

SYNTHESIS OF NOVEL POLYIMIDES FOR THE TESTING OF STRUCTURE-
PROCESSING AND PROPERTY RELATIONS WHEN USED TO FORM HIGH
TEMPERATURE POLYMER MATRICES

A Thesis

by

FRANCISCO TSCHEN MOLINA

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

December 2005

Major Subject: Materials Science and Engineering

SYNTHESIS OF NOVEL POLYIMIDES FOR THE TESTING OF STRUCTURE-
PROCESSING AND PROPERTY RELATIONS WHEN USED TO FORM HIGH
TEMPERATURE POLYMER MATRICES

A Thesis

by

FRANCISCO TSCHEN MOLINA

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Chair of Committee,
Committee Members,

Roger Morgan
Terry Creasy
Jaime Grunlan
Eric E. Simanek

Chair of Materials Science
and Engineering Faculty,

Joseph Ross

December 2005

Major Subject: Materials Science and Engineering

ABSTRACT

Synthesis of Novel Polyimides for the Testing of Structure-
Processing and Property Relations When Used to
Form High Temperature Polymer Matrices. (December 2005)

Francisco Tschen Molina, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Roger Morgan

High-performance polymers have found an extreme range of applications in the aerospace industry. Composites which have polymers incorporated in them can usually meet the needs of the design, and are the ideal materials for aerospace applications due to their light weight, high strength, and radar transparency. Phenyl-ethynyl terminated oligomers, for example, have found many uses in the aerospace industry. Phenyl-ethynyl terminated oligomers (AFR-PEPA-N) exhibit glass-transition temperatures of up to 450°C. Unfortunately crystals form due to interactions of the oligomers. These crystals do not melt until 360°C after 15 minutes when the resin is already 50% cured.

Investigation was performed to find any possible alteration to the end-caps and monomer chain elements of the current AFR-PEPA-N. Several siloxane related amines were added to the AFR-PEPA-N chain to form protective coatings when in service at high temperatures. The new poly(siloxane imide) showed an increase in processability while maintaining AFR-PEPA-N properties. In addition, phenyl-ethynyl end-caps were substituted with an ethynyl end-caps which showed no improvement in processability.

ACKNOWLEDGEMENTS

I would like to thank my advisor and mentor, Dr. Roger J. Morgan. His desire to be in the edge of technology motivates me to continue research and ultimately contribute to the latest developments in science and technology. His continuous guidance and support was extremely valuable to tackle the difficulties faced during research. I am also very thankful and privileged to work with Dr. Eric Simanek for his interest and insight into the chemical world and his extremely useful advice. Additionally, I would like to thank Dr. Terry Creasy and Dr. Jaime Grunlan for serving on my thesis committee.

I am indebted to the Simanek Research Group in the Chemistry Department for their kind help during the synthesis of chemical compounds. Specially, I would like to thank Karlos Moreno for all his time and effort he placed into this project. Karlos helped me and showed me chemical synthesis techniques and other valuable information.

I am also indebted to Charles Tapp, a very diligent undergraduate civil engineering student whose hard work and willingness to learn paved the way for this research. I am very grateful to the student colleagues in the Polymer Technology Center. Their advice and assistance have helped for the continuation and continual improvement of research. I want to express my gratitude to Jong-Il Weon, Yuntao Li, Jia Liu, Robert Browning, Woongjae Boo and Ben Ronck.

I want to express my gratitude and love to my parents, Francisco and Vera Tschen for their willingness to provide an excellent education for me. Because of their dedication I received an excellent high school education, which allowed me to continue my education in the United States. I would also like to thank my Uncle Jaime and Aunt Vilma Tschen for their unconditional help in every aspect of life.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	vi
LIST OF FIGURES.....	ix
LIST OF TABLES	xiii
1. INTRODUCTION.....	1
1.1 Background	1
1.2 Research Goals.....	3
2. LITERATURE REVIEW.....	5
2.1 Introduction	5
2.2 Polymers.....	5
2.2.1 Thermosetting Polymers	9
2.2.2 Polyimides.....	12
2.2.2.1 Synthesis of Polyimides	14
2.2.2.1.1 Synthesis of poly(amic-acids)	14
2.2.2.1.2 Structure-Property Relationships	19
2.2.2.1.3 History of Polyimides.....	21
2.2.2.1.3.1 Fluorinated Polyimides	23
2.2.2.1.3.2 Development of AFR-PEPA-N	27
2.2.2.1.3.2.1 PMR-15	27
2.2.2.1.3.2.2 AFR700B	28
2.2.2.1.3.2.3 PETI Oligomers	30
2.2.2.1.3.2.4 AFR-PEPA-N.....	33
2.3 End-Cap Units.....	35
2.3.1 Purpose.....	36
2.3.2 4-ethynyl phthalic anhydride.....	38
2.4 Carboranes.....	39
2.4.1 Structure	39
2.5 Polysiloxanes.....	41
2.5.1 Poly(imide-siloxanes)	43
3. REDUCTION OF VISCOSITY BY DISSOLUTION.....	45
3.1 Introduction.....	45

3.2 Experimental Techniques.....	47
3.2.1. AFR-PEPA-N Imide Solution.....	47
3.3 Results and Discussion.....	48
3.3.1 Dissolution Tests.....	48
3.3.1.1 AFR-PEPA-N/NVP.....	48
3.3.1.2 AFR-PEPA-N/NMP.....	50
3.4 Conclusions.....	52
4. ALTERATION OF CHEMICAL STRUCTURE OF AFR-PEPA-N.....	53
4.1 Introduction.....	53
4.2 Experimental Techniques.....	54
4.2.1 Poly(methyl-phenyl) siloxane studies.....	54
4.2.2 Poly(imide-siloxane) Composite Preparation.....	55
4.2.3 Poly(imide-siloxane) Composite Flexural Properties Testing.....	56
4.2.4 Poly(imide-siloxane) Composite Short-Beam Strength Testing.....	58
4.3 Results and Discussion.....	60
4.3.1 Poly(methyl-phenyl siloxane) Aging Tests.....	60
4.3.2 Poly(imide-siloxane) Samples.....	63
4.3.2.1 Poly(imide-siloxane) Flexural Properties.....	69
4.3.2.1.1 Preliminary Test.....	69
4.3.2.1.2 Second Test.....	74
4.3.2.1.2.1 Control Group.....	75
4.3.2.1.2.2 SD-APh.....	78
4.3.2.1.2.3 SD-4-100.....	81
4.3.2.1.2.4 SD-8-50.....	84
4.3.2.2 Poly(imide-siloxane) Short Beam Strength Testing.....	87
4.3.2.2.1 SD-APh.....	88
4.3.2.2.2 SD-4-100.....	89
4.3.2.2.3 SD-8-50.....	90
4.4 Conclusions.....	92
5. ALTERATION OF END CAP UNIT.....	93
5.1 Introduction.....	93
5.2 Experimental Technique.....	94
5.2.1 Synthesis.....	94
5.2.2 Characterization.....	95
5.2.2.1 FTIR.....	95
5.2.2.2 Mass Spectrometry.....	96
5.2.2.3 Thermal Gravimetric Analysis.....	96
5.2.2.4 Differential Scanning Calorimetry (DSC).....	96
5.2.2.5 Nuclear Magnetic Resonance.....	96
5.3 Results and Discussion.....	97

5.3.1 FTIR	98
5.3.2 Mass Spectroscopy	99
5.3.3 TGA	100
5.3.4 DSC	103
5.3.5 NMR	104
5.4 Conclusions	106
6. SUMMARY AND CONCLUSIONS	107
6.1 Conclusions	107
6.2 Future Work	108
REFERENCES	110
VITA	114

LIST OF FIGURES

	Page
Figure 1. Caprolactam Monomer and Polycaprolactam Polymer	6
Figure 2. Polymer Types: Linear, Branched, and Network.....	6
Figure 3. Damage in a Thermoset Matrix [5].....	11
Figure 4. Sulfone and Ether Functional Groups.....	12
Figure 5. Imide Functional Group.....	13
Figure 6. Linear Imide.....	13
Figure 7. Aromatic Heterocyclic Polyimide	13
Figure 8. Dupont's Kapton ® Polyimide	14
Figure 9. Formation of Poly(amic acid).....	15
Figure 10. Imide Formation	16
Figure 11. Chemical Structure of Phthalic Anhydride.....	16
Figure 12. Donor-Acceptor Charge Complex in a Polyimide.....	20
Figure 13. Effect of Charge Complex Between Polymer Chains.....	20
Figure 14. Some Commercially Available Dianhydrides [12].....	22
Figure 15. Some Commercially Available Diamines [12].....	23
Figure 16. Chemical Structure of PMR-15 Oligomer	28
Figure 17. Chemical Structures of BTDE and 6FDA Dianhydrides.....	29
Figure 18. Chemical Structure of AFR700B.....	29
Figure 19. Chemical Structure of PEPA	31
Figure 20. Precursors Used to Synthesize Different PETI Oligomers [35]	32

	Page
Figure 21. Partially Cross-linked Polyimide Oligomers [39]	33
Figure 22. Synthesis of AFR-PEPA-N Imide Oligomers [5].....	35
Figure 23. 4-ethynyl-phthalic Anhydride Monomer	38
Figure 24. Ortho, Meta, and Para Icosahedral Carborane Structures.....	40
Figure 25. Polysiloxane Formation	42
Figure 26. Sample Imide-siloxane Polymer Structure	44
Figure 27. NMP and NVP Chemical Structures	48
Figure 28. AFR-PEPA-N/NVP Solubility Diagram	49
Figure 29. AFR-PEPA-N/NMP Solubility Diagram.....	51
Figure 30. Poly(methyl-phenyl siloxane).....	54
Figure 31. Composite Labeling for Sectioning	56
Figure 32. Shear Strength Statistical Formulas	57
Figure 33. Silica Plot Standard [52]	61
Figure 34. IR Spectra of Silica Produced by Poly(siloxane) Decomposition	62
Figure 35. Siloxane Based Diamine Precursors	64
Figure 36. Formation of Siloxane Diamines	65
Figure 37. Siloxane Based Diamine	66
Figure 38. Potential Structure of Poly(imide siloxane) Oligomer	68
Figure 39. Chemical Structure N-18	70
Figure 40. Flexural Modulus of Samples Tested	71
Figure 41. Percent Weight Loss After Aging.....	72

	Page
Figure 42. Maximum Flexural Stress Experienced by Samples	73
Figure 43. Strain at Maximum Stress.....	73
Figure 44. Aged Sample N-17 After Cutting for Mechanical Testing.....	74
Figure 45. Control Sample Modulus at Different Testing Conditions.....	76
Figure 46. Control Sample Max. Stress at Different Testing Conditions	77
Figure 47. Comparison of Strain in Control Group at Different Conditions	78
Figure 48. Comparison of Modulus, Control vs. B2.....	79
Figure 49. Maximum Stress Comparison, Control vs. B2	80
Figure 50. Strain at Maximum Stress Comparison, Control vs. B2.....	80
Figure 51. Modulus Comparison, Control vs. B3-B6	82
Figure 52. Maximum Stress Comparison, Control vs. B3-B6	82
Figure 53. Strain Comparison, Control vs. B3-B6.....	83
Figure 54. Micrograph of Sample B5 After Aging.....	83
Figure 55. Micrograph of B8 Composite	85
Figure 56. Micrograph of B9 Composite After Aging.....	85
Figure 57. Modulus Comparison, Control vs. B7-B8	86
Figure 58. Maximum Stress Comparison, Control vs. B7-B8	86
Figure 59. Strain Comparison, Control vs. B7-B9.....	87
Figure 60. Inter-laminar Shear Strength of the Control Group.....	88
Figure 61. Interlaminar Shear Strength Comparison, Control vs. B2 (RT)	89
Figure 62. Short Beam Strength Comparison, Control vs. B3-B6 (RT)	90

	Page
Figure 63. Short Beam Strength Comparison Control vs. B7-B9 (RT)	91
Figure 64. Structure of Model Polymer Compound.....	98
Figure 65. FTIR Spectra of ETA Polyimide	99
Figure 66. Mass Spectroscopy Data.....	100
Figure 67. Plot Obtained From TGA Data.....	102
Figure 68. DSC Plot of Oligomer Powder (Rate:20°C/min).....	103
Figure 69. Carbon NMR Spectra 90-25ppm	104
Figure 70. Proton NMR 12-0 ppm	105

LIST OF TABLES

	Page
Table 1. Examples of Thermoplastic and Thermosetting Polymer Types	8
Table 2. Other Synthesis Polyimide Synthesis.....	17
Table 3. Important Polyimide Precursors [11]	18
Table 4. Properties Affected by Adding Fluorine to the Polymer Chain.....	25
Table 5. End-groups Considered for Oligomers Leading to Polymers [37]	37
Table 6. Bond Energies [45]	42
Table 7. Typical Failure Modes in the Short Beam Test	59
Table 8. Siloxane Diamines Created at P2SI	66
Table 9. Properties of Several Diamines Synthesized by P2SI.....	67
Table 10. Preliminary Siloxane Testing.....	69
Table 11. Inorganic Polyimide Samples	75
Table 12. Polymer Weight and Composition	97
Table 13. Melting Temperatures	101
Table 14. Boiling Temperatures.....	101

1. INTRODUCTION

1.1 Background

High-performance polymers have found an extreme range of applications in different industries. One such industry, the aerospace industry, has found that these polymers might be used for engines, airframes, missiles and rockets, to name a few. This use of polymers in industry is due to a demand for high performance materials with great strength to weight ratio. The materials must possess, in addition to a great strength to weight ratio, a fulfillment of performance and processing criteria.

Composites which have polymers incorporated in them, can usually meet the needs of the design, and are the ideal materials for aerospace applications due to their light weight, high strength, and radar transparency [1]. The performance of the composites used, often rely heavily on the properties of the polymer matrix. The polymer is a limiting factor together with the fiber-matrix interface in the composite due to the high thermal, and fatigue endurance of the fibers. In addition, the composites are exposed to a range of thermal gradients, hygrothermal and thermo-oxidative service environments, fatigue and high stresses, that might accelerate the degradation of the polymer matrix.

The durability of the materials used is a serious concern when these polymers are incorporated into parts. One vital requirement is that the components have a high glass-

This thesis follows the style of Polymer.

transition temperature, good high-temperature stability as well as meeting the mechanical property requirements. In order to obtain the desired part, the polymer and fibers must be processed first. Therefore, the polymer used must be processable by standard techniques such as resin-injection molding (RIM) or resin-transfer molding (RTM).

Polymers commonly implemented in aerospace composite matrices, are epoxies, polyimides, and bismaleimides [1]. It has been found that polyimides, particularly fluorinated polyimides, exhibit excellent thermal and mechanical properties ideal for aerospace applications. They have hydrolytic stability and good resistance to wear and radiation, as well as inertness to solvents. Polyimides are used as high-temperature adhesives, in microelectronics, optoelectronics, photo-resists, nonlinear optical materials, aerospace applications, composites, and fiber optics.

Aromatic polyimides are inherently stable and yield polymers with high glass-transition temperatures. Unfortunately, if the polymer chains are long they are impossible to process because of high viscosity, even though they exhibit high glass-transition temperatures. One approach to solving this problem is to synthesize these polymers with low weights and stop the polymerization by capping with reactive end-groups. The end-capped oligomers melt at lower temperatures, are soluble in a variety of solvents and are processable with standard techniques [2]. Upon heating of the oligomers, a stable 3-D

network forms. Phenyl-ethynyl terminated oligomers, for example, have found many uses in the aerospace industry.

1.2 Research Goals

Phenyl-ethynyl terminated oligomers (AFR-PEPA-N) have been studied heavily by Morgan and co-workers. It has been found that the polymer matrix formed exhibits glass-transition temperatures of up to 450°C. Unfortunately crystals form due to interactions of the oligomers, these crystals do not melt until 360°C after 15 minutes when the resin is already 50% cured [1]. This suggests that the oligomer crystals are the source of resin defects within the polymer matrix which leads to induced micro-cracking. In addition the high-cure temperature that the polymer network requires also leads to curing stresses in the matrix. These residual stresses might increase or accelerate the rate of micro-cracking.

This thesis will investigate any possible alteration to the end-caps and chain elements of the current AFR-PEPA-N system. If the oligomer is end-capped with different phthalic-anhydride related structures, the curing temperature might be reduced, leading to less residual stresses and easier processing. Incorporation of groups such as m-carborane to the end-cap might form protective coatings that lead to protection of the composite matrix when at high service temperatures. In addition alterations will be made to the original oligomer chain structure. The addition of siloxane and carborane groups to the

chain, will ultimately help form SiO_2 and B_2O_3 thermal protective coatings that will reduce thermo-oxidative degradation of the polymer and composites.

The thesis will specifically address several key items:

- Dilution of AFR-PEPA-N oligomers with reactive diluents.

- Synthesis of oligomers with altered end-cap units.
 - Chemical characterization of oligomers.
 - Identification of a reasonable processing window of oligomers.

- Synthesis of poly(imide-siloxane) oligomers.
 - Mechanical testing of poly(imide-siloxane) structures to determine best system.
 - Aging testing of poly(imide-siloxane) to observe thermal degradation in the different systems.

2. LITERATURE REVIEW

2.1 Introduction

This chapter will focus on basic premises that have led to the evolution of high-temperature polymers. There will be a brief introduction on the properties of polymers and types of polymers. In addition a brief history on the evolution of cutting edge oligomers synthesized at Air Force Research Labs, Performance Polymer Solutions Inc. (P2SI) and Texas A&M University (TAMU) labs will be given and why it has been done. Finally, there will be some information on smart synthesis of materials by combining cutting edge organic polymers with inorganic compounds to obtain desired properties such as is the case with imide-siloxane copolymers.

2.2 Polymers

Polymers are substances composed of very large molecules termed *macromolecules*. These macromolecules are made up of numerous small molecules, *mers* joined by chemical bonds. Polymers are synthesized from mers by a process called polymerization (Figure 1). There is a variety of properties and a diverse amount of mers utilized to form polymers, different mers impart different properties to the polymer.

Polymers are classified depending on the monomer chemical type; such as vinyl polymers, polyethers, polyesters, polyamides, polyimides, etc. In addition to the different type of monomers that can be used to create polymers, these monomers can react in different ways to form different structures: linear, branched, network (Figure 2). The different structures give the polymers different mechanical, chemical, and physical structures.

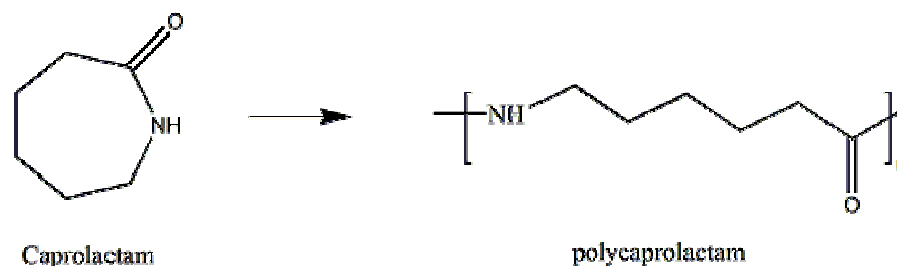


Figure 1. Caprolactam Monomer and Polycaprolactam Polymer

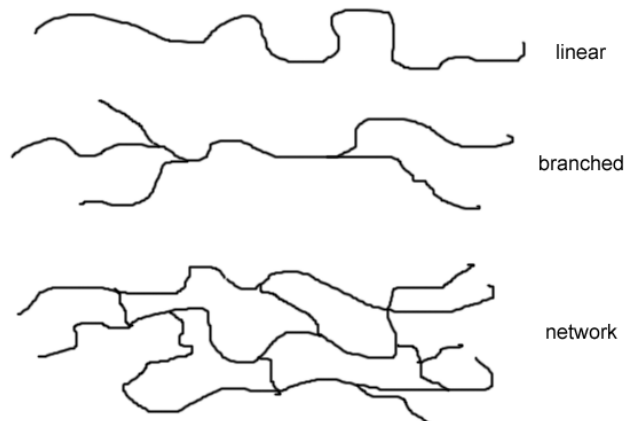


Figure 2. Polymer Types: Linear, Branched, and Network

There are two primary classes of polymeric materials: *thermoplastics* and *thermosets*. Thermoplastics have two-dimensional structure polymeric chains such as linear and branched polymers. Thermosets have three-dimensional structure polymeric chains such as network polymers. Thermoplastics can be reheated and cooled many times without appreciable change in the nature of the polymer. Thermosetting polymers may start as two-dimensional polymers but after heating and chemical action, branches can form a three-dimensional network. As a result of this three-dimensional structure thermosets cannot be reground and reprocessed into other parts.

The first polymerization is attributed to Leo Baekeland in the 1920s of phenol-formaldehyde thermosetting resins. Unfortunately during this time, little was known about the molecular structure of polymers. DuPont during the late 1920s made a major commitment to the development of synthetic polymers [2]. As more understanding of polymers came about during this time due to investment from different companies, the scientific community finally settled that polymers were made up of mers. After this major breakthrough much progress in the polymer area became about. Polymer materials started to take many forms and shapes. More importantly the physical properties of the polymers were tailored by controlling the shape, type and size of the mers. The use of the new knowledge led to the synthesis of polymers with excellent thermal and oxidative stability for use in high-performance applications.

As mentioned before, based on their response to temperature, polymers may be classified into two main categories, thermoplastic and thermoset polymers. A thermoplastic polymer behaves like a fluid above the Glass Transition temperature (T_g). On the other hand, thermoset polymers degrade before going through a fluid state. Several examples of these two types of polymers are shown in Table 1.

Table 1

Examples of Thermoplastic and Thermosetting Polymer Types

Thermoplastic Polymers	Thermosetting Polymers
Vinyl Polymers	Urea-formaldehyde resins,
Polyethers	Unsaturated polyesters,
Polyesters	Epoxy resins
Polyamides	Polyimides

To attain flow in a polymer, the condition is to have chains that are not bonded together but are held together by secondary bonding forces, such as *van der Waals* and Hydrogen bonding. All polymers in which the molecules can be separated by motion during flow will be referred to as thermoplastic polymers.

When dealing with polymers one important parameter to take into consideration is the Glass Transition Temperature or T_g . When a polymer reaches the T_g , it becomes hard and brittle, similar to glass; above the T_g the polymer becomes soft and flexible. In most

uses it is important to have the temperature in which the polymer is used (T_{use}) to be lower than the T_g . This allows for the polymer to behave as a glass during its use.

2.2.1 Thermosetting Polymers

In contrast to a thermoplastic polymer, a thermosetting polymer is a polymer in which all the chains are covalently bonded to each other, creating a giant macromolecule. Unless the covalent bonds are destroyed utilizing temperature or a solvent, the molecule will not flow. Thermosetting polymers may be defined therefore, as a network of polymers formed from chemical reaction of monomers with three or more reactive groups per molecule. During reaction, these multi-functional monomers should be in a significant percentage such that a gel forms at a particular conversion during synthesis.

It is to be noted that the polymer network formed is an irreversible synthesis. It is important then to polymerize while attaining final shape at the same time. As well, it is important to optimize the process for correct procedures, otherwise this leads to irreversible loss of material.

Thermosetting polymers are usually amorphous because there is no possibility of ordering the network structure due to the covalent bonding between the chains (*crosslinks*). There are some exceptions in the thermoset category; these include rigid

monomers which exhibit nematic-isotropic transitions. These monomers may align but the concentration of crosslinks may have to be kept at a low value [3].

Thermosets have encountered many areas in which their use is indispensable and other materials cannot compete because of their properties or costs. For example, epoxies and polyimides are employed in aeronautical and aerospace applications in which these help reduce weight as well as reduction in radar signature in planes.

When thermosetting polymers are used in high-performance applications, they could damage when subjected to high-temperature fluctuations, as well as impurities that might penetrate the polymer matrix. Figure 3 shows damage initiation and growth in the thermoset matrix.

Once impurities get inside the polymer matrix these could catalyze chain scission within the polymer. This chain scission is critical to the mechanical properties of the polymer. Morgan et.al. performed characterization on Kevlar 49 fibers (poly(p-phenylene terephthalamide) and found regions of high impurity concentrations in the fibers due to processing. In these regions there was preferential moisture diffusion. Trace quantities of other impurities found such as sulfuric acid accelerate hydrolytic and oxidative degradation in the fibers [4]. It is imperative that impurities are minimized during synthesis and processing of parts.

