THE APPLICATION OF SILOXANE MODIFIED POLYIMIDES AS HIGH PERFORMANCE TEXTILE COATINGS

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(ABSTRACT)

Novel poly(imide siloxane) copolymers were prepared and developed as high performance fiber coatings. These copolymers were synthesized and characterized extensively as a function of chemical composition. The polyimides were then utilized to coat prototype fibers which were subsequently evaluated regarding thermal stability, thermal behavior, and hydrophobicity.

The polymer series included poly(imide siloxane)s which were prepared in two steps, the first involving the generation of soluble poly(amic acid) intermediates which were then cyclodehydrated by heating in a coamide solution, at temperatures ranging from 140 to 170°C, resulting in soluble polymer which exhibited excellent thermal and mechanical properties. Because of the different nature of the imide and siloxane, a two phase microstructure developed at relatively low block molecular weight. X-ray photoelectron spectroscopy (XPS) and contact angle measurements indicated that the surface of the copolymer films was dominated by siloxane.

A series of coating solutions was prepared, controlling the solution concentration, solvent, and viscosity. Polybenzimidazole and Kevlar aramid multifilament yarns were immersion coated, dried, and evaluated. Due to the surface segregation of siloxane, these coated fibers advantageously displayed lower moisture sorption as measured in three environments of different humidities. Thus, the coating acted as a hydrophobic barrier. These coated fibers were also evaluated by thermogravimetric analysis (TGA) which displayed that the dynamic thermo-oxidative stability was improved. Finally, thermal expansion coefficients were measured in order to determine coating integrity or matrix/resin integrity under thermal stress. This thesis is dedicated to my nephew, Gregory David Hoover, who changed the lives of everyone he touched.

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TABLE OF CONTENTS

<u>Title</u>

<u>Page</u>

.

Abstract	ii
Dedication	iv
Acknowledgements	v
List of Schemes	xi
List of Figures	xii
List of Tables	xiv

Chapter I

Introduction

Chapter II - Literature Review

2.1	Introduction	5
2.2	High Performance Coatings	6
	2.2.1 High Performance Textile Coatings and Matrix Resins	8
2.3	. Polyimide Homo- and Copolymers	13
	2.3.1 Introduction	13
	2.3.2 Classical Polyimide Chemistry	14
2.4	Imidization Techniques	18
	2.4.1 Thermal Imidization	18
	2.4.2 Chemical Imidization	20
	2.4.3 Solution Imidization	22
2.5	Miscellaneous Synthetic Routes to Polyimides	24
	2.5.1 Polyimide Synthesis Via Isocyanate Route	24
	2.5.2 Nitro displacement Polymerization	26

Title	2	<u>Page</u>
	2.5.3 Diels-Alder Polymerization	26
2.6	Various Imide Containing Systems	27
2.7	Properties of Polyimides	31
	2.7.1 Introduction	31
	2.7.2 Thermal Properties	31
	2.7.3 Mechanical Strength	36
	2.7.4 Solubility	37
	2.7.5 Hydrolytic Stability	39
	2.7.6 Radiation Stability	39
2.8	Poly(Imide Siloxane) Copolymers	39
	2.8.1 Introduction	39
	2.8.2 Polyorganosiloxanes	41
	2.8.3 Synthesis of Siloxanes	43
	2.8.4 Synthesis and Characterization	
	of Poly(Imide Siloxane)s	45

Chapter III - Statement of the Problem

3.1	Introduction	51
3.2	Justification	52
3.3	Objectives	53
3.4	Assumptions and Limitations	54

Chapter IV - Methods and Materials

4.1	Introduction	55
4.2	Purification of Starting Materials	56
	4.2.1 Solvents	56
	4.2.2 Monomers	57

<u>Page</u>

<u>Title</u>		Pag
	4.2.3 Synthesis of Aminopropyl Terminated	
	Polydimethylsiloxane Oligomers	59
4.3	Synthesis of Polyimide Homo- and Copolymers	60
	4.3.1 High Molecular Weight Poly(Amic Acid)s	61
	4.3.2 Imidization	63
	4.3.2.1 Thermal (Bulk) Imidization	63
	4.3.2.2 Solution Imidization	64
4.4	Polymer Characterization	65
	4.4.1 Titration of Functional Monomers and Oligomers	65
	4.4.2 Gel Permeation Chromatography	66
	4.4.3 Intrinsic Viscosity	66
	4.4.4 Fourier Transform - Infrared Spectroscopy	67
	4.4.5 Proton Nuclear Magnetic Resonance	67
	4.4.6 Differential Scanning Calorimetry	68
	4.4.7 Thermomechanical Analysis	68
	4.4.8 Dynamic Mechanical Thermal Analysis	69
	4.4.9 Thermogravimetric Analysis	69
	4.4.10 Water Contact Angle	69
	4.4.11 Moisture Uptake	70
	4.4.12 Fiber Coating	.71

Chapter V - Results and Discussion

.

5.1	Introduction	72
5.2	Synthesis of High Molecular Weight Polyimide	72
	5.2.1 Synthesis of Functional Siloxane Oligomers	72
	5.2.2 Synthesis of Poly(Amic Acid) Precursors	74
	5.2.3 Imidization	76

	<u>Title</u>			<u>Page</u>
		5.2	3.1 Thermal Imidization	76
		5.2	3.2 Solution Imidization	77
	5.3	Struct	ural Characterization	78
		5.3.1	Fourier Transform- Infrared Spectroscopy	78
		5.3.2	Proton Nuclear Magnetic Resonance	78
	5.4	Solubi	ility	79
	5.5	Molec	cular Weight Characterization	81 ·
		5.5.1	Intrinsic Viscosity	81
		5.5.2	Gel Permeation Chromatography	82
	5.6	Surfac	ce Properties	82
	5.7	Water	Sorption Studies	83
	5.8	Therm	nal Properties	85
		5.8.1	Glass transition and Thermal Expansion Coefficients	85
		5.8.2	Thermooxidative Stability	88
Chapte	er VI	- C	onclusions	90
Refere	nces			94
Appendi	x 1			105
Appendi	x 2			121
Appendi	x3			141
Vita		•••••		159

List of Schemes

Appendix 1

1.	Synthesis of the First High Molecular Weight Polyimide	106
2.	Classical Synthesis of Polyimides	107
3.	Solvent Interaction During Thermal Imidization	108
4.	Undesirable Species Formed During Thermal Imidization	108
5.	Isoimide Formation During Chemical Imidization	109
6.	Synthesis of Polyimides by the Isocyanate Route	110
7.	Synthesis of Polyimides by Nitro Displacement Reaction	111
8.	Synthesis of Bismaleimides	112
9.	Synthesis of Poly(Amide Imide)s	113
10.	Synthesis of Heterocyclic Imides	114
11.	Synthesis of Ultem Polyetherimide	115
12.	Order of Stability of Polyimides as a Function of	
	Diamine Component	116
13.	Order of Stability of Polyimides as a Function of	
	Dianhydride Component	116
14.	Hydrolytic Degradation of Polyimides	117
15.	Synthesis of Cyclic Siloxanes by Hydrolysis of Chlorosilanes	118
16.	Synthesis of Functional Siloxane Oligomers	119
17.	Synthesis of Poly(Amic Acid) and Subsequent High	
	Temperature Solution Imidization of Poly (Imide Siloxane)s	120

List of Figures

Appendix 2

<u>Figure</u>		<u>Page</u>
1.	Thermogravimetric Analyses of Polypyromellitimides in	
	Dry Helium	122
2.	Apparatus Used for Distillation of Solvents	123
3.	Apparatus Used for Synthesis of Polydimethylsiloxane Oligomers	124
4.	Sample Calculations for Synthesis of Polydimethylsiloxane	
	Oligomers	125
5.	Apparatus Used for the Synthesis of Poly(Amic Acid)s	126
6.	Apparatus Used for High Temperature Solution Imidization	127
7.	Sample Tube Used for Measurement of Thermal Extension	
	Coefficient	128
8.	FT-IR of Solution Imidized Poly(Imide Siloxane)	129
9.	Proton NMR of a Solution Imidized Poly(Imide Siloxane)	130
10.	GPC of a Poly(Imide Siloxane)	131
11.	GPC of a Poly(Imide Siloxane)	131
12.	XPS Wide Spectrum of a Poly(Imide Siloxane)	132
13.	Moisture Uptake of PBI and Kevlar Aramid Fiber	133
14.	Moisture Uptake of PBI and Kevlar Aramid Fiber	134
15.	Moisture uptake of PBI and Kevlar Aramid Fiber	135
16.	Dynamic Mechanical Thermal Analysis of	
	Poly(Imide Siloxane)s	136
17.	Thermogravimetric Analysis of 3,3'-DDS	
	based Poly(Imide Siloxane)s	137

Attention Patron:

Page xiii omitted from numbering

List of Tables

Appendix 3

<u>Table</u>		<u>Page</u>
1.	Common Solvents for Poly(Amic Acid) Synthesis	142
2.	Common Dianhydrides used in Polyimide Synthesis	143
3.	Common Diamines used in Polyimide Synthesis	144
4.	Dehydrating Agents and Bases used in the Chemical	
	Imidization of Poly(Amic Acid)s	145
5.	Functional End Groups used with Addition Polyimides	146
6.	Glass Transition Temperatures for BTDA and PMDA	
	Based Polyimides	147
7.	Effect of Flexible Linkage on Glass Transition Temperatures	148
8.	Thermal Expansion Coefficients of Various Polyimides	149
9.	Mechanical Properties of Two Commercially Available	
	Polyimides	150
10.	Functional Endgroups for Organofunctionally Terminated	
	Disiloxanes	151
11.	Solvent Structures and Boiling Points Used in the Synthesis	
	of Poly(Amic Acid)s	152
12.	FT-IR Bands For Siloxanes	153
13.	Solubility of 3,3'-DDS Based polyimides	154
14.	Solubility of Bis P Based Polyimides	155
15.	Intrinsic Viscosity and Glass Transition Temperatures for	
	Polyimides	156
16.	Water Contact Angles for Various Polyimides	157
17.	Thermal Extension and Expansion Coefficients	
	for Various Polyimides	158

CHAPTER I

INTRODUCTION

Much of the effort to improve existing textile properties has resulted in the investigation of high performance polymer coatings. These coating materials are specialty resins or finishes which add to the textile to improve the product's features. The textile component provides tensile strength, tear strength, and elongation control, while an important function of the coating is protection against the environment to which the fabric is subjected (1,2). Efforts in the development of coatings for textiles have been directed in maximizing the desirable and minimizing the undesirable properties for a specific end use.

Advances in polymer technology helped to spur the textile coating sector of the apparel and textile industry to change significantly with respect to materials and machinery utilized, and particularly in terms of end product application (1,3). Due to the expansion of end uses such as industrial applications for textiles, the need for durable coatings and materials with special properties such as high strength and high temperature resistance is growing rapidly. Coated fabrics are being manufactured and improved for use in civil engineering, geotextiles, agriculture, and transportation (1, 3-6). Much research has involved specialty coatings for protective clothing and footwear (2,7). Coated fabrics are a necessity in the areas of hose reinforcement, conveyor belts, ropes and cables and aerospace and marine applications

(1,2,8). In addition, coated fiber technology is advancing rapidly due to the surge in utilization of fiber reinforced composites (9,10).

The development of high performance fibers such as the aramids has resulted in the development of coatings with comparable performance properties such as good thermo-oxidative stability and excellent durability. Other attractive properties such as surface modification and high strength are added benefits (11). In order to meet the stringent requirements necessary for protective coatings, a number of "high performance" thermoplastic and thermosetting polymers have been investigated and designed as coatings for either fiber, yarn, or fabrics. A number of parameters which must be considered when designing coatings includes adhesion and surface properties, thermal stability, thermomechanical behavior, and polymer processability. In addition, protective coatings should increase the textile's resistance to degradation by harsh environments such as water, oxygen, and ultraviolet radiation.

Several organic polymer systems have been developed which exhibit good properties when subjected to these harsh environments. Earlier work in this area includes polybenzimidazole(PBI), polyquinoxalines, aromatic polyamides (aramids), and aromatic polyimides (12,13). Since much of the work in this area has focused on increasing the thermooxidative stability and strength of these materials, these high performance polymers are generally not soluble in practical solvents. Due to the chemical nature of the chain backbone, i.e. a

rigid para-substituted and highly symmetric aromatic backbone, most of these aromatic polymers were rendered insoluble and thus, not processable. For this reason, much of the current research in this area has focused on increasing the solubility while retaining the thermal and mechanical properties.

The continuing effort for high performance, processable polymers has resulted in high molecular weight, soluble polyimides. By optimizing chemical architecture and synthetic procedure, it is possible to prepare fully imidized polyimides which are processable. Recent efforts in polyimide synthesis have included the incorporation of flexible bridging groups along the polymer backbone as well as dilution of the imide linkage along the backbone. This includes copolymers such as siloxane- , ether-, and amide-imide copolymers. In addition to imparting solubility to the imide systems, the siloxane provides added benefits such as ultraviolet stability, hydrophobicity, and lubricity to the imide surface. Because of these properties, soluble polyimides are excellent candiates for textile applications as protective and/or insulative coatings, adhesives, and matrix resins for fiber-reinforced composites.

The research described herein describes the design of polyimide homoand copolymers which could be successfully evaluated as protective coatings. First, this multidisciplinary approach involves the synthesis and characterization of a series of soluble, high molecular weight polyimide and poly(imide siloxane)s. Secondly, prototype fiber types (PBI and Kevlar aramid) were

coated with these polymers by immersion in a homogeneous polymer solution. Finally, the effect of the coating on these fiber types was determined by a variety of characteristics. The potential of this polymer as a textile coating was assessed by reviewing the corresponding textile properties.

CHAPTER II LITERATURE REVIEW

2.1 INTRODUCTION

The development of a novel textile coating is an extremely involved process and requires a multidisciplinary approach. First, a substrate must be selected and the need for improvements in its performance must be established. Next, a coating must be designed according to the nature of the substrate and the ultimate characteristics of the "improved" product. In addition, the type of coating must be known and well understood. The polymer which is used as the coating must be developed sufficiently to conform to the necessary requirements. In this research, a polymer which is sold commercially as a high temperature, high strength material has been investigated as a fiber coating. This polymer, called a polyimide, has historically been recognized as insoluble due to its chemical structure. By carefully designing the polyimide synthetic procedure, it is possible to retain these high performance properties while imparting solubility to the system. Thus, a generally insoluble, non-processable polyimide may be employed as a novel protective coating.

In order to demonstrate the importance of coatings in the textile industry, various coating types and their characteristics are described below. In addition,

some of the product end-use applications for coated textiles are reviewed. Likewise, the outstanding properties of polyimides are illustrated. The "quest for solubility" of these polymers is related by comparing different methods attempted at producing soluble polymers. The synthesis, characterization and properties of the polyimide are illustrated in depth, in order to emphasize the extreme importance and relevance to the textile and fiber industry.

2.2 HIGH PERFORMANCE COATINGS

High performance coatings are an integral part of the textile industry. Many of the coatings which are now taken for granted have existed for less than fifty years (14). Some older, conventional coating such as mineral oil, pyroxylin, and natural rubber have been replaced by cheaper, more technologically improved coatings such as poly(vinyl chloride), acrylics, synthetic rubbers, silicones, fluorocarbons, polyurethanes, and polyethylene (1,4,14). As an example, leather was first simulated by oilcloth, but since, has progressed to polyurethane coatings (2,5,14). It was evident that the trend in this industry was to formulate new and improved coatings which corresponded to new and expanded products.

It is important to note that the coating type, substrate, and process are specifically designed depending on the desired end use (1,14,15).

