a distinctly different appearance from the sample without BTO. Initially, the same surface morphology was seen for all the unexposed films. After exposure, the films with BTO showed the possible formation of a tin oxide layer. These pictures are shown in Figures 32 through 34.

This formation of the tin oxide layer was further confirmed by the EDAX studies (shown in Figures 35 through 37). The spectra of the unexposed samples showed the presence of carbon and oxygen where the predominant species on the surface of the film. After exposure, the spectra of the samples with BTO revealed that the predominant species on the surface was tin and oxygen.

a).



b).

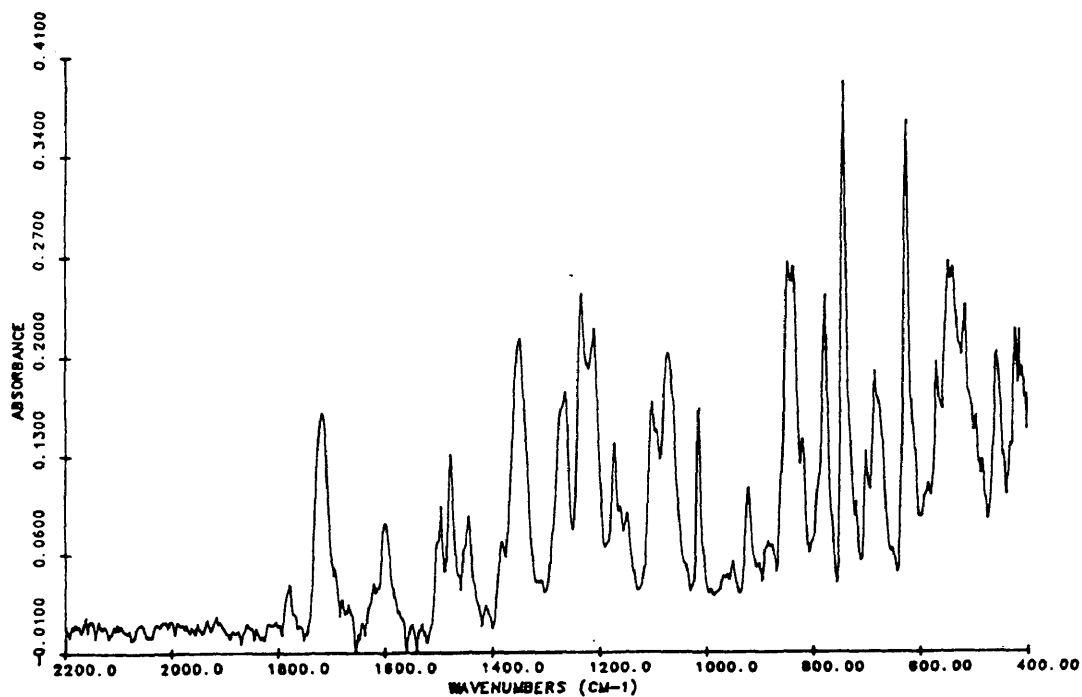
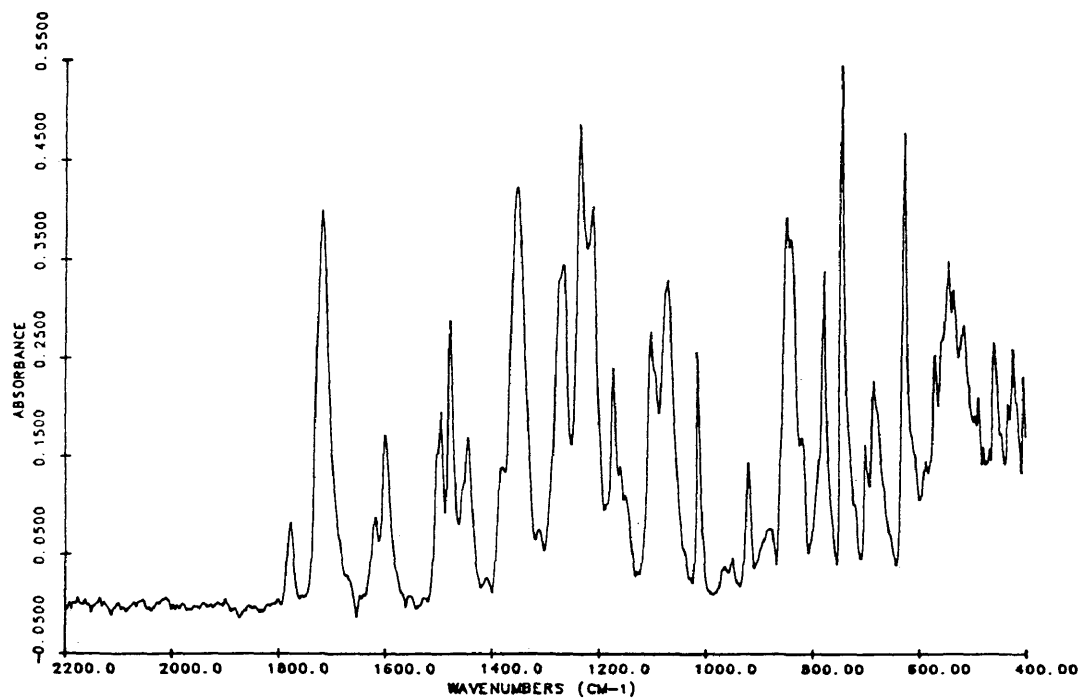


Figure 29: ATR-FTIR Spectra of PEI without BTO:  
a). Unexposed and b). Exposed

a).



b).