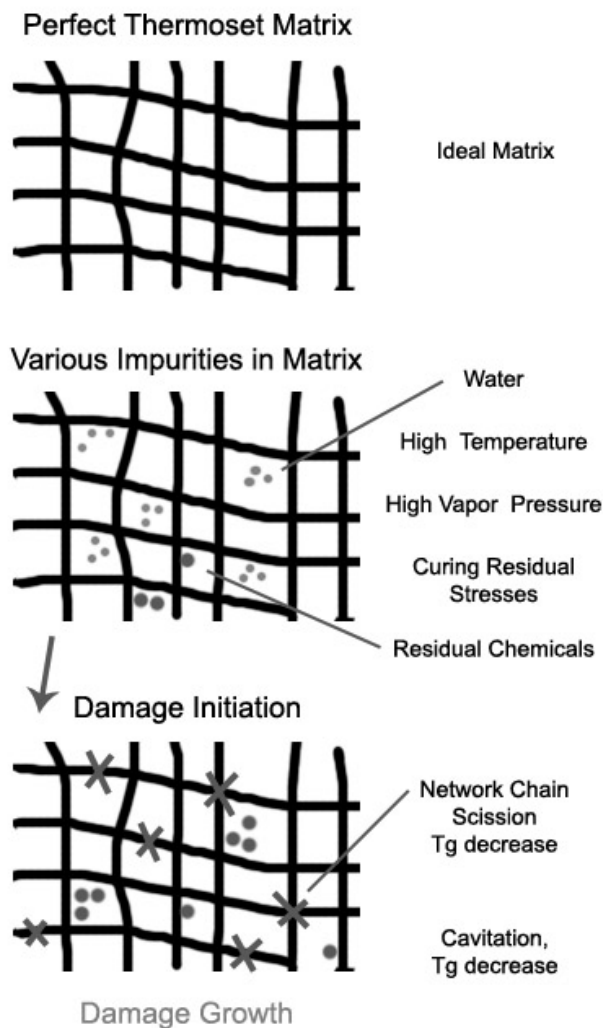


Figure 3. Damage in a Thermoset Matrix [5]

Due to the stability of aromatic compounds, many thermosets have aromatic chains. A wide variety of aromatic and thermally stable polymers has been developed in recent years. Many of these polymers have not found much commercial acceptance due to the high cost and poor processability. Aromatic polymers normally exhibit high transition temperatures, high melt viscosities, and low solubility due to these factors. Much

research has focused on introducing structural variations to allow improved processability. Some chemical functional groups added to the polymer are ether or sulfone groups, the problem is that thermal stability usually is decreased. Figure 4 shows the sulfone and ether functional groups, the new polymer would have these groups incorporated to its structure.

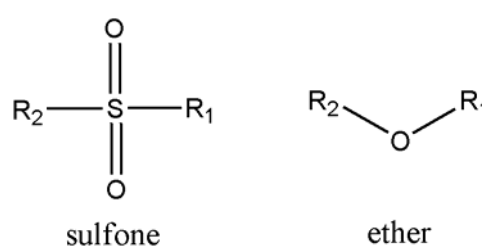


Figure 4. Sulfone and Ether Functional Groups

In recent years, the most productive approach for commercial development is the synthesis of aromatic oligomers with reactive end groups. The end-capped oligomers melt at relatively low temperatures and are soluble in a variety of solvents. Upon heating, there is thermal induced curing and formation of a stable network [6-10].

2.2.2 Polyimides

Polyimides are extremely strong, heat and chemical resistant polymers. Often their properties are so excellent that they replace glass and metals in demanding applications. Polyimides, as a polymer class, cover an extremely broad property range, from high-melting aromatic polyimides to melt processable polymers. Polyimides are formed from

monomers containing the imide link as shown in Figure 5. Imide links may take two different forms: linear and cyclic form.

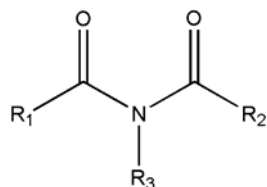


Figure 5. Imide Functional Group

In the linear version (Figure 6) the atoms in the imide group are part of a linear chain. In the cyclic version the imide group is part of a cyclic unit in the polymer chain (Figure 7).

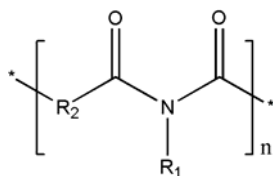


Figure 6. Linear Imide

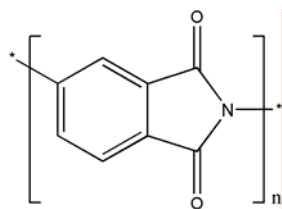


Figure 7. Aromatic Heterocyclic Polyimide

Aromatic heterocyclic polyimides are typical commercial polyimides such as DuPont's Kapton® seen in Figure 8. Aromatic polyimides have excellent mechanical and thermal properties. Which are used in high performance applications in electronics, automotive and most importantly the aerospace industry.

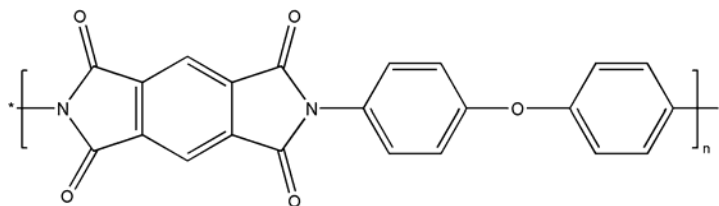


Figure 8. Dupont's Kapton® Polyimide

2.2.2.1 Synthesis of Polyimides

The field of polyimides developed very rapidly. It is also extremely broad due to the many types of polyimides structures available. Due to this, there is not a single section on polyimide synthesis in any book to describe all the possible synthesis variations. The procedures described following will be concerned with polyimides which are principally aromatic.

2.2.2.1.1 Synthesis of poly(amic-acids)

“The early attempts to prepare aromatic polyimides were unsuccessful because they attempted direct synthesis of final polyimide from the starting monomers [11].” After

many years, in 1962 a successful mechanism was found to create high molecular weight aromatic polyimides. The synthesis consists on two stages. To prepare a soluble poly(amic-acid) which is later converted into the desired polyimide.

The poly(amic-acid) is prepared by the reaction of an anhydride with a diamine at ambient temperatures in the presence of polar, aprotic solvents such as N-methyl-2-pyrrolidone (NMP) or N,M-Dimethylformamide (DMF); at room temperature poly(amic-acid) is formed rapidly. The reaction involves a nucleophilic attack of the amino group on the carbonyl atom of the anhydride group. This is followed by the opening of the anhydride ring to form the amic-acid group as seen in Figure 9.

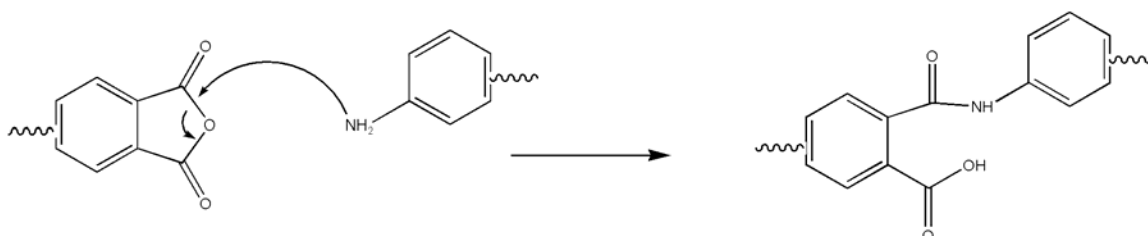


Figure 9. Formation of Poly(amic acid)

The poly(amic-acid) is later dehydrated into the polyimide. The closing of the ring, also called imidization (Figure 10), will then occur if it is induced using temperature or chemically. Thermal imidization is preferred for preparing films; the films are dried and gradually heated to 250-350°C. Chemical induced imidization is done using dehydrating agents such as acetic anhydride, propionic anhydride, n-butyric anhydride, among others. Catalysts can be used as well, some examples include pyridine, and methyl-pyridines.

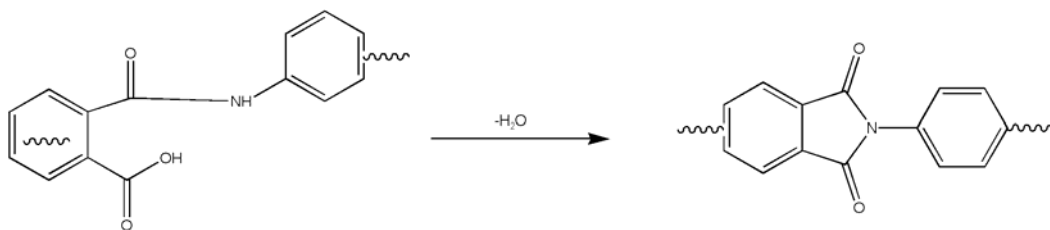


Figure 10. Imide Formation

The advantages of forming poly(amic-acid) is that these polymers can be cast into glass or metal plates and then vacuum dried. Fibers of poly(amic-acid) can also be spun from solution. End capping (to stop polymerization) of the amic-acid is done normally by incorporation of a phthalic anhydride (Figure 11), it is also possible to end-cap with maleic anhydride or nadic anhydride. The usefulness of end capping is that functional end-cap units might provide sites for subsequent cross-linking of the polymer.

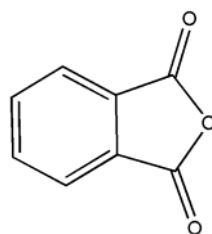


Figure 11. Chemical Structure of Phthalic Anhydride

The two-step synthesis is extremely useful even for different structural variations of the monomers, leading to hundreds or polyimides created. Other methods exist for polyimide synthesis, these will not be explained further but only mentioned (Table 2).

These synthesis methods are less common than the two-step process described above.

Table 3 summarizes a list of monomers of commercial utility or which possess special scientific interest to synthesize polyimides.

Table 2

Other Synthesis Polyimide Synthesis

- 1) One-step synthesis of polyimides in phenolic and other solvents.
- 2) Polyimide synthesis by vapor deposition.
- 3) Polyimides synthesis via reaction of dianhydrides with diisocyanates.
- 4) Polyimides synthesis via the Diels-Alder reaction.

Table 3

Important Polyimide Precursors [11]

Diamines	
Chemical name	Abreviation
p-phenylene diamine	PPD
m-phenylene diamine	MPD
4,4'-methylene dianiline	MDA
2-chlorophenylene diamine	CIPPD
benzidine	Bz
2,2'-dichlorobenzidine	2,2'-diClBz
3,3'-dimethylbenzidine	3,3'-diMeBz
4,4'-diaminodiphenyl ether	ODA
4,4'-diaminobenzophenone	4,4'-DABP
3,3'-diaminobenzophenone	3,Y-DABP
4,4'-diaminodiphenyl sulfone	4,4'-SO2D
4,4'-diaminodiphenyl sulfide	SDA
1,4-bis-(4-aminophenoxy)benzene	APB 4-1,4
1,4-bis-(3-aminophenoxy)benzene	APB 3-1,4
1,3-bis-(4-aminophenoxy)benzene	APB 4-1,3
1,4-phenylindane diamine	DAPI
2,2-bis-[4-(4'-aminophenoxyphenyl)] hexafluoropropane	4-BDAF
1, 1-bis(4-aminophenyl- 1-phenyl-2,2,2 trifluoroethane	3FDAM
2,2-bis(4-aminophenyl)hexafluoropropane	p,p'-6FDAM
Dianhydrides	
Chemical name	Abreviation
pyromellitic dianhydride	PMDA
3,Y,4,4'-benzophenonetetracarboxylic dianhydride	BTDA
3,Y,4,4'-biphenyltetracarboxylic dianhydride	BPDA
3,3',4,4'-oxydiphthalic anhydride	ODPA
4,4'-hexafluoroisopropylidenebis(phthalic anhydride)	6FDA
4,4'-bis(3,4-dicarboxyphenoxy) diphenylsulfide dianhydride	BDSDA
4,4',5,5'-sulfonyldiphthalic anhydride	DSO ₂ DA

2.2.2.1.2 Structure-Property Relationships

For a polymer to be considered thermally stable, it should not decompose below 400°C and should retain its mechanical properties at temperatures near decomposition temperature. It follows from this that the glass transition temperature (T_g) should be high. Thermal stability is primarily a function of bond energy [2]. When the temperature increases to the point where vibrational energy causes rupture, the polymer degrades. In the case of repeating cyclic units if one bond breaks within the ring, the molecular weight is maintained. The probability that two bonds break in the ring is low. The presence of oxygen causes different decomposition mechanisms in polymers. In most cases it has little effect on the initial decomposition temperatures. Bond rupture results from thermal processes rather than oxidative processes.

Polyimides show excellent stability and high temperature thermal degradation. The reason for this type of behavior, in addition to the aromaticity in the chain structure, is due to a charge transfer complex in the polymer. For a charge transfer complex to exist there must be donor and acceptor electrons. The donor contains many electrons such as Nitrogen atoms. The acceptor can pull electrons to it, the acceptors being the carbonyl groups (C=O) which suck the electron density from the N atoms. As seen in Figure 12, there are parts of the polymer in which the carbonyl groups (C=O) suck electron density away from the acceptor units. The N atoms have high electron density than the carbonyl groups and lend it to the acceptor.

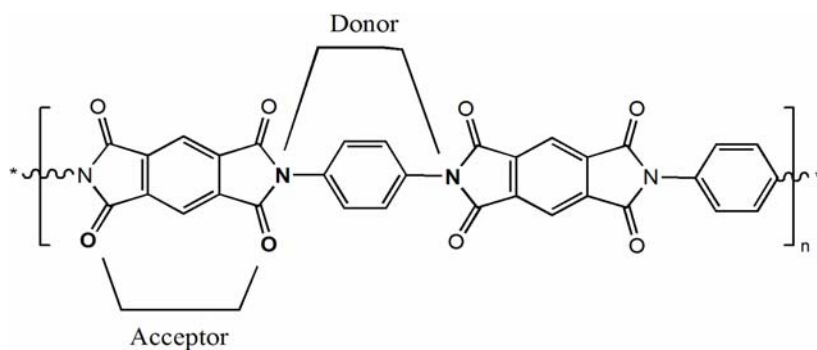


Figure 12. Donor-Acceptor Charge Complex in a Polyimide

In addition to the Donor-Acceptor charge complex within the chain, this can occur between adjacent units/chains (Figure 13). The chains may stack together when the electron donors and acceptors interact. The stacking allows the carbonyls chemical units of the acceptor on one chain, to interact with the nitrogen atoms of the donor between the chains. Due to this interaction, the chains have less mobility in the whole material and this increases the strength of the polymer bulk.

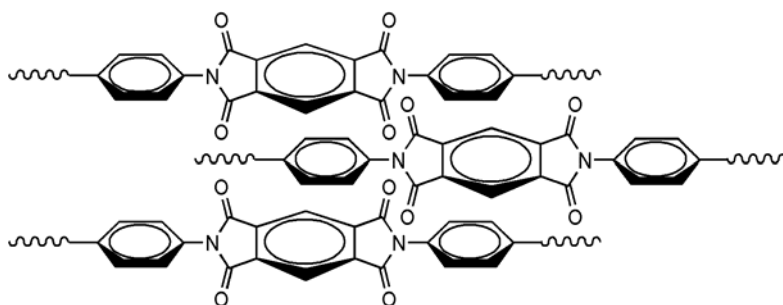


Figure 13. Effect of Charge Complex Between Polymer Chains

2.2.2.1.3 History of Polyimides

Synthesis of polyimides started in 1955 at DuPont's Film Department [5]. During the development of PI films, these showed that they had excellent thermal stability as well as good mechanical and electrical properties which promised for future industrial potentials. It wasn't long before several groups started researching on these new classes of polymers. Several processes were developed for large-scale processing and development. The first polyimide film, Kapton began in production in October 1965 with immediate success (Figure 8).

Due to the different chemical variations that can be achieved with both dianhydride and diamines, polyimide precursors, much research has focused on variation of structures (Figures 14, 15). The variation of structure in the polyimide is then compared to other structures and how chemical changes affect properties.

These materials have had extensive investigations during the 50 years after their discovery. Much of the research performed has focused on coupling high temperature capacity with physical, thermal, chemical and mechanical properties. In recent years, these materials have been designed to meet aerospace and aircraft applications. In addition, commercial applications of these polymers have focused on long shelf life at high service temperatures.

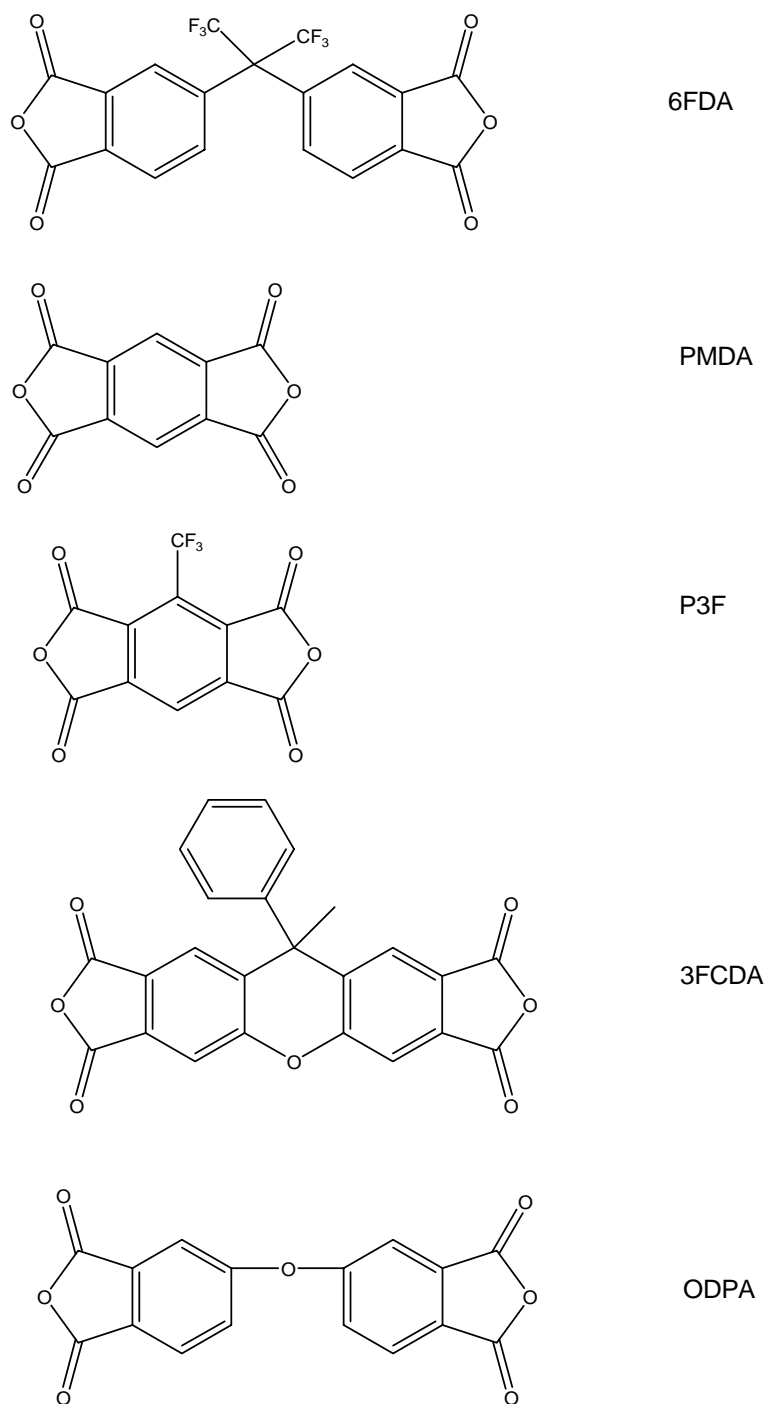


Figure 14. Some Commercially Available Dianhydrides [12]

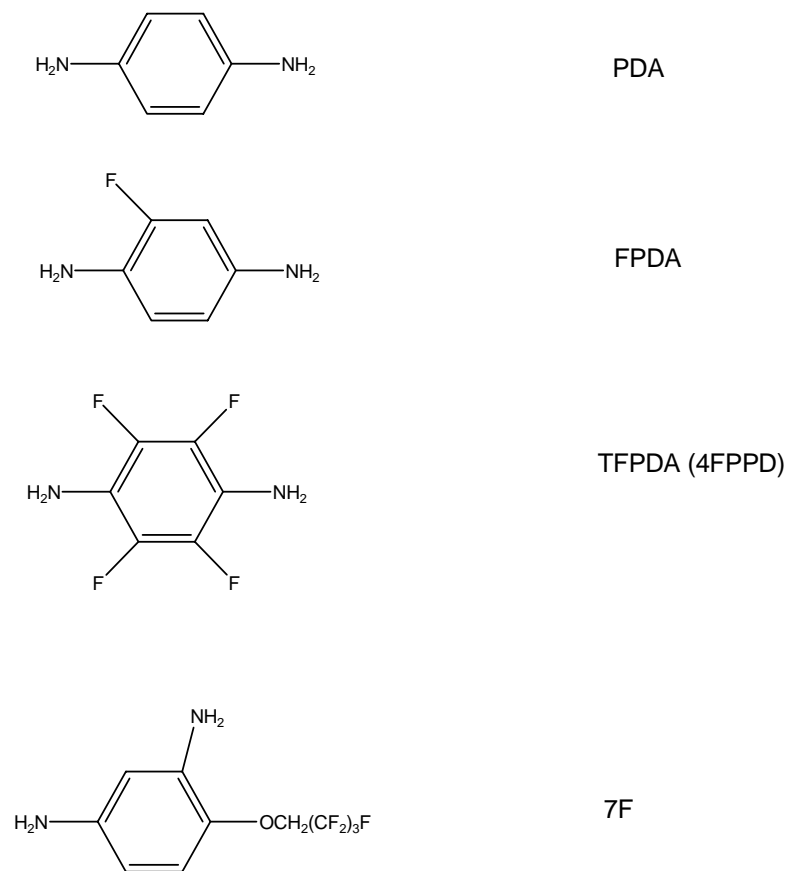


Figure 15. Some Commercially Available Diamines [12]

2.2.2.1.3.1 Fluorinated Polyimides

Of the many polyimides in the industrial market, only fluorine containing polyimides stand out for performing well thermally as well as mechanically. In addition to these qualities, they possess low dielectric permittivity and are processable as thin films,

therefore they are ideal for high-performance insulators in electronic devices, for example.

The imide group is among the most stable organic functional groups known, this in turn makes polymers incorporating it stable structures. The increase of knowledge in this field has been in part due to the extensive availability of di-anhydride and di-amine structures of wide structural variety commercially available. This gives way for structural optimization for applications or simply for academic studies.

The great variety of properties ranging from the different polyimide monomers has led to extensive studies on the matter. Numata, S. et. al. among others have performed thermal expansion behavior [13]. Other scientists have focused on optical properties [14,15], electronic structure [16], dielectric constants [17], spectroscopic properties [18,19] and molecular order to mention a few [20,21].

The addition of fluorine atoms incorporated into the polyimide, the chemical structure affects many properties that can add superior properties to the polymer. Many papers have focused on comparing monomers that have substituted the hydrogen atom for a fluorine atom. Sometimes these comparisons cannot be 100% reliable because the monomer is different but comparisons are often made regardless. Some of the properties that have been researched in different laboratories can be seen summarized in Table 4.

Table 4.

Properties Affected by Adding Fluorine to the Polymer Chain.

Properties	Fluorine-substitution
Optical	Decrease in refractive index, reduce optical loss
Water Absorption	Lower
Thermal Stability	Unchanged or increased
Radiation Resistance	Increase for some materials

Some fluorinated polyimides created will be discussed below. These polyimides have special characteristics that have been tailored by different research groups to meet specific demands. For example, the need of soluble, high optical transparency polyimides for coatings in space components such as solar cells, and thermal system was tackled by Matsuura and co-workers [17]. Matsuura found that polyimides composed of 6FDA and TFDB showed high transparency and solubility with common solvents such as acetone. In addition the polyimide exhibited a low dielectric constant, low refractive index and low water absorption rate.

Kowalczyk and co-workers have focused on the electronic structure of certain polyimides including mathematical modeling of the electronic structure [22]. Studies have revealed that the electronic processes of polyimides are highly localized. This quality makes polyimides successfully modeled using molecular calculations, [23].