Considerations in the coating process include the resin type and viscosity, and the adhesion of the coating on the substrate (1,9) Performance properties which vary according to coating type include durability, flexibility, hardness, abrasion resistance, fire retardance, and water repellency. Other properties include stability to ultraviolet light, oxidative stability and thermal- mechanical behavior (15,16). Coatings may be utilized to minimize costs while introducing properties comparable to expensive fibers. Thus, the purpose of coating technology is to manipulate the coating parameters in order to optimize these attractive properties.

The manufacture and utilization of protective surface coatings such as these is a highly developed technology. The first coatings utilized were applied as a substitute for leather in the "upholstery, garment, footwear, and luggage industries (4,5,7). As potential for coatings was recognized, the expertise grew. Acrylic based latices and styrene-butadiene coatings have been used widely as carpet and upholstery backings (2,14,17). Acrylic resins are used largely for shrinkage control and as a fiber fixative (17). Silicones and fluorocarbons have been used as coating materials for wind resistant and water repellent fabrics (1,17). Neoprene, butyl latex, and silicone rubber have also been important textile coatings (1,14,15,18).

Within the last decade, however, the necessity for new and improved coating types became apparent. New coating types are now developed

specifically for industrial textiles. This category includes geosynthetic, architectural, and transportation related textiles (1,3,6). In addition, due to the demand for high performance fiber reinforced composites, fiber/matrix considerations are extremely important. These end uses and specifications will be discussed below.

2.2.1 High Performance Textile Coatings and Matrix Resins

Geotextiles have been defined by ASTM as "permeable textiles used with geotechnical materials as an integral part of a manmade project, structure, or system" (1). The first reported uses of geotextiles in North America and Europe were in the late 1950's, but growth did not begin until the middle 1970's (1,6). These textiles have generally been used in separation, reinforcement, and combined functions. In all of these textiles, durable coated fabrics are required for successful products (6).

These fabrics must be highly abrasion resistant, as in acrylic resin coated fabrics which are used for erosion control and railroad track reinforcement (6,11). The coatings should increase mechanical properties such as tensile strength, trapezoidal tear strength, tensile modulus, and puncture resistance. Geomembranes are very low permeability membrane liners which control fluid migrations, and thus must be made of low permeability materials such as

poly(vinyl chloride) and high density polyethylene (1,6). In addition these materials must be solvent resistant.

Another industrial textile end use which is growing rapidly is high performance coated fabrics in structural materials (1,3). These fabrics have been developed as permanent lightweight, roofing materials which are supported by air or tension. Architectural fabrics are attractive since they make it possible to form enclosures without altering an existing structure. The coating for these structures must be extremely durable. Factors to consider when formulating these coatings are thickness, chemical and fire resistance, weight, light transmission, ultraviolet light resistance, and water repellency (3,15,17). Presently, fluorocarbon and silicon coatings are being utilized for these structures (15,18).

Finally, high performance coatings are being investigated in transportation applications (5,8). Often, safety and durability are the main concerns. One safety goal is installation of flame retardant coatings which emit little smoke when burned. These coatings should also emit non-toxic fumes when burned. In 1981, it was estimated that 20% of all textile fires resulted from flammable upholstered furniture and were responsible for more that 40% of all deaths due to textile fires (19). Often, fire retardant treatments decrease the rate of flame propagation, yet emit toxic gases and thick smoke. One approach to this problem was to include metal fabric interliners as a barrier to flame spread in

upholstered furniture (21). These fabrics were stiff and actual durability tests were not performed on the cloth. It was possible that durability, lubricity against the cover cloth, and comfort would have been decreased considerably. These materials have been of interest for use in confined situations such as aerospace applications (8). Fire retardant coatings have been considered for upholstery, or as barriers between foam and upholstery material to decrease flame and smoke propagation (19-21).

In addition to the multitude of coating types available, polymers with superior mechanical and thermal properties have been used extensively as matrix resins for fiber-reinforced composites (9,10,12). Many of the same principles apply for a matrix resin as for textile coatings. As in coatings, important factors for a successful composite structure include fiber/matrix adhesion, thermal-mechanical stress elements, and thermal-oxidative stability. Both the fiber and the matrix have distinct properties, which contribute to the ultimate properties of the composite. The fiber reduces the thermal expansion coefficient of the structure, and carries the in plane loads, thus providing stiffness and strength. The matrix protects, bonds, and holds the filaments in place. It also provides transverse strength and acts as a load transfer medium. The matrix should also provide interlaminar toughness and durability (9,22). Fiber properties which should be optimized include high strength/modulus, broad temperature use range and high temperature stability, low moisture

sensitivity, and low thermal expansion coefficient. The fiber/matrix interphase is affected by fiber sizing, chemical interaction between the two, environmental effects (moisture, high temperature, radiation), and thermally induced stresses (cure shrinkage, coefficient of thermal expansion) (9).

There has been a steady improvement over the years in basic fiber types and technology, which in part has led to the development of the high performance coatings mentioned (10,23). Chemical modification has added a great deal of versatility to existing fibers and provided solutions to major end use problems. In the case of polyester, nylon, and acrylics, anti-oxidants, antistatic modifiers, soil resistant additives, and flame proofing modifiers have advanced the state of technology (24). Aliphatic polyoxadiazoles have been. shown to impart flame resistance to silk fibers when coated onto fibers from a 10 % solution and dried (25).

Specialty fibers were designed to meet new levels of properties not attainable by modification of commercial high volume fibers. The most promising heat resistant fiber candidates are aromatic polymers where benzene rings are linked by amide, imide, or imidazole linkages. These heterocyclic polymers have gained much attention as high strength and thermally stable fibers. Popular high performance fibers include polyimide, polybenzimidazole, aromatic polyamides (Kevlar and Nomex aramids), phenolic based (Kynol novoloid), and carbon fibers (10). Inorganic fibers such as boron and silicon

carbide are also receiving attention as high performance fibers (10,23). Polyimide fibers are increasingly popular, due to the advances in polyimide chemistry (10,12). Many polyimide fibers are described in patents (26,27). However, most of these fibers are formed in the amic acid precursor stage, thermally cured, and result in inherently insoluble fibers in the final stage.

Development of these high performance fibers has led to research in coating technology. Coatings offer an advantage over fiber blends and bicomponent fibers in terms of ease of manufacturing, amount of material, and cost. Coatings have been designed which have thermal stabilities equal to or higher than the substrate while imparting other protective and functional propeties. Likewise, in composites, the matrix resin can be designed to exhibit thermal and mechanical properties comparable to or better than the fiber itself (9,22).

Advanced Composite Materials (ACM's) are a class of fiber reinforced plastics which have superior mechanical and/or functional properties which satisfy high level requirements of particular end uses. Reinforcing fibers for these include carbon, graphite, high modulus aramid, silicon carbide, boron, and superdrawn polyethylene. Although metal and ceramic composites exist, only polymer matrix composites have an industrial size market. The success or failure of these composites relies on fiber infrastructure (covalent bond strength, orientation) as well as fiber imperfections which may result from environmental

attacks such as temperature, moisture or chemicals, radiation, and fatigue. Examples of consumer products which are made of composite materials include tennis rackets, automobile interiors and exteriors, and various household appliances.

2.3 POLYIMIDE HOMO- AND COPOLYMERS

2.3.1 Introduction

The development of thermally stable polymers, during particularly the last 20 to 30 years, was achieved by designing appropriate pendant group structures or by introducing thermally stable groups such as aromatic rings into the chain, and are known for their excellent thermal and oxidative stability and outstanding mechanical properties (28,29). Polyimides are step growth or condensation polymers normally derived from primary diamines and bifunctional carboxylic acid anhydrides. The imide structure is formed as linear or heterocyclic units along the main chain of the polymer backbone as shown below. In the early development of these polymers, aliphatic polyimides were



synthesized, however, it was found that completely aromatic polymers had superior thermal and oxidative behavior as compared to aliphatic polymers (28). These aromatic polyimides have been used extensively as metal and glass replacements in aerospace, automotive, electronics, and packaging markets.

The first high molecular weight polyimide is believed to have been synthesized by Edwards and Robinson, who reacted an aliphatic diamine with an aromatic tetraacid or its diacid/diester (30). After initially forming a salt, the reaction was heated further evolving water and methanol, to form the polyimide as shown in Scheme 1 in Appendix 1. Aromatic diamines did not afford high molecular weight polymer in these early experiments. In order to maintain stable melt polymerization conditions, it was necessary to ensure that the resulting polyimides had sufficiently low melting points. This procedure was improved and refined by forming prepolymers and subsequently employing staged heating techniques (31,32).

2.3.2 Classical Polyimide Chemistry

Classical polyimide synthesis is a two-step polycondensation in which a soluble poly(amic acid) precursor is generated at ambient temperature and subsequently converted to a polyimide via thermal or chemical means (28). The overall process is illustrated in Scheme 2 (Appendix 1). The poly(amic

acid) is synthesized by the acylation of a diamine by a dianhydride of a tetracarboxylic acid in a polar solvent. Many aromatic diamines and dianhydrides have been successfully used in the polycondensation, however it is not feasible to utilize orthophenylene diamines or aromatic diamines possessing bulky ortho substituents (33,34). Since the process is a condensation polymerization, the synthesis of high molecular weight poly(amic acid) is highly dependant on many factors. These variables include solvent nature and purity, reaction time and temperature. Other important factors include sufficient monomer reactivity, high purity, solubility in the reaction mixture, and 1:1 stoichiometry. In general, these parameters are chosen according to monomers being used and the physical properties of the desired polymer. These will be discussed below.

The reaction rate of aromatic diamines and dianhydrides is highly dependent on the solvent. Dipolar, aprotic solvents afford reasonable reaction kinetics and solvate many aromatic diamine/dianhydride systems (11). Common solvents for poly(amic acid) synthesis are a function of the solubility of the monomers utilized and are listed in Table 1 in Appendix 3 (35). Polar solvents may be used in combination with less polar materials such as toluene and xylene as cosolvents which serve as a vehicle to remove the liberated water by azeotropic distillation. Ethers have become increasingly important in the synthesis of amic acids and include dioxane, tetrahydrofuran, diglyme, and

triglyme (35). St. Clair and coworkers have reported the use of ether solvents and suggested these solvents enhance the basicity of the amines via hydrogen bonding (36,37). The polyimides thus synthesized were successfully evaluated as structural adhesives and were reported to show good wetting of the adherends, generally metals. The solvents were easily volatilized, and were nonreactive at high bonding temperatures.

Polymer molecular weight optimization requires rigorously controlled reaction conditions. It is imperative that solvents be free of all impurities, including water. All solvents must be distilled after stirring over a drying agent; calcium hydride is generally sufficient, however, some past research has indicated that stirring amide solvents over phosphorous pentoxide followed by distillation is much more effective in removing moisture as well as amine impurities present which may cause side reactions. Impurities and water must be scrupulously excluded from the reaction in order to avoid side reactions (38,39).

Another important synthetic parameter is the reaction temperature. In some systems, above 50°C at least three side reactions which limit molecular weight are possible. Firstly, the amic acid may convert partially to polyimide, releasing water which may hydrolyze the unreacted amic acid or anhydride. At higher tempertures (100°C), this partially imidized portion may precipitate from the reaction as low molecular weight polymer. In addition, transamidation of the

amide acid with the amide reaction solvent is possible particularly with rigid polyimides (40,41).

A very large number of dianhydride and diamines have been studied. These are summarized in Table 2 and Table 3 in Appendix 3 (11,35). Perhaps the most important anhydrides currently utilized are pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride(BTDA).

Oxydianiline(ODA) is a widely utilized aromatic diamine, however, many newer diamines are commercially available. The order of addition of monomer is especially important in the synthesis of high molecular weight polymers. The preferred method of synthesizing poly(amic acid) precursors is by addition of the solid anhydride to a diamine solution at or below room temperature. This method of addition has been reported to yield slightly higher molecular weight polymers as compared to the addition of the diamine to an anhydride solution. Some workers have suggested that dissolving the anhydride first results in a complexation with the amide solvent. Also, by adding the dianhydride second, an upset in the 1:1 stoichiometry due to premature hydrolysis by residual water, is less likely (11,39).

2.4 IMIDIZATION TECHNIQUES

2.4.1 Thermal Imidization

High molecular weight polymers cannot be synthesized directly from many reactants due to the insoluble and infusible nature of polyimides. Thus, the polymer chains precipitate from the reaction media before high molecular weight is obtained. Therefore the soluble polyamic acid is formed in the first stage. In the second step, the imidization step may be accomplished either chemically or thermally. This imidization process is sensitive to the method employed. The goal is to quantitatively cyclize the amic acid to the imide form, releasing water as a by-product. Since the final polymer properties are a function of the molecular design of the polymer, the molecular architechture is extremely important.

The most common method of converting the amic acid to the imide form is by subjecting the films of the polymer solution to a thermal treatment, referred to as bulk imidization. Due to the evolution of water and residual solvent, thermal cyclization is only possible using thin films. It has been reported that the rate of cyclization depends on temperature (42), residual solvent (35,42), and the concentration and mobility of reactive groups (28,43-45). Because of these various factors, thermal imidization of thin films is generally carried out in a systematic manner. A common thermal cycle may consist of the following conditions:

1. One hour at 70°C

- 2. One hour at 100°C
- 3. One hour at 200°C
- 4. One hour at 300°C

5. Slow cooling down to ambient temperatures.

The cycle begins at lower temperatures in order to remove the casting solvent. Temperatures below 150°C may not exhibit significant amounts of imidization. Above this temperature, the ring closure increases at a rapid rate. In fact, a large fraction of imidization occurs between 150°C and 200°C. However, because the Tg increases as the fraction of imidization increases, the cure temperature must also be raised in order to afford efficient mobility within the system. Thus, higher temperatures are necessary to reach high degrees of imidization and thus, the desired physical properties. The extent of thermal cyclization has been studied extensively with many researchers concluding that the level of imidization is far from quantitative (46-48). Although controversy exists concerning the level of imidization in these polymers, there is general agreement that when cured properly, the extent of imidization should be greater than 95%.

Various aspects of the rates of imidization have been studied. Both the rapid (between 150°C and 200°C) and the slower cyclization stages can be interpreted as a first order process as determined by a logarithmic graphical

analysis of the data. The activation energies of the two processes were approximately the same, yet, the entropy of activation for the two processes was significantly different. The authors proposed that in the rapid cyclization process, the solvent promoted favorable orientation for ring closure, due to interaction with the amic acid. As more solvent is removed and conversion to imide increases, the polymer backbone stiffens, and the slow cyclization process follows (29,42). The solvent interaction has been described as shown in Scheme 3 in Appendix 1. Since the cyclization of the amic acid involves the attack of the amide nitrogen upon the carbonyl of the ortho carboxylic group, the solvent interaction may enhance the removal of water when assisted by heat or chemical treatment yielding the imide. It should be noted, also, that if the solvent removal is faster than water evolution or if the solvent does not facilitate the water removal, an undesirable species as shown in Scheme 4 (Appendix 1) may form (48-50).

2.4.2 Chemical Imidization

Polyamic acids may be converted to the polyimide by chemical reagents at ambient conditions. In the mid 1960's, Endrey reported that by employing dehydrating agents such as acetic anhydride, with basic catalysts such as triethylamine, it was possible to cyclize the amic acid. Table 4 (Appendix 3) lists various dehydrating agents and bases (51-53). These cyclizations,

however, first yield an intermediate, the isoimide, which at high temperatures, rearranges to form the imide structure. The entire reaction is illustrated in Scheme 5 in Appendix 1.

