Effect of polyhedral oligomeric silsesquioxane on gas transport properties of polyimide

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Gas Transport Properties of Polyimide

By

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An Abstract of

Effect of Polyhedral Oligomeric Silsesquioxane on Gas Transport Properties of Polyimide

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The transport properties of gases in polyimide – polyhedral oligomeric silsesquioxane (POSS) mixed matrix membrane were determined based on pure gas permeation and sorption experiments. Gas permeabilities, solubilities, diffusivities and selectivities (CO$_2$/CH$_4$, He/CH$_4$, O$_2$/N$_2$, He/N$_2$) are reported over a wide pressure, temperature for polyimide-POSS mixed matrix membranes containing various loadings of POSS.

Gas transport properties of mixed matrix membrane containing inorganic molecular sieving material depends on the sieving ability of the inorganic materials, the gas sorption capacity of the sieve, the interface between the sieve and the bulk polymer matrix and the inherent properties of the polymer matrix itself. Proper selection of both the polymer matrix and the molecular sieving materials is required to obtain mixed matrix membranes with enhanced gas transport properties.
Increase in both, diffusivity of smaller penetrants and diffusivity selectivity and consequently in permeability and permselectivity will be obtained in mixed matrix membranes containing molecular sieves with precise pore openings. The properties of the bulk polymer such as excess free volume, relative flexibility/rigidity affect the gas transport properties of mixed matrix membranes. A good interface between the two phases eliminates the possibility of non-selective gas transport and maintains selectivity.

Various inorganic materials such as zeolite, carbon molecular sieves are being incorporated into polymer matrices to form mixed matrix membranes. They possess precise pore openings and are mechanically and thermally stable. Polyhedral Oligomeric Silsesquioxanes (POSS) are three dimensional rigid cage structures made up of Si-O-Si linkages. They have dimensions in the nanometer range and possess a precise pore opening of 4.5 Å. They are also thermally and mechanically stable and hence are the inorganic filler of choice for this study.

The impact of POSS on the physical, mechanical and thermal properties of 6FDA-MDA polyimide is determined. The effect of functionalization of POSS on the dispersion and morphology of the polyimide-POSS composites are reported. A thorough investigation into the properties of POSS and polymer-POSS composites was done to understand the observed gas transport behavior of these membranes.

Pure gas permeation and sorption of penetrants was measured and analyzed based on understanding of pathways of gas transport in mixed matrix membranes. Specifically, pressure dependencies of gas permeabilities,
solubilities and diffusivities are discussed in terms of pre-established solution diffusion and dual mode sorption theory. Temperature dependence was also determined to evaluate the performance of these mixed matrix membranes at elevated temperatures.

In this study, the versatile properties of POSS particles were harnessed for yet another application. Octa functional POSS was covalently bound onto a carbon nanofiber to increase the overall functionality/reactivity of the fiber. The strong interface thereby generated would assist in effective load transfer under applied stress when incorporated within a polymer matrix. Confirmation of covalent attachment of POSS to the carbon nanofiber was obtained using various analytical techniques. Composites were formed using these functionalized carbon nanofibers within a polyimide matrix and their tensile properties were measured.
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# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................... iii

ACKNOWLEDGEMENTS ..................................................................................................................... vi

TABLE OF CONTENTS .................................................................................................................. vii

LIST OF TABLES .............................................................................................................................. x

LIST OF FIGURES .............................................................................................................................. xiii

1 INTRODUCTION ............................................................................................................................. 1

  1.1 MEMBRANES FOR GAS SEPARATION ...................................................................................... 1

  1.2 MIXED MATRIX MEMBRANES .............................................................................................. 3

  1.3 POLYHEDRAL OLIGOMERIC SILSESQUIOXANE ................................................................. 5

  1.4 CARBON NANOFIBER ............................................................................................................ 7

  1.5 PROPOSED RESEARCH OBJECTIVES .............................................................................. 8

2 THEORY AND BACKGROUND ........................................................................................................ 11

  2.1 TRANSPORT PROPERTIES OF GASES IN GLASSY POLYMERS .................................... 11

  2.2 GAS TRANSPORT IN POLYMIDES .................................................................................... 19

  2.3 LITERATURE REVIEW ON MIXED MATRIX MEMBRANES (MMM) ............................... 21

  2.4 STRUCTURE AND PROPERTIES OF POSS ...................................................................... 26

  2.5 BACKGROUND ON POLYMER-POSS COMPOSITES ...................................................... 29

  2.6 WHY POSS? .......................................................................................................................... 34

3 EXPERIMENTAL ........................................................................................................................... 36
3.1 MATERIALS ........................................................................................................ 36
3.2 TECHNIQUES TO FUNCTIONALIZE POSS, POLYIMIDE AND NANOCOMPOSITE FORMATION ................................................................................................................. 38
3.3 CHARACTERIZATION TECHNIQUES ........................................................................ 48

4 CHARACTERIZATION OF POLYIMIDE - POSS COMPOSITES ............ 61
4.1 FUNCTIONALIZATION OF OPS WITH AMINE GROUPS .................................. 62
4.2 SYNTHESIS OF POLYIMIDE ............................................................................... 65
4.3 BLENDED FILM FORMATION ............................................................................. 68
4.4 OPTICAL PROPERTIES ......................................................................................... 70
4.5 SEM MICROSCOPY ............................................................................................. 71
4.6 WIDE ANGLE X-RAY DIFFRACTION (WAXD) .................................................. 74
4.7 DENSITY MEASUREMENTS ............................................................................... 76
4.8 DYNAMIC MECHANICAL ANALYSIS .................................................................. 78
4.9 THERMOGRAVIMETRIC ANALYSIS ................................................................. 82
4.10 MECHANICAL PROPERTIES .............................................................................. 88

5 GAS TRANSPORT PROPERTIES – 35 °C ...................................................... 95
5.1 INTRODUCTION .................................................................................................. 95
5.2 BACKGROUND ................................................................................................... 98
5.3 OVERVIEW OF PHYSICAL PROPERTIES OF PI-OAPS MIXED MATRIX MEMBRANES ................................................................................................................. 100
5.4 PURE GAS PERMEATION STUDY ................................................................. 102
5.5 PURE GAS SORPTION STUDIES ................................................................. 119
5.6 PURE GAS DIFFUSIVITY ................................................................................. 133
# Table of Contents

5.7 **PRESSURE EFFECTS** .......................................................................................... 137  

6 **TEMPERATURE EFFECTS ON GAS TRANSPORT** .................................... 147  
   6.1 **INTRODUCTION** ......................................................................................... 147  
   6.2 **BACKGROUND** ......................................................................................... 148  
   6.3 **PURE GAS PERMEATION** ......................................................................... 150  
   6.4 **PURE GAS SORPTION STUDIES** ................................................................. 157  
   6.5 **PURE GAS DIFFUSIVITY** ........................................................................... 163  
   6.6 **ACTIVATION ENERGY** ............................................................................... 165  

7 **CARBON NANOFIBER - POSS COMPOSITE CHARACTERIZATION** .... 176  
   7.1 **INTRODUCTION** ......................................................................................... 176  
   7.2 **BACKGROUND** ......................................................................................... 179  
   7.3 **MATERIALS** .............................................................................................. 183  
   7.4 **CNF-OAPS REACTION MECHANISM USING CARBODIIMIDE CHEMISTRY** .... 183  
   7.5 **CNF-OAPS CHARACTERIZATION** .............................................................. 188  
   7.6 **POLYIMIDE-(CNF-OAPS) NANOCOMPOSITE** ...................................... 200  
   7.7 **TENSILE TESTING** .................................................................................... 202  

8 **CONCLUSIONS** ............................................................................................... 205  

9 **FUTURE WORK** ............................................................................................... 210  

10 **REFERENCES** .................................................................................................. 213  

11 **APPENDIX A** ................................................................................................... 225  

12 **APPENDIX B** ................................................................................................... 228  

13 **APPENDIX C** ................................................................................................... 229
LIST OF TABLES

TABLE 2.1: CHEMICAL STRUCTURES OF VARIOUS DIAMINES AND DIANYDRIDES USED TO FORM A POLYIMIDE.............................................................. 20

TABLE 3.1: PROPERTIES OF GAS PENETRANTS USED IN THIS STUDY.................. 55

TABLE 4.1: OPTICAL PROPERTIES OF PI-OAPS COMPOSITES DETERMINED BY UV-VIS SPECTROSCOPY. ................................................................. 70

TABLE 4.2: DENSITY MEASUREMENT ...................................................................... 77

TABLE 4.3: SUMMARY OF THERMAL PROPERTIES OF PI-OAPS COMPOSITES. .... 87

TABLE 4.4: TENSILE PROPERTIES OF PURE PI AND PI-OAPS COMPOSITES. ........ 90

TABLE 5.1: PHYSICAL PROPERTIES OF PI-OAPS MIXED MATRIX MEMBRANES. .... 100

TABLE 5.2: PERMEABILITY COEFFICIENTS AND PERMSELECTIVITIES OF PLAIN PI AND PI-OAPS MIXED MATRIX MEMBRANES FOR THE DIFFERENT GASES STUDIED. ........................................................................................................ 104

TABLE 5.3: PREDICTED AND EXPERIMENTAL VALUES OF PERMEABILITY COEFFICIENTS AT 35 °C OF ALL GASES STUDIED......................................................... 110

TABLE 5.4: SOLUBILITY COEFFICIENTS AND SOLUBILITY SELECTIVITIES OF PLAIN PI AND PI-OAPS MIXED MATRIX ................................................................. 122

TABLE 5.5: DUAL MODE PARAMETERS OF PI AND PI-OAPS MIXED MATRIX MEMBRANES. ........................................................................................................... 131

TABLE 5.6: CHANGE IN THE FRACTIONAL FREE VOLUME AND EXCESS FREE VOLUME OF POLYIMIDE WITH INCREASING CONCENTRATION OF OAPS .................. 131

TABLE 5.7: DIFFUSIVITY COEFFICIENTS OF PLAIN PI AND PI-OAPS MIXED MATRIX MEMBRANES FOR THE DIFFERENT GASES STUDIED.......................... 134
TABLE 6.1: PERMEABILITY COEFFICIENTS AND PERMSELECTIVITIES OF PLAIN PI AND PI-OAPS MIXED MATRIX MEMBRANES FOR THE DIFFERENT GASES STUDIED AT 35 °C. ................................................................. 154

TABLE 6.2: PERMEABILITY COEFFICIENTS AND PERMSELECTIVITIES OF PLAIN PI AND PI-OAPS MIXED MATRIX MEMBRANES FOR THE DIFFERENT GASES STUDIED AT 45 °C. ................................................................. 155

TABLE 6.3: PERMEABILITY COEFFICIENTS AND PERMSELECTIVITIES OF PLAIN PI AND PI-OAPS MIXED MATRIX MEMBRANES FOR THE DIFFERENT GASES STUDIED AT 60 °C. ................................................................. 156

TABLE 6.4: SOLUBILITY COEFFICIENTS OF PI AND PI-OAPS MIXED MATRIX MEMBRANES AT 45 °C AND 60 °C FOR O₂, N₂, CH₄ AND CO₂.......................... 160

TABLE 6.5: PURE GAS DIFFUSIVITY COEFFICIENTS OF O₂, N₂, CH₄ AND CO₂ IN PI AND PI-OAPS MIXED MATRIX MEMBRANES AT 45 °C AND 60 °C. .............. 164

TABLE 6.6: COMPARISON OF ACTIVATION ENERGY FOR PERMEATION, HEAT OF SORPTION AND ACTIVATION ENERGY FOR DIFFUSION IN PI AND PI-OAPS MIXED MATRIX MEMBRANES AT 35–60 °C. UPSTREAM PRESSURE WAS 10 ATM FOR HE, CO₂, O₂, N₂ AND CH₄. ................................................................. 166

TABLE 7.1: ATOMIC % OF EACH ELEMENT PRESENT IN THE FUNCTIONALIZED CNF DETERMINED FROM XPS. ................................................................. 191

TABLE 7.2: LIST OF VARIOUS TYPES OF CARBON NANOFIBERS USED IN THIS STUDY TO FORM NANOCOMPOSITES ALONG WITH THEIR TERMINOLOGIES............ 200
Table 7.3: Mechanical properties of PI-CNf composites determined using Instron tensile testing using functionalized and unfunctionalized CNF.

................................................................................................ 202
LIST OF FIGURES

FIGURE 1.1: RELATIVE POSITIONS OF SIEVING MATERIALS AND MIXED MATRIX MEMBRANES WITH RESPECT TO THE PERMEABILITY SELECTIVITY TRADEOFF CURVE FOR POLYMERS. ................................................................. 4

FIGURE 2.1: THE DIFFERENT MODES OF SORPTION WITHIN A POLYMER. .................... 14

FIGURE 2.2: SPECIFIC (OR MOLAR) VOLUME VERSUS TEMPERATURE FOR TYPICAL GLASSY POLYMERS............................................................... 16

FIGURE 2.3: FORMATION OF A “SIEVE-IN-A-CAGE” MORPHOLOGY IN MMMS. .............. 25

FIGURE 2.4: STRUCTURE OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (T₈). ......... 27

FIGURE 2.5: (A) T₁₀ AND (B) T₁₂ CAGE STRUCTURES OF POSS. .............................. 27

FIGURE 2.6: EXAMPLE OF SYNTHESIS OF A CYCLOHEXYL POSS BY USING TRICHLOROSILANE. ........................................................................ 28

FIGURE 3.1: STRUCTURE OF REPEAT UNIT OF 6FDA-MDA POLYIMIDE ...................... 36

FIGURE 3.2: STRUCTURE OF OCTAPHENYL SILSESQUIOXANE (OPS).......................... 37

FIGURE 3.3: DESCRIPTION OF THE BLENDING TECHNIQUE USED TO INCORPORATE OAPS WITHIN THE PI MATRIX......................................................... 47

FIGURE 3.4: SCHEMATIC OF GAS PERMEATION EXPERIMENTAL SET-UP .................... 56

FIGURE 3.5: SCHEMATIC OF DUAL VOLUME SORPTION SET-UP ................................ 58

FIGURE 4.1: CHANGE IN FTIR SPECTRUM OF (A) OPS ON NITRATION AND HYDROGENATION TO (B) ONPS AND (C) OAPS. ................................. 62

FIGURE 4.2: STRUCTURE OF OCTAPHTHALIMIDEPHENYL SILSESQUIOXANE (OPIPS) ... 64

FIGURE 4.3: FTIR SPECTRUM OF OPIPS .................................................................... 64

FIGURE 4.4: FTIR SPECTRUM OF 6FDA-MDA POLYIMIDE. ..................................... 65
FIGURE 4.5: VISUAL COMPARISON OF (A) PLAIN PI, (B) 5 WT% PI-OPS, (C) 5 WT% PI-OAPS, (D) 20 WT% PI-OAPS FILMS. ................................................. 69

FIGURE 4.6: SCANNING ELECTRON MICROGRAPH OF (A) PURE PI (B) PI-OAPS 10 WT% (C) PI-OAPS 20 WT% (D) PI-OAPS 50 WT% (E) EDS SPECTRUM OF PI-OAPS 50 WT% COMPOSITE WITH POLYMER FOCUS (F) EDS SPECTRUM OF PI-OAPS 50 WT% COMPOSITE WITH AGGREGATE FOCUS. .......... 72

FIGURE 4.7: WIDE ANGLE X-RAY DIFFRACTION (WAXD) PATTERNS OF (A) PLAIN PI (B) 5 WT% PI-OAPS (C) 10 WT% PI-OAPS (D) 20 WT% PI-OAPS (E) 30 WT% PI-OAPS (F) 50 WT% PI-OAPS (G) OAPS. ......................... 75

FIGURE 4.8: (A) TAN DELTA CURVE OVER A NARROW TEMPERATURE RANGE (B) GLASS TRANSITION TEMPERATURE DETERMINED FROM THE PEAK OF TAN DELTA CURVE (♦) PI-OAPS COMPOSITE, (♦) 5 WT% PI-OPS COMPOSITE. .. 80

FIGURE 4.9: TGA PLOT OF WEIGHT % VERSUS TEMPERATURE FOR OPS, ONPS AND OAPS IN N₂ .................................................................................. 83

FIGURE 4.10: DERIVATIVE THERMOGRAVIMETRY (DTG) CURVE FOR THERMAL DECOMPOSITION OF OPS (—), ONPS (-----), OAPS (— - —) IN N₂. .. 83

FIGURE 4.11: TG PLOT OF WEIGHT % VERSUS TEMPERATURE FOR PI AND PI-OAPS COMPOSITE FILMS. ................................................................. 85

FIGURE 4.12: DTG CURVES OF PLAIN PI AND THE PI-OAPS COMPOSITE FILMS........ 85

FIGURE 4.13: TYPICAL STRESS STRAIN CURVES FOR PI, 5 WT%, 10 WT% AND 20 WT% PI OAPS COMPOSITES. ............................................................. 89

FIGURE 5.1: SCHEMATIC OF A MIXED MATRIX MEMBRANE ................................................. 96
FIGURE 5.2: A PLOT OF (●) HE PERMEABILITY AND (♦) HE/CH₄ SELECTIVITY VERSUS OAPS CONCENTRATION (WT%). ................................................................. 105

FIGURE 5.3: A PLOT OF (●) O₂ PERMEABILITY AND (♦) O₂/N₂ SELECTIVITY VERSUS OAPS CONCENTRATION (WT%). ......................................................... 106

FIGURE 5.4: A PLOT OF (●) CO₂ PERMEABILITY AND (♦) CO₂/CH₄ SELECTIVITY VERSUS OAPS CONCENTRATION (WT%). ......................................................... 107

FIGURE 5.5: CORRELATION OF PURE GAS PERMEABILITY COEFFICIENTS WITH KINETIC DIAMETERS OF VARIOUS PENETRANTS AT 35 °C ......................... 108

FIGURE 5.6: INCORPORATION OF POSS WITHIN PI MATRIX AT (A) LOW CONCENTRATIONS (~5WT%) (B) INTERMEDIATE CONCENTRATIONS (~10 WT%) AND (C) HIGH CONCENTRATIONS (~50 WT%). ........................................ 114

FIGURE 5.7: POSITION OF PI-OAPS MIXED MATRIX MEMBRANES WITH RESPECT TO (A) CO₂/CH₄, AND HE/CH₄ UPPER BOUNDS ........................................ 117

FIGURE 5.8: CORRELATION OF SOLUBILITY COEFFICIENT WITH CRITICAL TEMPERATURES OF VARIOUS PENETRANTS AT 35 °C FOR PI AND PI-OAPS MIXED MATRIX MEMBRANES. .......................................................... 120

FIGURE 5.9: SORPTION ISOTHERMS OF (A) O₂, (B) N₂, (C) CH₄ AND (D) CO₂ FOR PI AND PI-OAPS MIXED MATRIX MEMBRANES ........................................ 126

FIGURE 5.10: CORRELATION OF SOLUBILITY COEFFICIENT WITH THE FRACTIONAL FREE VOLUME OF FILMS FOR VARIOUS PENETRANTS AT 35 °C WITH OAPS CONCENTRATION RANGING FROM 0 TO 20 WT%. ......................... 132

FIGURE 5.11: DISTRIBUTION OF FREE VOLUME WITHIN (A) PI MATRIX (B) PI-OAPS MMM. .............................................................................................................. 135
FIGURE 5.12: PICTORIAL REPRESENTATION OF DIFFUSIONAL JUMP OF (A) LARGE PENETRANT (B) SMALL PENETRANT THROUGH RIGIDIFIED POLYMER MATRIX. ................................................................................................................................................................. 136

FIGURE 5.13: PRESSURE DEPENDENCE OF PERMEABILITY COEFFICIENTS OF VARIOUS GASES IN 6FDA-MDA PI.................................................................................................................. 139

FIGURE 5.14: PRESSURE DEPENDENCE OF PERMEABILITY COEFFICIENTS OF VARIOUS GASES IN 5 WT% PI-OAPS.................................................................................................................. 139

FIGURE 5.15: PRESSURE DEPENDENCE OF PERMEABILITY COEFFICIENTS OF VARIOUS GASES IN 10 WT% PI-OAPS.................................................................................................................. 140

FIGURE 5.16: PRESSURE DEPENDENCE OF PERMEABILITY COEFFICIENTS OF VARIOUS GASES IN 20 WT% PI-OAPS.................................................................................................................. 140

FIGURE 5.17: PRESSURE DEPENDENCE OF SOLUBILITY COEFFICIENTS OF VARIOUS GASES IN 6FDA-MDA PI.................................................................................................................. 141

FIGURE 5.18: PRESSURE DEPENDENCE OF SOLUBILITY COEFFICIENTS OF VARIOUS GASES IN 5 WT% PI-OAPS.................................................................................................................. 141

FIGURE 5.19: PRESSURE DEPENDENCE OF SOLUBILITY COEFFICIENTS OF VARIOUS GASES IN 10 WT% PI-OAPS.................................................................................................................. 142

FIGURE 5.20: PRESSURE DEPENDENCE OF SOLUBILITY COEFFICIENTS OF VARIOUS GASES IN 20 WT% PI-OAPS.................................................................................................................. 142

FIGURE 5.21: A COMPARISON OF RELATIVE PERCENT REDUCTION IN PERMEABILITY, DIFFUSIVITY AND SOLUBILITY COEFFICIENT FOR 5 WT% PI-OAPS MEMBRANE. ................................................................................................................................................................. 144
Figure 5.22: A comparison of relative percent reduction in permeability, diffusivity and solubility coefficient for 10 wt% PI-OAPS membrane. ................................................................. 144

Figure 5.23: A comparison of relative percent reduction in permeability, diffusivity and solubility coefficient for 20 wt% PI-OAPS membrane. ................................................................. 145

Figure 6.1: Temperature effects on sorption isotherms for $N_2$ and $CH_4$ in (A) plain PI and (B) 20 wt% PI-OAPS ........................................................................................................ 162

Figure 6.2: Arrhenius correlations of permeability coefficients of penetrants in (A) plain PI and (B) 5 wt% PI-OAPS mixed matrix membrane. ............................................................... 167

Figure 6.3: Arrhenius correlations of permeability coefficients of penetrants in (A) 10 wt% PI-OAPS and (B) 20 wt% PI-OAPS mixed matrix membrane. ..................................................... 168

Figure 6.4: Arrhenius correlations of diffusion coefficients of various penetrants in (A) 6FDA-MDA PI and (B) 20 wt% PI-OAPS MMM. 171

Figure 7.1: Effect of functionalization on the interfacial properties of polymer-CNF nanocomposite. ................................................................. 181

Figure 7.2: Structure of anhydride terminated 6FDA-BiSP oligomer, where $n \cong 20$. .................................................................................................................. 185

Figure 7.3: XPS spectrum of oxidized carbon nanofiber functionalized with OAPS ................................................................................................. 189
FIGURE 7.4: XPS SPECTRUM OF CNF-OAPS FUNCTIONALIZED WITH ANHYDRIDE TERMINATED OLIGOMER. ................................................................. 190

FIGURE 7.5: A COMPARISON OF THE DTG CURVE OF OXIDIZED CNF AND CNF FUNCTIONALIZED WITH OAPS. .................................................. 193

FIGURE 7.6: A COMPARISON OF DTG CURVES OF OAPS AND CNF FUNCTIONALIZED WITH OAPS. .............................................................................. 193

FIGURE 7.7: A COMPARISON OF DTG CURVES OF 6FDA-BisP OLIGOMER AND CNF-OAPS–OLIGOMER. ............................................................... 194

FIGURE 7.8: (A) Z-CONTRAST STEM IMAGE OF CNF-OAPS-OLIG INDICATING BRIGHT SPOTS OF SI ON THE SURFACE. (B) EDS SPECTRUM OF ONE SUCH BRIGHT SPOT INDICATING A SHARP PEAK FOR SI. .............................................. 197

FIGURE 7.9: (A) TEM IMAGE OF CNF-OAPS-OLIG (B) CARBON MAP (C) SILICON MAP (D) FLUORINE MAP. .............................................................................................. 198

FIGURE 7.10: STRUCTURE OF REPEAT UNIT OF 6FDA-BisP POLYIMIDE. ................. 200

FIGURE 7.11: SCHEME FOR FORMATION OF (6FDA-BisP)-CNF NANOCOMPOSITE. 201

FIGURE 9.1: FORMATION OF A CONTINUOUS NETWORK OF POSS WITH PRECISE PORE STRUCTURE. ................................................................................... 211
1 INTRODUCTION

1.1 Membranes for Gas Separation

Growing energy requirements have become increasingly difficult to satisfy with the available energy resources. The increasing utility costs are clear evidence of the increasing difference between energy consumption rate and energy production rate. Chemical industry consumes a major portion of the energy produced. Amongst various chemical processes, downstream unit operations such as cryogenic distillation, pressure swing adsorption (PSA), distillation, used for separations consume a lot of energy, hence are also cost intensive. Since the early 1980’s, membrane technology has emerged as a low energy alternative separation technology [27]. Membranes have advantages over conventional unit operations in terms of their energy consumption and greater process flexibility.

Membranes have been applied successfully in the natural gas industry for natural gas purification, enhanced oil recovery and air purification. Removal of acid gases like CO$_2$ and H$_2$S from the natural gas streams using membranes is one of the biggest markets [28]. Other applications involve N$_2$ and H$_2$ removal from natural gas stream. Also, O$_2$/N$_2$ separation using membranes is one of the
oldest techniques used for this separation. Current developments in other fields have lead to the possible application of membranes, for example, hydrogen purification for fuel cells can be achieved using membranes. Polymers can also act as barrier materials and are used in both packaging and microelectronics industry. Majority of commercial membranes are made from synthetic polymers and can be glassy or rubbery depending upon the target gas separation. Examples of the most commonly used glassy polymeric membranes for gas separation are cellulose acetate (CA), polyimide (PI), polyamide (PA), polysulfone (PSF), polycarbonate (PC), polyetherimide (PEI) whereas, polydimethylsiloxane (PDMS) and silicone rubber (SBR) are the commonly used rubbery polymers for vapor separation [27,28].

Gas transport through polymers is characterized by their flux, proportional to permeability, which is a measure of membrane productivity and selectivity, which is a measure of membrane efficiency. Development of polymers with both high productivity and selectivity are prerequisites for their economic application towards any gas separation. Polymides are high temperature glassy polymers with very good gas separation characteristics and hence are subject for this study. However, the performance of glassy polymers can be limited by tradeoff between improved permeability and selectivity as identified by Robeson in 1991 [2]. Since then efforts are being made to develop polymers with performance above the tradeoff curve. Also, current process needs require high performance membranes with higher productivity and selectivity than that of traditional polymers with greater thermal, chemical and mechanical stability.
The development of strategies for structural optimization of polymers were necessary to target specific applications. Studies on polyimides have shown that systematic variations of the intrasegmental mobility and intersegmental chain packing can be used to achieve increase in productivity (or permeability) without losses in selectivity [25]. Similar results were also obtained for other families of polymers including polycarbonate, polyesters and polysulfones. While this led to enhancements in properties, the cost of new synthesis and incremental improvement seen for future materials has led to development of alternative approaches. However, such structural modifications failed to yield the required enhanced performance and hence other alternative routes are under investigation.

1.2 Mixed Matrix Membranes

Conventional gas separations like pressure swing adsorption (PSA) utilize molecular sieves to adsorb and separate gases. Molecular sieves such as zeolite have the ability to adsorb a particular gas due to their precise pore size. Tremendous improvements in transport properties would be achieved by forming inorganic membranes from such molecular sieving materials. However, immediate application of such inorganic membranes is hindered by the lack of technology to form continuous defect-free membranes, high membrane production costs and handling issues due to inherent brittleness. In view of this situation a novel approach to combine the excellent separating ability of molecular sieving materials with the processibility and cost effectiveness of polymers emerged in mid 1990’s. This approach involved dispersing molecular
sieving materials within a polymer matrix to form a “mixed matrix membrane”. Based on the precise molecular sieving ability of molecular sieves and the flexibility and processibility of polymers, the performance of such mixed matrix membranes can be thought to be above the limiting tradeoff curve as shown in Figure 1.1. The dispersed inorganic phase can be zeolite, carbon molecular sieve, fullerene or other nano-size particles.

Interesting gas transport properties have been obtained by incorporating sieving materials within a polymer matrix. Major contribution in developing and understanding these materials has been given by W. J. Koros and T. S. Chung and their coworkers [29,45,46].

![Figure 1.1: Relative positions of sieving materials and mixed matrix membranes with respect to the permeability selectivity tradeoff curve for polymers.](image-url)
Although these mixed matrix materials have shown some promising results, there are few challenges involved in their formation. The most common challenge is the formation of a defect free membrane. The defect formation process and factors affecting it have been described in greater detail in section 2.3.1. This, and other such processing challenges have hindered the commercial production of mixed matrix membranes till date. Current research focuses on overcoming these challenges and developing new materials which would eliminate the causes. Surface modifications of the inorganic sieving phase and changes in the membrane casting conditions have been suggested to overcome the formation of defects in large scale mixed matrix membranes. However, these approaches have still not yielded the desired simultaneous enhancements in both permeability and selectivity, with exception of a few reports.

1.3 Polyhedral Oligomeric Silsesquioxane

Polyhedral Oligomeric Silsesquioxane (POSS) has emerged as a new class of organic/inorganic hybrid material. POSS have three dimensional cage structure made up of Si-O. The overall diameter of POSS ranges between 1.5 – 3 nm. Further, the tetravalent Si atoms of POSS are bound to organic groups which can be tailored to be either reactive or non reactive. The nanoscopic size of POSS and the organic substitutions on its surface make them readily soluble in most organic solvents. Moreover, the organic groups can be reactive to enhance the compatibility with the surrounding polymer matrix by enabling strong physical / chemical interactions. These characteristic features of POSS make
them attractive materials for a host of other industrial applications including protective coatings, coatings on semi-conductors, flame resistant materials.

POSS particles have also found applicability in other industrial areas ranging from microelectronics to space survivable materials. The versatile nature of POSS enhances the properties of its polymer composite by increasing the $T_g$, increasing the decomposition temperature, enhancing oxidative stability, enhancing flame retardance and decreasing density. Also, POSS can be incorporated within a polymer matrix using different approaches that produce unique properties each way. The most prominent feature of POSS is that it is a molecular cage which is soluble in most organic solvents unlike other commonly used inorganic fillers. The ease of incorporation without modifying the commercial production techniques makes POSS cost effective as compared to other inorganic fillers, where special techniques may be needed to achieve uniform dispersion. Characterization of polyimide-POSS composites with focus on their morphology and thermo mechanical properties is discussed in Chapter 4.

Further, POSS is a building block of zeolite and hence can have similar sieving ability as that of zeolites, smaller size and reactive groups make them more attractive and promising. Therefore, this study will focus on the formation of polyimide-POSS mixed matrix membranes with enhanced gas transport properties, and mechanical and thermal stability. Chapter 5 and 6 will focus on the gas transport properties of polyimide-POSS mixed matrix membranes.
1.4 Carbon Nanofiber

The multifunctionality of POSS can be combined with the strength and stability of carbon nanofibers to give a hybrid nanoparticle with inherently good mechanical properties along with high degree of functionality. Since the discovery of carbon nanotubes (CNT) and carbon nanofibers (CNF), considerable interest has been generated in science and engineering due to their unprecedented physical and chemical properties. CNF have much higher surface area due to their nanometer size range, allowing greater interaction with composite matrices to obtain the required reinforcements. Their impressive mechanical properties (Young’s modulus – 100 to 1000 GPa, strength – 2.5 to 3.5 GPa) make them attractive as fillers in polymer matrices. The amount of reinforcement and property enhancement is largely dependent on the interface between CNF and the polymer. In order to maximize the use of CNF as reinforcing filler, the interface should be strong with no gaps or voids, as these would act as weak points where the composite could yield.

Functionalization of CNFs to enhance the interactions with the surrounding polymer matrix is done to minimize the weak interfacial bonds. Reactive organic groups with functional end groups can be attached to the CNFs after it has been oxidized to produce reactive –COOH groups on the surface. Different types of functional groups can be covalently reacted with the –COOH groups. However, oxidation results in fairly low concentration of reactive groups on CNF surface without affecting the inherent mechanical properties of CNFs. An approach to increase the functionality is to react POSS with a CNFs, the
multifunctionality of POSS will potentially increase the overall functionality on CNF by as much as 8 times. Further, the overall diameter of POSS is 1.5 nm, hence there is no possibility of steric hindrance or blockage due to POSS. Since the organic groups on POSS can be easily modified, they can be used to impart a wide range of functionalities on CNFs depending on the final application. Therefore, POSS can act as a multifunctional inorganic link between the polymer and CNFs. Chapter 7 will focus on the reaction scheme for CNF-POSS functionalization and the mechanical properties of their polymer composites.

This study will primarily focus on the impact of POSS on the gas transport properties of polyimide as a function of POSS loading, temperature and pressure. Also, the effect of POSS functionalization on the morphology and physical properties of the composites will be presented. Lastly preliminary results on CNF-POSS-polyimide nanocomposites will be presented.

1.5 Proposed Research Objectives

The overall goal of this project was to perform structure property analysis of polyimide-POSS mixed matrix membranes. In order to do this, following research objectives were proposed:

1. **Develop strategies to incorporate POSS into the PI matrix to form a defect free mixed matrix membrane with various percentages of POSS.**

Various methods of incorporating inorganic fillers into polymer matrices have been reported. Commonly used amongst them are blending, in situ polymerization and melt extrusion. Properties of the composite prepared via each of these methods would vary and an optimum method needs to be determined
which would enable easy, uniform and consistent incorporation of POSS into the PI matrix using various percentages of POSS. This may also involve functionalization of POSS to enhance its compatibility with the polyimide matrix.

