FUNDAMENTAL ASPECTS OF THE TRIBOLOGICAL BEHAVIOR OF
POLY(ETHER-ETHER-KETONE)-BASED IN-SITU COMPOSITES
AT ELEVATED TEMPERATURES

by

Jorge Hanchi

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHACY
in
Mechanical Engineering

APPROVED:

Prof. Norman S. Eiss, Jr., Chairman

Prof. Michael J. Furey

Prof. Herve Marand

Prof. Brian Vick

Prof. Ronald G. Kander

May, 1995
Blackburg, Virginia
FUNDAMENTAL ASPECTS OF THE TRIBOLOGICAL BEHAVIOR OF POLY(ETHER-ETHER-KETONE)-BASED IN-SITU COMPOSITES AT ELEVATED TEMPERATURES

by

Jorge Hanchi
Dr. Norman S. Eiss, Jr., Chairman
Mechanical Engineering

(ABSTRACT)

In-situ composites based on self-reinforcing blends of engineering thermoplastics and thermotropic liquid crystalline polymers (TLCPs) are recently developed, innovative polymeric materials, which have been reported to exhibit outstanding property profiles. These profiles include superior mechanical properties, excellent thermal and dimensional stabilities at high temperatures, and improved melt processabilities. Such characteristics make in-situ composites very attractive as performance polymer-based materials for tribological applications. To date, a thorough investigation of the tribology of in-situ composites has not yet been undertaken and, thus, the potential of these composites as performance tribomaterials has not been effectively assessed. The present research addresses this issue. An investigation is carried into the elevated temperature tribology of in-situ composite systems based on binary blends of Polyetheretherketone (PEEK) and HX-1000, a commercially available TLCP, as well as on ternary blends of PEEK, Polyetherimide (PEI) and HX-1000. The specific tribological phenomenon investigated is unlubricated sliding. Friction and wear measurements are performed at selected temperatures in the range from 20 °C to 250 °C using a pin-on-disk tribometer. Dynamic mechanical thermal analysis and morphological studies are carried out in conjunction with the tribological evaluation. The impact of operating temperature on tribological performance as well as active friction and wear mechanisms are discussed in terms of thermally activated molecular relaxation processes and the solid state morphology of the composite systems investigated. Basic knowledge of the way in which the structure, mechanical properties and tribological behavior of in-situ composites are interrelated is gained. Results from this research point to the validity of the concept of TLCP in-situ reinforcement as a means to produce thermoplastic-based performance tribomaterials.
Acknowledgments

I wish to express my gratitude to Professor Norman S. Eiss, Jr. for his guidance, encouragement, concern, enthusiasm, and constructive criticism provided throughout the course of my research. I also would like to express my appreciation to Professors M. Furey, R. Kander, H. Marand and B. Vick for serving as members of my Ph.D. advisory committee.

I am very grateful to my parents, Jorge and Mary Hanchi, for their support of my education, and to my wife, Satomi, for her love, patience and understanding during the years spent at Virginia Tech in the pursuit of my doctorate degree.

I would also like to thank Dr. Paulo de Souza, for his assistance with the processing of the polymer specimens used in this research, to Dr. Baoping He, for the help provided while conducting X-ray diffraction work, and, last but not least, to the Tribology Group, in particular Dr. Chiun-Chia Kang, Dr. Brian Weick, Dr. Bhawani Tripathy and Ed Lee, for their help and friendship.

The support of this research by the National Science Foundation Science and Technology Center for High Performance Polymeric Adhesives and Composites at Virginia Tech, through grant number DMR-9120004, is greatly appreciated.
# Table of Contents

Abstract................................................................................................................. ii  
Acknowledgments.................................................................................................. iii  
Table of Contents................................................................................................. iv  
List of Tables......................................................................................................... vii  
List of Figures........................................................................................................ viii  

Chapter 1. Introduction......................................................................................... 1  
1.1 Research Objectives...................................................................................... 4  
1.2 Research Plan................................................................................................ 5  

Chapter 2. Background........................................................................................... 7  
2.1 Thermotropic Liquid Crystalline Polymers: Their Nature and  
    Important Properties....................................................................................... 7  
2.2 In-situ Composites........................................................................................ 11  
2.3 Thermally Activated Molecular Relaxation Processes and  
    Dynamic Mechanical Thermal Analysis..................................................... 14  

Chapter 3. Test Materials and Experimental Details........................................ 19  
3.1 Test Materials................................................................................................. 19  
    3.1.1 Base Polymers...................................................................................... 19  
    3.1.2 Processing of Test Materials............................................................... 20  
3.2 Experimental Details..................................................................................... 23  
    3.2.1 Tribological Testing........................................................................... 23  
    3.2.2 Dynamic Mechanical Thermal Analysis.......................................... 31  
    3.2.3 Morphological Characterization of In-situ  
        Composite Systems.................................................................................. 32  

Chapter 4. Study of the Tribological Behavior of PEEK and  
PEEK/PEI Blends at Elevated Temperatures................................................. 33  
Synopsis............................................................................................................... 33  
4.1 Introduction.................................................................................................... 34
Chapter 5. Elevated Temperature Tribology of Blends of PEEK
and a Thermotropic Liquid Crystalline Polymer

Synopsis

5.1 Introduction

5.2 Experimental

5.2.1 Materials

5.2.2 Dynamic Mechanical Thermal Analysis

5.2.3 Viscosity Measurements

5.2.4 Microstructural Characterization

5.2.5 Tribological Evaluation

5.3 Results and Discussion

5.3.1 Dynamic Mechanical Thermal Analysis

5.3.2 Viscosity Measurements

5.3.3 Microstructural Characterization

5.3.4 Tribological Evaluation

5.3.4.1 Parent Polymers: PEEK and HX-1000

5.3.4.2 PEEK/HX-1000 Blends

5.4 Summary

Chapter 6. Elevated Temperature Tribology of Blends of PEEK,
PEI and a Thermotropic Liquid Crystalline Polymer

Synopsis
6.1 Introduction ........................................................................................................................................ 140
6.2 Experimental .................................................................................................................................. 141
  6.2.1 Materials ..................................................................................................................................... 141
  6.2.2 Dynamic Mechanical Thermal Analysis ..................................................................................... 142
  6.2.3 X-ray Diffraction Measurements .............................................................................................. 142
  6.2.4 Microstructural Characterization ............................................................................................... 143
  6.2.5 Tribological Evaluation .............................................................................................................. 143
6.3 Results and Discussion .................................................................................................................. 143
  6.3.1 Dynamic Mechanical Thermal Analysis ..................................................................................... 143
  6.3.2 Solid State Morphologies ......................................................................................................... 148
  6.3.3 Friction and Wear Measurements ............................................................................................. 151
6.4 Summary ......................................................................................................................................... 173

Chapter 7. Conclusions ..................................................................................................................... 175

References ............................................................................................................................................. 181

Appendix A. Numerical Friction and Wear Data for PEEK, PEI and HX-1000 ........................................ 188

Appendix B. Numerical Friction and Wear Data for PEEK/PEI Blends ................................................. 192

Appendix C. Numerical Friction and Wear Data for PEEK/HX-1000 Blends ........................................ 197

Appendix D. Numerical Friction and Wear Data for PEEK/PEI/HX-1000 Blends ................................. 203

Vita ......................................................................................................................................................... 208
List of Tables

3.1 Representative properties of PEEK, PEI and HX-1000............................... 22
3.2 Processing parameters for injection-molded test materials........................... 23
4.1 Glass transition temperature (Tg) and degree of crystallinity (Xc)
of PEEK/PEI blends.................................................................................. 38
List of Figures

2.1 Examples of main-chain TLCPs ................................................................. 9
2.2 Schematic of TLCP rheology ................................................................. 10
2.3 Schematic representation of the formation of an in-situ composite .......... 13
2.4 Schematic representation of the relaxation spectra of semicrystalline and amorphous polymers ................................................................. 17

3.1 Molecular Structures of PEEK and PEI .................................................. 21
3.2 Flash-gated injection molded plaque ...................................................... 21
3.3 Schematic representation of the pin-on-disk friction and wear apparatus ................................................................. 25
3.4 Schematic of the heating and loading schemes used in the sliding tests .... 26
3.5 Typical traces showing the evolution of the coefficient of friction, $\mu$, and linear wear, $h$, during the course of the sliding tests ......................... 27
3.6 Wear Parameters: Cumulative Linear Wear, $h$; Total Linear Wear, $H$; Net Cross-sectional Area, $A_{\text{net}}$; and Wear Volume, $W_{\text{vol}}$ ...................... 29
3.7 Schematic representation of wear tracks seen on worn polymer specimens when: (a) removal of material was the dominant wear mode; (b) viscoelastic-plastic plowing was the dominant wear mode; (c) both removal of material and viscoelastic-plastic plowing were significant ($A_{\text{net}}$: Net Cross-sectional Area; $H$: Total Linear Wear) ........................................... 30

4.1 DMTA results for PEEK/PEI blends: (a) As-molded blends; (b) As-molded (amorphous) and annealed (semicrystalline) PEEK/PEI 70/30 blends ........................................................................ 40
4.2 Glass transition temperature as a function of composition for PEEK/PEI as-molded blends ................................................................ 42
4.3 (a) Temperature dependences of the steady state coefficient of friction, $\mu$, and cumulative linear wear, $h$, for PEEK (bars show range of the
4.4 Temperature dependence of the recovery parameter for neat PEEK (bars show range of the data) ................................................. 46

4.5 Profiles of wear tracks generated during the sliding of PEEK ......................................................... 48

4.6 SEM micrographs of PEEK worn surfaces generated at: (a) 90 °C; (b) 152 °C; (c) 180 °C; and (d) 225 °C. Arrows indicate sliding direction ................................................. 50

4.7 WAXD scans of PEEK sliding surfaces taken before and after the tests performed at 180 °C (top) and 225 °C (bottom). For clarity, the “after” WAXD scans have been displaced upward by 1000 cps (counts per second) ......................................................... 54

4.8 (a) Temperature dependencies of the steady state coefficient of friction, \( \mu_s \), and cumulative linear wear, \( h \), for PEI (bars show range of the data). (b) Relaxation spectrum of PEI ......................................................... 55

4.9 Temperature dependence of the recovery parameter for neat PEI (bars show range of the data) ................................................. 56

4.10 Wear of PEI: profilometry traces of representative wear tracks ......................................................... 58

4.11 Typical evolution of the linear wear with the number of sliding cycles during the sliding of PEI in the severe wear regime ......................................................... 59

4.12 Severe wear of PEI (90 °C): (a) failure preceding the generation of wear particles; (b) PEI aggregate; (c) appearance of the wear track. Mild wear of PEI (180 °C): (d) appearance of the wear track ......................................................... 60

4.13 Temperature dependences of the steady state coefficient of friction (a) and cumulative linear wear (b) for the PEEK/PEI 85/15 blend. Bars show range of the data (PEEK and PEI data shown for comparison) ......................................................... 63

4.14 Temperature dependence of the recovery parameter for the PEEK/PEI 85/15 blend. Bars show range of the data (PEEK and PEI data shown for comparison) ......................................................... 64

4.15 SEM micrographs of worn surfaces of PEEK/PEI blends: (a) PEEK/PEI 85/15 (T = 152 °C); (b) as-molded PEEK/PEI 70/30 (T = 159 °C); (c) annealed PEEK/PEI 70/30 (T = 186 °C). Arrows indicate sliding direction ......................................................... 66

4.16 Temperature dependences of the steady state coefficient of friction (a) and cumulative linear wear (b) for the as-molded and annealed PEEK/PEI 70/30 blends. Bars show range of the data (PEEK and PEI data shown for comparison) ......................................................... 68
4.17 Temperature dependence of the recovery parameter for the as-molded and annealed PEEK/PEI 70/30 blends. Bars show range of the data (PEEK and PEI data shown for comparison). .......................... 69

4.18 Profiles of wear tracks generated during the sliding of the as-molded PEEK/PEI 70/30 blend .......................................................... 70

4.19 Profiles of wear tracks generated during the sliding of the annealed PEEK/PEI 70/30 blend .......................................................... 71

4.20 Temperature dependence of the steady state coefficient of friction (a) and cumulative linear wear (b) for the PEEK/PEI 50/50 blend. Bars show range of the data (PEEK and PEI data shown for comparison). ....................... 74

4.21 Temperature dependence of the recovery parameter for the PEEK/PEI 50/50 blend. Bars show range of the data (PEEK and PEI data shown for comparison) ........................................ 75

4.22 Profiles of wear tracks generated during the sliding of the PEEK/PEI 50/50 blend .......................................................... 76

4.23 SEM micrographs of the worn surfaces generated during the sliding of the PEEK/PEI 50/50 blend at 165 °C: (a) wear track; (b) fibrillar structures formed on the sliding surface. Arrows indicate sliding direction ........................................................................ 77

5.1 DMTA results for as-molded PEEK, HX-1000 and their blends; (a) Temperature dependence of the mechanical loss factor; (b) Temperature dependence of the dynamic modulus .......................................................... 85

5.2 Dynamic modulus as a function of TLCP concentration for as-molded PEEK/HX-1000 blends ........................................................................ 87

5.3 DMTA results for the as-molded and annealed PEEK/HX-1000 70/30 blends: (a) Temperature dependence of the mechanical loss factor; (b) Temperature dependence of the dynamic modulus ........................................... 88

5.4 WAXD scans for the as-molded (top) and annealed (bottom) PEEK/HX-1000 70/30 blends ........................................................................ 90

5.5 Variation of the dynamic shear viscosity as a function of TLCP concentration for the PEEK/HX-1000 blends ........................................................................ 92

5.6 Solid state morphology of injection molded HX-1000: (a) Schematic representation of fracture surface showing the skin-core structure (boxed areas correspond with micrographs 8(b)–(d)); (b) Cross-sectional view of one of the skin layers; (c) Cross-sectional view of the core; (d) Top skin sublayer (arrow coincides with the mold fill direction) ......................... 94
5.7 Pole Figures for HX-1000: (a) Skin layer; (b) Core layer (MFD: mold fill direction; TD: transverse direction)..........................................................95

5.8 Stereographic projection of a pole.................................................................96

5.9 Solid state morphology of the injection molded PEEK/HX-1000 50/50 blend: (a) Skin-core structure; (b) Skin layer; (c) Core layer; (d) Fibrillar structure of top skin sublayer (arrow coincides with the mold fill direction)........98

5.10 Pole Figures for the PEEK/HX-1000 50/50 blend: (a) Skin layer; (b) Core layer (MFD: mold fill direction; TD: transverse direction).............................................100

5.11 Solid state morphology of the injection molded PEEK/HX-1000 20/80 blend: (a) Fibrillar structure of top skin sublayer (arrow coincides with the mold fill direction); (b)–(c) Core layer.........................................................101

5.12 Solid state morphology of the injection molded PEEK/HX-1000 70/30 blend: (a) Skin-core structure; (b) Skin layer; (c) Core layer; (d) Top skin sublayer (arrow coincides with the mold fill direction).................................102

5.13 (a)–(b) Fracture surface of the PEEK/HX-1000 90/10 blend; (c) Fracture surface of neat PEEK.................................................................................................................104

5.14 Sliding test results for neat PEEK and HX-1000: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear (Bars show range of the data)........106

5.15 Temperature dependence of the recovery parameter for neat PEEK and HX-1000 (Bars show range of the data)..............................................................107

5.16 Profiles of wear tracks generated during the sliding of HX-1000..........109

5.17 Profilometry of an HX-1000 wear track onto which removed material extrudates have accumulated..........................................................110

5.18 SEM micrographs showing the appearance of an HX-1000 worn surface at different stages during the sliding at 140 °C: (a) at 300 cycles; (b)–(d) at 800 cycles; (e) at 1600 cycles. Arrows indicate sliding direction (SD: sliding direction; MFD: mold fill direction)........112

5.19 SEM micrographs of HX-1000 worn surfaces generated at: (a) 20 °C; (b) 80 °C; (c) 140 °C and (d) 180 °C. Arrows indicate sliding direction.................................................................113

5.20 Schematic representation of the mechanism of removal of material in HX-1000: (a) Disruption initiation sites (boxed regions); (b) Microcrack nucleation; (c) Skin sublayer splitting; (d) Fragmentation of skin sublayer
5.21 Sliding test results for the PEEK/HX-1000 20/80 and 50/50 blends: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear. Bars show range of the data (PEEK and HX-1000 data shown for comparison).................. 117

5.22 Temperature dependence of the recovery parameter for the PEEK/HX-1000 20/80 and 50/50 blends. Bars show range of the data (PEEK and HX-1000 data shown for comparison)........................................... 118

5.23 Profiles of wear tracks generated during the sliding of the PEEK/HX-1000 20/80 (top) and 50/50 (bottom) blends................................................................. 120

5.24 Sliding test results for the PEEK/HX-1000 70/30 blends: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear. Bars show range of the data (PEEK and HX-1000 data shown for comparison).......................... 121

5.25 Temperature dependence of the recovery parameter for the PEEK/HX-1000 70/30 blends. Bars show range of the data (PEEK and HX-1000 data shown for comparison)...................................... 122

5.26 Profiles of wear tracks generated during the sliding of the as-molded PEEK/HX-1000 70/30 blend................................................................. 125

5.27 Profiles of wear tracks generated during the sliding of the annealed PEEK/HX-1000 70/30 blend................................................................. 126

5.28 (a) PEEK/HX-1000 20/80 surface worn at 50 °C; (b) PEEK/HX-1000 50/50 surface worn at 180 °C; (c) As-molded PEEK/HX-1000 70/30 surface worn at 100 °C; (d) Annealed PEEK/HX-1000 70/30 surface worn at 225 °C. Arrows indicate sliding direction......................... 127

5.29 Sliding test results for the PEEK/HX-1000 90/10 blend: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear. Bars show range of the data (PEEK and HX-1000 data shown for comparison)....................................................... 129

5.30 SEM micrographs of PEEK/HX-1000 90/10 worn surfaces generated at: (a) 100 °C, low friction: $\mu = 0.15$; (b) 100 °C, high friction: $\mu = 0.28$; (c) 155 °C and (d) 225 °C. Arrows indicate sliding direction............... 131

5.31 Temperature dependence of the recovery parameter for the PEEK/HX-1000 90/10 blend. Bars show range of the data (PEEK and HX-1000 data shown for comparison)............................................... 132
5.32 Profiles of wear tracks generated during the sliding of the PEEK/HX-i000 90/10 blend.......................................................... 133

6.1 Temperature dependence of the mechanical loss factor for: (a) as-molded PEEK/PEI/HX-1000 blends; (b) as-molded parent polymers.......... 144