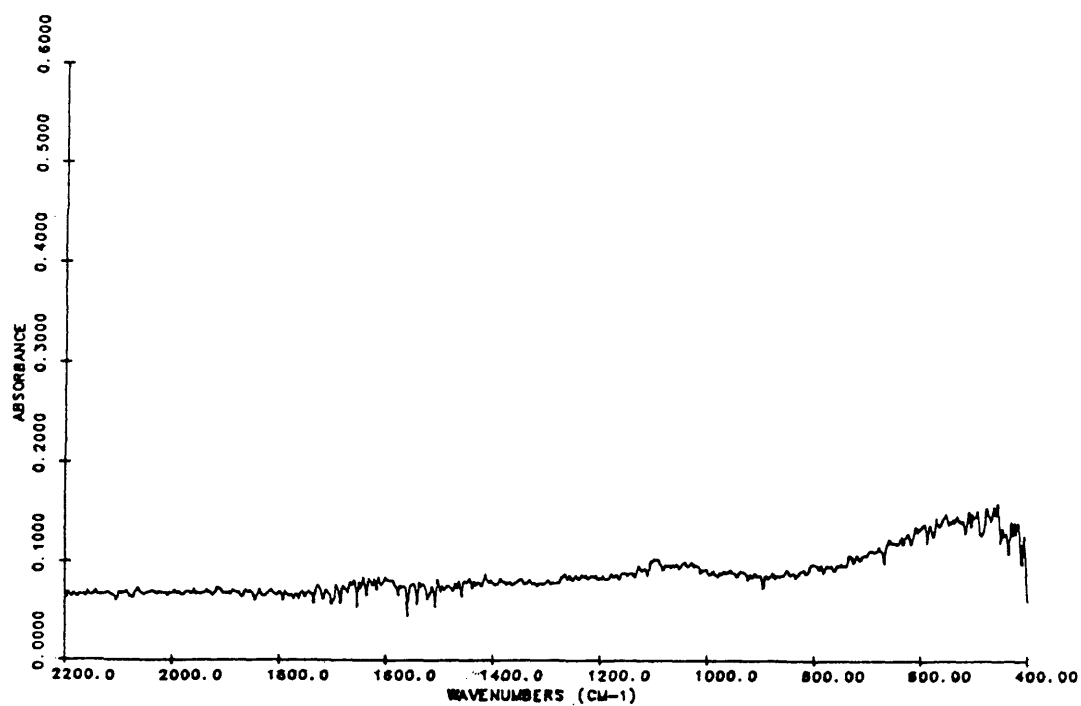
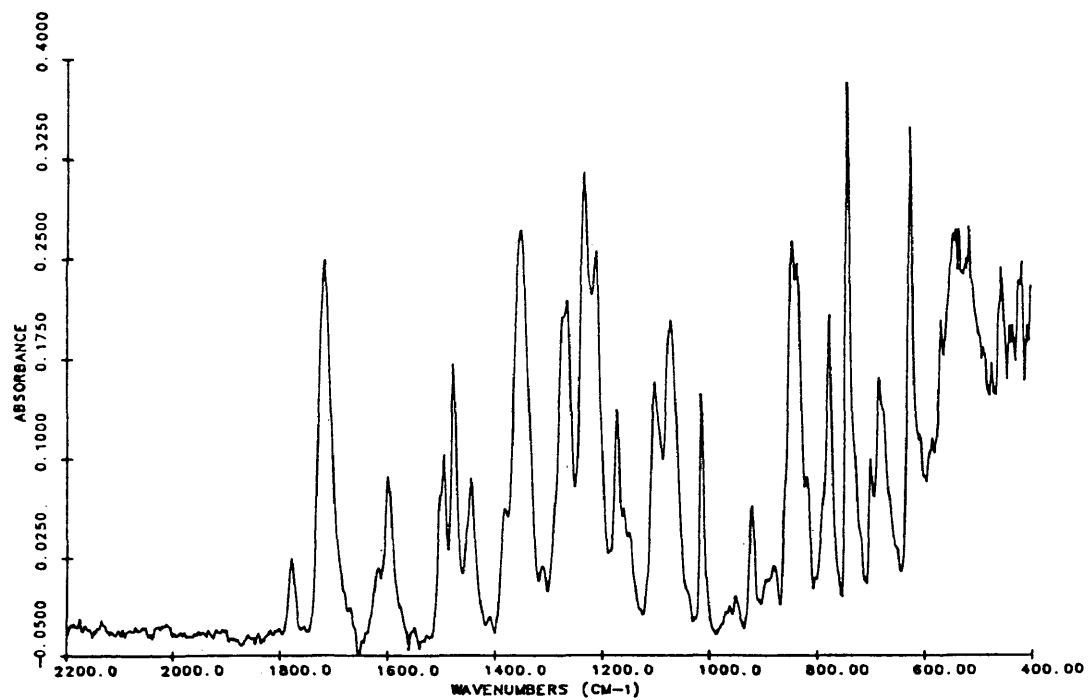


Figure 30: ATR-FTIR Spectra of PEI with 10.0% BTO:  
a). Unexposed and b). Exposed

a).



b).