2. Perform thorough characterization of the PI-POSS composite using various analytical techniques and determine the impact of POSS on the physical, mechanical and thermal properties of PI.

Since POSS are relatively new nanomaterials their impact on the polymer matrix is not very well known. Hence thorough characterization of POSS itself and the PI-POSS composites would determine the effect of incorporation of POSS on the physical, mechanical and thermal properties of PI. This would involve determination of dispersion of POSS within the PI matrix using techniques such as SEM and TEM, density determination. Determination of thermomechanical properties such as modulus, strength, glass transition temperature, decomposition temperature would evaluate the performance of these composites for other possible applications. Some of the observations from these experiments would be useful in understanding gas transport through these mixed matrix membranes.

3. Perform Gas permeation and sorption experiments at 35 °C and at elevated temperatures to determine the mode of gas transport through these mixed matrix membranes.

Since the primary goal of this project was to form novel mixed matrix membranes for gas separation, permeation and sorption experiments need to be done to evaluate their performance. A thorough investigation into the observed gas
transport properties of these membranes would determine whether POSS can be used as a molecular sieving material. Possible modes of transport through these membranes will be suggested and determined using results from other characterization experiments. Further, performance of these mixed matrix membranes at elevated temperatures were determined for high temperature gas separation applications.
2 THEORY AND BACKGROUND

2.1 Transport Properties of Gases in Glassy Polymers

2.1.1 Permeability and Permselectivity

The performance of a membrane is characterized by its flux and selectivity [1]. The first generation polymeric membrane materials were generally limited by a tradeoff of decreased flux with increased permeability [2,3,4,5]. An ideal membrane should have high flux and high selectivity combined with thermal and mechanical stability. The flux of a penetrant through a polymeric membrane can be determined by using Equation 2.1.

\[ \text{Flux} = \frac{P \Delta p}{l} \]  

2.1

where \( P \) is the permeability coefficient for a given membrane material, (units= barrer = \( 10^{-10} \) cm\(^3\)(STP) cm / cm\(^2\) sec cm Hg), \( \Delta p \) is the pressure driving force across the membrane (cm Hg) and \( l \) is the thickness of membrane in cm [6].

Ideal selectivity is then a ratio of permeability of penetrant A to the permeability of penetrant B through the membrane, given by Equation 2.2

\[ \text{Selectivity, } \alpha_{AB} = \frac{P_A}{P_B} \]  

2.2

Flux can therefore be increased by increasing the permeability of the membrane, decreasing the membrane thickness, or increasing the driving force.
Permeability of a penetrant through a membrane is a characteristic of the polymer itself, therefore any permeability enhancements would have to be achieved by altering the inherent structure of the polymer. Decreasing membrane thickness is a fairly easy approach to enhance flux and can be achieved by forming the polymer into asymmetric membrane which consists of a thin selective polymer layer on a porous support [7,8]. The asymmetric membrane technology was first discovered by Loeb et al. and has found practical industrial application since then. However, this approach would lead to enhanced flux for all the penetrants with no enhancement in selectivity. Selectivity can only be affected if the relative permeabilities of the penetrants are altered. So, the fundamental mechanism of gas transport through polymer membranes must be understood prior to initializing efforts towards improving membrane performance.

The fundamentals of gas transport in glassy polymers will be discussed in terms of solution-diffusion mechanism [9]. According to the solution-diffusion mechanism, gas molecules dissolve into the polymer on the high pressure feed side, diffuse through the thickness of the membrane and then desorb on the low pressure permeate side. The permeability coefficient can be described in terms of its solubility and diffusivity by relationship described in Equation 2.3

\[ P = D \times S \]  \hspace{1cm} 2.3

where \( D \) is the diffusivity coefficient (cm\(^2\)/sec), and \( S \) is the solubility coefficient \([\text{cm}^3(\text{STP}) / \text{cm}^3(\text{polymer}) \ \text{cm Hg}]\).
Diffusivity coefficient is a kinetic term and is a measure of the mobility of the penetrant through the membrane. It largely depends on the size and shape of the gas molecule, the relative thermal motions of the polymer chains and the relative polymer chain packing or free volume. Solubility of a penetrant is thermodynamic in nature and is determined by the relative condensability of penetrants, polymer-penetrant interactions and the amount of excess free volume in the glassy polymer.

The ideal selectivity can then be written as a product of solubility selectivity and diffusivity selectivity as shown in Equation 2.4

\[
\alpha_{AB} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B}
\]  

2.4

The solubility selectivity \((S_A/S_B)\) is the measure of relative condensabilities of penetrants A and B and their interactions with the polymer. The diffusivity selectivity is a measure of the shape and size selective nature of the polymer which depends on the intersegmental packing of polymer chains and segmental mobility.

**2.1.2 Dual Mode Theory for Gas Sorption**

The solubility of gases in glassy polymers can be described by the “Dual Mode” theory. Pressure dependent sorption measurements will be discussed in terms of dual-mode sorption model to gain an insight into the effect of incorporation of POSS on the free volume of the glassy polymer. While other
models have been suggested, the dual-mode model is the simplest and most widely employed model. This model states that gas sorption in glassy polymer occurs in two distinct environments \([10,11,12]\). The first environment into which penetrant can sorb in the amorphous densely packed region which is similar to sorption environments in liquids or rubbery polymers and is modeled using Henry’s Law. The second environment is a result of the nonequilibrium glassy state, in which pockets of excess free volume or packing defects serve as readily available sites for gas sorption \([\ldots,13]\). This mode gives rise to a hole filling population and follows Langmuir-type expression. The mathematical expression of the dual-mode model can be written as

\[
C = C_D + C_H
\]

\[
C = k_D p + \frac{b C'_H p}{1 + bp}
\]

Figure 2.1: The different modes of sorption within a polymer.

where \(C_D\) is the dissolved gas population and \(C_H\) corresponds to sorption into the penetrant size defects. The Henry’s law constant, \(k_D\) \((\text{cm}^3\text{(STP)} / \text{cm}^3\text{(polymer) atm})\) is a measure of the dissolved gas population, \(b\) \((1 / \text{atm})\) is the hole affinity constant and \(C'_H\) \((\text{cm}^3\text{(STP)} / \text{cm}^3\text{(polymer)})\) is the Langmuir sorption capacity.
All of the above parameters and constants can be determined by curve fitting the solubility versus pressure isotherm. The solubility coefficient can be determined from Equation 2.7

\[ S = \frac{C}{p} = k_d + \frac{bC''}{1 + bp} \quad (2.7) \]

Penetrant sorption in densely packed polymer region is largely dependent on the relative condensabilities of the penetrant molecules and on the interactions between the polymer and the penetrant. Another parameter on which sorption is dependent is the excess free volume of the polymer where Langmuir type sorption occurs [\text{.\.}]. A detailed explanation of this term is given in the subsequent paragraph.

As stated earlier, penetrant sorption can take place in the excess free volume of the polymer which is hypothetically described by Langmuir theory. Therefore a detailed understanding of the origin of excess free volume within a glassy polymer and factors affecting it is necessary to fully understand the dual-mode model.
Figure 2.2: Specific (or molar) volume versus temperature for typical glassy polymers.

Figure 2.2 illustrates this concept of excess free volume in glassy polymers. Above $T_g$ the polymer exists in a rubbery state, in which the polymer chains are more flexible and possess short chain mobility [14]. If the relationship between specific volume and temperature is extrapolated below the $T_g$, a theoretical or predicted equilibrium volume is obtained which is depicted by dashed line in the illustration [,15,16]. However, the polymer is in a non-equilibrium state and the actual specific volume of the polymer is much higher than the predicted [17]. The difference in volumes is defined as the excess free volume. Excess free volumes are regions of the matrix that are formed as polymer is quenched through $T_g$ hence are not well packed and remain as long
lived segmental-scale voids. The excess free volume is also sometimes referred to as unrelaxed volume.

The excess free volume of a glassy polymer can be affected by factors like aging, addition of an inorganic filler into the polymer matrix, structural modifications to the polymer backbone [18]. Both, aging and addition of inorganic fillers to polymer matrix leads to a decrease in the excess free volume []. Structural changes to the polymer backbone can either decrease or increase the excess free volume depending on the bulkiness of the monomers used []. Film casting conditions also affect the amount of excess free volume, they can be quenched from above $T_g$ temperature rapidly or allowed to slowly cool [19]. The excess free volume will be more in the former case than in the later as the polymer chains will be instantly frozen when they are quenched rapidly, whereas on slow cooling the polymer chains can relax leading to lower free volumes.

2.1.3 **Diffusion of penetrants in glassy polymers**

The penetrant molecule is initially sorbed into the polymer matrix by mechanisms described in the previous section and diffuses across the thickness of the membrane. The penetrant moves through the thickness of the membrane by making diffusive jumps within the polymer matrix [20,21]. In order to do this, the gap between two polymer chains must be greater than the kinetic or the sieving diameter of the penetrant molecule. Thermally activated motion of the polymer chain segments generate transient gaps through which diffusive jumps of the penetrant can occur. Diffusion in polymers is a thermally activated process and can be represented as
\[ D = D_0 \exp \left( -\frac{E_d}{RT} \right) \]  \hspace{1cm} (2.8)

Where \( D_0 \) is the pre-exponential factor and \( E_d \) is the activation energy for diffusion. The activation energy \( E_d \) can further be interpreted using the following equation in terms of the energy needed to open a cylindrical path of length \( \lambda \), and diameter \( \sigma \) (penetrant diameter), in the polymer matrix with a cohesive energy density, \( CED \) \[,22,23,24\].

\[ E_d = \frac{\lambda \Pi \sigma^2 CED}{4} \]  \hspace{1cm} (2.9)

From Equation 2.8 it is clear that small changes in \( E_d \) can cause significant changes in diffusivity selectivity because of the exponential dependence of \( D \) on \( E_d \). Equation 2.9 states that \( E_d \) has a squared dependence on \( \sigma \), the kinetic diameter of the penetrant. Hence diffusivity is a kinetic term and is largely dependent on the size and shape of the penetrant and also on the relative thermal motion of the polymer chains.

For systems that obey the “Dual Mode” model, the effective local diffusion coefficient can be interpreted using the following Equation (2.10) \[,25,26\]

\[ D_{\text{eff}} = D_D \frac{1 + FK / (1 + C_D b / k_D)^2}{1 + K / (1 + C_D b / k_D)^2} \]  \hspace{1cm} (2.10)

where \( F = D_H / D_D \) and \( K = C'_H b / k_D \). \( D_D \) and \( D_H \) represent the average local measure of mobility of a penetrant in the normally dissolved and Langmuir...
environments, respectively. The penetrant residing in the lower energy packing defects have much lower diffusivity than the dissolved molecules \( F \leq 0.1 \).

### 2.2 Gas Transport in Polyimides

Cellulose acetate (CA), polyimides, polyamides, polyetherimides are among the most commonly used polymers for membrane based separations \([27, 28]\). Prominent industrial gas separations where polymeric membranes are used include \( O_2/N_2 \), \( CO_2/CH_4 \), \( H_2/CH_4 \) and \( N_2/CH_4 \) separations \([29, 30, 31]\). The latter three separations are being studied in the natural gas industry whereas the former is used for air purification. Amongst various polymers being studied, polyimides show promising gas transport behavior and are also very thermally and mechanically stable \([32, 33, 34]\). Specifically, rigid aromatic polyimides have higher glass transition temperature \( T_g \) and have higher permeabilities and selectivities as compared to many other polymers.
Table 2.1: Chemical structures of various diamines and dianydrides used to form a polyimide.

<table>
<thead>
<tr>
<th>Dianhydride</th>
<th>Diamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Pyromelletic Dianhydride (PMDA)]</td>
<td>![Oxydianiline (ODA)]</td>
</tr>
<tr>
<td>![Hexafluoro dianhydride (6FDA)]</td>
<td>![Methylenedianiline (MDA)]</td>
</tr>
<tr>
<td>![Isopropylidenedianiline (IPDA)]</td>
<td>![Phenyldianiline (PDA)]</td>
</tr>
</tbody>
</table>

Different types of polyimides are available based on the functionality of the monomers used for polymerization. For example, a polyimide with an aliphatic backbone would be a relatively flexible with a lower $T_g$ with higher permeabilities and lower selectivities, whereas an aromatic backbone would make the polymer more rigid with a relatively higher $T_g$ and higher selectivities. Structures of some of the commonly used aromatic dianhydrides and diamines are given in Table 2.1.
The chemical nature of the constituent monomers will govern the permeability of a penetrant through the polymer matrix. PMDA and 6FDA are the most commonly studied dianhydrides which produce a variety of transport properties based on the nature of diamine. 6FDA has six bulky fluorine groups which impart considerable excess free volume relative to PMDA which is an important factor governing gas transport through polymers []. Also various aromatic diamines are available and gas transport then depends on the relative d-spacing between the polymer chains and the available excess free volume.

A polyimide with 6FDA and MDA constituent monomers was chosen for this study as it is a rigid aromatic polyimide with high \( T_g \) and good gas transport properties.

2.3 Literature Review on Mixed Matrix Membranes (MMM)

Although traditional polymers have good transport properties, their performance is limited by their flux and selectivity []. Current polymers have performance below a hypothetical curve called the “tradeoff curve” or “upperbound” which was first suggested by Robeson in 1991 []. Structural modifications to the polymer backbone were suggested as an alternative route to enhance flux and selectivity at the same time []. However, such efforts did not yield significant enhancements in gas transport properties. Current process requirements have necessitated the development of high performance membranes with performance above the upperbound curve.

Mixed matrix membranes are being researched and developed as they can potentially have performance above the upper bound curve [,35,36]. Mixed
matrix membranes are inorganic molecular sieving materials that are dispersed within a polymer matrix [37]. The goal is to combine the sieving ability of the inorganic sieve with the flexibility, processibility and low cost of the polymer matrix. Molecular sieves have been used for adsorption and separation of gas mixtures because of fine pore structure allowing precise separation [38]. Hence incorporation of molecular sieves such as zeolites, carbon molecular sieves (CMS), fullerene ($C_{60}$) into a polymer matrix can lead to the formation of a MMM with higher permeability and selectivity.

Transport of penetrants across a mixed matrix membrane can take place (i) through the pores of the molecular sieve based on the size and shape of the penetrant, (ii) through the rigidified bulk polymer matrix as the molecular sieves become inaccessible to the penetrant for various reasons, (iii) through the interface between the polymer and the inorganic sieve. Proper engineering of the interface can lead to enhancements in permeability as well as selectivity. Transport occurring by method (i) will lead to higher permeabilities and selectivities, however, if transport occurs by method (ii) then a decrease in permeability would be observed with a probable increase in selectivity. Some of the advantages of mixed matrix membrane are

a. Extended range of application
b. Enhanced thermal and mechanical stability due to the addition of inorganic fillers.
c. Greater processibility as compared to inorganic membranes.
Investigation of mixed matrix concept has predominantly focused on employing zeolites for the dispersed phase. Li et al. incorporated three types of zeolites, zeolite 3 Å, 4 Å and 5 Å with pore sizes of 3 Å, 3.8 Å and 4.5 Å respectively into polyethersulfone (PES) [39]. There was a decrease in permeability for all the gases studied with increase in zeolite loading which was counterintuitive to the molecular sieving ability of zeolite. Enhancements in O₂, CO₂, N₂ permeability and a decrease in CH₄ permeability should have been observed for zeolite 4A-PES MMM based on the kinetic diameters of penetrants. However, enhancements in selectivities was observed and the PES-zeolite 5 Å MMM showed improved performance than zeolite 3 Å and zeolite 4 Å. Gur et al. incorporated zeolite 13X into polysulfone but found no improvements in gas permeabilities [40]. On the contrary, Suer et al. successfully incorporated zeolite 4A and 13X into polyethersulfone and showed enhancement in O₂/N₂ selectivity from 3.7 to 4.4 [41,42]. A most prominent contribution to the development of MMM was done by Rojey et al. who observed significant enhancement in H₂/CH₄ selectivity in zeolite 4A containing Ultem® flat sheet membranes [43]. Pechar et al. studied polyimide-zeolite-L (7.1 Å) MMM and found enhancements in permeabilities of oxygen, nitrogen and methane with no substantial enhancements in selectivities [44]. The zeolite L was modified with aminopropyltriethoxy silane (APTES) and the observed decrease in helium and carbon dioxide permeability was attributed to partial pore blockage due to the APTES surfactant.
Extensive studies on incorporation of other molecular sieving materials like carbon molecular sieves (CMS), silicalite and fullerene have also been reported. Vu et al. incorporated CMS into two popular polyimides (Matrimid® and Ultem®) with enhancements in permeabilities along with significant increases in selectivities of some of the important gas pairs including CO$_2$/CH$_4$ (45%) and O$_2$/N$_2$ (20%) [45,46]. Chung et al. formed Matrimid®-C$_{60}$ MMM and observed a decrease in permeability with increase in C$_{60}$ content [47]. Also improvement in He/N$_2$ selectivity was observed but selectivity for O$_2$/N$_2$ and CO$_2$/CH$_4$ remained unchanged. This was again a counterintuitive observation as the pore size of C$_{60}$ is 7 Å, which is bigger than the kinetic diameters of the gases studied. The enhancements in selectivities were attributed to the polymer chain rigidification and decreased sorption which led to greater decrease N$_2$ permeability than He. A polycarbonate-zeolite 4A MMM study by D. Sen et al. also showed a decrease in pure gas permeabilities with significant enhancement in selectivities [48]. Significant variations in the gas transport behavior of polymer-zeolite mixed matrix membranes were observed which may be partly due to the polymer matrix chosen and partly due to the different preparation methods adopted. Therefore, a wise selection of polymer and molecular sieve are prerequisites to form mixed matrix membranes with enhanced gas transport properties.
2.3.1 Challenges in Forming Mixed Matrix Membranes

Although there has been some success in forming MMMs with molecular sieving materials like zeolite and CMS as the dispersed phase, these materials do not exhibit anticipated improvements in transport properties. One of the primary challenges in forming MMMs using such inorganic molecular sieving materials is the control of the interface between the polymer and the particle. Defects generated at the interface due to weak interactions between the two phases could lead to the formation of an interface void through which non-selective gas transport can take place [49]. This phenomenon is called “sieve-in-a-cage” morphology and is shown in Figure 2.2. Formation of such interfacial voids would typically lead to higher permeabilities with lower selectivities.

Figure 2.3: Formation of a “sieve-in-a-cage” morphology in MMMs.

Pechar et al. modified the surface of zeolite by an amine terminated silane coupling agent to enhance the compatibility between the two phases [ ]. Positive interactions between the two phases promoted adhesion between the two components which led to selectivity enhancements for O\textsubscript{2}/N\textsubscript{2} and N\textsubscript{2}/CH\textsubscript{4} gas pairs. Similar silane modified zeolite 4A-PES MMM were studied by Li et al, they
found enhanced permeabilities and selectivities as compared to the unmodified zeolite [50]. Another theory suggested by Mahajan et al. attributed formation of such interface void to the interfacial stresses generated during membrane formation and drying []. They suggested forming the membrane at its glass transition temperature which would eliminate these stresses as the polymer chains would be more flexible. Another approach suggested was the addition of plasticizers to lower the $T_g$ of the polymer and cast the membrane at that temperature []. Numerous studies have been carried on since then, and comprehensive reviews of some of the important contributions in MMM have been articulated by Chung et al [].

Newer mixed matrix materials are being investigated to form mixed matrix membranes with enhanced gas transport properties. The present work will focus on Polyhedral Oligomeric Silsesquioxane (POSS) as the mixed matrix material. The structure and properties of POSS will be described in the subsequent section along with a comprehensive review on polymer-POSS composites.

2.4 Structure and Properties of POSS

Polyhedral Oligomeric Silsesquioxanes (POSS) are a class of inorganic molecules with precise three dimensional cage structures that can be soluble in typical organic solvents and are readily dispersible in a polymer matrix. POSS consists of a Si-O cage formed by tetravalent Si atoms bound to three oxygen atoms and one functional group (R), which gives it unique properties [51,52,53]. The structure of POSS is illustrated in Figure 2.4. The R group can be tailored to
be inert or reactive using different chemistries depending upon the target application [54]. Commonly used $T_8$ type POSS with formula $(RSiO_{1.5})_8$ are cyclopentylsilsesquioxane, octaphenylsilsesquioxane, octaepoxysilsesquioxane. Two other structures of POSS exist, $T_{10}$ and $T_{12}$ as shown in Figure 2.5. However, extensive work has been focused on $T_6$ with very little experimental work reported on $T_{10}$ or $T_{12}$. In addition, $T_{10}$ and $T_{12}$ are not readily available in pure form []. POSS has a size of ~1.5 nm and mimics the basic building block of zeolites. POSS is synthesized via silane chemistry, an example of synthesis of a cyclohexyl POSS is shown in Figure 2.6. The R groups on the tetravalent Si atoms can be selected or modified at the time of synthesis of POSS or can be modified later using functionalization chemistries [].

![Figure 2.4: Structure of polyhedral oligomeric silsesquioxane ($T_8$).](image)

![Figure 2.5: (a) $T_{10}$ and (b) $T_{12}$ cage structures of POSS.](image)
Some of the property enhancements observed in polymer-POSS composites are as follows:

1. Increased decomposition temperature ($T_{dec}$).
2. Increased glass transition temperature ($T_g$).
3. Reduced flammability
4. Lower density.
5. Oxidation resistance.
6. Extended temperature range.
7. Enhanced blend miscibility.

POSS molecules can be thought of as the smallest particles of silica possible. However, unlike silica or modified clays, each POSS molecule has reactive functional groups suitable to form copolymers or blends with good adhesion. Further, these organic groups result in solubilities of POSS in common organic solvents. Therefore, POSS molecules can be used in the same manner as...
common organics and can be added to nearly all polymer types (glassy, rubbery, elastomeric, crystalline). In addition, the nanoscopic size of POSS alters the motion polymer chains while still maintaining processibility of the base polymer [].

### 2.5 Background on Polymer-POSS Composites

Recently, considerable research has focused on development of polymer-POSS composites targeting a wide range of applications. Broadly speaking, there are three types of polymer-POSS composite materials [,55,56]:

1. **Bead type**: A POSS with two functionalities is incorporated within a polymer backbone during polymerization.
2. **Pendant type**: A POSS with single functionality is polymerized within the polymer backbone to form a pendant group.
3. **Blend type**: An octa functional or a non-functional POSS is simply blended within a polymer matrix to provide reinforcement.

Monofunctional POSS molecules have also been used as comonomers to prepare copolymers. A series of block copolymers were prepared by Xu et al. using isobutyl styryl POSS in vinylpyrrolidone and acetoxylsyrylene [57]. A narrow molecular weight distribution was obtained with slight increase in the $T_g$. A similar study on styryl POSS copolymers was done by Haddad et al., where large changes in the thermal properties were observed with varying the amount of POSS [58]. Particularly, tailoring of the softening point and decomposition temperature was observed at different POSS loadings. Property enhancement in norbonyl-POSS copolymers was found to be dependent on the seven corner groups of POSS, as studied by Mather et al [59]. Different thermal
and mechanical properties of the copolymer were obtained with cyclopentyl and cyclohexyl POSS. The magnitude of dependence of $T_g$ on the composition of POSS in the copolymer was greater for cyclohexyl POSS than for cyclopentyl POSS. Also, a significant enhancement in the storage modulus below the $\beta$ relaxation temperature was observed only for cyclohexyl POSS-norbonyl copolymer. Therefore proper selection of polymer and POSS is necessary to obtain the necessary final material properties.

Grafting or in situ polymerization is one of the most commonly used techniques to prepare polymer-POSS nanocomposites. Lee et al. formed hybrid nanocomposites containing octaepoxy POSS (up to 10 wt%) by in situ polymerization within a polyimide backbone to form materials with low dielectric constant [60]. They observed a reduction in the dielectric constant which was explained on the basis of incorporation of nanovoids within the polymer which led to an overall increase in the free volume of the polymer. A new type of polyimide-poly(silsesquioxane)-like hybrid nanocomposite material was prepared by Tsai and coworkers by employing $p$-aminopropyltrimethoxysilane (APTS) to provide bonding between PSSQ-like and the polyimide [61]. These hybrid materials also had excellent transparency in visible light even at high silsesquioxane loadings. An octafunctional POSS was incorporated into an epoxy network via in situ polymerization by Ni and coworkers [62]. A uniform dispersion and improved flame retardance was observed when the POSS concentration was 10 wt%. The properties of POSS were harnessed for a relatively novel application by Gonzalez et al [63]. They investigated the resistance of polyimide-POSS
composite to atomic-oxygen attack. They found that POSS containing polyimide formed a passivating layer of SiO$_2$ on the surface which largely resisted atomic-oxygen attack and can have potential application on spacecrafts that operate in low-orbit earth atmosphere. The thermo-mechanical properties of polyimide-POSS nanocomposite formed by in situ polymerization were evaluated by Huang [64]. The PI-POSS nanocomposites exhibited excellent thermal mechanical properties such as high glass transition temperature and low coefficient of thermal expansion. Tamaki et al. utilized (octaaminophenyl) silsesquioxane as building blocks to form polyimide-POSS nanocomposites with enhanced properties [65,66]. The high reactivity of octafunctional POSS was used to form a continuous POSS network within the polyimide. Physical, thermal and mechanical properties of an organic/inorganic imide composite formed from aminophenylsilsesquioxanes were studied by Choi et al. [67]. Improved thermomechanical properties were obtained due to the stability induced by cross linking and perfect dispersion of silica particles.

Another approach to forming polymer-POSS hybrid nanocomposites is by blending, either in solution or in melt. The processing of the blended systems is simple and has a potential for commercial application without changing the processing technology. A series of composite materials were produced by incorporating POSS derivatives into polycarbonate by melt blending [68]. Trisilanolphenyl-POSS/PC composites possessed the best overall performance among the POSS materials tested. They further emphasized on the need for proper selection of POSS and polymer to get the desired properties.
Blanski et al. formed uniformly dispersed polystyrene-POSS hybrid materials by solution blending technique [69]. They demonstrated that by altering the organic side groups on POSS uniform dispersion can be obtained even in high molecular weight polystyrene, also a 30% increase in surface hardness was observed. Blends of poly(methyl methacrylate) (PMMA) with two acrylic POSS were studied by Kopeski et al. to determine the effect of well-dispersed POSS nanoparticles on the thermomechanical properties of PMMA [70]. A hydrogenated acrylic POSS was used and was compared with an unmodified acrylic POSS. The modified POSS had better dispersion and enhanced properties as compared to the unmodified POSS.

These studies indicate that proper selection of polymer matrix and POSS derivatives can result in hybrid nanocomposites with enhanced properties with respect to the base polymer. In addition, the wide range of applications where POSS can be potentially used are identified.

2.5.1 Computational Studies

Some interesting computation studies were also carried out by researchers on POSS and their polymer composites. Ab initio methods were employed by Tejerina et al. to determine the size of $T_8$, $T_{10}$ and $T_{12}$ POSS and the insertion mechanism of $N_2$ and $O_2$ into these silsesquioxane frameworks [71]. The diagonally opposite Si-Si distance for a $T_8$ POSS was determined to be 4.5 Å, $T_{10}$ and $T_{12}$ each had two or more isomeric structures with slightly bigger core size. Their work concluded that every POSS investigated showed higher permeability for $O_2$ than $N_2$ due to the differences in deformability of the electron
distribution of the molecular valence shell. Further the O$_2$/N$_2$ selectivity decreased as the number of faces increased from T$_8$ to T$_{12}$. This work was one of the basis for the selection of POSS as mixed matrix material in this study. A molecular simulation study done by Peng et al. revealed the effect of tether groups on the thermodynamic properties of POSS [72]. Effect of alkyl chain length of mono-substituted and octa-substituted POSS on the critical temperature, melting temperature and density was determined using SAFT-VR. The entire mechanism from silanol to T$_8$ was investigated by Kudo et al. using electronic structure theory calculations [73]. This study aided in understanding the actual reaction mechanism for the synthesis of silsesquioxanes.

Polymer-POSS blended systems were also modeled by many researchers to determine the aggregation behavior of POSS within a polymer matrix. The influence of blending cyclopentyl substituted POSS into a polyethylene matrix was probed by Capaldi et al. using atomistic simulations [74]. They showed that there is a decrease in the mobility of the polymer with increasing POSS content, and aggregates of POSS with clear internal ordering were formed. They also demonstrated that the orientation of the polymer at the POSS surface is such that it may influence diffusion of small molecules. A Monte Carlo study on the network structures of crosslinked POSS was done by Sheng and coworkers [75]. The effect of tether length and flexibility on the pore size and pore size distribution was determined. The reactivity of the linkers also plays an important role in the crosslinking density and pore formation in a continuous POSS network.
2.6 Why POSS?

Based on the ease of processibility and some unique properties, POSS was chosen as the inorganic component of our mixed matrix material. Extensive literature review suggested that POSS can be easily incorporated within a polymer matrix without compromising the inherent thermal and mechanical properties of the base polymer. Further, computational studies provided some evidence of possible selective transport of small gas species through POSS. Further, the structure and properties of POSS could overcome the most important challenge in the formation of mixed matrix membrane. The ready solubility of POSS in most organic solvents combined with the nanoscopic size enables incorporation into the polymer matrix on a molecular scale. This should enhance dispersion and affect the polymer matrix in a prominent way. Also, the organic functionalities on POSS surface create strong interactions with the surrounding polymer, thereby, reducing the formation of “sieve-in-a-cage” morphology.

Recently, POSS cages are being explored as porous gas permeable materials for gas separation. Rios-Dominguez et al. formed polystyrene-POSS mixed matrix membranes and studied O\textsubscript{2}, N\textsubscript{2} separation [76]. A styrylisobutyl POSS was polymerized with styrene monomer by free radical polymerization using 5, 10 and 20 wt% POSS concentration. The 5 and 10 wt% membranes showed higher O\textsubscript{2} and N\textsubscript{2} permeabilities but lower selectivities. The enhancements in permeabilities were attributed to increase in free volume because of the incorporation of bulky porous POSS cages within the polymer.
backbone. Increase in free volume led to higher diffusivities of \( \text{O}_2 \) and \( \text{N}_2 \) which led to decreased selectivities. The 20 wt% membrane showed higher \( \text{O}_2 \) solubility and lower \( \text{O}_2/\text{N}_2 \) selectivity.

A contrasting study done by Asuncion et al utilized POSS networks as barrier materials [77]. Continuous POSS networks were formed by reacting the R groups and their oxygen transmission rates (OTR) were measured at temperatures up to 70 °C. They observed that silsesquioxane films with high cross-link density and long flexible tethers gave maximum performance. A decrease in OTR was observed at lower temperatures, however, at higher temperatures (> 50 °C) the OTR increased. This loss in barrier property was attributed to the generation of nanosized cracks at elevated temperatures and also to the higher thermal motion of oxygen as well as the organic tether groups.

Further investigation need to be done using different polymer-POSS systems to determine the impact of POSS on the transport behavior of common polymers. Counterintuitive results have been obtained earlier with zeolite containing MMMs [1]. Therefore, speculations based on pore size and dimensions of POSS cannot be made without experimental evidence. This study discusses physical, mechanical and gas transport properties of polyimide-POSS nanocomposite by incorporating an octa functional POSS into a rigid aromatic polyimide.
3 EXPERIMENTAL

3.1 Materials

The polyimide used in this study, (6FDA-MDA) (Figure 3.1) was synthesized in the lab using standard procedure [78]. The dianhydride 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from Clariant Inc. (Charlotte, USA) and the diamine 4,4’-diaminediphenylmethane (MDA) from Aldrich (Milwaukee, USA). Acetic anhydride was purchased from Aldrich, distilled and used as a catalyst for imidization. Methanol and triethylamine (99.95%) were purchased from Fisher and used as is. N,N'-dimethylacetamide (DMAc) which is polar and aprotic was used as a solvent for the polyimide synthesis. Synthesis of high molecular weight polyimide requires anhydrous conditions, hence the monomers, solvents and reagents used for synthesis were purified prior to use. The monomers MDA and 6FDA were purified by sublimation. The solvent, DMAc was purified by refluxing over calcium
hydride for few hours and then collected by distillation. The catalyst acetic anhydride was also purified by distillation. Triethylamine was used without further purification.

![Structure of octaphenyl silsesquioxane (OPS).](image)

Figure 3.2: Structure of octaphenyl silsesquioxane (OPS).

The POSS used in this study was an octaphenyl substituted POSS, known as octaphenylsilsesquioxane (OPS) as shown in Figure 3.2. OPS was a fine white colored powder and was purchased from Aldrich. OPS was converted to octaaminophenyl POSS (OAPS) by a two step nitration-hydrogenation reaction. The 5 wt% Pd/C catalyst that was used in the hydrogenation step was also purchased from Aldrich. Other solvents and reagents including tetrahydrofuran (THF), hexanes, ethyl acetate, fuming nitric acid (99.99%) used in the functionalization of OPS were purchased from Fisher. The hydrogenation step required anhydrous THF in order to obtain pure product with good yield. THF refluxed over sodium/benzophenone and collected by distillation using a syringe under nitrogen just prior to use. Celite, sodium benzophenone, and sodium sulfate were also purchased from Aldrich.

Plain PI and PI-OAPS composite films were prepared in THF. Distilled THF was used for this purpose as well. PI-OPS films were cast using methylene
chloride as solvent without purification, as OPS was insoluble in THF. All the films in this study were cast in a glass dish. The commercially available petri dishes did not have a perfectly flat surface, which led to non-uniform films. Therefore, flat bottom dishes were specially made to obtain films with uniform thickness. These flat bottom dishes were custom made by the glassblower at the Department of Chemistry, University of Toledo.