6.2 Typical WAXD scans for as-molded PEEK (a), and PEEK/PEI/HX-1000 blends (b)-(d).................................................................................. 146

6.3 Temperature dependence of the storage modulus for the as-molded PEEK/PEI/HX-1000 blends......................................................... 147

6.4 Typical WAXD scans for the as-molded (top) and annealed (bottom) PEEK/PEI/HX-1000 60/10/30.............................................................. 149

6.5 Temperature dependence of the mechanical loss factor (a) and storage modulus (b) for the as-molded and annealed PEEK/PEI/HX-1000 60/10/30 blends.......................................................... 150

6.6 (a) PEEK/PEI/HX-1000 77/13/10 fracture surface; (b) skin-core structure of the PEEK/PEI/HX-1000 60/10/30 blend; (c) higher magnification view of PEEK/PEI/HX-1000 60/10/30 skin layer; (d) higher magnification view of PEEK/PEI/HX-1000 60/10/30 core layer.............................................................................................. 152

6.7 Solid state morphology of the PEEK/PEI/HX-1000 49/21/30 blend: (a) Skin-core structure; (b) skin layer; (c) core layer.......................... 153

6.8 Temperature dependence of the coefficient of friction (a) and cumulative linear wear (b) for the PEEK/PEI/HX-1000 77/13/10 blend. Bars show range of the data (PEEK/PEI 85/15 and HX-1000 friction and wear curves shown for comparison)............................................................... 154

6.9 SEM micrographs of PEEK/PEI/HX-1000 77/13/10 worn surfaces generated at 120 °C (top) and 205 °C (bottom). Arrows indicate sliding direction................................................................. 156

6.10 WAXD scans of PEEK/PEI/HX-1000 77/13/10 sliding surfaces taken before and after tribological evaluation at 180 °C (top) and 225 °C (bottom). For clarity, the “after” scans have been displaced upward by 1000 cps (counts per second).......................................................... 158

6.11 Temperature dependence of the recovery parameter for the PEEK/PEI/HX-1000 77/13/10 blend. Bars show range of the data (PEEK/PEI 85/15 and HX-1000 friction and wear curves shown for comparison)........................................................................................................... 159

6.12 Profiles of wear tracks generated during the sliding of the PEEK/PEI/HX-i000 77/13/10 blend............................................................... 160
6.13 Temperature dependence of the coefficient of friction (a) and cumulative linear wear (b) for the as-molded and annealed PEEK/PEI/HX-1000 77/13/10 blends. Bars show range of the data (PEEK/PEI 85/15 and HX-1000 friction and wear curves shown for comparison)........................................... 163

6.14 Temperature dependence of the coefficient of friction (a) and cumulative linear wear (b) for the PEEK/PEI/HX-1000 49/21/30 blend. Bars show range of the data (PEEK/PEI 70/30 and HX-1000 friction and wear curves shown for comparison).................. 164

6.15 SEM micrographs of PEEK/PEI/HX-1000 60/10/30 (a-b) and 49/21/30 (c-d) worn surfaces generated at 120 °C (top) and 205 °C (bottom). Arrows indicate sliding direction........................................ 165

6.16 Representative examples of WAXD scans of as-molded PEEK/PEI/HX-1000 60/10/30 (top) and 49/21/30 (bottom) sliding surfaces taken before and after tribological evaluation in the sliding regime above the glass transition. For clarity, the “after” scans have been displaced upward by approximately 1000 cps (counts per second).............................................. 166

6.17 Temperature dependence of the recovery parameter for the PEEK/PEI/HX-1000 60/10/30 (top) and 49/21/30 (bottom) blends. Bars show range of the data (PEEK/PEI 85/15, 70/30 and HX-1000 friction and wear curves shown for comparison).................. 168

6.18 Profiles of wear tracks generated during the sliding of the PEEK/PEI/HX-1000 60/10/30 blend......................................................... 169

6.19 Profiles of wear tracks generated during the sliding of the PEEK/PEI/HX-1000 49/21/30 blend......................................................... 170

6.20 Temperature dependence of the cumulative linear wear (top) and coefficient of friction (bottom) for the as-molded PEEK/HX-1000 70/30, PEEK/PEI/HX-1000 60/10/30 and PEEK/PEI/HX-1000 49/21/30 blends. Bars show range of the data........................................... 172

7.1 Friction trends observed during the reciprocating sliding of the PEEK/HX-1000 50/50 blend............................................................. 178

7.2 Electron micrographs of worn surfaces generated during the reciprocating sliding of the PEEK/HX-1000 50/50 blend: (a) SD perpendicular to the MFD; (b) SD parallel to the MFD (SD: sliding direction; MFD: mold fill direction). Arrows indicate sliding direction......................................................... 179
In recent years the selection of engineering thermoplastics over metals as materials for tribological components has become an increasingly common practice. This trend seems only natural when metals and engineering thermoplastics are compared on the basis of key material characteristics such as inherent lubricity, density (weight), specific strength, chemical inertness, ability to dampen shock and vibration, ability to operate with low levels of noise generation, and ease of fabrication into complex shapes. A recently developed engineering thermoplastic characterized by an outstanding property profile, and a promising potential as a high performance tribological material, is Polyetheretherketone (PEEK). PEEK is semicrystalline, and possesses superior thermal (glass transition temperature, \( T_g \), of 145–165 °C, and melting point, \( T_m \), of 335–350 °C), chemical, and engineering properties. It exhibits high mechanical strength and modulus, as well as an excellent resistance to dynamic fatigue [1-4]. In conjunction with these properties, PEEK shows very attractive tribological characteristics which include superior sliding wear properties [5-8]. This well balanced combination of mechanical and tribological properties is maintained at temperatures below the \( T_g \). At the \( T_g \) and higher temperatures, however, sharp drops in tensile and flexural strengths and moduli [1, 4] as well as marked increases in friction coefficients and wear rates are observed [9-11]. These phenomena clearly limit the high temperature operating potential of PEEK.

The usual approach to overcome the detrimental effects of high temperature on the tribological performance of PEEK has been to enhance its load-bearing capacity, strength, and low friction characteristics by means of the addition of glass or carbon fiber
reinforcement and/or an internal lubricating phase such as graphite or polytetrafluoroethylene (PTFE) fillers [11-13]. Although this approach can lead to improvements in tribological performance, an inhomogeneous material results; its mechanical and tribological properties are strongly dependent on factors such as the strength of the interface formed by the thermoplastic and the added phase, the distribution of fillers or fibers within the matrix, fiber aspect ratio, and fiber orientation [6, 14-16]. Moreover, the effective control and optimization of the latter factors in thermoplastic composites are tasks posing considerable difficulties [16, 17]. From the standpoint of processing, the inclusion of fiber reinforcement into a thermoplastic has two adverse effects; one is the need for higher processing pressures and temperatures due to increased melt-viscosities, and the other, the accelerated wear of the processing equipment.

A promising novel route to the development of high performance polymeric composites is the blending of isotropic engineering thermoplastics with thermotropic liquid crystalline polymers (TLCPs) [18-22]. The underlying strategy is to effectively exploit the excellent mechanical and physical properties as well as the unique rheological behavior of TLCPs to produce materials with property profiles comparable or superior to those of conventional thermoplastic composites while avoiding the property control and processing difficulties associated with the use of solid reinforcing phases and/or fillers.

TLCPs can be described as rigid, highly anisotropic macromolecules, usually fully aromatic polyesters, characterized by the formation of melts exhibiting high degrees of orientational order which, upon cooling, can easily transform into a solid whose morphology is dominated by the presence of highly oriented fibrous structures. Due to their nature, TLCPs possess many desirable properties that exceed those of conventional isotropic thermoplastics; such properties include very low melt viscosities, enhanced thermal and dimensional stabilities at elevated temperatures, and tensile moduli and strengths that are comparable or, in some cases, superior to those observed in fiber-
reinforced polymer composites [23-28]. By blending an isotropic thermoplastic and a TLCP, effective reinforcement of the thermoplastic phase can be achieved during processing, or in-situ, as the TLCP phase orients and forms high modulus fibrous domains. In addition, the oriented TLCP phase can effectively lubricate the thermoplastic phase during processing substantially reducing the overall melt viscosity of the blend.

In-situ reinforcement appears to have a promising potential as a means to develop high performance PEEK-based materials that could replace conventional fiber-reinforced and particulate-filled PEEK composites as materials for high temperature tribological applications. In principle, and relative to their conventional counterparts, PEEK-based in-situ composites should offer, in addition to a greatly improved melt processability, a much broader spectrum of possibilities in terms of the tailoring of key properties. Many of the added possibilities should be expected to arise from the ability to alter important attributes (e.g., strength, stiffness, degree of interaction with the thermoplastic matrix) of the reinforcing phase by varying, for instance, the structure of the molecular units composing the TLCP, or TLCP architecture. To date, however, data on the tribological behavior of in-situ composites, PEEK-based in-situ composites included, is not available in the open literature and an in-depth appraisal of the potential of these composites high performance tribological materials has not been made.

In the present work a systematic experimental study of the dry sliding friction and wear behavior of binary and ternary in-situ composite systems based, respectively, on blends of PEEK and a TLCP and PEEK, PEI (Polyetherimide), and a TLCP at elevated temperatures is undertaken. The research focuses on the development of a basic understanding of the elevated temperature tribology of the latter composite systems in terms of structure-property relationships and on the effective assessment of the potential of PEEK-based in-situ composites as high performance materials for tribological applications. The knowledge gained through this investigation should constitute an important initial
contribution towards the development of sound criteria for the rational design of both in-situ composites and in-situ-composite-based components for high performance tribological applications.

1.1 Research Objectives

The objectives of the present research are to:

- carry out a systematic experimental investigation into the effects of temperature on the dry sliding friction and wear behavior of PEEK-based in-situ composites.

- identify friction and wear mechanisms active during the dry sliding of PEEK-based in-situ composites at elevated temperatures.

- assess the potential of PEEK-based in-situ composites as high performance thermoplastic materials for high use temperature tribological applications.

- advance the understanding of the interrelationship between macro/micro-morphology, phase structure, thermal transitions, mechanical properties and tribological performance in isotropic-thermoplastic/TLCP in-situ composite systems.

The in-situ composite systems evaluated in this research were developed by Professor Donald Baird of the Virginia Tech NSF Science & Technology Center and consisted of binary blends of PEEK and HX-1000 (a commercially available TLCP), as well as of ternary blends of PEEK, PEI and HX-1000, respectively.

1.2 Research Plan

In order to achieve the objectives of this research three studies are conducted.
the first of these studies the effects of temperature on the tribological performance, and active friction and wear mechanisms of the isotropic engineering thermoplastics used as matrices for the in-situ composite systems evaluated in the present work, namely neat PEEK and PEEK/PEI blends, are investigated. Subsequently, the elevated temperature tribology of the PEEK/HX-1000 and PEEK/PEI/HX-1000 in-situ composite systems, is investigated in two separate studies.

For each of the above polymer systems, a series of un lubricated sliding friction and wear tests is conducted under controlled temperature conditions in order to determine the way in which friction and wear characteristics are affected by temperature. In addition, profilometry as well as light optical and scanning electron microscopy are applied to the analysis of wear process artifacts (e.g., wear tracks and debris, worn surfaces) with the intent of establishing the nature of the friction and wear mechanisms activated during the sliding of the polymer systems under investigation.

Furthermore, dynamic mechanical thermal analysis (DMTA) thermoscans are performed on each of the test polymers in order to obtain their relaxation spectra. Comparison of these spectra with the results from the sliding tests, enables the assessment of the effects of thermally activated molecular relaxation processes on the friction and wear behavior of the test polymers at elevated temperatures. DMTA also provides insight into the phase behavior (e.g., full or partial miscibility) of polymer systems investigated and thus affords a means to ascertain the impact of such behavior on tribological performance.

Central to the effective characterization of the tribological behavior of a given material is a good understanding of its microstructure. Accordingly, the details of the inner morphology of the in-situ composites investigated in the present research are studied using scanning electron microscopy (SEM) and wide-angle x-ray diffraction (WAXD) techniques. Important characteristics (e.g., geometry, size, distribution, and orientation) of the microstructural entities (e.g., fibrils, droplets) present in the in-situ composites are
revealed by SEM examination of the fracture surfaces of specimens broken at liquid nitrogen temperatures (-192 °C). In addition, the development of textures and crystallinity in the in-situ composite systems under scrutiny is investigated using WAXD.
2.1 Thermotropic Liquid Crystalline Polymers: Their Nature and Important Properties

The thermotropics constitute one of the two major classes of liquid crystalline polymers (the other being the lyotropics), and are characterized by the formation of thermally induced liquid crystalline phases or, as also termed, mesophases (where the term meso, which derives from the Greek word for middle, is used in view of the fact that liquid crystalline phases exhibit a degree of order which is intermediate between those observed in crystalline solids and isotropic fluids) [29, 30]. Thermotropic Liquid Crystalline Polymers (TLCPs) can be described as macromolecules consisting of rigid, highly anisotropic, usually fully aromatic, molecular species called mesogenic groups (since the formation of mesophases derive from their presence in the TLCP chain), and molecular units denominated spacers, which act as links between the mesogenic groups. The primary function of the spacers, which can take the form of flexible polymer molecules, non-linear molecular units, or mesogenic groups with different symmetry, is one of compromise, that is, they are to render the thermotropic polymer melt-processable while maintaining mesogenic behavior [29, 31]. The concentration of spacers in the thermotropic polymer chain is critical to the achievement of the latter. Too high a concentration would favor isotropic fluid behavior in the melt making the formation of a mesophase unlikely. On the other hand, the absence of spacers in the TLCP chain would result in the polymer being
intractable; in other words the formation of a liquid crystalline melt at a temperature below the degradation temperature of the TLCP would be highly improbable.

Based on the location of the mesogens with respect to the polymer backbone, two types of TLCPs have been distinguished, that is, the main-chain, and the side-chain TLCPs. In main-chain TLCPs, mesogens and spacers are incorporated into the backbone; in side-chain TLCPs, on the other hand, the mesogens are attached, via flexible spacers, as side groups to a flexible polymer backbone. In terms of industrial and commercial significance, main-chain TLCPs, usually based on aromatic polyesters, constitute the most important class of TLCP at the present time [28, 29, 31]; examples of main-chain TLCPs are shown in Figure 2.1. In what follows the term TLCP will be used to refer to main-chain TLCPs.

One of the most attractive features of TLCPs is their unique rheological behavior (see Fig. 2.2). In the melt, these polymers typically form a nematic liquid crystalline phase, that is, a mesophase characterized by the presence of domains consisting of TLCP molecules with their axes preferentially oriented parallel to each other. As a result of the high degree of orientational order exhibited by the nematic melt, the melt viscosities of TLCPs are substantially lower than those of conventional isotropic thermoplastics at a comparable molecular weight [20, 32, 33]. Two important implications of the latter fact are the following. First, TLCPs can be injection molded into components with complex geometries and thin section, and, secondly, TLCPs can be used as a processing aid, or melt lubricant, for conventional isotropic thermoplastics as has been demonstrated in a number of studies [20, 21].

Melt processed TLCPs can, depending on the degree of molecular orientation achieved during processing, show outstanding mechanical properties, particularly, tensile moduli and strengths in the direction of orientation. In fact, injection moldings of TLCPs have been found to possess mechanical properties that are superior to those of fiber
**Mesogenic Group**

```
[\text{O} \text{C} \text{O}]
```

**Flexible Spacer**

```
[\text{O} \text{CO(CH}_2\text{)}_{10} \text{OC}]
```

**Phenyl-based Molecular Units with different Symmetry**

```
[\text{C} \text{O} \text{O} \text{N}]
```

```
[\text{O} \text{C} \text{O}]
```

\[0.73\]

\[0.27\]

**VECTRA® (Hoechst-Celanese)**

**Figure 2.1** Examples of main chain TLCPs.
**Figure 2.2** Schematic of TLCP rheology.
reinforced composites; the latter has led to the use of the term *self-reinforcing* when describing TLCPs [25, 37, 38]. Melt processed TLCPs typically exhibit a highly anisotropic *skin-core* structure [29, 39, 40], which can be described as a layered structure in which molecular orientation changes from layer to layer. Molecular orientation is maximum in the skin layers, due to elongational flow, and minimum in the core, due to shear flow. Important factors determining the nature of the mechanical properties of melt processed TLCPs will be the thickness of the different layers and the degree of orientation of the TLCP chains within the layers. This factors, in turn, will largely depend upon the rheological conditions imposed on the TLCP melt, and on the intrinsic response of the polymer chains to such conditions.

Largely due to their unique molecular morphology, which undergoes little configurational changes during melt solidification, molded TLCPs have very low coefficients of thermal expansion, and exhibit minimal mold shrinkage and warpage compared to conventional isotropic thermoplastics [25, 29]. These attributes make TLCPs suitable for applications requiring high precision molded components with excellent dimensional stability.

### 2.2 In-situ Composites

In recent years, considerable effort has been devoted to the blending of isotropic thermoplastics with TLCPs with the objective of developing a new class of self-reinforcing, high performance polymeric material; this new class of polymeric material has been denominated *in-situ composite* [18-22]. The rationale behind the development of in-situ composites is that the key properties of TLCPs such as low melt viscosity, strength, stiffness, and excellent thermal and dimensional stabilities can be effectively exploited to
produce highly cost-effective thermoplastic materials with superior property profiles that can be tailored to meet the requirements encountered in high performance applications.

As shown schematically in Figure 2.3, an in-situ composite results when during the processing of a blend of an isotropic thermoplastic and a TLCP, the thermotropic liquid crystalline phase forms highly oriented domains which, under the appropriate flow conditions, subsequently transform into high modulus fibrous structures that reinforce the isotropic thermoplastic phase. The achievement of effective in-situ reinforcement depends strongly on the morphology (microfibrils with large aspect ratios being highly desirable), and degree of orientation of the TLCP phase in the solid state, as well as on the thermoplastic-TLCP interfacial strength. The viscosity ratio of the component polymers, the rheological characteristics of the isotropic thermoplastic, the TLCP concentration, and the processing conditions (in particular, to what extent elongational flow is promoted), have been found to be important factors having an impact on the morphology and degree of orientation attained by the TLCP phase in the solid state. The strength of the thermoplastic-TLCP interface will be determined by the magnitude of the adhesion between the phases, which, in turn, depends on the degree of interaction between the component polymers.

