

# Table of Contents

ABSTRACT

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION ..... 1

**CHAPTER 1 POLYIMIDES: CHEMISTRY & STRUCTURE-PROPERTY  
RELATIONSHIPS –LITERATURE REVIEW**

|         |  |    |
|---------|--|----|
| 1.1     | Introduction   | 3  |
| 1.2     | Two step method for polyimide synthesis  | 3  |
| 1.2.    | Formation of poly(amic acids)  | 5  |
| 1.2.2   | <i>Effect of monomer reactivity</i>  | 6  |
| 1.2.3   | <i>Effect of reaction conditions and solvents on the synthesis</i>                 | 8  |
| 1.2.4   | <i>Side reactions and other factors involved in the synthesis</i>                  | 9  |
| 1.2.5   | <i>Thermal imidization of poly(amic acid)</i>                                      | 11 |
| 1.2.5.1 | Determination of the degree of imidization:  | 12 |
| 1.2.5.2 | Changes in mechanical properties & molecular weight<br>during thermal imidization: | 13 |
| 1.2.6   | <i>Chemical imidization of the poly(amic acids)</i> :                              | 14 |
| 1.3     | One step method- high temperature solution polymerization:                         | 14 |
| 1.4     | Structure property relationships in linear aromatic polyimides                     | 15 |
| 1.4.1   | <i>T<sub>g</sub> – structure relationships</i>                                     | 15 |
| 1.4.2   | <i>Polyimide chain-chain interactions</i>  | 16 |

|       |  |    |
|-------|--|----|
| 1.4.3 | <i>Effect of chain length of the ether diamine on the glass transition</i> ..... | 20 |
| 1.4.4 | <i>Effect of isomeric attachment of the diamine:</i> .....                       | 22 |
| 1.4.5 | <i>Effect of the dianhydride structure on the glass transition:</i> .....        | 24 |
| 1.4.6 | <i>Effect of chain structure on the crystallinity:</i> .....                     | 25 |

## **CHAPTER 2 POLYMER CRYSTALLIZATION – LITERATURE REVIEW**

|      |  |    |
|------|--|----|
| 2.1  | Introduction .....   | 29 |
| 2.2  | Thermodynamics of crystallization and melting .....                  | 30 |
| 2.3  | Crystallization in polymers: structure, models & relationships ..... | 32 |
| 2.4  | The fringed micelle model.....                                       | 39 |
| 2.5  | Lamellar models .....  | 41 |
| 2.6  | Gibbs-Thomson equation:.....   | 44 |
| 2.7  | Lauritzen-Hoffman secondary nucleation theory' .....                 | 46 |
| 2.8  | Growth rate determination and regime kinetics .....                  | 57 |
| 2.9  | Primary nucleation:.....   | 62 |
| 2.10 | Spherulites .....  | 67 |
| 2.11 | Bulk crystallization kinetics-avrami analysis .....                  | 69 |

## **CHAPTER 3 SEMI-FLEXIBLE SEMICRYSTALLINE POLYIMIDES- LITERATURE REVIEW**

|     |   |    |
|-----|---|----|
| 3.1 | Introduction .....                                  | 80 |
| 3.2 | Crystallization behavior from the melt.....         | 81 |
| 3.3 | Crystallization kinetics .....                      | 85 |
| 3.4 | Morphology of semicrystalline polyimides.....       | 89 |
| 3.5 | Melting behavior of semicrystalline polyimides..... | 92 |
| 3.6 | Melt viscosity .....                                | 94 |

## CHAPTER 4 POLYIMIDES AS ADHESIVES: -LITERATURE REVIEW

|     |   |     |
|-----|---|-----|
| 4.1 | Introduction .....                            | 102 |
| 4.2 | Theories of adhesion .....                    | 103 |
|     | 4.2.1 Mechanical interlocking .....           | 103 |
|     | 4.2.2 Molecular inter-diffusion .....         | 103 |
|     | 4.2.3 Electronic theory .....                 | 104 |
|     | 4.2.4 Adsorption theory .....                 | 104 |
| 4.3 | Adhesion aspects of the present work .....    | 105 |
| 4.4 | Titanium as an adherend .....                 | 106 |
| 4.5 | Some aspects of various adhesion tests .....  | 110 |
| 4.6 | Lap-shear test .....                          | 110 |
| 4.7 | Crystallization aspects in adhesion.....      | 114 |
| 4.8 | Polyimides as high performance adhesives..... | 116 |