It has been reported that cyclization by dehydrating agents also produced side reactions which resulted in branching or crosslinking (54). These side reactions may result in amide formation which occurs during chemical imidization and may subsequently lead to crosslinking. Due to these side reactions, the isoimide exhibits poor thermal and mechanical properties compared to the high molecular weight polyimide. Aging experiments at 100°C for several days successfully converted some isoimide to imide, yet, an appreciable amount of isoimide remained (61). For this reason, chemical imidization is generally not used to convert polyamic acid to high molecular weight polyimide. It has been used to synthesize model imide compounds where the low molecular weight polyimide form may be easily separated, perhaps by recrystallization from the isoimide and other by-products.

An analytical tool which is invaluable in the measurement of the extent of imide formation is Fourier Transform Infrared Spectroscopy (FT-IR). As mentioned, the conversion to cyclic moieties dictates the mechanical properties. Infrared spectroscopy (35,48,56,57) has been used extensively to monitor the conversion of amic acid, and thus the extent of ring cyclization. Dine-Hart and

Imide I 1780-1770 cm-1 and 1730-1720 cm-1 Imide II 1400-1380 cm-1,1380-1360 cm-1, and 1360-1340 cm-1 Imide III 1140-1120 cm-1, 1120-1100 cm-1, and 1090-1070 cm-1 Imide IV 760-740 cm-1 and 740-720 cm-1

The two bands at Imide I are carbonyl absorptions and their intensity and position are easily identified for polyimides. The other imide bands are related to vibrations of the imide grouping. Imide II, III, and IV correspond to axial, transverse, and out-of-plane vibrations, respectively. In general, the Imide I and the Imide IV bands are used extensively due to their absolute positions and relative intensities. Much of the kinetic work which has been reported has utilized FT-IR. Using these techniques, various researchers have reported that solvent (58-60), temperature of imidization (43,58-63), polymer structure (60,64), and film thickness (57) all affect the rate of imidization.

2.4.3 Solution Imidization

There have been scattered attempts to prepare polymides by simply heating the amic acid in solution. In many earlier cases, the polyimide was synthesized but the polymer molecular weight was very low (61). Apparently, as the imidization proceeded, the water released was not removed from the
reaction mixture, and thus hydrolyzed the remaining uncyclized amic acid. Recently, it was reported (60) that by efficiently azeotroping the released water, the detrimental hydrolysis could be avoided. In this work, various polyetherimides were synthesized in phenol-type solvents with azeotroping agents such as chlorobenzene and toluene. Quantitative imidization was successful at temperatures 160-180°C, which was much lower than the Tg of the polyimide. It is proposed that since the imidizing species are solubilized throughout the reaction, the ring closure was quantitative at these temperatures. Apparently, this method allows for adequate mobility and chain flexibility throughout the imidization.

More recently, Summers and coworkers prepared high molecular weight polyimides by solution imidization technique (38,62,63,). A recently developed solvent-azeotroping agent combination was employed which quantitatively imidized the amic acid at temperatures in the range 155-160°C. By employing cyclohexylpyrollidinone to azeotrope the water of imidization, soluble, fully imidized polyimides were synthesized.

2.5 MISCELLANEOUS SYNTHETIC ROUTES TO POLYIMIDES

Many methods have been developed in the search for soluble polyimides. In order to illustrate the importance and potential applications of high molecular weight, soluble polyimides, it is necessary to understand how much research has been involved in this area. Some of the following synthetic procedures have been commercialized, and illustrate the commercial interest in these polymers.

Various synthetic methods have been described as alternatives to the diamine/dianhydride polycondensation described previously. Though the final polyimide is claimed to be identical to the above 'classical' polyimides, many of the processes have difficulty reaching high molecular weight. In most cases, the monomers are all somewhat similiar in structure, yet reaction conditions, and of course, intermediates are entirely different. Also, many of these processes attempted to synthesize soluble polyimides due to the alternative method of preparation. The most common alternate pathways include synthesis from isocyanates, nitro displacement chemistry, and the use of the Diels-Alder reaction. These are briefly discussed below.

2.5.1 Polyimide Synthesis Via Isocyanate Route

Since the late 1960's, workers have reported the reaction of a diisocyanate with either a tetraacid, its ester, or its dianhydride (64-72) in a

proposed that the addition of a partially polarized anhydride to the isocyanates will form a seven membered ring (66,73). This cyclic intermediate subsequently will decompose to evolve CO_2 and yield the polyimide. The formation of the intermediate and resultant polyimide synthesis is shown in Scheme 6 in Appendix 1.

Several reaction conditions which must be optimized in order to get high molecular polyimides include temperature and catalyst, monomer types, order of monomer addition, and residual moisture present. To avoid gelation, a tertiary amine catalyst is necessary, as well as a reaction temperature in the range of 10 to100°C. This temperature range permits the evolution of CO₂, yet temperatures >200°C are necessary to evolve theoretical amounts of CO₂. Due to solubility problems, which resulted in low molecular weight polyimides, Alvino and Edelman (71) used a mixture of aromatic dianydride and its tetraacid to obtain flexible aromatic high molecular weight polyimides. A small amount of water is necessary for the reaction, whereas large amounts can upset the stoichiometry, lowering molecular weight. Finally, it is necessary to add the solid diisocyanate to the acid/anhydride solution to afford high molecular weight. This route is currently used to prepare polyimides commercially developed by Upjohn Company and others (69,74,75).

2.5.2 Nitro-Displacement Polymerization

Nitro displacement reactions have been studied as alternative routes to polyimides. This polymerization involves the nitro displacement of bis-imides by a bisphenate in a dipolar aprotic solvent/azeotroping agent system (76). This nitro displacement reaction is illustrated in Scheme 7 in Appendix 1 . However, low to moderate molecular weight has been obtained but not high molecular weight. Nitro displacement, however, has been utilized in the monomer synthesis of a thermoplastic polyimide called Ultern, which has been commercialized by General Electric. This synthesis will be discussed later since it is a commercially available, processable polyetherimide.

2.5.3 Diels-Alder Polymerization

This reaction has been utilized to synthesize polyimides (77,78). One approach was to utilize this reaction to prepare a monomer with anhydride functionality, which was subsequently polymerized with diamines in the 'classical' synthesis, yielding high molecular weight polyimides. Another approach employed preimidized monomers which were reacted via Diels-Alder mechanisms, and after subsequent dehydrogenation, the reaction resulted in a phenylated polyimide. The resulting polymers were low molecular weight. This may be attributed to incomplete dehydrogenation, and the fact that the aromatization occurs after the polymer is formed, leading to partial degradation

of the polymer. Other Diels-Alder cycloaddition polymers are referenced (80-82).

2.6 VARIOUS IMIDE CONTAINING SYSTEMS

Due to the insoluble nature of many polyimides, much work has attempted to increase the processibility of these polymers. One idea of diluting the fraction of imide linkages has resulted in tremendous effort in the area of addition cured polyimide networks and polyimide copolymers. Again, the purpose here is to retain polyimide properties while increasing processability. It should also be noted that the following imide containing systems are used extensively in fiber reinforced composites, again illustrating the relationship between textiles and high performance polymers.

Addition polyimides are functionally capped imide oligomers which may be cured to the insoluble polyimide. These oligomers are low molecular weight organic compounds containing preformed imide structures terminated with reactive groups and were developed since they are processible precursors. The most common functional end groups are nadic (83,84), maleimide (85,86), and acetylene terminated (87,88). Table 5 (Appendix 3) lists various functional end groups which have been used (89).

The preparation of these oligomers is fairly straightforward. The molecular weight of the oligomers is controlled by excess amounts of capping agents and

the oligomers are prepared under conditions similar to those used for polyimide synthesis, forming the end group during the synthesis. The functional acetylene end group is prepared under the same conditions but this endgroup is incorporated after oligomer formation. Scheme 8 in Appendix 1 illustrates the oligomer formation for bismaleimides.

In a typical application, these oligomers are dissolved in a low boiling solvent, then solution cast or impregnated onto a substrate. The solvent is removed at low temperatures and then the temperature is raised above the crystalline melting point or glass transition temperature of the oligomers. The end groups react thermally via an addition type polymerization which yields a highly crosslinked network. Most of the endgroups crosslink without releasing volatiles. These polymers afford polyimides which are processable and stable in the oligomer stage but the networks formed are extremely brittle due to their high crosslink density. Current research involves toughening of these networks by lowering the crosslink density or by using diamines with extended structures or other flexibilizing units (90,91).

Copolymers containing the imide molety include poly(amide imide)s, poly(ester imide)s, poly(ether imide)s, poly(siloxane imide)s, and heterocyclic imides. Because of their significance in this research, siloxane-imides will be discussed in a separate section. Both the amide imides and ester imides were introduced in the early 1960's (92,93). Poly(amide imide)s have been

synthesized in various ways (94-97). There are three basic methods utilized which all follow the general classical two step synthesis for polyimide homopolymers. One method describes the formation of low molecular weight amine capped poly(amic acid) which is then reacted with diacid chlorides to form a poly(amide-amic acid). Another synthesis involves the reaction of excess diamine and diacid chlorides forming a low molecular weight amine capped polyamide which is subsequently cured to the amide imide. A third method involves the reaction of a diamine with trimellitic acid or its acid chloride, followed by thermal cyclization. Most amide imide copolymers are synthesized in this manner as illustrated in Scheme 9 (Appendix 1). Amoco Chemical Corp. has commercialized these materials under the trade name Torlon.

Polyester imides (101,102) are generally prepared by reacting diamines with bis(ester anhydrides) resulting in a poly(ester amic acid). Again, the ester amic acid is cyclized thermally. The bis(ester anhydride) may be conveniently prepared by reacting trimellitic acid chloride with an aromatic bisphenol. Various ester imides have been prepared and are available in patents.

Polyheterocyclic imides were successfully prepared in order to improve the processibility of polyimides while improving their thermal and mechanical properties. These polymers are an extremely important class of high performance polymers. These polymers are also used to make high

performance fibers, including polybenzimidazole and others. The overall synthesis of heterocyclic imides is illustrated in Scheme 10 (Appendix 1). In general, a diamine is reacted with a dianhydride which has been preformed. This dianhydride contains functional groups which will eventually become the heterocyclic portion of the polyimide. A thermal postcure follows the synthesis of the corresponding amic acid. This route is the most common and has been used to synthesize benzimidazoles, benzothiozoles, benzoxazinones, and benzoxazoles. Other procedures have been utilized to yield heterocyclic polyimides (12,98,99).

Other linkages which have been incorporated in polyimide copolymers include ketone, ether, sulfone, aliphatic meta linkages and bypyridyl (103-106). As mentioned previously, General Electric's Ultern is a commercially available polyether imide, which includes aromatic ether, aliphatic, and meta linkages to successfully achieve its thermoplastic nature while maintaining its excellent thermal and mechanical properties. It is believed that Ultern is prepared in the manner shown in Scheme 11 (Appendix 1) . In this reaction, a bis(arylene ether imide) is formed in the first step. In the second step, imide groups are hydrolyzed then dehydrated to form a bis(arylene ether anhydride). This anhydride is then reacted with a diamine to form the polyimide (11,35,76,102,107-108).

2.7 PROPERTIES OF POLYIMIDES

2.7.1 Introduction

The physical properties of polyimides have been studied extensively. The behavior of these polyimides is dependent upon the particular dianhydride and diamine used, as well as any other species present (11). Due to the multitude of monomers which have been reacted, the corresponding properties vary immensely between different polymer systems. Because of this, many general trends have been realized, relating polyimide chemical structure with thermal and mechanical behavior. As these properties are manipulated, other characteristics such as chemical resistance, solubility, and stability to harsh environments are affected.

In order to be a successful fiber coating, the polyimide must exhibit properties which improve upon or add to the uncoated specimen. To realize this goal, certain structure-property relationships must be identified. In this section, general trends will be discussed, relating the polyimide structure to these dependent properties.

2.7.2 Thermal Properties

The use temperature of polymeric materials relies on various factors including on various factors including phase changes, discoloration, modulus/strength variations, adhesive properties, and temperature of

degradation. Since the use temperature is most limited by the temperature of decomposition, this value is measured and associated with the use temperature of the polymer. Degradation is a function of chemical structure, but decomposition is further complicated by unknown factors such as initiator residues, sensitive terminal groups, impurities, and residual solvents (109).

The most common analytical method used to measure thermal stability of polyimides is Thermogravimetry (TG), also known as Thermogravimetric Analysis (TGA), where the loss of mass is measured as a function of time or temperature. This method has been used to measure various chemical processes such as pyrolysis, rates of evaporation, dehydration, reaction kinetic studies as well as to assess thermal oxidative degradation and thermal decomposition (109). Due to the complexity of polymer degradation, many factors must be controlled and reported when using thermogravimetry. Since weight loss is used to assess polymer stability, this method is sensitive to sample form, heating rate, atmosphere, time, temperature, and any stress applied to the system such as load or irradiation. The environment and thus the gas and flow rate, is extremely important since the removal or retention of volatile products or a reaction between the environmental gas and polymer has an effect on the weight loss. The thermal stability may be measured in a dynamic or isothermal mode. Heating rate affects the rate of reaction and /or devolatilization. Variation in sample form results in surface area variations, and

thus, difference in the observed weight loss. It should be noted that changes not accompanied by volatiles, such as oxidation, crosslinking, or phase changes, are not recorded. For this reason, other analytical techniques may be used in conjunction with thermogravimetry including gas chromatography, mass spectrometry, and evolved gas detection (11,12,109).

In general, polyimide films are stable in flowing air or under vacuum to temperatures greater than 500°C before a deterimental increase in the rate of degradation (110). Flexible units such as side or main chain aliphatic, ether, and sulfide groups or comonomers will lower the polyimide thermal stability (35,110). Thermal stability of the imide groups depends on the particular monomers used, also. The stability of polyimides based on various diamines generally follows that order shown in Figure 12 in Appendix 1 . Also, optimum thermal stability is obtained when rigid, para-substituted diamines are utilized instead of asymmetric, meta linkages. Likewise, the dianhydride thermal stability component generally follows the order shown in Scheme 13 in Appendix 1 . This trend is illustrated in the Figure 1 (Appendix 2) . The effect of various diamine components, with pyromelittic dianhydride (PMDA) as the anhydride component on thermal stability is demonstrated.

As mentioned above, degradation behavior is dependent upon the test atmosphere. The mechanism and kinetics of polyimide degradation have been studied by Clark, utilizing Thermogravimetric Analysis (TGA) (111). Clark

proposed that in an air atmosphere, oxidation is the major degradation mechanism with an activation energy of 24.5 kcal/mole in the temperature range of 507 to 602°C. A carbonization process also accompanies the degradation in air and is the most important mechanism in argon and vacuum. An activation energy of 76.5 kcal/mole was reported in argon in the temperature range of 498 to 597°C. Other researchers in the field have proposed that degradation in air proceeds by crosslinking primarily of the ether component (in PMDA/ODA) and of the imide to a small extent (112). Others have concluded that the thermal degradation in air proceeds by the formation of carbonyl and hydroxyl groups at the oxydiphenylene rings (113,114). These processes are subsequently followed by random chain scission of the polymer.

A distinctive feature of polymeric materials is that the properties can be influenced by the method of manufacturing and by processing. It is well known that glass transition values are highly dependent upon chemical structure, thermal history, and polymer molecular weight (115-119). In general, Tg temperatures of polyimides follow the same order as thermal stability (35,57). Depending on the method of evaluation, the glass transition temperatures have been reported in the range of 285 to 500°C (57). Table 6 (Appendix 3) lists the glass transition temperatures for BTDA and PMDA based polyimides varying the diamine segment. It is generally believed that this discrepancy between values from DSC and mechanical measurements is due to lightly

crosslinked high imide content aromatic polyimides. Table 7 (Appendix 3) illustrates the effect of flexible linkages on Tg (116). Polyimides with crystalline segments built into the polymer chain have been prepared by Hergenrother and others (120,121). These polymers have melting points in the range of 350°C to 442°C.