Kafafi has taken this knowledge and modeled polyimides for ionization potential, electron affinity and energy gap [24]

Factor and co-workers at IBM [21] have focused on the orientation of polyimide films and studied them utilizing x-ray diffraction. Factor found that near the surface of the films the polymers showed crystalline order. They also found that the presence of an interface may alter the ordering of the polymer. Some liquid crystallinity was found during the formation of poly(amic acid) and is maintained after the acid is imidized.

Due to the amount of research in the area, knowledge on the effects of fluorine on structure-property-processing relationships has grown. NASA Langley Research Center made improvements in the properties of fluorine-containing polyimides while studying dielectric constant changes. “This work contributed to the clear identification of kinked backbone structure as leading to lower dielectric constants when meta- and para- linked polyimides of many kinds were compared and to the relationship between the incorporation of fluorine and low dielectric constant, which was explained as being due in part to the reduction in chain-to-chain interactions and the packing efficiency that resulted [12]”.

In general, from the literature it can be summarized that incorporation of fluorine groups into the structure has the following effects: 1) Decrease dielectric constant but depends on the symmetry and frequency. Normally dielectric constants range from 3.0-4.0 with

fluorine they range from 2.6-3.3. Fluorine changes the dielectric constant by changing the polarizability, the hydrophobicity and the fractional free volume. The fluorine atoms might interfere with the chain-packing density. It might be possible for the fluorine atoms to repulse each other electrostatically which affects the packing [25,26] 2) Decrease moisture absorption even as free volume increases according to Mercer et. al [27,28]. 3) Decrease of Tg mostly when the fluorine atom is on a side chain, when in an aromatic backbone the decrease is smaller [12]. 4) Lastly, it can decrease the optical absorption.

Work continues in many labs to study the effect of the addition of fluorine and to better understand the structure-property relationships in polyimides.

2.2.2.1.3.2 Development of AFR-PEPA-N

2.2.2.1.3.2.1 PMR-15

During the 1970s NASA Lewis Research Center developed a processable polyimide comprised of a mixture of monomers in an alcohol solvent. These polyimide named PMR-15 (Figure 16) found use in composite materials, used to impregnate reinforcing fibers [29]. PMR-15 is a thermosetting polyimide made from three monomers : 5-norborene-2,3-dicarboxylic acid; 4,4'-methylenedianiline; and 3,3',4,4'-benzophenone tetracarboxylic dianhydride. PMR-15 had a service temperature of up to 260-316°C but was relatively brittle and suffered from inter-laminar matrix cracking. PMR-15 and its

polymerization monomer reactants approach are still used today in commercial and military systems, but new resins are preferred due to carcinogenic and mutagenic monomers, as well as its limited shelf life. [30,31]

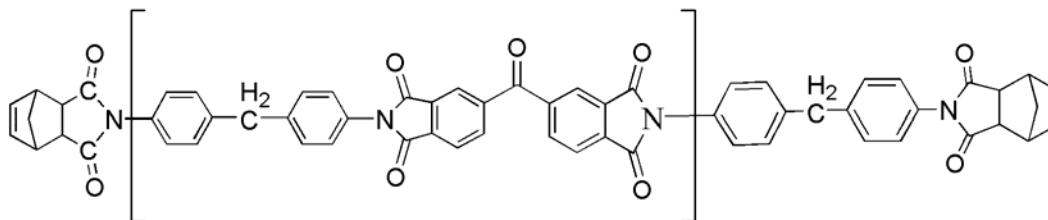


Figure 16. Chemical Structure of PMR-15 Oligomer

Due to the limited shelf life and toxicity as well as limited thermo resistance new polyimide oligomer systems were developed, these were: 1) NASA PMR-II-50, 2) AFR700B, 3) NASA-PETI and 4) Avimid ® materials.

2.2.2.1.3.2.2 AFR700B

AFR700B was created out of the need for a polymer system that had same mechanical properties of PMR-15 at 288°C, but at a service temperature of 371°C [32]. PMR-15 degraded at high temperatures and the need for a new polymer with better stability was desired. AFT700B fulfilled the requirements by replacing the BTDE monomer with 6FDA (Figure 17). The fluorinated portion of the polymer created a more stable oligomer. In addition p-PDA was added to the compound to reduce toxicity. The complete structure of AFR700B can be seen in Figure 18. The chemical compounds p-

PDA and 6FDA are reacted to form oligomers which are later end-capped with neoborene end groups to control the chain length and dramatically affect the overall properties of the network structure.

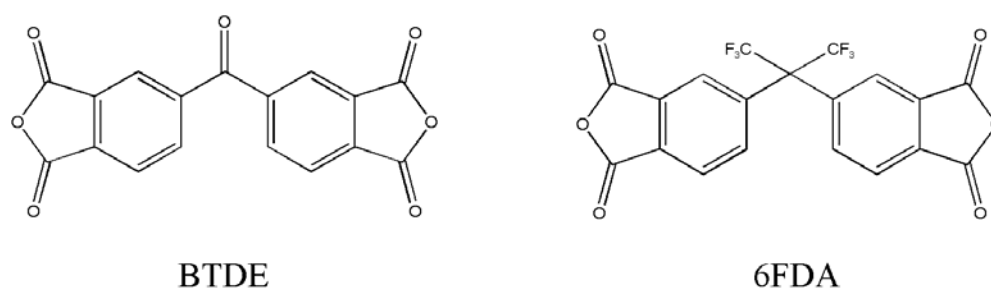


Figure 17. Chemical Structures of BTDE and 6FDA Dianhydrides

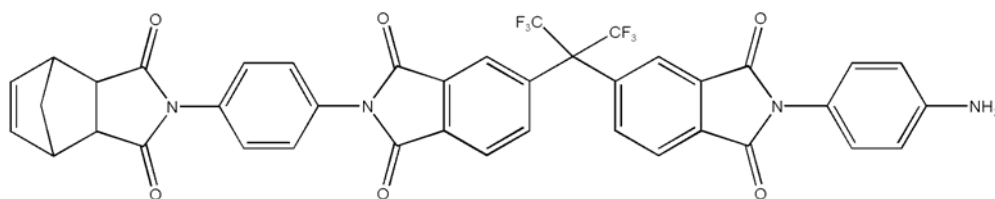


Figure 18. Chemical Structure of AFR700B

Upon heating of the oligomer, cross-linking reacting takes place forming a network structure similar to Figure 3. The AFR700B oligomer matrix proved to have excellent thermo-oxidative stability. Stealth fighter's fuselage trailing edges were replaced with the new polymer which were having heat damaging problems. AFR700B gave an additional 150°C of heat tolerance. "A total of 450 separate component parts were

fabricated at Sacramento ALC using this technology, with the last component being assembled in January 1999. [33]”

AFR700B is no longer used in hydro-thermal exposure applications. This was due to hydrolytic chain scission at the crosslinks rather than in inter-crosslink segments of the network. Chain scission at the crosslinks generates 1.5 to 2 times the greater disconnected network defects according to Lincoln [5]. Research was conducted in Air Force Research Laboratory where it was verified that the weak link in AFR700B was associated with the end-cap and not the fluorinated backbone [34]. It was concluded that end-caps such as norborene should be avoided to achieve a hydrolytically stable polyimide.

2.2.2.1.3.2.3 PETI Oligomers

NASA created PETI-5 a polyimide crosslinked with heat 350-371°C and 1MPa pressure. PETI-5 demonstrated excellent hot-wet properties, improved hydrolytic stability, high toughness (with strain to failure = 32%), excellent mechanical strength (130MPa) and 270°C Tg. In addition to PETI-5 several other polyimides were created using different precursors. There are several names given to the different variations, the current paper will focus on PETI-5 oligomers.

The purpose of NASA was to develop materials that were processable utilizing resin transfer molding (RTM), several chemical structures were prepared and evaluated for T_g, melt flow behavior and processability via RTM. Several resins were created exhibited the appropriate combinations of properties such as low and stable melt viscosity needed for RTM processing. Phenyl-ethynyl (Figure 19) terminated imide oligomers were prepared and evaluated. These oligomers exhibited low and stable melt viscosities capable of RTM processing that exhibit high T_g's [35-37]. In hygrothermal aging studies performed by Lincoln, PETI-5 was found to be more hydrolytically stable than AFR700B [5]. Figure 20 shows several precursors that were studied in NASA laboratories.

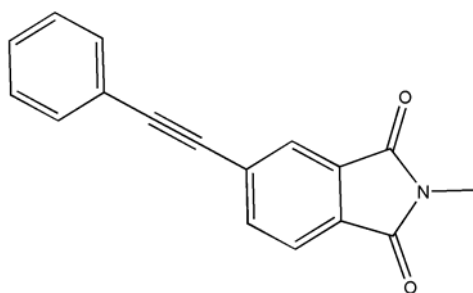
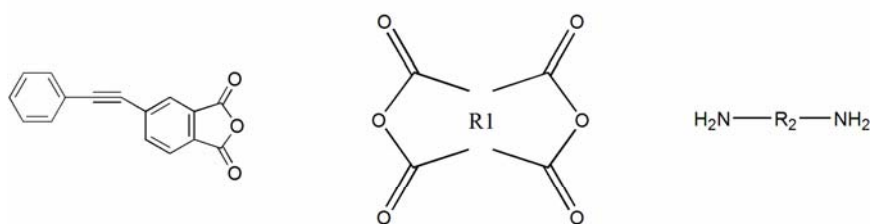


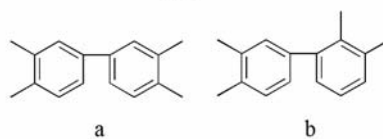
Figure 19. Chemical Structure of PEPA

The phenylethynyl end-caps in PETI-5 are thought to be the more stable link as compared to AFR700B neoborene end-caps. The phenylethynyl groups crosslink via the carbon triple bond, as seen in Figure 21 [38].

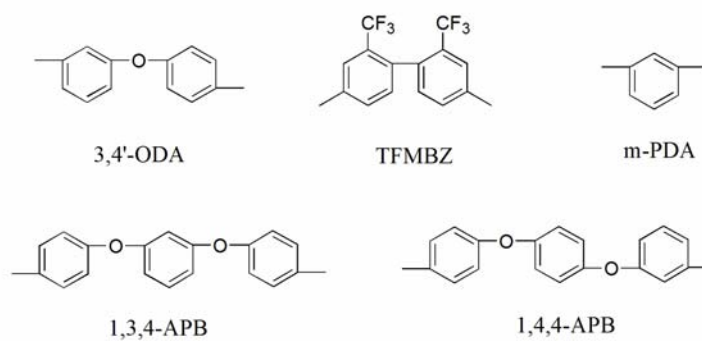
- Precursors -



- R1 -



- R2 -



PETIs

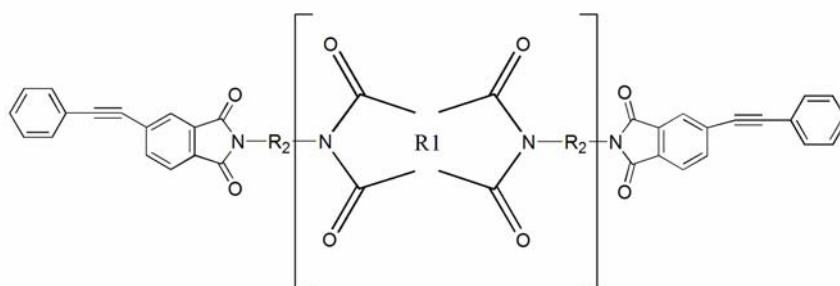


Figure 20. Precursors Used to Synthesize Different PETI Oligomers [35]

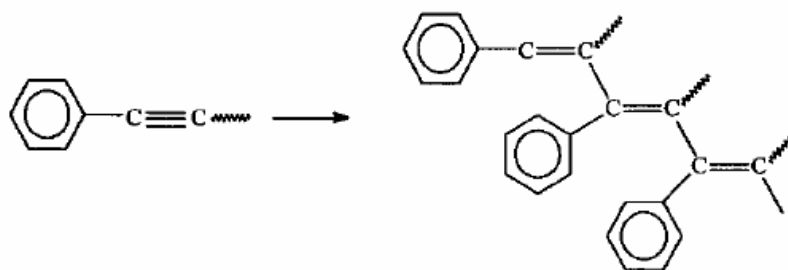


Figure 21. Partially Cross-linked Polyimide Oligomers [39]

2.2.2.1.3.2.4 AFR-PEPA-N

A new oligomer emerged from these two technologies labeled AFR-PEPA-N. The structure of the new compound had both technologies incorporated into it. The p-PDA, and 6FDA monomers end-capped with 4-phenylethynyl phthalic anhydride (PEPA).

The new AFR-PEPA-N oligomer showed Tg's up to 435-455°C. It was found that this polyimide had improved hydrolytic stability relative to AFR700B. AFR-PEPA-N experienced a moisture plasticized 3-5% Tg drop as opposed to 20% experienced by AFR700B. Most importantly AFR-PEPA-N had superior mechanical properties at the 300°C temperature range.

Lincoln and co-workers researched AFR-PEPA-N oligomers to confirm that the material met specifications set forth by the United States Air Force (USAF). Like NASA, the USAF also wanted a polyimide resin capable to be processable by RTM while displaying necessary properties at the 300°C temperature regime [5]. Additionally the polymer should have better hydrolytical and thermo-oxidative stability as compared to previous oligomers.

Lincoln found that the viscosity of the oligomer were in some instances acceptable for RTM processing. In other cases the viscosity was extremely high for RTM. It was recommended the addition of additives to the oligomer system to lower the viscosity and ease processing [5].

The synthesis of the AFR-PEPA-N system is shown in Figure 22. The oligomer is prepared by adding stoichiometric ratios of 6FDA and p-PDA. After formation of the 6FDA/p-PDA oligomer PEPA end cap is added to stop polymerization. After complete reaction of the PEPA end-cap, the chemicals are heated for thermally assisted imidization.

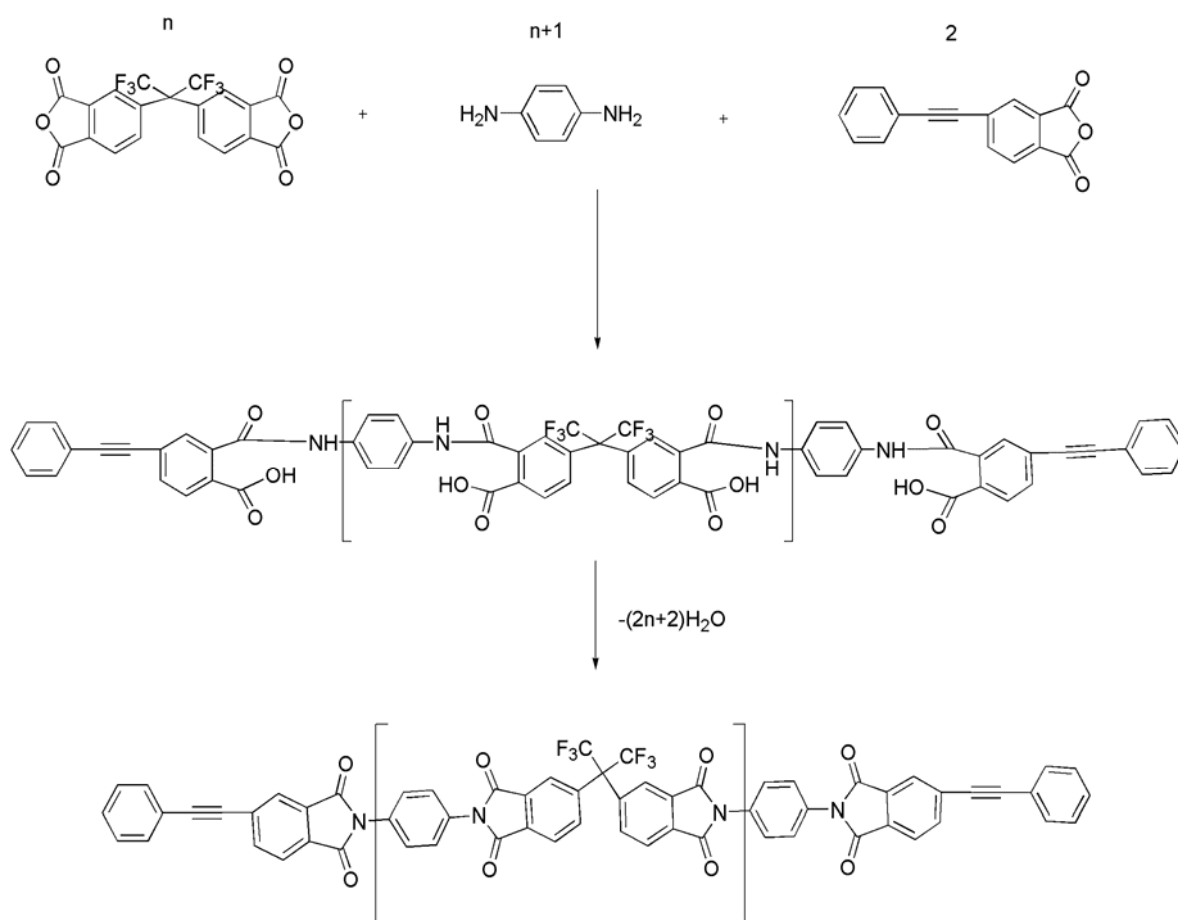


Figure 22. Synthesis of AFR-PEPA-N Imide Oligomers [5]

2.3 End-Cap Units

Current technology allows for the physical properties of polymers to be tailored by controlling the shape, type and size of the mers. The use of the new knowledge led to the synthesis of polymers with excellent thermal and oxidative stability for use in high-performance applications.


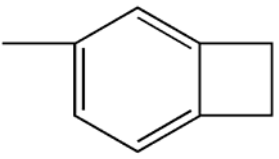
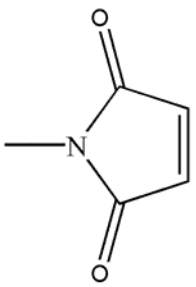
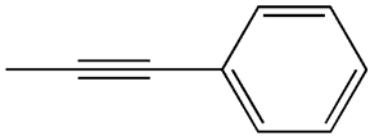

2.3.1 Purpose

From the standpoint of commercial development the synthesis of aromatic compounds is excellent in that they impart excellent thermal stability to the compound. These aromatic polymers are then capped with reactive end groups. There are several reasons for this end-capping: 1) by controlling the size of the oligomers the viscosity of the oligomer is lower; to facilitate manufacturing 2) oligomers melt at lower temperatures, 3) oligomers are soluble in a variety of solvents. Upon heating, these oligomers form a thermally stable network polymer. One commonly used end cap is phenyl-ethynyl phthalic anhydride. Phenyl-ethynyl terminated oligomers have been used in numerous aerospace applications [40]. In addition several other end-cap units have been studied, some commercially available are shown in Table 5.

The purpose of this project as mentioned before, was to improve the lifetime of components fabricated with AFR-PEPA-N oligomers by changing the end-caps utilized in the oligomer. This would reduce curing temperature, leading to induced stresses in the network. Due to the success of PEPA as an end-cap unit, our research wanted to focus on the creation of similar end cap units. One proposal included the creation of 4-ethynyl-phthalic anhydride (ETA) in which the phenyl group of the PEPA end cap was removed. It was found in the literature that the curing temperature of this end-cap was close to 250°C according to Hergenrother and co-workers at NASA Langley Research Center [37].

Table 5

End-groups Considered for Oligomers Leading to Polymers [37]

Reactive group structure	Name	Cure Temperature
	Cyanate	200-300
	Denzocyclobutene	220-250
	Maleimide	230-250
	Phenylethynyl	350-370
	Ethynyl	250

2.3.2 4-ethynyl phthalic anhydride

The initial intent of the research was to synthesize 4-ethynyl phthalic anhydride with a similar synthesis path as used by Johnston and co workers to create PEPA [41]. This would create a new end-cap that would be reactive as PEPA but would require lower temperatures to cure.

The reaction and synthesis to create the end-cap will not be described in this paper since poor yields of the final product were obtained, and the chemical produced was not utilized. Instead, 4-ethynyl phthalic anhydride (Figure 23) was bought from TCI America.

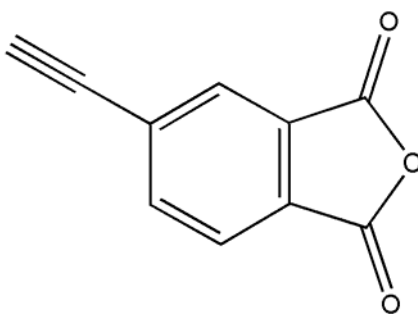


Figure 23. 4-ethynyl-phthalic Anhydride Monomer

2.4 Carboranes

Salts and esters of boric acid have been known to be excellent flame retardants, these can have greater combined effect with halogenated polymers or halogen additive/polymer systems. Boron compounds act by redirecting the composition process in favor of carbon formation rather than CO or CO₂. There have been some suggestions of that the formation of a surface layer/protective char that might be the reason for the flame retardancy. The layer would act as a barrier to prevent the access of oxygen to the polymer system. [42]

2.4.1 Structure

Carboranes are defined as “any member of a class of organometallic compounds having the general formula $C_2B_nH_{n+2}$, in which C, B, and H represent, respectively, carbon, boron, and hydrogen atoms and n an integer... the carboranes have polyhedral molecular structures based on networks of boron and carbon atoms...” [43]. Of special interest are icosahedron carboranes with ten boron atoms, these have optimal occupancy of 13 bonding molecular orbitals by 26 framework electrons [42]. This molecular arrangement allows for complete delocalization of the electrons giving them pseudo-aromatic character.

Of special importance is the icosahedron carborane $C_2B_{10}H_{12}$. The icosahedron carborane exists in three isomeric forms termed ortho-carborane, meta-carborane and para-carborane as seen in Figure 24. Figure 24 shows only the skeletal arrangement of the carboranes; one hydrogen is attached to each boron and carbon atom, the hydrogen atoms are sticking out of the carbon-boron cage. The melting temperature of the isomers are 534K, 546K and 570K for p-, m- and o-carborane respectively [44]

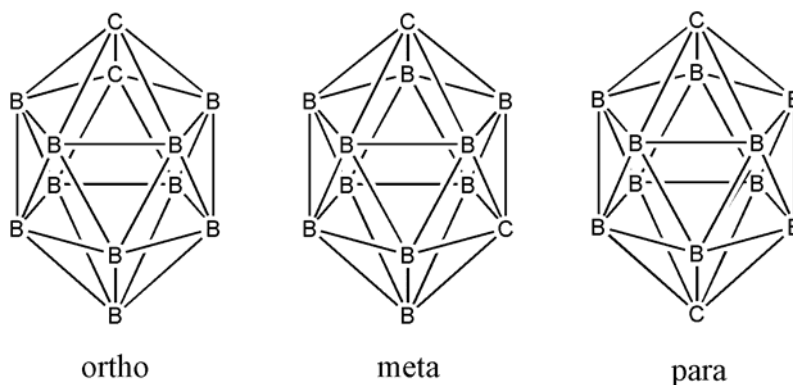


Figure 24. Ortho, Meta, and Para Icosahedral Carborane Structures

It is to be noted that the hydrogen attached to the carbons are more acidic than those attached to the boron atoms. This makes carborane useful since many derivatives can be synthesized by reaction with these carbon atoms. When these hydrogens are substituted with suitable functional groups they can be used in a variety of applications including polymers. Polymers containing these icosahedrals have been prepared over the years. Some polymers contain the carborane groups in the backbone of the chain such as vinylcarborane. Other polymers include the carborane units attached to the chain through another functional group such as an ester, amide, or others.

In general, adding icosahedral carboranes into polymer units, leads to enhanced thermal stability even when the percentage of the carborane is small. The protective layer formed by the carborane might also be helpful in the retardation of degradation of polymers during use.

Initial research led to the conclusion that the carborane cages could substitute the phenyl group in the PEPA end group. The addition of the carborane cages to the end group was not impossible but extremely costly. CATCHEM a company specializing in carborane compounds could perform the synthesis but the price to do this was extremely high. The research was abandoned due to the complexity and cost of the carborane group.