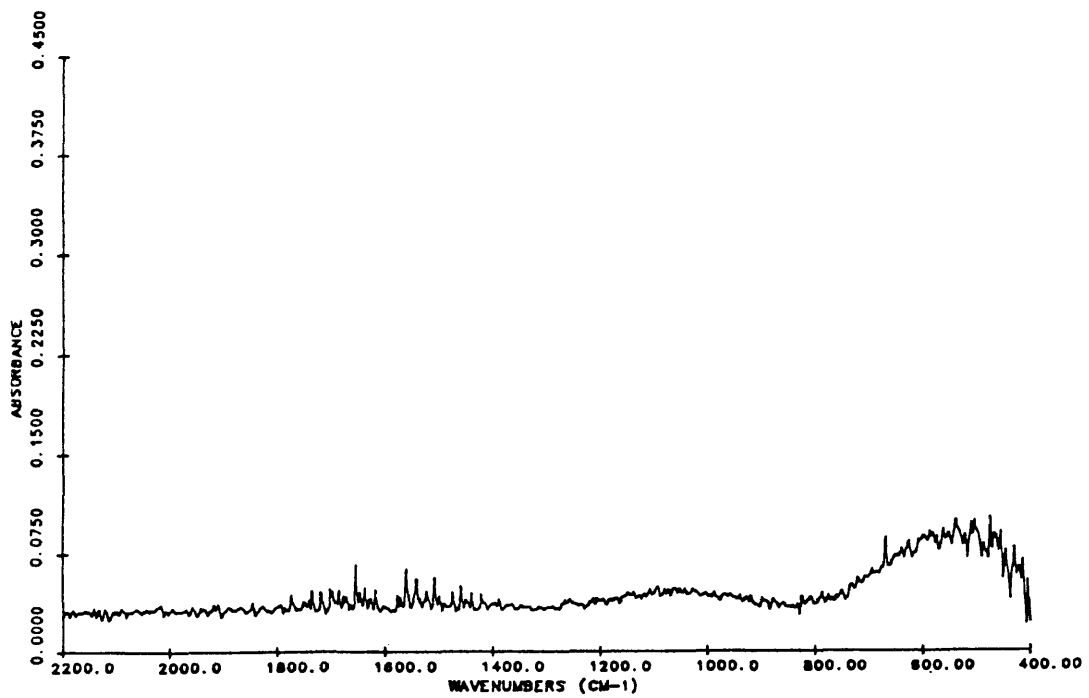
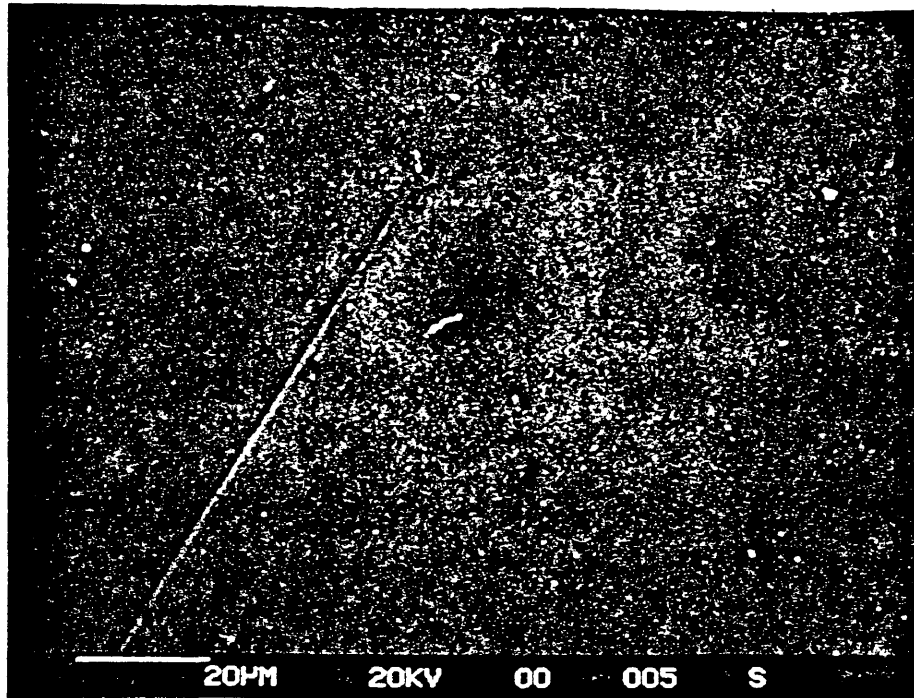


Figure 31: ATR-FTIR Spectra of PEI with 19.6% BTO:  
a). Unexposed and b). Exposed

a).



b).