One important thermal property of polyimides is the coefficient of thermal expansion. This parameter is becoming increasingly important in the area of electronics and composite engineering. In general terms, the Coefficient of Thermal Expansion (CTE) is defined as the change in length (with no load applied) as a function of temperature. The polymer chains expand greatest at its glass transition temperature. Likewise, the glass transition temperature is the intersection of the expansion curves of the glassy and supercooled rubbery states. A more rigid or cured material is generally characterized by a higher Tg, low thermal expansion coefficient, in both the glassy and rubbery states, and smaller difference in the expansion coefficients of the two states (109).

Expansion measurements on thin films such as polyimides present certain problems. Due to biaxial orientation in polyimide processing, the polymer has different expansion coefficients in the x, y, and z, direction. In the thin z direction, it is necessary to load the probe heavily to prevent buckling or warping and assure only thermal expansion is measured. In plane measurements (in the x-y direction) on thin samples are too thin to support

themselves and thus, are measured using an extension apparatus. Thus, both thermal extension and expansion coefficients may be measured.

In order for polymers to be practical in situations where thermal stress is generated, they must have matching CTE's. Although most polymers have high coefficients, polyimides have low values, comparable to metals, ceramics, and most high performance fibers. It has been observed that polyimides consisting of para-linked diamines and BTDA or PMDA result in low CTE polyimides. It is proposed that a low CTE is related to linearity and the absence of flexibilizing segments in the polymer backbone (122,123,124). Expansion coefficients have been reported for polyimides and poly(imide siloxane)s in Table 8 in Appendix 3 (124).

2.7.3 Mechanical Strength

Polyimides are high strength and high modulus materials, due to their chemical structure. Again, the mechanical properties of this class of polymers depends on diamine, dianhydride, and the presence of soft segments, which will lower the ultimate strength. As an example, mechanical properties of two commercially available polyimides, Kapton and Ultern, are listed in Table 9 (Appendix 3) (79,125). It should be noted that the mechanical properties for polyimides are higher than those for other common polymers such as polycarbonate, nylons, polysulfone, and polypropylene.

2.7.4 Solubility

Much of the work in the polyimide area has been involved in increasing the thermal stability and mechanical strength, however, at the expense of processability. The polyimide is generally molded or preformed in the amic acid form and then thermally cured to the polyimide. Disadvantages in this method include the evolution of volatiles, solvent, and the limitation of manufacturing in thin film form.

Much research has involved understanding the insolubility of polyimides. One popular theory involves a lightly crosslinked polyimide. In the middle 1960's, it was proposed that during thermal imidization of solution cast poly(amic acid)s, intermolecular condensation, i.e., the reaction between functionalities on adjacent chains in close proximity, occurred. Theoretically, this reaction could occur and yield a crosslinked structure (126). It is also possible that end groups or unreacted monomer may react in the same intermolecular fashion. Other workers have proposed that since the amount of imidization is not quantitative, the residual uncyclized amic acid may react to form a lightly crosslinked, insoluble polymer.

Opponents of the crosslinking idea have proposed that the insolubility was due to highly ordered structures, which result from high chain rigidity. By comparing the molecular weight of a fully cyclized polyimide dissolved in concentrated sulfuric acid with the molecular weight of the amic acid precursors,

it was proposed that no change in molecular weight or chain dimensions occurred on curing (39,127). Along these lines, other workers have proposed the formation of heterogeneous two phase structures involving ordered phases in the PMDA-ODA polyimide (128-130). An alternative theory suggested by St. Clair and coworkers states that charge transfer complexes form due to the alignment of adjacent polymer chains and thus, electronic interactions between electron donating and withdrawing groups on these chains (57,116,131).

In order to overcome the solubility problem, polyimides have been designed carefully. Much work has utilized dianhydrides and/or diamines which contain flexibilizing units. These may be bridging units such as sulfone, sulfur, fluoroalkyl, ether, carbonyl, as well as asymmetric, meta-linked isomers. These flexible units disrupt symmetry, and impart mobility to the polyimide backbone. Polyimides synthesized from monomers containing bulky side groups which disrupt chain packing, have also been used (132). Due to the importance of this area, recent improvements in polyimide solubility and processibility are referenced (133-136).

2.7.5 Hydrolytic Stability

As mentioned above, conventional aromatic polyimides are insoluble in most "normal" solvents. Concentrated sulfuric acid and cold fuming nitric acid have been used to dissolve these polymers. Polyimides are stable to weak

acids and weak bases but hydrolytic degradation can occur in the presence of stronger bases (137,138). It was shown by Delasi and Russell (139) that after soaking the Kapton polyimide in distilled water for various times at temperatures ranging from 25°C to 100°C, the polyimide film showed a loss of tensile strength. Scheme 14 (Appendix 1) illustrates possible hydrolytic degradation. Further hydrolysis would lead to a diacid group and an amine terminated group.

2.7.6 Radiation Stability

Polyimides exhibit fair ultraviolet light stability. As judged by exposure for 4000 hours ar 45°C in an Atlas Weather-O-Meter, both wet and dry polymer films showed substantial deterioration (140). In general, the radiation resistance is a function of imide and/or aromatic content.

2.8 POLY(IMIDE SILOXANE) COPOLYMERS

2.8.1 Introduction

Multiphase copolymer systems are of great interest due to their many advantages over simple polymer blends. Both blends and copolymers may exhibit tremendous enhancement of homopolymer properties, yet due to the positive enthalpy of mixing, many blends are immiscible or heterogeneous. These blends exhibit poor adhesion between the two polymer interfaces and this phase separation leads to poor mechanical properties. In a copolymer system, since the homopolymers are covalently bonded, this limits the degree of phase separation, maintains good interfacial adhesion, and thus results in improved mechanical properties. The resulting properties depend on the nature of the two polymers, segment lengths, and overall composition (140).

A class of homopolymers which received much attention in multiphase systems is the polyorganosiloxanes. Several siloxane modified systems which hve been studied include the siloxane-ureas and urethanes, siloxane-ester, siloxane carbonate, siloxane styrene, siloxane-aryl ether, siloxane imide, and siloxane amide imide (141). As mentioned previously, incorporation of flexible siloxane segments into the polyimide backbone structure can yield copolyimides with enhanced solubility. In addition, the polysiloxane component imparts many other beneficial properties such as reduced water sorption, improved mechanical properties at low temperatures, and resistance to degradation in aggressive atmospheres. Especially important is the ability of the nonpolar siloxane to modify the surface properties of the copolymer system. Because of these properties, siloxanes are attractive for use in various multiphase systems.

2.8.2 Polyorganosiloxanes

Early workers in silicon chemistry such as Friedel, Crafts, (142-144), and Ladenburg (145) synthesized organosilicon compounds as early as 1863-1871. In 1904, Kipping (146,147) discovered the principle of intermolecular condensation of silane diols and triols to polysiloxanes, however he failed to recognize the importance of polymerization in this field. Toward the end of the 1930's, workers at Corning Glass entered the field of siloxanes while trying to develop thermally stable resins for varnishes in electrical insulation. Once the unique and versatile character of silicone polymers was recognized, further development was rapid. By the 1940's, the usefulness of silicone products as lubricants and greases in gaskets, motors, and insulation in aircraft construction stimulated the research and development by large companies, including Dow Corning and General Electric (18). Today, silicone release agents, pressure sensitive adhesives, and textile treatments are examples of commercial uses of siloxanes (18,141). In textile treatments, various silicones have been used in water repellency of nylon, abrasion resistance of triacetate yarns, antipilling of fabrics, as well as many other applications (17,18).

Organosilicon compounds comprise a class which have at least one direct Si-C bond in the molecule. Polymers of this type which also have oxygen bridges between silicon atoms are called polysiloxanes (18,141). The repeat unit of a polysiloxane consists of two monovalent organic radicals attached to

the silicon atoms, which are attached to oxygen atoms in an alternating fashion as shown below. The most common silicon substituents are methyl groups.



R = methyl, phenyl, trifluoropropyl, hydrogen, vinyl, etc.

The methyl group can be replaced by other organic radicals such as phenyl, hydrogen, vinyl or 1,1,1-trifluoropropyl in order to arrive at different properties.

Siloxanes offer many attractive physical properties which include the following: good thermal stability, high gas permeability, hydrophobic behavior, surface activity, and physiological inertness (18,148). In addition, siloxanes exhibit low intermolecular forces, resulting in a low glass transition temperature (-123°C), low surface energy, low dielectric constant, and a low solubility parameter (18,149). It has been shown by spectroscopic studies and thermodynamic considerations that these low intermolecular forces are a consequence of the unusal ease of rotation of the methyl groups around the (Si-O) bonds (149-151). The thermal stability of siloxanes is partly due to the fact

that the Si-O bond is one of the the most thermally stable bonds formed by silicon and has a bond dissociation energy of 110kcal/mole compared with 85.5 for C-O, 82.6 for C-C, and 76 for Si-C bonds (149,153). Finally, polydimethyl siloxanes are transparent to ultraviolet and visible light, stable against atomic oxygen, and highly resistant to ozone and corona discharge (18,149,152).

2.8.3 Synthesis of Siloxanes

Organosiloxane cyclics may be prepared by hydrolysis of chlorosilanes (18,141,149) as shown below in Scheme 15 in Appendix 1. Presently, the most important polyorganosiloxanes used in step growth polymers affording novel copolymers are, α, ω -organofunctionally terminated siloxane oligomers. These linear polysiloxanes of high molecular weight are readily prepared by catalyzed ring opening of the corresponding cyclic trimer or tetramer. Due to the markedly different electronegativities of the silicon and carbon atoms, or the polarity of the bonds, groups attached to the Si atom have much higher reactivities towards nucleophilic reageants when compared with analagous groups attached to the carbon atom. In fact, the ring opening polymerization proceeds by an ionic mechanism, due to the partially ionic (50%) character of the Si-O bond. This bond is cleaved by strong acids and bases. During these reactions, the catalyst may only cleave Si-O bonds in the cyclic or linear species, while the Si-C and C-C bonds are stable (150,151). Equilibration

reactions are the major route to functionally terminated oligomers. Equilibration of siloxanes is the process where the Si-O linkages in a mixture of linear and cyclics are continuously broken and reformed until the system reaches its thermodynamically most stable equilibrium state. At equilibrium, the reaction consists of approximatey 10-15% cyclics, with the remaining amount consisting of linear species. This position of equilibrium is determined by the temperature, concentration of siloxane units in the system, and the nature of the organic radical attached to the silicon atom. An increase in the size and polarity of these substituents increases the amount of equilibrium cyclics.

In work done by McGrath, Yilgor, and others, reactive difunctional siloxane oligomers were prepared by ring opening of octamethylcyclotetrasiloxane , or D_4 , in the presence of strong acid or base catalysts. The molecular weight of the oligomer obtained was controlled by the addition of a linear disiloxane as an endblocker. A variety of α , ω -organofunctionally terminated disiloxanes used as endblockers are listed in Table 10 (Appendix 3). The overall reaction scheme used to prepare these oligomers is illustrated in Scheme 16 in Appendix 1 . After decomposition of the catalyst, nonfunctional cyclic side products were removed by vacuum distillation at elevated temperatures. These oligomers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance (NMR) for structural determination. The number average molecular weight was determined by Vapor Phase Osmometry and

potentiometric titration of end groups. Thermal transitions were detected using Differential Scanning Calorimetry (141).

2.8.4 Synthesis and Characterization of Poly(imide siloxane)s

Combining siloxanes and imides had been a popular goal of many researchers. As mentioned above, the copolymers exhibit many interesting properties such as surface modification and ultraviolet radiation stability. These copolymers retain their thermal stability and exhibit a service or use range of approximately 400°C due to the extreme differences in glass transition temperatures. The siloxane also imparts flexibility into the polymer backbone, thus affording a more processable polyimide. For these reasons, polyimide siloxanes have been of great interest.

Poly(imide siloxane)s have been reported as early as 1966 by Kuckertz where pyromelittic dianhydride(PMDA) was reacted with an amine terminated siloxane dimer and subsequently imidized thermally. Two years later, Greber reported the synthesis of a series of poly(ester imide siloxane)s and polyimide siloxanes using different backbones. Again, the disiloxane was utilized for both of these copolymers, but physical properties were not reported (38,141). After these early reports, a multitude of siloxane imide copolymer systems have been reported. Much of this available information is in patents, and often chemical

structures are not disclosed, yet many interesting polymers and applications have been achieved.

In most of these systems, the aliphatic amine terminated silicone dimers have been utilized. The disiloxane simplifies the reaction chemistry as the siloxane solubility is close to that of the other reactants. Several disadvantages are associated with incorporating the disiloxane into the polymer. Due to the low molecular weight of the dimer, the copolymer is phase mixed and does not allow for surface modification by the siloxane (154). In order to render the copolymer soluble in low boiling solvents, a large concentration of disiloxane must be incorporated (155). Because phase separation is not possible, a single copolymer Tg is observed, which is significantly depressed due to large amounts of disiloxane. Likewise, the thermal stability and performance is decreased greatly (156-158).

Despite these disadvantages, many publications have reported polyimides made from bis(amino alkyl)disiloxanes in high concentrations in order to obtain soluble polymers with improved toughness. The siloxane component has been used extensively in both linear (159-162) and addition (163-164) polyimides. More recently, St. Clair and coworkers (165) reacted varying amounts of bis(amino propyl) tetramethyl disiloxane with benzophenone tetracarboxylic dianhydride (BTDA) and the diamine analog (DABP). The resulting polymers exhibited increased processability and were soluble in dipolar aprotic solvents such as N-methyl pyrollidinone (NMP) and at high siloxane concentrations the copolymers were soluble in low boiling solvents such as tetrahydrofuran (THF) and digylme(2-methoxy ethyl ether). Since the dimer was incorporated, the Tg dropped and the thermooxidative stability decreased sharply with increasing siloxane composition (166). The mechanical properties of the copolymer are also highly dependent upon disiloxane content. Lee reported that copolymers with low amounts of siloxane behave essentially as unmodified polyimides whereas at high amounts of siloxane, the copolymers are elastomeric in nature (156-158).

Because of the shortcomings of disiloxane-based poly(imide siloxane)s, researchers have begun to focus on incorporation of low molecular weight oligomers into the polyimide backbone. Poly(imide siloxane) segmented copolymers commercialized by M+T Chemicals have utilized higher molecular weight siloxane equilibrates which produce microphase separated segmented copolyimides (167-169). Several advantageous properties of siloxane blocks over disiloxane includes higher Tg, better dielectric properties, and less sensitivity to water sorption. St. Clair and coworkers (170) reported the use of aromatic amine terminated polydimethyl siloxane oligomers of varying molecular weight to modify various thermoplastic polyimides. These copolymers were reported to have two phase morphologies due to two separate glass transition temperatures, a low Tg corresponding to siloxane segment and

an upper Tg corresponding to the imide portion. These polymers also exhibited improved adhesive strengths and better thermal stability.

Lee (171) and Berger (172) have reported several new siloxane-imide coplymers. Although chemical compositions are not reported, the authors claimed that the polymers were solution or melt processable, and that multiphase copolymers were synthesized, again due to the presence of a low (-20 to -120°C) and a high (>230°C)Tg. Lee elucidated the advantages of disiloxane over dimer in a recent paper.