Compared to their fiber-reinforced counterparts, in-situ composites offer distinct advantages. One of such advantages is evidenced by the emergence of in-situ composites with mechanical properties comparable to, and significantly better melt processabilities than those of conventional fiber-reinforced composites [18, 21]. Other advantages, deriving directly from the absence of a solid reinforcing phase in in-situ composites, are given by improved process equipment lifetime (since the accelerated wear of components by glass or carbon or fibers is eliminated); more energy-efficient processing schemes; and a much lower risk of processing temperatures reaching levels near the degradation temperature of the isotropic thermoplastic phase. Thus, in view of the combination of good mechanical properties, and improved processability exhibited by in-situ composites, their potential as
Figure 2.3 Schematic representation of the formation of an in-situ composite.
materials for high performance engineering applications (tribological applications included) where the utilization of fiber-reinforced thermoplastics has been predominant, seems certainly promising.

2.3 Thermally Activated Molecular Relaxation Processes and Dynamic Mechanical Thermal Analysis

A distinct characteristic of polymeric materials is the strong dependence upon temperature of their mechanical properties. The sudden, in cases dramatic, drops in elastic modulus seen in amorphous and semicrystalline polymers when exposed to increasing temperatures are clear manifestations of this dependence. The origins of the temperature dependence of mechanical properties in polymers have been found in the onset of thermal relaxation processes involving specific types of molecular motions including main chain (long range and local, or restricted) motions in amorphous and crystalline domains, side group motions in amorphous materials, motions of crystalline defects, and interlamellar shear in crystalline domains [41-46]. Since material mechanical properties and tribological behavior are intimately related, it is evident that the understanding of thermal relaxation processes is of crucial importance for the effective specification of the tribological application of a polymer; in addition, such understanding may prove invaluable in the characterization of friction and wear phenomena in polymeric materials. Furthermore, it is also important to recognize that knowledge of the nature of the molecular motions associated with the activation of relaxation processes may constitute a distinct advantage in terms of the effective manipulation of properties in polymeric materials.

A technique widely used to study thermal relaxation processes in polymers is Dynamic Mechanical Thermal Analysis (DMTA). The principle of the DMTA technique is
as follows [42, 43, 46, 47]. The application of a sinusoidal mechanical stress onto a viscoelastic material results in a dynamic strain which is not in phase with the applied stress. This phase lag arises from the time necessary for molecular rearrangements and is associated with relaxation phenomena. The dynamic stress is resolved into an elastic, or storage, component and a viscous, or loss, component. These two components are, respectively, in phase and out of phase with the strain response. With the in-phase and out-of-phase stress components and the resulting strain the storage and loss components of the dynamic modulus (Young's or Shear) are computed as follows:

\[
\text{Storage Modulus} = \frac{\text{In-phase Stress Amplitude}}{\text{Strain Amplitude}}
\]

\[
\text{Loss Modulus} = \frac{\text{Out-of-phase Stress Amplitude}}{\text{Strain Amplitude}}
\]

For a viscoelastic material, it must be pointed out, the former of the above components constitutes a measure of its stiffness while the latter provides a measure of its ability to dissipate mechanical energy in connection with the activation of relaxation processes. Customarily, the terms \(E'\) and \(E''\) are used to refer to the Young's storage and loss moduli, respectively. Analogously, \(G'\) and \(G''\) are used to represent the shear storage and loss moduli. The dynamic modulus (\(E^*\) or \(G^*\)), which is treated as a complex entity and, therefore, usually referred to as the complex modulus, is defined, in terms of the storage and loss components, as:

\[E^* = E' + iE'' \quad \text{(Young's Modulus)}\]

or

\[G^* = G' + iG'' \quad \text{(Shear Modulus)}\]
In addition, the mechanical loss factor of the material, or tan δ, is obtained as the ratio of the loss modulus to the storage modulus, that is

$$\tan \delta = \frac{E''}{E'} = \frac{G''}{G'}$$

with δ being the phase angle (lag of strain behind stress). The dimensionless parameter tan δ is physically the ratio of energy lost, or dissipated, to the energy stored, during cyclic deformation.

DMTA results are usually presented in the form of plots of tan δ, and/or storage modulus (a measure of the stiffness) versus temperature. For a given polymer, a plot showing the temperature dependence of tan δ and/or storage modulus with temperature is referred to as its relaxation spectrum. Sudden drops in modulus and the occurrence of tan δ peaks as temperature is increased correspond with the onset of some particular type of molecular motion, and therefore, with the inception of a relaxation process. Thus, there are two important mechanical effects associated with the occurrence of relaxation processes in polymers: a decrease in stiffness (a phenomenon also known as thermal softening) and the dissipation of increasing amounts of mechanical energy when undergoing deformation, as shown schematically in Figure 2.4.

Relaxation processes in polymers are customarily termed, in order of their appearance with decreasing temperature, α, β, γ, and so on. The α relaxation process is generally attributed to long range amorphous main chain motions occurring at the glass transition. In amorphous polymers, the onset of the α relaxation process is accompanied
Figure 2.4  Schematic representation of the relaxation spectra of semicrystalline and amorphous polymers.
by a drastic drop (typically, 2-3 orders of magnitude) in modulus, and a marked increase in mechanical loss factor, or tan δ. In semicrystalline polymers, the presence of crystallites restrict the mobility of the amorphous chains, and therefore, the drop in modulus, and rise in tan δ at the glass transition are not as pronounced as in amorphous polymers. The remaining relaxation processes, i.e., the β, γ, and so on, which are known as secondary relaxation processes, are ascribed to molecular motions such as local, or restricted, main chain motions, side group motions, and small motions within molecules dissolved in the polymer (e.g., a plasticizer molecule) [45, 46]. The variations in modulus and tan δ associated with the occurrence of secondary relaxations are, in general, much less prominent than those seen in connection with the onset of an α relaxation. It is important to point out that secondary relaxations may, nonetheless, have a significant impact on the mechanical behavior of a polymer; for instance, a ductile-brittle transition may occur as a polymer undergoes a β relaxation process involving main chain molecular motions [45].
CHAPTER 3

Test Materials and Experimental Details

3.1 Test Materials

3.1.1 Base Polymers

Two isotropic engineering thermoplastic resins, Polyetheretherketone (PEEK) and Polyetherimide (PEI), and the commercially available TLCP HX-1000 were the base polymers used in the present research. PEEK was selected by virtue of its excellent property profile and promising potential as a matrix material for composites for high temperature tribological applications [4, 5, 7, 8]. HX-1000 was chosen on the basis that it has a processing temperature range that overlaps those of the thermoplastics to be used as matrix materials, possesses good mechanical and thermal properties and exhibits partial miscibility, over the whole range of composition, with PEI [48, 49], which in turn is fully miscible with PEEK [50, 51]. Noticing that miscibility is not a common occurrence in isotropic–thermoplastic/TLCP systems [21], PEI could, in principle, act as a compatibilizer in the ternary system PEEK/PEI/HX-1000, promoting interfacial activity between the PEEK and TLCP phases (i.e., enhancing interfacial strength) and improving the mechanical properties and tribological performance of the system. The potentially beneficial role it could play as a compatibilizer in the ternary PEEK/PEI/HX-1000 system was an important consideration prompting the selection of PEI as one of the base polymers.
Moreover, through the formation of PEEK/PEI phases the mechanical integrity of PEEK at high temperatures can be enhanced [50]. This occurs on the basis of the full miscibility of PEEK and PEI, and the superior thermal properties of PEI (e.g., glass transition and heat deflection temperatures) [2, 52-55].

The specific PEEK and PEI resins used in this investigation were, respectively, Victrex® PEEK 380-G, supplied by ICI Advanced Materials, and Ultem® 1000, provided by General Electric Plastics. The molecular structures of these engineering thermoplastics are shown in Figure 3.1 [5, 53]. HX-1000, an amorphous thermotropic liquid crystalline copolyester was made available by DuPont. The formulation of this TLCP is proprietary DuPont information and has not been disclosed; it is believed, however, to be based on terephthalic acid, hydroquinone and other hydroquinone derivatives [56].

For comparison, representative properties of PEEK, PEI and HX-1000 have been compiled in Table 3.1.

3.1.2 Processing of Test Materials

The melt processing operation selected to produce the test specimens of the materials evaluated in this research, namely PEEK, PEI, HX-1000 and selected PEEK/PEI, PEEK/HX-1000 and PEEK/PEI/HX-1000 blends, was injection molding. Prior to injection molding, all materials, which were in pellet form, were dried in a vacuum oven at a temperature of 150 ºC for at least 24 hours in order to minimize moisture absorption, which may give rise to the formation of voids within the moldings. The PEEK/PEI, PEEK/HX-1000, and PEEK/PEI/HX-1000 pellets were produced by compounding pellet mixtures, pre-tumbled according to desired weight ratios, of the pertinent base polymers using a Killion KL-100 single screw extruder.
**Figure 3.1** Molecular structures of PEEK and PEI.

**Figure 3.2** Flash-gated injection molded plaque.
<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>PEEK</th>
<th>PEI</th>
<th>HX-1000</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>[MPa]</td>
<td>100</td>
<td>105</td>
<td>126</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>[GPa]</td>
<td>3.60</td>
<td>2.97</td>
<td>11.50</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>[%]</td>
<td>50</td>
<td>60</td>
<td>1.77</td>
</tr>
<tr>
<td>Notched Izod Impact Strength</td>
<td>[J/m]</td>
<td>84</td>
<td>53</td>
<td>—</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass Transition Temperature, $T_g$</td>
<td>[°C]</td>
<td>145</td>
<td>217</td>
<td>185</td>
</tr>
<tr>
<td>Melting Point, $T_m$</td>
<td>[°C]</td>
<td>335</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Heat Deflection Temperature (@ 264 psi)</td>
<td>[°C]</td>
<td>160</td>
<td>200</td>
<td>—</td>
</tr>
</tbody>
</table>

*a Adapted from references [2], [5], [49], [52], [54] and [55].

b Room temperature values.
### Table 3.2 Processing Parameters for Injection–molded Test Materials

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK/PEI Blends</td>
<td>390-410</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>PEEK/HX-1000 Blends</td>
<td>360</td>
<td>110</td>
<td>40</td>
</tr>
<tr>
<td>PEEK/PEI/HX-1000 Blends</td>
<td>370</td>
<td>115</td>
<td>40</td>
</tr>
</tbody>
</table>

Injection molding was performed in an Arburg 221-55-250 Allrounder injection molding machine. The processing parameters have been summarized in Table 3.2. All of the test materials were molded into flash–gated square plaques measuring 76 x 76 x 1.6 mm, as shown in Figure 3.2, above. The test specimens needed for the tribological, DMTA, and morphological characterization studies carried out in this research were all machined from the molded plaques.

### 3.2 Experimental Details

#### 3.2.1 Tribological Testing

The elevated temperature dry sliding friction and wear characteristics of all the test polymers were studied using a pin-on-disk tribometer. The tribometer and other components of the test apparatus used in this investigation are depicted schematically in
Figure 3.3. For each of the test polymers, a series of sliding tests at different temperatures was conducted. The ball-on-flat contact configuration was used. In all cases, a stationary steel ball (AISI 52100) with a diameter of 3.175 mm was pressed, under a known normal load, against a rotating polymer plate of dimensions 38 x 38 x 1.6 mm machined from the injection molded plaques of the test polymers (Fig 3.2).

The sliding tests were conducted at a sliding speed of 0.15 m/s, a normal load of 15 N and under controlled temperature conditions. For each of the test materials, duplicate sliding tests were conducted at selected temperatures in the range from 20 °C to 250 °C. In all cases, sliding contact was maintained until the rotating polymer specimen completed 3000 revolutions (sliding cycles). Upon completion of 3000 sliding cycles, the normal load was removed and the polymer specimens were allowed to cool down to room temperature and undergo viscoelastic recovery on the pin-on-disk machine. Figure 3.4 shows, schematically, the heating and loading schemes followed in each of the sliding tests.

Linear wear, i.e., the depth of penetration of the steel ball into the polymer specimen and a displacement proportional to the friction force were continuously monitored during the sliding tests by means of two noncontacting proximity sensors (see Fig. 3.3) having a resolution of 0.25 μm. The output signals of the sensors were filtered using an antialiasing filter and subsequently processed, conditioned, and recorded in a data acquisition system. In this way, continuous traces showing the evolution of linear wear and friction coefficient (computed as the ratio of the friction force to the applied normal load) with time were generated for all the materials tested. Representative examples of these traces are shown in Figure 3.5.

After completion of each of the sliding tests, initial assessment of the effects of friction and wear processes on the contact surfaces of the sliding partners was performed.
Figure 3.3 Schematic representation of the pin-on-disk friction and wear apparatus.
Figure 3.4  Schematic of the heating and loading schemes used in the sliding tests.
Figure 3.5  Typical traces showing the evolution of the coefficient of friction, $\mu$, and linear wear, $h$, during the course of the sliding tests.
using a light optical microscope. Following this, profilometry traces across the wear tracks on the polymer disks were obtained. Total linear wear (i.e., the maximum depth of the wear track measured at room temperature and after viscoelastic recovery had occurred) and wear track net cross-sectional area measurements were obtained from the profilometer traces. Multiplication of wear track net cross-sectional areas by the track circumference allowed wear volumes to be determined. 

Of the parameters available to quantify the cumulative effects of wear on the test polymers (see Fig. 3.6 below), that is, linear wear—cumulative, at 3000 sliding cycles, and/or total—and wear volume, the former was selected to report wear results in the present work. Justification for this selection was found in the following. Worn polymer disks specimens exhibited three general types of wear tracks, shown in Figure 3.7: 1) tracks corresponding to materials whose wear behavior was dominated by processes resulting in the separation or loss of material from the sliding surface (Fig. 3.7(a)); 2) tracks resulting from wear processes in which the dominant wear mechanism was viscoelastic-plastic deformation, or plowing, with removal of material being negligible (Fig. 3.7(b)); and, 3) tracks corresponding to materials in which wear of the sliding surface involved both appreciable loss of material and plowing (Fig. 3.7(c)). Important to notice at this point is that in all the cases represented in Figure 3.7 wear has resulted in damage to the sliding surface and that, regardless of the wear mechanism/s involved, there is always a positive linear wear, or wear depth, associated with such damage. In contrast to this, and although damage to the polymer sliding surface may be substantial, wear volumes corresponding to cases in which plowing is the dominant wear mechanism—a common case in the present research—are insignificant (notice in Fig 3.7(b) that $A_{\text{net}}$ is virtually zero in this case). Thus, since linear wear appeared to more clearly represent the effects of wear in terms of damage to the polymer surface (see ASTM [57] definition of wear) than
Figure 3.6 Wear Parameters: Cumulative Linear Wear, $h$; Total Linear Wear, $H$; Net Cross-sectional Area, $A_{\text{net}}$ and Wear Volume, $W_{\text{vol}}$. 
Figure 3.7 Schematic representation of the wear tracks seen on worn polymer specimens when: (a) removal of material was the dominant wear mode; (b) viscoelastic-plastic plowing was the dominant wear mode; (c) both removal of material and viscoelastic-plastic plowing were significant ($A_{\text{net}}$: Net Cross-sectional Area; $H$: Total Linear Wear).
wear volume, the selection of the former parameter to report wear results seemed appropriate.

Finally, with the aim of ascertaining the nature of the surface failure mechanisms activated during sliding, selected worn surfaces and wear debris were examined by means of scanning electron microscopy.

### 3.2.2 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) studies were carried out for each of the polymer systems evaluated in this research in order to identify thermal transitions, assess the effects of thermally activated molecular relaxation processes on both mechanical behavior and tribological performance, and elucidate their phase structure. Two fully automated DMTA measuring systems were used in these studies, namely a Perkin–Elmer DMA–7 Dynamic Mechanical Analyzer and a Polymer Laboratories Dynamic Mechanical Thermal Analyzer. Both systems were interfaced with temperature controllers and equipped with computer-based data acquisition systems. Small strips measuring 15 x 3 x 1.6 mm, which were machined from injection molded plaques of the test polymers (Fig. 3.2), were used as DMTA test specimens. For each of the polymers tested, temperature scans were conducted across the range from 20 °C to 250 °C, which coincided with the range of test temperatures within which tribological behavior was investigated. A heating rate of 3 °C/min was used in all cases. All DMTA tests were carried out in the bending mode, with a constant amplitude sinusoidal strain applied to the test specimens at a frequency of 2 Hz. Storage modulus and mechanical loss factor (tan δ) measurements were recorded during the DMTA tests; based on these measurements, relaxation spectra for the material systems under scrutiny were generated.
3.2.3 Morphological Characterization of In-situ Composite Systems

The morphology of the in-situ composite systems investigated in this research was studied using scanning electron microscopy (SEM). Techniques developed for polymeric materials [58, 59] were employed. A International Scientific Instruments SX-40 scanning electron microscope was used to carry out the morphological studies. An accelerating voltage of 20 KV was used in all cases.

Specimens for SEM were machined from the injection molded plaques of the test polymers (Fig. 3.2). Subsequently, these specimens were notched, cooled down to cryogenic temperatures by immersing them in liquid nitrogen (-192 °C) for at least 5 minutes and, finally, fractured through the application of reversed bending stresses. In order to expose internal textures, appropriate sections of selected SEM specimens were prepared using a peel back technique (nicking with a scalpel followed by peel back using small forceps). Prior to observation under the electron microscope, the SEM specimens were coated with gold using an Edwards S150-B sputter coater; sputtering was performed in an argon atmosphere at a pressure of 7 mbar.

Furthermore, crystallization and the development of textures in the in-situ composite systems under evaluation were investigated using wide-angle X-ray diffraction (WAXD) techniques suitable for the analysis of polymeric materials [59-61]. Two machines were used for this purpose. One of them was a Scintag XDS–2000 X-ray diffractometer equipped with a computerized data acquisition system, and the other, a Philips PW–1840 diffractometer. In all cases, CuKα1 radiation (wavelength, \( \lambda = 1.5405 \) Å) was used.
CHAPTER 4

Study of the Tribological Behavior of PEEK and PEEK/PEI Blends at Elevated Temperatures

Synopsis

The elevated temperature tribological behavior of injection molded blends of semicrystalline Polyetheretherketone (PEEK) and amorphous Polyetherimide (PEI) is investigated, under unlubricated sliding conditions, using a pin-on-disk tribometer. PEEK, PEI, and three PEEK/PEI blends with weight ratios of 85/15, 70/30 and 50/50 are the materials evaluated. To assess the effects of the development of crystallinity on tribological performance, the PEEK/PEI 70/30 blend is tested in the as-molded and annealed conditions. For each of the test polymers, a series of sliding tests is conducted at selected temperatures within the range from 20 °C to 250 °C. The friction and wear test results are correlated to results obtained from DMTA (dynamic mechanical thermal analysis) thermoscans performed on each of the test polymers. It is found that tan δ peaks corresponding to α transitions occurring in the vicinity of the glass transition temperature ($T_g$) coincide with catastrophic tribological failure in the case of PEI and the as-molded PEEK/PEI blends. PEEK and the annealed PEEK/PEI 70/30 blend, do not fail catastrophically at the $T_g$; however, marked increases in friction and wear are observed at and above the $T_g$. The absence of catastrophic tribological failure in PEEK and the annealed 70/30 blend in the vicinity of the $T_g$ is found to correspond to α transitions of significantly lesser strength (i.e. lower tan δ peak values) than those observed in PEI and
the as-molded blends. Between 90 °C and 105 °C for PEI, and 45 °C and 70 °C for the PEEK/PEI 50/50 blend, severe-mild friction and wear transitions are observed. DMTA results showing secondary tan δ peaks centered at 75 °C for PEI, and 38 °C for the PEEK/PEI 50/50 blend evidence the occurrence of β transitions in these materials. A substantial change in ductility associated with these β transitions appears to have resulted in the observed transitional tribological behavior.