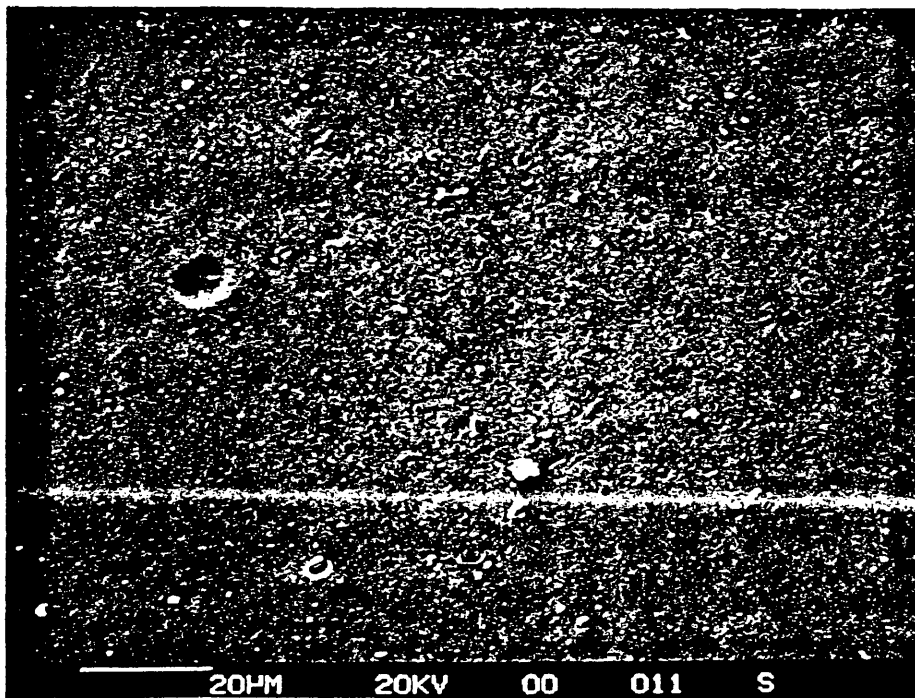
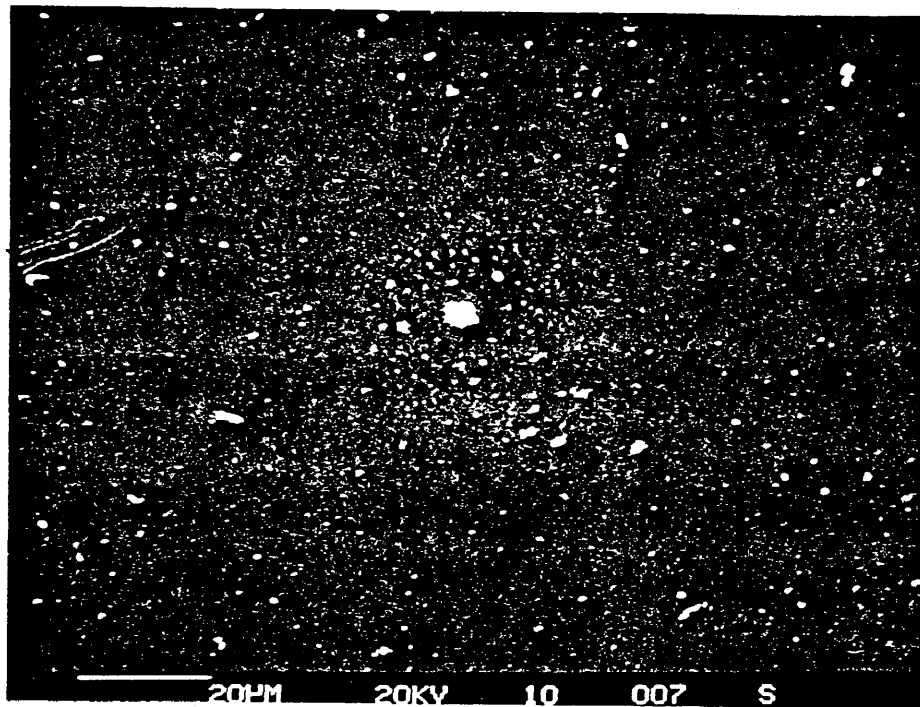


Figure 32: SEM Studies on PEI without BTO:  
a). Unexposed and b). Exposed

a).



b).