Previous work at Virginia Tech has addressed the siloxane modification of polyimides. Amine terminated polydimethyl siloxane oligomers and oxydianiline (ODA) were reacted with PMDA or BTDA (79), varying the molecular weights and amounts of siloxane incorporated. In order to keep the reaction solvated, a cosolvent system consisting of tetrahydrofuran (THF) and dimethylacetamide (DMAC) was necessary. Complete imidization of the poly(amic acid siloxane)s was achieved by a thermal cure cycle. FT-IR was utilized to follow the transformation from amic acid to imide. These copolymers exhibited multiphase behavior. Even at low siloxane compositions, contact angle and X-Ray Photoelectron Spectroscopy (XPS) demonstrated that the copolymer film surfaces were mostly siloxane. Thermal and mechanical properties were fairly good, yet even at high siloxane compositions, the copolymers were insoluble.

Synthesis of soluble, thermoplastic imide siloxane copolymers was recently reported Summers and others (38,141). Aminopropyl terminated siloxane oligomers and 3,3'-DDS were reacted with BTDA. The incorporated polydimethyl siloxane oligomer was varied from 5 to 70 weight percent with molecular weight in the range of 800 to 10,000g/mole. The polymers were synthesized in THF/DMAC co-solvent solution at room temperature. The precursor was cured in a high temperature thermal cycle as described previously. Alternatively, a solution imidization method was employed which utilized NMP/CHP at 150-160°C as a unique solvent/azeotroping agent combination, quantitatively imidizing the amic acid. The overal process is depicted in Scheme 17 in Appendix 1.

Yilgor and coworkers have also prepared similar siloxane imides for protective coatings (141). Low and high temperature glass transitions corresponding to siloxane and imide were observed, indicating the formation of two phase structures. Copolymers were soluble in NMP and DMAC, and at higher siloxane content, in THF and chloroform (CHCl₃). Intrinsic viscosities qualitatively confirmed fairly high molecular weight. Contact angle and XPS showed siloxane rich surfaces which resulted in dramatic reduction of equilibrium water absorption levels of the films. This siloxane modification was shown to increase the atomic oxygen resistance of these materials (38,173) Thermogravimetric analysis indicated thermal stabilities >400°C even with high

amounts of siloxane. Mechanical properties were a function of copolymer composition and these polymers have also been evaluated in preliminary adhesive studies.

The desired physical properties associated with poly(imide siloxane) copolymers can be achieved by varying the quantity of siloxane and its molecular weight. Because of these advantageous properties which can be obtained by varying the siloxane component, applications for siloxane imides are numerous. Gas separation membranes (174), electronic parts and printed circuit boards are important applications (175). Aerospace and marine applications include protective coatings, matrix resins, structural adhesives, and textile components. A portion of this thesis addresses the structure-property relationships of a series of poly(imide siloxane) copolymers and subsequently, their potential application as a matrix resin and fiber coating/primer.

Chapter III

STATEMENT OF THE PROBLEM

3.1 INTRODUCTION

Manmade fibers which were insignificant prior to 1940 now represent half of the total world textile prodluction. Because of this fact, as well as the slow development of new fiber types for traditional uses such as apparel, the future growth and vitality of the fiber and textile industry is increasingly depending upon non-traditional uses of fibrous materials. Aramids, carbon, glass, and ultraoriented polyethylene have joined traditional nylon, polyethylene, and polypropylene as reinforcing fibers in aircraft, appliances, construction, marine equipment, automobiles, and consumer products.

The unique combination of physical properties of fibrous materials, coupled with their high specific surface areas make them ideally suited for many innovative applications. The challenge for the fiber and textile science community lies in new and innovative uses for fibrous materials. A relatively easy and inexpensive way to tailor these fibers to certain applications involves the use of specialty coatings and/or finishes. Coatings offer many improvements in fiber performance at a relatively low cost. An inexpensive fiber

may be coated with a high performance coating and behave equal to or better than a more expensive, highly developed fiber.

3.2 JUSTIFICATION

In the past, coating was restricted to reputable, specialized coating firms that produced heavy, general all-purpose coatings such as polyurethanes, for outdoor articles. Today, a new philosophy has evolved based on manufacturing as few as possible raw materials and creating entirely different end use applications for both apparel and industrial goods by mechanical and chemical finishing operations. The popularity of fine-coated apparel is increasing at a steady rate, as is the area of high performance industrial coatings for textiles. Coatings have been improved very impressively in the last few years and can satisfy a range of specifications by efficiently utilizing existing technology.

When developing a coating for a specific fiber, certain properties of the coating and fiber must be identified. In the case of poly(imide siloxane) copolymers, the outstanding properties include high strength, high temperature stability and hydrophobicity. These properties may be "transferred" to fiber in the form of a coating. In addition, other fiber properties may change as a result of the coating.

This research, specifically, involves poly(imide siloxane) coatings and polybenzimidazole and Kevlar aramid fiber substrates. Coating these fibers will increase the thermooxidative stability and increase the hydrophobicity, which is essential for various novel applications. Because this project is exploratory and will not encompass a matrix of fiber properties, only these aspects of the coating and coated fibers will be addressed.

3.3 OBJECTIVES

An investigation as broad as this include synthesis and characterization of the polymer, coating the fibers, and characterization of the final coated fiber. Specifically, the three main objectives of this work were:

1. To refine and further develop the poly(imide siloxane) synthesis since it is a fairly new procedure. In addition, it is necessary to vary the diamines and dianhydrides and to test the resulting polymers in order to optimize solubility and thermal behavior.

2. To optimize the coating process. This included testing different solvents, different drying times, and temperatures.

3. To test the coated and uncoated fibers for hydrophobicity and thermal stability. From these results, it was to be decided if this polymer could reasonably be effective as a protective fiber coating.

3.4 ASSUMPTIONS AND LIMITATIONS

Polyimides are very high strength, high temperature polymers which are not processable or soluble in most cases. Kevlar aramid and polybenzimidazoles are high performance fibers with some properties which may be improved by combining the fibers with the polyimides. Both fibers and polyimides are highly polar moieties, and thus it is assumed that the polymer adheres well to the fibers. Since the polymer exhibits unique surface properties and high temperature stability, these are the properties which were tested. Thus, an assumption was that other properties such as mechanical strength were not adversely affected by the coating. It is also assumed that the surface was dominated by siloxane, and thus was very nonpolar. Thus, it is also assumed that siloxane surface may also impart other beneficial properties to the fiber which were not tested such as ultraviolet light resistance and abrasion resistance of the fiber surface.

Chapter IV

METHODS AND MATERIALS

4.1 INTRODUCTION

This section will include all the experimental conditions concerning polymer synthesis, characterization, fiber coating, and fiber characterization. As mentioned previously, the synthesis of high molecular weight polyimides is highly dependant on the purity of starting materials and the reaction conditions employed. Monomers and solvents were extremely pure, and the system remained anhydrous throughout the polymerization. Solvents were dry and free of impurities in order to synthesize high molecular weight polymers and to optimize the solution coating of fibers.

Because of these requirements, polymerization and coating solvents were stirred over drying agents, generally phosphorous pentoxide, and distilled utilizing the apparatus shown in Figure 2 (Appendix 2). For high boiling solvents, reduced pressure distillations were possible using this apparatus. In all distillations, the solvent was allowed to reflux and a constant boiling middle fraction was collected. This middle fraction was stored in a round bottom flask fitted with a rubber septum, the amount of residual water determined using a Karl-Fischer water titrator, and subsequently handled using syringe techniques

to minimize atmospheric exposure. For polymer synthesis, the solvents were distilled daily and contained less than 100 ppm water. For coating purposes, the distilled solvents were used within two weeks and contained between 200 and 500 ppm water. The solvent structures and their boiling points are listed in Table 11, Appendix 3.

4.2 PURIFICATION OF STARTING MATERIALS

4.2.1 Solvents

Tetrahydrofuran(THF:Fisher) was dried by stirring over phosphorous pentoxide or finely crushed calcium hydride for at least eight hours. The dried solvent was then distilled at atmospheric pressure under inert gas purge.

N,N-Dimethylacetamide(DMAC:Fisher) was dried by stirring over phosphorous pentoxide for at least 10 hours. The dried solvent was then distilled under reduced pressure generated by a mechanical vacuum pump to avoid significant degradation.

N-Methyl-2-Pyrrolidone(NMP:Fisher) was dried by stirring over phosphorous pentoxide for at least 10 hours. Phosphorous pentoxide is very effective in removing amine impurities which may be present in amide solvents. The dried solvent was then distilled under mechanically generated vacuum conditions. N-Cyclohexyl-2-Pyrrolidone(CHP:GAF) was dried by stirring over phosphorous pentoxide for at least 10 hours. The dried solvent was then distilled under reduced pressure generated by a mechanical vacuum pump.

4.2.2 Monomers

4,4"-[1,4-phenylene-bis-(1-methyl ethylidene)] bisaniline(Bis P:Air Products) was obtained in high purity as a fine white powder and was further purified by recrystallization from deoxygenated ethanol. To a 1 liter erlenmeyer flask, 900 ml of 100% ethanol was added and nitrogen bubbled through the solvent for 4 hours to deoxygenate the solvent. Deoxygenated ethanol, as well as mild heating and vigorous stirring were necessary to avoid oxidation of the diamine. Approximately 50 grams of Bis P were added slowly to the flask at the reflux temperature. When complete solvation of the Bis P had occurred, the clear, greyish solution was allowed to cool to room temperature in the absence of agitiation. To further induce crystallization, the capped flask was place in a refrigerator for approximately eight hours. The recrystallized Bis P was then isolated via vacuum filtration and washed with cold, deoxygenated ethanol. The crystals were crushed and dried in a vacuum oven for 12 hours at 70°C. Extended drying and /or heating resulted in oxidized material. The monomer was then bottled and stored in a dessicator until needed.

3,3'-Diaminodiphenyl sulfone(DDS:FIC Corporation) was obtained as a relatively pure compound but further purification was necessary to produce high molecualr weight materials. To a 1 liter erlenmeyer flask, 500 ml of deoxygenated methanol was added. Approximately 50 grams of DDS were added to the flask forming a saturated solution while at the solvent reflux. Next, a small amount of deoxygenated water was added to the solution until the precipitation point was approached. White crystals formed upon cooling the solution to room temperature and it was further cooled in a refrigerator for approximately 10 hours. The crystals were isolated by vacuum filtration, washed with cold deoxygenated methanol, crushed, and dried in a vacuum oven for 12 hours at 70°C. The monomer was transferred to a brown bottle, and stored in a dessicator until used.

3,3',4,4'-Benzophenonetetracarboxylicacid Dianhydride(BTDA:Allco Co.) was obtained in monomer grade purity and was white in color. The monomer was essentially monomer grade, however, it was first placed in a forced air convection oven at 150°C for 12 hours immediately before use. This thermal treatment was necessary to remove residual water and dehydrate any remaining diacid groups back to the dianhydride. The BTDA was stored in a dessicator between thermal treatments.
Bis(3-aminopropyl)tetramethyldisiloxane(DSX:Petrarch Systems, Inc., or Silar Laboratories) was acquired in high purity form and was utilized in the synthesis of siloxane oligomers without further purification.

Octamethylcyclotetrasiloxane(D₄:Petrarch Systems, Inc., or Union Carbide) was obtained in high purity and used successfully without further purification.

4.2.3 Synthesis of Aminopropyl Terminated

Polydimethylsiloxane Oligomers

As mentioned previously, the siloxane oligomers used in this work were synthesized through the redistribution of the aminopropyl endblocker with the cyclic tetramer. This anionic equilibration is carried out in bulk utilizing a 3necked round bottom flask equipped with a mechanical stirrer, inert gas inlet, thermometer, condenser, and drying tube as shown in Figure 3, Appendix 2. The reaction quantities were determined by the molecular weight of the desired oligomer as illustrated by the sample calculations in Figure 4, Appendix 2. In a typical reaction, to prepare an aminopropyl terminated siloxane of <Mn>=2500g/mole, 50 grams(0.2012 moles) of bis(3-aminopropyl)disiloxaneand 4.5302 grams(1.5273 moles) of D₄ were introduced to the flask. The flaskwas heated to 80°C with stirring and 5.03 grams(1 wt. %) of tetramethyl ammonium siloxanolate catalyst was added. The reaction proceeded for 48 hours under N_2 at 80°C to ensure complete equilibration. Next, the reaction temperature was raised to 150°C for 3 hours in order to decompose the transient quaternary catalyst. After cooling, the mixture was transferred to a vacuum distillation apparatus, which removed the remaining cyclics and decomposed catalyst. The number average molecular weight, as determined by titration of the primary amine endgroups with 0.1N alcoholic HCI, and confirmed by proton NMR, was 2465 g/mole.

4.3 SYNTHESIS OF POLYIMIDE HOMO- AND COPOLYMERS

All of the imide containing homo- and copolymers were prepared utilizing the classical two step method mentioned previously. The amic acid precursors were then cyclized to the imide via thermal treatment as well as a novel solution cyclodehydration procedure. Representative synthetic procedures will be outlined for each amic acid-siloxane as well as for subsequent imidization by the two techniques mentioned.

The amic acid precursors were synthesized in the apparatus in Figure 5, Appendix 2. This apparatus consisted of a 3-necked round bottom flask fitted with a mechanical stirrer, inert gas inlet, drying tube, and addition funnel (optional). This reaction apparatus was assembled, purged with inert gas, and

flamed immediately prior to each synthesis in order to remove any residual moisture on the glassware. The amic acid siloxanes were synthesized in a series of 10, 20, 30, and 50 weight percent siloxane compositions utilizing the 2465 g/mole oligomer. Typical synthesis quantities and procedures will be described for a 10 and a 50 weight percent siloxane-amic acid copolymer.

4.3.1 High Molecular Weight Poly(Amic Acid)s

The amic acids using BTDA/Bis P and BTDA/DDS were synthesized by an identical procedure except that the Bis P is not soluble in NMP, and thus was synthesized in DMAC. No addition funnel was used in the synthesis of the homopolymers. After flaming and purging the apparatus (Figure 5, Appendix 2) with N₂, 10.6756 grams(0.0310 moles) of Bis P were quantitatively added to a 250 ml flask, while rinsing with DMAC, and stirring. After the diamine had dissolved, 10.0000 grams(0.0310 moles) BTDA were then added to the reaction flask with NMP. At this point, the reaction product became viscous and a slight exotherm (~10°C) was observed. The reaction was allowed to proceed for eight hours, during which time the solution viscosity increased dramatically. The final Bis P based poly(amic acid) was clear and golden yellow in color while the DDS based amic acid was a clear golden orange. Total DMAC (or NMP) used was 110 ml.

10 Weight Percent Siloxane Composition: (Siloxane <Mn> = 2465 g/m) Total reactant and solvent quantities were 8.0000 grams(0.0248 moles) BTDA, 8.2879 grams(0.0241 moles) Bis P, 1.8098 grams(0.0007 moles) polysiloxane oligomer, 60 ml DMAC, and 70 ml THF. The standard reaction setup was assembled, flamed and purged. First, 8.0000 grams of BTDA were added to a 250 ml flask with 40 ml DMAC and 40 ml THF. After the BTDA had dissolved, the siloxane was dissolved in 15 ml THF in an addition funnel and added dropwise to the solution over a period of 10 minutes; after addition was complete, the addition funnel was rinsed with 5 ml of THF. Next, the Bis P was dissolved in the addition funnel in 10 ml DMAC and 10 ml THF, then added dropwise to the solution, and the addition funnel rinsed with 10 ml DMAC. This resulted in a clear, viscous solution and the reaction was allowed to proceed for eight hours.