2.5 Polysiloxanes

Although the element silicon is located directly below the periodic table to carbon it has properties completely different to it. The normal oxidation state of silicon is 4, but unlike carbon it contains electrons in its 3d shell which can be used for bonding. A significant difference between carbon and silicon is that Si-Si bonds have about 30kcal/mol less bond energy than C-C bonds [45]. Therefore $\text{Si}_n\text{H}_{2n+2}$ compounds are less stable than $\text{C}_n\text{H}_{2n+2}$ compounds. On the other hand, Si-O bonds have about 90 kcal/mol more energy than C-O bonds and C-C bonds, consequently more stable. Table 6 shows several bond energies for comparison purposes. Polymers which have recurring Si-O bonds are termed polysiloxanes. Polysiloxanes are prepared by hydrolysis of alkylsilicon or

arylsilicon halides. Hydrolysis of the halides gives silanols which are very unstable; once the silanols condense they form siloxane linkages which are more stable (Figure 25).

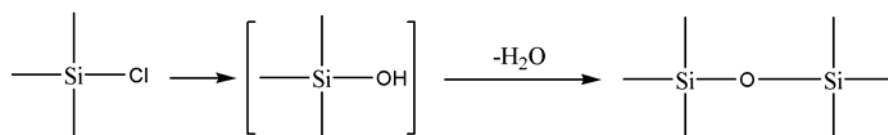


Figure 25. Polysiloxane Formation

Table 6

Bond Energies [45]

Bond	Bond Energy (kJ/mol)
C-H	109
Si-Si	225
C-Si	300
C-C	348
C-O	360
Si-O	450
C=C	614
C≡C	839

To obtain a high-molecular-weight polymer, siloxane cyclic units are normally purified and polymerized with acid or base catalysts. The catalyst helps with the ring-opening reactions. Polymerization of cyclic units give oils that have good thermal stability [42].

One example of a siloxane product is silicon rubber, useful for electrical parts because it has good thermal and oxidative stability, chemical resistance and dielectric properties. Polysiloxanes have also found usefulness in wire coatings, gaskets, adhesive, among others. Much research has focused on modification of polysiloxanes in structure, chemical units or copolymerization with other monomers.

2.5.1 Poly(imide-siloxanes)

The research effort has focused on investigating a stable thermoset based on organic-inorganic polyimides. Incorporation of siloxanes into the polyimide matrix could help thermal stability of the neat polyimide. It has been known that upon heating many polysiloxanes form protective chars, these chars ultimately would improve the thermostability of the oligomers, as well as the thermoset matrix made from these oligomers [42].

Poly(imide-siloxanes) have been developed as high performance heat resistant polymers applied to advanced microelectronics and aerospace applications. [46-49]. It has been shown that thermal and mechanical properties are strongly affected by the siloxane

structure. The structure of the siloxane depends on the original siloxane monomers in addition to the length of the poly(siloxane) created. [50]

Combining flexible siloxane molecules with polyimide oligomers for use in a matrix resin of carbon fiber-matrix composites, not only would give for the possibility of silicon dioxide protective coatings, but the addition will give a class of polyimides with flexible segments and reactive side-chains. These polyimides have shown to increase melt-processability before crosslinking while maintaining excellent thermal properties. Figure 26 shows a model structure for the an imide-siloxane based polymer.

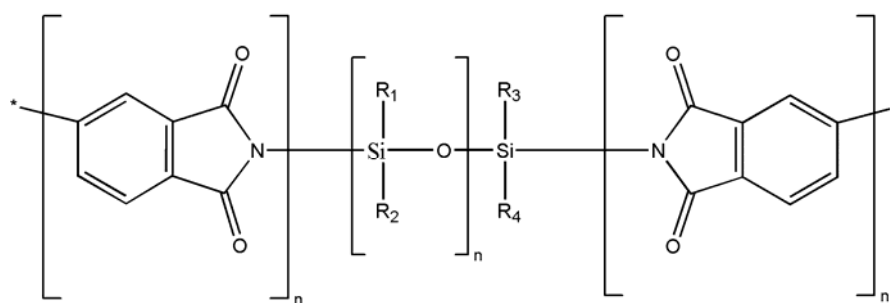


Figure 26. Sample Imide-siloxane Polymer Structure

3. REDUCTION OF VISCOSITY BY DISSOLUTION

3.1 Introduction

One objective in the synthesis of polyimide oligomers is to attain both mechanical properties while maintaining manufacturing of parts feasible by common industrial techniques. In the case of AFR-PEPA-N the viscosity of the oligomer during processing was extremely high and only in some cases low enough for manufacturing. Only AFR-PEPA-2 had a borderline viscosity for use in manufacturing methods such as Resin Transfer Molding (RTM). Several techniques exist to help in reducing viscosity of a polymer, such as: 1) Increase of temperature sample during processing, 2) Dissolve with reactive agents that help reduce the viscosity while maintaining properties of the oligomer. 3) Change the chemistry of the polymer to include functional groups that aid in the reduction of viscosity. The second technique was studied for the AFR-PEPA-N system and the results will be shown in the next few pages.

Several reactive diluents exist commercially, but one common solvent utilized in industry and academia is N-vinyl-2-pyrrolidone or simply NVP. Lorenz and coworkers have found that NVP increases the efficiency of energy use in systems by activating curing. In addition NVP has shown good solvency and pigment dispersion properties that are good in UV manufacturing processes [51]. The second solvent utilized in the

study was N-methyl-2-pyrrolidone (NMP). The idea behind utilizing this chemical was its use during the synthesis of the oligomer itself.

When utilizing these solvents the idea behind it was that only small percentages of the solvent were going to be used to allow for the final properties of the polymer to remain equal if not very close to neat AFR-PEPA-N. Ideally a small amount of liquid would form a pasty substance upon processing and heating.

Another potential use of dissolving the oligomer would be to reduce residual crystals that act as stress concentrators and initiators of microcracking. According to Murphy and co-workers, AFR-PEPA-N polyimide oligomers do not melt until 360°C after 15 minutes when the resin is already 50% cured. Murphy concluded that oligomer crystals are the source of resin defects [1].

The research described in this section will focus upon:

- Reduction of residual oligomer crystals as stress concentrators and initiators of micro-cracking through dissolution with reactive diluents.
- Reduction of viscosity utilizing reactive diluents.

3.2 Experimental Techniques

3.2.1. AFR-PEPA-N Imide Solution

In a small glass vial, AFR-PEPA-4 oligomer powders were dissolved using both NVP and NMP (Figure 27). The percentage by weight of NVP and NMP was varied. The solutions were stirred vigorously for approximately 10 minutes.

The glass vials were heated from room temperature until 120°C on a Corning Hot Plate until the crystals appeared to dissolve. The temperature at which the samples dissolved was noted. Upon dissolution the samples were removed from the Hot Plate. Three samples were taken at each temperature to observe any changes in cooling rates. One sample was cooled using 1) acetone-water-ice bath, 2) air at room temperature, 3) oil bath until the temperature reached room temperature. The samples were observed for any changes, and noted.

The solutions were also analyzed under cross-polarized light using an Olympus BX60 Optical Microscope. Micrographs of the solutions were taken utilizing FlashPoint FPG Software.

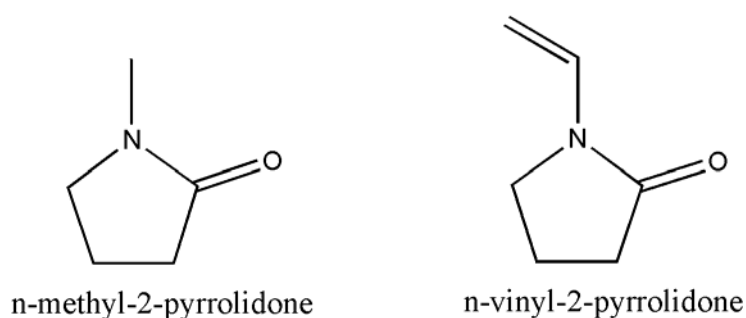


Figure 27. NMP and NVP Chemical Structures

3.3 Results and Discussion

3.3.1 Dissolution Tests

In addition to reducing the viscosity of the oligomer, another purpose of the dissolution tests was to minimize the amount of crystals that lead to defect induced micro-cracking according to Murphy and co-workers [1].

3.3.1.1 AFR-PEPA-N/NVP

According to Lincoln and co-workers [5] dilution of polymers with 10% by weight will reduce the viscosity and improve processing conditions. The initial test concluded that 90% by weight of NVP was needed to dissolve the oligomer at room temperature (25°C). To obtain a 50/50 oligomer/solvent solution it was necessary to increase the temperature to 126°C as shown in Figure 28.

By preparing several samples of the AFR-PEPA-N/NVP at different concentrations and heated until the crystals dissolve a dissolution curve was obtained using statistical methods. The formula obtained was extremely accurate with an correlation coefficient (R) value of 0.99. The temperature at which a certain percentage of oligomer will melt between 50% and 90% is given by: Temperature = -230.57 * percentage NVP by weight + 244. 13.

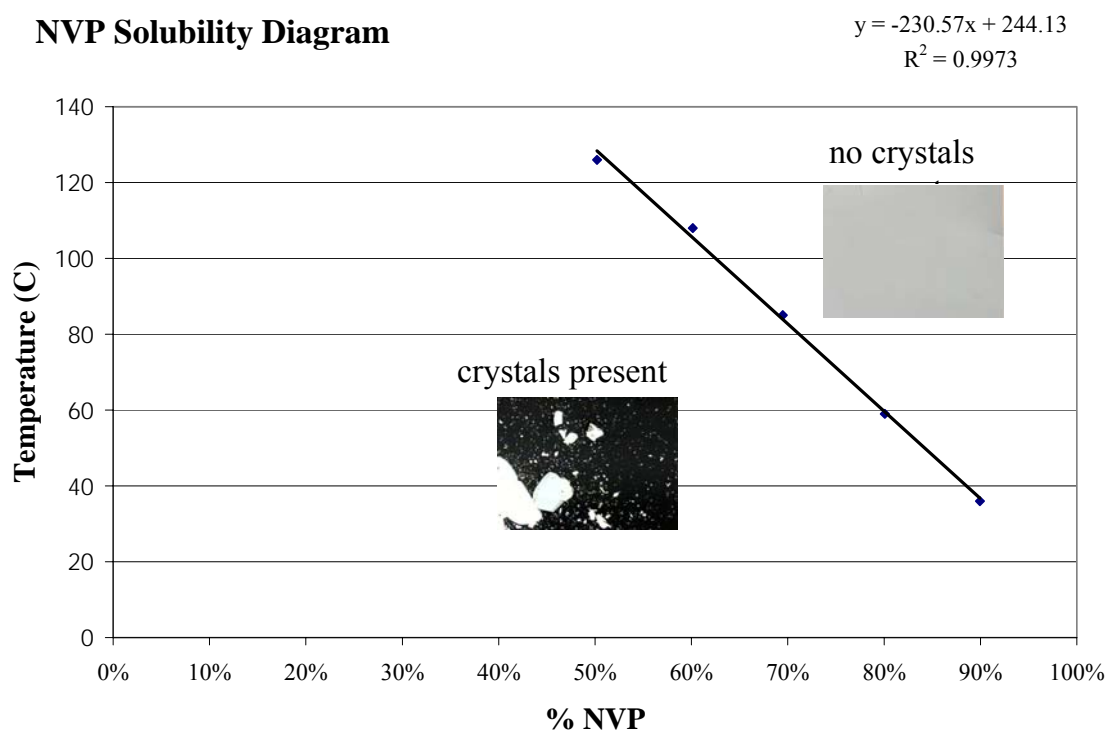


Figure 28. AFR-PEPA-N/NVP Solubility Diagram

Since the properties of AFR-PEPA-N are desired for their high-performance capacity, it was decided not to use this system for further study.

3.3.1.2 AFR-PEPA-N/NMP

The second test performed with the oligomer was done utilizing NMP as the solvent. As seen in Figure 29, the percentage of NMP needed to dissolve the oligomer at room temperature was less than for the NVP system. Only 80% by weight of NMP solvent was needed to dissolve the AFR-PEPA-N at 25°C.

This system proved more promising than with the NVP system. At 118°C the amount needed of NMP by weight is 35%. If the processing of the samples takes place at higher temperatures this solvent promises to work. In the case for room temperature processing the amount of NMP is too high (80%).

A time window was found in which the samples crystallized several hours after cooling to room temperature if the samples were heated for about 1 hour at the temperature indicated by the graph. Therefore, crystallization of the mixture is inevitable, but there is a potential composite processing time within this re-crystallization range.

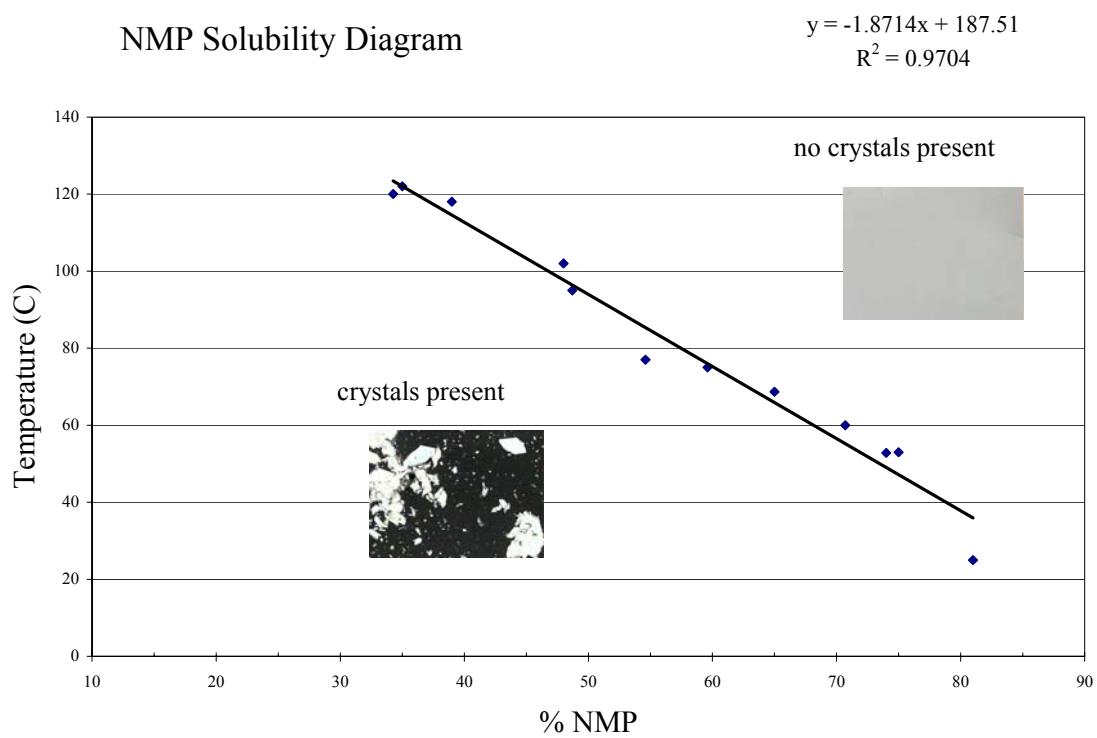


Figure 29. AFR-PEPA-N/NMP Solubility Diagram

3.4 Conclusions

Due to the high amounts of solvents (both NMP and NVP) needed for reduction of crystallinity and reduction of viscosity, this method would not allow for better and easier processing of AFR-PEPA-N composites and parts.

In addition there seems to be a small reduction of crystals in the different systems but at low concentrations of solvent, AFR-PEPA-N crystals would still remain a source of micro-defects.

4. ALTERATION OF CHEMICAL STRUCTURE OF AFR-PEPA-N

4.1 Introduction

Another objective in the synthesis of polyimide oligomers is to attain a large usable life of polymer composites. It was found that the AFR-PEPA-N oligomer had major defect induced microcracking [44]. These defects would cause a reduction in the life of parts made from these thermosets. Performance Polymer Solutions Inc. (P2SI) has developed a new generation of thermal stable thermoset organic-inorganic polyimides based on siloxane with phenyl-ethynyl reactive functionality.

The research described in this section will focus upon:

- Mechanical Testing of poly(imide-siloxane) composites.

4.2 Experimental Techniques

4.2.1 Poly(methyl-phenyl) siloxane studies.

Model compound methyl-phenyl siloxanes were utilized for a preliminary study in order to understand the degradation mechanism of a siloxane-based system. The siloxane compound utilized for this experiment was poly(methyl-phenyl siloxane) and used as received from Aldrich Chemical (Figure 30). The chemical was heated to temperatures of 100°C, 200°C, 300°C, 400°C and 500°C for periods of 1 hr. The liquid samples were then placed between KBr plates and FTIR Spectra was generated. The solid samples were placed grinded into KBr pellets and likewise Spectra was generated as well. The intensity of the Si-O-Si (1100 cm^{-1}) related peaks were recorded and normalized to Si-Ph ($3080\text{-}3030\text{ cm}^{-1}$) readings.

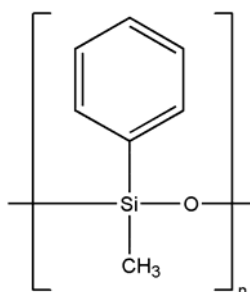


Figure 30. Poly(methyl-phenyl siloxane)

4.2.2 Poly(imide-siloxane) Composite Preparation

Poly(imide-siloxane) composites were received from P2SI. Two sets of samples were obtained for each chemical composition. One set of composites was aged at 400°C for 100 hours utilizing a 48000 Barnstead Furnace. The other set of composites was left at room temperature during that time.

After the aging of the samples, all composites were labeled for cutting as shown in Figure 31. The composites were cut utilizing a (aerospace machine). After the cutting of the samples, these were washed with water and a small amount of detergent.

Immediately after washing the samples, these were rinsed with water and dried with paper towels. The samples were labeled and their dimensions (length, width and thickness) were measured using calipers. The samples were then placed in a VWR Vacuum Oven at 100°C for 24 hours. Upon drying the samples were placed in glass vials and sealed until mechanical testing was performed.

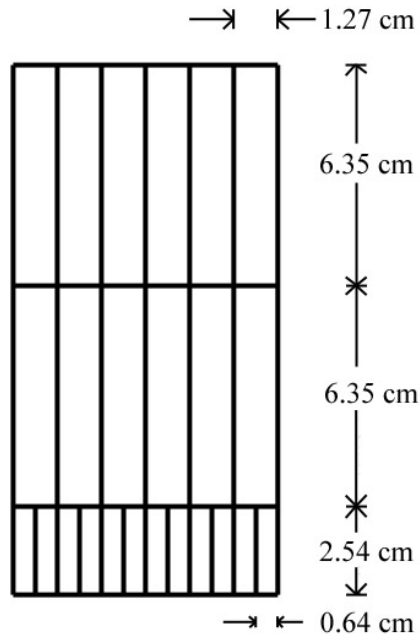


Figure 31. Composite Labeling for Sectioning

4.2.3 Poly(imide-siloxane) Composite Flexural Properties Testing

Dried composite samples were tested using an Instron 1125 machine. ASTM D790-03 was utilized as the testing standard. The Instron machine was equipped with a SATEC Furnace model F0-1 for high temperature testing of the samples. The machine was set up with a support span of 16 times the average thickness of the samples. The crosshead motion was selected using the formula in the ASTM D790-03 standard. Since the Instron machine had set crosshead motion, rate 0.05 in/min was selected as the closest to the number given by the formula.

Ten specimens were tested for each chemical composition, five of these samples were tested at room temperature; the other five samples were tested at a temperature of 260°C. The samples were placed inside the furnace until equilibrated (~6 min) and tested at 260°C. Testing of samples stopped until either of the following occurred: 1) fracture occurred or 2) max strained was reached (0.05 mm/mm). Maximum stress, strain at break and resilience were recorded for each sample. The data was averaged utilizing statistical formulas as shown in Figure 32.

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$$

$$s_{n-1} = \sqrt{\frac{\sum_{i=1}^n x_i^2 - n(\bar{x})^2}{n-1}}$$

$$CV = 100 \times \frac{s_{n-1}}{\bar{x}}$$

where :

\bar{x} = mean strength

s_{n-1} = standard deviation of strength

CV = % variance of data

Figure 32. Shear Strength Statistical Formulas

The data was collected and processed utilizing formulas given by ASTM D790-03 standard in Microsoft Excel and Visual Basic Software.

4.2.4 Poly(imide-siloxane) Composite Short-Beam Strength Testing







Dried composite samples were tested using an Instron 1125 machine. ASTM D2344/D2344M - 00 was utilized as the standard. The Instron machine was equipped with a SATEC Furnace Model F0-1 for high temperature testing of the samples. The machine was set up with a support span of 4 times the average thickness of the samples. The crosshead motion was selected as 0.05 in/min as specified in the ASTM D2344/D2344 test method.

Ten specimens were tested for each chemical composition, five of these samples were tested at room temperature. The other five samples were tested at a temperature of 260°C. The samples were placed inside the furnace until equilibrated (~6 min) and tested at 260°C. Testing of samples stopped until either of the following occurred: 1) load drop-off of 30%, 2) travel exceeded the specimen nominal thickness. After testing was concluded the samples were examined to determine the failure mode: 1) Interlaminar Shear, 2) Compression, 3) Tension or 4) Inelastic Deformation (Table 7).

The data was collected and processed utilizing the formulas shown in Figure 28 where the sample mean, sample standard deviation and sample coefficient of variation are given by given by the ASTM standard in Microsoft Excel and Visual Basic Software.

Table 7

Typical Failure Modes in the Short Beam Test

Sample	Failure Mode
	Untested sample
	Interlaminar Shear
	Interlaminar Shear
	Compression
	Tension
	Inelastic Deformation

4.3 Results and Discussion

4.3.1 Poly(methyl-phenyl siloxane) Aging Tests

The purpose of this test was to see the reaction of a model siloxane oligomer at high temperatures; formation of silica was expected.

The aging test was done to observe any changes in the siloxane structure due to thermal-induced changes. The objective of the test was to observe any production of silicon dioxide during decomposition of the siloxane for in-situ thermal protection. Figure 33 shows IR spectra of non-crystalline silicon dioxide, these were used as standards to compare if silica was indeed produced during decomposition of the siloxane [52,53]. After testing the siloxane at 500°C for 1 hr a thick film of white powder formed in the vial. The white powder was grinded and formed into a KBr pellet and tested in the IR machine. Figure 34 shows the spectra obtained. It was determined that indeed silica was produced during thermal exposure to 500°C.

Indeed as the poly(siloxane) was heated in the furnace the siloxane decomposes and oxidizes, producing silicon dioxide. The siloxane would follow the following reaction $R-Si-R + O_2 \rightarrow SiO_2$. If the siloxane is incorporated into composites these will likely add unique surface thermal protection properties to poly(imide siloxanes).