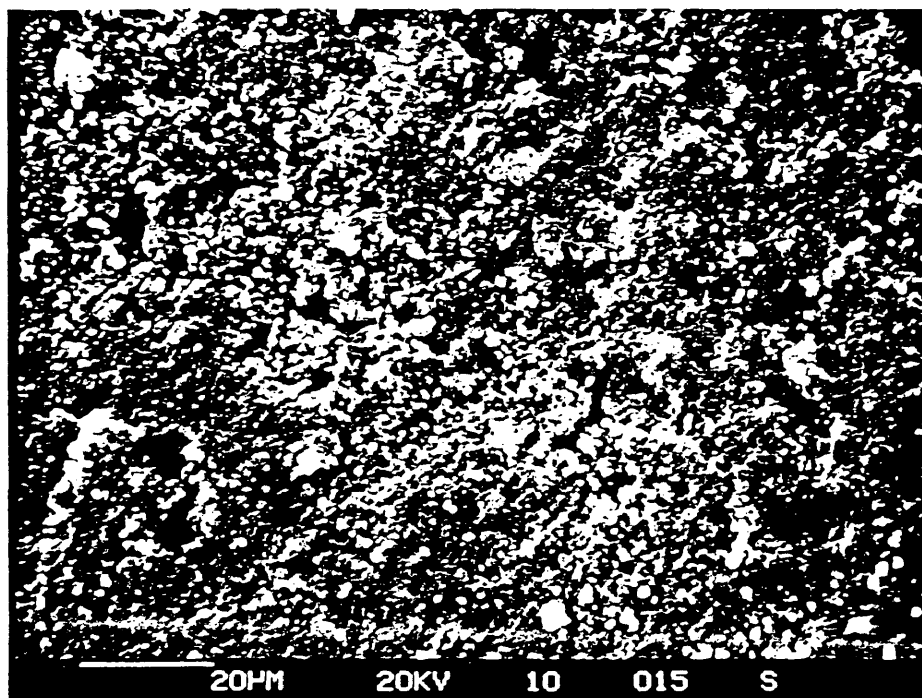
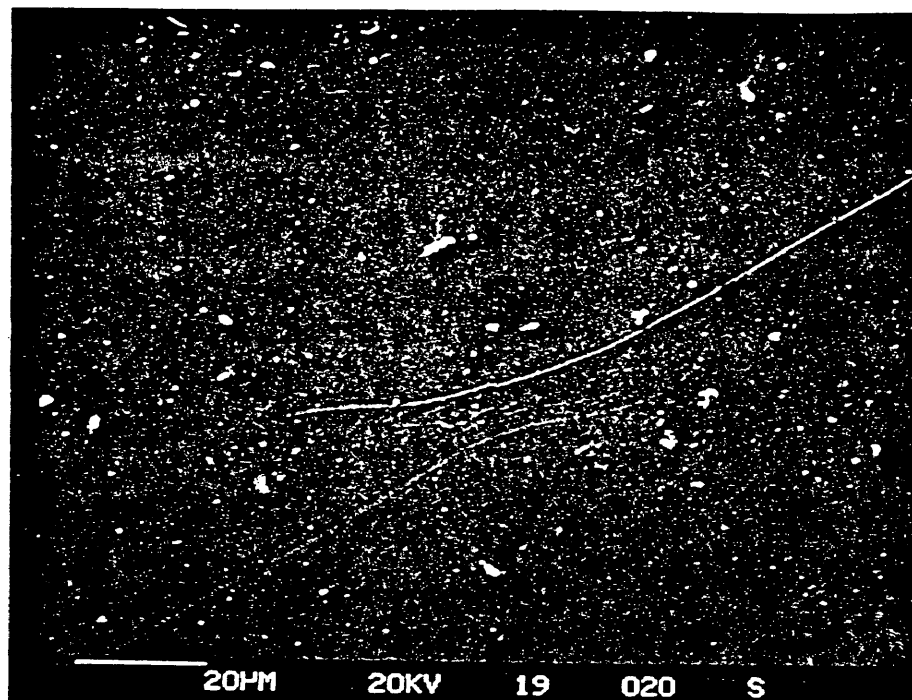


Figure 33: SEM Studies on PEI with 10.0% BTO  
a). Unexposed and b). Exposed

a).



b).