4.1 Introduction

This chapter focuses on the elucidation of the elevated temperature dry sliding friction and wear behaviors of Polyetheretherketone (PEEK) and blends of PEEK and Polyetherimide (PEI), that is, the isotropic engineering thermoplastic materials used as matrices for the in-situ composite systems investigated in this research. Such elucidation is central to the effective assessment of the usefulness of in-situ reinforcement as a means to enhance the tribological performance of neat PEEK as well as PEEK/PEI blends.

As stated in the preceding chapter, a major incentive for the selection of PEI to form ternary PEEK/PEI/HX-1000 in-situ composite systems, was found in the potentially beneficial effects (in particular, improved levels of tribological performance linked to enhancements in mechanical properties) that could result from the compatibilization of the PEEK and the reinforcing liquid crystalline HX-1000 phases by PEI. The latter compatibilization, a net effect of which would be the strengthening of the PEEK–HX-1000 interface, should be expected to occur in light of two factors, that is, the partial miscibility of PEI and HX-1000 [48, 49] and the full-miscibility of PEEK and PEI [50, 51].

Moreover, in in-situ composite systems based on PEEK/PEI/HX-1000 blends, the presence of PEI could have an additional beneficial effect, namely the enhancement of the
thermal stability of the PEEK phase. The latter should be expected to occur on the basis of the mutually soluble nature of PEEK and PEI and the superior thermal properties of PEI. Notice that in homogeneous polymer mixtures properties may be additive or even synergistic [62]. In reference to the thermal properties of PEI, an amorphous high performance engineering thermoplastic, it must be pointed out that the polymer is characterized by a glass transition temperature of 217 °C [52, 53] (i.e., approximately 70 °C higher than that of PEEK), room-temperature mechanical properties that are comparable to those of PEEK and, most importantly, a superior retention of these properties at elevated temperatures.[52, 55]. The higher heat-deflection temperature under load exhibited by PEI (see Table 3.1) attests to the latter. In the area of tribological properties, however, PEEK has a clear advantage over PEI. The fact that PEI has been found to exhibit significantly higher, even catastrophic, sliding wear rates [12, 63] corroborates the latter observation. Thus, it becomes apparent at this point that while the addition of PEI could lead to an enhancement of the thermal stability of PEEK, it could also have detrimental effects on PEEK's tribological performance.

In the context of the present research it is of particular interest to know how the elevated temperature tribology of PEEK/PEI blends is affected by blend composition. Obviously, such knowledge is needed for the rational selection of potentially useful binary isotropic thermoplastic matrix systems for PEEK/PEI/HX-1000 in-situ composites. Data on the tribological behavior of blends of PEEK and PEI in the open literature is, however, virtually nonexistent. In fact, a study conducted recently by Yoo and Eiss [64] constitutes the first available report on the tribology of these blends. In this study the friction and wear characteristics of PEEK/PEI blends with different compositions and morphologies were evaluated at room temperature. A series of sliding tests were conducted at four different combinations of sliding speeds and normal loads. It was found that as the content of PEI
in the blends increased wear rates also increased and that rising the degree of crystallinity of the PEEK phase resulted in reduced wear rates. Reported dominant wear mechanisms were plowing in PEEK dominated blends and fatigue in PEI rich blends. It must be added that the latter blends were found to exhibit the highest coefficients of friction.

The study reported in the present chapter had three main objectives: 1) to assess the impact of the addition of PEI on the thermal stability and elevated temperature tribological performance of PEEK; 2) to elucidate the nature of friction and wear mechanisms active during the sliding of PEEK/PEI blends at elevated temperatures; and, 3) to gain a basic understanding of the tribological behavior of the PEEK/PEI system in terms of structure-property relationships. Accordingly, the dry sliding friction and wear of PEEK, PEI, three amorphous blends, and a semicrystalline blend were studied in the temperature range of 20 °C to 250 °C. Dynamic mechanical properties of these materials were measured over the same temperature range. This permitted the identification of relaxation processes associated with molecular motions which have significance in terms of structure-property relationships. Finally, the observed friction and wear phenomena are discussed and correlations between tribological behavior and structure-property relationships are established.

4.2. Experimental

4.2.1 Materials

Victrex PEEK 380 G, manufactured by ICI, and PEI Ultem 1000, produced by General Electric Plastics, were the starting materials used in the present study (See Fig.3.1 for molecular structures). Blending of these thermoplastics was performed on a single
screw extruder at 335–380 °C. PEEK/PEI blends with weight ratios of 85/15, 70/30 and 50/50 were produced. Subsequently, the neat polymers as well as the blends were injection molded into plaques according to the specifications described in Section 3.1.2 of the preceding chapter. In the as-molded condition, the PEEK plaques were opaque; the opacity of these plaques indicated that PEEK had crystallized during molding. The remaining plaques—with the exception of some of the PEEK/PEI 85/15 ones, which were partially opaque (in the vicinity of the gate region)—were transparent, which was an indication of the amorphous nature of the polymers in the plaques.

In order to study the effects of crystallinity on tribological behavior at elevated temperatures, a number of the PEEK/PEI 70/30 plaques were annealed at 205 °C for 24 hours. Differential scanning calorimetry (DSC) was used to determine the glass transition temperature and the degree of crystallinity of each of the test materials. Results from DSC revealed that the amorphous and annealed PEEK/PEI blends exhibited single T_g 's. Additionally, the variation of T_g with composition in the amorphous blends was found to be in good agreement with the Fox equation [65]. The latter two factors confirmed the previously reported miscible nature of PEEK and PEI in the amorphous state [50, 51]. Additional details concerning sample preparation and DSC characterization can be found elsewhere [64]. The glass transition temperatures and degrees of crystallinity of the materials evaluated in the present study are summarized in Table 4.1 below.

4.2.2 Dynamic Mechanical Thermal Analysis

A Perkin-Elmer DMA-7 dynamic mechanical analyzer was used to obtain the relaxation spectra of the test polymers across the temperature range from 20 °C to 250 °C.
Table 4.1 Glass Transition Temperature ($T_g$) and Degree of Crystallinity ($X_c$) of PEEK/PEI Blends

<table>
<thead>
<tr>
<th>Blend Composition [wt % PEEK/wt %PEI]</th>
<th>$T_g$ [°C]</th>
<th>$X_c$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-molded</td>
<td>Annealed</td>
</tr>
<tr>
<td>100/0</td>
<td>144.6</td>
<td>—</td>
</tr>
<tr>
<td>85/15</td>
<td>152.3</td>
<td>—</td>
</tr>
<tr>
<td>70/30</td>
<td>159.4</td>
<td>186.0</td>
</tr>
<tr>
<td>50/50</td>
<td>178.1</td>
<td>—</td>
</tr>
<tr>
<td>0/100</td>
<td>213.0</td>
<td>—</td>
</tr>
</tbody>
</table>

The test configuration and operating mode utilized were, respectively, three-point-bending and fixed-frequency, constant-amplitude, forced flexural oscillation. Other experimental details pertaining dynamic mechanical testing, such as specimen geometry and dimensions as well as operating parameters, can be found in Section 3.2.2.

Due to its increased sensitivity to the onset of relaxation processes [45, 47], tan δ measurements were preferentially recorded during dynamic mechanical testing (storage modulus data were also recorded, but only for the parent homopolymers). With these data, relaxation spectra (i.e., plots showing the temperature dependence of tan δ—and storage modulus in the case of the parent homopolymers—within the range of test temperatures)
were generated for the test polymers. Tan δ peaks seen in these spectra allowed the identification of main and secondary thermal transitions associated with the onset of molecular relaxations processes. Comparison of the relaxation spectra with friction and wear results enabled the assessment of the effects of thermally activated relaxation processes on tribological behavior.

4.2.3 Tribological Evaluation

The dry sliding friction and wear characteristics of PEEK, PEI and their blends were studied within the 20 °C–250 °C temperature range using a pin-on-disk friction and wear tester. A schematic representation of the friction and wear test apparatus can be found in Figure 3.3. The applied normal load, sliding speed and test duration were kept constant throughout the tribological evaluation of the test polymers; the respective values of these parameters were 15 N, 0.15 m/s, and 3000 sliding cycles (disk revolutions). For further experimental details, the reader should refer to Section 3.2.1, where a thorough description of all the important aspects concerning the friction and wear testing of materials throughout the course of the present research is offered.

4.3 Results and Discussion

4.3.1 Dynamic Mechanical Thermal Analysis

The relaxation spectra of PEEK, PEI and the PEEK/PEI blends, generated based on the results from the DMTA tests, are presented in Figure 4.1. A well defined tan δ
Figure 4.1 DMTA results for PEEK/PEI blends: (a) As-molded blends; (b) As-molded (amorphous) and annealed (semicrystalline) PEEK/PEI 70/30 blends.
absolute maximum or, as usually termed, $\alpha$ peak, is seen in the spectra of each of the polymers. Since $\alpha$ peaks are associated with the glass transition [41, 42, 43, 46], the temperatures at which the $\alpha$ peaks in Figure 4.1 are centered ($T_\alpha$) can be regarded as the glass transition temperatures of the polymers tested. The presence of single $\alpha$ peaks and their location in the relaxation spectra of the as-molded PEEK/PEI blends, shown in Figure 4.1(a), confirmed the miscible character of PEEK and PEI in the amorphous state. The $\alpha$ peaks of the as-molded PEEK/PEI blends are located between the $\alpha$ peaks of the parent homopolymers and are seen to shift to higher temperatures with increasing PEI content. The associated monotonic increase in $T_g$ with increasing PEI content was found to be in good agreement with the Fox equation as well as with the results obtained from DSC (see Table 4.1). In Figure 4.2 the $T_g$'s of the amorphous PEEK/PEI blends measured by DSC and DMTA have been plotted along with the Fox equation for comparison.

Further inspection of the spectra shown in Figure 4.1(a) reveals that PEI and the PEEK/PEI 50/50 blend exhibited a tan $\delta$ relative maximum, or secondary tan $\delta$ peak, in the region below the glass transition at about 75 °C and 38 °C, respectively. In each case, it is seen that the magnitude of the tan $\delta$ relative maximum is considerably smaller than the magnitude of the corresponding $\alpha$ peak; this fact evidences the much more restricted nature of the molecular motions associated with the secondary tan $\delta$ peak. The glassy region, "low strength," tan $\delta$ peaks observed in PEI and the PEEK/PEI 50/50 blend have been previously identified and related to a secondary, or $\beta$, relaxation process seen in polyimides and ascribed to complex oscillations along the main chain involving the aromatic and benzimide rings [50]. It should be noted that in glassy amorphous polymers, $\beta$ relaxation processes involving main chain motions may result in increases in ductility and impact strength [42] or even determine the onset of a ductile-brittle transition [45]. These
Figure 4.2  Glass transition temperature as a function of composition for PEEK/PEI as-molded blends.
changes in mechanical behavior, it should be noted, can have a marked impact on tribological performance.

Figure 4.1(b) shows the temperature dependence of tan δ for the as-molded (amorphous) and annealed (semicrystalline) PEEK/PEI 70/30 blends. The position of the α peaks seen in Figure 4.1(b) reveals that the crystallinity induced (within the PEEK phase) by annealing caused the T_g of the PEEK/PEI 70/30 blend to increase. In addition, a noticeable reduction in the strength of the α relaxation is apparent in the annealed blend. The increase in T_g can be regarded as a consequence of the restriction imposed by crystalline domains on the mobility of the polymer chains within the amorphous phase of the material [41]. Notice that the increased PEI content present in the amorphous fraction of the annealed blend—since only PEEK crystallizes—can also lead to an increase in T_g [51]. The reduced strength of the α relaxation in the annealed blend can be related, primarily (although restricted mobility of the amorphous phase could also lead to a reduction in relaxation strength), to the decrease in the amount of amorphous material present in the blend as a result of the development of crystalline domains during annealing. In other words, since the glass transition is a phenomenon affecting only the amorphous regions of a polymer, as increasing numbers of polymer chains are incorporated into crystalline domains the strength of the α relaxation should be expected to decline [41, 66]. The same rationale can be used to explain the reduced strength of the α relaxation exhibited by as-molded PEEK (27% crystalline) as seen in Figure 4.1(a). In fact, in a study on PEEK crystallization [67], the constraining effect of crystalline domains on the mobility of the amorphous phase was reported as the cause for both a drop of one order of magnitude (from about 2.0 to approximately 0.2) in the α peak and a 10 °C rise in T_g as the degree of crystallinity increased from 0% to 32%.
4.3.2 Tribological Evaluation

4.3.2.1 PEEK/PEI 100/0: Neat PEEK

The results from the sliding tests performed on PEEK are presented in Figures 4.3 and 4.4. Shown in Figure 4.3 are plots of the steady state coefficient of friction and cumulative linear wear at 3000 sliding cycles (hereafter, when referring to this parameter, the term "at 3000 sliding cycles" will be omitted) as functions of the sliding temperature are shown—for comparison, a plot of the relaxation spectrum of PEEK has been included in Figures 4.3. Figure 4.4 shows a plot of the temperature dependence of the parameter \([1 - (H/h)]\), which hereafter will be referred to as the "recovery parameter." In the expression for the recovery parameter, "H" and "h" represent, respectively, the total and cumulative linear wear (see Fig. 3.6). Important to recognize and bear in mind is that the magnitude of the recovery parameter at a given sliding temperature, provides a measure of the viscoelastic fraction of the deformation energy dissipated in the contact region at such temperature.

From Figure 4.3(a), it can be seen that at sliding temperatures of up to 140 °C, the coefficient of friction of PEEK varied within the range from 0.1 to 0.25 and showed a tendency to decrease with increasing temperatures. As the sliding temperature rose from 140 °C to 180 °C, a marked increase in friction was observed; the coefficient of friction was seen to rise from about 0.14 at 140 °C to approximately 0.5 at 180 °C. Coefficients of friction of about 0.5 were also measured at 200 °C and 225 °C. Clearly, three regimes of frictional performance can be identified for PEEK in the temperature range from 20 °C to 225 °C: a low friction regime at temperatures below the \(T_g\) (ca. 150 °C); a transitional friction regime at temperatures within the glass transition region; and a high friction regime
Figure 4.3  (a) Temperature dependences of the steady state coefficient of friction, μ, and cumulative linear wear, h, for PEEK (bars show range of the data). (b) Relaxation spectrum of PEEK.
Figure 4.4  Temperature dependence of the recovery parameter for neat PEEK (bars show range of the data).
at temperatures well above the T_g. In direct correspondence with the regimes just described were three regimes of wear performance, as substantiated by the wear data for PEEK also included in Figure 4.3(a).

Comparison of the data in Figures 4.3(a) and 4.3(b) reveals the existence of a direct correspondence between the distinct changes in tribological behavior taking place above 140 °C and the onset of the α relaxation, or glass transition. At the T_g and higher temperatures, due to the substantial increase in molecular mobility that characterizes the transition from the glassy to the rubbery state, the polymer chains in the amorphous regions of semicrystalline PEEK are able to undergo large scale configurational readjustments. Associated with the latter phenomenon are two important effects, that is, a significant decline in stiffness, a phenomenon also known as "thermal softening," and the dissipation of considerable amounts of energy (high mechanical losses) when undergoing mechanical deformation. Thus, the wear intensification, namely the generation of deeper wear tracks, experienced by PEEK at sliding temperatures above 140 °C can be attributed to thermal softening of the polymer as it undergoes the glass transition. Further, the latter wear intensification combined with the enhanced ability to dissipate mechanical energy brought about by the onset of the α relaxation appeared to have led to the sharp increase in friction exhibited by PEEK at and above the T_g.

With values for the recovery parameter ranging from 84% to 96% (see Fig. 4.4), it is evident that viscoelastic plowing was the dominant wear mechanism during the sliding of PEEK as seen in the present study. Examination of the temperature dependence of the recovery parameter in conjunction with profilometry traces of the cross-sections of the wear tracks generated at each of the test temperatures (see Fig. 4.5 for representative examples) was very informative in terms of ascertaining the nature of the mechanisms by which wear
Figure 4.5 Profiles of wear tracks generated during the sliding of PEEK.
occurred during the sliding of PEEK in the temperature range between 20 °C and 225 °C.

By so doing, it became apparent that at sliding temperatures of up to 120 °C, the wear of PEEK occurred by viscoelastic and plastic plowing with material removal being either negligible or nonexistent. Wear tracks characterized by the presence of ridges of plastically deformed material on the sides of the groove produced by the rider (steel ball) and net cross-sectional areas (see Fig. 3.6) of virtually zero magnitude attested to the occurrence of plastic plowing with no removal of material [68]. As can be established from Figure 4.5, plastic plowing intensified with increasing temperatures. SEM examination of the wear tracks produced on PEEK specimens tested at temperatures between 20 °C and 120 °C revealed that they all were characterized by a very smooth appearance. A micrograph showing the typical appearance of the wear tracks generated in the 20 °C–120 °C regime is shown in Figure 4.6(a).

At sliding temperatures within the glass transition region (i.e., 140 °C and 152 °C), viscoelastic and plastic plowing as well as moderate removal of material emerged as the active wear modes of PEEK. A significant intensification of the plastic plowing mechanism appeared to have occurred in correspondence with thermal softening of the thermoplastic in the vicinity of its Tg. In line with the latter and the activation of a material removal mechanism, the magnitude of the recovery parameter of PEEK (Fig. 4.4) was seen to decline and reach a minimum (84% at 152 °C) in the glass transition region. Removal of material from the sliding surface of PEEK in the glass transition region seemed to have occurred by tearing. Under the action of frictional forces, lips of stretched material, oriented perpendicularly to the sliding direction, were first formed on the PEEK contacting surfaces; contacting surfaces becoming increasingly "rubbery" in the vicinity of the Tg would seem to have favored lip formation at 140 °C and 152 °C. Upon repeated sliding
Figure 4.6  SEM micrographs of PEEK worn surfaces generated at: (a) 90 °C; (b) 152 °C; (c) 180 °C; and (d) 225 °C. Arrows indicate sliding direction.
passes, these lips underwent significant plastic deformation and eventually fractured giving way to the generation of wear fragments (see Fig. 4.6(b)). A superior toughness [5] and/or an enhanced strength in the sliding direction, which could have arisen from the preferential alignment of polymer chains in the direction of the surface tractions [69], are factors that could account for the minimum levels of material removal seen during sliding of PEEK in the glass transition region.