3.2 Techniques to Functionalize POSS, Polyimide and Nanocomposite Formation

3.2.1 Synthesis of octaaminophenyl silsesquioxane (OAPS)

Scheme 3.1: Reaction scheme for the functionalization of OPS to OAPS.
The two step functionalization method to convert OPS to OAPS was adopted with slight modifications from a method described by Huang and co-workers []. The reaction scheme for the functionalization of OPS to OAPS is given in Scheme 3.1. In the first step, OPS was nitrated to octanitrophenyl POSS (ONPS), followed by hydrogenation to octaaminophenyl POSS (OAPS). For this reaction, 10 g of octaphenylsilsesquioxane (OPS) were added to a 500 ml round bottom flask and kept in a water/ice bath at 0 °C. Then fuming nitric acid (50 ml) was added in parts using a glass pipette. The reaction mixture was stirred for half hour at 0 °C and for 20 h at room temperature. The reaction mixture was poured over ice to obtain a faint yellow precipitate. This precipitate was filtered, washed with distilled water two times and dried at 70 °C to obtain octanitrophenylsilsesquioxane (ONPS). The reaction was confirmed by FTIR and NMR.

A catalytic hydrogenation reaction was used to convert ONPS to OAPS. For this reaction 5 g ONPS (3.58 mmol, -NO₂ 28.7 mmol) was added to a 300 ml three neck flask with a condenser under nitrogen. Freshly distilled THF (40 ml) was added via syringe and stirred until the ONPS completely dissolved. 5 wt% Pd/C catalyst (0.61 g, 0.287 mmol) and 40 ml triethylamine (0.287 mol) were added to the reactor. Following this, the mixture was heated to 60 °C and 98% formic acid (4.4 ml, 0.115 mol) was added dropwise over a period of 2 h using a pressure equalizing dropping funnel. The reaction was carried out for 14 h and filtered over a bed of celite to remove the Pd/C catalyst from the reaction mixture. The filtrate was then transferred to a separating funnel to which 40 ml
ethyl acetate was added and then extracted with distilled water (20 ml, 3x). The organic phase was collected and dried over sodium sulfate to remove the residual water. The dry organic mixture was precipitated by dropwise addition to 1L of hexane to obtain a pale yellow precipitate which was collected by filtration and dried under vacuum for 2 days. The OAPS was further purified by dissolving it in THF/ethyl acetate (30:50) mixture and removing the undissolved impurity by filtration. The filtrate was precipitated in 600 ml of hexane to obtain pure OAPS. The resulting compound was dried under vacuum for 3 days to obtain a white powder of pure OAPS.

3.2.2 Octaphthalimidephenyl silsesquioxane (OPIPS)

The reactivity of the amine groups on POSS were tested by reacting it with phthalic anhydride and further imidizing the amide bond (Scheme 3.2). For this reaction 5 g of OAPS (0.433 mmol) were added to a 50 ml round bottom flask. Then, 10 ml of freshly distilled THF was added to the reaction mixture and stirred
until the OAPS completely dissolved. Phthalic anhydride (0.539 g, 3.64 mmol) was added and the solution stirred for 2 h. The excess THF in the mixture was evaporated using a Bucchi rotovap and the resulting powder was transferred to a glass dish. The glass dish was kept in a vacuum oven at 110 °C for 6 h. The final imidization step was carried out at 300 °C under vacuum. The formation of OPIPS from OAPS was confirmed using FTIR.

### 3.2.3 Polyimide Synthesis

An aromatic rigid polyimide 6FDA-MDA with structure given in Figure 1. was synthesized and used in this study. The materials used for the synthesis and the purification techniques have been illustrated in section 3.1. The polyimide was synthesized using the condensation polymerization method described by Husk et al [78]. A schematic of this reaction is shown in Scheme 3.3. A dry three neck round bottom flask with a condenser was purged with nitrogen for some time and 5 mmol MDA (1.98 g, 10 mmol) were added to the reactor followed by 50 ml distilled DMAc and stirred until the MDA completely dissolved. An equimolar amount of 6FDA (4.44 g, 10 mmol) was added to the reactor and stirred for 4 h. The diamine reacted with the dianhydride to form a polyamic acid which was pale yellow in color. The polyamic acid was then chemically imidized to form polyimide using catalysts, acetic anhydride and triethylamine. Then 40 mmol of triethylamine and acetic anhydride (1:1) were added to the polyamic acid solution. The temperature was increased to 50 °C and the mixture was stirred for 1 h.
Scheme 3.3: Reaction scheme for the synthesis of 6FDA-MDA polyimide.

The final imidization step was carried out by increasing the temperature to 100 °C for 30 min, during which cyclic dehydration takes place to form an imide bond. During this step the color of the solution slightly darkened, sometimes turning red. The solution was allowed to cool to room temperature and then precipitated in 1 L methanol to form polymer coils. This precipitate was crushed in a blender using fresh methanol to give polyimide powder. Finally, the product was filtered, washed with methanol two times and collected by vacuum filtration. It was dried in an oven at 80 °C for 2 days and then at 260 °C for 16 h under vacuum to ensure complete removal of the solvent. The formation of an imide bond was confirmed by FTIR and the molecular weight was determined using gel permeation chromatography (GPC) with THF as the eluting solvent.
3.2.4 Nanocomposite formation

There are a number of different ways to incorporate inorganic filler within a polymer to form a nanocomposite. The properties of the composite may vary with the formation technique. Hence, optimization of the technique based on the desired properties is necessary. Various methods of incorporating OAPS in PI were investigated and an optimum method was selected based on ease of preparation and physical properties.

3.2.4.1 In-situ polymerization

In situ polymerization was initially used to incorporate OAPS within the backbone of the polyimide. Two routes of imidization were tested (a) chemical imidization, wherein the polyamic acid formed during the polymerization reaction is imidized by using catalysts, acetic anhydride and triethylamine (b) thermal imidization, wherein the polyamic acid is heated to high temperatures (~300 °C).

Chemical imidization

(i) Within the backbone (Scheme 3.4): A 2 wt% PI-OAPS composite was prepared by adding MDA (0.99 g, 5 mmol) to a dry three neck reactor with a condenser and purged with nitrogen. DMAc (30 ml) was added till the MDA completely dissolved. To this OAPS (64.2 mg, 0.05 mmol) was added and stirred for some time. The dianhydride 6FDA (2.22 g, 5 mmoll) was added and the reaction mixture stirred for 4 h. After this point the standard chemical imidization procedure was adopted. Finally, the PI-OAPS composite was obtained by precipitating the reaction mixture in methanol and drying it in a vacuum oven.
Scheme 3.4: Reaction mechanism for in situ polymerization of PI-OAPS by incorporating OAPS in the PI backbone.
Scheme 3.5: Reaction scheme for in situ polymerization of PI-OAPS by incorporating OAPS as side groups.
(ii) As side groups (Scheme 3.5): A 2 wt% PI-OAPS composite with OAPS attached to the polymer chain as side groups was prepared by forming polyamic acid using equimolar amounts of MDA and 6FDA (5 mmol). After the formation of polyamic acid, OAPS (64.2 mg, 0.05 mmol) was added and allowed to react for 2 h. This was followed by the standard chemical imidization and drying protocol as discussed earlier.

**Thermal imidization**

A method to directly obtain PI-OAPS composite film was to do thermal imidization. For this, polyamic acid-OAPS reaction mixture was prepared by either of the methods described above. The reaction mixture was diluted with 25 ml THF and cast onto a glass dish. The dish was kept in an oven at 80 °C under dry air flow for several days (until the film dried). The film was then peeled off from the glass dish and kept on a glass plate and heated stepwise to 80 °C, 120 °C, 200 °C. The final imidization was carried out by heating the film to 300 °C under inert atmosphere.

3.2.4.2 Blending technique

The pure 6FDA-MDA film and the PI-OAPS composite films were made by simple blending technique as shown in Figure 3.3 using THF as the casting solvent. Plain PI films were prepared by dissolving PI (5 wt%) in THF (30 ml) to form a solution. Foreign particles that would induce defects in the film and result in a loss of selectivity were removed by filtering the solution under vacuum prior to casting.
Figure 3.3: Description of the blending technique used to incorporate OAPS within the PI matrix.

The polymer solution was cast in a flat bottom dish. The dish was kept in a glove bag with THF environment to facilitate slow evaporation of solvent and to obtain films with uniform thickness. After all the solvent had evaporated, the dish was submerged in water and the film peeled off from the glass surface. The film was dried at 80 °C for 2 days and annealed at 260 °C under vacuum for 16 h. To prepare PI – OAPS composite films, PI (5 wt%) and OAPS were dissolved separately in THF and kept for complete dissolution overnight. The two solutions were then mixed and blended for 15 min and cast in a flat bottom dish. Composite films of octaphenylsilsesquioxane (OPS) and PI were prepared in methylene chloride (as OPS was insoluble in THF) to determine the effect of functionalization on the appearance and mechanical properties of the composite. All composites were dried in a similar fashion as the plain PI.
3.3 Characterization Techniques

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

A Digilab FTS 4000 FTIR was used to determine the presence of functional groups on POSS, polyimide and the composite. POSS samples which were in powder form were prepared using a standard KBr pellet technique. For this FTIR grade KBr was dried in an oven at 100 °C. The sample was also dried under vacuum for several days. KBr and the sample (1 to 3 wt%) were mixed thoroughly in a glass mortar and pestle. Pellets of approximately 1 mm thickness were prepared using a Thermoelectron pelletizer and applying hand pressure. Care was taken to form transparent pellets. The pelletizer along with the pellet was mounted in the internal workbench of the FTIR and scanned at least 1024 times. A Background spectrum (1024 times) was collected prior to collecting the sample spectrum. Attenuated total reflectance (ATR) technique was used to obtain spectra of polymer films with the FTIR-microscope. Plain PI and blended films were tested using FTIR to determine complete imidization of the base polyimide, and the appearance and intensity of the Si-O-Si peak. Before starting the experiment the microscope was filled with liquid nitrogen to keep it cool while in operation. The microscope ATR accessory was mounted onto the microscope. Small film samples were kept on the microscope stage with a glass slide underneath for support. To collect a spectrum, the ATR was lowered so that it just touched the sample film. A background spectrum was collected and subtracted from the sample spectrum.
3.3.2 $^1$H Nuclear Magnetic Resonance Spectroscopy (NMR)

$^1$H NMR was used to confirm the functionalization of OPS to OAPS. A Varian VXRS-400 MHz spectrometer at The University of Toledo Instrumentation Center was used for this purpose. Deuterated acetone $d_6$ was used as the solvent and tetramethylsilane was used as the internal standard. Samples were prepared by dissolving small amounts of POSS in acetone-$d_6$ in a NMR tube. The tube was inserted in the NMR spectrometer and the spectrum was collected using standard procedures.

3.3.3 Gel Permeation Chromatography (GPC)

Molecular weight of the PI used for blending with POSS was determined using a Shimadzu SCL-10A VP series gel permeation chromatograph (GPC) with a $300 \times 7.8$ mm Phenomenex phenogel column ($5 \mu$, $10^4$ Å). Consistency of molecular weight from different batches of synthesized polyimide was determined using GPC. Chromatography grade THF (purchased from Aldrich) was used as the eluting solvent. Samples were prepared by dissolving 1 to 2 mg/ml PI in GPC grade THF. A standard GPC start-up and operating procedure was adopted. The sample solution was filtered under vacuum to remove any particulate foreign objects which are likely to block the column.

3.3.4 Density Measurements

The bulk densities of the plain PI and the PI-OAPS composite films were measured in a density gradient column with CaNO$_3$ aqueous solution at the University of Toledo, Polymer Institute. The density measurements were
performed on solution cast films that had been thoroughly dried. The density gradient column was maintained at 25 °C and contained an aqueous solution of CaNO$_3$. Glass beads of known densities were immersed into the column to develop the calibrated gradient. Small pieces of the sample film were cut and carefully dropped into the column to avoid bubbles on the surface. After attaining equilibrium the position of the sample film relative to the glass beads were noted. Density calculations were carried out using the following Equation.

\[
d = a + \frac{(x-y)(b-a)}{(z-y)}
\]

where,

d = density of the sample film (g/cm$^3$) (to be determined)

a = density of bead 1 (lighter)

x = position of the sample film (cm)

y = position of bead 1 (cm)

b = density of bead 2 (heavier) (g/cm$^3$)

z = position of bead 2 (cm)

3.3.5 UV-vis Spectroscopy

A UV-visible spectrophotometer was used to determine the optical properties of the PI-OAPS composite films. A dual beam Shimadzu UV2401 PC spectrophotometer was used to determine absorbance in the visible range of 400 to 700 nm. Thin samples of the polymer films were cut and placed directly onto the slits. The thickness of the films was almost constant and ranged from 0.08 to
0.09 mm. Air was used as the reference. The obtained absorbance data was converted to percent transmittance by using the following Equation:

\[ A = 2 - \log_{10} T \]  

where \( A \) is the absorbance and \( T \) is transmittance. The optical clarity of the composite films was determined from the relative values of percent transmittance the different PI-OAPS composites.

### 3.3.6 Wide Angle X-ray Diffraction (WAXD)

Wide angle x-ray diffraction (WAXD) measurements were carried out on a Panalytical X’Pert Pro diffractometer with Cu K\(_{\alpha}\) radiation, \( \lambda = 1.54 \) Å. The powder diffraction technique was used to collect diffraction patterns of pure OAPS. For this the powder was ground finely and neatly packed in an aluminum sample holder. Extra care was taken while grinding and packing the sample as improper sample preparation could lead to erroneous diffraction patterns. Diffraction patterns of the films were collected by cutting rectangular strips of the film and neatly sticking them onto the stage by using a double sided scotch tape. Care was taken to make sure that the scotch tape did not appear in the path of the x-ray beam and that the film was precisely stuck to the stage without any unevenness. A symmetric gonio scan was performed from \( 2\theta = 2.5^\circ \) to \( 40^\circ \) and the intensity was collected by an X’celerator detector.

### 3.3.7 Dynamic Mechanical Analysis (DMA)

A TA Instruments dynamic mechanical analyzer (DMA) Q 800 was used to measure thermal - mechanical properties of the nanocomposite films. In DMA,
the sample film is subjected to a dynamic strain and the resultant stress is recorded. Storage modulus, loss modulus and tan delta were determined using a temperature ramp frequency sweep program with a tension clamp on thin sample films. Storage modulus is the measure of energy stored and loss modulus is a measure of energy lost under oscillatory strain. Tan delta is the ratio of loss and storage modulus, the peak of the tan delta curve was used as the glass transition temperature \((T_g)\) of the sample. The samples were heated from room temperature to 400 °C by using a ramp rate of 2 °C/min and a frequency of 1 Hz. Sample preparation was done by cutting the film into thin strips of approximately 5 mm wide, 0.1 mm thick and 16 mm long. The sample dimensions were kept approximately constant from run to run to maintain consistency. Position calibration was done followed by clamp calibration before each run. No sub \(T_g\) transition was observed for any of the samples. The sample glass transition temperatures of the films studied ranged from 295 °C to 325 °C.

### 3.3.8 Thermogravimetric Analysis

Thermal degradation of POSS and PI-OAPS nanocomposites were analyzing using a TA Instruments thermogravimetric analyzer (TGA) Q 50. The % weight versus temperature curve was used to determine the onset decomposition temperature. The derivative thermogravimetric curve (DTG) was used to qualitatively describe the nature of degradation observed in either POSS or in films. A platinum sample pan was used and the temperature range studied was up to 1000 °C. A heating rate of 5 °C/min was used for all the samples. A fine powder of 5 to 10 mg of POSS samples was ground and packed carefully.
into the pan to form a uniform layer. The PI and PI-OAPS (5 to 10 mg) films were cut into small rectangular pieces and placed in the pan. Dry nitrogen gas was purged through the balance (40 ml/min) and the sample chamber (60 ml/min).

3.3.9 Instron Tensile Testing

Mechanical properties including Young’s modulus, strength and strain at yield were determined as a function of OAPS concentration using tensile testing on a Universal Tensile Tester. The sample specimen was held between the two pneumatically operated grips and subjected to a fixed load using a fixed drawing rate. Samples were cut using a dogbone according to ASTM standard 683. At least 5 specimens from each film were tested, the thickness and gauge length were measured for each specimen by using a caliper. The gauge length was the distance between the upper and the lower grip. A stress-strain curve characteristic of a polyimide was obtained when the dogbone samples were subjected to a 100 N load. The drawing rate was kept constant at 1 mm/min and a load cell of 100 N was used. The initial slope of the stress strain curve was used to calculate the Young’s modulus, strength was determined from the maximum stress at yield. Toughness was determined from the area under the stress strain curve or simply strain at yield divided by the volume of the specimen.

3.3.10 Scanning Electron Microscopy (SEM)

A FEI Nova 200 scanning electron microscope at the University of Michigan’s Electron Microbeam Analysis Laboratory (EMAL) was used to obtain
micrographs of fracture surface of the composite films. The SEM was equipped with an x-ray EDAX UTW detector to perform (energy dispersive spectroscopy) EDS analysis. An electron beam (15 kV, 0.14 nA) was focused on the sample and the image obtained was collected at various magnifications. The image was stabilized by adjusting the x and y stigmator. Typical sample preparation involved snapping the polymeric film under liquid nitrogen and mounting it on a stub with a double sided carbon tape. Since the polymeric films were non-conducting, they were coated with gold before mounting in the SEM. A very thin layer (~10 nm) of gold was sputtered onto the sample using a gold coater with an argon plasma. Qualitative elemental analysis on the 50 wt% PI-OAPS film was carried out by collecting EDS spectra at different spots as discussed in Chapter 4.

3.3.11 Gas Penetrants Used in this Study

The gases used in this study were obtained from Linde Inc., and were used as received. The purity of each gas was at least 99.95%. The various gas penetrants studied and their physical properties are listed in Table 3.1. The permeability and sorption of these gases through the membranes were studied and the coefficients determined. The penetrants were chosen to allow the determination of permeability and selectivity of several industrially important gas pairs, such as O₂/N₂, CO₂/CH₄ and He/CH₄.
Table 3.1: Properties of gas penetrants used in this study.

<table>
<thead>
<tr>
<th>Penetrant</th>
<th>He</th>
<th>CO₂</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Diameter (Å)</td>
<td>2.89</td>
<td>3.3</td>
<td>3.46</td>
<td>3.64</td>
<td>3.8</td>
</tr>
<tr>
<td>Critical Temperature (K)</td>
<td>33.2</td>
<td>304.2</td>
<td>154.6</td>
<td>126.2</td>
<td>190.6</td>
</tr>
</tbody>
</table>

The kinetic diameters of penetrants have been correlated with the diffusivity coefficients in polymers. Amongst other factors, the solubility of a penetrant into the polymer at a given pressure is dependent on the critical temperature of the penetrants. Higher critical temperatures of the penetrant indicate more condensability or solubility in the polymer. All gas transport studies are based on pure gases.

### 3.3.12 Gas Permeation System

Pure gas permeabilities were measured using a constant volume variable pressure permeation set-up as shown in Figure 3.4. It consists of a downstream and upstream volume cylinders separated by the permeation cell in which the membrane is mounted. The downstream volume is equipped with a pressure transducer whereas the upstream pressure is measured using a pressure gauge (Heise, 1000 psia). The upstream volume, permeation cell and the downstream volume were kept in a constant temperature enclosure. The downstream pressure was measured using a BOC Edwards Barocell 600 pressure transducer with a pressure range up to 10 torr and an accuracy of 15%. The upstream volume was used as a buffer volume to allow the gas to equilibrate at a particular
temperature and to modulate any small delivery pressure variations from cylinder. The membrane was mounted in the permeation cell and the gas permeated through the membrane was collected in the downstream volume whose pressure was measured by the pressure transducer. The membrane was masked on both sides using an adhesive aluminum tape in order to confine permeation through a fixed area.

Prior to use the system was refurbished and was calibrated using the following procedure:

1. The downstream side was isolated from the upstream side and connected (after the downstream valve) to a sample cylinder of known volume.
2. Both the downstream volume and the sample cylinder were evacuated for some time. The sample cylinder was evacuated for a longer time. The downstream pressure was noted.

3. Then vacuum was shut off and the valve between the sample cylinder and the downstream volume was opened and change in the reading of the pressure transducer was noted down.

4. The total downstream volume was determined by using the ideal gas law. A typical permeation run would involve mounting the membrane in the permeation cell and then evacuating the entire system overnight. Vacuum to the system was then shut off and the gas was slowly pressurized to the desired pressure on the upstream side. As the gas permeated through the membrane it was collected in the downstream volume (calibrated). The steady state increase in the downstream pressure was recorded by the transducer-readout assembly. Prior to second run, the downstream was evacuated for sufficient time.

The permeability in barrers was calculated from the steady state rate of increase in the number of moles of gas \(\frac{dn}{dt}\) in the downstream volume using Equation 3.3

\[
P = \frac{10^{10} \times \left(\frac{dn}{dt}\right) \times l \times 22400}{\left(p_0 \times \left(\frac{196.5}{38}\right)\right) \times A}
\]

The thickness of the membrane \(l\) was accurately measured using a caliper and \(p_0\) is the upstream pressure measured from the pressure gauge. The permeation area \(A\) was determined from the diameter of the unmasked portion of the
membrane. Gases studied were helium, oxygen, nitrogen, methane and carbon
dioxide in that order up to 200 psia (~ 14 atm) at 35 °C, 45 °C and 60 °C.

3.3.13 Gas Sorption Equipment and Measurement

Pure gas sorption measurements were done using a dual volume sorption
set-up. A schematic of the experimental set-up is shown in Figure 3.5. The
sample chamber volume \(V_A\) and the reservoir volume \(V_B\) are separated by a
valve A. Two MKS pressure transducers with integrated display are mounted on
the \(V_A\) and \(V_B\). The valve B allows inlet of vacuum/gas into the system. The entire
set-up was kept in a constant temperature bath. The polymer sample in the form
of thin films was placed in \(V_A\).

Sorption set-up was calibrated to determine the volumes \(V_A\) and \(V_B\) as follows:

1. The entire system was evacuated overnight. Valve A was closed and \(V_B\)
   was pressurized using nitrogen gas.

![Figure 3.5: Schematic of dual volume sorption set-up.](image-url)
2. Valve B was closed and the pressure reading was noted after attaining equilibrium. Then Valve A was opened to expand the gas into the $V_A$ and closed quickly.

3. Pressure readings from both the transducers were noted after 30 minutes.

4. Steps 1 - 3 were repeated for pressure ranges from 100 psi to 900 psi.

5. A mole balance between the two chambers gave the ratio $V_A/V_B$.

6. To determine the volumes of the two chambers, a ball bearing of known volume was kept inside the sample chamber and steps 1 - 4 were repeated.

7. A mole balance between the two chambers again yielded one more equation for $V_A/V_B$. The two equations were solved and numerical values of $V_A$ and $V_B$ were determined.

A typical run started by placing the known mass of polymer sample (1.2 g – 1.5 g) in the form of thin strips inside the sample chamber $V_A$. The entire system was evacuated overnight to remove adsorbed air or gases. After sufficient evacuation, valve A was closed and gas was introduced to the reservoir chamber to a desired pressure, following which the valve B was closed. After attaining steady state the pressure reading from the reservoir chamber was noted. By using ideal gas law the number of moles of gas trapped inside $V_B$ was determined. Valve A was then opened and the gas was allowed to expand into the sample chamber. The valve was closed back again almost instantaneously. Pressure reading in both the chambers was noted after sufficient equilibration time. Pressure reading remained almost constant for the reservoir chamber, whereas a continuous
decay in pressure was observed in the sample chamber as the gas gets sorbed into the polymer. The decay in pressure was maximum for CO₂ and less for CH₄, N₂, O₂, He in that order. The number of moles of gas in Vₐ was determined using ideal gas law using the volume of sample chamber minus the sample volume as the actual volume for calculation. The difference between the sum of these amounts and that originally trapped gave the quantity of a gas sorbed by the polymer. A more detailed procedure and calculations can be found elsewhere [10,12]. Sorption of gases into the polymer was modeled by a dual mode sorption theory which has been described in detail in Chapter 2. Gas sorption measurements were performed using helium, oxygen, nitrogen, methane and carbon dioxide at three temperatures, 35 °C, 45 °C and 60 °C. Gas sorption measurements using He, N₂, CH₄ and CO₂ were carried out up to 850 psia whereas O₂ was measured up to 200 psia due to safety reasons.
4 Characterization of Polyimide - POSS Composites

This Chapter will discuss the results obtained during synthesis and characterization of PI-OAPS composites. Characterization of each functionalization step in the synthesis of OAPS was necessary to ascertain the chemistry utilized in this study. Prior to performing gas transport studies, a thorough analysis of PI-OAPS composites was necessary as POSS is a relatively new nanoparticle with limited reports on the behavior of polymer-POSS blended systems [68,76]. Since the polyimide was synthesized in our laboratory, its characterization in terms of FTIR and GPC was useful in monitoring the consistency from batch to batch. Visual photographs along with the electron micrographs were used to observe the dispersion and homogeneity of the composite films. A detailed thermogravimetric analysis (TGA) of POSS ensured the thermal stability of the Si-O cage and allowed us to determine the effect of addition of functional groups on this cage. TGA analysis of plain PI and composites provides insights into the thermal degradation process of the films and the relative stability of PI-OAPS films with respect to pure polyimide. Similarly, DMA and Instron tensile tester were used to probe the impact of POSS on the thermal – mechanical properties. Specifically, the $T_g$ obtained from DMA
provided vital information which later was used to explain the observed gas transport in the mixed matrix membranes. In addition, density and d-spacing analysis were used to explain the impact of POSS on the free volume which is critical for gas transport.

4.1 Functionalization of OPS with amine groups

The functionalization of OPS to OAPS involved a two step reaction, in the first step OPS was nitrated to ONPS, and in the second step ONPS was converted to OAPS by catalytic hydrogenation using Pd as catalyst [64]. Fourier transform infrared spectroscopy (FTIR) was used as a primary characterization tool to determine the presence of functional groups on POSS. Figure 4.1 gives a comparative overlay of the FTIR spectra of OPS, ONPS and OAPS.

![FTIR Spectra](image)

Figure 4.1: Change in FTIR spectrum of (a) OPS on nitration and hydrogenation to (b) ONPS and (c) OAPS.
The FTIR spectrum of OPS showed only one distinct peak for Si-O-Si at 1100 cm\(^{-1}\). When the OPS was converted to ONPS two new peaks appeared at 1348 cm\(^{-1}\) and 1530 cm\(^{-1}\) which are characteristic of N=O. Further, when ONPS was hydrogenated to form OAPS the two N=O peaks disappeared and a new broad peak that is characteristic of N-H in the amines appeared at 3467 cm\(^{-1}\). The prominent Si-O-Si peak was observed for both ONPS and OAPS. Therefore, FTIR analysis clearly confirmed that both reactions were successful and that ONPS and OAPS were formed.

\(^1\)H NMR was used as a secondary tool to monitor the formation of ONPS and OAPS. Since all the protons on the phenyl ring in ONPS are identical, a triplet corresponding to 4 protons was observed at a chemical shift of 8.7 ppm in the NMR spectrum of ONPS. This chemical shift of the phenyl protons was at 9 ppm on hydrogenation and a new peak corresponding to two protons of –NH\(_2\) appeared at 4.2 ppm for OAPS. Therefore, FTIR and NMR analysis confirm modification of OPS to OAPS.

Further, in order to check the reactivity of the amines, OAPS was reacted with phthalic anhydride to form OPIPS (Figure 4.2).
Successful imidization and formation of an imide bond would further confirm the presence of reactive amine groups on OPS. The FTIR spectrum of OPIPS is shown in Figure 4.3. A sharp peak at 1700 cm\(^{-1}\), which is characteristic of C=O in carbonyl in the FTIR spectrum of OPIPS confirmed the reaction.
between phthalic anhydride and OAPS. Also a C-N peak at 1420 cm\(^{-1}\) indicated that the amide bond between the amine and the anhydride had been successfully imidized. This confirmation of the reactivity of the amine groups on OAPS was necessary to study the in-situ polymerized PI-OAPS systems.

4.2 Synthesis of polyimide

The 6FDA-MDA polyimide was synthesized by condensation polymerization method. Equimolar amounts of diamine and dianhydride were reacted to form a polyamic acid. The polyamic acid was imidized by using chemical catalysts to form a polyimide. FTIR was used to monitor the formation of the imide bond and also other characteristic peaks of the polyimide. The FTIR spectrum of 6FDA-MDA polyimide is shown in Figure 4.4.

![FTIR spectrum of 6FDA-MDA polyimide](image)

Figure 4.4: FTIR spectrum of 6FDA-MDA polyimide.
The FTIR spectrum of plain PI was analyzed for the characteristic C=O and the C-N peaks. The C=O peak at 1700 cm\(^{-1}\) appeared which came from the carbonyl of 6FDA. The imidization of the amide bond to an imide bond was confirmed from the C-N peak at 1420 cm\(^{-1}\). Also there are no peaks for \(-\text{NH}\) originating from the amide bond in the FTIR spectrum of 6FDA-MDA polyimide.

4.2.1 \textit{In-situ polymerization of PI-OAPS}

Possible methods of incorporating OAPS into the PI matrix were explored including in situ polymerization and blending which were the two approaches chosen for this study. As described earlier the reactivity of the amine groups on OAPS with anhydride was tested prior to polymerization of PI in presence of OAPS. This section will describe the results of the in-situ polymerization method. The detailed synthesis procedure is outlined in section 3.2.4. Two approaches were taken to produce films (1) chemical imidization, and (2) thermal imidization.

Chemical imidization

(i) Within the backbone: OAPS was added to the reactor along with the diamine (MDA) in DMAc. An equimolar amount of dianhydride (6FDA) was added to this mixture. The polyamic acid-OAPS thus formed was chemically imidized using catalyst and precipitated in methanol. After complete drying of PI-OAPS, it was redissolved in THF in order to cast films. However, it was observed that the in-situ polymerized PI-OAPS did not completely dissolve in THF. Insoluble gel like globules were observed. Partial crosslinking had occurred during the polymerization
step. The eight amine groups on OAPS led to the partial crosslinking. Several attempts were made, but none were successful.

(ii) As side groups: Another approach was to form polyamic acid initially and add OAPS at end of reaction, so that OAPS are attached as side groups on to the polyimide chain. The OAPS acted as crosslinking agent and gelation was observed as soon as it was added to the polyamic acid solution. The reaction mixture could not be further imidized and therefore no further analysis was possible.

Since, chemically imidized PI-OAPS did not completely dissolve in THF, thermal imidization was considered as an alternative. Thermal imidization would yield PI-OAPS films, thereby eliminating the redissolution step.

4.2.2 Thermal imidization:

Since chemical imidization of in situ polymerized PI-OAPS composite formed a highly crosslinked network that was insoluble, thermal imidization was used as a direct route to form PI-OAPS films. A similar approach to producing the initial polyamic acid was used for thermal and chemical imidization. However, for thermal imidization, the polyamic acid was diluted using THF to avoid immediate gelation of the reaction mixture. The polyamic acid-OAPS reaction mixture was then pipetted into glass dishes and thermally imidized using the protocol described in Chapter 3. The final imidization step in each case was performed by heating the film to 300 °C under a continuous nitrogen flow. Formation of small bubbles was observed which suggested that there was some residual DMAc in the film. Also the films were very non-uniform, and could not be used for gas
transport studies. Several drying protocols were tested, but none yielded a good uniform film.

From this study, it was concluded that in-situ polymerization was very difficult to achieve due to the high reactivity of the amines on OAPS which led to gelation of the reaction mixture. Therefore, further studies are based on the PI-OAPS blended system only.

4.3 Blended Film Formation

Composite films of PI-OPS and PI-OAPS were formed using the procedure described in section 3.2.4. A 5 wt% PI-OPS film was cast using methylene chloride as solvent (Figure 4.5-b) as OPS was insoluble in THF. The PI-OAPS blended films were cast using THF as solvent. Prominent phase separation was observed for 5 wt% PI-OPS film as the OPS separated out from the polyimide phase during film formation and drying resulting in a non-homogenous film which suggested lack of favorable interactions between OPS and PI. Therefore, the OPS was converted to OAPS since the amine functionalities should favorably interact with the 6FDA-MDA to improve the miscibility of POSS in the polymer phase. In addition, the presence of amine groups improved solubility of OAPS in the casting solvent, which was THF in our study.
Figure 4.5: Visual comparison of (a) plain PI, (b) 5 wt% PI-OPS, (c) 5 wt% PI-OAPS, and (d) 20 wt% PI-OAPS films.

Blended films were produced with OAPS at loading from 0 to 50 wt%. Figure 4.5 gives a comparison of visual appearances of the different POSS loadings studied. The pure 6FDA-MDA film (Figure 4.5a) was pale yellow and transparent. Films formed by blending 0 to 50 wt% OAPS in PI were also transparent with color darkening from pale yellow to brown. Marked differences were observed between the 5 wt% PI-OPS (Figure 4.5b) and 5 wt% PI-OAPS films (Figure 4.5c). The 5 wt% PI-OPS film was hazy, brittle and showed clear phase separation, whereas the 5 wt% PI-OAPS was transparent, homogenous and not brittle. Films with higher OAPS loading were also transparent up to 50 wt%. When the OAPS
concentration in PI reached 50%, visible phase separation was observed. Also, all the 30 wt% and 50 wt% films were fairly brittle. The optical transparency of PI-OAPS blended films indicates that the OAPS is incorporated into the PI matrix with no visible phase separation. Thus functionalization of OPS with amine groups facilitated blending with the polyimide over the full concentration range.