50 Weight Percent Siloxane Composition: (Siloxane <Mn> = 2465 g/m) Total reactant and solvent quantities were 5.0000 grams(0.0155 moles) BTDA, 4.0718 grams(0.0118 moles) Bis P, 9.0718 grams(0.0037 moles) polysiloxane oligomer, 40 ml DMAC, and 120 ml THF. The standard reaction setup was again assembled, flamed and purged. First, 5.0000 grams of BTDA were added to a 300 ml flask with 30 ml DMAC and 40 ml THF. After the BTDA had dissolved, the siloxane was dissolved in 40 ml THF in an addition funnel and added dropwise to the solution over a period of 20 minutes, and the funnel rinsed with 10 ml THF. Next, the Bis P was dissolved in the addition funnel in 10 ml DMAC and 20 ml THF, added dropwise to the solution, and the addition funnel rinsed with 10 ml THF. The reaction generally was allowed to proceed for eight hours. Often at high siloxane contents, it was necessary to add more THF (~30 ml) in order to keep the solution clear and homogeneous. In cases where the solids concentration went below 10%, the reaction was allowed to run for 24 hours in order to reach high molecular weight.

4.3.2 Imidization

4.3.2.1 Thermal (bulk) imidization

All of the poly(amic acid)s synthesized were cyclodehydrated to the polyimide (in bulk) via a thermal curing cycle for two reasons: first, to check that the amic acid was high molecular weight, before solution imidization, and second, as a control to assure that the solution imidized polymers exhibited similar or identical properties to the conventionally cured polyimides. The amic acid solution was taken from the reaction flask and poured onto a clean dry glass plate and drawn into a smooth, flat film with a doctor blade, set at thicknesses ranging from 20 to 40 mils. The glass plate was then placed in a vacuum oven at ~ 70°C and vacuum was gradually raised to full vacuum over a period of 1 hour, using a mechanical pump. The film was left under vacuum an additional hour to remove as much of the reaction solvent as possible. Next, the

glass plate was set in a 100°C forced air convection oven for 1 hour. The temperature was then raised to 200°C for 1 hour, then 300°C for another hour. The film remained in the oven as it cooled slowly to ~100°C at which time the glass plate was taken out of the oven and the film was gently removed using a razor blade to pry up a corner. Some specimens required immersion in distilled water to remove the film.

4.3.2.2 Solution Imidization

As mentioned previously, a novel solution imidization can be used to cyclize amic acid while retaining high molecular weight. This method employed a high boiling solvent/azeotroping agent combination to imidize the amic acids. The reaction setup was comprised of a 250 ml 4 necked round bottom flask, condenser, Dean-Stark trap, thermometer, mechanical stirrer, and stopper; the flask was immersed in a silicon oil bath as illustrated in Figure 6, Appendix 2. Solvent values were determined solely on the amount of polymer and corrected for the amount of solvent in the amic acid solution. Any THF was neglected, as it boiled rapidly at imidization temperatures, and was quickly collected in the Dean-Stark trap. These imidizations were run at a total solids concentration of ~15% using an NMP/CHP cosolvent ratio of 80/20.

The NMP/CHP mixture was stabilized at 160°C at which point the amic acid solution was added slowly in order to maintain temperatures greater than

150°C. After all the amic acid solution was added, the reaction was allowed to proceed for at least 14 hours at 160°C, after which time the solution was dark brown and viscous. For lower boiling solvent mixtures such as DMAC/CHP, the reaction was allowed to proceed at 150°C for 24 hours. Finally, the solution was cooled and diluted with DMAC or NMP to 10% solids, then precipitated in a 50/50 methanol/water mixture. Higher siloxane composition copolymers were precipitated in mixtures with higher proportions of water. Finally, the polymer was dried in vacuum 24 hours at ~100°C resulting in an 80% yield.

4.4 CHARACTERIZATION

4.4.1 Titration of Functional Monomers and Oligomers

A Fisher Scientific Titrimeter II automated potentiometric titrator was used to titrate aminopropyl terminated polydimethylsiloxane oligomers and aromatic diamines used in the syntheses. A standard calomel electrode and a reference electrode were utilized as the titrator automatically determined endpoints.

Solutions were prepared containing the functional monomer and an appropriate solvent. The electrodes were then immersed in the solution and the sample was titrated until an endpoint was obtained. At this point, a computer recorded the endpoint volume as judged by the potential (in millivolts). To alleviate changes due to solvent, a solvent blank was also titrated with the same titrant until the endpoint potential was reached. This volume was then

subtracted from the sample endpoint volume. The molecular weight of the sample could be calculated as follows:

Mn = (number of endgroups per molecule) x (sample weight)

(titrant concentration) x (corrected titrant volume)

The aminopropyl terminated siloxane oligomers were dissolved in ~100 ml isopropanol and the primary amine endgroups were successfully titrated with 0.1N HCI. Aromatic diamines were dissolved in 50 ml distilled chlorobenzene and 25 ml glacial acetic acid and titrated with 1N HBr. These molecular weights were determined to assess diamine monomer purity.

4.4.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography was used as a qualitative analysis of molecular weight and molecular weight distribution of soluble polyimides and siloxane oligomers. Samples were run in THF using a Waters instrument fitted with ultrastyrogel columns and ultraviolet and refractive index detectors. Flow rate used was 1.0 ml / min.

4.4.3 Intrinsic Viscosities

Intrinsic viscosities were used as a qualitative measure of relative molecular weight. The viscosity measurements were obtained using Cannon-

Ubbelohde dilution viscometers with capillary sizes 75 and 100. Samples were run at 25°C in distilled NMP. Four concentrations were analyzed and a linear regression was calculated in order to extrapolate to zero concentration.

4.4.4 Fourier Transform Infrared Spectroscopy (FT-IR)

Monomer and polymer structures were identified using a Nicolet MX-1 spectrophotometer. Monomers were run as KBr pellets. Polymers were analyzed as either free standing thin films or as thin solution cast coatings on salt plates. The appearance of the imide bands at 1778 cm-1 and 725 cm-1 and the disappearance of the amic acid band at 1546 cm-1 were evaluated in order to identify imide structures.

4.4.5 **Proton Nuclear Magnetic Resonance (1H-NMR)**

An IBM 270 MHz analyzer was used to obtain structural and compositional information for these copolymers. The Bis P based samples were generally dissolved in deuterated chlorform in a 5% solution and run at room temperature. Monomers and DDS based polyimides were dissolved in deuterated DMSO in 5-10% solutions. The amount of siloxane incorporated was calculated by ratioing the integrated peak intensity due to siloxane methyls and the aromatic protons.

4.4.6 Differential Scanning Calorimetry (DSC)

Glass transition temperatures of the polymers and melting points of monomers were analyzed on a Perkin Elmer Model-2 DSC and a Dupont Model 2100 DSC. Samples were run at ambient temperatures under nitrogen and at subambient temperature under helium, since liquid nitrogen was the coolant. Both upper(imide) and lower(siloxane) transitions were obtained and the scan of the second heating of each specimen was used. The samples were generally run at 10°C/min and the Tg was taken as the midpoint of the change in slope of the baseline.

4.4.7 Thermomechanical Analysis (TMA)

In evaluation of extension and expansion data, a Perkin Elmer System Thermomechanical Analyzer was used. Since specimens were thin films, they often had to be stacked to obtain usable thicknesses. Expansion measurements were run at 10°C/min using a quartz probe at zero loading. Extension measurements were run at 10°C/min using an extension analysis probe and sample tube(shown in Figure 7, Appendix 2), used with the Perkin Elmer TMS-1. Coefficients of thermal expansion and extension were reported in unitless quantities (10⁻⁶ or ppm per °C⁻¹).

4.4.8 Dynamic Mechanical Analysis (DMTA)

In order to determine primary mechanical transitions as a function of temperature, a Polymer Laboratories Dynamic Mechanical Thermal Analyzer was used. Free standing films with thicknesses 3-10 mils were used. Frequency was set at 1 Hz and heating rate 5°C/min. This allowed for determination of upper and lower transitions, by obtaining both Tan δ and storage modulus (E").

4.4.9 Thermogravimetric Analysis (TGA)

Thermal stability of both fibers and films was investigated with a Perkin-Elmer System-2 Thermogravimetric Analyzer and a Dupont 2100 Thermogravimetric Analyzer. All samples were run at 10°C/min in a flowing air environment. Polymers were run as thin films and fibers were knotted loosely (5 or 6 times) and handled carefully with tweezers while placing in a platinum pan connected to an electronic microbalance. Temperature ranges were usually 50°C to 725°C. Weight loss was monitored as a function of time or temperature.

4.4.10 Water Contact Angle

Water contact angle measurements were conducted using a Kernco Model G-1 Goniometer. Samples were prepared by taping thin films to

ferrotype plates using double sided tape, and insuring a flat surface.

Measurements were conducted at room temperature using distilled water drops of ~2 microliters in size. An average of five readings on various parts of the film was taken as the value reported, while considering an error of \pm 2°.

4.4.11 Moisture Uptake

In all cases, the moisture uptake of coated and uncoated fibers was followed gravimetrically as a function of time until a constant value was reached. All fibers were dried in a vacuum oven at 120°C for 24 hours before weighing. The fibers were then exposed to three environments, each having a different relative humidity. For the fibers, each sample was suspended in a wire mesh screen in a l liter jar filled with 300 ml distilled water. The water was kept at approximately 95°C and the system was covered with a watch glass. The fibers were removed, and carefully blotted in order to remove any condensed water droplets before weighing. This system was a qualitative measure of approximate 100% relative humidity environment in order to set the shortest time limit in which the fibers became saturated. In the second case, fibers were dried and set in a conditioning room (65% relative humidity and 70°F+/- 2°F) and weighed periodically until a constant weight was reached. In the third experiment, fibers were suspended in beakers above a 51 % (by weight) solution of concentrated aqueous sulfuric acid solution which when

held at 25°C corresponds to a 35% relative humidity atmosphere. The percent of moisture uptake was calculated by the formula:

% moisture uptake = <u>conditioned weight - dry weight x 100</u> conditioned weight

4.4.12 Fiber coating

The fibers used in this research were 1.2 denier/filament polybenzimidazole (PBI) and 1.6 denier/ filament Kevlar aramid multifilament yarns which were supplied by Hoechst-Celanese and Dupont, respectively. Both fiber types were drawn, unsized, and had no surface pretreatments. Before coating, both fiber types were dried at 120°C for 24 hours to reduce the moisture present. The multifilament yarns were coated by immersion in a polyimide solution, and pulled through rollers to remove excess coating. The concentration of the coating was determined by the solution viscosity, solubility, and coating uptake on the fibers. Generally, solutions of 15-20% solids in NMP or DMAC were used in order to minimize the amount of solvent used and to optimize "homogeneous wetting" characteristics of the solution. Coated fibers were then dried in a vacuum oven at 220°C for 48 hours. Approximately 0.3% solvent remained, which is due to the highly polar solvents, coating, and fibers.

Chapter V RESULTS AND DISCUSSION

5.1 INTRODUCTION

The research which is discussed in this chapter is divided into three general sections. First, the synthesis of precursors and final polymer types is discussed. The second section will be concerned with structural determination and pertinent polymer characterization. A third section will discuss the coated fibers and characterization which is relevant to final performance properties.

5.2 SYNTHESIS OF HIGH MOLECULAR WEIGHT POLYIMIDES

5.2.1 Synthesis of Functional Siloxane Oligomers

Aminopropyl terminated polydimethyl siloxane oligomers were successfully prepared by equilibration reactions of a cyclic species(D_4) with an appropriate disiloxane endblocker(DSX). As illustrated previously, a basic catalyst attacks the electropositive silicon of the D_4 , which opens the ring and generates siloxanolate ions. Because of the similar reactivities of the Si-O bonds in the dimer and the cyclic, an exchange reaction between the two results in a growing siloxane chain. In addition, the silicon-carbon chain is

more covalent in nature than the silicon-carbon bond, and thus is stable during the polymerization.

The oligomers used in this research were prepared in bulk at 80°C under anhydrous conditions. After 48 hours, the temperature was raised to 150°C to decompose the transient catalyst into methanol and trimethylamine. Vacuum distillation removed these by-products as well as remaining cyclics. The amount of cyclics at equilibration was found to be ~8% as determined by chromatographic methods. As was shown by the calculations of oligomer molecular weight, the D₄-DSX ratio is used to predict the set point which thermodynamically favors a high concentration of linear species and thus the siloxane molecular weight.

These oligomers were characterized to determine <Mn>, structure, and presence of cyclics. The <Mn> was determined accurately by potentiometric titration with alcoholic 0.1N HCI. GPC was used to confirm the absence of low molecular weight cyclics. Infrared spectroscopy and proton NMR were used to identify the siloxanes. Important IR Bands are listed in Table 12, Appendix 3, for siloxanes (38). In proton NMR, a sharp singlet at 0.3 ppm corresponding to the silicon methyl protons is normally used to determine the presence of a silicone compound. It is possible to calculate the <Mn> in oligomers up to a certain molecular weight (up to 10,000g/mole) by ratioing the peak area integrations of the end groups with silicon methyl group integrations.

5.2.2 Synthesis of Poly(Amic Acid) Precursors

The classical two step process for imidization was utilized to synthesize the polyimides used in this research. All synthetic procedures involved the generation of an amic acid or amic acid siloxane through the reaction of an aromatic dianhydride with an aromatic diamine and the appropriate aminopropyl terminated siloxane oligomer. Synthetic conditions are discussed below.

The reaction conditions during the synthesis of high molecular weight poly(amic acid)s were extremely critical. In general, any step growth reaction such as this requires highly pure (>99.5%) monomers. Side reactions, branching, and low molecular weight polymers with inferior qualities are direct consequences of impure starting materials. In the case of polyimides, it has been reported that the highest molecular weight polyimide is prepared by adding solid dianhydride to a rapidly strirred diamine solution. This minimizes the atmospheric exposure of the dianhydride and thus, minimizes the possibility of hydrolysis.

Two major reaction considerations include the choice of solvent, and exclusion of moisture in the system. Water severely limits molecular weight due to hydrolysis causing degradation, side reactions and a low molecular weight polymer. The major sources of water include solvents, dianhydrides, and

premature imidization which may evolve water. For these reason, dianhydrides are dried immediately prior to use, solvents are distilled, and reactions are performed at room temperature or below. The reaction apparatus is flamed previous to use, and the reaction is run under a dry nitrogen atmosphere.

Solvents are extremely important, not only because of residual moisture or impurities, but also other factors including the solubilizing power, and the practical limitations of these solvents. Solubility is crucial, because the monomers must stay in a homogeneous solution in order to react in a 1:1 ratio. Dipolar aprotic solvents such as DMAC or NMP were excellent solvents for the diamines, dianhydrides, and amic acids, but did not dissolve the siloxane oligomers. Conversely, the oligomers were soluble in solvents such as THF, methylene chloride, and chloroform, which did not dissolve the other starting materials. Because of this, a DMAC/THF or NMP/THF cosolvent system was used. Although DMAC and NMP are high boiling amide solvents, and are difficult to quantitatively remove from the resultant polymers, they were determined the best in overall terms after investigation of other solvents.

In the polyamic acid siloxane, another important synthetic parameter must not be overlooked. In order to achieve a random copolymer, the order of siloxane addition was regulated in order to avoid premature chain extension of the siloxane oligomer. This "agglomeration" of oligomer was avoided by a very slow addition of the siloxane oligomer into a solution of the overall

stoichiometric equivalent of anhydride. In addition, this BTDA-capped siloxane oligomer was more soluble in the dipolar aprotic solvating medium. The difficulty in maintaining a homogeneous solution occurs at the beginning of the addition of siloxane due to insolubility of the siloxane and at the addition of the diamine. At this final point, as the diamine is added, the reaction product solution was slightly cloudy due to the solubility change of growing polymer in the THF/NMP solution.