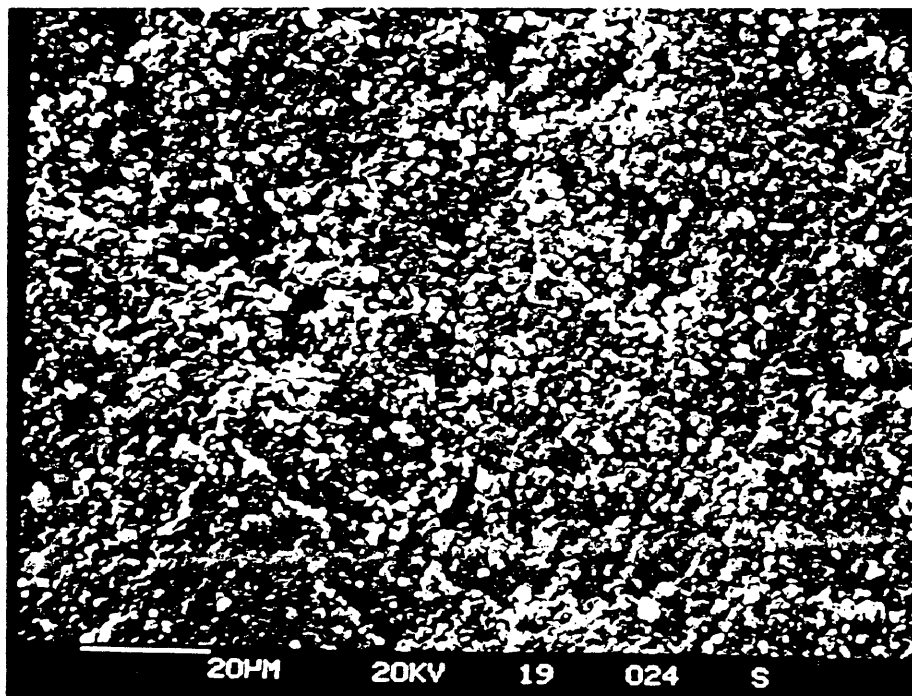
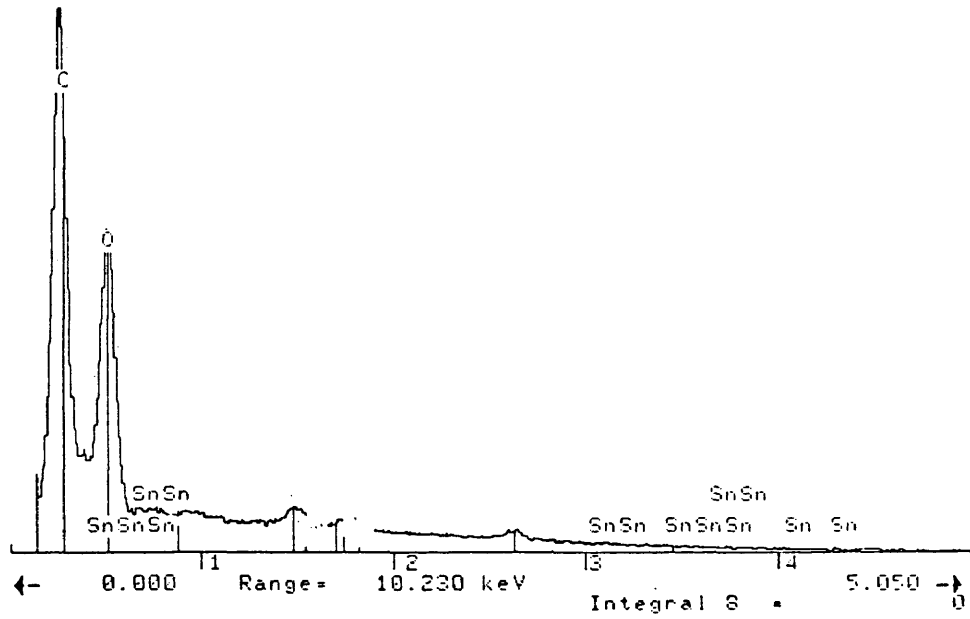


Figure 34: SEM Studies on PEI with 19.8% BTO:  
a). Unexposed and b). Exposed

a).



b).