4.4 Optical Properties

The transparency of PI-OAPS composites compared to plain PI was determined using UV-vis spectroscopy. Percent transmittance of a composite is an important characteristic for applications in the electronic industry. As shown in Figure 4.5, incorporation of OAPS within the PI matrix changes the color from pale yellow to dark brown with increasing OAPS concentration. Table 4.1 gives the cut-off wavelength and percent transmittance in the visible range for the different compositions studied. The visible range is from 400 nm to 700 nm, therefore percent transmittance at 650 nm was determined.

Table 4.1: Optical properties of PI-OAPS composites determined by UV-vis spectroscopy.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Color</th>
<th>Cut-off Wavelength, $\lambda_0$</th>
<th>%T at 650 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Pale yellow</td>
<td>381</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>Pale yellow</td>
<td>391</td>
<td>88</td>
</tr>
<tr>
<td>10</td>
<td>Dark yellow to light brown</td>
<td>419</td>
<td>70</td>
</tr>
<tr>
<td>20</td>
<td>Dark brown</td>
<td>441</td>
<td>70</td>
</tr>
<tr>
<td>30</td>
<td>Dark brown</td>
<td>473</td>
<td>45</td>
</tr>
</tbody>
</table>
As seen in Table 4.1, the 5 wt% PI-OAPS film shows optical properties very similar to that of plain PI with a high percent transmittance of 88%. As the concentration of OAPS increases, the value of cut-off wavelength increases combined with a decrease in percent transmittance. However, even at relatively high OAPS concentrations of 10 and 20 wt% the percent transmittance is 70% which means that the composites are still very transparent. However, for 30 wt%, transmittance drops to 45%. At lower OAPS concentration (5 wt%), the distribution of POSS is quite uniform within the PI matrix. With increase in concentration, aggregation of POSS causes additional diffraction of light. This leads to significant change in color for 10, 20 and 30 wt%. As the concentration increase, the number and size of these aggregates increase thereby intensifying the color change. At 30 wt%, the significant drop in %T could be due to phase separation.

### 4.5 Scanning Electron Microscopy (SEM)

Analysis of the morphology of a polymer-filler blended film can give valuable information regarding the homogeneity and dispersion of the filler within a polymer matrix. For example, in case of molecular scale inorganic fillers, agglomeration and phase separation can be monitored using techniques such as SEM. The morphology of the plain PI and the blended films was observed using scanning electron microscope (SEM). Micrographs of pure PI, 10 wt%, 20 wt% and 50 wt% composites are shown in Figure 4.6(a-d) respectively. The pure PI, 20 wt% and 50 wt% composite SEM images are at 1 µm resolution, whereas 10 wt% composite is at a resolution of 500 nm.
Figure 4.6: Scanning electron micrograph of (a) pure PI, (b) PI-OAPS 10 wt%, (c) PI-OAPS 20 wt%, (d) PI-OAPS 50 wt%, (e) EDS spectrum of PI-OAPS 50 wt% composite with polymer focus, and (f) EDS spectrum of PI-OAPS 50 wt% composite with aggregate focus.
The 10 and 20 wt% micrographs show a uniform cross section with no visible phase separation. The fracture surfaces are similar to that of the pure PI and are typical for brittle fracture surfaces. However, very small nanosized agglomerates of POSS are seen for both 10 wt% and 20 wt% PI-OAPS composites.

The SEM micrograph of the 50 wt% film shows distinct phase separation with formation of distinctive micron size aggregates. Individual POSS particles are of molecular size (1.5 nm) as compared to the polymer matrix [51]. Addition of increasing amounts of POSS within the polymer leads to aggregation of inorganic filler, at 50 wt%, a regular array of micron size aggregates of POSS were observed. A similar fracture surface with silica rich domains was observed by Wahab et al. for a 30 wt% hybrid composite of PI and polyvinylsilsequioxane (PVSSQ) [79,80]. They also observed that as compared to other commonly used sol-gel precursors like TEOS, the organic PVSSQ gave better interfacial interaction and enhanced properties.

EDS spectra of a spot of the bulk polymer matrix and the aggregates were used to probe the chemical nature of the aggregates (Figure 4.6(e) & (f)). Qualitative peak identification reveals high Si concentration in the aggregates as compared to the bulk polymer. The presence of a strong carbon peak in Figure 4.6(f) suggests that there may be some entrapped polymer in this region. Thus, homogenous distribution of OAPS was observed for concentration up to 20 wt% with formation of a regular distribution of larger particles of POSS with some trapped PI at 50 wt%. In contrast to many nanomaterials that have one dimension in nanometer range, POSS are spherical with an overall diameter of
1.45 nm so that amine functionalization significantly aids in favorable interactions between POSS and PI matrix. There is also potential for controlled formation of particles within polymer matrix with some polymer trapped in these aggregates to improve interfacial interactions and reduce gap formation which is critical for many applications.

4.6 Wide Angle X-ray Diffraction (WAXD)

The impact of addition of POSS on the intersegmental packing of the 6FDA-MDA PI was determined using a wide angle x-ray diffractometer (WAXD). X-ray patterns of the plain PI and the PI-OAPS composites are given in Figure 4.7. The information from diffraction patterns of amorphous polymers is far less definite and precise than for crystalline structures. In amorphous polymers there is no long range order, but there is a minimal kind of short range order due to the average distance between neighboring polymer chains. This order is responsible for the diffraction pattern observed for noncrystalline polymers such as 6FDA-MDA polyimide used in this study.

The broad peak shown in pattern (a) for plain PI at $2\theta \approx 16^\circ$ can be attributed to interference from intersegmental d-spacing. This corresponds to a d-spacing of $\sim 6$ Å. There is another very broad peak peak at $2\theta \approx 5^\circ$ which corresponds to a d-spacing of $\sim 10$ Å. Diffraction at such low angle can come from some long range regularity along the polymer chains. The XRD pattern for OAPS (g) also shows a broad peak at $2\theta \approx 7^\circ$ which corresponds to a d-spacing of $\sim 1.1$ nm. This d-spacing corresponds roughly to the core diameter of OPS [67].
There is no shift in the amorphous 2θ peak (~16°) of PI with the incorporation of OAPS in increasing concentrations. There is only a slight shift to higher angle for the 50 wt% PI-OAPS composite which means that there is a slight decrease in the d-spacing. Therefore incorporation of OAPS within the PI matrix has not affected the intersegmental distance or packing of the polymer chains up to high concentrations of 50 wt%. However, there is a significant change occurring at lower angles or higher d-spacing’s with increasing OAPS concentration. At 5 wt% and 10 wt% OAPS, there is just a very slight shift to higher angle. This peak for the PI-OAPS composites can be a combination of diffraction from the POSS cages as well as some long range ordering of the polymer chains. At 20 wt%, there is a significant increase in the peak intensity.
due to the increase in POSS concentration. For 30 wt% and 50 wt%, the peak position shifts more toward higher angle and appears very similar to the diffraction peak of pure OAPS.

Therefore, it can be concluded from WAXD studies that the intersegmental packing of the polymer chains is not disrupted by the incorporation of OAPS.

4.7 Density Measurements

Density comparison of the plain PI and the PI-OAPS blended films was essential to explain the gas transport behavior. Also, it has been reported in the literature that incorporation of POSS into a polymer can make the composite lighter, in other words decrease its density with respect to the plain polymer. Since POSS have a hollow cage like structure, its incorporation into the polymer can lead to the addition of hollow pockets which would be responsible to decrease in density. However, this phenomenon would be more applicable to an in-situ polymerized polymer-POSS system wherein individual POSS particles are copolymerized within the polymer backbone [64]. For a simple blended system this may not always hold true. It is known that as we decrease the size of particles, they tend to aggregate. Nanoparticles are more prone to aggregation, POSS (1.5 nm) can be considered to be a molecular sized particles when compared to the polymer chains. Hence, they are more likely to aggregate in a blended system than in in-situ polymerized systems since they are covalently bound within the polymer matrix. These aggregates or individual OAPS can readily occupy the excess free volume that exists in the polymer. These packets of free volume are formed in glassy polymers, and fluorinated polymers like
6FDA-MDA have a high concentration of excess free volume available for space filling by POSS molecules due to the presence of bulky fluorine groups. The term excess free volume and its significance was explained in greater detail in section 2.1.2.

Table 4.2: Results of density measurements.

<table>
<thead>
<tr>
<th>OAPS concentration (wt%)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.379</td>
</tr>
<tr>
<td>3</td>
<td>1.396</td>
</tr>
<tr>
<td>5</td>
<td>1.398</td>
</tr>
<tr>
<td>10</td>
<td>1.402</td>
</tr>
<tr>
<td>20</td>
<td>1.401</td>
</tr>
<tr>
<td>30</td>
<td>1.403</td>
</tr>
<tr>
<td>POSS</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The densities of plain PI and the PI-OAPS blends were determined using a density gradient column. The density of each film was determined by comparing its position in the column as compared to standard beads of known density. Table 4.2 gives the densities of plain PI and PI-OAPS blend with increasing concentration of OAPS.

The density of plain PI determined experimentally was 1.379 g/cm³, with addition of OAPS in increasing concentrations the density increases to 1.4 g/cm³ for 10 wt% PI-OAPS blend. The density difference is not significant because, incorporation of POSS into PI makes it denser but at the same time the hollow cages of POSS induces some air pockets into the blend. However, overall increase in density suggests that the polymer matrix has become denser and that
there is reduction in the excess free volume of the polymer due to the occupation of these POSS aggregates. This is supported by the results of x-ray diffraction studies which indicate that there was no shift in d-spacing of the polymer with addition of POSS at all loadings.

4.8 Dynamic Mechanical Analysis

Glass transition temperatures (T_g) are indicative of the flexibility/rigidity of the polymer chains in a film as it is the temperature at which there is a cooperative motion of polymer chains that transforms it from a glassy state to a rubbery state. More flexible polymers would have a lower T_g, whereas a rigid polymer like 6FDA-MDA would have a relatively higher T_g. Techniques like dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) can be used to determine the T_g of a polymer.

In this study dynamic mechanical analysis (DMA) was used to measure the glassy state transitions in pure PI and the composites. Plots of tan delta versus temperature measured at a frequency of 1 Hz by using a TA Instruments DMA for PI and PI-OAPS blends are shown in Figure 4.8(a). Hence the tan delta plot in Figure 4.8(a) is shown over a narrow temperature range from 200 °C to 400 °C to better understand the impact of incorporation of POSS into PI.

Shifts in the location and width of the tan delta peak of a composite can be used as a measure of the extent of interaction between the polymer matrix and the filler. A strong interaction with rigid inorganic filler will typically lead to an increase in T_g whereas a weak interaction can cause the T_g to decrease [81].
Since OAPS is rigid molecular scale filler, incorporation and dispersion within the polyimide matrix is expected to impact the polymer chain rigidity.

The beta transition or sub-$T_g$ was also determined from the tan delta curve of DMA. The sub-$T_g$ transitions are related to a combination of vibrational motions of all the units of the polymer chains, and generally vary with structural variations to either the diamine or the dianhydride moiety of the polyimide. There is a well established broad sub-$T_g$ transition for aromatic polyimides at temperatures near 150 °C. Neither the intensity nor the position of sub-$T_g$ transitions changed with the incorporation of POSS within the polyimide matrix. This indicated that POSS did not affect the vibrational motions of the polymer chains.
Figure 4.8: (a) Tan delta curve over a narrow temperature range, (b) Glass transition temperature determined from the peak of tan delta curve, (✦) PI-OAPS composite, and (◼) 5 wt% PI-OPS composite.
The \( T_g \) was determined from the peak of the tan delta curve. There was a shift in peak position to higher temperatures with increase in OAPS concentration up to 30 wt\%. Distinctive peak broadening of the tan delta curve was also observed for the composites containing 20 wt\% and higher OAPS concentration. As shown in Figure 4.8(b), there is a gradual increase in \( T_g \) as the OAPS concentration approached 10 wt\%. The plain PI film had a \( T_g \) of 297 °C, 10 wt\% PI-OAPS film had a \( T_g \) of 318 °C. For PI-OAPS blends of intermediate concentrations between 0 and 10 wt\%, the \( T_g \) increased in a regular fashion linearly. Beyond 10 wt\%, the \( T_g \) remained constant up to 30 wt\% and exhibited a slight decrease at 50 wt\%. However the 5 wt\% PI-OPS films showed a lower \( T_g \) compared to that of the plain PI. This decrease in \( T_g \) may be due to an increase in localized free volume in gaps near the OPS surface that would result in greater chain mobility.

The shift in \( T_g \) to higher temperatures suggests that the segmental chain mobility was restricted due to the interactions between the flexible polymer and the rigid inorganic POSS. For higher concentrations of OAPS (20 wt\% and 30 wt\%) \( T_g \) does not change, however a reduction in peak height or peak broadening was observed. Xiong et al. have attributed such tan \( \delta \) peak broadening and decreased peak height in titania containing acrylic resin to an increase in entrapment of polymer chains within inorganic networks, resulting in reduction of polymer chain mobility [1]. In addition to the physical entrapment of the polymer chains, the positive interactions of amines on OAPS with the polyimide matrix can result in local reduction in chain mobility. A distribution of
such interactions within a polymer matrix results in broadening of the glass transition behavior. The decrease in $T_g$ and peak broadening for 50 wt% PI-OAPS can be attributed to phase separation which would lead to formation of two populations of polymers within the composite. The polymer chains in the bulk matrix would be expected to be less rigid than those entrapped in the POSS aggregates leading to a short, broad peak. In general, the results for DMA agree with SEM observations, which suggest that the distribution of OAPS within PI matrix is uniform with visible phase separation occurring only when the concentration reaches 50 wt%. The impact of OAPS on the storage modulus will be discussed in section 4.10 with Instron Tensile testing.

### 4.9 Thermogravimetric Analysis

Polyimides are known to be thermally stable and are being used for various high temperature applications. Therefore, a polyimide-POSS composite should also retain if not enhance the thermal stability of the polyimide in order to find commercial application. The Si-O cage of POSS is known to be thermally stable, however it is necessary to determine whether addition of functional groups has in any way altered the thermal stability. TA instruments thermogravimetric analyzer (TGA) was used to determine the effect of functional groups on the thermal degradation of POSS. The thermal degradation behaviors of OPS, ONPS and OAPS in nitrogen are presented in the form of % weight mass loss and derivative thermogravimetry curves (DTG) in Figure 4.9 and Figure 4.10 respectively.
Figure 4.9: TGA plot of weight % versus temperature for OPS, ONPS and OAPS in N₂.

Figure 4.10: Derivative thermogravimetry (DTG) curve for thermal decomposition of OPS (---), ONPS (-----), and OAPS (— - —) in N₂.
The TG curves of OPS, ONPS and OAPS in Figure 4.9 indicate that the mass loss is very similar for all three POSS, approximately 40% at 700 °C (~60% char residue). The char residue of a material is dependent on the content of organic and inorganic components in the molecules and whether there are more stable compounds forming during the decomposition process [82]. The higher the content of inorganic groups in the material, the higher the char yield. The weight percentage of the inorganic Si-O cage in POSS is 35% – 40% in theory. However, a much higher char yield is obtained (60%) upon thermal decomposition for OPS, ONPS and OAPS. This indicates that either there is only partial degradation of the organic corner groups on POSS or there are some unknown reactions taking place during the heating process with the formation of certain new thermally stable compounds besides SiO₂.

The DTG peaks of OPS, ONPS and OAPS shown in Figure 4.10 further aids in the understanding of the thermal degradation process. The DTG peaks of OPS and ONPS at 420 °C and 380 °C respectively suggest rapid decomposition within a narrow temperature range. In contrast, the broad peak of OAPS from 300 °C to 650 °C, suggest that it undergoes a very slow degradation. A small peak for OAPS at 100 °C can be attributed to the loss of some water in the sample as OAPS is very hygroscopic compared to OPS and ONPS. Further, the broad nature of the OAPS DTG peak suggests that the degradation of the organic groups has been slowed down due to the presence of amine groups.
Figure 4.11: TG plot of Weight % versus temperature for PI and PI-OAPS composite films.

Figure 4.12: DTG curves of plain PI and the PI-OAPS composite films.
The $\text{-NH}_2$ groups resonance stabilize the phenyl rings on the Si – O cage because the lone pair of electrons on nitrogen is stabilized by the hydrogen atoms. A sharp degradation peak for OPS and ONPS (absence of $\text{-NH}_2$) also support this hypothesis. In case of ONPS, the electronegative oxygen atoms pulls the lone pair of electrons from nitrogen making the phenyl rings unstable resulting in a sharp degradation. Similarly, the phenyl rings on OPS show a sharp degradation.

In order to determine the effect of addition of OAPS on the thermal stability of PI, TGA analysis of pure PI was compared with blended PI-OAPS films in nitrogen. The weight % versus temperature (TG plot) curves for plain PI as well as the PI-OAPS composites are shown in Figure 4.11. A slight increase in the onset decomposition temperature is observed for 5 wt% PI-OAPS film as compared to the plain PI. Composites with higher percentage of OAPS do not show any significant change in their thermal behavior. The 50 wt% PI-OAPS composite shows a considerable reduction in the onset decomposition temperature. The char residue yield for PI-OAPS composites are similar to the plain PI (~ 55%) due to the small mass fraction of POSS. A summary of the thermal properties of the PI-OAPS composites is given in Table 4.3. Similar to the increase in onset decomposition temperature for 5 wt% composite, there is an increase in the 5% mass loss temperature as well.
Table 4.3: Summary of thermal properties of PI-OAPS composites.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Temperature at 5% mass loss (°C)</th>
<th>Char Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>485</td>
<td>56.0</td>
</tr>
<tr>
<td>5</td>
<td>504</td>
<td>55.7</td>
</tr>
<tr>
<td>10</td>
<td>479</td>
<td>54.5</td>
</tr>
<tr>
<td>20</td>
<td>487</td>
<td>57.3</td>
</tr>
<tr>
<td>50</td>
<td>407</td>
<td>55.7</td>
</tr>
</tbody>
</table>

A significant reduction in the 5% mass loss temperature of 50 wt% composite suggests that the decomposition behavior is intermediate between the plain PI and OAPS. Therefore, the thermal properties of the composites are affected at low and very high weight percentages of OAPS in the composite with no significant changes for intermediate OAPS loadings.

The derivative thermogravimetry (DTG) curves of plain PI and the composite films are shown in Figure 4.12. The thermal decomposition behavior of all the composites was similar to the pure PI with a shift towards higher temperatures at concentrations up to 20 wt%. For composites with 20 wt% and higher OAPS loading, a prominent peak due to mass loss of POSS appeared in the DTG plot indicating beginning of phase separation. For 50 wt%, the DTG plot showed two distinct mass loss peaks, one of the OAPS at around 480 °C and the other at around 500 °C of the polyimide itself. Strong interactions between the thermally stable Si-O cage and the polyimide matrix cause the onset decomposition temperature to increase. However, this prominent change is observed primarily in the 5 wt% film as the effect of addition of filler is known to be more significant at
lower filler concentrations. As the POSS concentration increases to 50 wt% the onset decomposition temperature decreases as phase separation takes place. The onset decomposition temperature lies between that of the pure PI and OAPS itself. Huang et al. reported a 25 °C increase in decomposition temperature for an *in-situ* polymerized PI - POSS system [5]. It was attributed to the thermal stability of POSS itself and also to the stable covalent bonds between the PI and the POSS. In case of our blended PI-POSS system, any additional thermal stability only comes from POSS as there are no covalent bonds, and so we see only a slight increase in the decomposition temperature.

### 4.10 Mechanical Properties

Mechanical testing of plain PI and the composite films was performed in this study since addition of inorganic filler within a polymer matrix can result in increased brittleness or moderation of mechanical properties. In addition, one of the main objectives of this project was to develop PI-POSS mixed matrix membranes with good transport properties without compromising the thermo-mechanical properties of plain PI. Mechanical properties such as strength, toughness and Young’s modulus were determined on an Instron Tensile Tester. Strength was determined from the maximum stress at yield, and the area under the stress strain curve (at yield point) was used as a measure of toughness. The nature of the stress strain curve obtained from Instron for plain PI and 5 wt%, 10 wt% and 20 wt% PI-OAPS composite is shown in Figure 4.13. Polyimides are a class of thermoplastic polymers whose stress strain curve shows a brittle
fracture. There is no specific yield point unlike in other polymers,

![Graph showing stress-strain curves for PI, 5 wt%, 10 wt% and 20 wt% PI OAPS composites.](image)

Figure 4.13: Typical stress-strain curves for PI, 5 wt%, 10 wt% and 20 wt% PI OAPS composites.

which show ductile behavior beyond the yield point and finally break. A clean fracture was observed without the occurrence of crazing or necking. The composite films also show a similar type of fracture when tested under Instron. The nature of the stress strain curve matches very well with that of plain PI.

The plain PI and the composite films were tested for storage modulus, Young’s modulus, strength and strain at yield. The storage modulus was determined from DMA analysis, a detailed procedure has been outlined in section 3.3.7. Particularly, the storage modulus was determined by subjecting the film to oscillatory strain and measuring the resulting stress. Young’s modulus, strength, and strain at yield were determined from Instron tensile testing. Table
4.4 lists the storage modulus (determined from DMA), Young’s modulus, strength and strain at yield of the pure PI and the composites. Young’s modulus which was the initial slope of the stress strain curve did not change significantly with the addition of OAPS, strength and toughness (measured indirectly from strain at yield) of the PI-OAPS composites up to 5 wt% were comparable with that of the pure PI. However, for OAPS concentrations beyond 5 wt%, strain at yield decreased considerably which would lead to an overall decrease in toughness. In general, addition of inorganic filler into a polymer can weaken the inherent properties of the polymer due to the lack of favorable interactions between the two phases which may lead to defects. For concentrations up to 5 wt%, strength and strain at yield are retained. This can be attributed to good interfacial adhesion and to the incorporation of nanovoids into the polymer matrix which increases its ability to dissipate energy.

Table 4.4: Tensile properties of pure PI and PI-OAPS composites.

<table>
<thead>
<tr>
<th>Film</th>
<th>Storage Modulus* (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Strength (MPa)</th>
<th>Strain at Yield (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PI</td>
<td>2800 ± 136</td>
<td>2900 ± 74</td>
<td>103 ± 5</td>
<td>0.064±0.004</td>
</tr>
<tr>
<td>1 wt% PI-OAPS</td>
<td>2500 ± 326</td>
<td>3100 ± 100</td>
<td>108 ± 3</td>
<td>0.068±0.003</td>
</tr>
<tr>
<td>1.5 wt% PI-OAPS</td>
<td>2500 ± 57</td>
<td>3100 ± 58</td>
<td>103 ± 2</td>
<td>0.064±0.002</td>
</tr>
<tr>
<td>2.5 wt% PI-OAPS</td>
<td>-</td>
<td>3000 ± 100</td>
<td>106 ± 5</td>
<td>0.064±0.003</td>
</tr>
<tr>
<td>5 wt% PI-OAPS</td>
<td>2900 ± 133</td>
<td>3100 ± 68</td>
<td>105±1</td>
<td>0.065±0.002</td>
</tr>
<tr>
<td>10 wt% PI-OAPS</td>
<td>2500 ± 293</td>
<td>3200 ± 72</td>
<td>105 ± 2</td>
<td>0.056±0.001</td>
</tr>
<tr>
<td>20 wt% PI-OAPS</td>
<td>2700 ± 89</td>
<td>3100 ± 46</td>
<td>104 ± 4</td>
<td>0.05±0.002</td>
</tr>
</tbody>
</table>

* Measured using DMA

The composites with greater than 5 wt% OAPS were increasingly brittle as reflected in the decrease in strain at yield. However, it should be noted that modulus and strengths were retained even at very high filler loadings. Huang et
al. reported an initial increase in strength and modulus and then a large drop off as OAPS content increased in \textit{in-situ} polymerized polyimide composite (for amine group ratio $>0.1$) \cite{}. A study on polycarbonate-POSS composites by Zhao et al. suggested no significant mechanical property enhancements in composites up to 10 wt\% POSS \cite{}. It can be concluded from the mechanical study that the composite formed by simply blending POSS with PI maintains but does not enhance the superior properties of the polyimide.

\textbf{Summary}

Composites of 6FDA-MDA polyimide were prepared by incorporating POSS nanoparticles within the polymer matrix. An octaphenyl substituted POSS (OPS) was chosen and a 5 wt\% composite was prepared by simple blending technique using methylene chloride as solvent. However, the resulting composite was brittle and had visible phase separation. Therefore, OPS was functionalized with reactive amine groups to enhance the compatibility with the PI. OAPS was readily soluble in most organic solvents and therefore made composite formation very easy. The functionalization chemistry of OPS to OAPS was confirmed using FTIR and NMR.

There were two ways of incorporating OAPS within the PI matrix, in situ polymerization and blending. Both techniques were tried and it was concluded that blending was the fastest, easiest and most effective way of incorporating OAPS into the PI matrix. Tetrahydrofuran (THF) was used as the solvent to form the composite films as it is relatively polar and has a slightly higher vapor
pressure than methylene chloride. Higher loadings of OAPS could be incorporated into the PI matrix by this method without any visible phase separation. Composites with OAPS loading as high as 50 wt% were prepared.

The morphology of the fracture surface of the composite films was probed using SEM. 5, 10, and 20 wt% PI-OAPS composites showed uniform cross section similar to the plain PI, typical for a brittle fracture with no phase separation. However, formation of nanosized aggregates was observed for OAPS compositions up to 20 wt%. When the OAPS loading in the composite was 50 wt%, micron size aggregates were observed. EDS analysis showed that the aggregates were rich in POSS compared to the other phase.

Wide angle x-ray diffraction (WAXD) was carried out on plain PI and the PI-OAPS composite films to determine the impact of OAPS on the intersegmental packing or the d-spacing between polymer chains. The d-spacing of the 6FDA-MDA PI appeared at ~6 Å, and it remained unchanged up to OAPS loadings of 30 wt%, and a slight decrease in d-spacing was observed at 50 wt%.

Primary goal of this project was to develop polyimide-POSS mixed matrix membranes with not only enhanced gas transport properties but also good thermal and mechanical stability. Dynamic mechanical analysis (DMA) was used to determine the impact of incorporation of POSS on the glass transition temperature ($T_g$) of the polymer. It gave an insight to the molecular level impact of POSS on the polymer matrix, specifically segmental mobility of the polymer chains. An increase in $T_g$ was observed with increasing OAPS loading up to 20
wt%. The 50 wt% PI-OAPS composite showed a decrease in $T_g$. This increase in $T_g$ was attributed to the increase in polymer chain rigidity due to the addition of OAPS. Also, significant peak broadening of the tan delta curve was observed as the POSS loading increased. This was attributed to the distribution of localized areas of enhanced rigidity throughout the polymer matrix. DMA analysis of 5 wt% PI-OPS composite indicated a decrease in $T_g$ which was due to unfavorable or weak interactions between the two phases. Therefore, amine functionalization of OPS resulted in enhanced polymer POSS interactions and composites with higher glass transition temperatures.

The thermal degradation behavior of OPS, ONPS and OAPS was studied using TGA to determine the impact of organic functional substitutions on the otherwise thermally stable Si-O-Si cage. A comparison of the degradation behavior of the OPS, ONPS and OAPS in $N_2$ atmosphere revealed that amine groups on OAPS makes the POSS more thermally stable by slowing down its decomposition rate. Further, the residual char yield was higher than the theoretically calculated value for the Si-O cage, suggesting either partial decomposition of the organic groups or formation of other thermally stable compounds during the degradation process. Thermal stability of the composites was also tested using TGA and were found to be as thermally stable as plain PI with slightly enhanced stability observed for 5 wt% PI-OAPS composite.

Mechanical properties such as Young’s modulus, strength and strain at yield were determined using an Instron Tensile Tester, the storage modulus was determined using DMA. The composites showed no change in Young’s modulus
with the incorporation of OAPS in increasing concentration. Strength and toughness were also comparable to the plain PI for composites up to 5 wt% OAPS loading. For higher OAPS loadings, a decrease in the strain at yield was observed due to increase in brittleness of the composite. However, even at higher OAPS loadings, the modulus (both storage and Young's) and strength were comparable to the plain PI. Therefore, addition of inorganic POSS maintained the inherent mechanical and thermal properties of 6FDA-MDA polyimide. This can be attributed in part to the good interfacial adhesion between POSS and the polyimide matrix, which was facilitated by the reactive amine groups.
5 Gas Transport Properties – 35 °C

5.1 Introduction

Numerous strategies are being developed to structurally optimize polymeric membranes to allow high membrane productivity (permeability) and selectivity [18]. Such high performance membranes have the potential to replace traditionally used unit operations for separations, due to their low cost and ease of production. For this, the membrane should not only have good permeability and selectivity but it should also have good thermal and mechanical stability in order to be used in harsh environments and at high temperatures.

Currently used polymeric membranes such as cellulose acetate (CA), polyimides (PI), polyamides (PA), polysulfones (PSF), and polyethersulfones (PES) are limited by their flux and selectivity [27]. Generally, glassy polymers exhibit a tradeoff between permeability and selectivity which gives the maximum operating efficiency of a particular membrane [2]. Efforts to develop membranes that have performance beyond the tradeoff are underway and various theories have been suggested based on the fundamental principles of membrane based separations. Inorganic molecular sieving membranes were developed for precise separation and for high temperature applications. However, mechanical instability of the membranes and processing difficulties limited their potential commercial
applicability. A novel concept developed over the last decade is to combine the inorganic molecular sieving materials with the conventional polymeric materials to form a “mixed matrix membrane”.

Considerable research has been done in recent years on developing mixed matrix membrane materials that consist of an inorganic sieving phase dispersed within a polymeric matrix. A schematic representation of a mixed matrix membrane is given in Figure 5.1. The inorganic phase can provide a secondary selective pathway for gas transport along with diffusion in the polymer phase. Such membranes combine the advantages of inorganic materials (rigidity, stability, highly selective transport) and the organic polymers (flexibility, ductility and processibility).

![Mixed Matrix Membrane Schematic](image)

Gas transport across a mixed matrix membrane can take place by either one or a combination of the following pathways:

1. Through the pores of the molecular sieves (continuous or discontinuous):
   Precise pore dimension and proper selection of the molecular sieve can lead to size selective gas transport through the membrane. For example a
A molecular sieve with a pore dimension of 3.5 Å should allow oxygen (3.46 Å) to pass through and block nitrogen (3.64 Å).

2. Through the bulk polymer: Molecular sieves dispersed in the polymeric membrane may not be accessible to the gas penetrants. This can happen due to pore blockage of the molecular sieve by polymer chains or formation of agglomerates of the molecular sieve which make them inaccessible to the gas molecules. Gas transport will occur through the rigidified bulk polymer.

3. Through the interface: the interface between the molecular sieve and the polymer can be engineered in such a way that it allows selective gas transport.

The pathways described above are in addition to gas transport through the bulk polymer. If gas transport occurs by either method 1 or method 3 then an increase in both permeability and selectivity would be observed. However, if transport takes place by method 2 then a decrease in permeability with a probable increase in selectivity would be observed. Gas transport through mechanism 1 is the most desired pathway as it leads to highly selective membranes with high permeability for the fast penetrant.

However, formation of defects in mixed matrix membranes has been the biggest obstacle as these defects will allow non-selective transport of gas molecules. Hence formation of a defect free membrane is a prime criterion for a good mixed matrix membrane with desired gas transport behavior. Lack of interaction between the inorganic molecular sieve and the organic polymer matrix has been the primary source of defects and the various ways to overcome this
problem suggested by researchers in the past have been discussed in section 2.3.1.

This chapter presents the results of an attempt to form mixed matrix membranes of 6FDA-MDA polyimide and polyhedral oligomeric silsesquioxane (POSS). The effect of addition of POSS in varying concentrations to the polyimide on the transport properties will be discussed. All the studies in this chapter are limited to 35 °C, higher temperature studies will be discussed in the Chapter 6. POSS was chemically modified with amine groups to form octaminophenyl silsesquioxane (OAPS). A detailed procedure for the synthesis has been described in Chapter 3 and properties were presented in Chapter 4.

5.2 Background

The permeation of a penetrant in a polymeric membrane occurs through a solution-diffusion mechanism. The gas molecules dissolve into the polymer on the high pressure feed side, diffuse through the polymer and desorb at the low pressure permeate side. The permeability $P$ is then a product of diffusivity coefficient $D$, and a solubility coefficient $S$. The separation efficiency of the membrane is defined in terms of its selectivity $\alpha_{AB}$, which is simply the ratio of permeability of gas molecule A to the permeability of gas molecule B. A Robeson’s tradeoff curve which is a plot of selectivity of a gas pair A B versus the permeability of the gas A gives the upper bound limit for all known polymeric membranes.

Permeability of gas penetrants through polymers is dependent on the structure and properties of the polymer. Rubbery or flexible polymers with lower
glass transition temperatures show very high permeabilities but very poor selectivities. On the other hand, rigid glassy polymers with higher glass transition temperatures show moderate permeabilities and high selectivities which make them attractive candidates for commercial separations. Further, permeation in rigid polymers is governed by diffusivity and solubility of penetrants which in turn is dependent on the structure of the polymer backbone [83]. For example, polymer with a high free volume will have higher solubility and hence higher permeability. Numerous studies on structural modification to enhance gas transport properties have been reported. Hoehn et al suggest that it is desirable to do two things simultaneously when changing the structure within a family of polymers: inhibit intersegmental packing while simultaneously hindering backbone mobility [84].