5.2.3 Imidization

5.2.3.1 Thermal imidization

Bulk thermal and solution thermal imidizations were used and properties of the two polymers were compared. The thermal cyclodehydration (in bulk) was carried out by casting a thin film onto a glass plate and drawing it into uniform thickness with a drawing bar set at 20-40 mils. It was extremely important to cure the amic acids in a consistent stepwise fashion. The stages from 70°C (in a vacuum oven) to 100°, 200° and 300° C in a forced air convection oven were necessary to accomodate the rising glass transition temperature of the polyimide. Since the Tg continually increased as more imide groups were formed, it was necessary to maintain the oven temperature above the Tg to allow sufficient chain mobility necessary for quantitative ring closure. These films were insoluble at low siloxane concentration, which was an obvious disadvantage, since no solution characterization was possible, and thus no fiber coating. The siloxane segments were not harmed by the extremely high oven temperatures, as illustrated by the polymers' excellent thermal and mechanical properties.

5.2.3.2 Solution Imidization

In this research, NMP (and/or DMAC) was used to solvate the polymer system while CHP was used as an efficient azeotroping agent which removed the water of imidization from the system preventing the hydrolytic degradation of the remaining amic acid. CHP was chosen for this purpose since it has high boiling and good solvating characteristics. In addition, below 150°C it is miscible with water, yet above 150°C, the two are immiscible. Earlier efforts revealed the need for both NMP and CHP since using just one resulted in molecular weight degradation or premature polymer precipation from solution. Based on previous work, and NMP/CHP cosolvent ratio of 80/20 was used to imidize the poly(amic acid)s. The poly(amic acid) synthesis and subsequent solution imidization are depicted in Scheme 17, Appendix 1.

5.3 STRUCTURAL CHARACTERIZATION

5.3.1 Fourier Transform Infrared Spectroscopy

In both of these imidizations, FT-IR was used to monitor the progress of imidization. The amic acid can be identified by amide and carboxylic acid bands around 3300 cm⁻¹ and a saturated region between 1750-1000 cm⁻¹ which is due to tremendous hydrogen bonding interactions between polar groups. After imidization, as shown in Figure 8, Appendix 2, the broad absorbances around 3300 cm⁻¹ have disappeared and the broad region between 1750-1000 cm⁻¹ has sharpened immensely due to the reduction of highly polar hydrogen bonding groups. New bands appeared at ~1778 and 725 cm⁻¹ which are due to imide groups. The siloxane methyl stretch around 3000 cm⁻¹ is visible and its shape and intensity are highly dependent upon the siloxane content. Other siloxane bands occur at 1260 cm⁻¹, 1094 cm⁻¹, and 1028 cm⁻¹.

5.3.2 Proton Nuclear Magnetic Resonance

In addition to FT-IR, structural information and copolymer composition were analyzed by proton NMR. NMR was used to determine <Mn> of siloxane oligomers. After determining that the system was free of cyclics, the strong resonance at 0.3 ppm was indicative of the methyl groups attached to the silicon. As mentioned, by integration of the amine end groups and the siloxane methyl groups, it is possible to calculate molecular weight up to a limiting value, which depends on the amount of endgroups detected.

Proton NMR was also valuable in determining residual amic acid, copolymer structure, and composition. A typical solution imidized polyimide is illustrated in Figure 9, Appendix 2. The absence of peaks above 10 ppm due to carboxylic structures demonstrates the quantitative conversion of amic acid to imide. This spectrum shows the expected aromatic and aliphatic proton resonances as labelled. By ratioing the aromatic proton region to the siloxane methyl groups, it is possible to determine the amount of siloxane incorporated. When higher amounts of siloxane are charged into the reaction vessel, it is more difficult to incorporate all the siloxane. Generally, 80-90% charged is incorporated. Finally, a relatively small amount of residual solvent is observed in the aliphatic region at approximately 2 ppm (CHP/NMP). The small amount of solvent and absence of amic acid groups indicated that the polymer solubility was not due to solvent plasticization and/or incomplete conversion to imide.

5.4 SOLUBILITY

One basic premise of this research is the fact that these polyimides are soluble yet totally imidized. This fact opens up the potential of solution properties advantageous for practical applications as well as determination of molecular weight and structure. Solubility was affected by both the

incorporation of flexible siloxane segments, as well as the method of imidization. By observing the sample trends, it was evident that solubility depended on the weight % of siloxane oligomer and not the siloxane molecular weight. Table 13, Appendix 3 illustrates the solubility for 3,3'-DDS based polyimides. It is evident that the solubility increases as the siloxane content is increased. The effect of imidization method on solubility is also illustrated in this table. Bulk (conventionally thermal) imidized samples were not soluble until high siloxane compositions were attained. Finally, the effect of a more flexible diamine, Bis P, is illustrated in Table 14, Appendix 3. These BTDA-Bis P based polymers were more soluble than the DDS based , however, the trends are similar as the siloxane contents were increased.

The reasons for this enhanced solubility are not actually clear. For some of the polyimide systems which are rendered soluble by solution imidization, it may be proposed that crosslinking and/or branching reactions which occur during thermal cyclization may be avoided due to less rigorous temperatures used in solution. In addition, highly symmetric monomers are not rendered soluble, as they precipitate before complete imidization. This fact supports high chain rigidity as the reason for polyimide insolubility. One final observation regarding these solution imidized polyimides was that solutions greater than 20 weight percent solids which were heated to ~200°C (i.e. in a drying oven) or sat

in solution for 3 or 4 days at room temperature in DMAC or NMP seemed to gel. When diluted and heated slightly in solution, the gel redissolved.

One possibility for this is that after solution imidization, the sudden polymer isolation into a nonsolvent may 'lock' the polyimide chains into a unique conformational state. When in solution, the chains may be driven to their thermodynamically stable state. At high concentrations, at room temperature in solution, chain mobility is adequate enough for a conformationally favorable chain reorganization to occur. It is evident that more research should be done in this area.

5.5 MOLECULAR WEIGHT CHARACTERIZATION

5.5.1 Intrinsic Viscosity

Relative molecular weights were determined in distilled NMP at 25°C. Values for solution imidized samples are listed in Table 15, Appendix 3. In polyimide jargon, since these polymers have been historically insoluble, a film which was "finger-nail creasable" and exhibited acceptable mechanical properties was considered high molecular weight. In general, polyimides with excellent mechanical properties and creasable films had intrinsic viscosities of 0.5 dl/g or higher as illustrated in Table 15.

5.5.2 Gel Permeation Chromatography

Gel permeation chromatography was used as a qualitative indication of molecular weight and molecular weight distribution. Figures 10 and 11 (Appendix 2) are GPC curves for a 30 and 50% siloxane (2465g/mole) in THF. Successful analysis was only possible in THF soluble samples. After stringent precipitation, a monomodal, Gaussian distribution was evident. In general, the symmetry, breadth, and shape of these curves was noted relative to physical properties of films. Polyimides with lower intrinsic viscosities generally eluted at high volumes, indicating low molecular weight. As higher amounts of siloxane were incorporated (50% vs. 30%), the distribution had a low molecular weight skew, probably due to low molecular species which did not react because of unincorporated siloxane. In general, however, the polymers had no extremely low or high molecular weight segments and the distribution of polymer chains was fairly symmetric.

5.6 SURFACE PROPERTIES

A unique property of siloxane containing polyimides is the ability of low energy nonpolar siloxane to migrate to the surface of the polymer. Because of this, polymers, and thus coated fibers will exhibit a predominately nonpolar surface. This low surface energy corresponds to surface properties such as low abrasion and friction, high lubricity, good adhesion of coating to fiber, and

excellent water and soil repellency. The migration of silicon to the surface is evident by X-Ray Photoelectron Spectroscopy (XPS), an analytical technique which probes the first few hundred angstroms of a solid surface. Figure 12, Appendix 2 shows DDS based polyimides which exhibit silicon on the surface. In addition, a qualitative measurement of siloxane surface segregation is water contact angle. Due to its high surface energy, water placed on the low energy surface beads up. A higher contact angle corresponds to more siloxane on the surface. Table 16 (Appendix 3) lists the water contact angle of various DDS and Bis P based films.

5.7 WATER ABSORPTION STUDIES (LIQUID AND VAPOR)

Moisture regain and moisture uptake are important properties for various textile applications. For apparel concerns, a high fiber regain is desired to improve heat and moisture transmission, which in turn provides comfort to the garment. In this case, certain functional groups such as carboxyl, hydroxyl, and amide groups employ hydrogen bonding to absorb water. These polar groups are generally advantageous in designing comfortable apparel.

These high moisture uptake values, however, are detrimental to fibers being employed as high strength, high thermal stability fibers for aerospace and industrial applications. Some research suggests that heat properties are affected by moisture transport. Polybenzimidazole, for example, absorbs ~15%

water, while Kevlar aramid absorbs ~7% under standard conditions (65% R.H @ 21°C). Amounts such as these render the fiber inferior in such uses as fiber reinforced composites and in applications such as heat shielding fabrics.

Water absorption is also a detrimental property of polyimides, themselves. Depending on the chemical structure, i.e. the polymer polarity, these materials can absorb up to 5 weight percent water as determined by soaking in distilled water at 25°C. Water absorption characteristics affect dimensional stability, corrosion resistance, and insulating properties. The presence of water in these systems also severely affects ultimate thermal and mechanical properties. In both fibers and films, the lowest possible water absorption is desirable in terms of increasing electrical resistance, limiting stress build up due to swelling in humid environments, preventing protected metals from corrosion, increasing insulating properties, and increasing thermal and mechanical properties.

Siloxanes, although very water permeable, absorb typically less that 0.3% by weight and have been well recognized as encapsulants for various applications. A benefit of siloxane block incorporation thus includes water repellence, and preservation of fiber and polymer properties in humid environments. To evaluate the effectiveness of decreased water absorption due to siloxane incorporation in the copolymer and as a protective coating for the fibers, the samples were exposed to varying water environments and

removed, then weighed to determine water or moisture uptake versus time until a constant weight was achieved.

Fibers were exposed to three different humidity conditions: a simulated 100%, 65% @21°C, and 45% relative humidity. The fibers were extended in the vapor above the solutions, checked for any vapor condensation, and weighed. Figures 13, 14, and 15, Appendix 2, illustrate the effect of coating on fiber moisture uptake. For the times examined, it is evident that moisture absorption was significantly reduced upon siloxane incorporation and continued to decrease with increasing siloxane content.

5.8 THERMAL PROPERTIES

5.8.1 Glass Transition Temperature

The glass transition temperature is an important property of polymers in general since this softening point defines their upper and lower use temperatures. A distinguishing feature of polyimides is their high Tg's in the range of 250-500°C, depending on the chemical structure and method of determination. Likewise, siloxanes are known for their extremely low Tg's, ranging from -123°C (high molecular weight) to -115°C (low molecular weight oligomer). Because of these extreme differences, these polyimides behaved as two phase systems possessing both 'hard' and 'soft' segments.

Differential scanning calorimetry was used as an analytical technique to determine Tg's. The upper Tg values of BTDA/3,3'DDS polyimides are listed in Table 15 (Appendix 3). First, it was observed that bulk and solution imidized values were quite close, the solution imidized materials only slightly depressed from bulk counterparts. This depression may be due to small amounts of crosslinking in the bulk polymer, as well as a small amount of residual solvent in the solution polymers, which acted as a plasticizer. Second, the values illustrate more of a Tg depression in lower <Mn> siloxane segments, as compared to higher molecular siloxane segments. From this, it was observed that the higher molecular weight siloxane oligomers allowed for a certain degree of a microphase separated morphology while lower molecular weight oligomers tended to phase mix with the imide phase. This allowed for the incorporation of moderate amounts of siloxane without sacrificing upper use temperature.

For this reason, the siloxane molecular weight used in the preparation of copolymers was ~2500g/mole. This microphase separated system is again evident by the two (both high and low) glass transition temperatures; the upper Tg values of a BTDA/Bis P and a BTDA/3,3'-DDS series of copolymers are listed in Table 15, Appendix 3. In general the lower Tg values (not listed in table) range from -123°C for 50% siloxane to -100°C for lower amounts, such as 10%, whose lower transition temperatures were detected by Dynamic

Mechanical Thermal Analysis. Again, the upper Tg values were slightly depressed, depending on the amount of siloxane incorporated. When the dimer is used, microphase separation does not occur, a single copolymer Tg is observed, and a Tg depression is highly sensitive to siloxane content. Figure 16 (Appendix 2) illustrates the Dynamic Mechanical Thermal (1Hz, 5°C/min) behavior of a Bis P based homopolymer, 20%, and 50% (2500g/mole) copolymers, indicating a distinct upper and lower transition for siloxane and imide components.

The extension and expansion behavior of some of these materials was measured in order to match the thermal mechanical behavior of the various fibers and polyimide films. The extension behavior of coated fibers was measured in order to evaluate the effect of the coating on thermal-mechanical properties of the fibers. The coefficents of the coated fiber did not change, which was expected since the fiber substrate mechanical properties should dominate over the thin polymer coating. The expansion coefficients increase as the amount of siloxane was increased, demonstrating the potential to tailor the properties to the desired substrates. The volume expansion coefficients and extension coefficients for various polyimide copolymers and fibers are listed in Table 17, Appendix 3.

5.8.2 Thermooxidative stability

The thermal stabilities of both polyimides and siloxanes have been well documented. Thus, the copolymers were expected to have excellent thermal stabilities. Thermooxidative stabilities were assessed using Thermogravimetric Analysis. Unless otherwise noted, samples were run in air at 10°C/min from 50°C to 750°C. TGA scans of representative BTDA/DDS and BTDA/BisP based copolymers are shown in Figures 17 and 18 (Appendix 2). In general, as siloxane content was increased, the onset of degradation occurred at lower temperatures. These copolymers still maintained good thermal stability even at high levels of siloxane. These solution imidized polyimides exhibited thermal stabilities which were identical to the bulk imidized counterparts. In an oxidative atmosphere, the char yields at high temperatures were found to be proportional to siloxane content. This suggested that a silicate type structure was the principal degradation product in air. Although not studied in depth, the degradation begins initially at temperatures ~400°C first by depolymerization of linear siloxane back into cyclics, followed by a degradation of the aliphatic portion of the polymer. In addition to random chain scission at even higher temperatures, BTDA based polyimides may undergo crosslinking reactions.

The poly(imide siloxane) coated fibers were examined for thermooxidative stability. In order for the coating to be protective, the coated fibers needed to exhibit an equal or greater thermal stability than the uncoated. The reason for

this limiting thermal behavior requirement was that the other benefits such as decreased water absorption and increased lubricity could be imparted without sacrificing original fiber thermal properties.

For PBI fibers, an important property is stability at high temperatures for short times. At longer times, however, the PBI is susceptible to oxidation which renders the fiber impractical for extended time at high temperatures. Figure 19, Appendix 2, illustrates the thermal degradation behavior of PBI fibers coated with a homopolymer and a 10%(2500) siloxane-imides containing different amounts of siloxane. Figure 20, Appendix 2 illustrates the same effect (with identical coatings) on the thermal stability of Kevlar fibers. Although not an absolute method of thermal stability, Thermogravimetric Analysis of low siloxane content coatings demonstrated the similarities of polyimide and fiber stabilities. Also evident is the amount of water present in uncoated fibers as evidenced by a weight loss at 50-100°C.