In the temperature range from 180 °C to 225 °C, the active sliding wear mechanisms of PEEK remained unchanged. However, as corroborated by the appearance of the pertinent wear track cross-sections in Figure 4.5, removal of material replaced plastic plowing as the second dominant wear mode. It must be noted that the weakening, after progressive intensification between 20 °C and 152 °C (see Fig. 4.5), of the plastic plowing mechanism in the region above the glass transition seemed to be in conflict with the fact that in polymers [70, 71], PEEK included [55], the temperature dependence of the yield strength parallels that of the modulus. Another observation of interest is that values for the recovery parameter ranging from 92% to 96% indicated that viscoelastic plowing at temperatures above the T_g reached, after undergoing an attenuation in the glass transition region, intensity levels similar to those attained at temperatures well below the T_g (see Fig. 4.4).

Furthermore, in the temperatures interval from 152 °C to 225 °C, a clear change in the mechanism by which material was removed from the PEEK contacting surface was seen to occur. The most notable effect associated with this change was a marked reduction in the ability of the material in the PEEK contacting surface to flow plastically. This was evidenced by the progressive disappearance of the "lips" from the wear tracks as sliding temperatures increased from 152 °C to 225 °C (see Figs. 4.6(b), (c) and (d)). Removal of material from the PEEK sliding surface at and above 180 °C appeared to occur by brittle
crumbling and involved the generation of minute plate-like debris which tended to aggregate in small clusters. With increasing temperatures wear intensified and larger volumes of material were removed. At 200 °C and 225 °C, wear debris trapped in the contact zone were compacted into relatively large agglomerates such as those seen in the central area of the wear track shown in Figure 4.6(d).

Recognizing the fact that at temperatures above the Tg PEEK can crystallize [72] rather rapidly [73], then the changes in tribological behavior described in the preceding two paragraphs can be rationalized as follows. While sliding at and above 180 °C, an annealing effect (the total times of exposure to the sliding temperature of the polymer specimens tested at 180 °C and higher temperatures ranged from 45 to 90 minutes) and intense directional plastic straining, led to the formation of highly oriented crystalline structures within the surface layers of PEEK in the contact region. As a result, a morphology that could be visualized as that of a two-layered material consisting of a hard coating on a viscoelastic substrate developed.

Two effects that can be associated with the hardening of the PEEK surface layers in contact region at 180 °C and higher temperatures are a marked reduction in the amount of plastic flow preceding the detachment of a wear fragment from the sliding surface and the onset, when under the action of contact stresses, of a mostly viscoelastic state of deformation in the regions beneath the hard surface layers. These two effects would seem to explain, in a plausible manner, the shift in material removal mechanism and the intensification of the viscoelastic plowing mechanism that characterized the tribological behavior of PEEK in the region above the glass transition.

In order to address the question of crystallization during testing, WAXD scans of the sliding surfaces of PEEK specimens tested at and above 180 °C were obtained prior to and after the sliding tests. Representatives examples of these WAXD scans can be found in

52
Figure 4.7. Sharper and higher intensity crystalline reflections in the WAXD scans obtained after completion of the sliding tests indicated that enhancements in crystallinity did in fact occur during the tests conducted at 180 °C and higher temperatures [74].

4.3.2.2 PEEK/PEI 0/100: Neat PEI

The friction and wear results from the sliding tests carried out on PEI are presented in Figures 4.8 and 4.9. Shown in Figure 4.8, along with the relaxation spectrum of PEI (included for comparison), are plots of the steady state coefficient of friction and cumulative linear wear as functions of the sliding temperature. Figure 4.9 shows the dependence upon the sliding temperature of the recovery parameter.

Examination of the friction and wear data in Figure 4.8(a) reveals the two most salient features of the tribological behavior of PEI as seen during the course of the present study, namely a severe-to-mild friction and wear transition taking place as the sliding temperature varied from 90 °C to 105 °C, and the occurrence of catastrophic tribological failure at 213 °C. High friction and linear wear levels characterized the tribological behavior of PEI at sliding temperatures between 20 °C and 90 °C; steady state coefficients of friction and cumulative linear wear levels exceeded those exhibited by PEEK, within the same temperature interval (see Fig. 4.3(a)), by factors of about 2-3 and 3-5, respectively. At 105 °C, substantial drops in both cumulative linear wear and friction coefficient evidenced the transition to a mild-wear, low-friction sliding regime, which persisted at temperatures of up to 180 °C. At a sliding temperature of 213 °C catastrophic tribological failure, in the form of seizure accompanied by gross loss of form of PEI disk specimens, occurred during the first few cycles of frictional interaction.
Figure 4.7  WAXD scans of PEEK sliding surfaces taken before and after the tests performed at 180 °C (top) and 225 °C (bottom). For clarity, the "after" WAXD scans have been displaced upward by 1000 cps (counts per second).
Figure 4.8  (a) Temperature dependences of the steady state coefficient of friction, $\mu$, and cumulative linear wear, $h$, for PEI (bars show range of the data). (b) Relaxation spectrum of PEI.
Figure 4.9  Temperature dependence of the recovery parameter for neat PEI (bars show range of the data).
Recovery parameter data (Fig. 4.9) and profilometry traces of the wear track cross-sections (see Fig. 4.10 for representative examples) provided important information about the wear mechanisms active during the sliding of PEI. Low recovery parameter values (see Fig. 4.9) and deep wear tracks with virtually no ridges of plastically deformed material on their edges (see the 20 °C and 90 °C traces in Fig. 4.10) indicated that the severe wear of PEI involved the removal of sizable amounts of material from the sliding surface, minimal viscoelastic plowing and practically no plastic plowing. By contrast, in the mild wear regime (i.e., between 105 °C and 180 °C), viscoelastic plowing of the sliding surface appeared to be the dominant wear mechanism of PEI. Plastic plowing and removal of material, both moderate in intensity, were also found to be active wear mechanisms during the sliding of PEI in the mild wear regime. Recovery parameter values in the 80%–90% range within the 105 °C–180 °C temperature interval (see Fig. 4.9) and the appearance of the 105 °C and 180 °C wear track profiles in Figure 4.10 corroborate the observations made in reference to the mild wear of PEI.

The process of removal of material in the severe wear regime of PEI was characterized by the generation of large volumes of minute flake-like wear particles. This, however, did not occur as soon as sliding commenced but after a number of sliding cycles during which no appreciable change in linear wear was apparent. In other words, wear debris generation was preceded by an “incubation” period, as shown in Figure 4.11. This type of phenomenon, which has been previously reported for PEI [63, 64] and other polyimides [75–77], indicated that wear was initiated by a fatigue mechanism. The type of fatigue failure that preceded the generation of wear particles is shown in Figure 4.12(a). Notice that, although limited, some plastic shear straining appears to occur in the surface layers prior to the generation of wear particles. Once wear particles were being generated, a large portion of them was transported outside of the contact region and accumulated on
Figure 4.10 Wear of PEI: profilometry traces of representative wear tracks.
Figure 4.11  Typical evolution of the linear wear with the number of sliding cycles during the sliding of PEI in the severe wear regime.
Figure 4.12  Severe wear of PEI (90°C): (a) failure preceding the generation of wear particles; (b) PEI aggregate; (c) appearance of the wear track. Mild wear of PEI (180°C): (d) appearance of the wear track.
the sides of the wear track. The portion that remained on the wear track formed compacted aggregates (see Figs. 4.12(b)), which, when entrapped at the sliding interface, appeared to plow the surface of the wear track, as shown in Fig. 4.12(c). It must be observed at this point that the high levels of friction observed during the severe wear of PEI can be associated with the dissipation of large amounts of energy (due to the nature and intensity of the wear process) occurring in the contact region during sliding.

SEM examination of the worn polymer surfaces generated during the sliding of PEI in the mild wear regime revealed the presence of a layer of what appeared to be back-transferred material covering the sliding surface. As corroborated by the micrograph shown in Figure 4.12(d), stretching of the latter material in the sliding direction was apparent. It has been reported that a high degree of molecular orientation in the direction of sliding can result in a reduction in the wear of a polymer surface (due to an increased strength in the direction of orientation) [69] and, at the same time, in decreased coefficients of friction (due to a substantial reduction in the amounts of energy dissipated by plastic reorientation of molecules) [78]. It then would seem reasonable to postulate that the above layer of back-transferred material consisted of polymeric chains aligned, preferentially, in the sliding direction, and that the latter contributed to the improved frictional and wear performance of PEI at sliding temperatures of 105 °C up to 180 °C.

Implicit in the above discussion is that the key factor controlling the onset of the severe–mild wear transition in PEI was a dramatic change in mechanical behavior, namely, a marked increase in ductility as the sliding temperature increased from 90 °C to 105 °C. A “thermally activated” increase in ductility in the glassy state could have only occurred in association with the onset of a secondary relaxation process. It must therefore be concluded that the onset of the β relaxation at about 75 °C (see Fig. 4.8(b)) resulted in the change in ductility that led to the transition from the severe to the mild wear regime in PEI.
It should be added that, based on the observed effects on ductility, the $\beta$ relaxation of PEI appears, as pointed out in [50], to involve main chain segmental motions [42, 45].

The catastrophic tribological failure of PEI at 213 °C can be attributed to the drastic thermal softening undergone by the amorphous polymer in connection with the glass transition, or $\alpha$ relaxation. Notice in Figure 4.8(b) that the latter thermal softening translates into an abrupt drop in modulus of approximately two orders of magnitude. It should be noted that such occurrence, typical in amorphous polymers [42, 43, 45], has been previously reported for PEI [50].

4.3.2.3 PEEK/PEI Blends

The temperature dependence of the coefficient of friction, cumulative linear wear and recovery parameter for the as-molded PEEK/PEI 85/15 blend are shown in Figures 4.13(a), 4.13(b) and 4.14, respectively. The results in Figure 4.13 show that, at sliding temperatures under the $T_g$ (ca. 152 °C), the tribological performance of this PEEK-dominated amorphous blend did not differ much from that of PEEK. However, at higher sliding temperatures, and in connection with the onset of the $\alpha$ relaxation, a dramatic change in tribological behavior took place. Marked increases in coefficient of friction and cumulative linear wear at 160 °C, followed by catastrophic tribological failure (seizure accompanied by gross loss of form due to severe thermal softening) during the initial stages of sliding at 175 °C, were seen to occur. Comparison of the tribological and $\tan \delta$ data for the PEEK/PEI 85/15 blend shown in Figures 4.13 and 4.1(a), respectively, substantiates the latter observation.

The active wear mechanisms during the dry sliding of the PEEK/PEI 85/15 blend appeared to be plowing and polymer transfer. At temperatures of up to 100 °C,
Figure 4.13  Temperature dependences of the steady state coefficient of friction (a), and cumulative linear wear (b) for the PEEK/PEI 85/15 blend. Bars show range of the data (PEEK and PEI data shown for comparison).
Figure 4.14  Temperature dependence of the recovery parameter for the PEEK/PEI 85/15 blend. Bars show range of the data (PEEK and PEI data shown for comparison).
viscoelastic (predominantly) and plastic plowing of the sliding surface occurred preferentially; removal of material due to polymer transfer was minimal. Validating these observations were recovery parameter values above 90% (see Fig. 4.14) as well as wear tracks with negligible net cross-sectional areas, which bore a strong resemblance to those generated during the sliding of PEEK in the region below the glass transition (see Fig. 4.5). Furthermore, SEM examination of PEEK/PEI 85/15 worn surfaces produced at sliding temperatures within the 20 °C–100 °C range revealed only one distinct feature, namely a very smooth appearance.

As sliding temperatures from 130 °C to 160 °C, the combined action of the normal and tangential forces appeared to have resulted in the formation of “lips” of plastically deformed material (elongated in the direction of sliding, and lying across the wear track) on the sliding surface. After repeated sliding passes these lips seemed to be torn away and relatively large wear fragments were generated, as shown in Figure 4.15(a). Some of the latter fragments were transferred to the counterface and eventually displaced from the contact region, while others appeared to be back–transferred to the sliding surface and to form, after repeated sliding passes, large agglomerates. With increasing sliding temperatures, and probably due to a decline in shear strength attributable to thermal softening, the lips on the PEEK/PEI 85/15 sliding surface were more closely spaced (presumably, as a result of lips rupturing almost immediately after formation), wear fragments were generated at higher rates and the rate of wear increased. Accompanying the occurrence latter phenomenon, it must be pointed out, was an increasing decline in the ability of the PEEK/PEI 85/15 blend to undergo viscoelastic/plastic deformation, or plowing. Rapidly falling recovery parameter values (see Fig. 4.14) and wear tracks with barely perceptible ridges of plastically deformed material on their flanks corroborated the preceding assertion.
Figure 4.15  SEM micrographs of worn surfaces of PEEK/PEI blends: (a) PEEK/PEI 85/15 (T = 152 °C); (b) as-molded PEEK/PEI 70/30 (T = 159 °C); (c) annealed PEEK/PEI 70/30 (T = 186 °C). Arrows indicate sliding direction.
Plots of the steady state coefficient of friction, cumulative linear wear and recovery parameter as functions of the sliding temperature for the as-molded (amorphous) and annealed (semicrystalline) PEEK/PEI 70/30 blends are presented in Figures 4.16(a), 4.16(b) and 4.17, respectively. Additionally, representative examples of wear track cross-sections generated during the sliding of the as-molded and annealed PEEK/PEI 70/30 blends are shown, respectively, in Figures 4.18 and 4.19.

It is seen from Figures 4.16(a) and 4.16(b) that at temperatures below their respective T_g's, both the as-molded and annealed blends exhibited very similar frictional and wear behaviors. At room temperature (20 °C), the wear of the two blends involved viscoelastic and plastic plowing as well as fatigue of the sliding surface followed by the generation of appreciable volumes of wear particles (see Figs. 4.17 through 4.19). Plowing, it must be pointed out, was mostly viscoelastic in nature. Further, it appeared that in direct correspondence with the relatively high intensity of the wear process, the room temperature coefficients of friction of the PEEK/PEI 70/30 blends were comparatively high. As the sliding temperatures increased from 20 °C to about 50 °C, the fatigue mechanism subsided, removal of material was mitigated and friction coefficients showed a tendency to decrease with sliding temperature. At temperatures above 50 °C but below the respective T_g's of the PEEK/PEI 70/30 blends, viscoelastic and plastic plowing as well as moderate polymer transfer became the active wear mechanisms; evidence of this can be found in Figures. 4.17 through 4.19. For both blends, the observed friction and wear levels in this temperature range were comparatively low and commensurable with those exhibited by PEEK, as shown in Figure 4.16.

At sliding temperatures in the vicinity of the T_g, the onset of the α relaxation in the as-molded PEEK/PEI 70/30 blend led to drastic changes in tribological behavior (see Figs. 4.16 and 4.1(b)). Steep increases in both friction coefficient and cumulative linear
Figure 4.16  Temperature dependences of the steady state coefficient of friction (a), and cumulative linear wear (b) for the as-molded and annealed PEEK/PEI 70/30 blends. Bars show range of the data (PEEK and PEI data shown for comparison).
Figure 4.17  Temperature dependence of the recovery parameter for the as-molded and annealed PEEK/PEI 70/30 blends. Bars show range of the data (PEEK and PEI data shown for comparison).
Figure 4.18  Profiles of wear tracks generated during the siding of the as-molded PEEK/PEI 70/30 blend.
Figure 4.19 Profiles of wear tracks generated during the sliding of the annealed PEEK/PEI 70/30 blend.
wear followed by catastrophic tribological failure. The presence of crystallinity significantly reduced the strength of the $\alpha$ relaxation (due to a reduction in the amount of amorphous material present in the blend, and the constraint imposed by the crystalline domains on the mobility of the remaining amorphous phase, as discussed earlier) in the annealed PEEK/PEI 70/30 blend. As a result, thermal softening at the glass transition was less severe and, thus, the heat treated PEEK/PEI 70/30 blend was able to sustain load and maintain dimensional stability while sliding at temperatures well in excess of the $T_g$. The tribological performance of the annealed blend at temperatures beyond the $T_g$ was, however, rather poor; friction and wear levels were high and increased rapidly with the sliding temperature (see Fig. 4.16). The sliding of the PEEK/PEI 70/30 blends at and above their respective $T_g$'s resulted in the removal of appreciable volumes of material. The latter appeared to involve, as in the case of the 85/15 blend, the formation of “lips” which, after repeated traversals, ruptured giving way to the formation of wear fragments, a fraction of which was, in turn, removed from the wear track. In line with the marked declines in stiffness and strength associated with the phenomenon of thermal softening, the latter process intensified with increasing sliding temperatures. Lips underwent less deformation before rupturing, wear fragments were generated at higher rates, and larger volumes of wear fragments were removed from the contact region. Figures 4.15(b) and 4.15(c) show lips formed during the sliding of the PEEK/PEI 70/30 blends at their respective $T_g$'s. It is noticed that the lips formed on the sliding surface of the annealed blend appeared to be more closely spaced than those formed on the corresponding surface of the as-molded blend. It would seem that due to a reduction in ductility, a condition ascribable to the development of crystallinity, shorter, less extended, lips were formed on the sliding surface under the action of the frictional forces.
Results from the sliding tests performed on the PEEK/PEI 50/50 blend are presented in Figures 4.20 through 4.22. Figure 4.20(a) and 4.20(b) show, respectively, the temperature dependence of the steady state coefficient of friction and cumulative linear wear; Figure 4.21 shows the variation of the recovery parameter as a function of the sliding temperature; and Figure 4.22 presents profilometry traces of representative wear track cross-sections.

Except for the shifting toward lower temperatures of the main (α) and secondary (β) relaxations and corresponding tribological phenomena, the relaxation and tribological behaviors of the PEEK/PEI 50/50 blend were remarkably similar to those of PEI (see Figs. 4.1, 4.8, 4.9 and 4.10). Active friction and wear mechanisms during the sliding of the PEEK/PEI 50/50 blend remained the same as those active during the sliding of PEI. At sliding temperatures near the T_g, however, the wear of the blend appeared to be somewhat more intense than that of PEI and involved severe transfer as well as the formation of fibrillar structures on the sliding surface, as illustrated by the micrographs in Fig. 4.23.