However, there is a limit to the structural modifications that can be made on any polymer which would give membranes with both high permeability and high selectivity. Considerable research is now being done on developing mixed matrix membranes using different molecular sieving materials. Encouraging results have been obtained in the past molecular sieving materials such as zeolites, carbon molecular sieves (CMS) when uniformly dispersed within polymer matrices [44,45,47,48]. Polyhedral Oligomeric Silsesquioxane (POSS) are three dimensional porous silica cage structures; hence offer an opportunity to be used as molecular sieving materials.

In this Chapter the permeability and solubility coefficients obtained for the PI-POSS mixed matrix membranes will be discussed. The structure and
properties of POSS has been described in section 2.4. Specifically, an octaamine substituted POSS was used to enhance the compatibility between the flexible aromatic polyimide and the rigid inorganic POSS. Also, tradeoff curves for a few gas pairs are plotted and discussed in this section.

5.3 Overview of Physical Properties of PI-OAPS Mixed Matrix Membranes

An investigation into the physical properties of PI-OAPS mixed matrix membranes was carried out and the results are described in Chapter 4. Various characterization techniques were used to determine the impact of incorporation of POSS into the polyimide matrix. The important results from Chapter 4 are summarized in Table 5.1. The observations and results were useful in our understanding of the observed gas transport in these mixed matrix membranes.

Table 5.1: Physical Properties of PI-OAPS mixed matrix membranes.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Density (g/cm³)</th>
<th>T_g (°C)</th>
<th>Sub-T_g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.379</td>
<td>297</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>1.398</td>
<td>309</td>
<td>120</td>
</tr>
<tr>
<td>10</td>
<td>1.402</td>
<td>318</td>
<td>120</td>
</tr>
<tr>
<td>20</td>
<td>1.401</td>
<td>319</td>
<td>120</td>
</tr>
</tbody>
</table>

A gradual increase in density was observed with an increase in OAPS content. Also, a significant increase in the glass transition temperature (T_g) was observed with increased OAPS loading. This suggested restriction to co-operative segmental mobility of the polymer chains induced by the incorporation of OAPS. However, no effect was observed on the sub-T_g transition temperature of 6FDA-MDA polyimide. The beta transitions are related to a combination of vibrational
motions of all the units of the polyimide chain. Therefore changes in the beta
transition temperatures are usually associated with structural modifications within
the polymer backbone. Since OAPS was simply blended within the PI matrix it
did not affect the vibrational motions of the polymer chain. Only the cooperative
motions of segments of polymer chains were affected due to incorporation of
POSS which is evident from the significant increase in $T_g$.

Based on the discussion of transport in mixed matrix membranes in
section 2.4, the possible pathways of transport through PI-POSS mixed matrix
membranes can be as follows:

(i) through the Si-O cage of POSS.
(ii) through the aggregates of POSS formed within the PI matrix
(iii) through the interface between POSS and bulk polymer matrix
(iv) only through the polymer matrix.

Gas transport by any of the first three ways would be in addition to the transport
through the polymer matrix. Further, transport by the first three ways would also
lead to an increase in the pure gas permeabilities of penetrants with either an
increase or a decrease in selectivities.

Earlier computational works on silsesquioxanes have emphasized on the
presence of energy barriers that may prevent permeation of gas molecules
through the cages [71]. The SEM images of PI-POSS composites in section 4.5,
revealed formation of small aggregates of POSS. The number and size of these
aggregates increases with increased POSS content in the composite. Formation
of such aggregates may further aggravate this problem by creating tortuous
pathways for permeation of penetrant molecules. Evidence of a strong interface between POSS and the polymer was obtained from DMA studies in section 4.8. The significant increase in $T_g$ clearly indicated strong favorable interactions existed between the two phases. Also with the presence of eight amine groups on the Si-O cage of POSS, it is expected that it would enhance the interactions, thereby reducing any interfacial gaps or voids that may exist between the two phases. Therefore, transport of penetrants through interfacial voids is also unlikely, this leaves only two possible pathways, either through the aggregates and the polymer or only through the polymer matrix. Only after a detail analysis of gas permeation and sorption through these membranes it would be possible to conclude the mode of transport. The following sections will describe the results obtained from pure gas permeation and sorption studies.

5.4 Pure Gas Permeation Study

A constant volume variable pressure gas permeation set-up was used to determine pure gas permeabilities of He, CO$_2$, O$_2$, N$_2$, and CH$_4$. A detailed description of the set-up and the experimental procedure has been outlined in section 3.3.12. PI-OAPS mixed matrix membranes with OAPS concentrations of 0, 5 wt%, 10 wt% and 20 wt% were studied. The 30 wt% and 50 wt% PI-OAPS films were very brittle and could not be used successfully in the permeation set-up. The permeability of each gas was determined at pressures up to 200 psi (14 atm). The pure gas permeabilities and selectivities for all the gases studied are listed in Table 5.2 for OAPS loading from 0 to 20 wt%. The ideal selectivities obtained of some of the important gas pairs are listed in Table 5.2. A general
trend of decreasing permeability with increasing OAPS concentration was observed. Also, an increase in the ideal selectivities of the various gas pairs studied was observed as the OAPS loading increased from 0 to 20 wt%.
Table 5.2: Permeability coefficients and permselectivities of plain PI and PI-OAPS mixed matrix membranes for the different gases studied.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Permeability Coefficients (P) (Barrer)</th>
<th>Permselectivity (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He (10 atm)</td>
<td>O₂ (10 atm)</td>
</tr>
<tr>
<td>0</td>
<td>50±1</td>
<td>3.76±0.1</td>
</tr>
<tr>
<td>5</td>
<td>46±0.8</td>
<td>3.54±0.09</td>
</tr>
<tr>
<td>10</td>
<td>43±0.5</td>
<td>2.9±0.12</td>
</tr>
<tr>
<td>20</td>
<td>43±0.4</td>
<td>2.6±0.08</td>
</tr>
</tbody>
</table>

1 Barrer = 10⁻¹⁰ cm³(STP).cm/cm².sec.cm Hg
A general trend of a decrease in permeability with an increase in OAPS concentration was observed. Also, an increase in the ideal selectivities of the various gas pairs studied was observed as the OAPS loading increased from 0 to 20 wt%. A double Y plot of He permeability and He/CH\textsubscript{4} selectivity versus % OAPS concentration is shown in Figure 5.2.

![Double Y plot of He permeability and He/CH\textsubscript{4} selectivity versus OAPS concentration](image)

**Figure 5.2:** A plot of (●) He permeability and (♦) He/CH\textsubscript{4} selectivity versus OAPS concentration (wt%).

Helium exhibited a 14% decrease in permeability as the OAPS concentration increased from 0 to 10 wt%. For 20 wt% the permeability leveled off without further decrease. On the contrary, CH\textsubscript{4} which is the largest of all the gas molecules studied showed a continuous decrease in permeability from 0 to 20 wt% OAPS concentration. The 20 wt% PI-OAPS mixed matrix membrane showed a 40% decrease in CH\textsubscript{4} permeability. Due to this large difference in
percentage decrease in permeability, a significant increase in He/CH\textsubscript{4} selectivity (~44\%) was observed. A similar plot for O\textsubscript{2}/N\textsubscript{2} gas pairs is shown in Figure 5.3. It is a double Y plot of O\textsubscript{2} permeability and O\textsubscript{2}/N\textsubscript{2} selectivity versus the OAPS concentration (wt\%) in the mixed matrix membrane.

![Graph showing O\textsubscript{2} permeability and O\textsubscript{2}/N\textsubscript{2} selectivity versus OAPS concentration](image)

Figure 5.3: A plot of (●) O\textsubscript{2} permeability and (♦) O\textsubscript{2}/N\textsubscript{2} selectivity versus OAPS concentration (wt\%).

There was a 15\% increase in O\textsubscript{2}/N\textsubscript{2} selectivity with a two fold decrease (~30\%) in O\textsubscript{2} permeability. Enhancements in O\textsubscript{2}/N\textsubscript{2} selectivity is very difficult to achieve because of their close kinetic diameters and relatively low solubilities, so even a 15\% increase is significant. The selectivity enhancement suggests that the permeability of N\textsubscript{2} which is larger in size than O\textsubscript{2} decreases to a greater extent than O\textsubscript{2}. 
CO₂/CH₄ is another industrially important gas separation which has attracted considerable interest, especially in the natural gas industry. A plot of CO₂ permeability and CO₂/CH₄ selectivity versus OAPS concentration is shown in Figure 5.4. CO₂ is the second smallest gas penetrant after He and also the most condensable of all the gases. As stated earlier, CH₄ is the largest of all gas molecules and the second most condensable of the gases studied.

![Figure 5.4: A plot of (●) CO₂ permeability and (♦) CO₂/CH₄ selectivity versus OAPS concentration (wt%).](image)

The permeability behavior of CO₂ with increasing OAPS loading is different from all the other gases studied. The CO₂ permeability remained constant up to 10 wt% OAPS concentration, at 20 wt% there was a 9% decrease in permeability. This marginal decrease in CO₂ permeability led to a significant increase in CO₂/CH₄ selectivity (55%) as the OAPS concentration reached 20 wt%.
5.4.1 Effect of OAPS Incorporation on Permeability

The effect of addition of OAPS in a 6FDA-MDA matrix on pure gas permeabilities has been listed in Table 5.2. Enhancements in pure gas selectivities with a slight decrease in permeabilities were observed. Figure 5.5 shows the effect of addition of OAPS in PI on the pure gas permeabilities of penetrants as a function of the kinetic diameters.

![Figure 5.5: Correlation of pure gas permeability coefficients with kinetic diameters of various penetrants at 35 °C.](image)

As shown in Figure 5.5, the permeability coefficient is a decreasing function of kinetic diameter. 6FDA-MDA polyimide shows a gradual decrease in permeability coefficients with increase in the kinetic diameters of the penetrants. PI-OAPS mixed matrix membranes containing various amounts of OAPS also follow a similar decreasing trend of permeability coefficient with increase in
kinetic diameters. However, there is a slight decrease in permeability for each penetrant with increase in OAPS concentration. Further, Figure 5.5 shows that this decrease in permeability is more pronounced for N\textsubscript{2} and CH\textsubscript{4} than He and CO\textsubscript{2}. Since the relationship between permeability coefficient and kinetic diameters for PI-OAPS mixed matrix membranes is similar to that of 6FDA-MDA PI, it is possible that transport may be occurring through the bulk polymer matrix and not through POSS cages.

5.4.2 Maxwell Prediction for performance of PI-OAPS mixed matrix membrane

The impact of OAPS concentration on the permeability of penetrants will be discussed in terms of Maxwell’s model for PI-OAPS mixed matrix materials. Mathematical determination of gas transport through a mixed matrix medium is a complex problem. Several models have been suggested in the past to determine the permeability of a penetrant through a mixed matrix material as a function of the permeability of the continuous polymer phase and permeability of the dispersed phase. A simple and particularly useful model was developed by Maxwell in 1873.

\[ P_{\text{eff}} = P_{c} \left[ \frac{P_{d} + 2P_{c} - 2\phi_{d}(P_{c} - P_{d})}{P_{d} + 2P_{c} + \phi_{d}(P_{c} - P_{d})} \right] \]  

5.1

where, \( P_{c} \) is the permeability of the continuous phase, \( P_{d} \) is the permeability of the dispersed phase and \( \phi_{d} \) is the volume fraction of the dispersed phase. The predicted and experimental values of permeabilities for He, O\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} are given in Table 5.3.
Table 5.3: Predicted and experimental values of permeability coefficients at 35 °C of all gases studied.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>( P_{\text{He}} ) (Barrer)</th>
<th>( P_{\text{O}_2} ) (Barrer)</th>
<th>( P_{\text{N}_2} ) (Barrer)</th>
<th>( P_{\text{CH}_4} ) (Barrer)</th>
<th>( P_{\text{CO}_2} ) (Barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pred</td>
<td>Expt</td>
<td>Pred</td>
<td>Expt</td>
<td>Pred</td>
</tr>
<tr>
<td>5</td>
<td>46</td>
<td>46</td>
<td>3.45</td>
<td>3.54</td>
<td>0.64</td>
</tr>
<tr>
<td>10</td>
<td>43</td>
<td>43</td>
<td>3.22</td>
<td>2.9</td>
<td>0.6</td>
</tr>
<tr>
<td>20</td>
<td>37</td>
<td>43</td>
<td>2.79</td>
<td>2.6</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Pred = Predicted; Expt = Experimental

The predicted values of permeabilities listed in the above Table 5.3 are calculated using Maxwell’s Equation 5.1 by considering the permeability of dispersed phase to be zero. The volume fraction of OAPS at each concentration was determined from their corresponding weight percentages in the PI-OAPS composites. The decreasing permeability trend in the experimental permeability data suggested that the POSS cages may be inaccessible to the penetrants. As can be seen from the table, the experimental permeability values for \( \text{O}_2 \), \( \text{N}_2 \) and \( \text{CH}_4 \) are consistently lower than predicted for higher OAPS loadings (10 wt% and 20 wt%). This can be attributed to the rigidification of the polymer matrix due to the incorporation of POSS which is clearly indicated by \( T_g \) increase. Recall that the chain rigidification is same for higher loadings than 10 wt% and sub-\( T_g \) are same for all the composites. The Maxwell model does not take into consideration other physical effects the inorganic material would have on the polymer matrix and hence in most cases predicts higher permeability values than experimental [46]. However, for \( \text{CO}_2 \), the experimental values of permeability are higher than
the predicted. This disagreement may be due to some interactions between the POSS cages and CO$_2$, which was evaluated by using sorption measurements and will be described in section 5.5.

Various such models to predict gas transport through mixed matrix membranes have been developed but none have proven to predict values close to the experimentally determined values. Vu et al. compared various models with their experimental values for a polyimide-CMS MMM [45]. They observed that the predicted values fit closely with the experimental for one type of polyimide (Ultem®) but not for the other (Matrimid®) [45,46]. For PES-zeolite 4A MMM studied by Li et al., the experimental permeability values were much lower than those predicted by the Maxwell model [50].

Transport properties of mixed matrix membranes depend on many factors and no single model can be applied successfully to describe their behavior. Variation in predictions with change in either the polymer phase or the dispersed phase makes application of such models very difficult. A conceptual model of probable transport mechanism needs to be developed for each polymer-molecular sieve mixed matrix membrane based on the experimentally observed gas transport behavior. Thorough characterization of the mixed matrix membranes using other techniques such as dynamic mechanical analysis (DMA), scanning electron microscopy (SEM) and positron annihilation lifetime spectroscopy (PALS) further helps in understanding and explaining gas transport through these membranes. An effort to understand the experimentally observed gas transport was made and is described in detail in section 5.4.4.
5.4.3 Gas Transport through PI-POSS MMM

An effort to understand the effect of OAPS concentration on the performance and separation efficiency of PI-OAPS mixed matrix membranes was made from the above pure gas permeation results. A decrease in permeability for all the gases suggests that the effective gas transport may be occurring through the PI matrix and not through POSS itself. If the POSS cages were accessible to even the smallest penetrant, helium, it would have led to an increase in permeability of He relative to larger penetrants like N₂ and CH₄. But experimental data suggests a decrease in permeability of He which means that none of the penetrants studied are able to permeate through individual POSS cages.

There may be a couple of reasons why penetrants are unable to permeate even though the pore opening of POSS is larger than the kinetic diameters of penetrants studied. Although, the pore opening of POSS is approximately 4.5 Å, there may be energy barriers which may be too high to prevent insertion of penetrants through the cage. Tejerina et al. computationally showed that such barriers exist which may inhibit penetrants from permeating through the cage [71]. The second reason may be the tendency of POSS particles to aggregate and form clusters. The nanometer size of POSS (1.45 nm) increases its tendency to agglomerate. SEM micrographs of 10 wt% and 20 wt% OAPS shown in section 4.5 provide some evidence of formation of small nanosized aggregates which get transformed to micron size when the OAPS concentration in PI increases to 50 wt%. The formation of aggregates would create a more tortuous pathway for permeation of penetrant molecules.
Formation of such agglomerates can affect gas transport in many ways. Small penetrant size defects may be present within the agglomerates due to inefficient packing. Diffusion of smaller penetrants through these defects may also affect the overall permeability and hence selectivity of the membrane. The number of such defects would determine whether or not it would have a noticeable impact on permeability. From the experimental data obtained for PI-OAPS MMMs in this study, it cannot be concluded for sure whether or not there are any packing defects within the agglomerates of POSS big enough for permeation of penetrants.

The other pathway of gas transport suggested in section 5.3 is through the interface between the aggregates of POSS and the polymer matrix. In other words penetrant size defects or interfacial voids created between the aggregates and the polymer matrix would affect the pure gas permeabilities of the penetrants. High resolution SEM images of 10 and 20 wt% PI-OAPS composites did not indicate formation of such interfacial voids. Further, POSS are soluble within the polymer up to higher concentrations and the process of forming nanoparticles is in situ and slow which would allow plenty of time for rearranging polymer chains near the surface. At 50 wt% POSS concentration large interfacial voids were observed between the micron size aggregates of POSS and the surrounding polymer matrix. Moreover, non selective transport of penetrants would have occurred through such voids leading to loss in selectivities. The experimental data in Table 5.2 indicates enhancements in selectivities which suggest that
there are no interfacial voids present and non selective gas transport does not take place.

Figure 5.6 gives the schematic picture of possible distribution of POSS particles/aggregates at low, intermediate and high loadings. As can be seen from Figure 5.6(A), at low concentrations, POSS is uniformly distributed within the PI matrix. Small aggregates of POSS are formed and get distributed within the bulk polymer and can occupy the available excess free volume. The excess free volume is the unoccupied space which arises as a result of inefficient packing of disordered chains in the amorphous region of glassy polymers. Polyimides are relatively high free volume polymers which accounts for their excellent gas transport properties. The presence of an octafunctional POSS within the PI matrix can result in rigidification of the polymer segments which is demonstrated by increase in $T_g$. As the POSS concentration increases the number and size of aggregates within the polymer increase. Up to 10 wt% POSS loading (Figure 5.6B)) the increase in the number of aggregates is prominent where as for
composites beyond 10 wt%, the increase in the size of aggregates is prominent. This is supported by the increase in $T_g$ up to 10 wt%, and remains constant for higher POSS loadings. The bulk polymer acts as a solvent for the POSS particles. When high enough concentration of POSS is reached (~50 wt%), POSS precipitates out from the bulk polymer giving rise to large micron size aggregates (Figure 5.6C)). However, note that even at very high loading, OAPS will be dissolved in the matrix at equilibrium with the particles. As these POSS particles come close to each other there is a possibility of some polymer entrapment. Therefore, the aggregates of POSS may also have some entrained polymer. This possible distribution and aggregation of POSS is supported by the SEM micrographs as shown in Figure 4.6, section 4.5.

Dynamic mechanical analysis (DMA) in section 4.8 revealed that the glass transition temperature ($T_g$) increased OAPS concentration. Since, the glass transition temperature is used to determine the flexibility/rigidity of a polymer matrix and higher the $T_g$ the more rigid is the polymer, increase in $T_g$ suggests restriction to polymer chain motions (increase in rigidity of the polymer matrix). It can be seen from Figure 5.6 that there can be matrix rigidification occurring when the octafunctional POSS comes in close proximity with the surrounding PI matrix. The amine groups enable strong interactions between the two phases thereby leading to rigidified motion of the polymer chains. The implication of this matrix rigidification on diffusion of gas molecules will be discussed in greater detail in section 5.6.
Occupation of the FFV by POSS and the matrix rigidification may lead to decrease in solubility as well as diffusivity of all the gas penetrants. This would cause a decrease in the permeability. Increase in selectivity for small to large gas pairs can be from the differences in the amounts of reduction in permeability as described in section 5.4. Analysis of pure gas sorption studies further aided in the explaining the transport behavior and is described in section 5.5.

Similar studies in the past with different polymer-filler systems have confirmed such counter intuitive reduction in permeability. A study on PES-zeolite 4A MMM done by Li et al. reported reduction in permeability which was attributed primarily to the inhibition of polymer chain motions [50]. Chung et al. studied the matrimid/C\textsubscript{60} MMM system and found that permeability decreased in spite of the large pore opening of fullerene (7Å) [47]. Another cause for the decrease in permeability would be pore blockage due to polymer chains. But its contribution towards the observed transport behavior cannot be precisely quantified. To summarize, the pure gas permeation data for plain PI and PI-OAPS mixed matrix membranes suggests incorporation of POSS in increasing concentration causes the permeation of larger gas molecules to decrease to a greater extent than the smaller gas molecules which lead to an overall increase in the ideal selectivities of the gas pairs studied. Therefore, the observed permeability behavior of PI-OAPS mixed matrix membranes can be attributed to the transport of penetrants through the rigidified polymer matrix.
5.4.4 Trade-Off Curve

Figure 5.7: Position of PI-OAPS mixed matrix membranes with respect to (a) CO$_2$/CH$_4$, and (b) He/CH$_4$ upper bounds.
Based on the above permeability and permselectivity results, the mixed matrix membranes were plotted on a tradeoff curve of CO\textsubscript{2}/CH\textsubscript{4} and He/CH\textsubscript{4} as shown in Figure 5.7. Tradeoff plots of other gas pairs (O\textsubscript{2}/N\textsubscript{2} and He/N\textsubscript{2}) are given in Appendix B.

Trade-off curve or the upper bound gives correlation between selectivity and permeability coefficient of a gas pair and most polymers show performance below the upper bound (shown as solid line). This correlation was first developed by Robeson and is being used as a guideline to choose polymer for a particular separation. Incorporation of inorganic fillers into the polymers will affect their transport behavior and may shift the performance either towards the upper bound or away from it depending on its impact on the polymer matrix. The membrane performance would shift upwards and to the right if precise molecular sieving of penetrants occurred through the dispersed inorganic sieving phase. On the other hand membrane performance would shift downwards and to the left if either there were interfacial voids present between the sieving phase and the polymer phase or if the sieving phase did not perform precise sieving of the penetrant molecules.

The 20 wt% PI-OAPS mixed matrix membrane lies on the upper bound of CO\textsubscript{2}/CH\textsubscript{4} with only a slight decrease in CO\textsubscript{2} permeability as shown in Figure 5.7(a). Note that 6FDA-MDA PI has performance way below the upper bound. The 5 wt% and 10 wt% PI-OAPS mixed matrix membranes also show a progressive increase in selectivity without any loss in permeability. Thus, for CO\textsubscript{2}/CH\textsubscript{4} gas pair the addition of OAPS shifts the trend upwards towards the upper bound without affecting the CO\textsubscript{2} permeability. In other words, addition of
OAPS enhances the performance as compared to the plain PI. However, for He/CH₄, the trend shifts upwards and slightly to the left with the addition of OAPS into PI in increasing concentration as shown in Figure 5.7(b).

5.5 Pure Gas Sorption Studies

Pure gas sorption isotherms for He, CO₂, O₂, N₂ and CH₄ in plain PI and PI-OAPS mixed matrix membrane were measured using a dual volume sorption set-up as described in section 3.3.13. Carbon dioxide at elevated pressures has been shown to increase the free volume of glassy polymers which will affect the solubility of other gases tested. Therefore, the order of gases studied were He, O₂, N₂, CH₄, CO₂. The pressure ranges studied for He, N₂, CH₄, and CO₂ were from 0 to 900 psia (~60 atm) and 0 to 200 psia (10 atm) for O₂. Oxygen was studied at relatively low pressures due to safety reasons. The solubility coefficients were calculated from the sorption isotherms at 10 atm for He, N₂, CH₄ and CO₂ and 2 atm for O₂. The solubility coefficients are listed in Table 5.4 along with solubility selectivities.

Gas sorption in glassy polymers can be described by the dual mode model. The dual-mode equation and the various constants associated with it have been described in section 2.1.2. The amount of gas sorbed at a particular pressure depends on the condensability of the gas, interactions between the polymer matrix and the gas molecule, sorption in the densely packed amorphous region of the polymer (Henry’s regime), and on the excess free volume of the polymer where Langmuir type sorption occurs. Since the interactions between penetrant and polymer remain unchanged, factors affecting gas sorption into a
MMM are limited to chain packing, excess free volume, interactions between penetrants and inorganic filler and the gas sorption capacity of the filler (if any). Langmuir type sorption dominates at lower pressures (into the excess free volume), and increases rapidly with pressure as the Langmuir sites are saturated, whereas, Henry’s law sorption dominates at higher pressures.

![Graph showing solubility coefficients vs critical temperatures for various penetrants](image)

Figure 5.8: Correlation of solubility coefficients with critical temperatures of various penetrants at 35 °C for PI and PI-OAPS mixed matrix membranes.

The solubility coefficients (S) of gases within a polymer in the absence of strong polymer-penetrant interactions are correlated with the critical temperature. A plot of the solubility coefficient as a function of penetrant critical temperature for the mixed matrix membrane is shown in Figure 5.8. The solubility coefficient increases with increase in critical temperature of the penetrant for the base polyimide. The critical temperature directly corresponds to the condensability of the penetrant in the polymer matrix. CO₂ has the highest Tₖ, hence is most
condensable whereas, He has the lowest $T_c$ and is the least condensable of all the penetrants.

The solubility coefficients in the PI-OAPS mixed matrix membranes exhibit a similar correlation with $T_c$ to that of plain PI. However, decrease in solubility coefficient is observed for all penetrants except CO$_2$ with increase in OAPS concentration. Solubility of CO$_2$ does not decrease until the OAPS concentration reaches 20 wt% in the MMM. The different sorption behavior of CO$_2$ compared to other penetrants suggests some interactions may be taking place between the membrane and CO$_2$. 
Table 5.4: Solubility coefficients and solubility selectivities of plain PI and PI-OAPS mixed matrix membranes for the different gases studied.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Solubility Coefficient (cm^3(STP)/cm^3 polymer.atm)</th>
<th>Solubility Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He (10 atm)</td>
<td>O_2 (2 atm)</td>
</tr>
<tr>
<td>0</td>
<td>0.14</td>
<td>0.86</td>
</tr>
<tr>
<td>5</td>
<td>0.14</td>
<td>0.83</td>
</tr>
<tr>
<td>10</td>
<td>0.14</td>
<td>0.8</td>
</tr>
<tr>
<td>20</td>
<td>0.14</td>
<td>0.72</td>
</tr>
</tbody>
</table>
As seen in Table 5.4, the solubility coefficient follows the trend CO$_2$, CH$_4$, O$_2$, N$_2$, He as CO$_2$ is the most condensable of all the gases with the highest critical temperature. A decrease in solubility is observed for all gases except CO$_2$ as the content of OAPS in the polyimide increases from 0 to 20 wt%. The solubility coefficient of He remains unchanged on incorporation of POSS within the PI matrix. Since, helium is the least condensable amongst the gases studied, any change in its sorption is difficult to discern. For the other penetrants, O$_2$, N$_2$, and CH$_4$, there was a continuous decrease in solubility coefficient with increasing OAPS loading. There was a corresponding increase in the solubility selectivity for O$_2$/N$_2$ and CO$_2$/CH$_4$ gas pairs.

The sorption isotherms for O$_2$ for the different membranes studied are shown in Figure 5.9(a). The isotherms for O$_2$ are relatively flat as they were collected at a lower pressure range. A continuous reduction in the solubility was observed as the OAPS loading increased from 0 to 20 wt%. At 20 wt% there is a 16% decrease in sorption. A similar trend of sorption isotherm was observed for N$_2$ as shown in Figure 5.9(b). The sorption isotherms for N$_2$ are concave to the pressure axis, which is typical characteristic of dual mode sorption in glassy polymers. N$_2$ being less condensable than O$_2$ has lower sorption in the membranes. However, a 30% decrease in solubility was observed for 20 wt% PI-OAPS mixed matrix membrane. Further, the nature of the N$_2$ sorption isotherm curve for 20 wt% film became more linear indicating decrease in Langmuir type sorption.
The sorption isotherm plots for CH$_4$ and CO$_2$ for all the membranes are shown in Figure 5.9(c) and Figure 5.9(d) respectively. The solubility of CH$_4$ in the PI-OAPS mixed matrix membranes decreases continuously, at 20 wt% the isotherm somewhat loses its Langmuir behavior and becomes more linear. However, for CO$_2$, there is no change in sorption for 5 wt% and 10 wt% PI-OAPS films. But a decrease in observed for 20 wt% composite membrane. The distribution of sorbed penetrants between densely packed regions and packing defects will be described using dual-mode in the subsequent section 5.5.1.

5.5.1 Dual Mode Sorption Isotherms

Gas sorption in glassy polymers can be described by dual-mode sorption. The Langmuir type sorption of penetrants in the excess free volume of the polymer increases rapidly at low pressures and becomes concave to the pressure axis as these low energy sites become saturated. In contrast, sorption in regions between polymer chains is linear to pressure axis and can be described using Henry’s model. Sorption into the packing defects tends to dominate at lower pressures and sorption in the densely packed regions dominates at higher pressures.

The sorption isotherms for all gases studied at 35 °C are shown in Figure 5.9(a-d). There is a general flattening of the sorption isotherms at low pressures for most gases studied which suggests that there is a reduction in solubility of gases due to the overall decrease in the available low energy Langmuir sorption sites. The nanosized aggregates of POSS may occupy the excess free volume
(a) Oxygen concentration (cm$^3$(STP) / cm$^3$ (polymer)) vs. pressure (atm)

(b) Nitrogen concentration (cm$^3$(STP) / cm$^3$ (polymer)) vs. pressure (atm)
Figure 5.9: Sorption isotherms of (a) O₂, (b) N₂, (c) CH₄, and (d) CO₂ for PI and PI-OAPS mixed matrix membranes.
within the polymer matrix, which would otherwise be available for sorption as can be seen in Figure 5.6. An even distribution of OAPS is obtained throughout the matrix at low concentrations. However, the packets of free volume are very accessible for occupancy by the OAPS molecules and small aggregates. As the number and size of aggregates increases with increase in POSS concentration, the amount of available Langmuir sorption sites decreased and hence a continuous decrease in sorption is observed for all gases except He and CO₂.

When the OAPS loading in the polyimide matrix is high enough (20 wt%), the sorption isotherm becomes slightly linear, thereby losing some of its typical Langmuir type behavior. Density measurement results (section 4.7) showed that the density increased continuously from plain PI (1.379 g/cm³) to 10 wt% PI-OAPS (1.402 g/cm³) and remained constant for higher OAPS loadings as shown in Table 4.2, section 4.7. Therefore, the density results also indicated the space filling effect of POSS when incorporated into the polyimide matrix. The observed decreased sorption behavior of the PI-OAPS mixed matrix membranes is only observed for O₂, N₂, and CH₄.

On the contrary, CO₂ which is a highly condensable polar gas molecule showed a sorption behavior that was somewhat different from the other penetrants. The solubility coefficient did not show any change until the OAPS concentration reached 20 wt%. This phenomenon could be attributed to the inherent high condensibility of CO₂ and also to the numerous NH₂ groups of OAPS which makes the membrane more polar. The presence of amine groups has been shown to increase solubility of acid gases in polymers. At lower OAPS
concentrations (5 wt% and 10 wt%) the effect of reduced excess free volume due to the addition of OAPS is compensated by the high polarity induced due to the NH$_2$ groups. However, at 20 wt%, the Langmuir effect becomes dominant and a slight reduction (~9%) in sorption is observed. The CO$_2$ permeability data also supports this hypothesis, where permeability remains constant up to 10 wt% and then decreases at 20 wt%.

5.5.2 Dual Mode Sorption Parameters

The dual mode sorption model was fitted to the sorption isotherms to investigate the impact of OAPS on sorption in the two environments. The dual mode sorption parameters, $k_d$, $C'_H$ and $b$ for N$_2$, CH$_4$ and CO$_2$ for all the membranes are listed in Table 5.5.

\[
C = k_d p + \frac{bC'_H p}{1 + bp}
\]  
5.2

The Henry’s constant, $k_d$, which characterizes the sorption in Henry’s regime depends on the condensibility of the penetrants, packing density of polymer chains, and polymer-penetrant interactions. The Langmuir capacity, $C'_H$ and the Langmuir affinity constant, $b$, describe sorption in the excess free volume (Langmuir sites). $C'_H$ directly corresponds to the number of available Langmuir sites within the polymer matrix whereas, $b$ largely depends on the polymer-penetrant interactions. Therefore, change in the intersegmental packing (d-spacing) or increase in polymer-penetrant interactions would result in changes in values of $k_d$ different from the plain PI. In contrast, a decrease in the excess free
volume or the Langmuir sites would result in decrease in the Langmuir capacity constant $C'_H$.

The dual-mode parameters, $k_d$, $C'_H$ and $b$ were determined by curve fitting using equation 2.6. The $k_d$ and $b$ values increase in the order $N_2$, $CH_4$ and $CO_2$. This sequence is in agreement with the increasing sequence of their critical temperature as listed in Table 5.5. The Henry’s constant $k_d$ changed subtly over all the OAPS composition ranges for $N_2$, and $CH_4$. This suggests that the Henry’s type sorption is not affected by the incorporation of POSS into the PI matrix, and that the intersegmental packing of the polymer chains is not greatly affected. There is a slight increase in $k_d$ for $CO_2$ with increase in OAPS concentration. Since the intersegmental packing or d-spacing is not affected (section 4.6), this increase may be due to penetrant interactions with the dissolved OAPS. However, there is a continuous decrease in the Langmuir capacity constant $C'_H$ with increase in OAPS concentration which directly corresponds to the excess free volume within a polymer. A decrease in $C'_H$ clearly indicates that there is a decrease in Langmuir type sorption which occurs due to a decrease in the excess free volume. The values for Henry’s law and Langmuir sorption at 10 atm were calculated using the dual mode parameters and are listed in Table 5.5.