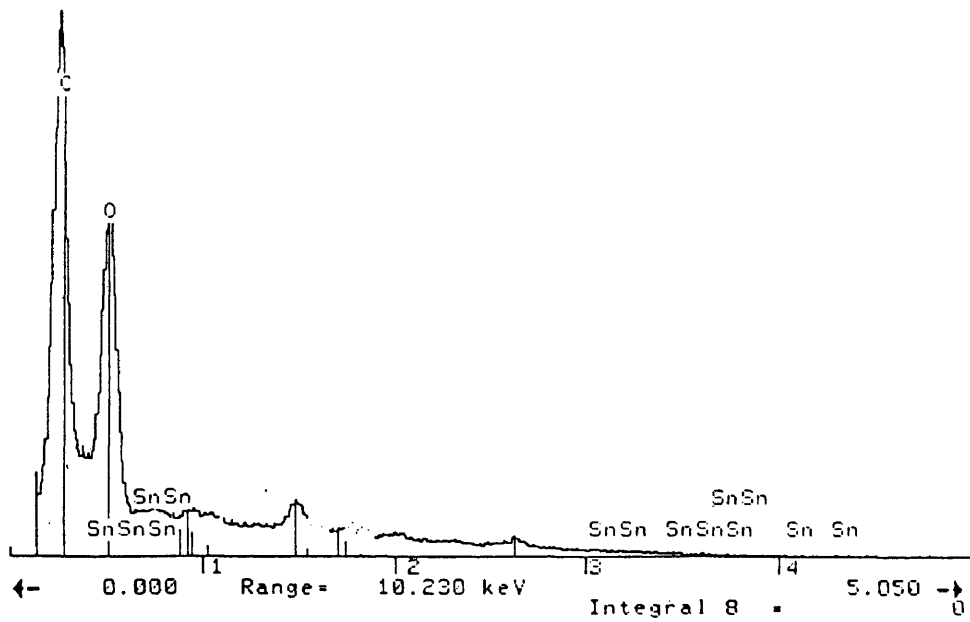
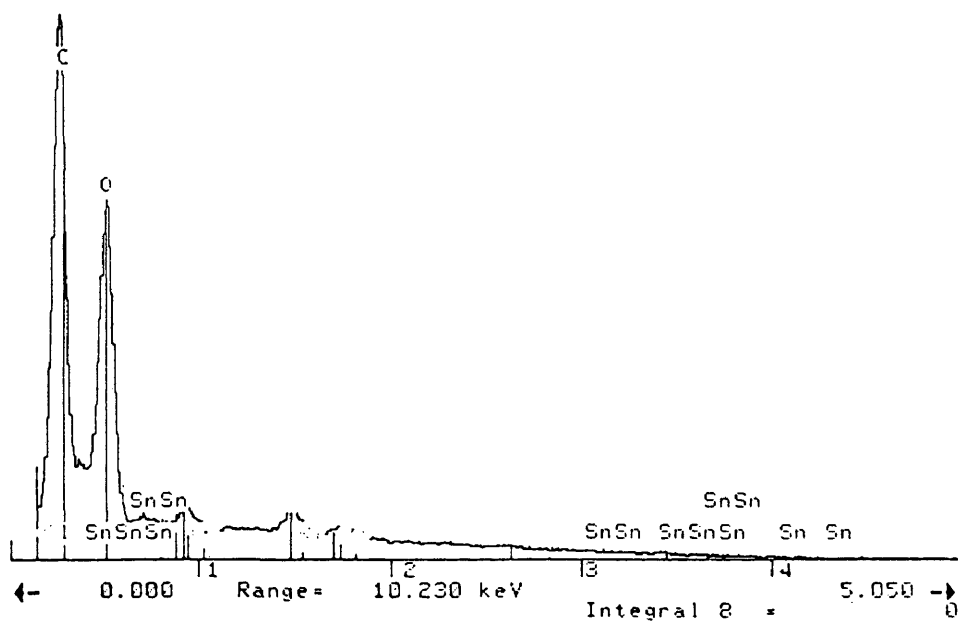
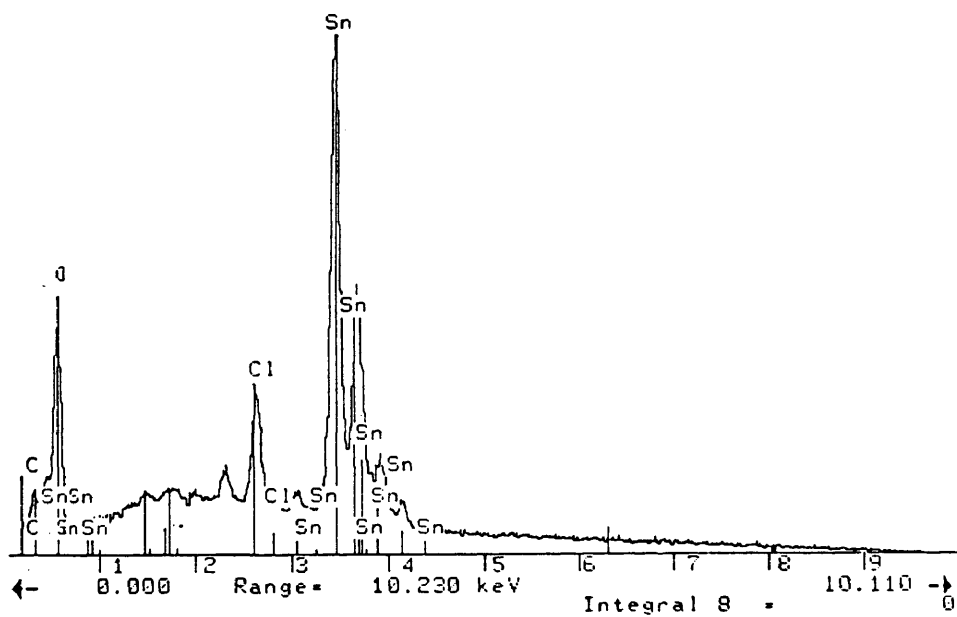


Figure 35: EDAX Studies on PEI without BTO:  
a). Unexposed and b). Exposed

a).