## CHAPTER 5 A MELT PROCESSABLE SEMICRYSTALLINE POLYIMIDE STRUCTURAL ADHESIVE BASED ON 1,3-BIS(4- AMINOPHENOXY) BENZENE AND 3,3',4,4'- BIPHENYLTETRACARBOXYLIC DIANHYDRIDE

|     |  |     |
|-----|--|-----|
| 5.1 | Introduction .....                     | 125 |
| 5.2 | Experimental .....                     | 129 |
|     | 5.2.1 Synthesis.....                   | 129 |
|     | 5.2.2 Characterization:.....           | 132 |
|     | 5.2.3 Surface treatment: .....         | 134 |
| 5.3 | Results and Discussion .....           | 135 |
|     | 5.3.1 Thermal stability: .....         | 135 |
|     | 5.3.2 Melt rheology .....              | 138 |
|     | 5.3.3 Morphology of TPER-BPDA-PA:..... | 140 |
|     | 5.3.4 Surface preparation:.....        | 148 |

|       |  |     |
|-------|--|-----|
| 5.3.5 | <i>Optimization of bonding process:</i> .....      | 149 |
| 5.3.6 | <i>Durability studies on lap-shear bonds</i> ..... | 158 |
| 5.3.7 | <i>Effect of various solvents:</i> .....           | 164 |
| 5.4   | Conclusions .....                                  | 166 |
| 5.5   | Acknowledgments.....                               | 167 |

**CHAPTER 6 THERMAL STABILITY, CRYSTALLIZATION KINETICS AND MORPHOLOGY OF A NEW SEMICRYSTALLINE POLYIMIDE BASED ON 1,3-BIS (4-AMINOPHENOXY) BENZENE AND 3,3', 4,4'-BIPHENYLTETRACARBOXYLIC DIANHYDRIDE**

|         |   |     |
|---------|---|-----|
| 6.1     | Introduction .....  | 170 |
| 6.2     | Experimental .....  | 172 |
| 6.3     | Results and Discussion .....  | 174 |
| 6.3.1   | <i>Effect of melt residence time and melt temperature on crystallization kinetics</i> ..... | 189 |
| 6.3.2   | <i>Rheological studies</i> .....  | 200 |
| 6.3.2.1 | Isothermal frequency sweeps at 430°C.....   | 200 |
| 6.3.2.2 | Isothermal time sweeps at various melt temperatures .....                                   | 203 |
| 6.3.2.3 | Complex viscosity on cooling from various melt temperatures .....                           | 208 |
| 6.3.2.4 | Activation energy ( $E_a$ ) values on cooling from various melt temperatures.....           | 209 |
| 6.3.3   | <i>Growth rates as a function of melt histories and non-isothermal behavior:</i> .....      | 210 |
| 6.4     | Conclusions .....   | 216 |
| 6.5     | Acknowledgments.....  | 219 |

**CHAPTER 7 WEDGE AND DOUBLE CANTILEVER BEAM TESTS ON A  
HIGH TEMPERATURE MELT PROCESSABLE POLYIMIDE  
ADHESIVE, TPER-BPDA-PA**

|     |   |     |
|-----|---|-----|
| 7.1 | Introduction .....  | 221 |
| 7.2 | Wedge test (experimental methodology): .....                        | 222 |
| 7.3 | Double cantilever beam (DCB) Test (experimental methodology): ..... | 225 |
| 7.4 | Experimental: .....   | 227 |
| 7.5 | Results and Discussion .....  | 229 |
|     | 7.5.1 <i>Wedge tests</i> .....                                      | 229 |
|     | 7.5.2 <i>Double cantilever beam tests</i> .....                     | 234 |
| 7.6 | Conclusions .....   | 239 |

**CHAPTER 8 CRYSTALLIZATION AND MULTIPLE MELTING BEHAVIOR  
OF A NEW SEMICRYSTALLINE POLYIMIDE BASED ON 1,3-  
BIS (4-AMINOPHENOXY) BENZENE (TPER) AND 3,3', 4,4'-  
BENZOPHENONETETRACARBOXYLIC DIANHYDRIDE  
(BTDA)**

|     |                                     |     |
|-----|-------------------------------------|-----|
| 8.1 | Introduction .....                  | 244 |
| 8.2 | Experimental .....                  | 249 |
|     | 8.2.1 <i>Synthesis</i> :.....       | 249 |
|     | 8.2.2 <i>Characterization</i> ..... | 251 |
| 8.3 | Results and Discussion .....        | 252 |
| 8.4 | Conclusions .....                   | 288 |

**CHAPTER 9 SUMMARY AND RECOMMENDATIONS FOR FUTURE  
WORK**

|     |                                      |     |
|-----|--------------------------------------|-----|
| 9.1 | Summary .....                        | 292 |
| 9.2 | Recommendations for Future Work..... | 294 |