The decrease in the Langmuir sorption capacity is associated with the decrease in the fractional free volume or the excess free volume within the polymer matrix upon incorporation of OAPS in increasing concentration. Excess free volume is the specific volume of the film which is not occupied by the polymer chains ($V-V_o$), and FFV is the fraction of the excess free volume with
respect to the total volume. Table 5.6 gives the values of FFV and the excess free volume determined by using Equation 5.3

\[ FFV = \frac{V - V_o}{V} \]  

where, \( V \) = specific volume in glassy state, \( V_o \) = specific volume in the hypothetical rubbery state. The FFV and the excess free volume of 6FDA-MDA were determined from the experimentally determined density and the specific volume of polymer chains determined from group contributions obtained from literature [85,86]. FFV and excess free volume for PI-OAPS composites were calculated using Equation 5.3 by incorporating the volume fraction of OAPS and polymer in each case. A continuous decrease in FFV and the excess free volume with increasing OAPS content was observed. This decrease in the excess free volume corresponds very well with the decrease in the Langmuir capacity constant as listed in Table 5.6.
Table 5.5: Dual mode parameters of PI and PI-OAPS mixed matrix membranes.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>k_d (a)</th>
<th>C'_H (b)</th>
<th>b (c)</th>
<th>C_D*</th>
<th>C_H*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO_2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain PI</td>
<td>0.84</td>
<td>44</td>
<td>0.29</td>
<td>8.4</td>
<td>32.7</td>
</tr>
<tr>
<td>5 wt% PI-OAPS</td>
<td>0.97</td>
<td>41.4</td>
<td>0.33</td>
<td>9.7</td>
<td>31.8</td>
</tr>
<tr>
<td>10 wt% PI-OAPS</td>
<td>1.12</td>
<td>40.9</td>
<td>0.37</td>
<td>11.2</td>
<td>32.2</td>
</tr>
<tr>
<td>20 wt% PI-OAPS</td>
<td>0.75</td>
<td>37</td>
<td>0.3</td>
<td>7.5</td>
<td>27.8</td>
</tr>
<tr>
<td><strong>CH_4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain PI</td>
<td>0.375</td>
<td>30.28</td>
<td>0.1</td>
<td>3.75</td>
<td>15.2</td>
</tr>
<tr>
<td>5 wt% PI-OAPS</td>
<td>0.32</td>
<td>26.45</td>
<td>0.16</td>
<td>3.2</td>
<td>16.2</td>
</tr>
<tr>
<td>10 wt% PI-OAPS</td>
<td>0.28</td>
<td>24.82</td>
<td>0.097</td>
<td>2.8</td>
<td>12.2</td>
</tr>
<tr>
<td>20 wt% PI-OAPS</td>
<td>0.34</td>
<td>20.52</td>
<td>0.077</td>
<td>3.4</td>
<td>9.0</td>
</tr>
<tr>
<td><strong>N_2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain PI</td>
<td>0.17</td>
<td>6.67</td>
<td>0.064</td>
<td>1.7</td>
<td>2.6</td>
</tr>
<tr>
<td>5 wt% PI-OAPS</td>
<td>0.155</td>
<td>5.44</td>
<td>0.044</td>
<td>1.5</td>
<td>1.66</td>
</tr>
<tr>
<td>10 wt% PI-OAPS</td>
<td>0.14</td>
<td>5.07</td>
<td>0.047</td>
<td>1.4</td>
<td>1.62</td>
</tr>
<tr>
<td>20 wt% PI-OAPS</td>
<td>0.12</td>
<td>4.8</td>
<td>0.041</td>
<td>1.2</td>
<td>1.39</td>
</tr>
</tbody>
</table>

(a) cm^3(STP) / cm^3(polymer) atm] [b) cm^3(STP) / cm^3(polymer)]
(c) 1 / atm

*C_D and C_H determined at 10 atm.

Table 5.6: Change in the fractional free volume and excess free volume of polyimide with increasing concentration of OAPS.

<table>
<thead>
<tr>
<th>OAPS %</th>
<th>d-spacing (Å)</th>
<th>V_0*</th>
<th>FFV</th>
<th>Excess free volume (cm^3/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.23</td>
<td>0.609</td>
<td>0.16</td>
<td>0.116</td>
</tr>
<tr>
<td>5</td>
<td>6.23</td>
<td>0.616</td>
<td>0.137</td>
<td>0.098</td>
</tr>
<tr>
<td>10</td>
<td>6.23</td>
<td>0.621</td>
<td>0.136</td>
<td>0.096</td>
</tr>
<tr>
<td>20</td>
<td>6.23</td>
<td>0.631</td>
<td>0.115</td>
<td>0.082</td>
</tr>
</tbody>
</table>

* Calculated using theoretical volume of 6FDA-MDA polymer chains obtained from literature, volume of OAPS, and the respective volume percent of each in the composite.
Figure 5.10: Correlation of solubility coefficients with the fractional free volume of films for various penetrants at 35 °C with OAPS concentrations ranging from 0 to 20 wt%.

As shown in Figure 4.7, at lower POSS concentrations, the small agglomerates of POSS do not affect the d-spacing between the polymer chains. XRD analysis (discussed in section 4.6) showed that the d-spacing between the polymer chains is not affected up to 30 wt%, however, a slight decrease in d-spacing was observed for 50 wt% OAPS concentration. Visible phase separation occurs at such high OAPS loadings and the size of aggregates increases to almost 1 μm as discussed in section 4.5. The almost constant values of Henry's constant, k_d for 5, 10 and 20 wt% PI-OAPS films also supports this hypothesis. Addition of POSS into the PI matrix does not disrupt the chain packing; it occupies the excess free volume, which is evident from the almost constant
values of $k_d$ and continuous decreasing values of $C'_H$. The correlation between solubility coefficient and FFV is given in Figure 5.10. As can be seen from the figure, a linear relationship exists between the solubility coefficient and FFV for $O_2$, $N_2$ and $CH_4$. However, this relationship becomes non-linear for $CO_2$. This non-linear behavior indicates that there are other factors affecting $CO_2$ solubility in the MMM other than FFV. This increase in $CO_2$ solubility is with the addition of OAPS can be attributed to the penetrant-OAPS interactions. The polar –NH$_2$ groups of OAPS increases the overall polarity of the MMM and hence increases interactions with $CO_2$, which can also be concluded from the increasing values of Henry’s constant, $k_d$ with increasing OAPS loading.

**5.6 Pure Gas Diffusivity**

The pure gas diffusivities were calculated from the permeability and solubility coefficients using equation 2.3. Diffusivity of a penetrant in a polymer matrix depends largely on the size and shape of the gas molecule. It also depends on the relative packing and thermal motion of the polymer chains. Table 5.7 gives the diffusivities of all the gases studied for plain PI and PI-OAPS mixed matrix membranes. Diffusivity coefficients increase in order He, $O_2$, $CO_2$, $N_2$ and $CH_4$ as helium is the smallest penetrant and $CH_4$ is the largest.
Table 5.7: Diffusivity Coefficients of plain PI and PI-OAPS mixed matrix membranes for the different gases studied.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Diffusivity Coefficient (×10^8 cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
</tr>
<tr>
<td>0</td>
<td>270</td>
</tr>
<tr>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>10</td>
<td>233</td>
</tr>
<tr>
<td>20</td>
<td>233</td>
</tr>
</tbody>
</table>

The 5 wt% PI-OAPS membrane shows 8% decrease in the diffusivity for helium as compared to the plain PI. Whereas, 10 and 20 wt% PI-OAPS membranes show equal reduction in diffusivity (~14%). The diffusivity coefficients of O_2, N_2, and CH_4 also decrease with the incorporation of POSS, but this decrease in diffusivity is maximum for 10 wt% OAPS loading and then remains almost constant for 20 wt%. As discussed in section 5.4.4, the reduction in diffusivity may be due to the restriction induced by POSS to the motion of the polymer chains. This phenomenon of enhanced polymer chain rigidity was also confirmed using DMA, which showed an increase in T_g with increasing OAPS content. Further, the pure gas diffusivity data suggests that the polyimide matrix experiences a maximum restriction to motion when the OAPS loading reaches 10 wt%. In other words maximum rigidification is attained at 10 wt% OAPS loading and any further increase of OAPS in the polyimide matrix will result only in the filling of its excess free volume. DMA studied also indicated a maximum increase
in $T_g$ at 10 wt% OAPS concentration, no significant change in $T_g$ was observed beyond that.

5.6.1 Impact of FFV on Diffusion

It is useful to visualize the impact of FFV on the diffusion of penetrants through the membrane. The impact of incorporation of POSS within the PI matrix has been discussed in section 5.5.2 and the values of FFV with increasing OAPS concentration are listed in Table 5.2. A pictorial representation of free volume distribution within a polymer matrix is given in Figure 5.11(a). The effect of addition of POSS at an arbitrary POSS loading is given in Figure 5.11(b).

![Figure 5.11: Distribution of free volume within (A) PI matrix, (b) PI-OAPS MMM.](image)

The open pockets in Figure 5.11 represent the specific free volume and is defined as the difference between the specific volume of the polymer, $V$ (determined from density measurements) and the volume occupied by the polymer chains, $V_0$ (determined from group contribution estimation). Addition of POSS increases the total occupied volume, thereby decreasing the excess volume within the polymer matrix as seen in Figure 5.11(b). This free volume or free space exists as disconnected packets that slowly exchanges positions...
because of thermally activated chain motions. Activated diffusional jumps of penetrants takes place by a combination of the above processes through the polymer. Therefore, reduction in the excess free volume in combination with inhibition to segmental mobility of polymer chains results in reduction in diffusivity of the penetrant.

A rocking motion of the polymer chains provides penetrant scale gap through which gas molecule can translate via diffusional jumps (Figure 5.12). These diffusional jumps of penetrants in the transient gaps are size and shape dependent and an impact on the formation of these transient gaps affects their diffusion to a certain extent.

Figure 5.12: Pictorial representation of diffusional jump of (a) large penetrant, and (b) small penetrant through rigidified polymer matrix.

Due to the induced restriction to the motion of polymer chains, the transient gaps are large enough for smaller penetrants like helium to make a dissusional jump but are small for larger penetrants like methane to make a diffusional jump. A distribution of such restricted motions causes the diffusivity of larger penetrants to decrease to a greater extent than the diffusivity of larger penetrants. A point is reached at 10 wt% OAPS loading where almost all the
polymer chains have been affected and addition of excess POSS does not affect the diffusivity of the penetrants as shown in Table 5.7.

### 5.7 Pressure Effects

The pressure dependence of permeability predicted by the dual mode model is given by Equation 5.3

\[
P = k_D D_D + \frac{D_H C_H b}{1 + bp}
\]

where \( D_D \) and \( D_H \) are the diffusion coefficients through the continuous phase (Henry’s type) and adsorptive sites (Langmuir mode) respectively. Diffusion of penetrants through the polymer takes place primarily by mobility through Henry’s mode. Langmuir sites are locations where the gas molecules are in a low energy state and do not participate in the diffusional process. Therefore, it can be safely assumed that \( D_H \) is very low, and the permeability coefficient hardly shows any dependence on upstream pressure.

A similar pressure dependence was observed for 6FDA-MDA PI as shown in Figure 5.13. He, O\(_2\), and N\(_2\) did not show much variation with increase in upstream pressure, while a decrease in the permeability coefficient of CH\(_4\) and CO\(_2\) was observed. This is due to a greater drop in CH\(_4\) and CO\(_2\) solubility with increase in pressure. Figure 5.14 gives the pressure dependence of permeability coefficient of 5 wt% PI-OAPS membrane. A trend similar to the plain PI was observed with no change in He, O\(_2\), N\(_2\) and slight drops is CH\(_4\) and CO\(_2\). As discussed in section 5.5, decrease in Langmuir type sorption was observed with the addition of OAPS into the PI matrix. The Henry’s type sorption was not
significantly affected as incorporation of POSS does not disrupt the intersegmental chain packing. From equation 5.3, since the permeability coefficient has very little dependence on diffusion in Langmuir sites, a decrease in Langmuir type sorption does not affect the pressure dependency of the permeability coefficient.

Figure 5.15 and Figure 5.16 give similar permeability coefficient versus pressure plots for 10 wt% and 20 wt% PI-OAPS membranes. The pressure dependence of solubility coefficients for various gases in plain PI, 5 wt% PI-OAPS, 10 wt% PI-OAPS and 20 wt% PI-OAPS films is given in Figure 5.17 to Figure 5.20 and they all agree with the dual-mode sorption model. A decrease in solubility coefficients with increase in pressure was observed for all gases in all membranes. The influence of pressure on S for He, O₂, N₂ and CH₄ is much less than that for CO₂. S for CO₂ drops dramatically with increase in pressure at low pressure range and then tends to level-off at high pressure range. This indicates that the effect of pressure on S of CO₂ in the Langmuir sites is significant at low pressures and can be ignored once all the Langmuir sites are occupied by the penetrant at high pressure. This strong pressure dependence of S for CO₂ gives rise to a strong dependence of P on pressure in the low pressure range.

Pressure dependence of both P and S for the PI-OAPS mixed matrix membranes was similar to that of the Plain PI. This further validates the theory that incorporation of OAPS within the PI matrix leads to decrease in Langmuir sites and increase in polymer chain rigidity without disrupting polymer chain packing or affecting Henry's sorption/diffusion.
Figure 5.13: Pressure dependence of permeability coefficients of various gases in 6FDA-MDA PI.

Figure 5.14: Pressure dependence of permeability coefficients of various gases in 5 wt% PI-OAPS.
Figure 5.15: Pressure dependence of permeability coefficients of various gases in 10 wt% PI-OAPS.

Figure 5.16: Pressure dependence of permeability coefficients of various gases in 20 wt% PI-OAPS.
Figure 5.17: Pressure dependence of solubility coefficients of various gases in 6FDA-MDA PI.

Figure 5.18: Pressure dependence of solubility coefficients of various gases in 5 wt% PI-OAPS.
Figure 5.19: Pressure dependence of solubility coefficients of various gases in 10 wt% PI-OAPS.

Figure 5.20: Pressure dependence of solubility coefficients of various gases in 20 wt% PI-OAPS.
Summary of Gas Transport

Pure gas permeation and sorption studies were carried out on the plain PI and the PI-OAPS mixed matrix membranes to determine the effect of incorporation of POSS into the polyimide matrix. Diffusivity coefficients were calculated from the experimentally determined values of permeability and solubility coefficients using equation 2.3. An overall decrease in permeability was observed for He, O₂, N₂ and CH₄ for increasing OAPS loading (5, 10 and 20 wt%). CO₂ permeability remained constant for 5 wt% and 10 wt% and showed 9 % decrease for 20 wt% OAPS loading. It was determined from this data that the pores of POSS cages were not accessible to the penetrants and the primary mode of gas transport is through the bulk polymer. Amongst the other possible modes of transport described in section 5.3, interfacial transport is not possible due to strong interactions between OAPS and PI. Transport through aggregates of OAPS may be possible, but is difficult to quantify or characterize.

The decrease in permeability was attributed partly to a decrease in solubility and partly to a decrease in diffusivity. A comparison of the relative reduction in the permeability, diffusivity and solubility of He, O₂, N₂ and CH₄ for 5 wt% PI-OAPS membrane is shown in Figure 5.21. The Y axis indicates the total reduction in property (i.e permeability, diffusivity, solubility) and on the X axis are the different penetrants. Similar plots for 10 wt% and 20 wt% PI-OAPS membranes are shown in Figure 5.22 and Figure 5.23 respectively.
Figure 5.21: A comparison of relative percent reduction in permeability, diffusivity and solubility coefficient for 5 wt% PI-OAPS membrane.

Figure 5.22: A comparison of relative percent reduction in permeability, diffusivity and solubility coefficient for 10 wt% PI-OAPS membrane.
Figure 5.21 indicates that the decrease in $O_2$ and $N_2$ permeabilities is in part due to a decrease in diffusivity and in part due to decrease in solubility, decrease in solubility being greater than that in diffusivity. For $CH_4$ there is an equal contribution from these two factors. For 10 wt% PI-OAPS mixed matrix membrane (Figure 5.22), the diffusivity and solubility both decrease further, with percent decrease in diffusivity greater than that in solubility. Finally for 20 wt% membrane, the contribution from diffusivity remains constant with a significant decrease in solubility. In other words, solubility factor dominates at higher OAPS loading whereas, diffusivity dominates at lower loadings.

In conclusion, the incorporation of POSS into the polyimide matrix had two primary effects, reduction in diffusivity and reduction in solubility. The OAPS
restricted the motion of polymer chains when blended into it which led to a
decrease in diffusion. At 10 wt% OAPS concentration a point was reached where
all the polymer chains had been affected (restricted) and any further addition of
OAPS led to a further reduction in the excess free volume of the polyimide.
Reduction in FFV also led to a decrease in diffusivity coefficient as the amount of
FFV and mobility of polymer chains together determine the diffusivity coefficient
of a penetrant within a polymer.

The dual mode sorption parameters showed a continuous decrease in
Langmuir capacity constant (C'_H) and no significant change in the Henry’s
constant (k_d) for N_2 and CH_4. This suggested a decrease in excess free volume
with increase in OAPS concentration. The decrease in the excess free volume
was determined using experimentally determined densities, and they correspond
very well with the decrease in C'_H at various OAPS loadings. The pressure
dependence of P and S of PI-OAPS mixed matrix membranes is similar to that of
plain PI, indicating transport through the PI matrix. Polar interactions between
OAPS and CO_2 led to higher solubilities and permeabilities than expected for 5
wt% and 10 wt% PI-OAPS mixed matrix membranes. This was also indicated by
the higher values of Henry’s constant, k_d. Also, unlike other penetrants, solubility
coefficient of CO_2 did not have a linear relationship with FFV.

The significant enhancements in selectivities of CO_2/CH_4, He/CH_4 and
O_2/N_2 with only slight decrease in permeabilities showed that though POSS could
not be used as a molecular sieve (as intended), it enhanced the overall transport
properties of the 6FDA-MDA polyimide.
6  Temperature Effects on Gas Transport

6.1  Introduction

In Chapter 5, gas transport properties of (6FDA-MDA) PI-OAPS mixed matrix membranes at 35 °C were discussed. Decreases in pure gas permeabilities with enhancements in selectivities were observed. Especially, significant enhancements in CO$_2$/CH$_4$, He/CH$_4$ and He/N$_2$ were observed with performance tending towards the upperbound on the trade-off curve for these gas pairs. Significant improvement in CO$_2$/CH$_4$ selectivity was obtained due to the favorable polar interactions between CO$_2$ and OAPS. Amongst the various possible pathways of gas transport, it was concluded from the study that the transport was occurring through the polymer matrix with no evidence of transport within either the OAPS molecules or aggregates.

Since significant enhancements in selectivities were observed at 35 °C, this chapter will describe the results obtained at higher temperatures, 45 °C and 60 °C. Further, the behavior of these mixed matrix membrane materials at high temperature will be used to test conclusions from Chapter 5 regarding the mode of transport through these membranes. A detailed understanding of temperature effects on gas permeation properties is essential to determine the commercial applications of these membranes. Relative insensitivity of permeability and
permselectivity to high temperatures is desirable. Pure gas permeation and sorption studies were performed at 45 °C and 60 °C using methods described in section 3.3.12. Also, activation energies of permeation and diffusion and heat of sorption were determined for various penetrants using pre-established theories.

6.2 Background

The pure gas permeability of penetrants through glassy polymers typically increases with increasing temperature. However, a significant loss in selectivities of small to large gas pairs is obtained [83]. An increase in temperature causes increase in frequency and size of thermal motions of polymer chains. This leads to formation of penetrant size gaps which leads to an increase in permeability of all the penetrants. This increase is greater in case of larger penetrants than smaller penetrants resulting in loss of selectivity. While diffusivity is increasing function of temperature, solubility is a decreasing function of temperature. The decrease in solubility is due to decrease in Langmuir sites with increase in temperature. Also, there is a decrease in condensability of gas molecules with a shift in temperature away from the critical temperature ($T_c$). Decrease in Langmuir type sorption occurs, this leads to flattening of the typical dual mode concave nature of the sorption isotherm. The effect of temperature on permeability, diffusivity and solubility coefficients are expressed in terms of Arrhenius type equations.

Gas permeability of a membrane, $P$, can be expressed by an Arrhenius type equation for a reasonable temperature range.

$$ P = P_0 \exp\left(\frac{-E_p}{RT}\right) \quad 6.1 $$
where $P_0$ is the pre-exponential factor, $E_p$ is activation energy for permeation and $R$ is the gas constant.

Further according to the solution-diffusion mechanism, gas permeability is determined by two contributions, diffusivity, $D$ and solubility, $S$ of a penetrant.

$$P = D \times S$$ \hspace{1cm} 6.2

Both diffusivity and solubility can also be expressed by Arrhenius type equations 6.3 and 6.4:

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right)$$ \hspace{1cm} 6.3

$$S = S_0 \exp\left(-\frac{H_s}{RT}\right)$$ \hspace{1cm} 6.4

where $D_0$ and $S_0$ are pre-exponential factors for diffusivity and solubility respectively. $E_d$ is the activation energy for diffusion and $H_s$ is the heat of sorption.

The activation energy for permeation is equal to the sum of activation energy for diffusion and heat of sorption as shown below,

$$E_p = E_d + H_s$$ \hspace{1cm} 6.5

The heat of sorption, $H_s$, defines the effect of temperature on gas solubility coefficients in a polymer. It is primarily governed by the negative average enthalpy change associated with the gaseous penetrants being sorbed into the polymer matrix, and the positive enthalpy required to create a site into which penetrant can sorb. An additional factor associated with the magnitude of polymer-penetrant interactions or “heat of mixing” may also affect the overall heat of sorption.
The activation energies of diffusion, $E_d$, are more easily correlated to the physical characteristics of the penetrants. It is well known that the diffusion process is dependent on size and shape of the gas molecules. Large scale motions greatly enhance the diffusivity of relatively large gas molecules by producing gaps of sufficient size to allow these molecules to pass, while smaller molecules are affected to a lesser extent. The activation energy for diffusion describes the energy required for a penetrant to make a diffusive jump from one site to another. The more rigid the polymer, the higher will be the energy required. Therefore, matrix rigidification would cause an increase in $E_d$.

Since, activation energy for permeation, $E_p$, is a sum of $E_d$ and $H_s$ and $E_d$ is positive (endothermic) and $H_s$ is negative (exothermic), $E_p$ is positive ($|E_d| > |H_s|$). This positive value of activation energy for permeation results in permeability being an increasing function of temperature.

### 6.3 Pure Gas Permeation

Pure gas permeabilities of He, CO$_2$, O$_2$, N$_2$ and CH$_4$ were determined using a constant volume variable pressure gas permeation set-up. Gas permeation experiments were performed on each gas with a maximum upstream pressure of 200 psi at 45 °C and 60 °C. PI-OAPS mixed matrix membranes with OAPS concentrations of 0, 5 wt%, 10 wt% and 20 wt% were studied. The pure gas permeabilities and selectivities at 45 °C and 60 °C are listed in Table 6.2 and Table 6.3 respectively. The pure gas permeabilities of penetrants in PI and PI-OAPS mixed matrix membranes at 35 °C are given in Table 6.1 for sake of
comparison. As discussed in Chapter 5, the permeability of penetrants at 35 °C, decreased with increase in OAPS concentration with the exception of CO₂. The magnitudes of permeabilities in PI as well as PI-OAPS MMMs at 45 °C and 60 °C are in the same order as permeabilities at 35 °C. Helium has the smallest kinetic diameter and the highest permeability and is followed progressively by CO₂, O₂, N₂ and CH₄. This order of permeabilities is similar to those in other typical glassy polymers. As expected, an overall increase in permeability with increase in temperature for plain PI was observed for all the gases. A similar increasing trend of permeability with temperature was observed for PI-OAPS mixed matrix membranes (5 wt% - 20 wt%). Permselectivities of a few gas pairs studied are also listed in Table 6.2. An overall increase in selectivity was observed for each gas with increase in OAPS concentration at both the temperatures. However, The PI-OAPS MMMs show an overall loss in selectivity with increase in temperature from 35 °C to 45 °C. This loss in selectivity with increase in temperature is characteristic of transport through polymeric membranes. However, at any given temperature the selectivity of PI-OAPS mixed matrix membrane is higher than that of plain PI.

From the pure gas permeability values at 45 °C listed in Table 6.2, the permeability of all penetrants decreases with increase in OAPS concentration. There was a similar increase in permeability and loss in selectivity at 45 °C relative to 35 °C. For example, there is a 7% increase in He permeability for plain PI with a 10 °C increase in temperature. The 5, 10 and 20 wt% PI-OAPS MMMs show only a marginal increase in permeability of ~3 %. For CH₄ which is the
largest penetrant, the permeability of PI increases by 30% with a 10 °C increase in temperature. The percentage increase for PI-OAPS MMMs increases progressively from 10%, 30%, to 58% with increase in OAPS concentration. No change in CO₂ permeability was observed even at 45 °C for OAPS concentrations up to 10 wt%, at 20 wt% there is a 6% decrease in permeability with respect to plain PI. The corresponding enhancements in selectivity of CO₂/CH₄ and He/CH₄ at 45 °C for 20 wt% PI-OAPS MMM are ~30% and ~13% respectively over that of plain PI. The enhancements in selectivities are lower at 45 °C as compared to 35 °C.

The permeability coefficients and permselectivities of plain PI and PI-OAPS MMMs for various penetrants at 60 °C are given in Table 6.3. A 15 °C increase in temperature causes 18% increase in He permeability for plain PI, 22% increase for 5 wt% PI-OAPS MMM, 30% increase for 10 wt% and 20 wt% PI-OAPS MMM. For CH₄, the permeability increases by 73% for plain PI and 63% for 20 wt% PI-OAPS MMM. There is an enhancement of 30% in the selectivity of CO₂/CH₄ and He/CH₄ for 20 wt% PI-OAPS MMM over that of plain PI.

It should be noted that as in the case of plain PI, the percent increase in permeability of larger penetrants in the MMMs are greater than that of the smaller penetrants. This behavior is characteristic of transport through glassy polymers and causes loss in selectivity with increase in temperature. Though decrease in selectivity was observed for MMMs with increase in temperature from 35 °C to 60
°C, they were still higher than the selectivities of penetrants in plain PI at that temperature.
Table 6.1: Permeability Coefficients and permselectivities of plain PI and PI-OAPS mixed matrix membranes for the different gases studied at 35 °C.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>He (10 atm)</th>
<th>O₂ (10 atm)</th>
<th>N₂ (10 atm)</th>
<th>CH₄ (10 atm)</th>
<th>CO₂ (10 atm)</th>
<th>O₂/N₂</th>
<th>CO₂/CH₄</th>
<th>He/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50±1</td>
<td>3.76±0.1</td>
<td>0.7±0.02</td>
<td>0.4±0.022</td>
<td>16.3±0.5</td>
<td>5.3±0.08</td>
<td>41±3</td>
<td>125±4</td>
</tr>
<tr>
<td>5</td>
<td>46±0.8</td>
<td>3.54±0.09</td>
<td>0.62±0.02</td>
<td>0.37±0.028</td>
<td>16.4±0.35</td>
<td>5.8±0.04</td>
<td>44±2.4</td>
<td>123±7</td>
</tr>
<tr>
<td>10</td>
<td>43±0.5</td>
<td>2.9±0.12</td>
<td>0.51±0.014</td>
<td>0.31±0.007</td>
<td>16.5±0.35</td>
<td>5.5±0.05</td>
<td>53±1</td>
<td>139±2</td>
</tr>
<tr>
<td>20</td>
<td>43±0.4</td>
<td>2.6±0.08</td>
<td>0.425±0.02</td>
<td>0.24±0.01</td>
<td>15±0.14</td>
<td>6.1±0.2</td>
<td>63±2</td>
<td>180±6</td>
</tr>
</tbody>
</table>

1 Barrer = 10⁻¹⁰ cm³(STP).cm/cm².sec.cmHg
Table 6.2: Permeability Coefficients and permselectivities of plain PI and PI-OAPS mixed matrix membranes for the different gases studied at 45 °C.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Permeability Coefficients (P) (Barrer)</th>
<th>Permselectivity (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He (10 atm)</td>
<td>O₂ (10 atm)</td>
</tr>
<tr>
<td>0</td>
<td>53.6±0.5</td>
<td>4.4±0.03</td>
</tr>
<tr>
<td>5</td>
<td>47.4±0.5</td>
<td>4±0.04</td>
</tr>
<tr>
<td>10</td>
<td>44±1</td>
<td>3.98±0.04</td>
</tr>
<tr>
<td>20</td>
<td>44±0.3</td>
<td>3.4±0.08</td>
</tr>
</tbody>
</table>

1 Barrer = 10⁻¹⁰ cm³(STP).cm/cm².sec.cmHg
Table 6.3: Permeability Coefficients and permselectivities of plain PI and PI-OAPS mixed matrix membranes for the different gases studied at 60 °C.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Permeability Coefficients (P) (Barrer)</th>
<th>Permselectivity (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He (10 atm)</td>
<td>O₂ (10 atm)</td>
</tr>
<tr>
<td>0</td>
<td>63</td>
<td>5.1</td>
</tr>
<tr>
<td>5</td>
<td>57.8±0.4</td>
<td>5±0.06</td>
</tr>
<tr>
<td>10</td>
<td>56±0.3</td>
<td>4.8±0.1</td>
</tr>
<tr>
<td>20</td>
<td>56±0.5</td>
<td>4.3±0.08</td>
</tr>
</tbody>
</table>

1 Barrer = 10⁻¹⁰ cm³(STP).cm/cm².sec.cmHg
The permeation behavior of PI-OAPS MMMs at higher temperatures follows a similar trend as that of plain PI. However, the matrix rigidification due to incorporation of OAPS is evident at higher temperatures and leads to an overall increase in selectivity compared to that of plain PI. Though there is an increase in thermal motion of polymer chains due to increase in temperature, the restriction to motion induced by OAPS assists in maintaining higher selectivities. The activation energies for permeation were determined and will be discussed in detail in section 6.6. The impact of temperature on the penetrant solubility of PI and PI-OAPS MMM will be discussed in section 6.4.

6.4 Pure Gas Sorption Studies

Pure gas sorption of plain PI and PI-OAPS mixed matrix membranes were performed at 45 °C and 60 °C on He, O₂, N₂, CH₄ and CO₂ in that order. He, N₂ and CH₄ were measured up to pressures of 850 psi (~60 atm) whereas CO₂ and O₂ were measured up to 200 psi (~14 atm). The solubility isotherms for CO₂ were measured at lower pressures to avoid penetrant induced conditioning or hysteresis which can affect transport properties in these non-equilibrium materials. The solubility coefficients at 45 °C and 60 °C are listed in Table 6.4 for O₂, N₂, CH₄ and CO₂. Helium solubility at 35 °C is very low, and decreases further with increase in temperature. Hence, the values of helium solubility are not reported for higher temperatures since they cannot be accurately measured. A decrease in solubility was observed for 6FDA-MDA PI and the PI-OAPS MMMs for all the OAPS compositions at 45 °C and 60 °C. The solubility of O₂, N₂ and CH₄ at 45 °C and 60 °C decreases with increase in OAPS concentration due to
the space filling effect of OAPS which occupies the FFV within the polymer matrix. Similar to 35 °C, the solubility of CO₂ remains unchanged with the addition of OAPS. The decrease in penetrant condensability and Langmuir sites caused by the increase in temperature affects the PI-OAPS mixed matrix membranes in a similar fashion as that for the plain PI with the exception of CO₂. As discussed earlier, the interactions between OAPS and CO₂ would result in an enhanced solubility relative to base PI.

The sorption isotherms for N₂, CH₄ and CO₂ of plain PI and 20 wt% PI-OAPS MMM at 35 °C, 45 °C and 60 °C are given in Figure 6.1 (a) & (b) respectively. For both, plain PI and 20 wt% PI-OAPS MMM, N₂ and CH₄ solubility is a decreasing function of temperature. Also, it should be noted that the typical Langmuir nature of the isotherm that is concaving to the pressure axis becomes relatively linear at 60 °C. This clearly indicates decrease in sorption in the Langmuir sites of the polymer matrix. Other penetrants also follow a similar solubility behavior at 45 °C and 60 °C.

The relative amounts of reduction in sorption of penetrants with increase in OAPS concentration decreases with increase in temperature. As discussed in section 5.5, at 35 °C, reduction in FFV causes an overall decrease in solubility of penetrants except CO₂. At higher temperatures, there is an inherent decrease in Langmuir sites of plain PI which leads to a decrease in solubility of penetrants. Therefore, the relative difference in sorption of penetrants in PI-OAPS MMM as compared to plain PI decreases with increase in temperature. The sorption characteristics of CO₂ in PI-OAPS MMMs at 45 °C and 60 °C are similar to that
at 35 °C. There is no decrease in sorption of CO₂ until the OAPS concentration reaches 20 wt% in the MMM.
Table 6.4: Solubility coefficients of PI and PI-OAPS mixed matrix membranes at 45 °C and 60 °C for O\(_2\), N\(_2\), CH\(_4\) and CO\(_2\).