Amorphous silica - Diatomaceous earth		4661
0251	PREP: Cal disc .5/300 mg PATH REGION SOLVENT	NSRDS-COBLENTZ CLASS III structure verified
SiO ₂	SPECTROMETER Beckman IR-12 Gratings blazed at 3330, 1330, 445, 220 cm ⁻¹	STATE solid M.P. B.P. CONTRIBUTOR DeSoto, Inc. DATE RECORDED

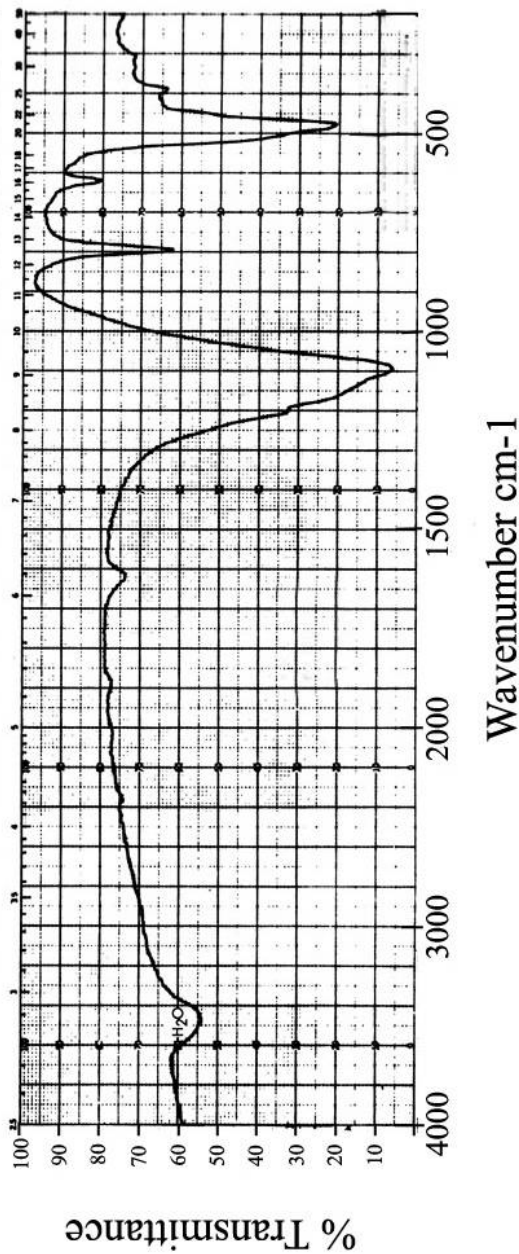


Figure 33. Silica Plot Standard [53]

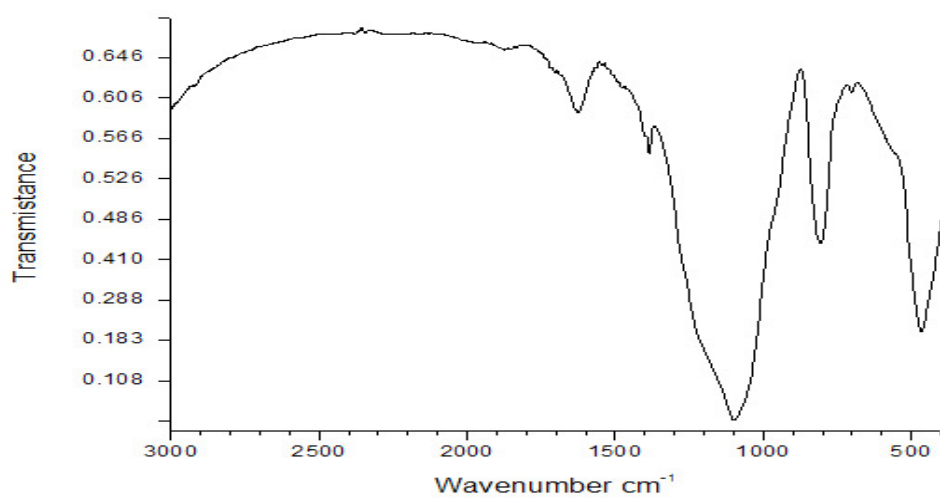


Figure 34. IR Spectra of Silica Produced by Poly(siloxane) Decomposition

4.3.2 Poly(imide-siloxane) Samples

Due to the availability of commercially available siloxanes, studies were made by P2SI to select the most appropriate siloxane system for this study. The selection was focused in selecting siloxanes with good thermal stability. P2SI decided to select poly(dimethyl siloxanes) with fractions of the methyl groups substituted with phenyl groups. To incorporate the siloxane group into the polyimide chain it was necessary to also add siloxane diamines that would react with the dianhydrides of the 6FDA monomer and the PEPA endcaps.

There were several siloxane based diamines prepared by P2SI to be used for the poly(imide siloxane) samples as seen in Table 8. Figure 35 shows the different monomers utilized by P2SI to create the different siloxane systems. Figure 36 shows how reactions of these precursors occur. Upon addition of a strong acid such as Sulfuric Acid, siloxane rings tend to open which allows them to react with Bis(γ -aminopropyl) methyl siloxane (Figure 35). These precursors were utilized to form the model siloxane diamines shown in Figure 37. The three siloxane diamines created by P2SI are shown in Table 8. The name of the siloxane diamines (SD) refers to the repeating units of in the middle of the chain as well as the % of phenyl in the diamine. For example, SD-8-50 has 4 repeating units of di-phenyl siloxane and 4 repeating units of di-methyl siloxane. Since 50% of the groups are phenyl the number 50 appears in the name. Table 9 mentions properties of the siloxane diamines created by P2SI.

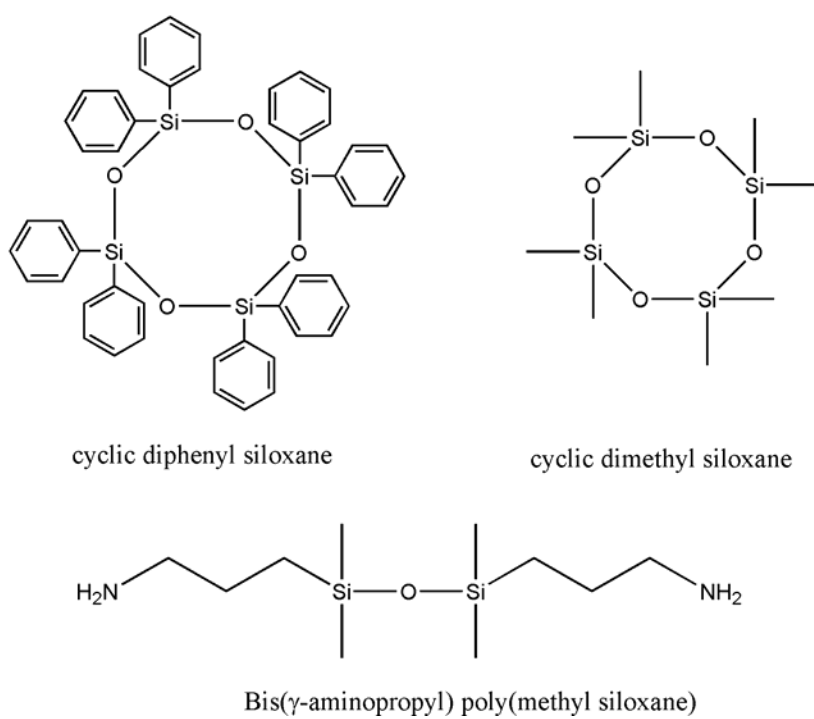


Figure 35. Siloxane Based Diamine Precursors

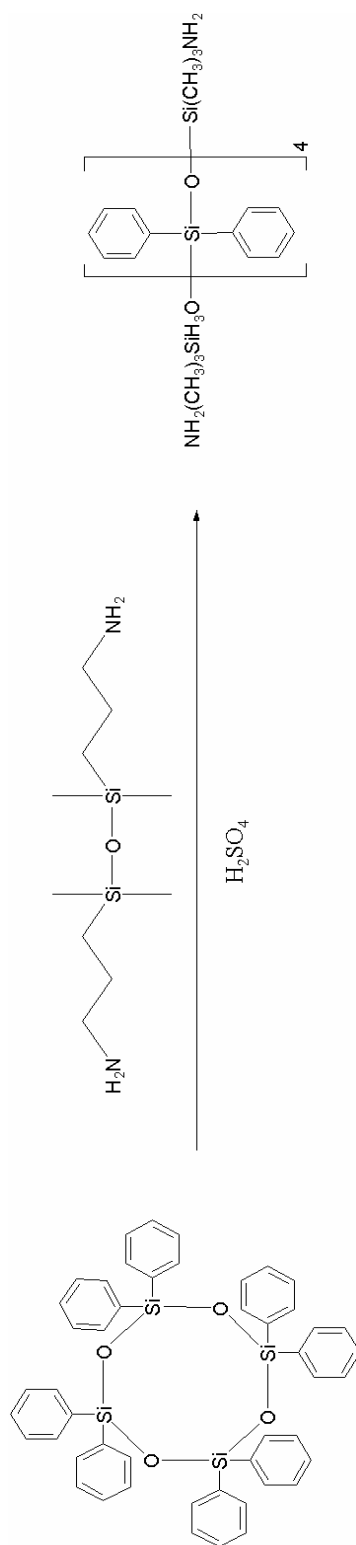


Figure 36. Formation of Siloxane Diamines

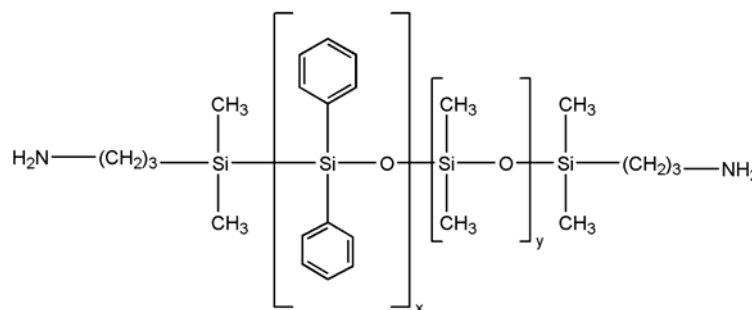


Figure 37. Siloxane Based Diamine

Table 8.

Siloxane Diamines Created at P2SI

Name	Chemical Structure
SD-4-100	
SD-8-50	
SD-APh-0	

After synthesis of the different siloxane diamines, the siloxane oligomers were added to the p-PDA and 6FDA solution to form poly(amic acids) in NMP solutions, once these had formed the desired oligomers, these were end-capped with PEPA.

Table 9.

Properties of Several Diamines Synthesized by P2SI

Name	$x + y = n$	% Phenyl	M_n (g/mol)
SD-2-50	2	50	521
SD-2-100	2	100	645
SD-4-50	4	50	793
SD-4-100	4	100	1042
SD-8-50	8	50	1338
SD-16-50	16	50	2428

Stoichiometric fractions of p-PDA 25%, 50% and 75% were substituted with the siloxane system to form the imide-siloxane as seen in Figure 38. The variable z seen in Figure 38 has a maximum value of five. Stoichiometrically the AFR-PEPA-4 oligomer requires five groups of p-PDA to form the compound. As the number of siloxane diamine (SD) is increased to substitute p-PDA the number of Z goes down to 0 when no p-PDA is present (when only siloxane is present).

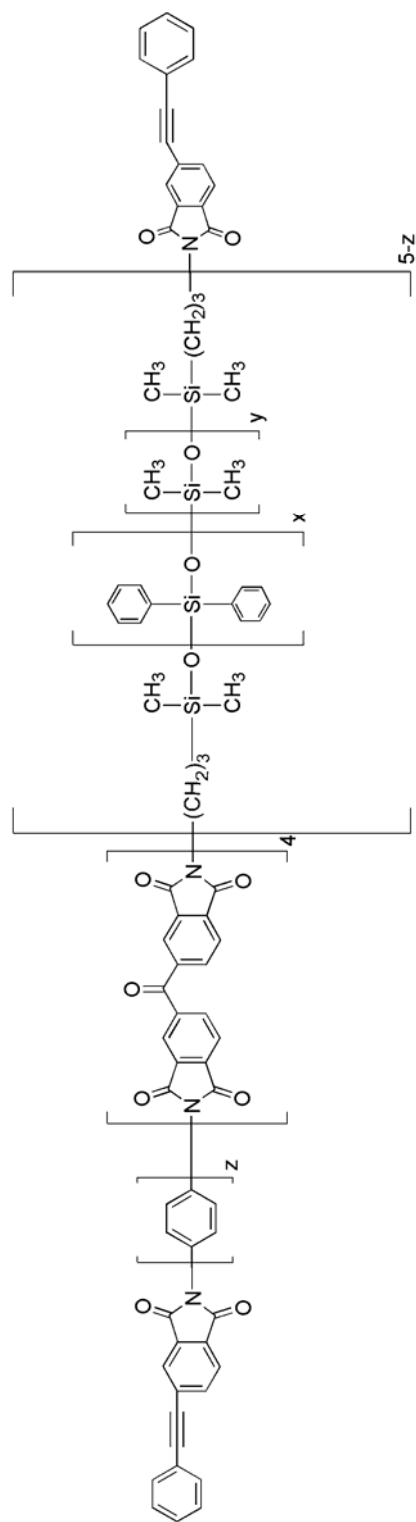


Figure 38. Potential Structure of Poly(imide siloxane) Oligomer

4.3.2.1 Poly(imide-siloxane) Flexural Properties

P2SI fabricated several composites using standard polyimide composite fabrication techniques. 7-ply S-2 glass fiber and carbon fiber composites were fabricated for flexural and shear testing.

4.3.2.1.1 Preliminary Test

The first test was done with poly(imide siloxane)/ S-2 glass fiber composites to determine what properties the samples would exhibit. The four systems were tested as shown in Table 10. For system N-18 the chemical structure is shown in Figure 39.

Table 10.

Preliminary Siloxane Testing

Name	Diamine	p-PDA substitution %
N-16	SD-4-100	25
N-17	SD-4-100	50
N-18	SD-4-100	75
N-20	SD-8-50	50

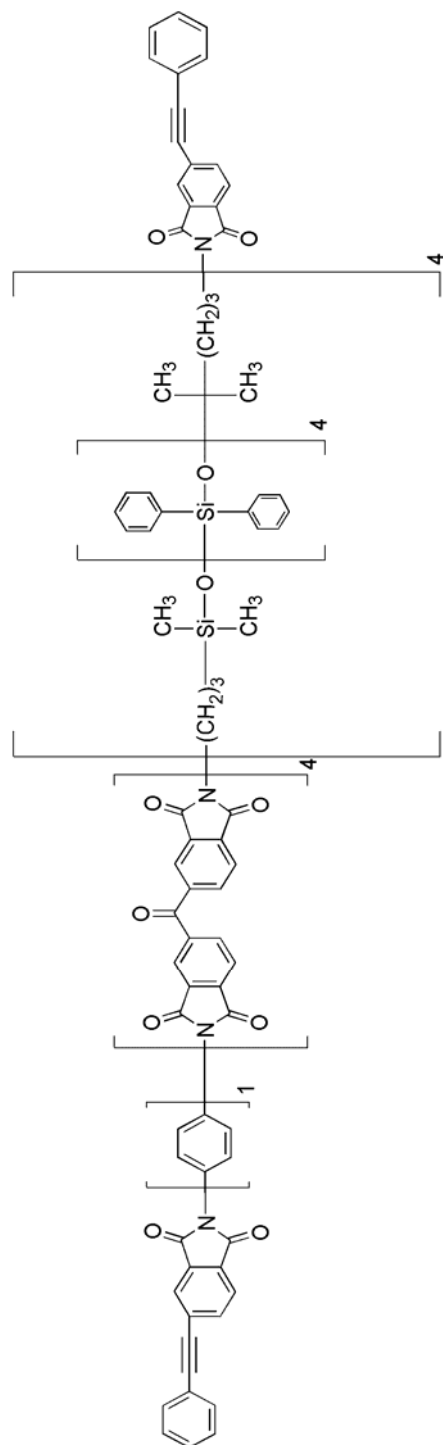


Figure 39. Chemical Structure N-18

The preliminary results showed that for a 100% phenyl siloxane diamine system, as the percentage substitution of p-PDA increased the flexural modulus increased (Figure 40). In addition to this finding, for a 50% of phenyl and 50% methyl siloxane system, with only a 50% substitution of p-PDA a comparable modulus was obtained as with 75% substitution with SD-4-100 diamine.

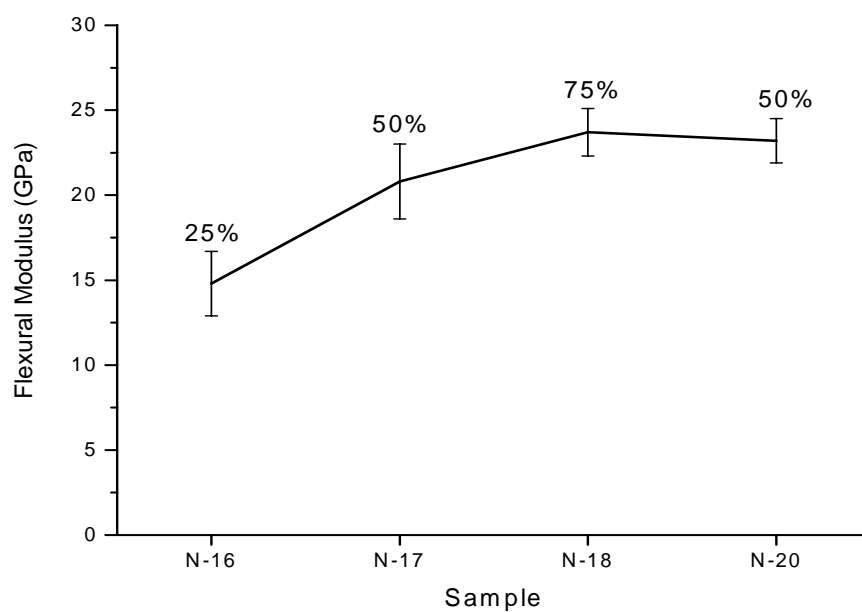


Figure 40. Flexural Modulus of Samples Tested

After 100 hours at 371°C the samples were weighed and the percent of weight loss was calculated. From the data, in Figure 41 it can be seen that the samples that had higher modulus also degraded less. This result was excellent because the next set of testing would focus in samples which degrade less and have better mechanical properties.

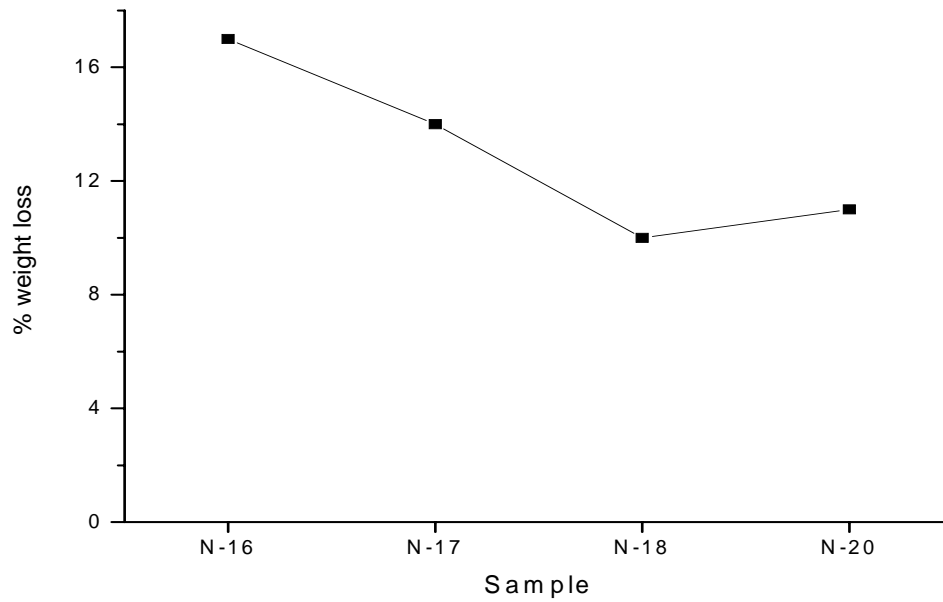


Figure 41. Percent Weight Loss After Aging

In addition to the correlation of modulus and aging the same correlation was obtained for maximum stress during testing, strain at max stress (Figures 42,43).

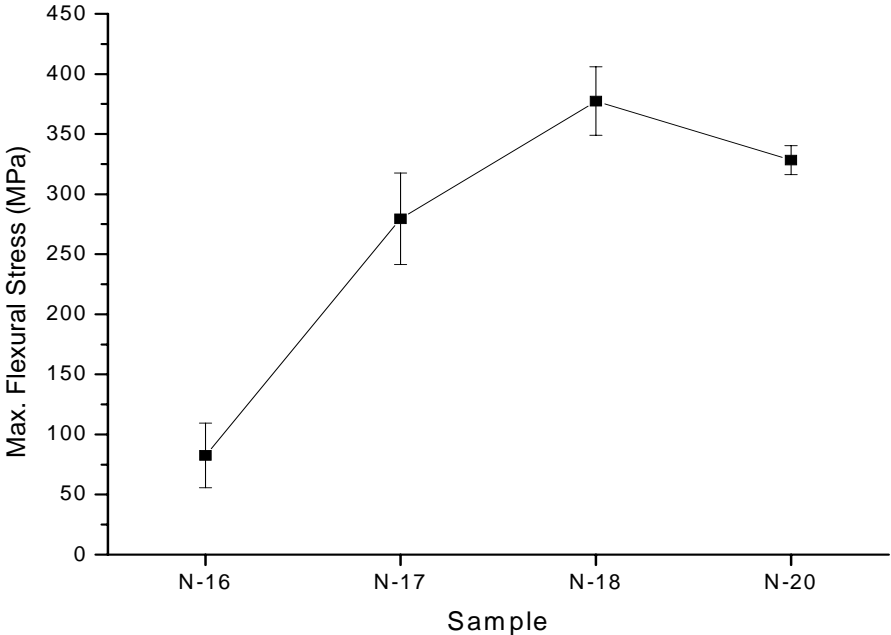


Figure 42. Maximum Flexural Stress Experienced by Samples

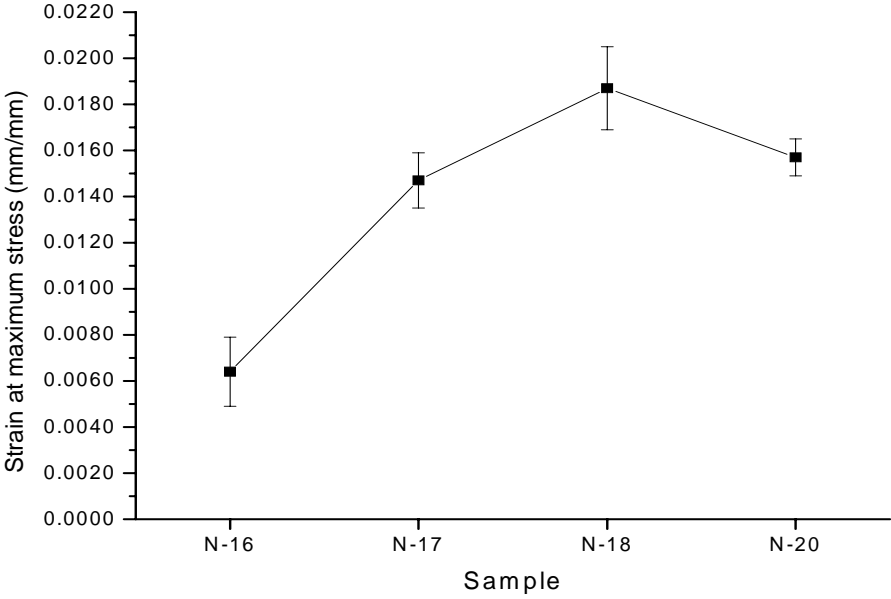


Figure 43. Strain at Maximum Stress

There was no mechanical testing on aged composites due to their brittle nature. These samples would delaminate easily when being cut. Figure 44 shows sample N-17 where fibers are readily separating from the composite and delamination is easily achieved as well.



Figure 44. Aged Sample N-17 After Cutting for Mechanical Testing

4.3.2.1.2 Second Test

After the preliminary test was performed three siloxane diamine systems were selected for future testing. These were used in different concentrations to form inorganic modified polyimides. Twelve composites were fabricated for mechanical and aging testing using T650-35/UC309 8HS carbon textiles (15.24 cm x 15.24 cm x 0.254 cm, 8 plys) as shown in Table 11. After subsequent cutting and preparation of samples as

described earlier these were ready for testing. Sample B1 was utilized as the control group being a purely poly(imide) sample.

Table 11.

Inorganic Polyimide Samples

Name	Diamine	p-PDA % substitution
B1	None (Control Group)	0%
B2	SD-APh	20%
B3	SD-4-100	5%
B4	SD-4-100	20%
B5	SD-4-100	50%
B6	SD-4-100	100%
B7	SD-8-50	5%
B8	SD-8-50	20%
B9	SD-8-50	50%

4.3.2.1.2.1 Control Group

The control group properties are very important to provide a comparison. This is the system that will provide a reference to the usefulness of the chemical changes in the structure.