The presence of PEEK in the PEEK/PEI 50/50 blend appeared to have caused, in addition to the shifting toward lower temperatures of the α and β relaxations, an increase in ductility relative to PEI. As corroborated by the recovery parameter data presented in Figure 4.21, the latter translated into the PEEK/PEI 50/50 blend exhibiting an improved ability to accommodate frictional energy as deformation during sliding. In line with this, PEEK/PEI 50/50 disk specimens appeared to undergo less severe wear than their PEI counterparts when sliding at temperatures between 20 °C and 45 °C. With respect to that of PEEK, the tribological performance of the PEEK/PEI 50/50 blend in the range from 20 °C to 45 °C was poor. As shown in Figure 4.20, the blend exhibited coefficients of friction and cumulative linear wear levels that were, respectively, about 2-3 and 3-4 times larger than those measured for PEEK at comparable sliding temperatures. However, in the
Figure 4.20  Temperature dependences of the steady state coefficient of friction (a), and cumulative linear wear (b) for the PEEK/PEI 50/50 blend. Bars show range of the data (PEEK and PEI data shown for comparison).
Figure 4.21  Temperature dependence of the recovery parameter for the PEEK/PEI 50/50 blend. Bars show range of the data (PEEK and PEI data shown for comparison).
Figure 4.22 Profiles of wear tracks generated during the sliding of the PEEK/PEI 50/50 blend.
Figure 4.23  SEM micrographs of the worn surface generated during the sliding of the PEEK/PEI 50/50 blend at 165°C: (a) wear track; (b) fibrillar structures formed on the sliding surface. Arrows indicate sliding direction.
temperature range from 70 °C to 150 °C, the PEEK/PEI 50/50 blend appeared to possess friction and wear performance levels that were comparable to those of PEEK.

4.4 Summary

In this chapter, the results of an experimental study aimed at determining the impact of operating temperature and composition on the dry sliding friction and wear behavior of the isotropic thermoplastic systems to be used as matrices for PEEK-based in-situ composites have been presented. The materials evaluated, all of them in the injection-molded condition, were semicrystalline PEEK, amorphous PEI, three amorphous PEEK/PEI blends with weight ratios of 85/15, 70/30 and 50/50, and an annealed (semicrystalline) PEEK/PEI 70/30 blend. Summarized below are the most important findings of this study:

1. In all the materials tested, the onset of thermally activated molecular relaxation processes coincided with the occurrence of distinct changes in tribological behavior.

2. The onset of the $\alpha$ relaxation, or glass transition, resulted in catastrophic tribological failure in PEI and the PEEK/PEI amorphous blends, and in marked increases in friction and wear in PEEK and the annealed PEEK/PEI 70/30 blend.

3. The nature of the tribological phenomena accompanying the glass transition appeared to depend on the “strength” (as gauged by the magnitude of the $\alpha$ peak of $\tan \delta$) of the $\alpha$ relaxation. The factor controlling the strength of the $\alpha$ relaxation is long range mobility of the amorphous chains. The presence of crystallinity restricted the mobility of the amorphous chains, reduced the strength of the $\alpha$ relaxation and,
therefore, prevented the occurrence of catastrophic tribological failure in PEEK and the annealed PEEK/PEI 70/30 blend.

4. PEI and the PEEK/PEI 50/50 blend were found to exhibit secondary, or $\beta$, relaxations at about 75 °C and 45 °C, respectively. The activation of these relaxation processes resulted in marked increases in ductility in both materials. The latter phenomenon appeared to have induced severe-to-mild friction and wear transition as sliding temperatures increased from 90 °C to 105 °C, in the case of PEI, and from 45 °C to 75 °C, in the case of the PEEK/PEI 50/50 blend.

5. The $\beta$ transition of PEI was seen, centered at a lower temperature, in the PEEK/PEI 50/50 blend. This suggested that the $\beta$ transition (and accompanying transitional tribological behavior) shifts to lower temperatures as the PEI content decreases. In order not to significantly impair tribological performance in the region below the glass transition, the concentration of PEI in PEEK/PEI blends should not exceed 30 wt% (although not pronounced, friction and wear transitions were seen to occur between 20 °C and 50 °C in the PEEK/PEI 70/30 blends).
CHAPTER 5

Elevated Temperature Tribology of Blends of PEEK and a Thermotropic Liquid Crystalline Polymer

Synopsis

An investigation is carried out into the effects of temperature on the friction and wear behavior of injection molded in-situ composites based on blends of Polyetheretherketone (PEEK) and a thermotropic liquid crystalline polymer (TLCP) under unlubricated sliding conditions. Results from sliding tests conducted on a pin-on-disk tribometer at selected temperatures in the 20 °C–250 °C range are reported. Active friction and wear mechanisms are described in relation to the microstructure of the polymer systems investigated. Additionally, the impact of TLCP concentration and thermally activated molecular relaxation processes on the mechanical properties and tribological performance of the PEEK/TLCP blends are discussed in conjunction the potential of in-situ reinforcement as a route towards the development of performance thermoplastic-based tribomaterials for high use temperatures.

5.1 Introduction

Recently, a new class of self-reinforcing polymeric material based on blends of isotropic thermoplastics and thermotropic liquid crystalline polymers (TLCPs) has been
developed. This new class of polymeric material has been termed in-situ composite. In in-situ composites, key characteristics of TLCPs, such as low melt viscosities, excellent mechanical properties and superior thermal and dimensional stabilities at elevated temperatures, are effectively exploited to produce thermoplastic materials with superior property profiles that can be tailored to meet the requirements encountered in high performance engineering applications.

In-situ composites appear to have a promising potential as high performance polymer-based tribomaterials, an area of application currently dominated by fiber-reinforced and particle-filled engineering thermoplastics. This observation is supported by the emergence of in-situ composites which, in addition to exhibiting mechanical properties that are comparable to those of their conventional counterparts, possess, due to the absence of the solid phase—i.e., fibers and/or fillers, significantly improved melt processabilities [18, 21].

In this chapter, the question of the potential of in-situ composites as performance tribomaterials is addressed. Presented below are the results from a study aimed at assessing the effectiveness of TLCP in-situ reinforcement as a means to enhance the high temperature tribological performance of Polyetheretherketone (PEEK), as well as at advancing the understanding of the tribological behavior of in-situ composites in terms of structure-property relationships. The specific tribological phenomenon investigated was the unlubricated sliding of self-reinforcing blends of PEEK and HX-1000, a commercially available TLCP, under controlled temperature conditions. The microstructure, phase behavior, impact of TLCP concentration and thermally activated molecular relaxation processes on mechanical properties and tribological performance and active friction and wear mechanisms of the materials investigated are discussed.
5.2 Experimental

5.2.1 Materials

The base materials used in this study were semicrystalline Victrex® PEEK 380-G supplied by ICI, and the TLCP HX-1000, an amorphous DuPont copolyester. Four PEEK/HX-1000 blends with TLCP concentrations of 10 wt%, 30 wt%, 50 wt% and 80 wt% were compounded using a single screw extruder. Following this, the blends as well as the parent polymers were injection molded into plaques according to the specifications given in section 3.1.2. In order to investigate the effects of annealing on tribological performance, a number of injection molded plaques of the PEEK/HX-1000 70/30 blend were heat treated in a vacuum oven at 230 °C for 12 hours.

5.2.2 Dynamic Mechanical Thermal Analysis

The dynamic mechanical properties of the polymer systems under study were investigated within the 20 °C–250 °C temperature range using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer. The selected test configuration and operating mode were, respectively, single cantilever bending and fixed-frequency, constant-amplitude forced flexural oscillation. Mechanical loss factor (tan δ) and dynamic storage modulus were measured and recorded during thermoscans performed across the temperature range of interest. With the recorded data, relaxation spectra were generated for the test polymers. For further experimental details on DMTA testing refer to Section 3.2.2.

The results from DMTA enabled the assessment of the effects of thermally activated
molecular relaxation processes on the mechanical properties and tribological performance of the test polymers. They also allowed the phase structure of the PEEK/HX-1000 blends to be determined.

5.2.3 Viscosity Measurements

In order to assess the processability of the test polymers, dynamic oscillatory shear viscosity measurements were performed in a Rheometrics Mechanical Spectrometer RMS-800. The test configuration used was parallel plates. All measurements were conducted at a shear rate of 1000 s\(^{-1}\) and at a temperature of 360 °C, which coincided with the temperature at which the test polymers were processed.

5.2.4 Microstructural Characterization

The microstructures of PEEK, HX-1000 and their blends were investigated using scanning electron microscopy (SEM) and wide-angle x-ray diffraction (WAXD) techniques. SEM was carried out on an International Scientific Instruments (ISI) SX-40 scanning electron microscope. WAXD studies were performed on a fully automated Scintag XDS 2000 x-ray diffractometer. Details on experimental setup and procedures pertinent to the microstructural characterization of materials in this study can be found in Section 3.2.3.

5.2.5 Tribological Evaluation

The elevated temperature dry sliding friction and wear characteristics of the test polymers were investigated using a pin-on-disk apparatus (see Fig. 3.3). For each of the
materials under study, a series of sliding tests were conducted at selected temperatures in
the range from 20 °C to 250 °C. For a complete description of experimental procedures,
test setup and other important experimental details concerning tribological evaluation, refer
to Section 3.2.1.

5.3 Results and Discussion

5.3.1 Dynamic Mechanical Thermal Analysis

DMTA data showing the temperature dependence of the mechanical loss factor, or
tan δ, and storage modulus for PEEK, HX-1000, and the PEEK/HX-1000 blends in the
as-molded condition are shown in Figure 5.1. Bearing in mind that the temperature at
which the storage modulus curve has an inflection point and tan δ goes through a maximum
is generally regarded as the glass transition temperature (T_g) of a polymer [43], the T_g's of
PEEK and HX-1000 were determined to be 148 °C and 183 °C, respectively. These
temperatures are in close agreement with those reported in the literature [4, 48]. The
presence of two peaks in the tan δ curve for HX-1000 suggests that the chemical
composition of the liquid crystalline copolyester is heterogeneous in nature. The latter
would seem to be in line with the observation made in [27] indicating that liquid crystalline
polymers typically exhibit multiphasic solid structures.

Blends of mutually soluble, or miscible, polymers show a single T_g, the location of
which, between the T_g's of the constituent polymers, is composition-dependent.
Incompatible polymer blends, on the other hand, show multiple T_g's which coincide with
those exhibited by the component polymers in the neat condition [43, 46]. The number and
location of the peaks in the tan δ curves for the PEEK/HX-1000 blends indicate that PEEK
Figure 5.1 DMTA results for as-molded PEEK, HX-1000 and their blends:
(a) Temperature dependence of the mechanical loss factor; (b) Temperature dependence of the storage modulus.
and HX-1000 exist as separate phases in the blended state. Further examination of the tan δ curves for the PEEK/HX-1000 blends reveals that a direct relationship appears to exist between the height, or intensity, of the tan δ peaks and the relative concentration of the parent polymers in the blends. Two points are worth introducing here; first, tan δ peak intensity is a measure of the ability of a polymer to dissipate energy under dynamic deformation conditions [43]. Secondly, bearing in mind the dissipative nature of the friction process, the extent of such ability could certainly have a significant impact on the frictional performance of a polymer [79].

Judging from the modulus data shown in Figure 5.1(b) it could be said that, up to a temperature of about 200 °C, the addition of the TLCP phase had a reinforcing effect on PEEK. A more precise assessment of the effectiveness of TLCP reinforcement can be made, however, by replotting the data in Figure 5.1(b) in the way shown in Figure 5.2. Using significant increases in modulus with TLCP concentration as the discerning criteria, Figure 5.2 shows that TLCP reinforcement can be regarded as effective at temperatures of up to 180 °C. At 200 °C, despite the fact that an increase in modulus with TLCP concentration is still perceivable, the effectiveness of the TLCP as a reinforcing agent is significantly impaired; notice that at 200 °C the difference in modulus between PEEK and HX-1000 is not substantial. At temperatures above 200 °C the modulus of HX-1000 falls under that of PEEK and, consequently, the reinforcing action of the TLCP phase vanishes. Clearly, the pronounced drop in modulus occurring in connection with the glass transition constitutes the factor effectively limiting the high temperature reinforcing potential of the amorphous HX-1000.

In Figure 5.3 the DMTA results for the as-molded and annealed PEEK/HX-1000 70/30 blends are compared. Annealing appeared to have three main effects on the dynamic
Figure 5.2  Storage modulus as a function of TLCP concentration for as-molded PEEK/HX-1000 blends.
Figure 5.3  DMTA results for the as-molded and annealed PEEK/HX-1000 70/30 blends: (a) Temperature dependence of the mechanical loss factor; (b) Temperature dependence of the storage modulus.
mechanical properties of the PEEK/HX-1000 70/30 blend. First, a noticeable reduction in the intensity of the tan δ peaks of the TLCP and PEEK phases. Second, an increase in the \( T_g \) of the PEEK phase, as evidenced by the shift towards higher temperatures of the relevant tan δ peak (notice that due its drop in intensity and shift towards higher temperatures, the PEEK tan δ peak appears as a shoulder on the low temperature side of the HX-1000 tan δ peak at 183 °C). Third, and last, an appreciable rise in dynamic stiffness combined with a moderate improvement in modulus retention. The latter improvement, it should be added, can be linked to the increase in \( T_g \) undergone by the PEEK phase upon heat treatment.

In order to explain the effects just described, two facts ought to be recognized first. One is that in the PEEK/HX-1000 system only one of the polymers, namely PEEK, is crystallizable. The other is that the glass transition is a phenomenon involving the onset of long-range main-chain segmental motions within the amorphous regions of a polymer [43, 46]. With this in mind, the effects of annealing on the dynamic mechanical behavior of the PEEK/HX-1000 70/30 blend can be explained as follows [41, 43, 66]. The stiffening of the blend upon heat treatment can be ascribed to a densification (reduction in free volume) process which, as can be qualitatively determined from the WAXD scans shown in Figure 5.4, involved the development of crystallinity in the PEEK phase (notice the sharper PEEK crystalline reflections, or peaks, at \( 2\theta = 18^\circ, 22^\circ \) and \( 28^\circ \) in Figure 5.4(b)) [60, 80]

Furthermore, the reduction in intensity and shift towards higher temperatures of the PEEK tan δ peak upon heat treatment can be attributed, respectively, to the following two factors. First, the reduction in the fraction of amorphous PEEK present in the annealed 70/30 blend that must have occurred as PEEK crystallites developed and, secondly, the constraint imposed by the newly developed crystallites on the mobility of the remaining
Figure 5.4  WAXD scans for the as-molded (top) and annealed (bottom) PEEK/HX-1000 70/30 blends.
amorphous regions within the PEEK phase.

Restained mobility, also arising from the presence of newly developed PEEK crystallites, and densification of the amorphous TLCP phase, are factors to which the depression of the HX-1000 tan δ peaks in the annealed 70/30 blend could be linked.

5.3.2 Viscosity Measurements

The results from the viscosity measurements performed on PEEK, HX-1000 and their blends are shown in Figure 5.5 in the form of a plot of dynamic shear viscosity as a function of TLCP concentration. Two facts are important to recognize from the data in Figure 5.5. First, the viscosity of HX-1000 is over an order of magnitude lower than that of PEEK and, secondly, reductions in viscosity (although modest at TLCP concentrations up to 30 wt%) occurred as the TLCP weight fraction in the PEEK/HX-1000 blends increased. The observed drop in viscosity evidences the ability of liquid crystalline HX-1000 to lubricate isotropic PEEK in the melt. It is of interest to point out that the results from the viscosity measurements together with those pertaining to the storage modulus in the previous section show that, in contrast to conventional solid phase reinforcement, TLCP in-situ reinforcement can lead to the simultaneous enhancement of both mechanical properties and melt processability. Worth noting here, in relation to the preceding observation, is that data presented in [5] shows that while the addition of 30 wt% carbon fiber reinforcement to PEEK 450-G (an injection molded grade similar to the one used in this research) significantly enhances the mechanical properties of the resin, it also leads to a rise in melt viscosity (at 360 °C and a shear rate of 1000 s⁻¹) of about 40%.

5.3.3 Microstructural Characterization

Examination of the fracture surface of injection molded HX-1000 revealed a "skin-
Figure 5.5  Variation of the dynamic shear viscosity as a function of TLCP concentration for the PEEK/HX-1000 blends.
core" solid state morphology, that is, a morphology consisting of three macrolayers, two "skins," with a "core" in between [39, 40], as shown schematically in Figure 5.6(a). This type of morphology, it should be noted, appears to be a recurrent development in moldings of both TLCPs and blends of isotropic thermoplastics and TLCPs [21]. SEM micrographs of the HX-1000 skin and core layers are presented in Figures 5.6(b) through 5.6(d). The skin layers (Fig. 5.6(b)) were found to be composed of a series of sublayers in which a high level of molecular orientation, in the mold fill direction (MFD), was apparent. Molecular orientation appeared to be maximum in the outermost skin sublayers, which were characterized by a highly fibrillar nature. The micrograph in Figure 5.6(d), which shows one of these sublayers, namely the top one, illustrates the latter observation. In contrast to the skin layers, the core (Fig. 5.6(c)) did not show a well defined sublayered structure and exhibited a lesser degree of molecular orientation in the MFD. This was corroborated by the pole figures (see [60] and [61] for detailed discussions on the topic) shown in Figure 5.7, which were obtained through WAXD analysis of microtomed samples from the skin and core layers of molded HX-1000. Prior to proceeding with the interpretation of the results in Figure 5.7, however, the introduction of some brief explanatory comments on the subject of pole figures seems appropriate.

Pole figures are stereographic projections (see Fig. 5.8) that can be described as contour maps depicting the spatial distribution and density (number) of the normals to specific lattice planes, or poles, within a sample. As such, pole figures afford a means to effectively assess the distribution of molecular orientation in ordered polymers [81–83]. A contour line in a pole figure is an isointensity line, or in more explicit terms, a line along which the diffracted x-ray beam intensity remains invariant. The latter intensity, it is important to bear in mind, is directly proportional to pole density. As could be inferred, in
Figure 5.6  Solid state morphology of injection molded HX-1000: (a) Schematic representation of fracture surface showing the skin-core structure (boxed areas correspond with micrographs 8(b)-(d)); (b) Cross-sectional view of one of the skin layers; (c) Cross-sectional view of the core; (d) Top skin sublayer (arrow coincides with the mold fill direction).
Figure 5.7  Pole figures for HX-1000: (a) Skin layer; (b) Core layer (MFD: mold fill direction; TD: transverse direction).
Figure 5.8  Stereographic projection of a pole.
the absence of orientation a pole figure will show poles scattered all over its surface and no marked intensity, or pole density, gradients will be apparent. If preferred orientation exists, on the other hand, pole figures will display distinct patterns reflecting the tendency of poles to concentrate about certain directions. Lastly, a comment on the poles of noncrystalline HX-1000. The poles of molded HX-1000 result from the fact that in the solid state this amorphous TLCP exhibits a morphology that can be described as that of an ordered glass. In connection with the latter, it is instructive to point out that an ordered amorphous polymer can be treated within the context of diffraction theory as a limiting case of a crystalline polymer having one dimensional (along the molecular axis) structural regularity [82].