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Solubility Coefficient (cm(^3)(STP)/cm(^3)polymer.atm) 45 °C</th>
<th>Solubility Coefficient (cm(^3)(STP)/cm(^3)polymer.atm) 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(_2) (2 atm)</td>
<td>N(_2) (10 atm)</td>
</tr>
<tr>
<td>0</td>
<td>0.72</td>
<td>0.31</td>
</tr>
<tr>
<td>5</td>
<td>0.67</td>
<td>0.28</td>
</tr>
<tr>
<td>10</td>
<td>0.63</td>
<td>0.23</td>
</tr>
<tr>
<td>20</td>
<td>0.6</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Sorption of penetrants in polymers is an exothermic process and is usually associated with the evolution of heat of sorption. The sorption process can be pictured as taking place in two stages: (i) an endothermic process which involves forming a hole of penetrant size in the polymer and (ii) condensation of penetrant from gaseous into the polymer matrix which is an exothermic process. Condensation of penetrants being a more dominant process, the overall sorption process becomes exothermic. The heat of sorption evolved for $O_2$, $N_2$, $CO_2$ and $CH_4$ for PI and PI-OAPS MMMs were determined and will be discussed in section 6.6.
Figure 6.1: Temperature effects on sorption isotherms for N\(_2\) and CH\(_4\) in (a) plain PI and (b) 20 wt% PI-OAPS.
6.5 Pure Gas Diffusivity

The pure gas diffusivity coefficients of penetrants at 45 °C and 60 °C were calculated from the experimentally determined permeability and solubility coefficients at their respective temperatures. Diffusivity coefficient is an increasing function of temperature. Increase in temperature increases the thermal motions of the polymer chains thereby enhancing diffusivity of penetrants. The diffusivity coefficients of O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4} and CO\textsubscript{2} in plain PI and PI-OAPS mixed matrix membranes at 45 °C and 60 °C are given in Table 6.5.

The diffusivity coefficients of all the penetrants at 45 °C are higher than at 35 °C. However, the diffusivity coefficients of PI-OAPS mixed matrix membranes decreases with increase in OAPS concentration. This indicates that the matrix rigidification effect of OAPS still exists at 45 °C. Although, the polymer chains gain thermal motion as a result of increase in temperature, they are still restricted by either individual OAPS molecules or aggregates. The diffusivity coefficient of CO\textsubscript{2} for the PI-OAPS MMMs remains unchanged due to the almost constant values of permeability and solubility at 45 °C.

At 60 °C, the diffusivity coefficient of all the penetrants in plain PI further increases. The PI-OAPS MMMs also have higher diffusivities at 60 °C as compared to 45 °C. The diffusivity coefficients for O\textsubscript{2} and N\textsubscript{2} in PI-OAPS MMMs at 60 °C showed slightly higher values than expected. This could be due to some experimental error as these values are obtained from a single run. Again for CO\textsubscript{2}, there is little variation in the diffusivity coefficients with increase in OAPS concentration.
Table 6.5: Pure gas diffusivity coefficients of O$_2$, N$_2$, CH$_4$ and CO$_2$ in PI and PI-OAPS mixed matrix membranes at 45 °C and 60 °C.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>Diffusivity Coefficient ($\times 10^8$ cm$^2$/s) 45 °C</th>
<th>Diffusivity Coefficient ($\times 10^8$ cm$^2$/s) 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_2$</td>
<td>N$_2$</td>
</tr>
<tr>
<td>0</td>
<td>4.64</td>
<td>2.23</td>
</tr>
<tr>
<td>5</td>
<td>4.53</td>
<td>2.17</td>
</tr>
<tr>
<td>10</td>
<td>4.8</td>
<td>2.4</td>
</tr>
<tr>
<td>20</td>
<td>4.26</td>
<td>2.9</td>
</tr>
</tbody>
</table>
6.6 Activation Energy

The activation energy for permeation and diffusion and heat of sorption were computed from data in Figure 6.2 to Figure 6.4 using Arrhenius equations. The activation energy for permeation was determined from the slope of linear fits of log of permeability versus inverse temperature. Figure 6.2(a & b) are Arrhenius plots for plain PI and 5 wt% PI-OAPS MMM. Figure 6.3(a & b) are Arrhenius plots for 10 wt% and 20 wt% PI-OAPS MMMs respectively. As shown in Figure 6.2(a) there is a stronger dependence of N\textsubscript{2} and CH\textsubscript{4} permeability on temperature as compared to He, and CO\textsubscript{2} for PI. The Arrhenius plots of PI-OAPS MMMs, Figure 6.2(b) to Figure 6.3(a & b) indicate similar stronger temperature dependence of N\textsubscript{2} and CH\textsubscript{4}. The computed activation energies are listed in Table 6.6. The values of activation energies for plain PI obtained are comparable with those reported in the literature for other types of polyimides [83,87]. The activation energies reported in this study are applicable only for the temperature range studied.

The activation energy for permeation (E\textsubscript{p}) is the energy required for permeation of penetrant through the polymer. This activation energy increases with increase in the kinetic diameter of the penetrants. Therefore, CH\textsubscript{4} has highest E\textsubscript{p} followed by N\textsubscript{2}, O\textsubscript{2}, He and CO\textsubscript{2} in that order. Although CO\textsubscript{2} is bigger than He, it has a lower E\textsubscript{p} than He due to the fact that it is a highly condensable gas. It can then be thought that the addition of OAPS into the polyimide matrix will cause a further increase in E\textsubscript{p} of penetrants as more energy would be required for permeation of penetrants through the rigidified polymer matrix.
Accordingly, it can be seen from Table 6.6 that the activation energy increases for almost all penetrants with increase in OAPS composition. This increase in activation energy of permeation supports the hypothesis that matrix rigidification is induced by the addition of POSS particles. Due to restriction to thermal motions of polymer chains induced by the incorporation of OAPS, the penetrants require more energy to permeate through the matrix.

Table 6.6: Comparison of activation energy for permeation, heat of sorption and activation energy for diffusion in PI and PI-OAPS mixed matrix membranes at 35 °C–60 °C. Upstream pressure was 10 atm for He, CO\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4}.

<table>
<thead>
<tr>
<th>% OAPS</th>
<th>He</th>
<th>CO\textsubscript{2}</th>
<th>O\textsubscript{2}</th>
<th>N\textsubscript{2}</th>
<th>CH\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.86</td>
<td>0.364</td>
<td>1.11</td>
<td>2.26</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>0.94</td>
<td>0.427</td>
<td>1.23</td>
<td>2.47</td>
<td>2.37</td>
</tr>
<tr>
<td>10</td>
<td>0.99</td>
<td>0.21</td>
<td>1.85</td>
<td>2.51</td>
<td>3</td>
</tr>
<tr>
<td>20</td>
<td>0.99</td>
<td>0.35</td>
<td>1.80</td>
<td>2.72</td>
<td>3.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Activation Energy for Permeation, E\textsubscript{p} (kcal/gmol)</th>
<th>Heat of Sorption, H\textsubscript{s} (kcal/gmol)</th>
<th>Activation Energy for Diffusion, E\textsubscript{d} (kcal/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% OAPS</td>
<td>He</td>
<td>CO\textsubscript{2}</td>
<td>O\textsubscript{2}</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-1.42</td>
<td>-1.31</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-1.12</td>
<td>-1.49</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-1.71</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-0.621</td>
<td>-1.48</td>
</tr>
</tbody>
</table>

166
Figure 6.2: Arrhenius correlations of permeability coefficients of penetrants in (a) plain PI and (b) 5 wt% PI-OAPS mixed matrix membrane.
Figure 6.3: Arrhenius correlations of permeability coefficients of penetrants in (a) 10 wt% PI-OAPS and (b) 20 wt% PI-OAPS mixed matrix membrane.
The heats of sorption for PI and PI-OAPS MMMs were determined by plotting penetrant solubility versus inverse of temperature. Since solubility is a decreasing function of temperature, the slope of the linear fit is negative. The heat of sorption ($H_s$) which is determined from the slope is also negative. Further as explained in section 6.4, the overall sorption process is exothermic giving rise to negative $H_s$. Generally, in glassy polymers, $H_s$ is more negative for CO$_2$ which is the most condensable of all penetrants. The overall heat of sorption in polymers is associated with heat of sorption in the Henry’s environment which is less negative and the heat of sorption in the Langmuir environment which is more negative. The less negative value of $H_s$ for CO$_2$ in the plain has been reported earlier and no clear understanding is available at this time [83,88]. PI-OAPS MMMs exhibit less negative values of $H_s$ with increase in OAPS concentration. To begin with, PI shows this counterintuitive behavior for CO$_2$, and further interactions between OAPS and CO$_2$ may induce some artifact. A detailed analysis of the heat of sorption in the Henry’s mode $H_D$ and in the Langmuir mode $H_H$ need to be performed along with dual mode parameter evaluation at elevated temperatures to better understand the phenomenon.

Figure 6.4(a & b) are Arrhenius correlations for diffusion coefficients of penetrants in plain PI and 20 wt% PI-OAPS MMM respectively. As can be seen from these plots, N$_2$ and CH$_4$ have strong temperature dependence than CO$_2$ and O$_2$. The activation energy for diffusion ($E_d$) is computed from experimentally determined values of activation energy for permeation ($E_p$) and the heat of sorption ($H_s$) using equation 6.5. The activation energy for diffusion of helium can
be expected to be very small as it has the smallest kinetic diameter. On the other hand, $E_d$ for CH$_4$ will be the highest since it has the largest kinetic diameter.

The values of $E_d$ for various penetrants in PI and PI-OAPS MMMs are given in Table 6.6. As expected, the value of $E_d$ decreases with decrease in kinetic diameter of the penetrant. The energy of activation for diffusion of helium could not be accurately measured because the heat of sorption of helium could not be accurately determined from high temperature sorption studies of helium. This was due to the very low inherent solubility / condensibility of helium which further decreases at elevated temperatures. It can be further observed from Table 6.6 that for each penetrant $E_d$ increases with increase in OAPS composition in the membrane.
Figure 6.4: Arrhenius correlations of diffusion coefficients of various penetrants in (a) 6FDA-MDA PI and (b) 20 wt% PI-OAPS MMM.
This is consistent with expectations since more energy is required for diffusion of penetrants through the polymer matrix on incorporation of OAPS cages. As discussed in section 5.5, additional diffusional resistance exists due to matrix rigidification as well as reduced FFV. Therefore, the high temperature gas permeation and sorption results compliment very well with the transport properties at 35 °C. The high temperature studies are consistent with the primary mode of transport through the PI-OAPS mixed matrix membranes is through the bulk polyimide matrix.

**Summary**

The temperature dependence of permeability, diffusivity and solubility coefficients in 6FDA-MDA PI and the PI-OAPS mixed matrix membranes can be correlated well with Arrhenius equation. The heats of sorption of each penetrant (CO₂, CH₄, N₂ and O₂) are negative (exothermic) as in other typical glassy polymers. Both, the activation energy for permeation and diffusion are positive (endothermic). Permeability in 6FDA-MDA PI has stronger temperature dependence for larger penetrants, N₂ and CH₄ as compared to He and CO₂. The thermal motion of polymer chains at elevated temperatures leads to formation of gaps through which larger penetrants can diffuse easily. This makes penetrant gaps available to the large penetrants that were available at lower temperatures to small penetrants. This lead to increase in the overall pure gas permeability of all penetrants in 6FDA-MDA PI with a decrease in selectivity of smaller to larger gas molecules. This is characteristic of transport through glassy polymers.
The pure gas permeabilities of penetrants in PI-OAPS mixed matrix membranes also increased with increase in temperature. However, the percentage increase at a given temperature was lower than that of plain PI. This difference led to enhanced selectivities even at elevated temperatures. Although the polymer chains gained thermal motion at higher temperatures, the matrix rigidified by OAPS retained the selectivity. Temperature dependence of permeability, diffusivity and solubility were studied using Arrhenius plots. Temperature dependence of transport properties of penetrants in PI-OAPS MMMs was similar to that in plain PI.

In general, the values of activation energy for permeation and diffusion increased with increase in OAPS concentration in PI-OAPS MMM. The increase in activation energy for permeation in mixed matrix membranes has been attributed in the past to matrix rigidification [29]. There was a decrease in solubility that is typical of polymers due to loss in condensability of penetrants. Therefore, high temperature transport studies of PI-OAPS mixed matrix membranes supported the hypothesis that transport of penetrants was occurring through the polyimide matrix.

The results from physical, mechanical and transport properties of PI-OAPS mixed matrix membranes compliment each other very well. The visual appearance and SEM micrographs of PI-OAPS mixed matrix membranes indicated uniform dispersion of OAPS within the polyimide matrix up to 20 wt% OAPS composition. Thermo-mechanical analysis showed that there was an increase in $T_g$ with incorporation of OAPS in increasing concentration. The
increase in $T_g$ was due to enhanced polymer chain rigidity induced by POSS particles. The $-\text{NH}_2$ functional groups on the POSS cage ensured strong interface without formation of interfacial void. The decreasing pure gas permeability of all penetrants further confirmed that there were no interfacial gaps or voids present between POSS and the polyimide matrix.

Further, the pure gas permeability experiments showed enhanced selectivities with slightly reduced permeabilities. It was ultimately concluded from this study that transport was occurring through the polyimide matrix and not through the pore openings of the POSS cages or through aggregates. The reduction in permeability was attributed in part to reduction in diffusivity and in part to reduction in solubility. The reduction in diffusivity was very well supported by increase in $T_g$ which was due to matrix rigidification. Decrease in penetrant sorption was due to reduction in FFV as XRD studies showed that the polymer chain d-spacing was not affected by the incorporation of POSS. The reduction in FFV was also supported by density measurements which showed an increase with the addition of OAPS. Further, the almost constant values of Henry's constant, $k_d$, and the decreasing values of Langmuir capacity constant, $C'_H$, confirmed that incorporation of POSS into the PI matrix did not disrupt intersegmental packing but only decreased the FFV. SEM images provided evidence of formation of aggregates within the polymer matrix which increase in shape and size with increase in OAPS concentration.

Finally, high temperature gas permeation and sorption was performed to determine the effect of temperature on these mixed matrix membranes. The PI-
OAPS MMMs showed an overall increase in pure gas permeability of penetrants with decrease in selectivity which is typical of transport through glassy polymers. However, selectivity of PI-OAPS MMMs at any of the three studied temperature was always higher than plain PI. Further, an increase in the activation energy for permeation was observed with increase in OAPS concentration which is typical of matrix rigidification effect in mixed matrix membranes.

Therefore, this study concludes that POSS behaved more like a filler than as a molecular sieving material for the temperature, pressure and composition range in which the PI-POSS system was studied. The enhanced gas transport properties of PI-OAPS mixed matrix membranes at 35 °C can be attributed to the octa functionality of POSS and the nanometer size range (1.45 nm).
7 Carbon Nanofiber - POSS Composite Characterization

This chapter will discuss our efforts to explore alternative applications that take advantage of the unique properties of poly(orthosiloxanes). The structure and properties of POSS has been described in great detail in section 2.4. Based on initial studies with octaphenyl POSS in polyimides, the individual POSS molecules did not allow transport of gas molecules and provide a secondary transport mechanism. It is possible that larger POSS molecules would provide an open enough structure that would provide better transport properties, but study of those materials is outside the scope of this project. However, due to other features like high functionality and nanometer size enhanced transport properties were observed at 35 °C. These attractive features of POSS were used to modify the surface of carbon nanofiber (CNF) to form a hybrid nanomaterial which could then be used as reinforcing filler within polymer matrices to form nanocomposites.

7.1 Introduction

Carbon nanofibers (CNFs) and carbon nanotubes (CNT) have attracted a lot of interest in science and engineering industry [89,90]. Due to their inherent mechanical strength, they have been studied as nanofillers within polymer matrices to form hybrid nanocomposites with enhanced mechanical properties.
Typically, the Young’s modulus of a CNFs ranges from 100 to 1000 GPa and strength ranges from 2.5 to 3.5 GPa [91]. Such superior mechanical properties of CNFs can be harnessed to provide property reinforcement within a polymer matrix. The overall diameter of a CNFs ranges from 50 to 100 nm and the length can be up to 100 μm. These small dimensions lead to high surface area and high surface energy, and can lead to significant improvement in properties of polymer-CNF nanocomposites. A drawback of these nanoscale dimensions is that CNF tend to agglomerate due to strong Van der Waal’s forces, thereby affecting the properties of the composite. Many techniques such as sonication and shear mixing have been used to improve blending of nano-fillers into polymers and to reduce aggregation [92]. Dispersion of CNFs in a solvent or within a polymer matrix can also be enhanced by modifying the surface of CNFs with organic functional groups [93].

Functionalization of nanomaterials is a common technique used to improve compatibility between nanoparticles with the polymer matrix and eliminate gaps. Property enhancements in a nanocomposite depend largely on the distribution of nanofiller into the bulk polymer and the interface between the two. A good interface is one in which the gap between the filler and the bulk polymer matrix is minimized with very little or no property variation. In order to obtain polymer-CNF with enhanced mechanical properties, the interface between the two should be strong, an interfacial gap would lead to a weak point where the composite can yield under applied mechanical stress. In addition, A good interface would enable effective load transfer from the polymer matrix to the CNF thereby making the
nanocomposite mechanically strong. The pristine CNF does not have functional
groups on its surface to improve compatibility with polymer matrix, and therefore
when mixed within a polymer matrix tend to form non-uniform agglomerates. In
an effort to overcome this problem, ways to graft organic groups on the surface
of CNFs have been discovered. The pristine CNFs are readily oxidized to obtain
fibers with carboxylic groups on the surface. However, there is a limitation to the
number of carboxylic groups that can be formed without affecting the inherent
mechanical properties of the CNFs. Various reactive functional groups can be
covaiently bound to the CNFs via the carboxylic linkage. Type of functionality
would then depend on the polymer matrix into which it will be incorporated to for
a nanocomposite.

Enhancing the functionality by using an octafunctional POSS was the goal
of this part of the project. Since OAPS has eight amine groups on its surface, it
can be covalently reacted with the carboxylic groups on the oxidized CNFs, then
the total amount of functionality would increase by seven fold. Also, since POSS
is a spherical particle with an overall diameter of only 1.5 nm, it would not create
any steric hindrances and would bring the CNFs in close contact with the
polymer matrix. The other most attractive feature of grafting POSS onto CNFs is
the ability to modify the functionality based on the polymer matrix. For example,
an octaamine POSS can be used when the polymer matrix is a polyimide, an
octaepoxy POSS can be used when the CNFs has to be incorporated into an
epoxy network or an acrylic POSS can be used if the polymer matrix is
poly(methyl)methacrylate. In addition, the OAPS can impart properties to the
polymer nanocomposite including hardness and flame retardance. Therefore, 
OAPS functionalized CNFs would be expected to have improved compatibility 
with the polymer matrices and potentially multiple functionalities.

Functionalizing the surface of CNFs with POSS not only increases but 
also fine tunes the functionality based on the target application. It opens an entire 
ew array of functionalization chemistries that can be used on a CNF to 
maximize its use as a reinforcement agent within a polymer matrix. Therefore, 
POSS can act as a bridging link between CNF and the polymer matrix.

This Chapter will discuss the carbodiimide functionalization chemistry 
used to covalently bind OAPS to CNFs. Further, a method to graft short chain 
oligomers of polyimide onto CNF-OAPS will be discussed. Various 
characterization tools used to determine the success of each functionalization 
step will be described and their results will be discussed in some detail. Finally, 
mechanical properties of the polymer nanocomposite formed using these 
materials will be presented.

7.2 Background

In recent years carbon nanofibers have been used as a nanofiller within 
polymer matrices to enhance its thermal and mechanical properties. It is believed 
that the superior inherent mechanical properties of the CNFs would assist in load 
transfer when under stress thereby making the composite stronger [94]. 
Laboratory scale tests have shown that the performance of composite materials 
can be significantly enhanced by the addition of small percentages of CNFs. 
However, these enhancements are still lower than the estimated performance,
mainly due to aggregation and poor interfacial interactions between the polymer and the CNFs. Various approaches to identify the reason behind this have been adopted in the past and different techniques have been suggested to overcome these problems.

Sonication of CNFs by using ultrasound waves is a method proposed to increase the dispersion of CNFs within a solvent or a polymer solution [96]. The agglomerates of CNFs break down due to high energy ultrasound waves, however, they can also damage the CNFs if exposed to prolonged sonication times. Surface modifications of CNFs to enhance its compatibility with the polymer matrix have been proposed to eliminate the interfacial voids which may form to due to poor interactions and lead to weak point where the composite can yield under stress. A simple nanofiber oxidation technique was studied by A. Rasheed et al. to determine the dispersibility and mechanical performance of the surface modified CNFs [95]. They found that oxidative groups not only aid in dispersion but also assist in enhancement of mechanical properties. Significant enhancement in storage modulus was observed for a composite of polystyrene 20% vinyl phenol copolymer containing 1 wt% oxidized CNF. These enhancements were attributed to the intermolecular hydrogen bonds formed between the copolymer matrix and the oxidized CNFs, which improved dispersion. The effect of plasma surface modification on the mechanical properties of CNF-polycarbonate composites was investigated by P. He et al [96]. Their experimental results concluded that plasma coating significantly
enhanced dispersion of CNFs in polycarbonate which led to improvements in mechanical properties of the nanocomposite.

Significant efforts are being made to modify the surface of CNFs to further enhance its dispersion within a polymer matrix. In addition to grafting oxidative groups on the surface, reactive functional groups would not only enhance dispersion but would also enable positive interactions between the polymer matrix and the CNFs [97,98,99].

![Diagram](image.png)

**Figure 7.1**: Effect of functionalization on the interfacial properties of polymer-CNF nanocomposite.

As shown in Figure 7.1 the interfacial void between the CNF and the polymer matrix can be greatly reduced by grafting reactive functional groups on the surface of CNF. The choice of functional groups will then depend on the polymer matrix into which the CNFs will be incorporated. The positive interactions would create strong bonds between the two phases and assist in load transfer when the composite material is subjected to mechanical stress. Baek et al. functionalized CNF via Friedel Crafts acylation with 2,4,6-trimethylphenocycbenzoic acid and found enhanced thermal and mechanical properties of its polymer composites [100]. Polyimide-CNF nanocomposites can
be formed by functionalizing the CNFs with diamine monomers similar to that of the polyimide and then either blend it with the polyimide or included in in situ polymerization reaction [101]. Polyimides are versatile polymers with a wide range of applications, therefore, forming their composites with enhanced properties has attracted a lot of research interest.

Our research group has used several diamines to functionalize CNFs have following different chemistries which have all proven successful each time. Functionalization with elastomeric oligomers like polydimethyl siloxane (PDMS) has also been done. All the functionalization reactions are carried out on oxidized CNFs with reactive –COOH groups on the surface. Functional groups are then covalently reacted with these –COOH on CNFs, therefore, the amount of functionality depends on the number of –COOH groups. Further, the number of –COOH groups that can be grafted onto the surface of CNFs are limited so as not to destroy the inherent properties of the CNFs.

This Chapter will describe our efforts to enhance the surface functionality of CNFs with the available surface oxidative groups. An octafunctional POSS if reacted with the oxidized fiber would increase the overall functionality of CNF seven fold. Also, the nanoscopic size of POSS (~1.5 nm) is very small as compared to that of CNFs, and hence would react readily with all the available –COOH groups on CNFs. In this study the octaaminophenyl silsesquioxane (OAPS) was reacted with oxidized CNFs as our target polymer matrix was a polyimide. The OAPS functionalized CNFs were subsequently functionalized with an oligomer to provide potential chain entanglement with the polymer matrix.
7.3 Materials

The oxidized CNF (Pyrograf PR-24-PS-OX) were obtained from Applied Sciences Inc. (ASI, Cedarville, OH), octaaminophenyl POSS (OAPS) was synthesized from octaphenyl POSS (OPS) by reaction scheme described in section 3.2.1. N-ethyl-N(-3-dimethylyaminopropyl) carbodimide (EDC, 97%) & 4-dimethylaminopropyl (DMAP) were obtained from Sigma-Aldrich and used without further purification. THF was obtained from Fisher Scientific and was distilled over Na/benzophenone prior to use.

7.4 CNF-OAPS Reaction Mechanism using Carbodiimide Chemistry

Functionalization of CNFs with OAPS was done using carbodiimide chemistry by following a reaction scheme shown in Scheme 7.1. For this, oxidized CNFs obtained from Applied Sciences Inc. were purified using an acid treatment prior to reaction. To do this, 5 g CNFs was suspended in HNO$_3$ (2M, 250 ml) and refluxed for 48 h. The suspension was filtered and washed thoroughly with deionized water to remove the residual acid and make it neutral. The purified oxidized CNFs were then dried in a vacuum oven for several days. The number of moles of reactive –COOH groups on the surface were determined by Dr. Ling Hu to be $\sim 2 \times 10^{-4}$ moles per gram CNFs by titration analysis. This was used as the basis for further functionalization reaction.
Scheme 7.1: Reaction scheme for the functionalization of CNF with OAPS.

For the first step of functionalization, 0.5 g CNFs (1.2 × 10^{-4} moles – COOH) was dispersed in 15 ml THF, sonicated for about 15 mins to uniformly disperse them into the solvent and to minimize agglomeration. Dry distilled THF was used for this reaction and the reactor was continuously purged with dry nitrogen. To this, DMAP (50 mg) and EDC (41 μL, 2.4 × 10^{-4} moles) were added and stirred to obtain a uniform suspension. The OAPS (0.3 g, 2.48 × 10^{-4} moles) was separately dissolved in 5 ml THF and stirred until completely dissolved. The OAPS solution was added to the CNFs reaction mixture and stirred at 60 °C under reflux for 12 h. After completion of the reaction, the CNFs were filtered using Teflon filter paper and washed several times using THF. The fibers were dried for 1 day, ground and mounted in a soxhlet extraction apparatus. Since excess OAPS was used, the unreacted OAPS was removed by during soxhlet extraction using THF. Finally the functionalized CNFs were filtered and dried.

7.4.1 CNF-OAPS-Oligomer Functionalization

The OAPS functionalized CNFs were further reacted with anhydride terminated polyimide oligomers to enhance reactivity and chance of chain
entanglement with the base PI matrix. The amine groups on OAPS would readily react with the anhydride end groups of the oligomer, thereby forming dendrimer-like structures on the surface of the carbon nanofiber. This will make the CNF-polyimide interface more reactive, and a good interface would enable the desired reinforcement in the composite. Anhydride terminated oligomer based on 6FDA and BisP monomers was synthesized prior to the reaction using the method described below. The reason behind choosing these polyimide precursors for this study is to enable comparison of final composite properties based on CNFs functionalized with BisP monomer and with 6FDA-BisP oligomer produced by another member of our group.

7.4.2 Oligomer Synthesis

![Structure of anhydride terminated 6FDA-BisP oligomer, where n ≅ 20](image)

Figure 7.2: Structure of anhydride terminated 6FDA-BisP oligomer, where $n \cong 20$

The structure of anhydride terminated 6FDA-BisP oligomer is given in Figure 7.2. Polyimide molecular weight (or number of repeat units) and end group control can be achieved by altering the stoichiometric ratio of the dianhydride and the diamine using a Carother’s equation. A step by step derivation of the various equations and terms used is given below,
\[ X_n = 2 \left( \frac{M_n - M_{eg}}{M_{ru}} \right) \]  

where,

\( X_n \) = Degree of polymerization

\( M_n \) = Number average molecular weight of oligomer

\( M_{eg} \) = Molecular weight of end group (6FDA in this case)

\( M_{ru} \) = Molecular weight of repeat unit (mol. Wt. of 6FDA + mol. Wt. of BisP – 2(mol. Wt. of H\(_2\)O))

Carother's equation,

\[ X_n = \frac{1 + r}{1 - r}, \]  

\[ r = \frac{N_{AA}}{N_{BB}} = \frac{\text{Moles of difunctional monomer } A}{\text{Moles of difunctional monomer } B} \]  

Using the equations 7.1-7.3, the \( r \) calculated by considering \( M_n = 7,500 \) (approximately 10 repeat units) and 5 g oligomer as basis was 0.897. However, after actual synthesis of the oligomer, the average molecular weight determined using GPC was very high. Therefore, an \( r \) value of 0.625 was chosen arbitrarily to obtain oligomers with shorter chain length. A dry two neck flask equipped with a condenser was purged with nitrogen. BisP (1.43 g, 4.15 mmoles) was added to the reactor and dissolved in 15 ml distilled DMAc. To this, 6FDA (2.95 g, 6.64 mmoles) was added and stirred for 3 h to form a polyamic acid. A 1:1 mixture of triethylamine (TEA) and acetic anhydride (AA) were added to the reaction mixture as catalyst for the imidization step. The reaction mixture was then heated to 50 °C for 1 h and the final imidization step was done by heating to 100 °C for
20 min. After cooling, the oligomer was precipitated into 600 ml of methanol, filtered, washed with fresh methanol and dried in a vacuum oven at 80 °C for 2 days and at 260 °C for 16 h. The molecular weight of the oligomer was determined using GPC with methylene chloride as solvent and polystyrene as standard. The weight average molecular weight was \( M_w = 20,000 \) g/mol.

![Scheme 7.2: Reaction scheme for the functionalization of CNF-OAPS with anhydride terminated oligomer.](image)

The CNF-OAPS was reacted with the dianhydride end-capped oligomer by using the reaction given in Scheme 7.2. For this reaction, CNF-OAPS (0.2 g, 0.336 mmol NH\(_2\)) was added to a two neck reactor with a condenser under nitrogen purge. Distilled DMAc (15 ml) was added and the fibers were dispersed in the solvent by sonicating for 15 – 20 min. Meanwhile, the anyhydride terminated oligomer (6.72 g, 0.336 mmol dianhydride) was dissolved in 10 ml DMAc. The oligomer solution was added to the suspended CNF-OAPS solution and the reaction allowed to take place for 4 h at room temperature. The –CONH
bond between the OAPS and the oligomer was imidized using TEA and AA by using method described in the previous section. After complete imidization, the fibers were collected by filtration and washed several times using THF. They were then dried for two days, ground and again mounted in a soxhlet extraction set-up to remove any unreacted oligomer. The fibers were again collected by filtration and dried in a vacuum oven for several days.

7.5 CNF-OAPS Characterization

7.5.1 X-ray photoelectron spectroscopy (XPS)

The reaction of carboxylic group on the surface of the oxidized CNFs with the amine group on OAPS was facilitated using water soluble carbodiimide EDC. The EDC facilitates the formation of amide linkage between the carboxylate group and the amine group without leaving a spacer molecule. The formation of covalent linkage between the CNFs and OAPS was monitored using XPS to detect presence of surface functional groups. XPS is a sensitive analytical tool used to study the surface composition, electronic state and elemental composition of a sample. Specifically, the binding energy of a peak is characteristic for each element and can be shifted by local environment which makes this an ideal tool for confirming surface functionalization. The XPS spectrum of oxidized CNFs functionalized with OAPS is shown in Figure 7.3. Each element is determined from its peak at a characteristic binding energy. The characteristic peaks for the oxidized CNF are at 284 eV for C 1s and at 531 eV for O 1s.
Figure 7.3: XPS spectrum of oxidized carbon nanofiber functionalized with OAPS.

A strong peak at 399 eV is characteristic of nitrogen which was in the form of NH$_2$ groups on OAPS. Also two small peaks at 100 eV and 150 eV are characteristic of silicon from OAPS. A qualitative confirmation of the functionalization of CNFs with OAPS was obtained from the XPS spectrum. Moreover, since the functionalized fibers were extracted using THF to remove unreacted OAPS, the strong peaks from XPS indicate covalent bond (not physically adsorbed) between the CNFs and OAPS. Note that our group has demonstrated that sohxlet extraction successfully removes unbound reactants from CNFs. Further, when anhydride terminated oligomer were reacted with the OAPS functionalized CNFs, the characteristic peaks for the modified CNFs should be different due to
presence of the oligomer. The XPS spectrum of CNF-OAPS-Oligomer is shown in Figure 7.4.

A new peak appeared at 690 eV when the CNF-OAPS was reacted with oligomer. This peak was attributed to fluorine and comes from the fluorine of the hexafluoroisopropylidene groups of 6FDA of the oligomer. Successful covalent binding between the anhydride group of oligomer and the amines of OAPS was evident from Figure 7.4. Also, the strong intensity of fluorine peak qualitatively suggests that more than one oligomer chain was attached to the OAPS and that the reaction was not hindered due to steric hindrances. This would have to be confirmed by detailed experiments including area analysis for the peaks which is beyond the scope of this work. The successful binding of the

Figure 7.4: XPS spectrum of CNF-OAPS functionalized with anhydride terminated oligomer.
oligomer chains to the OAPS also indicate that the oligomer synthesized was indeed anhydride terminated. If multiple amine groups on the OAPS reacted with the oligomers, a highly branched tethered structure had been created on the surface of carbon nanofiber. This would enhance its compatibility with the surrounding polymer matrix resulting in a strong interface and possibly good mechanical properties.

Quantitative analysis of the relative peak areas in XPS was performed to determine the percentage of each element in the carbon sample. Table 7.1 gives the quantitative amounts of each element present (i.e; C, N, O, F, Si). The table also lists two other types of functionalities that were studied for comparison purposes, CNF-BisP and CNF-Olig. These two functional CNFs were prepared in our groups by Javed Mapkar [102].