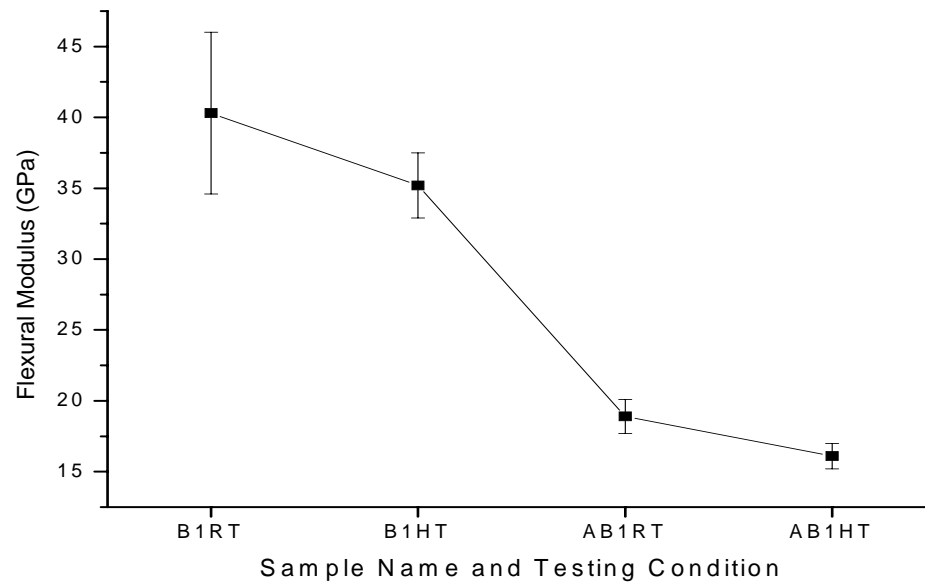


Figure 45. Control Sample Modulus at Different Testing Conditions

Figure 45 shows the general trend of most of the samples tested. For the non-aged samples (B1) the modulus at room temperature is 12% higher than samples tested at 260°C (HT). The aged samples (AB1) significantly lose modulus as compared to non-aged samples. Again, there is a loss of modulus of 14% at HT as compared to RT.

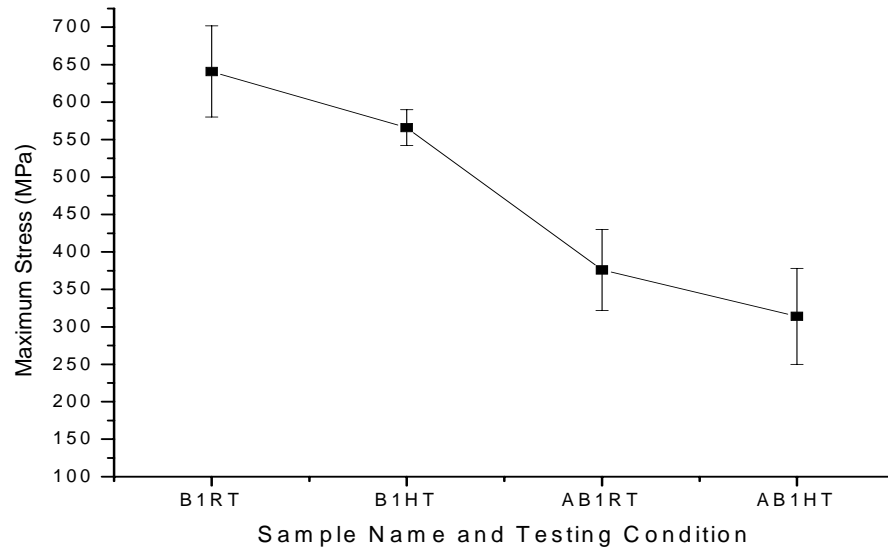


Figure 46. Control Sample Max. Stress at Different Testing Conditions

The same correlation is seen for maximum stress endured by the sample during testing (Figure 46). For B1RT samples the max. stress at room temperature is 12% higher than B1HT samples. AB1 samples significantly lower strength as compared to B1 samples. Again, there is a loss of modulus of 14% for AB1HT as compared to AB1RT.

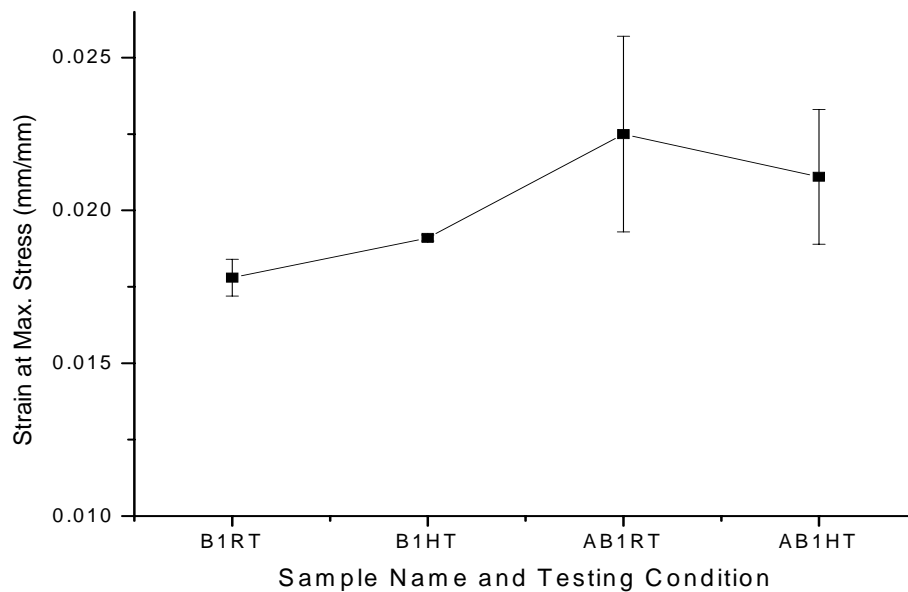


Figure 47. Comparison of Strain in Control Group at Different Conditions

In regards to strain at maximum stress during testing, there is little correlation that can be made from the tests performed (Figure 47). The samples have a value that oscillates between 0.017 mm/mm to 0.022 mm/mm but due to the error involved in aged samples the value of the strain could be close to 0.0189 mm/mm for the control group at all testing conditions.

4.3.2.1.2.2 SD-APh

Only one sample was tested with an SD-APh composition at 20% as shown on Table 11. The samples were tested at room temperature (RT) and 260°C (HT), both aged and non-aged samples.

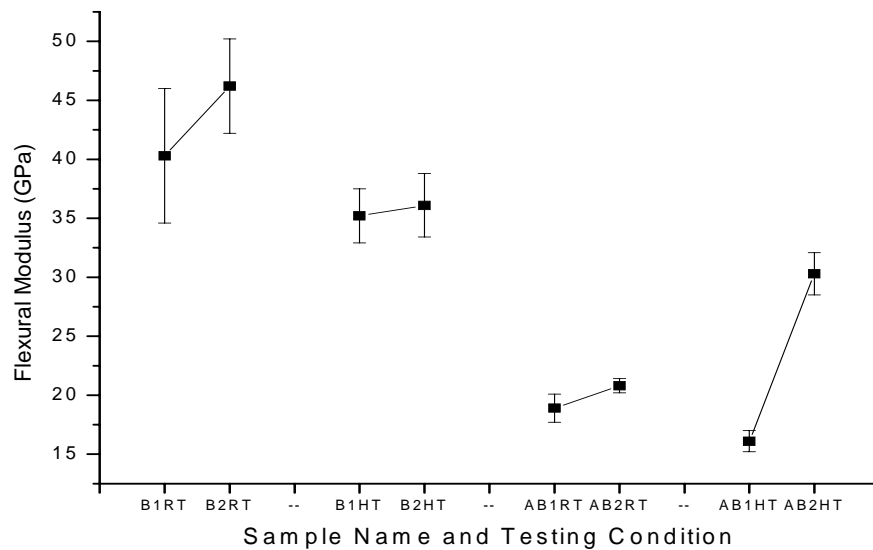


Figure 48. Comparison of Modulus, Control vs. B2

Initially from what can be seen in Figure 48 the modulus of the poly(imide-siloxane) ranges within the values of the property of the control group. Upon aging of the sample it appears that the properties of the poly(imide-siloxane) composite are improved, specially at high temperature testing of the sample. This could be attributed to less damage during aging for the sample tested at high temperature.

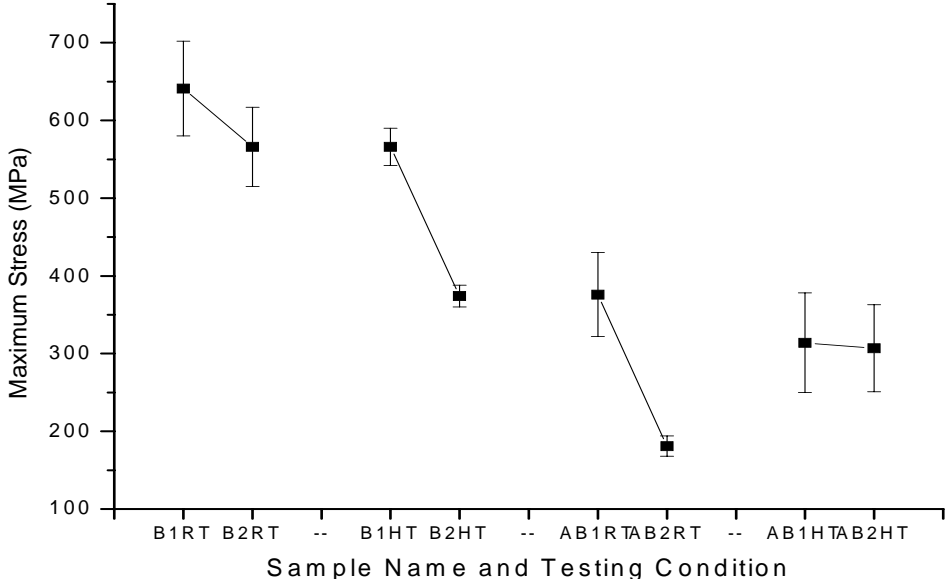


Figure 49. Maximum Stress Comparison, Control vs. B2

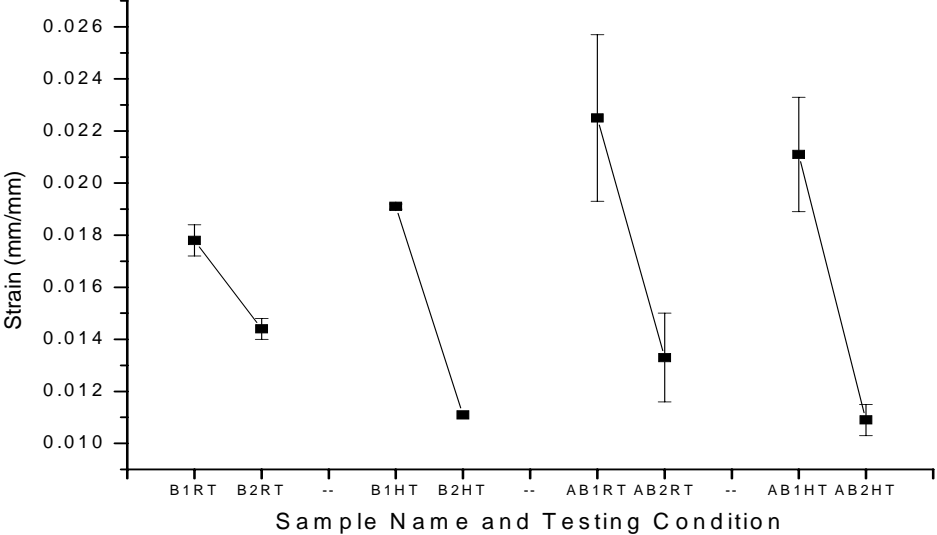


Figure 50. Strain at Maximum Stress Comparison, Control vs. B2

It can be concluded that the modulus is improved in the case of the aged SD-Aph poly(imide-siloxane) system. There appears to be no correlation with regards to stress and strain except that these are lower than the control group at all testing conditions (Figures 49, 50).

4.3.2.1.2.3 SD-4-100

Several composites were tested with different percentages of SD-4-100 substitution of p-PDA. Due to the large amount of data, only samples tested at room temperature will be described. It is known that at high temperature testing, samples properties tend to decrease. Figure 51 shows that the modulus for SD-4-100 siloxane non-aged samples is higher or within the same range as the control group. This seems promising in the fact that these samples have better processability than the original AFR-PEPA-N oligomer composites [5]. In addition maximum stress (Figure 52) was increased at concentrations of 20% SD-4-100 substitution. It was seen that the strain at maximum stress was also higher for non aged siloxane samples (Figure 53). In this case the range of usefulness of the SD-4-100 siloxane diamine substitution is between the values of 10% and 35% substitution.

For aged samples it appears that the same range (10-35%) maintains properties that are better or equal to the control group (Figures 51-53). Since these samples are thermally damaged these values fall below non-aged sample values. Figure 54 shows a micrograph

of a composite with siloxane substitution and the damage produce within the polymer matrix.

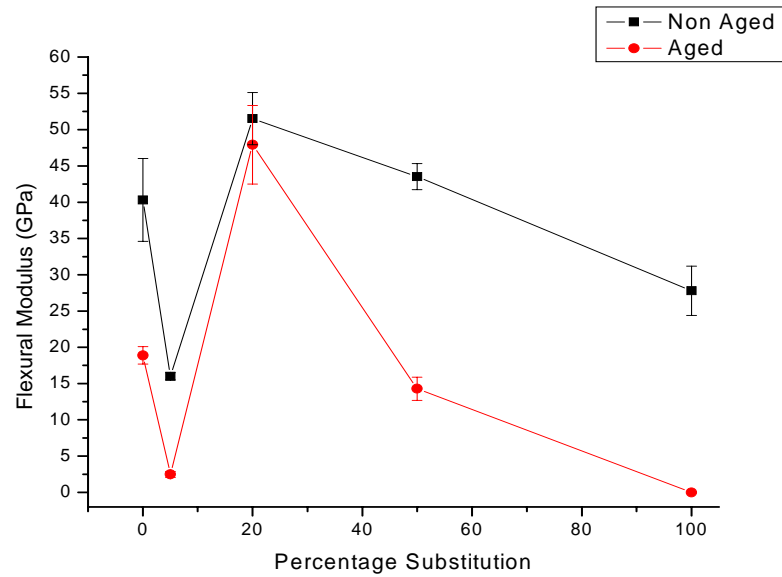


Figure 51. Modulus Comparison, Control vs. B3-B6

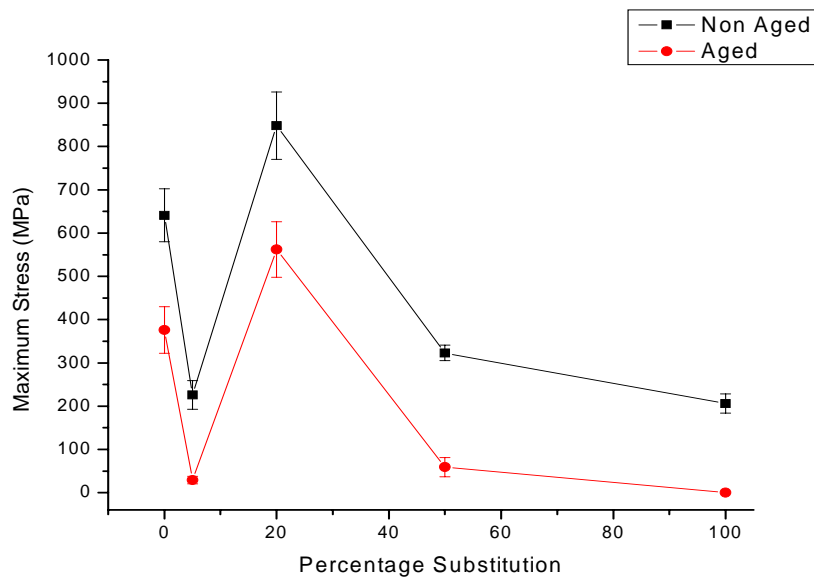


Figure 52. Maximum Stress Comparison, Control vs. B3-B6

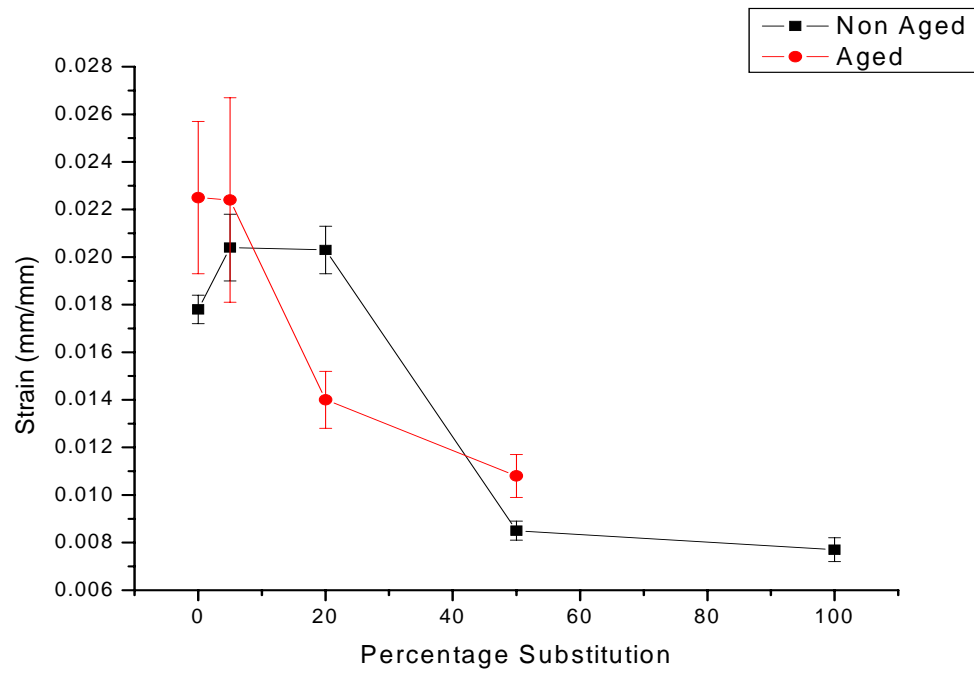


Figure 53. Strain Comparison, Control vs. B3-B6

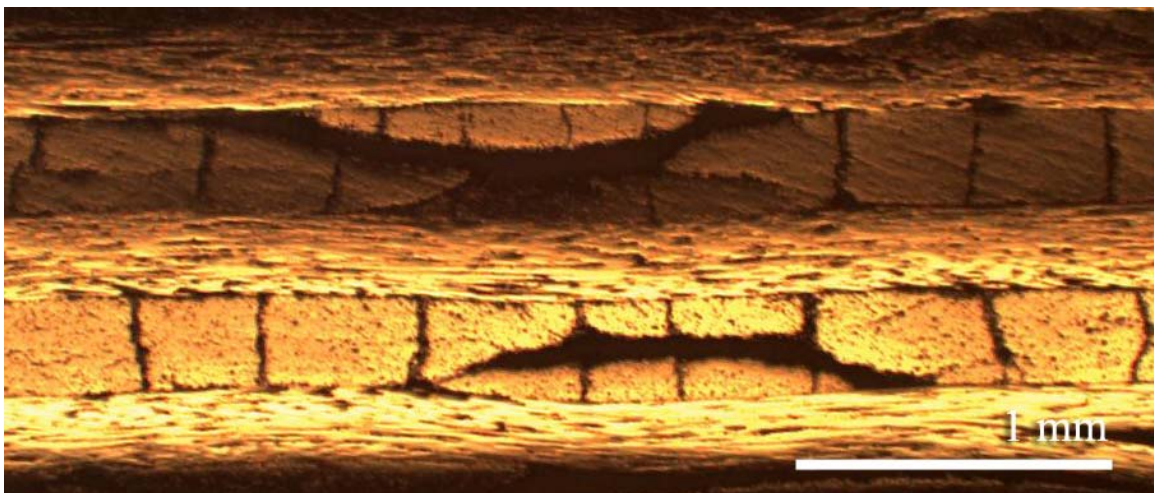


Figure 54. Micrograph of Sample B5 After Aging

There is an initial decrease in properties observed at SD-4-100 siloxane concentrations of less than 10%. This phenomenon was consistent for different inorganic diamines evaluated by Lincoln and co-workers, therefore it is not believed to be an artifact or experimental error. An SD-4-100 concentration of 10-35% provides the best mechanical performance after environmental aging as mentioned before. At concentrations in excess of 35%, the resin matrix behaves more as an elastomer than a thermoset matrix.

4.3.2.1.2.4 SD-8-50

The third group tested involved different percentage molar substitutions of p-PDA with DS-8-50 in the original AFR-PEPA-N system. The results are quite similar to the SD-4-100 siloxane system. The range of substitution was found to be 0-35%, quite similar to the SD-4-100 system. Again, at a concentration in excess of 35%, Lincoln has reported that the resin behaves more as an elastomer than a thermoset matrix.

Several micrographs were taken of samples, Figure 55 is a micrograph taken from a non aged B8 sample. Figure 56 shows a micrograph of sample B9 after aging.

With regards to the properties themselves it can be seen that there is a small increase in properties but these values are extremely close to the control group values (Figures 57-59). Therefore, it can be concluded that the only reason for the substitution of p-PDA would be to facilitate processing.