With the above information in mind, it can be inferred from the data in Figure 5.7 that preferred orientation was in fact present in both the skin and core layers of molded HX-1000, and, moreover, that the direction of preferred orientation coincided with the MFD. Additionally, a less pronounced diffraction beam intensity gradient and a somewhat wider spread of the iso-intensity lines about the MFD axis in the core pole figure, suggested that the degree of axial orientation in the core was less marked than in the skin layers.

Skin-core morphologies were also exhibited by the molded PEEK/HX-1000 blends with TLCP concentrations of 30 wt% and above. Figure 5.9 shows SEM micrographs of the fracture surface of the PEEK/HX-1000 50/50 blend. As attested by the images in Figures 5.9(a) and 5.9(b), the skin layers of the latter blend were structurally very similar to the corresponding layers of neat HX-1000. All the characteristic features of the HX-1000 skin layers, namely the sublayered structure, the anisotropy of molecular orientation and the high degree of fibrillation in the outermost skin sublayers (see Fig. 5.9(d)) were present in the skin layers of the 50/50 blend. Clear differences, however, were found to
Figure 5.9  Solid state morphology of the injection molded PEEK/HX-1000 50/50 blend: (a) Skin-core structure; (b) Skin layer; (c) Core layer; (d) Fibrillar structure of top skin sublayer (arrow coincides with the mold fill direction).
exist between the core structures of HX-1000 and the 50/50 blend (see Figs. 5.6(c) and 5.9(c)). Unlike the HX-1000 core, the core of the 50/50 blend appeared to consist of elongated, fiber-like TLCP domains, 1–3 µm in diameter and profusely disseminated throughout the PEEK phase. Close examination of the core of the 50/50 blend revealed the presence of numerous cavities which appeared to be the empty sites left by TLCP fibrous domains pulled out as specimens were fractured prior to observation under the electron microscope. Such cavities evidenced the poor nature of the interfacial adhesion between the PEEK and HX-1000 phases, a fact which, given the immiscible character of these polymers, was not at all surprising. The pole figures shown in Figure 5.10 were obtained in order to ascertain the degree of orientation of the TLCP phase within the skin and core layers of the 50/50 blend. They indicated that an axial texture along the MFD existed in the skin layers and that no preferred orientation developed in the core.

As in the case of the 50/50 blend, the PEEK/HX-1000 20/80 blend showed a skin structure which, to a large extent, resembled that of neat HX-1000; notice for instance, in Figure 5.11(a), the highly fibrillar nature of the 20/80 top skin sublayer. Fibrillation of the TLCP phase in the core however, appeared to be more pronounced in the 20/80 blend than in that of the 50/50 blend. Core TLCP fibrils in the 20/80 blend were finer and exhibited larger aspect ratios than those in the 50/50 blend (see Figs. 5.11(b), 5.11(c) and 5.9(c)). From the standpoint of axial texture development, no significant differences were found to exist between the 20/80 and 50/50 blends; the TLCP phase in the 20/80 blend was highly oriented along the MFD in the skin and unoriented in the core.

Micrographs showing the general appearance of the fracture surface and important microstructural details of the PEEK/HX-1000 70/30 blend are presented in Figure 5.12. Relative to neat HX-1000 and the blends with 50 wt% and 80 wt% TLCP content, the
Figure 5.10 Pole figures for the PEEK/HX-1000 50/50 blend: (a) Skin layer; (b) Core layer (MFD: mold fill direction; TD: transverse direction).
Figure 5.11  Solid state morphology of the injection molded PEEK/HX-1000 20/80 blend: (a) Fibrillar structure of top skin sublayer (arrow coincides with the mold fill direction); (b)-(c) Core layer.
Figure 5.12  Solid state morphology of the injection molded PEEK/HX-1000 70/30 blend: (a) Skin-core structure; (b) Skin layer; (c) Core layer; (d) Fibrillar structure of top skin sublayer (arrow coincides with the mold fill direction).
70/30 blend was found to exhibit skin layers composed of significantly thinner sublayer which, densely packed across the thickness, imparted the skin a finely textured appearance (see Fig. 5.12(b)). Close examination of the top skin sublayer in the 70/30 blend (Fig. 5.12(d)) revealed that, although a high degree of orientational anisotropy had developed during processing, fibrillation was not as marked as in the corresponding sublayers in HX-1000 or the blends with higher TLCP fractions (see Figs. 5.6(d), 5.9(d) and 5.11(a)). As can be determined from Figure 5.12(c), the core structure of the 70/30 blend resembled that of the 50/50 blend (Fig. 5.9(c)); the fiber-like domains into which the TLCP phase aggregated were, however, less prominent in the 70/30 blend. The degrees of orientation attained by the TLCP phase in the skin and core layers of the 70/30 blend were similar to those attained in the corresponding layers of the 50/50 blend (see Fig. 5.10).

Images showing the appearance of the fracture surfaces of the PEEK/HX-1000 90/10 blend and neat PEEK can be found in Figure 5.13. The skin-core morphology exhibited by HX-1000 and the blends with 30 wt% and higher TLCP concentrations was not observed in the 90/10 blend. In fact, the morphology displayed by the 90/10 blend consisted of a PEEK matrix throughout which finely dispersed TLCP droplets were found. At liquid nitrogen temperatures, such morphology seemed to render the 90/10 blend the toughest among the test polymers. The latter first became apparent when the number of reversed bending cycles required to fracture a 90/10 sample was found to be significantly greater than the number required to break samples of the other test polymers. Tangible evidence of the superior toughness of the 90/10 blend is provided by the micrographs shown in Figures 5.13(a) and 5.13(b), which clearly show that a great deal of plastic work was exerted during the generation of the 90/10 fracture surfaces. It would seem that the effective introduction of an energy-absorbing mechanism, presumably crazing (notice, in
Figure 5.13  (a)-(b) Fracture surface of the PEEK/HX-1000 90/10 blend; (c) Fracture surface of neat PEEK.
Fig. 5.13(b). the highly drawn fibrillar structures in the PEEK matrix), by the rigid TLCP droplets resulted in the enhanced toughness exhibited by the 90/10 blend.

Figure 5.13(c) shows the appearance of a PEEK fracture surface. A typical brittle failure characterized by macroscopically smooth fracture surfaces in which hardly any traces of deformation can be recognized, was seen in this case. Close SEM examination of the PEEK fracture surfaces did not reveal any unusual microstructural features.

5.3.4 Tribological Evaluation

5.3.4.1 Parent Polymers: PEEK and HX-1000

Plotted for comparison in Figures 5.14(a), 5.14(b) and 5.15 are, respectively, the temperature dependences of the steady state coefficient of friction, cumulative linear wear (i.e., depth of penetration of the rider–steel ball– into polymer counterface as measured at 3000 sliding cycles) and the recovery parameter for PEEK and HX-1000.

The tribological behavior of PEEK, as seen during the course of this research, has been described in detail in Section 4.3.2.1. In view of this, the topic is omitted here and the remainder of this section is devoted to the discussion of the tribology of HX-1000.

As evidenced by the data in Figures 5.14(a) and 5.14(b), the dry sliding tribological performance of HX-1000 differed significantly from that of PEEK; higher friction and wear levels were exhibited by the TLCP over the entire range of test temperatures. From the same figures, it becomes apparent that temperature had the same impact on both the frictional and wear behaviors of HX-1000; moderate increases in friction and wear with temperature were followed by catastrophic failure at 180 °C. The catastrophic tribological failure of HX-1000 took place during the first stages of sliding (after approximately 200
Figure 5.14  Sliding test results for neat PEEK and HX-1000: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear. Bars show range of the data.
Figure 5.15  Temperature dependence of the recovery parameter for neat PEEK and HX-1000. Bars show range of the data.
sliding cycles) and was characterized by the occurrence of severe frictional oscillations (chatter), pronounced warping of test specimens under the applied normal load and, ultimately, seizure.

A correlation appeared to exist between the friction and wear performance and dynamic mechanical behavior of HX-1000; comparison of the results for HX-1000 in Figures 5.1 and 5.14 validates this observation. The catastrophic tribological failure at 180 °C is ascribable to the severe thermal softening of HX-1000 in the glass transition region. Clearly, the latter phenomenon, a characteristic of amorphous polymers [43], effectively limits the high temperature operating potential of HX-1000.

Recovery parameter data (Fig. 5.15) and wear track cross-sectional profiles (Fig. 5.16) indicated that viscoelastic and plastic plowing as well as material removal were the active wear modes during the sliding of HX-1000. Comparison of the recovery parameter data in Figure 5.15 shows that in the temperature range between 20 °C and 160 °C, viscoelastic plowing in HX-1000 was roughly half as intense as it was in PEEK. Furthermore, at all sliding temperatures under and up to 160 °C, removal of material was, by a large margin, more intense than plastic plowing. The relative proportions of the cross sectional areas of the ridges and grooves in the wear tracks shown in Figure 5.16 attest to the dominance of the material removal wear mode. It must be added, in connection with the latter, that due to the accumulation of removed material extrudates (see text below) on the sides of the wear track, as shown schematically in Figure 5.17, the profilometry traces of certain wear track cross-sections showed larger-than-actual "ridges" of plastically deformed material on one or both sides of the wear groove. The traces for 110 °C and 140 °C in Figure 5.16 constitute examples of the situation just described and consequently, wear track net cross-sectional area measurements based on these traces would not yield
Figure 5.16  Profiles of wear tracks generated during the sliding of HX-1000.
Figure 5.17 Schematic of profilometry of an HX-1000 wear track onto which removed material extrudates have accumulated.
accurate estimates of the relative intensities of the plastic plowing and material removal wear modes at the indicated temperatures. The extent to which HX-1000 underwent plastic plowing in the present study was minimal and can be gauged from the cross-sectional profiles of the wear tracks shown in Figure 5.16 for 20 °C, 80 °C and 160 °C. It is apparent that, commensurate with its rigid nature, HX-1000 exhibited a wear behavior typical of a brittle material.

Investigation of worn surfaces generated during sequential and full-length sliding tests by means of optical light and scanning electron microscopy provided insight into the nature of the mechanism of removal of material in HX-1000. SEM micrographs of HX-1000 worn surfaces are provided in Figures 5.18 and 5.19. Figure 5.18 shows SEM micrographs taken at different stages during the sliding of HX-1000 at 140 °C and Figure 5.19 illustrates the evolution of the wear of HX-1000 from comparatively mild, at 20 °C, to catastrophic, at 180 °C.

Removal of material in HX-1000 appeared to occur by the sequential disruption of the sublayers composing the skin of the TLCP. The disruption process began with the nucleation, during the early stages of sliding, of microcracks along the central region of the wear track—where contact stresses are most intense—at locations where the sliding direction (SD) was perpendicular to the MFD (see Figs. 5.20(a) and 5.20(b)). The nucleated microcracks, a micrograph of which is shown in Figure 5.18(a), were closely spaced and oriented parallel to the MFD. Based on the micrographs shown in Figures 5.18(a) and 5.6(d) it would seem reasonable to associate the onset of microcrack nucleation in HX-1000 with the failure, under the action of the surface tractions, of the interface between the fibrous domains present in the outermost, highly anisotropic skin sublayer of the TLCP. The inherent transverse weakness of oriented TLCPs [84, 85], a manifestation
Figure 5.18  SEM micrographs showing the appearance of an HX-1000 worn surface at different stages during the sliding at 140 °C: (a) at 300 cycles; (b)-(d) at 800 cycles; (e) at 1600 cycles. Arrows indicate sliding direction (SD: sliding direction; MFD: mold fill direction).
Figure 5.19  SEM micrographs of HX-1000 worn surfaces generated at (a) 20 °C; (b) 80 °C; (c) 140 °C; and (d) 180 °C. Arrows indicate sliding direction.
Figure 5.20  Schematic representation of the mechanism of removal of material in HX-1000: (a) Disruption initiation sites (boxed areas); (b) Microcrack nucleation; (c) Skin sublayer splitting; (d) Fragmentation of skin sublayer (SD: sliding direction; MFD: mold fill direction).
of which, it must be noted, is the proclivity of these materials to fibrillate—i.e., to easily fracture along the direction of preferred orientation [29], is a fact adding merit to the latter observation.

Upon repeated sliding passes, the nucleated microcracks grew into cracks and propagated sideways. In time, as TLCP fibrils in the top skin sublayer broke, these cracks coalesced within the zone where the nucleation process commenced. Crack coalescence resulted in the splitting of the top skin sublayer along the central region of the wear track (see Fig. 5.20(c)). As sliding continued, the cracks propagating sideways reached the edges of the wear tracks and, eventually, they too coalesced. As this occurred, sizable fragments of the splitted top skin sublayer were torn-off by the surface tractions (see Fig. 5.20(d)). Evidence of the activation of the disruption mechanism depicted schematically in Figure 5.20 can be found in Figures 5.18 and 5.19. The crack tips protruding from the upper edge of the wear track in Figure 5.18(b) (seen at higher magnification in Figure 5.18(c)), the absence of transverse cracks on the wear track in Fig 5.18(d), and the tearing of material from the sliding surface as seen at the bottom of the micrograph in Figure 5.18(b) and in Figure 5.19(d), constitute such evidence.

Once disruption had occurred at locations where the SD and MFD were mutually perpendicular, the break-up of the top skin sublayer at other locations followed on by splitting and fragmentation by tearing as well; fracture along the MFD continued to be predominant during fragmentation at the latter locations. Figure 5.19(a), which shows an HX-1000 surface worn at a location where the SD was parallel to the MFD, illustrates the process of disruption of the top skin sublayer at locations other than where the process commenced.

Following the deterioration of the top skin sublayer, other skin sublayers were
sequentially disrupted in a manner analogous to the one described above. With increasing sliding temperatures, the material removal mechanism of HX-1000 intensified, a greater number of skin sublayers were disrupted, larger volumes of wear debris were generated and the wear of HX-1000 became progressively more severe. It must be added at this point that coupled to the fact that a significant fraction of the wear debris generated during the sliding of HX-1000 tended to remain in the wear track, the disruption of the sublayers beneath the top skin sublayer was somewhat mitigated. More explicitly, repeated deformation at the contact interface resulted in the debris remaining in the wear track being flattened, agglomerated and eventually extruded towards the edges of the wear track (see Fig. 5.19(b)). When wear volumes were substantial (i.e., as sliding temperatures approached the \( T_g \)), this situation translated into the formation of a layer of highly deformed material covering the extensive portions of the wear track (see Figs. 5.18(e) and Fig. 5.19(c)). For as long as they resisted extrusion out of the contact zone, agglomerates and layers of highly deformed material protected the sliding surface and reduced the rate at which damage was inflicted.

The highly energy-dissipative nature of the processes associated with the sliding wear of HX-1000, namely tearing, fracture, and repeated deformation and extrusion of wear debris, explain the high sliding friction coefficients exhibited by the TLCP prior to catastrophic tribological failure at the \( T_g \).

5.3.4.2 PEEK/HX-1000 Blends

The temperature dependences of the steady state coefficient of friction, cumulative linear wear, and recovery parameter for the PEEK/HX-1000 20/80 and 50/50 blends are shown in Figures 5.21(a), 5.21(b) and 5.22, respectively. It can be seen from Figure 5.21
Figure 5.21 Sliding test results for the PEEK/HX-1000 20/80 and 50/50 blends: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear. Bars show range of the data (PEEK and HX-1000 data shown for comparison).
Figure 5.22  Temperature dependence of the recovery parameter for the PEEK/HX-1000 20/80 and 50/50 blends. Bars show range of the data (PEEK and HX-1000 data shown for comparison).
that at temperatures below 150 °C no significant differences in tribological performance existed between the 20/80 and 50/50 blends. Both blends exhibited friction and wear levels that were intermediate to those of the parent polymers. At sliding temperatures above 150 °C both the 20/80 and the 50/50 blend failed catastrophically; the 20/80 blend at 180 °C and the 50/50 blend at 225 °C. Apparently, the lower concentration of HX-1000 in the 50/50 blend led to a comparatively better high temperature mechanical stability and, consequently, to an improved ability to sustain load at higher sliding temperatures. The catastrophic failure of the 20/80 and 50/50 blends at sliding temperatures above 150 °C appeared to be a consequence of the high temperature mechanical stability of both blends being controlled by the thermal softening characteristics of the amorphous HX-1000 phase. Clearly, the addition of HX-1000 in high concentrations to PEEK was not beneficial in terms of enhancing the high temperature tribological performance of PEEK.

Inspection of the recovery parameter data in Figures 5.22 and comparison of the wear track profiles shown in Figure 5.23 with those in Figure 5.16 reveal that practically no differences existed, in terms of active wear modes and their relative intensities, between the wear processes of neat HX-1000 and the PEEK/HX-1000 20/80 and 50/50 blends. As in the case of HX-1000, the sliding wear of the 20/80 and 50/50 blends involved viscoelastic plowing and material removal, as the dominant wear modes, and minimal plastic plowing. It should be noted, however, that coupled to the presence of the PEEK phase within them, the 20/80 and 50/50 blends were able to accommodate larger fractions of frictional work in the form of viscoelastic deformation than neat HX-1000 (see Fig. 5.22).

The results from the sliding tests performed on the as-molded and annealed PEEK/HX-1000 70/30 blends are presented in Figures 5.24 and 5.25. Inspection of the
Figure 5.23  Profiles of wear tracks generated during the sliding of the PEEK/HX-1000 20/80 (top) and 50/50 (bottom) blends.
**Figure 5.24** Sliding test results for the PEEK/HX-1000 70/30 blends: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear. Bars show range of the data (PEEK and HX-1000 data shown for comparison).
Figure 5.25  Temperature dependence of the recovery parameter for the PEEK/HX-1000 70/30 blends. Bars show range of the data (PEEK and HX-1000 data shown for comparison).
friction data in Figure 5.24(a) reveals that at temperatures below 150 °C both the as-molded and annealed 70/30 blends slid with higher coefficients of friction than PEEK. At sliding temperatures above 150 °C annealing in conjunction with TLCP in-situ reinforcement were more effective than in-situ reinforcement alone in terms of improving the frictional characteristics of PEEK above its T_g. Further, by first noticing from Figure 5.24(b) that the wear levels attained by the as-molded and annealed 70/30 blends at temperatures above 150 °C did not differ significantly, it becomes apparent, after comparison of the data in Figures 5.24(a) and 5.3(a), that a direct connection exists between coefficient of friction and tan δ for the PEEK/HX-1000 70/30 blends. Notice that depressed tan δ peaks or, equivalently, a decreased ability to dissipate mechanical energy during frictional interaction, corresponded with lower coefficients of friction in the annealed 70/30 blend at sliding temperatures over 150 °C.