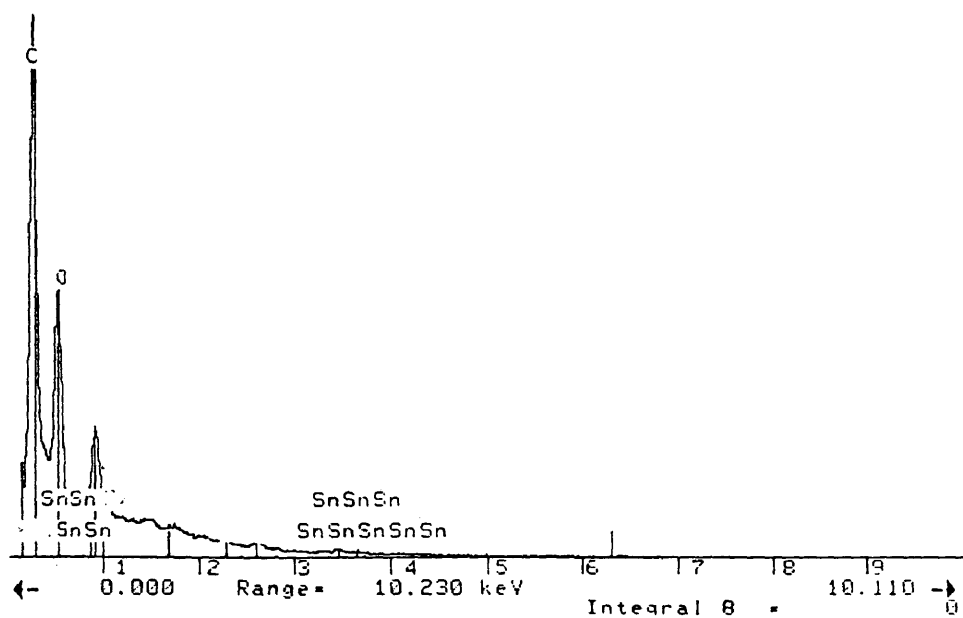


b).



**Figure 36: EDAX Studies on PEI with 10.0% BTO:  
a). Unexposed and b). Exposed**

a).



b).

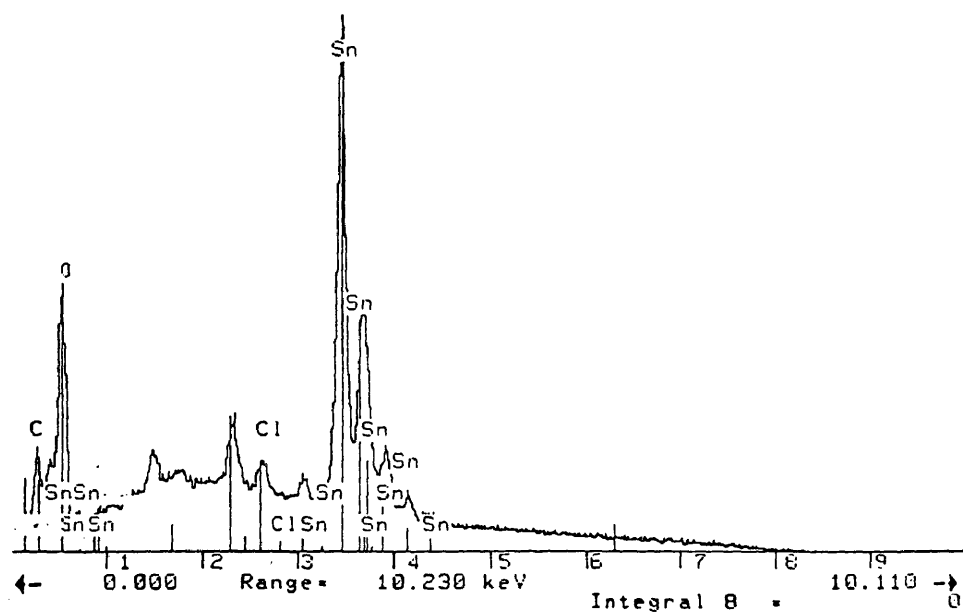


Figure 37: EDAX Studies on PEI with 19.8% BTO:  
 a). Unexposed and b). Exposed

## CONCLUSION

Two types of polymeric materials were made and tested in an asher. The first test material was a siloxane modified epoxy resin. Two types of siloxane modifiers were synthesized anionically in the lab using a siloxanolate catalyst: piperazine terminated polydimethylsiloxane oligomers and poly(dimethyl-co-diphenyl)siloxane oligomers. The first modifier is known to form an incompatible network with an epoxy resin due to its lower solubility parameter. The poly(dimethyl-co-diphenyl)siloxane oligomers were synthesized to raise the solubility parameter of the modifier. Even though this oligomer had a higher solubility parameter, the modifier still was immiscible with the epoxy resin.

The films formed by the modification of the epoxy resin were still tested in the asher. The results obtained showed no improvement in the protection of the material from atomic oxygen attack. In fact, the rate of degradation was greater than the unmodified network and increased as exposure time increased.

The second material tested was a film polyetherimide (PEI) containing an additive. Several additives were tested for their solubility in polyetherimide. One additive, bis(triphenyltin) oxide (BTO), was found to be soluble up to

40% by weight in PEI.

Several films of PEI with BTO were made with different concentrations of the additive. The rates of erosion of films with BTO, although initially very high, were found to decrease quickly to a rate lower than a film without BTO. This decrease in rate was attributed to the formation of a tin oxide layer.

The formation of a tin oxide layer was verified by FTIR, SEM, and EDAX analysis. In each technique, the exposed films with BTO distinctly varied from the unexposed films and the exposed film without BTO. In the case of the FTIR spectra, all the peaks attributed to PEI disappeared for the films with BTO. The SEM pictures showed a definite difference in surface morphology, and the EDAX scans showed the disappearance of a carbon surface to a tin oxide surface.

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