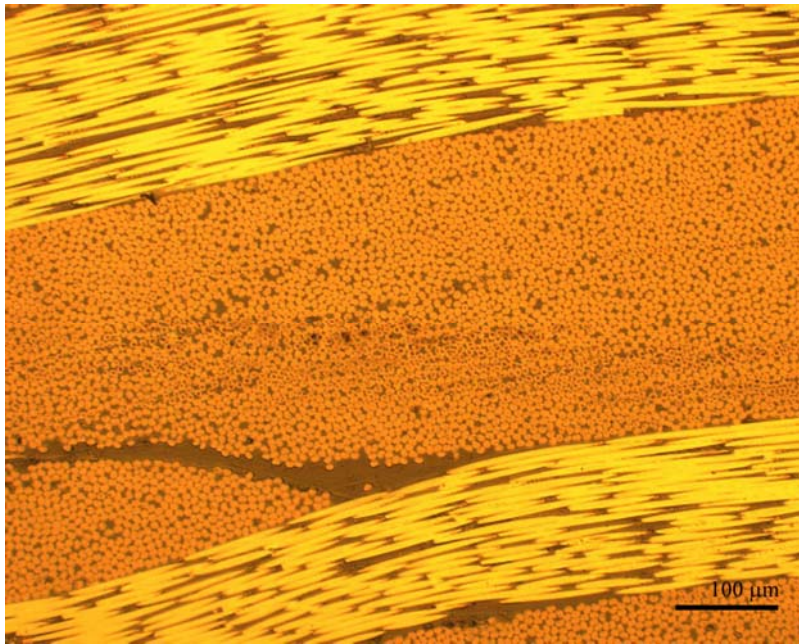


Figure 55. Micrograph of B8 Composite

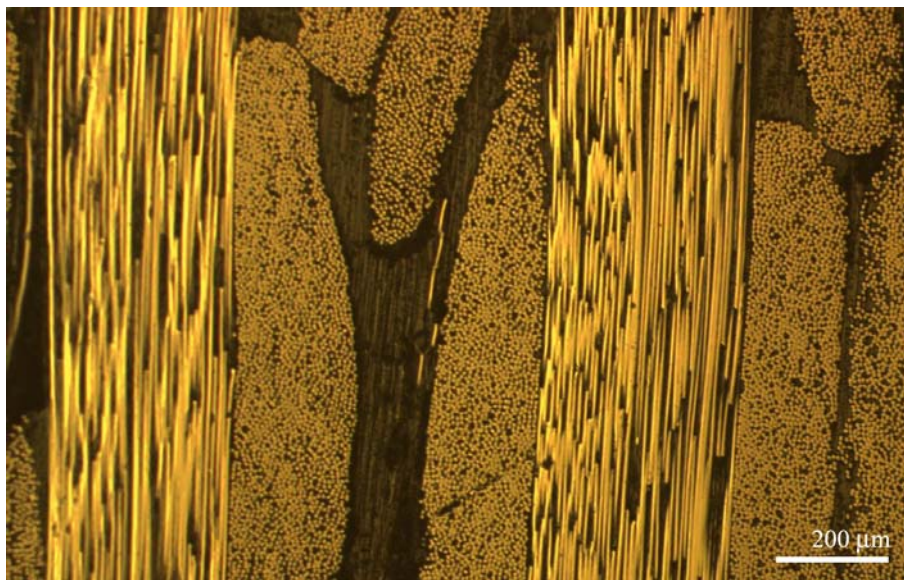


Figure 56. Micrograph of B9 Composite After Aging

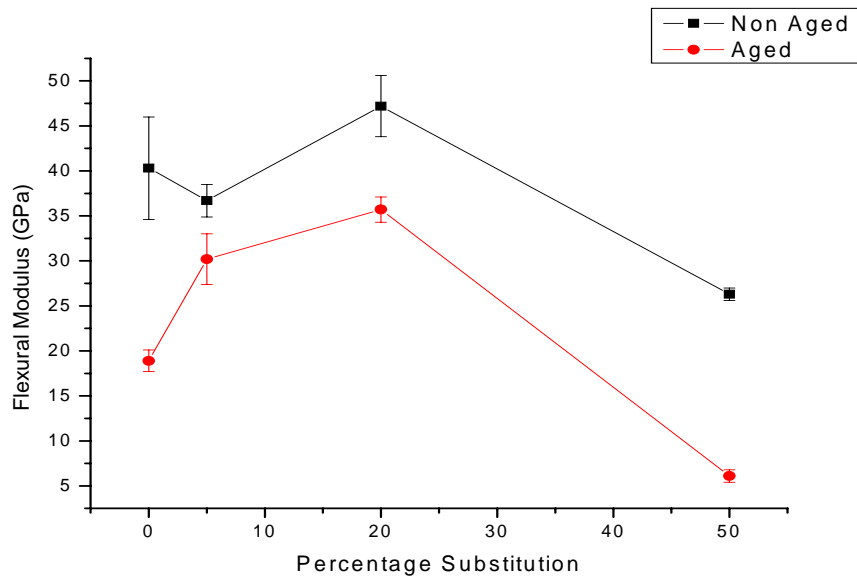


Figure 57. Modulus Comparison, Control vs. B7-B8

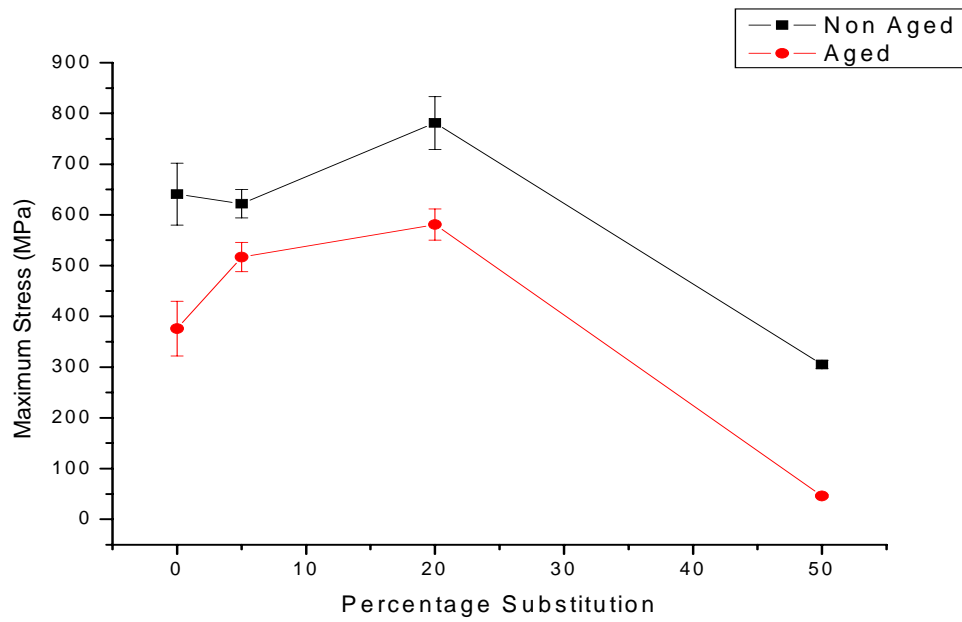


Figure 58. Maximum Stress Comparison, Control vs. B7-B8

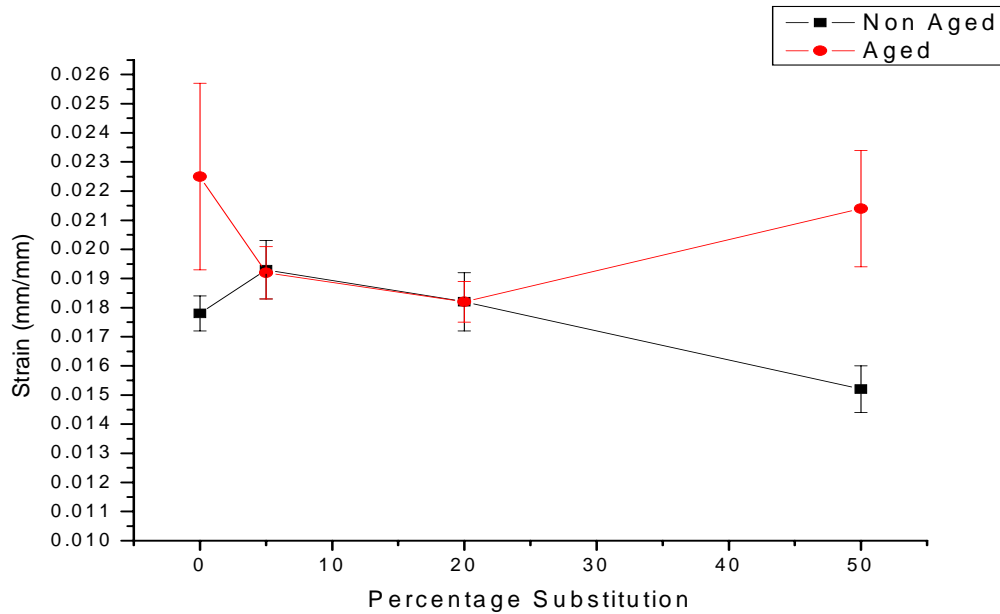


Figure 59. Strain Comparison, Control vs. B7-B9

4.3.2.2 Poly(imide-siloxane) Short Beam Strength Testing.

Figure 60 shows the trend of the control group aged and non-aged for room and high temperature testing. The same trend found for flexural properties is seen in the short-beam strength. One interesting characteristic is that non-aged samples tested at 260°C have the same range of properties than aged samples tested at room temperature. This means that there is no need for aging of the samples to drop 16% in inter-laminar shear strength (short beam strength) when exposed to high temperatures.

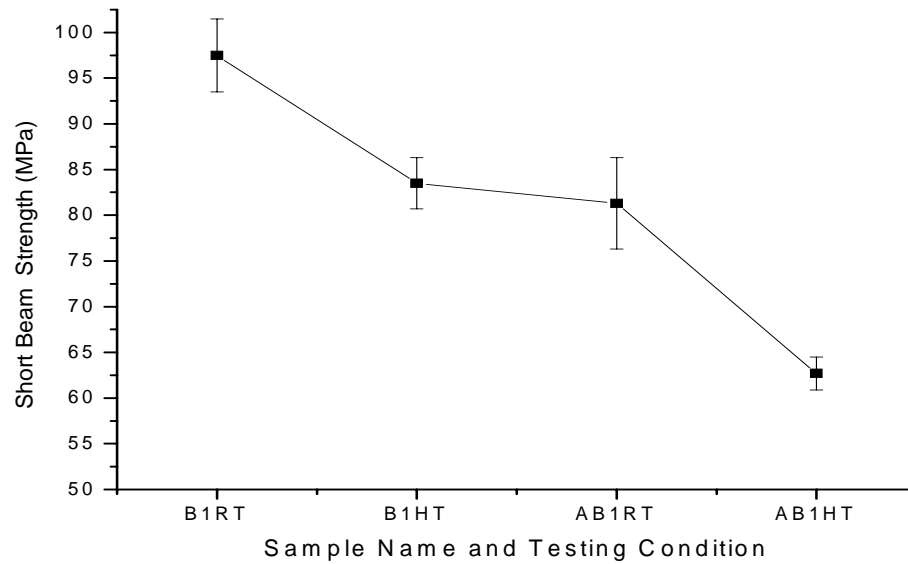


Figure 60. Inter-laminar Shear Strength of the Control Group

4.3.2.2.1 SD-APh

At 20% substitution of p-PDA by SD-APh there seems to be no improvement in properties. The short-beam strength is decreased 16%, this is the same amount the control group decreases when aged (Figure 61).

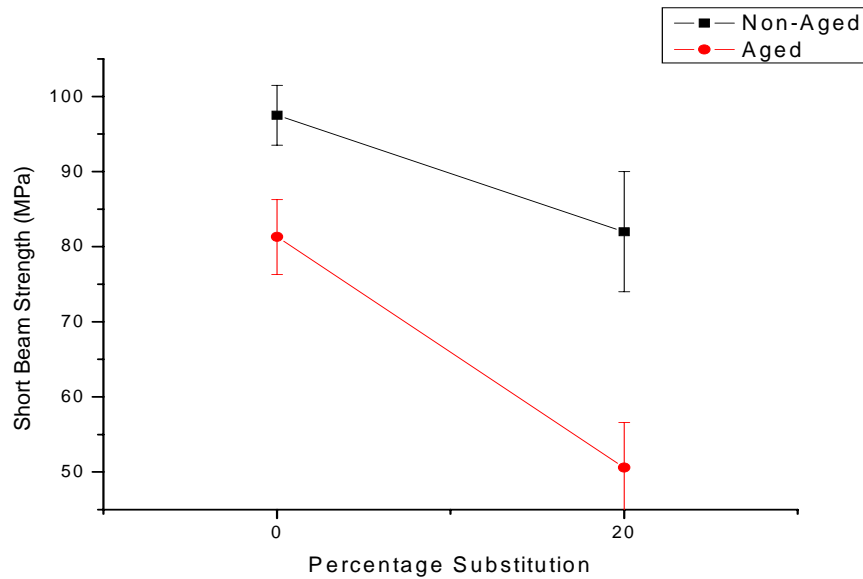


Figure 61. Interlaminar Shear Strength Comparison, Control vs. B2 (RT)

4.3.2.2.2 SD-4-100

The properties of this system seem to agree with the flexural properties of the composites as mentioned before (Figure 62). There is an initial decrease at 5% substitution but at 20% the properties are increased to the range of the control group.

The percentage between 15%-35% as proposed before would allow for the properties of the polymer to behave as the aged control group. Only at 20% substitution does the SD-4-100 system have comparable properties to the non-aged control group.

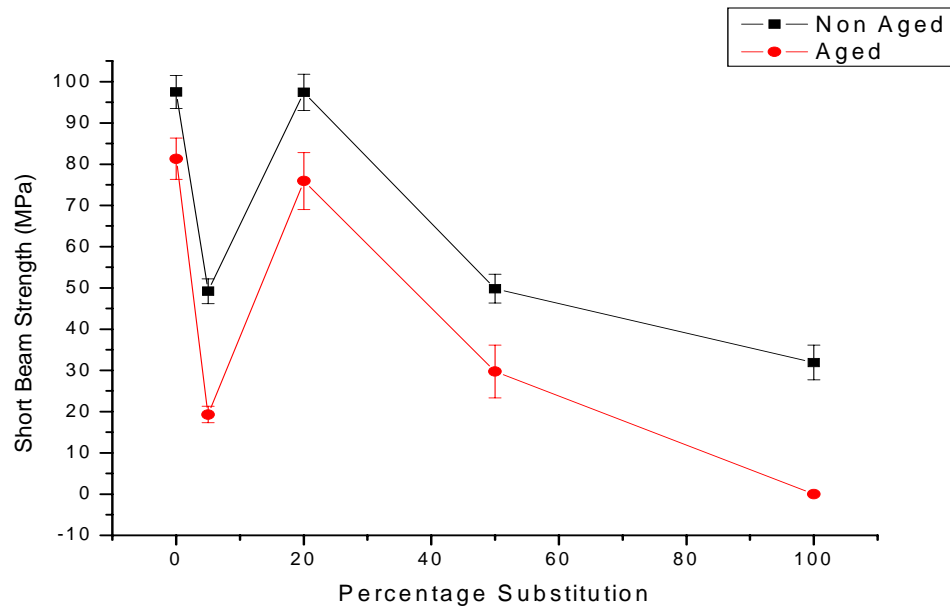


Figure 62. Short Beam Strength Comparison, Control vs. B3-B6 (RT)

4.3.2.2.3 SD-8-50

In comparison to the other siloxane systems SD-8-50 outperformed both the control group and the other siloxane systems. Figure 63 shows that the short beam strength goes up as high as 8% from the control group strength. This final test would allow us to say that the optimal substitution for this system would range from 10% to 25% to avoid loss of inter-laminar strength.

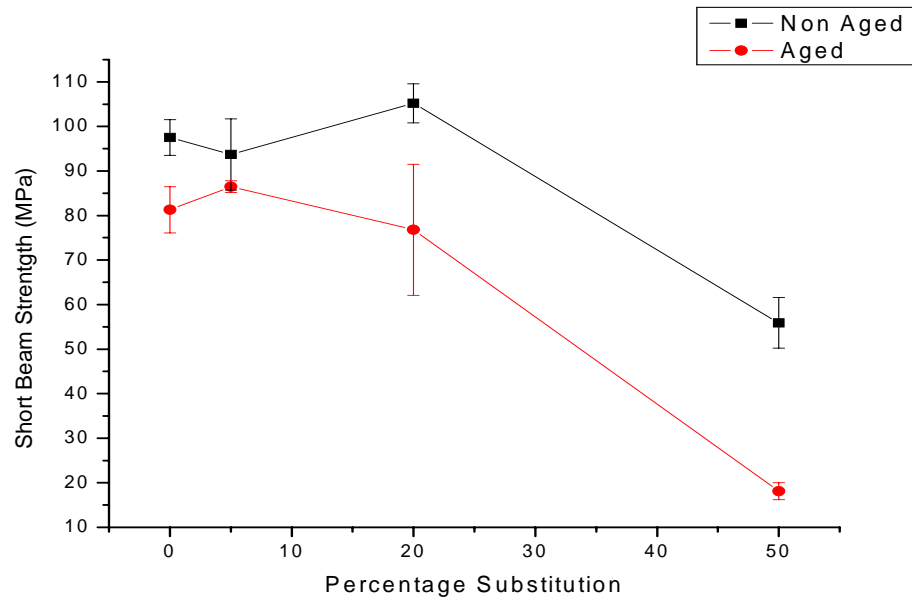


Figure 63. Short Beam Strength Comparison Control vs. B7-B9 (RT)

4.4 Conclusions

The siloxane diamine SD-4-100 promises to maintain or improve properties at concentrations of 10% to 35% substitution. SD-8-50 siloxane diamine maintain properties for substitution percentages of 10% to 25% of p-PDA.

Even though the original intent was not focused on improvement of processing, the advantage of utilizing siloxane diamines is that processing is improved. If the properties are equal to AFR-PEPA-N with substitution of p-PDA with SD, there is an advantage in adding the siloxane oligomers. Additionally it was proven that indeed there is a probability that these oligomers form protective thermal barriers upon decomposition and oxidation of the siloxane oligomers.

In order to improve the processability of the AFR-PEPA-N system the best route found during this study was the alteration of the original chemistry utilizing siloxane compounds. If the siloxane oligomers are incorporated into composites, these will likely add unique surface thermal protection properties to poly(imide-siloxanes). Additionally the siloxane diamines that substitute p-PDA in the polyimide system that outperform the AFR-PEPA-N system are SD-4-100 and SD-8-50.

5. ALTERATION OF END CAP UNIT

5.1 Introduction

Due to the many advantages of aromatic polyimides in processability and material properties these have increased in use for high-performance applications. Phenyl-ethynyl terminated imide oligomers have demonstrated superior performance over other systems. One problem encountered with the phenyl-ethynyl group is that the temperature to initiate curing is high (360°C). This constitutes a problem because high curing temperatures cause thermal gradients within the polymer; upon cooling, these gradients contribute to the creation of residual stresses within the matrix.

Polyimide chains have been terminated with end groups to avoid having either an amine or an anhydride at the end of each chain. These amine or anhydride groups can react with the surroundings and decrease the stability of the polyimide. Adding chain groups to both ends of the chains is a good way to increase the stability of polyimides.

With phenyl-ethynyl terminated imide polymers the triple bond is expected to react by chain extension, crosslinking, and branching, but the actual mechanism is not clearly understood. As the ethynyl group reacts, this causes the polymer to form a crosslinked network and increase its T_g.

5.2 Experimental Technique

The synthesis involved produces a poly(amic acid) composed of p-PDA diamine and 6FDA dianhydride, the poly(amic acid) is later capped with 4-ethynyl-phthalic anhydride (EPA, Figure 23). The structure obtained is similar to AFR-PEPA-N, the difference in structures is the end-cap. EPA promises to reduce the curing temperature of the oligomers as compared to PEPA end-capped oligomers.

5.2.1 Synthesis

6FDA was utilized as received from Performance Polymer Solutions, Inc. p-PDA with a purity of 98% was obtained from Spectrum Quality Products, Inc. EPA 99% purity was obtained from TCI America. NMP was obtained from Aldrich, Inc. All chemicals were used as received.

The monomer solids were measured 10% solids 90% NMP by weight. A molar ratio of 4:5:2 was utilized for 6FDA, p-PDA and EPA respectively. In a two-neck round bottom flask a solution of p-PDA and NMP was stirred with a Teflon® coated stir-bar under a nitrogen atmosphere at room temperature. Utilizing another two-necked round bottom flask a solution of 6FDA and NMP was prepared stirred under a nitrogen atmosphere. After both solutions are completely dissolved p-PDA is added drop wise over a period of 4 hours. The solution is mixed continuously under a nitrogen atmosphere for 24 hours at

room temperature. Once all the 6FDA and p-PDA have formed poly(amic acids) 4-EPA is added to the solution. The solution is mixed for 4 more hours. The solution is then heated to 120C for 12 hours. This aids with the imidization of the poly(amic acid).

After temperature aided imidization was performed, a dark brown slurry is obtained. The slurry is added to distilled water in a beaker, mixed and filtered. A yellowish powder was obtained which was washed with boiling water. The powder is also washed with warm methanol to aid in the removal of NMP solvent. The remainder brownish yellow powder is dried under vacuum at 100°C for 24 hours.

5.2.2 Characterization

Four tests were performed on the powder to determine if the synthesis of the polyimide oligomer was successful; Fourier Transform Infrared Spectroscopy, Mass Spectrometry, Gel Permeation Chromatography, Differential Scanning Calorimetry, and Thermogravimetric Analysis.

5.2.2.1 FTIR

The IR Spectra of TAMU-ETA-N was measured using a A Nicolet AVATAR 360 spectrometer. The samples were prepared as KBr pellets. The resolution was set to 2cm-1 with 64 scans.

5.2.2.2 Mass Spectrometry

Mass Spectrometry was performed on a PE SCIEX QSTAR mass spectrometer with Electrospray Ionization (ESI). Acetone was used as the solvent.

5.2.2.3 Thermal Gravimetric Analysis

Thermo-gravimetric analysis was performed on a TGA Q500 thermal analyzer. An air atmosphere was utilized for the testing. The samples were heated to 500°C with a heating rate of 10°C/min.

5.2.2.4 Differential Scanning Calorimetry (DSC)

Tests were performed on Perkin Elmer Pyris 7 DSC with a heating rate of 20°C/min under nitrogen atmosphere.

5.2.2.5 Nuclear Magnetic Resonance

80 mg of the sample was dissolved in 1mL of chloroform-d, filtered and transferred to a 5mm NMR tube. Varian Unity Inova 400 NMR spectrometer with an Oxford standard bore magnet housed in Chemistry department was used for ^1H (400MHz) and ^{13}C (100MHz) room temperature measurements. Waltz proton decoupling scheme was

employed to observe ^{13}C resonances. The ^{13}C spectrum was obtained with about 8000 scans and 8 sec delay between pulses. While the ^1H spectrum reported used no line broadening, the ^{13}C spectrum was obtained using ^1Hz line broadening. In both cases the solvent peak was used for internal referencing.

5.3 Results and Discussion

The major goal of the program was to create a polymer with four (p-PDA/6FDA) repeat units, end capped with ETA end groups (Figure 64). Lincoln and co-workers studied AFR-PEPA-4 (4-p-PDA/6FDA repeat units) for RTM processing [37], so this route was decided for the new polymer. Due to the nature of polymerization there is a wide dispersion with regards to molecular weight. Table 12 shows the dispersion in molecular weights that theoretically could be encountered during the polymerization process.

Table 12.

Polymer Weight and Composition

Repeating Units	Composition	Molecular Weight
2	$\text{C}_{76}\text{H}_{32}\text{F}_{12}\text{N}_6\text{O}_{12}$	1448
3	$\text{C}_{101}\text{H}_{42}\text{F}_{18}\text{N}_8\text{O}_{16}$	1964
4	$\text{C}_{126}\text{H}_{52}\text{F}_{24}\text{N}_{10}\text{O}_{20}$	2480
5	$\text{C}_{151}\text{H}_{62}\text{F}_{30}\text{N}_{12}\text{O}_{24}$	2998

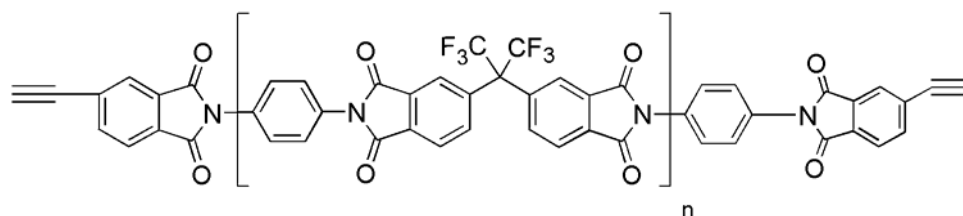


Figure 64. Structure of Model Polymer Compound

5.3.1 FTIR

FTIR Results (Figure 65) showed that indeed there was a presence of the imide bond (1726 cm^{-1}). In addition there is a weak presence of the triple bond around 2100 cm^{-1} . Due to the inaccuracy of IR to distinguish the triple bond, it was necessary to additionally confirm the presence of it utilizing Nuclear Magnetic Resonance.

It was found that some p-PDA monomer was unreacted. This was detected when in presence of acetone a precipitate formed. This was later confirmed utilizing IR to determine if there was indeed a formation of the imine group. Imine group formation may happen in the presence of ketones such as acetone and an amine.

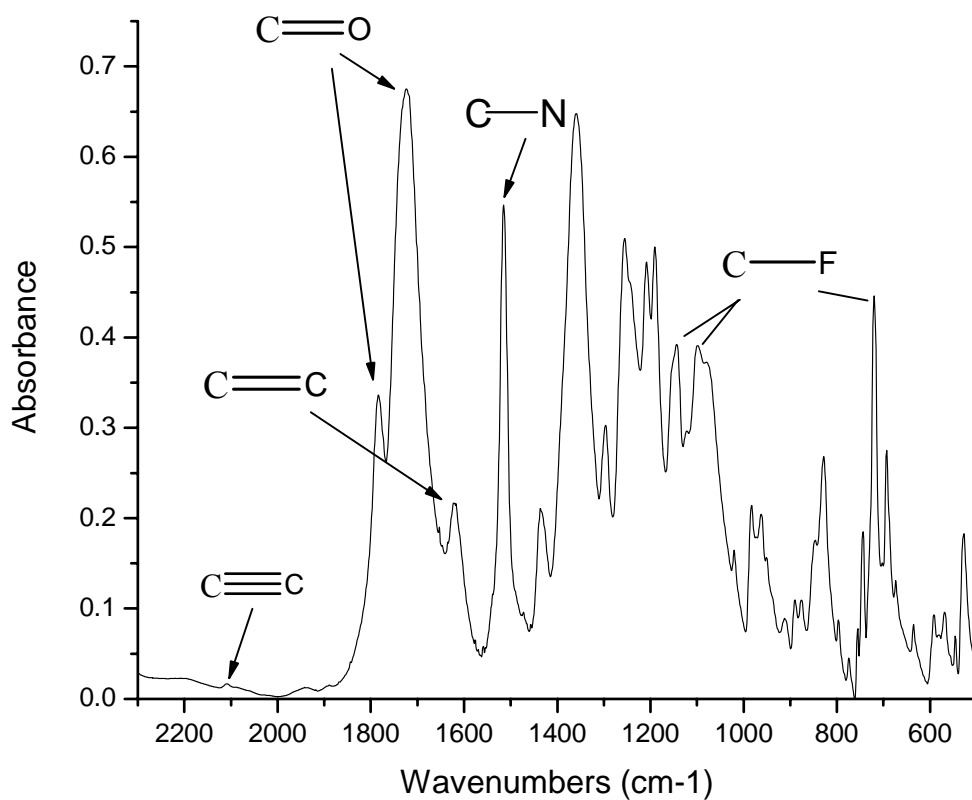


Figure 65. FTIR Spectra of ETA Polyimide

5.3.2 Mass Spectroscopy

The mass spectroscopy results were positive, there were several peaks located in the spectra separated by 516 molecular weight (Figure 66). This indicated the presence of several molecular weights in the oligomer distribution. Nothing can be concluded with respect to the distribution of the molecular weight from the Mass Spectroscopy data but this can be estimated from NMR Data. The Mass detected from Mass Spectroscopy has a difference of 21 from the molecular weight values as shown in Table 12. This

discrepancy in molecular weight might be attributed to sodium ions in solution attaching to the molecules during Mass Spectroscopy testing.