Chapter VI

CONCLUSIONS

This research had three main objectives. The first objective was to synthesize and characterize soluble, high molecular weight polyimide and poly(imide siloxane) copolymers by a novel solution technique. Secondly, these polymers were formulated into coatings for fibers by controlling the coating process, solution concentration and thus viscosity and coating uptake. Finally, these fibers were characterized according to the predicted changes in properties, namely hydrophobicity, thermal behavior, and thermooxidative stability.

A series of thermally stable poly(imide siloxane) copolymers was achieved by the incorporation of flexible aliphatic siloxane segments into the polymer backbone. The polymers were synthesized in two steps. The first step included the generation of a poly(amic acid) precursor. In this step, a THF/DMAC cosolvent system was used to solvate all species. The final polymers were synthesized in the second step, which employed a novel high temperature solution imidization of the amic acid precursor. In this step, a "coamide" solvent system was developed which consisted of a mixture of CHP/NMP, where the

NMP performed the task of solvation while the CHP was necessary to eliminate the water of imidization.

A series of poly(imide siloxane) copolymers were prepared where the siloxane content was 10, 20, 30, and 50% of the total copolymer. All physical properties were found to be dependent upon siloxane oligomer molecular weight, weight % of siloxane in the copolymer, and the particular diamine (3,3' DDS or Bis P) copolymerized. Upper glass transition temperatures decreased from ~270°C for the homopolymers to ~205°C for copolymers with 50% siloxane. The onset temperature of degradation as measured by Thermogravimetric Analysis, decreased as siloxane content increased. Thermal expansion coefficients increased as the siloxane content increased from ~5, for a homopolymer, to ~30, for a 70% siloxane-imide (units are expressed as 10⁻⁵ ppm /°C). XPS and water contact angles of poly(imide-siloxane) film surfaces confirmed the presence of a siloxane dominated surface. This siloxane dominated surface established the basis of the coating's hydrophobic nature.

Once the polymers were synthesized and characterized, they were dissolved in different solvents at different concentrations. It was determined gravimetrically that approximately 25-30% of the polymer remained on the fiber after coating and drying. Solvent residues were made negligible by employing concentrated solutions and by drying the fibers meticulously after coating.

Fiinally, the coated fibers were evaluated with respect to moisture uptake, thermooxidative stability, and thermal expansion coefficient. Coatings with 10% siloxane were found to significantly lower the amount of moisture uptake as measured at three different relative humidities. In general, the moisture uptake of PBI fibers was decreased from ~14% for the uncoated fibers to 6% for fibers coated with a 10%(2500) siloxane-imide. Likewise, the moisture uptake for the Kevlar aramid fibers was reduced from ~7% for the uncoated fibers to less than 2% for the coated fibers. Evidently, the coatings contained sufficient amounts of siloxane, imparting a hydrophobic surface. These coatings acted as a barrier, decreasing the driving force for water vapor diffusion.

Although measured dynamically, the thermal stability of the coated fibers was enhanced by the 10% siloxane copolymer and the homopolymer coatings. The coated fibers exhibited an increase in the onset of degradation temperature of approximately 15°C. This apparent increase in thermal stability was indicative of increased resistance to oxidation in a high temperature environment.

The purpose of measuring thermal extension and expansion coefficients was to establish a basis for matching the thermal-mechanical behavior of fibers with the polymers in order to predict the potential "combined" thermalmechanical behavior of the substrate and the polyimide. Thermal expansion and extension coefficients were found to be relatively similar, depending on the

amount of siloxane present, indicating that the potential existed for these polyimides and poly(imide siloxane)s to be used as matrix resins for reinforcing fibers such as polybenzimidazole and Kevlar aramid.

Although these tests were not conclusive as to the marketability and overall properties of this polymer as a fiber coating, they did demonstrate that these coatings were effective as protective fiber coatings for specific applications and environments. A poly(imide siloxane) containing 10% (<Mn>= 2500g/mole) siloxane exhibited a hydrophobic protective surface without sacrificing high temperature mechanical properties and thermooxidative stability.

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APPENDIX I

SCHEMES







(R and R' are aromatic structures)

Scheme 2 Classical Synthesis of Polyimides (28)







Scheme 4 Undesirable Species Formed During Thermal Imidization (48-50)









ISOIMIDE

Scheme 5 Isoimide Formation During Chemical Imidization (51-53)





.







ADDITION THROUGH DOUBLE BOND

Scheme 8

Synthesis of Bismaleimides (85, 86)







Scheme 10 Synthesis of Heterocyclic Imides (12)



Scheme 11 Synthesis of Ultem Polyetherimide (102, 107, 108)



Scheme 12 Order of Stability of Polyimides as a Function of Diamine Component (35, 110)



Scheme 13 Order of Stability of Polyimides as a Function of Dianhydride Component (35, 110)



Scheme 14 Hydrolytic Degradation of Polyimides (137, 138)











Scheme 17 Synthesis of Poly(Amic Acid) and Subsequent High Temperature Solution Imidization of Poly(Imide Siloxane)s (38)

APPENDIX 2

FIGURES





Thermogravimetric Analysis of Polypyromelltimides in Dry Helium;

(R represents the sructure of the diamine component,

heating rate = $3^{\circ}C/min$) (35)









Desired molecular weight of oligomer = 2500 g/mole Molecular weight of disiloxane (DSX) = 248.5 g/mole

2500.0 g/m (total oligomer desired molecular weight) <u>- 248.5 g/m</u> (disiloxane molecular weight) 2251.5 g/m (D₄ tetramer required)

From this point, calculations depend on only the amount of disiloxane used and thus, the amount of oligomer desired. If the amount of DSX chosen is 50g, then:

grams of D₄ necessary = $\frac{2251.5 \text{ g/m} \times 50 \text{ g DSX}}{248.5 \text{ g/m}}$ = 453.02 grams D₄

Total amount of oligomer will be:

50g + 453.02 g = 503.02 g of <Mn>= 2500 g/mole oligomer

Figure 4 Sample Calculations for Synthesis of Polydimethylsiloxane Oligomers



Figure 5 Apparatus Used for Synthesis of Poly(Amic Acid)s



Figure 6 Apparatus Used for High Temperature Solution Imidization














Figure 10 GPC of a Poly(Imide Siloxane) (30% <Mn>=2500g/mole, Bis P based)



(50% <Mn>= 2500g/mole, Bis P based)





























(atmosphere = air, heating rate = 10°C/min.)













APPENDIX 3

TABLES

 Table 1

 Common Solvents for Poly(Amic Acid) Synthesis(35)

N,N - dimethylformamideN,N - DimethylacetamideN,N - diethylformamideN,N - DimethylmethoxyacetamideN - methylcaprolactamdimethyl sulfoxideN - methyl - 2 - pyrrolidonepyridinehexamethylphosphoramidedimethyl sulfonedioxanetetrahydrofuran

diglyme

triglyme

Table 2Common Dianhydrides Used in Polyimide Synthesis(11,35)

MONOMER

STRUCTURE

pyromellitic dianhydride(PMDA)

benzophenone tetracarboxylic acid dianhydride

2,2-bis(3,4-dicarboxyphenyl)propane dianhydride

2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride

bis(3,4-dicarboxyphenyl) dianhydride R= O(ether), S(thioether), SO₂(sulfone)

2,3,6,7-naphthalenetetracarboxylic acid dianhydride

3,3',4,4'-biphenyltetracarboxylic acid dianhydride

0 "

o o

ο

bisphenol A bisether dianhydride



Common Diamines Used in Polyimide Synthesis(11,35)

MONOMER

STRUCTURE



Dehydrating Agents and Bases Used in

the Chemical Imidization of Poly(Amic Acid)s (51-53)

Acetic anhydride

Acetic benzoic anhydride

Propionic anhydride

n-Butyric anhydride

4-methyl pyridine

Phosphorous trichloride

Pyridine

3,5-Lutidine

N-methyl morpholine

3-methyl pyridine

Isoquinoline

Trimethylamine



Functional Endgroups Used with Addition Polyimides (89)



CYCLOHEXENE



MALEIC



N-PROPARGYL



ACETYLENE







Cl6-NADIC

Glass Transition Temperatures for

BTDA and PMDA based Polyimides (57)

.

		METHOD OF
DIAMINE STRUCTURE	<u>Tg(oC)</u>	MEASUREMENT
FROM PYROMELLITIC DIA	NHYDRIDE	
OXYDIANILINE	325	DSC
	380	Torsional Braid
	385	Dissipation Factor
	>500	Tensile Modulus
METHYLENE DIANILINE	390	Torsional Braid
BENZOPHENONE	285	Torsional Braid
PHENYL	>320	Torsional Braid
-(CH2) ₉ -	110	

FROM BENZOPHENONE TETRACARBOXYLIC ACID DIANHYDRIDE

OXYDIANILINE	290	Torsional Braid
METHYLENE DIANILNE	290	Torsional Braid
BENZOPHENONE	277	Torsional Braid
PHENYL	294	Torsional Braid
ULTEM®	217	DSC

Effect of Flexible Linkages on Glass Transition Temperatures (116)

<u>Dianhydride</u>	<u>Diamine</u>	<u>Tg(oC)</u>	
PMDA	p,p-ODA	399	
	p,p-DABP	412	
	m,m-DABP	321	
BTDA	p-PDA	333	
	m-PDA	300	
ODPA	p-PDA	342	

*For structures, refer to Table 2 and 3

PMDA = pyromellitic dianhydride

BTDA = benzophenone tetracarboxylic dianhydride

ODPA= oxydiphthalic anhydride

ODA= oxydianiline

DABP= diaminobenzophenone

PDA= phenylene diamine

Та	ble	8
10	DIG	- u

Thermal Expansion Coefficients

for Various Polyimides (124) (unit:×10 ⁻⁵ K ⁻¹)				
		(1) D	(2) Dig Di	3 70 07
ω	· ©•	-	2.10	0.26
(B)	Ø	3.20	2.94	4.00
G	Ø _{CHs}	-	3.95	3.19
Ð	-©- -0-	0.04	2.59	0.58
Œ	Ŭ 	3.48	3.95	4.00
(F)		1.61	-	-
G		0.59	2.17	0.54
0-0	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0.20	1.54	0.56
(II)		1.37	4.91	4.64
(J)	-0-0-0-	0.56	1.83	0.59
80		-	-	1.72
പ	-0	1.58	1.60	1.13
3	- O- O-O-	2.16	4.28	4.56
~	-@-s- @ -	4.15	5.24	4.61
Ø		4.57	4.50	4.18
(P)	ૻઌ૾ૢૢૢૢૢૢૡૡ૱ૡૢૼૻ	5.76	5.36	4.85
Q	Q	-	2.61	1.00
(R)	-@o@-@o@	5.33	5.43	5.32
ග	<u>అంఅర్డ్తిం</u> ల	5.01	5.39	5.69
n	୶୶୶ୖୄୢ୵୶୶୶	4.57	5.47	5.61
a di	000 SO, O00	5.14	-	4.90

Mechanical Properties of Two Commercially

Available Polyimides (79, 125)

Property	<u>Ultem®</u>	Kapton®
Tensile Yield (ksi) 15.2 (25°C)		
Tensile Strength (ksi)		25.0 (25°C)
		17.0 (200°C)
Tensile Modulus (ksi)	430 (25°C)	430 (25°C)
		260 (200°C)
Elongation to Break	60% (25°C)	38% (25°C)
Elongation to Yield	7-8% (25°C)	



α, ω- Organofunctionally Terminated Disiloxanes (141)



CI----(CH₂)3-

Solvent Structures and Boiling Points

Used in the Synthesis of Poly(Amic Acid)s

SOLVENT NAME	SOLVENT STRUCTURE	BOILING POINT °C
N,N-Dimethylacetamide (DMAC)	0 H ₃ C 1 H ₃ C 1 H ₃ C 1	165
N-methyl-2-pyrrolidone (NMP)	□ =0 CH ₃	202
N-cyclohexyl-2-pyrrolidone (CHP)		290
Tetrahydrofuran (THF)		76

FT-IR Bands for Siloxanes

Frequency (cm ⁻¹)	Assignment
3000	C-H methyl stretch
1410	$Si(CH_3)_2O$ asymmetric deformation
1260	Si(CH ₃) ₂ O symmetric deformation
1130-1000	Si-O-Si stretch vibration
800	Si(CH ₃) ₂ O stretch; methyl rock
715	Si(CH ₃) ₂)O stretch
510	Si-O-Si bend vibration
1090-1080	Cyclic tetramers
1080-1050	Cyclics larger than tetramers
1070-1040	Disiloxanes
1020-1010	Cyclic trimers

Solubility of

3,3'-DDS Based Polyimides

Polyimide	NMP	THE	CH ₂ Cl ₂	<u>oDCB</u>	TOL
BTDA-DDS	SOL	IS	IS	IS	IS
BTDA-DDS- 10 PSX 950	SOL	IS	IS	IS	IS
BTDA-DDS- 20 FSX 950	SOL	IS	IS	IS	IS
BTDA-DDS- 40 PSX 950	SOL	SOL	SOL	SOL	IS

SOL=SOLUBLE IS=INSOLUBLE SS=SPARINGLY SOLUBLE

Solubility of Bis P Based Polyimides

<u>Polvimide</u>	NMP	THE	CH ₂ Cl ₂	oDCB	TOL
BTDA/BIS P	SOL	SS	SOL ,	SS	IS
BTDA/BIS P- 10 PSX 800	SOL	SS	SOL	SS	IS
BTDA/BIS P- 10 PSX 2465	SOL	SS	SOL	SS	IS
BTDA/BIS P- 30 PSX 2465	SOL	SOL	SOL	SS	IS
BTDA/BIS P- 50 PSX 2465	SOL	SOL	SOL	SOL	SOL

SOL=SOLUBLE IS=INSOLUBLE SS=SPARINGLY SOLUBLE

.

Intrinsic Viscosity and Glass Transition

Temperatures for Polyimides

<u>Polvimide</u>	(η)	<u>Tg ºC (DSC)</u>
BTDA-DDS	1.36	265
BTDA-DDS-10PSX 900	1.88	251
BTDA-DDS-20PSX 900	0.67	240
BTDA-DDS-40PSX 950	0.58	218
BTDA-BIS P	0.72	264
BTDA-BIS P-10PSX 800	0.60	241
BTDA-BIS P-10PSX 2465	0.65	258
BTDA-BIS P-20PSX 2465		245
BTDA-BIS P-30PSX 2465	0.74	242
BTDA-BIS P-50PSX 2465	0.63	205

Water Contact Angles for

Various Polyimides

.

<u>Siloxane <mn></mn></u>	Contact Angle
	82 ⁰
800	990
2465	1010
2465	1040
2465	106 ⁰
	68 ⁰
950	92 ⁰
2100	1000
2100	102 ⁰
950	106 ⁰
2100	106 ⁰
	SIIOXANE

Thermal Extension and Expansion

Coefficients for Various Polyimides

POLYIMIDE		α x 10 ⁵ ,ppm ⁰ C	
	< <u>Mn> PSX</u>	EXT	<u>EXP</u>
BTDA/3,3'-DDS		4.28	5.48
10% PSX/BTDA/3,3'-DDS	950	5.51	6.20
30% PSX/BTDA/3,3'-DDS	1000	10.75	13.43
50% PSX/BTDA/3,3'-DDS	1000	12.22	24.75
70% PSX/BTDA/3,3'-DDS	1200	16.04	30.15
BTDA/BIS P		3.87	5.86
10% PSX/BTDA/BIS P	2465	4.32	6.93
PBI FIBER		-1.71	
KEVLAR FIBER		-0.17	6.63

The vita has been removed from the scanned document