<table>
<thead>
<tr>
<th>Functionality on CNF</th>
<th>%C</th>
<th>%N</th>
<th>%O</th>
<th>%F</th>
<th>%Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized CNF</td>
<td>91.7</td>
<td>-</td>
<td>8.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CNF-BisP</td>
<td>91.4</td>
<td>2.2</td>
<td>6.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CNF-OAPS</td>
<td>75</td>
<td>4.8</td>
<td>14.2</td>
<td>-</td>
<td>5.9</td>
</tr>
<tr>
<td>CNF-Olig</td>
<td>88.2</td>
<td>1.8</td>
<td>9</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>CNF-OAPS-Olig</td>
<td>76</td>
<td>3.7</td>
<td>10.9</td>
<td>5.5</td>
<td>3.7</td>
</tr>
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</table>

The CNF-BisP and CNF-OAPS can be compared as they both are amine functionalized carbon nanofibers. The %N content in CNF-OAPS is almost two times that of the CNF-BisP. Also, the atomic % reported in the table are relative values, the %C in CNF-OAPS is reduced greatly to 75% whereas the %C for
CNF-BisP is 91%. A %Si of 5.9 in CNF-OAPS indicates that the surface of CNF is covered with large number of OAPS cages. These comparative values suggest that there are more functional amino groups on the surface of CNF-OAPS than on CNF-BisP. Further, CNF-Olig and CNF-OAPS-Olig can be compared and the increase in the amount of functionality due to OAPS can be discussed. The difference in the %N content in the two (1.8% & 3.7%) suggests that the number of oligomers on CNF-OAPS-Olig are more than CNF-Olig. Further, the %F content in CNF-OAPS-Olig is almost six times that of CNF-Olig, which suggests that almost all the reactive –NH₂ groups on OAPS have reacted with the anhydride terminated oligomer and a highly tethered structure has been formed. The relative % C is the lowest for CNF-OAPS and CNF-OAPS-Olig as compared to other type of functionalities. This supports the conclusion that OAPS has significantly increased the amount of surface functionality on CNF and has aided in the growth of dendrimer like structures which can have many potential applications.

7.5.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used as a second characterization tool for determination of successful functionalization on CNFs. TGA runs were performed under inert nitrogen atmosphere, the functional groups on CNFs will decompose and the decomposition temperature and mass loss can be used to compare functionalization. A comparative plot of the derivative thermogravimetry curves of oxidized CNFs and CNF-OAPS is shown in Figure 7.5.
Figure 7.5: A comparison of the DTG curve of oxidized CNF and CNF functionalized with OAPS.

Figure 7.6: A comparison of DTG curves of OAPS and CNF functionalize with OAPS.
Figure 7.7: A comparison of DTG curves of 6FDA-BisP oligomer and CNF-OAPS–oligomer.

Oxidized CNFs has two prominent broad mass loss peaks, one ranging from 200 °C to 400 °C and the other from 400 °C to 750 °C. The short broad peak at around 300 °C is due to the mass loss of functional groups on the surface of oxidized CNFs. The other very broad peak is mass loss due to graphitic carbon in CNFs. Unlike carbon nanotubes, carbon nanofibers have disorder in their surface structure and the graphitic mass loss occurs only in CNFs. For CNF-OAPS a sharp mass loss peak appears at around 200 °C. Also a very broad peak corresponding to the graphitic carbon mass loss occurs at 600 °C. The origin of the mass loss peak at 200 °C can be understood in light of Figure 7.6 which is a comparative DTG plot of OAPS and CNF-OAPS. In OAPS, a prominent mass loss peak appears at around 100 °C. Preliminary mass loss calculations suggest that it is due to the mass loss of amines on the phenyl rings.
of OAPS. The peak at 200 °C in the DTG curve of CNF-OAPS is similar in nature to that of the –NH₂ peak in OAPS. However, it has slightly shifted to higher temperatures because the OAPS is covalently bound to a thermally stable CNF. Moreover, total mass loss of the CNF-OAPS is almost equivalent to the oxidized CNFs which suggest that OAPS has not completely decomposed. In fact, it appears that only the amines have decomposed. Also, the mass loss peak due to –COOH has disappeared, which is further indication of successful functionalization.

A similar comparative DTG plot of oligomer and CNF-OAPS-Oligomer is shown in Figure 7.7. The DTG curve of 6FDA-BisP oligomer shows a single sharp mass loss peak at around 500 °C. A similar relatively strong peak appears in the DTG curve of CNF-OAPS-Olig at around 530 °C, which suggests that the short chain oligomers have been successfully attached to the OAPS on CNF. Here again, the peak has shifted slightly to higher temperatures because the oligomer chains are stabilized not only by CNFs but also by the POSS cages. A small shoulder to this peak can be observed at 600 °C which may be due to the graphitic carbon mass loss. However, the broad nature and intensity of this peak has been greatly suppressed due to the large number of functional groups covering the surface of CNFs. These functional groups form a protective layer on the surface of CNFs, thereby reducing its decomposition.

### 7.5.3 Transmission Electron Microscopy (TEM) Studies

Although XPS provides qualitative as well as quantitative confirmation of functionalization, the CNF-OAPS-Olig was observed under transmission electron
microscope (TEM) to visually observe the surface covered by functional groups. Z contrast imaging in scanning transmission electron microscope (STEM) mode and elemental mapping in TEM mode using EELS was done on CNF-OAPS-Olig at the EMAL Instrumentation Center at the University of Michigan. A 2010F Jeol TEM was used. Figure 7.8(a) shows z contrasting image taken in STEM mode. Since in z contrasting, heavier elements appear brighter, for our CNF-OAPS-Olig sample, the silicon atoms in OAPS should appear brighter than carbon. A close observation of the image indicates the presence of such bright spots on the surface. The composition of one such bright spot was determined by using EDS analysis of that spot. Figure 7.8(b) shows the EDS spectrum of the bright spot indicated by the circle in the STEM image.
Figure 7.8: (a) Z-contrast STEM image of CNF-OAPS-Olig indicating bright spots of Si on the surface. (b) EDS spectrum of one such bright spot indicating a sharp peak for Si.
Figure 7.9: (a) TEM image of CNF-OAPS-Olig (b) carbon map (c) silicon map (d) fluorine map.
A sharp silicon peak was observed at 100 – 200 eV along with the carbon peak at ~ 300 eV. Therefore, this confirms that all the bright spots that appear on the surface are indeed OAPS.

Further, the extent of functionalization was visualized using elemental mapping in the TEM mode. Carbon, silicon and fluorine mapping were performed on the TEM image of CNF-OAPS-olig. Figure 7.9(a) is the bright field TEM image of the CNF, Figure 7.9(b), (c), (d) are the carbon, silicon and fluorine maps respectively. The carbon map in Figure 7.9(b) shows bright spots all over the CNF, whereas the silicon map (Figure 7.9(c)) shows bright spots on the surface with dark hollow region in the center where there is no silicon present. A similar fluorine map (Figure 7.9(d)) shows the presence of surface fluorine atoms which come from the 6FDA monomer of the oligomer. The fluorine map is not as bright as carbon and silicon because it lies to the opposite end of the binding energy spectrum and requires more exposure time. Also the fluorine atoms are easily burned by the high energy electron beam and destroyed in the process.

Therefore, TEM images of the CNF-OAPS-Olig not only confirm the functionalization but also demonstrate that the CNF were uniformly functionalized along the surface. Silicon mapping clearly indicates that the surface of CNF is covered with OAPS. Since each OAPS has eight reactive functional groups, the surface of CNF is in turn covered by functional groups. This surface modification should result in strong interaction between the CNF and the surrounding polymer matrix enabling more effective load transfer under applied stress. The
subsequent section will describe the formation of polyimide-CNF nanocomposites and their mechanical properties.

7.6 Polyimide-(CNF-OAPS) Nanocomposite

An aromatic relatively rigid polyimide, 6FDA-BisP was chosen to form composites using CNF functionalized with OAPS by reaction scheme described in section 3.2.3. The structure of repeat unit of 6FDA-BisP polyimide is given in Figure 7.10.

![Figure 7.10: Structure of repeat unit of 6FDA-BisP polyimide.](image)

The plain PI and the composite films were prepared by simply blending the functionalized CNF with PI using THF as solvent. Nanocomposites were formed using Pristine CNF, oxidized CNF, OAPS functionalized CNF and oligomer functionalized CNF-OAPS fibers. The terminologies used for these composites are listed in Table 7.2.

Table 7.2: List of various types of carbon nanofibers used in this study to form nanocomposites along with their terminologies.

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Terminology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine CNF</td>
<td>CNF-Pr</td>
</tr>
<tr>
<td>Oxidized CNF</td>
<td>CNF-Ox</td>
</tr>
<tr>
<td>OAPS functionalized CNF</td>
<td>CNF-OAPS</td>
</tr>
<tr>
<td>Oligomer functionalized CNF-OAPS</td>
<td>CNF-OAPS-Olig</td>
</tr>
</tbody>
</table>
Plain PI film was prepared by dissolving 6FDA-BisP (5 wt%) in 30 ml THF. The solution was kept on a shaker for dissolution overnight. Following this, the solution was cast on glass dishes coated with silane and kept in a glove bag with THF environment for slow evaporation of solvent. The glass dish was coated with a repel silane to make all the surface –OH groups on glass non-reactive.

![Scheme for formation of (6FDA-BisP)-CNF nanocomposite.](Image)

Figure 7.11: Scheme for formation of (6FDA-BisP)-CNF nanocomposite.
This glass treatment enabled easy removal of the film once it had dried in the glove bag. The film was dried at 80 °C for 2 days and annealed at 260 °C under vacuum for 16 h. The polyimide-CNF nanocomposites were formed by following a protocol given in Figure 7.11 which was very similar to process described for base polyimide with exception of a CNFs dissolution and sonication step.

7.7 Tensile Testing

Instron Universal Tensile Tester was used to determine the mechanical properties of the nanocomposites. Properties such as Young’s modulus, strength and strain at yield were determined using a dogbone shaped die according to ASTM standard 683. The strain rate was 1 mm/min and tests were done under a load of 100 N. Thickness and gauge length was measured for each sample at atleast ten points and an average value was used. Table 7.3 gives the Young’s Modulus, stress at yield and strain at yield for all the PI-CNF composites studied. The concentration of CNFs in each composite was 1.5 wt% and 6FDA-BisP with an average molecular weight of 70,000 g/mol was used to form films.

Table 7.3: Mechanical properties of PI-CNF composites determined using Instron Tensile testing using functionalized and unfunctionalized CNFs.

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Young’s Modulus (MPa)</th>
<th>Stress at Yield (MPa)</th>
<th>Strain at Yield (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FDA-BisP PI</td>
<td>2777±100</td>
<td>90±2</td>
<td>0.05±0.002</td>
</tr>
<tr>
<td>1.5 wt% CNF-Pr</td>
<td>3200±200</td>
<td>95±4</td>
<td>0.044±0.003</td>
</tr>
<tr>
<td>1.5 wt% CNF-Ox</td>
<td>3220±300</td>
<td>99±3</td>
<td>0.047±0.002</td>
</tr>
<tr>
<td>1.5 wt% CNF-OAPS</td>
<td>3150±200</td>
<td>100±2</td>
<td>0.05±0.001</td>
</tr>
<tr>
<td>1.5 wt% CNF-OAPS-Olig</td>
<td>3000±100</td>
<td>100±3</td>
<td>0.05±0.002</td>
</tr>
</tbody>
</table>
The average thickness of each specimen was 0.15 mm and five dogbone specimens were cut from each film. The values reported in Table 7.3 are average values for two such films. As can be seen from the table, CNF-Pr shows improved mechanical properties as compared to the base PI. Enhancements in Young’s Modulus, strength was observed with a slight reduction in strain at yield. The incorporation of pristine CNFs made the composite stronger and more brittle. 1.5 wt% CNF-Ox showed similar properties with only slight improvements in strength and strain at yield over 1.5 wt% CNF-Pr. The 1.5 wt% CNF-OAPS and CNF-OAPS-Olig composites did also showed similar properties as that of CNF-Ox composite. Expected enhancements were not observed inspite of functionalizing the CNFs with multi-functional groups.

The reason behind this may be in the dispersibility of the functionalized carbon nanofiber in the polymer solution. THF was used as the casting solvent for all the composite films. The order of polarity between the various solvents that could be used is methylene chloride (CH$_2$Cl$_2$) < THF < dimethylacetamide (DMAc). Clearly DMAc is the most polar solvent, and a better solvent for 6FDA-BisP polyimide. It is well known that solvent used to cast a polymer film can have significant impact on its thermal and mechanical properties [103]. Due to favorable solvent-polymer interactions, the polymer chains are able to open up and dissolve in DMAc to a greater extent than in THF or CH$_2$Cl$_2$. Further, the relative solubility of functionalized CNFs were studied by suspended them in THF, methylene chloride and DMAc for extended period of time. It was observed that the CNF-OAPS fibers settled in THF and CH$_2$Cl$_2$ but remained well
suspended in DMAc for several weeks. This clearly indicates that DMAc would be the best solvent for dissolving PI as well as for suspending the CNF’s.

Settling of CNF-OAPS fibers in THF was unexpected as OAPS is readily soluble in THF. Therefore, it was expected that functionalization of CNFs with OAPS would enhance the overall solubility of CNFs in the solvent. The exact reason behind this counterintuitive phenomenon is still unclear. A possible reason could be that OAPS groups on CNFs create attractive forces between neighboring CNFs bringing them close together to cause settling. The more favorable interactions between CNF-OAPS and DMAc inhibit such aggregation of fibers, and thus enable good suspension. Therefore, enhancements in mechanical properties could be observed if the composite films were cast in DMAc rather than in THF, and a proper choice of solvent is essential to obtain the desired property enhancements. A detailed investigation into the solvent effect on the properties of base polymer and the composites needs to be done to fully understand the phenomenon.
8 Conclusions

This study investigated the synthesis, formation and characterization of a novel mixed matrix membrane material based on a molecular scale inorganic filler. The potential application of polyhedral oligomeric silsesquioxane as molecular sieving material was studied and several conclusions were drawn based on gas transport properties at three different temperatures and at various POSS compositions. Also, a thorough characterization of the composite was performed in order to understand the impact of incorporation of POSS on the physical, thermal and mechanical properties of the polyimide matrix. An effort was made to understand the gas transport behavior based on current knowledge of transport through polymeric membranes. Results obtained physical characterization methods were also used to further validate and explain the behavior of the mixed matrix membranes.

Polyhedral Oligomeric Silsesquioxane (POSS) is a novel nano particle and has several known advantages when incorporated within a polymer matrix. An effort was made to develop (6FDA-MDA) PI-OPS composites, as the aromatic substitutions would create favorable interactions with the aromatic backbone of 6FDA-MDA. However, the resulting 5 wt% PI-OPS composite was non-uniform and very brittle. This necessitated the functionalization of OPS with amine groups to form OAPS as the amine groups were thought to enhance the compatibility of
OPS with the surrounding PI matrix. Various techniques of incorporating OAPS within the PI matrix were studied and a simple blending technique was found to be most convenient, reproducible and easily processible. The PI-OAPS films formed using the blending approach were (i) optically clear (ii) uniform up to 20 wt% when probed under SEM (iii) retained mechanical stability of the base PI (iv) maintained the thermal stability of PI.

Incorporation of OAPS at different loadings impacted the physical properties of the composite in many ways. Increase in $T_g$ with increase in OAPS concentration was indication of strong positive interactions of rigid OAPS with PI. This also indicated restriction were induced to the motion of the polymer chains. Although the composite films were optically clear, nanoscale aggregates of OAPS was observed under SEM which increased in size with increase in concentration. Increase in density with increase in OAPS concentration was also observed which suggested that POSS may be occupying the readily available excess free volume within the polymer.

POSS had some very distinct advantages over commonly used mixed matrix materials. The amine functionality of OAPS resulted in solubility in most organic solvents, which made its dispersion within the polymer matrix much easier. Further, the octa functionality enabled OAPS for complete mixing with the polyimide matrix so as to reduce the interface gaps which would have led to unfavorable properties. Interfacial gaps or voids are very detrimental to the formation of a good mixed matrix membrane and is one of the biggest challenge in mixed matrix membrane formation. Both the nanoscopic size and high
functionality eliminated any interface issues and led to the successful formation of a defect free mixed matrix membrane.

The formation of a defect free mixed matrix membrane was evident from the decreasing trend of pure gas permeabilities of all the gases studied. It was further observed that the decrease in permeability for larger penetrants like N₂ and CH₄ was greater than for smaller penetrants like He and O₂. This resulted in a general trend of increase in permselectivity which would not occur if there were interfacial gaps that provided low resistance transport pathways. Enhancement in the selectivity of the most difficult gas separation, O₂/N₂ was also observed. This suggested that OAPS had a definite impact on the PI at a molecular level. Significant enhancements in CO₂/CH₄ selectivity was observed, the 20 wt% PI-OAPS mixed matrix membrane exhibited performance very close to the upper bound. This was due to interactions between the polar CO₂ and OAPS which led to higher solubilities and permeabilities for CO₂ than expected.

These results were further analyzed by using the solution diffusion model which describes the mechanism of gas transport in polymers. The continuous decrease in pure gas permeabilities with increasing OAPS loading supported the hypothesis that the pores of POSS were not accessible to the gas penetrants and that the transport may be occurring primarily through the polymer matrix. Therefore, the two primary components of permeability were analyzed in greater detail, namely diffusivity and solubility to probe this hypothesis. All evidence from physical characterization suggested that POSS had densified the polymer matrix and additionally induced restrictions to the segmental motions of polymer chains.
Further, individual POSS molecules or agglomerates of POSS may have led to a decrease in the excess free volume or the fractional free volume (FFV) within the polymer. Both diffusivity and solubility of penetrant molecules were found to decrease as a result of the decrease in FFV with increasing OAPS concentration. Additional reduction in diffusivity may be due to the rigidification of polymer chains which inhibited the diffusional jumps of gas molecules.

The changes in transport properties of CO$_2$ following addition of OAPS to polyimides were found to be different from the other gas molecules. No evident decrease in permeability and solubility was observed for OAPS loadings up to 10 wt%, however only a slight decrease (~9%) was observed for 20 wt% PI-OAPS MMM. The amine functionalities on OAPS increased the overall polarity of the membrane which would improve solubility of acid gases. Therefore, the permeability of CO$_2$ (which is a polar gas molecule) was not as affected by the decreased FFV or the increased chain rigidity. All these combined phenomena led to an increase in the overall performance of the PI-OAPS mixed matrix membranes. Significant improvements were observed for CO$_2$/CH$_4$, He/CH$_4$ and He/N$_2$ gas pairs and showed promising behaviors when plotted on the trade-off curve.

High temperature studies supported that the gas transport mechanism occurring through the PI-OAPS mixed matrix membranes. Increase in permeability with a decrease in selectivity was observed which is characteristic of transport through polymers. However, at any given temperature, the PI-OAPS MMMs showed greater selectivity than plain PI. The increasing trend of activation
energies for permeation with increasing OAPS concentration provides more evidence of matrix rigidification. Similar trends in diffusivity and solubility with increase temperature was observed which finally confirmed that the POSS cages were acting more like a filler than a molecular sieve for the various compositions, temperature and pressure ranges studied.

The versatile nature of POSS was used for another purpose. This part of the project exploited the multifunctional behavior of POSS to increase the functionality on CNFs. CNFs are being studied for their potential application as reinforcing fillers within polymer matrices. OAPS was successfully reacted on oxidized CNFs to give nanofibers with high functionality without compromising on its mechanical strength. These functionalized CNFs were incorporated within a polymer matrix at low loading and tensile tests were performed. The addition of CNFs resulted in improvements in tensile strength relative to base polymer.
9 Future Work

Several recommendations can be made based on the physical, thermal, mechanical and gas transport properties of PI-OAPS mixed matrix membranes. The recommendations for future work suggested are based on the current progress and requirements in materials development research.

(1) **Measure gas transport properties of POSS blended within a more flexible polymer matrix:** The tendency of POSS to aggregate in a very regular fashion at higher loadings can be utilized to form nanosized particles within the polymer matrix. Also, POSS structure is similar to basic building blocks of a zeolite, so if POSS is able to aggregate in a regular fashion it can form zeolite type materials which may exhibit unusual gas transport properties. The 6FDA-MDA PI matrix chosen for our study was very rigid and formed very brittle composites when blended with high loadings of POSS. Therefore, a more flexible polymer matrix like PDMS can be chosen for this study to probe transport properties at much higher loadings.

(2) **Formation of a continuous network of POSS to give precise porous inorganic type membranes:** POSS can be readily reacted with each other through the reactive R groups which are covalently bound to the eight Si atoms. The length of this R group will determine the pore diameter through which gas transport can take place. Figure 9.1 gives a schematic of how the network will
appear if the surface R groups are made to react with each other to form a continuous network.

Figure 9.1: Formation of a continuous network of POSS with precise pore structure.

The pore diameter can be tailored depending on the gases to be separated by changing the length of the R group. This would be an interesting route for making inorganic membranes. For example an octavinyl substituted POSS can be reacted to form a continuous network by free radical polymerization. The mechanical stability of such structures would be a further topic of investigation. The core cage of POSS is made up of silica and hence
is known to be thermally stable, therefore, such membranes can find applications for high temperature gas separations as well.

(3) **Detail SEM and TEM analysis of the composite films**: Probing the composites using electron microscopy would give more information on the nature of aggregation of POSS and the precise manner in which it affects the surrounding polymer matrix. Silicon mapping using SEM would also assist in understanding the distribution of POSS within the polymer matrix. Since POSS are only 1.5 nm in diameter, TEM imaging would be useful in understanding critical concentration required for agglomeration and also the mechanism of formation of regularly shaped agglomerates at high loadings. TEM can also be used to investigate actual structure of POSS itself, whether functionalization techniques has caused any distortion to the size and shape of the Si-O core cage.
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## Appendix A

### Calibration of Sorption Cell

**Date**: 9/6/2006  
**Temperature**: 308.15 K  
**Pressure (psi)**:  
**Gas**: nitrogen

**Forward calibration without ball bearing**

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AVG = 0.84257
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**AVG =** 0.833727

### Forward Calibration with ball bearing

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**AVG =** 0.806634
### Reverse Calibration with ball bearing

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**AVG = 0.795252**

### Dia of ball bearing

- **Volume:** 10.99 mm \(\times\) 0.432 in = 1.099 cm

### Volume of reservoir

- **Volume:** 2.27 in\(^3\) = 37.1986 cc

### Volume of Polymer chamber

- **Volume:** 1.9033 in\(^3\) = 31.1895 cc
Appendix B

Tradeoff Curves

Figure B-1: Trade-off curves for (a) O2/N2 and (b) He/N2 gas pairs for PI-OAPS MMMs.
Appendix C

Pure Gas Permeation
### Table C-1: Permeability Coefficients of various penetrants in 6FDA-MDA PI at 35°C. (Sample #1)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
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<td>50</td>
<td>0.48</td>
<td>65</td>
<td>19</td>
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(a) psi (b) Barrer

### Table C-2: Permeability Coefficients of various penetrants in 6FDA-MDA PI at 35°C. (Sample #2)

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<th>Press CH₄ (a)</th>
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<th>Press CO₂ (a)</th>
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(a) psi (b) Barrer
Table C-3: Permeability Coefficients of various penetrants in 5 wt% PI-OAPS at 35°C. (Sample #1)

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<th>Press He (a)</th>
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<th>Press O₂ (a)</th>
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<th>Press N₂ (a)</th>
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Table C-4: Permeability Coefficients of various penetrants in 5 wt% PI-OAPS at 35°C. (Sample #2)

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(a) psi (b) Barrer
Table C-5: Permeability Coefficients of various penetrants in 10 wt% PI-OAPS at 35°C. (Sample #1)

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(a) psi (b) Barrer

Table C-6: Permeability Coefficients of various penetrants in 10 wt% PI-OAPS at 35°C. (Sample #2)

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(a) psi (b) Barrer
Table C-7: Permeability Coefficients of various penetrants in 20 wt% PI-OAPS at 35°C. (Sample #1)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>43</td>
<td>43</td>
<td>2.78</td>
<td>57</td>
<td>0.51</td>
<td>42</td>
<td>0.319</td>
<td>54</td>
<td>17</td>
</tr>
<tr>
<td>66</td>
<td>43.3</td>
<td>78</td>
<td>2.72</td>
<td>110</td>
<td>0.47</td>
<td>112</td>
<td>0.283</td>
<td>87</td>
<td>16.3</td>
</tr>
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<td>43</td>
<td>117</td>
<td>2.68</td>
<td>150</td>
<td>0.43</td>
<td>158</td>
<td>0.24</td>
<td>155</td>
<td>15</td>
</tr>
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<td>113.5</td>
<td>42.8</td>
<td>155</td>
<td>2.62</td>
<td>203</td>
<td>0.41</td>
<td>196</td>
<td>0.232</td>
<td>190</td>
<td>14.2</td>
</tr>
</tbody>
</table>

Table C-8: Permeability Coefficients of various penetrants in 20 wt% PI-OAPS at 35°C. (Sample #2)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
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<tbody>
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<td>0.34</td>
<td>54</td>
<td>17.6</td>
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<td>76</td>
<td>43.1</td>
<td>85</td>
<td>2.67</td>
<td>103</td>
<td>0.45</td>
<td>105</td>
<td>0.3</td>
<td>103</td>
<td>16.8</td>
</tr>
<tr>
<td>112</td>
<td>43</td>
<td>145</td>
<td>2.6</td>
<td>155</td>
<td>0.44</td>
<td>151</td>
<td>0.23</td>
<td>148</td>
<td>15.2</td>
</tr>
<tr>
<td>162</td>
<td>43.2</td>
<td></td>
<td></td>
<td>200</td>
<td>0.39</td>
<td>186</td>
<td>0.2</td>
<td>196</td>
<td>14.8</td>
</tr>
</tbody>
</table>

(a) psi (b) Barrer
### Table C-9: Permeability Coefficients of various penetrants in 6FDA-MDA PI at 45°C. (Sample #1)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>55.6</td>
<td>43</td>
<td>4.43</td>
<td>48</td>
<td>1.1</td>
<td>46</td>
<td>0.54</td>
<td>52</td>
<td>19</td>
</tr>
<tr>
<td>93</td>
<td>55.36</td>
<td>84</td>
<td>4.43</td>
<td>98</td>
<td>0.99</td>
<td>81</td>
<td>0.531</td>
<td>74</td>
<td>18.2</td>
</tr>
<tr>
<td>149</td>
<td>53.23</td>
<td>114</td>
<td>4.29</td>
<td>149</td>
<td>0.915</td>
<td>115</td>
<td>0.52</td>
<td>104</td>
<td>17.5</td>
</tr>
<tr>
<td>199</td>
<td>52.8</td>
<td>150</td>
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<td>220</td>
<td>0.878</td>
<td>140</td>
<td>0.51</td>
<td>160</td>
<td>17</td>
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### Table C-10: Permeability Coefficients of various penetrants in 6FDA-MDA PI at 45°C. (Sample #2)

<table>
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<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>56</td>
<td>50</td>
<td>4.5</td>
<td>52</td>
<td>1.2</td>
<td>45</td>
<td>0.57</td>
<td>62</td>
<td>20</td>
</tr>
<tr>
<td>113</td>
<td>55.2</td>
<td>102</td>
<td>4.4</td>
<td>88</td>
<td>1.05</td>
<td>105</td>
<td>0.54</td>
<td>114</td>
<td>19</td>
</tr>
<tr>
<td>150</td>
<td>54</td>
<td>145</td>
<td>4.38</td>
<td>160</td>
<td>0.895</td>
<td>155</td>
<td>0.53</td>
<td>165</td>
<td>17.5</td>
</tr>
<tr>
<td>210</td>
<td>54.2</td>
<td></td>
<td></td>
<td>200</td>
<td>0.85</td>
<td></td>
<td></td>
<td>198</td>
<td>16.5</td>
</tr>
</tbody>
</table>

(a) psi (b) Barrer
Table C-11: Permeability Coefficients of various penetrants in 5 wt% PI-OAPS at 45°C. (Sample #1)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>48.02</td>
<td>60</td>
<td>4.04</td>
<td>54</td>
<td>1.13</td>
<td>75</td>
<td>0.44</td>
<td>64</td>
<td>18.6</td>
</tr>
<tr>
<td>117</td>
<td>47.37</td>
<td>113</td>
<td>4.1</td>
<td>105</td>
<td>0.95</td>
<td>115</td>
<td>0.42</td>
<td>105</td>
<td>17.6</td>
</tr>
<tr>
<td>168</td>
<td>47</td>
<td>163</td>
<td>4.08</td>
<td>157</td>
<td>0.88</td>
<td>155</td>
<td>0.39</td>
<td>152</td>
<td>17.2</td>
</tr>
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<td>47.48</td>
<td>215</td>
<td>3.92</td>
<td>220</td>
<td>0.86</td>
<td>210</td>
<td>0.35</td>
<td>200</td>
<td>16.4</td>
</tr>
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</table>

Table C-12: Permeability Coefficients of various penetrants in 5 wt% PI-OAPS at 45°C. (Sample # 2)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>49</td>
<td>63</td>
<td>3.98</td>
<td>62</td>
<td>1</td>
<td>46</td>
<td>0.5</td>
<td>66</td>
<td>19</td>
</tr>
<tr>
<td>100</td>
<td>48.5</td>
<td>102</td>
<td>4.03</td>
<td>112</td>
<td>0.92</td>
<td>105</td>
<td>0.48</td>
<td>104</td>
<td>17</td>
</tr>
<tr>
<td>145</td>
<td>47.8</td>
<td>142</td>
<td>3.98</td>
<td>148</td>
<td>0.83</td>
<td>147</td>
<td>0.42</td>
<td>150</td>
<td>16.7</td>
</tr>
<tr>
<td>215</td>
<td>48</td>
<td>142</td>
<td>3.98</td>
<td>148</td>
<td>0.83</td>
<td>217</td>
<td>0.37</td>
<td>200</td>
<td>16.4</td>
</tr>
</tbody>
</table>

(a) psi (b) Barrer
Table C-13: Permeability Coefficients of various penetrants in 10 wt% PI-OAPS at 45°C. (Sample #1)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
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<td>4.12</td>
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<td>0.749</td>
<td>40</td>
<td>0.421</td>
<td>55</td>
<td>18.3</td>
</tr>
<tr>
<td>103</td>
<td>44.1</td>
<td>105</td>
<td>4.03</td>
<td>116</td>
<td>0.728</td>
<td>104</td>
<td>0.415</td>
<td>104</td>
<td>17.6</td>
</tr>
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<td>157</td>
<td>44.7</td>
<td>153</td>
<td>4.02</td>
<td>171</td>
<td>0.73</td>
<td>155</td>
<td>0.41</td>
<td>165</td>
<td>16.7</td>
</tr>
<tr>
<td>203</td>
<td>44.3</td>
<td>198</td>
<td>3.95</td>
<td>222</td>
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<td>0.396</td>
<td>190</td>
<td>16.3</td>
</tr>
</tbody>
</table>

(a) psi (b) Barrer

Table C-14: Permeability Coefficients of various penetrants in 10 wt% PI-OAPS at 45°C. (Sample # 2)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
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<td>3.95</td>
<td>54</td>
<td>0.77</td>
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<td>42</td>
<td>19</td>
</tr>
<tr>
<td>95</td>
<td>43</td>
<td>102</td>
<td>4</td>
<td>104</td>
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<td>106</td>
<td>0.42</td>
<td>86</td>
<td>18.2</td>
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<td>43.3</td>
<td>145</td>
<td>3.96</td>
<td>156</td>
<td>0.735</td>
<td>152</td>
<td>0.396</td>
<td>164</td>
<td>16</td>
</tr>
<tr>
<td>215</td>
<td>43.6</td>
<td></td>
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<td>210</td>
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<td></td>
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<td>196</td>
<td>15.6</td>
</tr>
</tbody>
</table>

(a) psi (b) Barrer
### Table C-15: Permeability Coefficients of various penetrants in 20 wt% PI-OAPS at 45°C. (Sample #1)

<table>
<thead>
<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
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<td>65</td>
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<td>0.972</td>
<td>110</td>
<td>0.386</td>
<td>68</td>
<td>18</td>
</tr>
<tr>
<td>115</td>
<td>44.31</td>
<td>113</td>
<td>3.39</td>
<td>115</td>
<td>0.652</td>
<td>160</td>
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</tr>
<tr>
<td>167</td>
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<td>163</td>
<td>3.3</td>
<td>167</td>
<td>0.652</td>
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<td>0.373</td>
<td>155</td>
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</tr>
</tbody>
</table>

(a) psi  (b) Barrer

### Table C-16: Permeability Coefficients of various penetrants in 20 wt% PI-OAPS at 45°C. (Sample # 2)

<table>
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<tr>
<th>Press He (a)</th>
<th>Perm He (b)</th>
<th>Press O₂ (a)</th>
<th>Perm O₂ (b)</th>
<th>Press N₂ (a)</th>
<th>Perm N₂ (b)</th>
<th>Press CH₄ (a)</th>
<th>Perm CH₄ (b)</th>
<th>Press CO₂ (a)</th>
<th>Perm CO₂ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
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<td>65</td>
<td>4.02</td>
<td>52</td>
<td>0.85</td>
<td>44</td>
<td>0.4</td>
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<td>17.6</td>
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<tr>
<td>95</td>
<td>44</td>
<td>115</td>
<td>3.56</td>
<td>112</td>
<td>0.73</td>
<td>96</td>
<td>0.39</td>
<td>120</td>
<td>16.6</td>
</tr>
<tr>
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<td>43.8</td>
<td>175</td>
<td>3.42</td>
<td>150</td>
<td>0.67</td>
<td>152</td>
<td>0.38</td>
<td>165</td>
<td>15.4</td>
</tr>
<tr>
<td>210</td>
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<td>0.6</td>
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<td>14.8</td>
</tr>
</tbody>
</table>

(a) psi  (b) Barrer