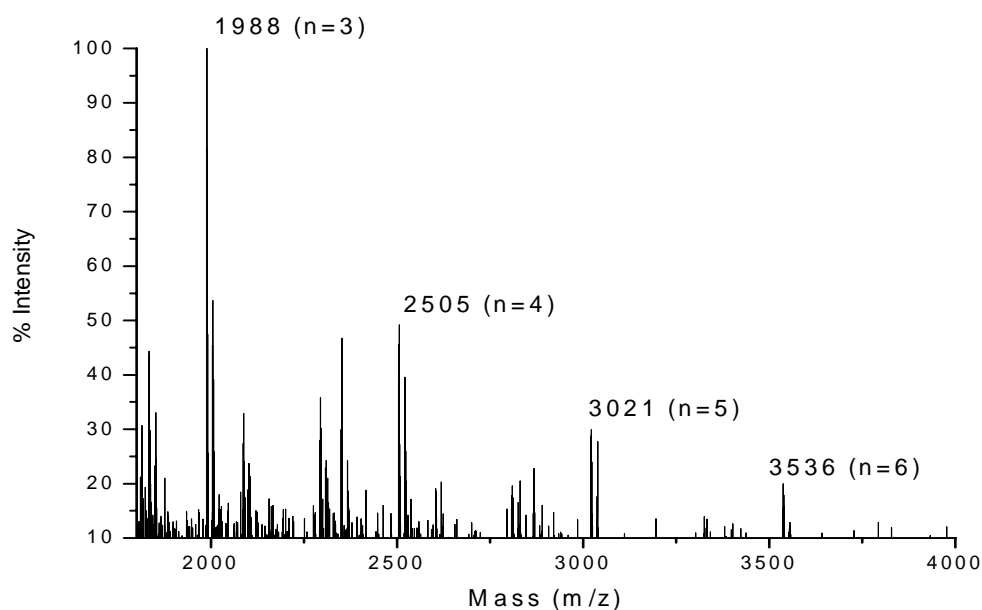


Figure 66. Mass Spectroscopy Data

5.3.3 TGA

TGA analysis of the oligomer sample as seen in Figure 67 shows that the oligomer powders start decomposing at a temperature of about 455°C. This result proved to be significant in that it was believed that the precursors were present in the yellow powder. It was seen previously that indeed there was a certain amount of unreacted monomer but the percentage of it seems to be low. In addition, there was no evidence of melting in the TGA sample holder. Tables 13 and 14 show some reference temperature for melting

and boiling of the monomers utilized during the reaction. There might be some indication from the boiling point of 4ETA that there seems to be some evaporation of the monomer around 335°C.

Table 13.

Melting Temperatures

Chemical Compound	Temperature (°C)
6FDA[54]	244-245°C
p-PDA[55]	140°C
4-ETA[56]	120°C

Table 14.

Boiling Temperatures

Chemical Compound	Temperature (°C)
6FDA[54]	494.5 ± 45°C
p-PDA[55]	267.4 ± 13°C
4-ETA[56]	352.4 ± 25°C

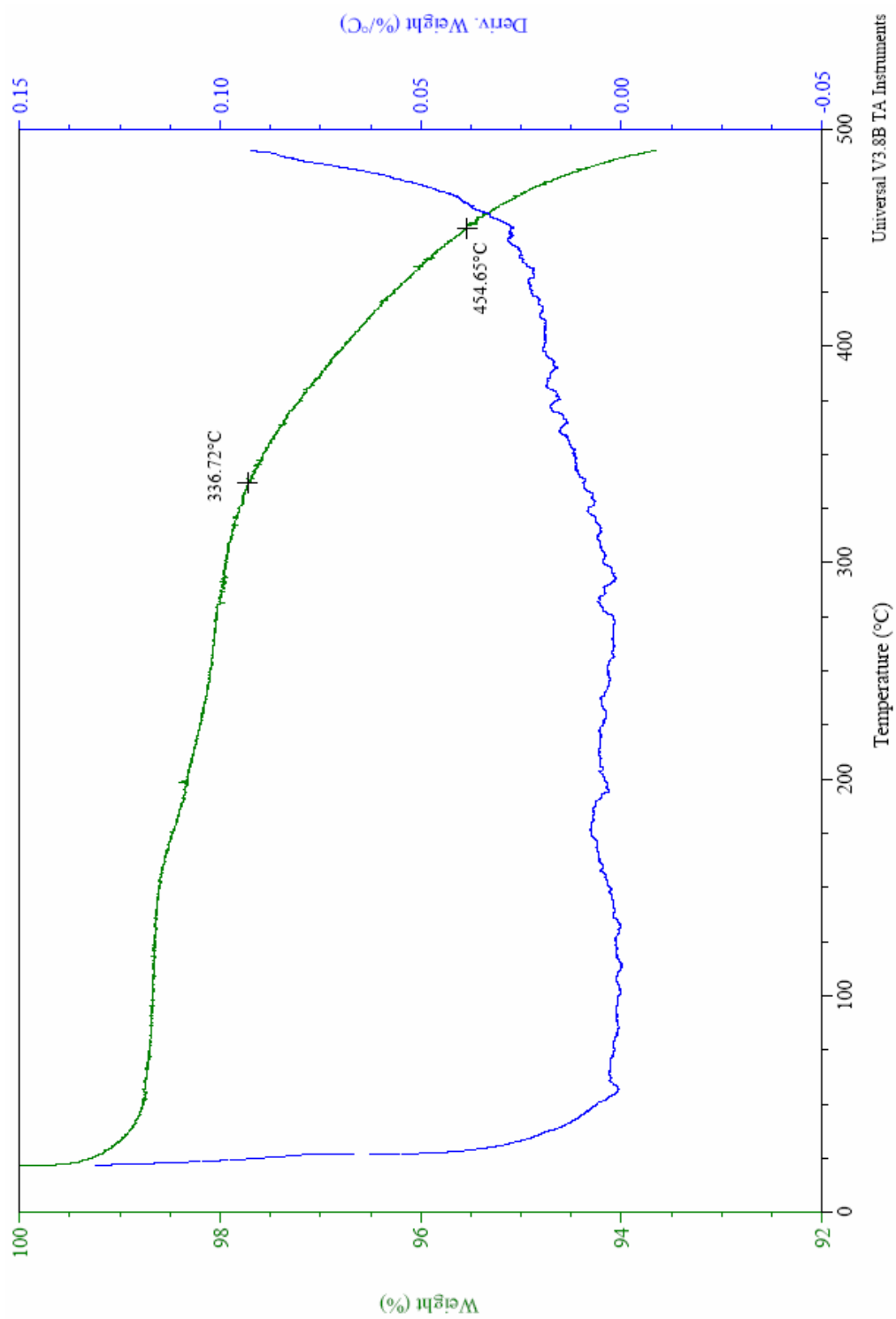


Figure 67. Plot Obtained From TGA Data

5.3.4 DSC

From the DSC Graph obtained (Figure 68) there are several observations that can be made. There appears to be a peak around 80°C. Another peak is present around 220°C this is attributed to a cross-linking reaction of the ethynyl group from the literature [36]. This is a positive result in that there is cross-linking occurring. The oligomer itself might not be melting and therefore the crosslinking is localized and not throughout the entire sample.

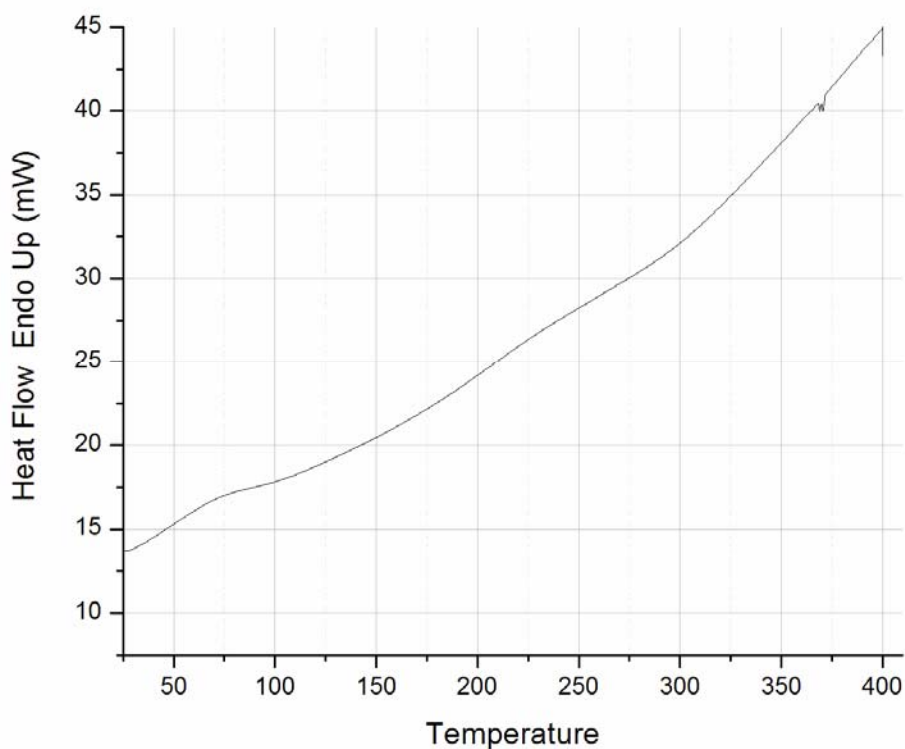


Figure 68. DSC Plot of Oligomer Powder (Rate:20°C/min)

5.3.5 NMR

The results from the Carbon NMR indicated the presence of the ethynyl group in the system (Figure 69). This is shown in the region of Figure 70 around 80ppm; there is a small peak at 82ppm which is attributed to the ethynyl group. In addition, from Proton NMR it can be deduced that the most abundant oligomer would be of the order of $n=5$ (Figure 70). This is confirmed from integration of the peaks around 3.25 - 3.75 ppm and 1 - 1.5 ppm gave a value close to 5. In addition the ethynyl proton is observed in the 4 ppm area [57,58].

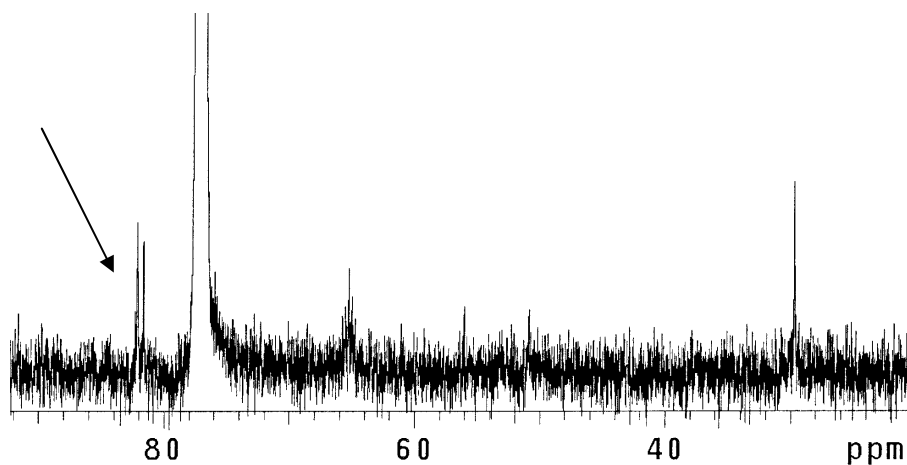


Figure 69. Carbon NMR Spectra 90-25ppm

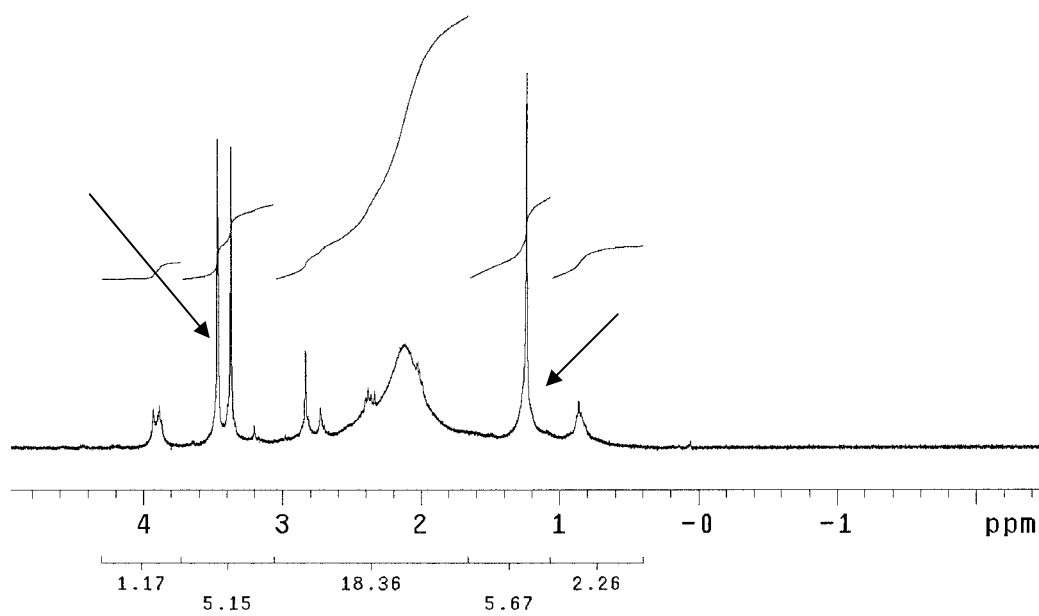


Figure 70. Proton NMR 12-0 ppm

5.4 Conclusions

It was determined that when the oligomer was synthesized there appears to be a percentage of unreacted amine that reacts with acetone. In addition NMR results indicated a molecular distribution with $n=5$ as the dominant oligomer. TGA results confirm the presence of some ETA monomer that evaporates at temperatures of about 336°C .

From the current DSC observations there is evidence that the oligomer does crosslink. The crosslinking appears to be occurring around 220°C . The crosslinking seems to be localized within the oligomer powder. The temperature of decomposition of the oligomer is about 454°C . This might be useful if the oligomer itself is incorporated into a composite matrix.

6. SUMMARY AND CONCLUSIONS

6.1 Conclusions

This thesis focused on four basic elements: 1) Reduction of crystal defects in AFR-PEPA-N to produce defect free matrices, 2) Alteration of chemistry to provide protective coatings for extreme conditions, 3) Reduction of viscosity in the AFR-PEPA-N system to allow for processability of the compound and 4) Alteration of end-caps to AFR-PEPA-N to reduce curing temperatures and test for additional properties.

The problem of crystal presence and viscosity seemed to be eliminated at high concentration of solvent (~90%). This is a problem since at low concentrations (~20%) crystals remain to be a source of micro-defects. Due to the high amounts of solvents (both NMP and NVP) needed for reduction of crystallinity and reduction of viscosity, this method would not allow for better and easier processing of AFR-PEPA-N composites and parts.

The addition of siloxane groups to the chain, will ultimately help form SiO₂ thermal protective coatings that will reduce thermo-oxidative degradation of the polymer and composites. The siloxane diamine SD-4-100 promises to maintain or improve properties at concentrations of 10% to 35% substitution. SD-8-50 siloxane diamine maintains properties for substitution percentages of 10% to 25% of p-PDA. Also, the advantage of

utilizing siloxane diamines is that processing is improved. If the properties are equal to AFR-PEPA-N with substitution of p-PDA with SD, there is an advantage in adding the siloxane oligomers.

The synthesis of the 4-ETA/6FDA/p-PDA oligomer was successful. NMR results indicate a molecular distribution with $n=5$ as the dominant oligomer. Even though the oligomers react creating a crosslinked network, the oligomers stay solid, the reaction does not occur throughout the sample. A small percentage of unreacted amine is filtered out with the help of acetone solvent, which creates a precipitate containing imine groups. In addition, TGA results confirm the presence of some ETA monomer that volatilizes at temperatures of about 336°C . The temperature of decomposition of the oligomer is about 454°C .

6.2 Future Work

Future work might focus on producing different siloxane systems that might help with processability of the AFR-PEPA-N system. In addition other alternatives in inorganic polymers might also prove useful such as sulfur polymers added during polymerization and matrix formation.

Other end-cap units might also prove useful in the development of new poly(imides) with better properties and processability. New synthesis techniques are needed for the

synthesis of diamine carborane groups that would add protective coatings to the polymer for their use in extreme conditions.

REFERENCES

- [1] Murphey L. Morphological Investigation of AFR-PEPA-N Imide Oligomers and Their Cured Polyimides and the Remodification of AFR-PEPA-N to Achieve Liquid-crystalline Behavior. M.S. Thesis Texas A&M University 2003. pp.10-70.
- [2] Stevens, M. Polymer chemistry: an introduction. New York: Oxford University Press; 1999. pp. 96-128, 364-394, 425-446.
- [3] Pascault, JP. Thermosetting polymers. New York: Marcel Dekker, Inc; 2002. pp.1-5, 67-75.
- [4] Morgan RJ, Pruneda CO. Polymer 1987;28(2):340.
- [5] Lincoln JE. Structure-property-processing Relationships and the Effects of Physical Structure on the Hygrothermal Durability and Mechanical Response of Polyimides. Ph.D Dissertation, University of Michigan, 2001. pp.78-105.
- [6] Hergenrother PN, J. Macromol. Sci.,Rev Macromol Chem 1980;C19:1.
- [7] Stenzenberger HD, Hertzog M, Römer W, Scheiblich R, Reeves NJ. Br. Polym. J 1983;15:1.
- [8] Stevenson WTK, Goldfard IJ. J. Appl. Polym. Sci. 1991;42:665.
- [9] Stevenson WTK, Goldfard IJ, Soloski EJ, Houtz MJ. J. Appl. Polym. Sci. 1991;42:679.
- [10] Delos SE, Shellenber RK, Smedley JE, Kranbuehl DE. J. Appl. Polym. Sci. 1982; 27:4295.
- [11] Snoog, CE. Prog. Polym. 1991; 16:561.

- [12] Gareth H: Hougham G, Cassidy PE, Johns K, Davidson T, editors. Fluoropolymers 2: properties, vol. 2. New York: Kluwer Academic/Plenum Publishers; 1999. pp. 233-271.
- [13]. Numata S, Fijusaki K, Kinjo N. Polymer 1987;28:2282.
- [14]. Arjavalingham G, Hougham G, LaFemina JP. Polymer 1990;31:840.
- [15]. Kafafi SA. Chem. Phys. Lett. 1990;169:561.
- [16]. Kowalczul SP, Stafstron S, Dredas JL, Salaneck WR, Jordan-Sweet JL. Phys. Rev. B 1990;41:1965.
- [17]. Matsuura T, Hasuda Y, Nishi S, Yamada N. Macromolecules 1991;24:5001.
- [18] Wellinghoff S, Ishida H, Koenig J, Baer E, Macromolecules 1980;13:834.
- [19] Ishida H, Wellinghoff S, Baer E, Koenig J, Macromolecules 1980;13:826.
- [20] Takahashi N, Yoon DY, Parrish W. Macromolecules 1984;17:2583.
- [21] Factor BJ, Russell TP, Toney MF. Phys. Rev. Lett. 1991;66:1181.
- [22] Kowalczyk SP, Stafström S, Brédas JL, Salaneck WR, Jordan-Weet JL. Physical Review B 1990;41:1645.
- [23] LaFemina JP, Arjavalingham G, Hougham G, J. Chem. Phys. 1989;90:5154.
- [24] Kafafi SA, Chemical Physics Lett. 1990 ;169:561.
- [25] Hougham G, Tesoro G, Viehbeck A. Macromolecules 1996;29:3453.
- [26] Hougham G, Zhang Q, Jean YC. Polym. Preprints 1998;39(2):871.
- [27] Mercer FW, McKenzie MT. High Perf. Polym. 1993;5:97.
- [28] Mercer FW, Goodman TD. High Perf. Polym. 1991;3:297.
- [29] Bowles KJ, SAMPE Quarterly, 1990;21(4):6.

- [30] Hartness T, Porter D, Reardon JP. 34th International SAMPE Symposium 1989;211.
- [31] Kantz M, *Plastics Engineering*, 1990;46:27.
- [32] Russell JD, Kardos JL, *Polymer Composites* 1997;18,64.
- [33] Coleman F. *Hilltop Times* 1999:
[www:http://www.hilltopimes.com/archive/19990715/parts.html](http://www.hilltopimes.com/archive/19990715/parts.html). accessed: July 2005.
- [34] Thorp K, Curliss D, *Proceedings from High Temple Conference XXI* 2001;Paper L.
- [35] Smith JG, Connell JW, Hergenrother PM, Yokota R, Criss JM, *SAMPE Meeting* 2002:12.
- [36] Hergenrother PN. *Polymer* 2000;41(13):5073.
- [37] Hergenrother PN, Thomson CM. *Macromolecules* 2002;35:5835.
- [38] Lincoln JE, Morgan RJ, Shin EE. *Journal of Polymer Science Part B* 2001;39:2947.
- [39] Fang X. *Polymer Chemistry* 1998;36:461.
- [40] Wilson D, Stenzenberger HD, Hergenrother PM, editors, *Polyimides*. New York: Chapman and Hill; 1990. pp. 71-120.
- [41] Johnston JA, Li FM, Harris FW, Takekoshi T. *Polymer*, 1994;35(22):4865.
- [42] Lu SY. *Prog. Polym. Sci.* 2002;27(9):1661.
- [43] *Encyclopædia Britannica*. *Encyclopædia Britannica Premium Service*, 2005
[www:http://www.britannica.com/eb/article-9020268?query=carborane&ct=](http://www.britannica.com/eb/article-9020268?query=carborane&ct=).
accessed: June 2004.
- [44] Grimes R, *Carboranes*, New York: Academic Press; 1970. pp. 151-180.

- [45] Olmsted J, Williams GM. Chemistry: the molecular science. Iowa: Wm. C Brown; 1997. p. 407.
- [46] Progar DJ, St. Clair TL, J. Adhesion 1989;30:185.
- [47] Progar DJ, St. Clair TL, J. Adhesion Sci. Tech. 1991;5:711.
- [48] Bott RH, Summers JD, Arnold CA, Taylor LT, Ward TC and McGrath JE, J. Adhesion 1987;23:67.
- [49] Furukawa N, Yamada Y, Kimura Y, High Perform. Polym. 1997;9(1):17.
- [50] Kaltenecker KJ, Ward TC, J. Adhesion 1993;42:113.
- [51] Lorenz DH, Azorlosa JL, Tu RS, Radiat. Phys. Chem. 1977;9:843.
- [52] Socrates G, Infrared and Raman characterisit group frequencies. Chichester, UK: John Wiley and Sons, Ltd. 2001. pp. 82-88, 343.
- [53] Craner CD, The coblantz society desk book of infrared spectra. Kirkwood, Missouri: The Coblantz Society; 1982. pp. 471.
- [54] Sinnreich J, Synthesis 1980;7:578.
- [55] Roehrscheid F, Patent No: DE 3826572. 1990.
- [56] Sabourin ET, Journal of Organic Chemistry 1983;48(25):5135.
- [57] Johnson LF, Jankowski WC, Carbon-13 NMR spectra. New York: John Wiley and Sons; 1972. pp. 19, 58.
- [58] Abraham RJ, Fisher J, Loftus P, Introduction to NMR spectroscopy. Chichester, UK: John Wiley and Sons; 1988. pp.1-33.

VITA

Francisco Tschen Molina was born in Guatemala City, Guatemala on January 25, 1981. He graduated Cum Laude and received a B.S. degree from Texas A&M University in chemical engineering in May 2003. He continued his education that same year in the area of materials science with a focus on high-performance polymers. Francisco obtained his M.S. degree in materials science and engineering in December 2005.

Permanent Address:

2228 Southgate Blvd. Houston, TX 77030

e-mail address:

itschen@gmail.com