From Figure 5.24(b) it is seen that at temperatures below 150 °C, the 70/30 blends exhibited wear performance levels that varied from lower than PEEK's, at temperatures under 100 °C, to comparable to PEEK's, at 100 °C and 140 °C. At temperatures above 150 °C, and up to 200 °C, the maximum temperature at which HX-1000 could be expected to have a reinforcing effect on PEEK (see Fig. 5.2), the 70/30 blends showed better wear characteristics than neat PEEK. This suggests that at 30 wt% concentration, the presence of the HX-1000 reinforcing phase proved effective in ameliorating the post-glass-transition wear performance of PEEK. The latter, it is of interest to point out, seemed to have resulted from a synergistic interaction between the PEEK and HX-1000 phases. It is clear from the data in Figure 5.24(b) that heat treatment did not have any significant effect on the wear performance of the PEEK/HX-1000 70/30 blend.

Recovery parameter data and wear track profiles for the 70/30 blends are shown in
Figures 5.25 through 5.27. With the exception of an enhanced ability to undergo viscoelastic deformation during sliding and the absence of catastrophic tribological failure, the wear of the 70/30 blends resembled that of HX-1000 and the PEEK/HX-1000 blends with higher TLCP concentrations. As was the case with the latter materials, there were three active wear modes during the sliding of the as-molded and annealed 70/30 blends, namely viscoelastic and plastic plowing and material removal. At all sliding temperatures, plastic plowing of the 70/30 sliding surfaces was moderate and viscoelastic plowing and material removal emerged as the dominant wear modes.

The process by which material was removed from the sliding surfaces of the PEEK/HX-1000 20/80, 50/50 and the two 70/30 blends remained essentially the same as that observed for neat HX-1000. As in the case of HX-1000, loss of material during the sliding of the 20/80, 70/30 and 50/50 blends arose as a consequence of the activation of the mechanism of sequential disruption of the skin sublayers. It must be pointed out that given the microstructural similarities that existed between the skin layers of HX-1000 and the 20/80, 50/50 and 70/30 blends (see Figs. 5.6, 5.9, 5.11 and 5.12), the activation of the mechanism of sequential disruption of the skin sublayers during the sliding of the latter blends seemed natural. Comparison of the images in Figure 5.28, which shows representative PEEK/HX-1000 20/80, 50/50 and 70/30 worn surfaces, with those of in Figures 5.18 through 5.20 is instrumental in verifying the similar nature of the processes by which material removal occurred in HX-1000 and the 20/80, 50/50 and 70/30 blends.

Common to the PEEK/HX-1000 20/80, 50/50 and 70/30 blends were friction trends that, within the selected range of tests temperatures, paralleled those followed by wear. Hence, for these blends friction can be regarded, for the most part, as a direct measure of the deformation and fracture energies dissipated during the wear process. At
Figure 5.26  Profiles of wear tracks generated during the sliding of the as-molded PEEK/HX-1000 70/30 blend.
Figure 5.27 Profiles of wear tracks generated during the sliding of the annealed PEEK/HX-1000 70/30 blend.
Figure 5.28  (a) PEEK/HX-1000 20/80 surface worn at 50 °C; (b) PEEK/HX-1000 50/50 surface worn at 180 °C; (c) As-molded PEEK/HX-1000 70/30 surface worn at 100 °C; (d) Annealed PEEK/HX-1000 70/30 surface worn at 225 °C. Arrows indicate sliding direction.
temperatures above 150 °C, configurational readjustments of amorphous polymer chains, which become possible via the thermal activation of molecular relaxation processes within the constituent phases (see Fig 5.1(a)), afford an extra energy dissipation mechanism contributing to the friction of the 20/80, 50/50 and 70/30 blends.

Friction and wear results for the PEEK/HX-1000 90/10 blend are shown in Figure 5.29. In general, the coefficient of friction showed a relatively ample variability within the range of test temperatures, as seen in Figure 5.29(a). At sliding temperatures under 150 °C, the coefficient of friction of the 90/10 blend varied between 0.13 to 0.30 attaining values ranging from lower to noticeably higher than those attained by PEEK within the same temperature range. At temperatures over 150 °C, a propensity to slide with lower friction than PEEK appeared to exist. By recalling that the 90/10 blend had a morphology consisting of HX-1000 droplets dispersed in a PEEK matrix, and by recognizing that such droplets can be viewed as filler particles which are rigid below and increasingly soft above 180 °C (see data for HX-1000 in Figure 5.1(b)), the following speculation on the observed frictional behavior of the 90/10 blend can be made.

During processing, the degree of dispersion of the HX-1000 droplets throughout the bulk of the molded plaques from which the PEEK/HX-1000 90/10 sliding test specimens were cut varied from plaque to plaque. At sliding temperatures below 180 °C, 90/10 specimens with a low concentration of TLCP droplets in the subsurface region adjacent to the contact interface would then exhibit frictional characteristics quite similar to those of PEEK. In this case, highly deformed contacting surfaces characterized, presumably as a result of plastic reorientation of molecules by the surface tractions, by high degrees of molecular orientation in the direction of rubbing, provided smooth PEEK–like, low friction sliding counterfaces. By contrast, 90/10 specimens with a more uniformly
Figure 5.29  Sliding test results for the PEEK/HX-1000 90/10 blend: (a) Temperature dependence of the coefficient of friction; (b) Temperature dependence of the cumulative linear wear. Bars show range of the data (PEEK and HX-1000 data shown for comparison).
dispersed TLCP phase or high concentrations of HX-1000 droplets within the subsurface dissipation zone would tend to show higher coefficients of friction. This tendency can be tentatively ascribed to the activation of an additional energy dissipation mechanism in the contact region, namely brittle cracking, due to a significant drop in ductility in the surface layers in connection with the presence of the hard HX-1000 phase. The micrographs in Figures 5.30(a) and 5.30(b), which show PEEK/HX-1000 90/10 sliding surfaces worn at 100 °C, would seem to corroborate the preceding observations.

At sliding temperatures above 180 °C, 90/10 specimens with the expected or higher concentrations of HX-1000 droplets within their surface layers, would exhibit a tendency to slide with lower friction than PEEK. Low friction coefficients would arise when HX-1000 droplets removed from the PEEK matrix are easily deformed (due to their liquid crystalline nature), under the action of the intense highly directional strain field prevailing in the contact zone, into structures possessing a high degree of molecular orientation in the direction of sliding, which effectively lubricate the sliding interface. Conversely, low degrees of dispersion of the HX-1000 phase within the dissipation zone beneath the sliding surface would result in coefficients of friction as high in magnitude as those which characterized the sliding of PEEK in the region above the glass transition.

Inspection of the data in Figure 5.29(b) indicates that the elevated temperature wear performance of the 90/10 blend was, with the exception of the noticeable improvement seen above 180 °C, very similar to that of neat PEEK. Furthermore, examination of recovery parameter data (Fig. 5.31), wear track profiles (Fig. 5.32) and worn surfaces (Fig. 5.30) reveals that, within the temperature range between 20 °C and 225 °C, the wear process of the 90/10 resembled, to a large extent, that of PEEK. Active wear mechanisms and their relative intensities remained practically unchanged. Moreover, the shift in material removal
Figure 5.30  SEM micrographs of PEEK/HX-1000 90/10 worn surfaces generated at: (a) 100 °C, low friction: $\mu = 0.15$; (b) 100 °C, high friction: $\mu = 0.28$; (c) 155 °C; and (d) 225 °C. Arrows indicate sliding direction.
Figure 5.31  Temperature dependence of the recovery parameter for the PEEK/HX-1000 70/30 blend. Bars show range of the data (PEEK and HX-1000 data shown for comparison).
Figure 5.32 Profiles of wear tracks generated during the sliding of the PEEK/HX-1000 90/10 blend.
mechanism undergone by PEEK at temperatures above 150 °C did also occur in the case of the 90/10 blend (see Figs. 4.6(b)–(d) and 5.30(c)–(d)). Crystallization of the PEEK phase while sliding at temperatures above its T_g, as explained in section 4.3.2.1 (see Fig. 4.7), can be regarded as the effect leading to the latter occurrence.

At present, the nature of the synergy leading to the improvement in wear performance exhibited by the 90/10 blend above 180 °C (see Fig. 5.29(b)) has not been investigated thoroughly. However, it is speculated that lubrication of the sliding interface by the HX-1000 phase combined with the ability of the PEEK phase to crystallize while sliding at temperatures above the T_g, resulted in the observed lower linear wear levels. This could have occurred as follows. As in the case of PEEK, hardening of the surface layers occurred during sliding of the 90/10 blend at 200 °C and 225 °C. However, in the latter case, the lubricating action of the HX-1000 phase retarded the process of disruption of the sliding surface allowing the development of PEEK crystallites with higher degrees of perfection in the subsurface regions. Leading to this development would be increased times of exposure of the subsurface regions to the crystallization temperatures [73, 86]. Higher degrees of crystalline perfection within the 90/10 surface layers translated into a superior hardness and, therefore, into an enhanced resistance to penetration by the rider (steel ball) during sliding.

5.4 Summary

A study aimed at assessing the potential of TLCP in-situ reinforcement as a means to enhance the elevated temperature tribological performance of PEEK, as well as at advancing the understanding of the tribology of in-situ composites in terms of structure-
property relationships has been conducted. The study involved the examination of the dry sliding friction and wear behavior of injection molded blends of PEEK and HX-1000 (an amorphous thermotropic liquid crystalline copolyester) within the temperature range from 20 °C to 250 °C. The compositions (in weight ratios) of the PEEK/HX-1000 blends selected as test materials were 100/0, 90/10, 70/30, 50/50, 20/80 and 0/100. The dynamic mechanical behavior (also across the 20 °C–250 °C temperature range), morphology and processability (via dynamic shear viscosity measurements) of the selected test materials were investigated in conjunction with their tribology.

Dynamic mechanical thermal analysis (DMTA) results showed that PEEK and HX-1000 coexisted as separate phases in the blended state. Further, dynamic modulus measurements indicated that the addition of HX-1000 had a reinforcing effect on PEEK. The latter effect, however, was prevalent at temperatures under the $T_g$ of the TLCP (ca. 180 °C); marked thermal softening above the glass transition prevented the HX-1000 from being effective as a reinforcing agent at higher temperatures. Morphological examination revealed that HX-1000 and the PEEK/HX-1000 blends with TLCP concentrations of 30 wt% or more developed skin-core morphologies (i.e., morphologies consisting of three well defined macrolayers: 2 skins with a core in between). The skin layers were composed of a series of sublayers in which a high degree of molecular orientation in the mold fill direction was apparent. Orientational anisotropy was less pronounced in the HX-1000 core and not present in the core layers of the blends. PEEK and the PEEK/HX-1000 90/10 blend did not show skin-core morphologies; both materials were isotropic in nature. The blend, however, showed a heterogeneous microstructure consisting of minute TLCP droplets finely dispersed throughout the PEEK matrix. Dynamic shear viscosity measurements performed at 360 °C (the temperature at which the test polymers were
processed) indicated that the addition of liquid crystalline HX-1000 to PEEK can, through a melt-lubricating effect, enhance the processability of the isotropic thermoplastic resin.

In all the polymers tested, the activation of the molecular relaxation process associated with the glass transition resulted in marked changes in tribological performance. HX-1000 and the PEEK/HX-1000 20/80 and 50/50 blends failed catastrophically when sliding at temperatures within the glass transition region. In PEEK and the PEEK/HX-1000 70/30 and 90/10 blends, the onset of the glass transition brought about significant increases in friction and wear. Viscoelastic plowing and removal of material occurred predominantly during the sliding of HX-1000 and the PEEK/HX-1000 20/80 and 50/50 and 70/30 blends. The process of removal of material in these polymers was found to involve the sequential disruption of the highly anisotropic skin sublayers. Fibrillation (easy fracture along the direction coinciding with the axis of anisotropy) in the latter sublayers appeared to mark the onset of the disruption mechanism. Viscoelastic and plastic plowing of the sliding surface predominated during the wear of PEEK and the PEEK/HX-1000 90/10 blend in the region below the glass transition. Above the glass transition, however, moderate removal of material appeared to replace plastic plowing as one of the dominant friction and wear mechanisms.

The results from the sliding tests performed on the PEEK/HX-1000 70/30 blend appeared to indicate that TLCP in-situ reinforcement was instrumental in ameliorating the tribological performance of PEEK in the region above the glass transition. The observed improvements were, however, moderate and restricted to the temperature range between 150 °C and 200 °C. Marked thermal softening of HX-1000 in the glass transition region was found to be the factor effectively limiting the potential of the TLCP as load-bearing capacity and tribological performance enhancer for PEEK at elevated temperatures.
Interestingly, in spite of being inconsequential in terms of improving the thermal softening characteristics of PEEK at temperatures above 180 °C, the addition of 10 wt% HX-1000 to the engineering thermoplastic was seen to result in appreciable improvements in wear performance at and above 200 °C. The nature of the synergistic interaction between the PEEK and TLCP phases leading to such development is not well understood at the present time. It is speculated, however, that the ability of PEEK to crystallize while sliding at temperatures above its T_g in combination with the acting of the HX-1000 phase (in the form droplets) as an effective solid lubricant—which protected the subsurface regions in the contact zone while they hardened as a result of PEEK crystallization—are factors contributing to the observed synergy.

Results from this study appeared to indicate that the potential of TLCP in-situ reinforcement as a means to produce thermoplastic-based performance tribomaterials is real. Mechanical property, tribological performance and processability enhancements were all seen to occur in connection with the incorporation of liquid crystalline HX-1000 into PEEK. Effectively limiting the potential of HX-1000 as elevated temperature tribological performance enhancer for PEEK was a stability of mechanical properties at high temperatures which was not significantly better than that of PEEK's (notice that the softening temperatures of PEEK and HX-1000 are only about 30 °C apart). The utilization of a TLCP with a superior retention of mechanical properties at high temperatures (e.g., a semicrystalline TLCP) could lead to improved results. The inherent anisotropy of in-situ composites is another factor that could be exploited to achieve superior tribological performance. For instance, sliding along the axis of anisotropy could, in principle, lead to lower coefficients of friction and improved wear resistance. Factors to which the latter effects would be coupled are the elimination of plastic reorientation of molecules as an
interfacial energy dissipation mechanism, and superior mechanical properties, strength in particular, along the axis of anisotropy.
CHAPTER 6

Elevated Temperature Tribology of Blends of PEEK, PEI and a Thermotropic Liquid Crystalline Polymer

Synopsis

The dry sliding friction and wear behavior of in-situ composite systems based on blends of Polyetheretherketone (PEEK), Polyetherimide (PEI) and a thermotropic liquid crystalline polymer (TLCP) was investigated as a function of operating temperature. Friction and wear measurements were performed at selected temperatures within the range from 20 °C to 250 °C. The specific in-situ composite systems investigated consisted of binary PEEK/PEI 85/15 and 70/30 isotropic thermoplastic matrices, and HX-1000, a thermotropic liquid crystalline copolyester, acting as the reinforcing phase. Although individually both PEEK/PEI matrices and HX-1000 were seen to undergo catastrophic tribological failure at their respective glass transition temperatures \( T_g \), the ternary PEEK/PEI/HX-1000 blends were able to maintain sliding at temperatures well in excess of the \( T_g \)s of their constituent phases. This synergistic behavior is explained in terms of TLCP reinforcement and PEEK cold-crystallization. The presence of PEI, a potential compatibilizer for immiscible PEEK and HX-1000 (PEI exhibits miscibility with both PEEK and HX-1000), in the ternary PEEK/PEI/HX-1000 blends did not appear to be beneficial in terms of enhancing tribological performance at elevated temperatures. Active friction and wear mechanisms are described in relation to the microstructure of the polymer.
systems investigated. Additionally, the effects of TLCP concentration and thermal transitions on the mechanical properties and tribological performance of the PEEK/PEI TLCP blends are discussed.

6.1 Introduction

This chapter describes an experimental study of the elevated temperature tribology of ternary in-situ composite systems based on blends of Polyetheretherketone (PEEK), Polyetherimide (PEI) and HX-1000, a thermotropic liquid crystalline polymer (TLCP).

It has been reported that compatibilization (enhancement of interfacial strength) of an immiscible polymer mixture can be achieved through the addition of a third polymer which exhibits miscibility with both of the constituent polymers of the original mixture [87]. In this study the viability of this concept is explored. PEI, which exhibits full miscibility with PEEK [50, 51] and partial miscibility with HX-1000 [48, 49], is used with the intent of bringing together immiscible PEEK and HX-1000 (see Section 5.3.1). The hypothesis that the incorporation of PEI can, through the promotion of interfacial activity between PEEK and HX-1000, enhance mechanical behavior and, ultimately, tribological performance is examined.

The ternary systems chosen for study were PEEK/PEI/HX-1000 77/13/10, 60/10/30 and 49/21/30. The former two compositions are equivalent to those of (PEEK/PEI 85/15)/HX-1000 90/10 and 70/30 blends, respectively. Similarly, the third ternary composition is equivalent to that of a (PEEK/PEI 70/30)/HX-1000 70/30 blend. In Chapter 4, it was shown that PEI possess rather undesirable friction and wear characteristics (see Section 4.3.2.2) and that PEI fractions larger than 30 wt% would result in PEEK/PEI blends with poor tribological performances. Knowledge of these facts was
used as the criterion for selection of the PEI fractions present in the ternary PEEK/PEI/HX-1000 blends chosen as test materials in the present study.

In what follows, the results from dry sliding tests carried out on the polymers systems under investigation under controlled temperature conditions are reported. The sliding tests were conducted at selected temperatures across the range from 20 °C to 250 °C. The tribological behavior of the test materials is discussed in relation to their microstructure and thermally activated molecular relaxation behavior. Active sliding friction and wear mechanisms are also discussed.

6.2 Experimental

6.2.1 Materials

The base materials used in this study were Victrex® PEEK 380-G, supplied by ICI. PEI Ultem® 1000, manufactured by GE Plastics, and HX-1000, an amorphous thermotropic liquid crystalline copolyester produced by DuPont. Three PEEK/PEI/HX-1000 blends with weight ratios of 77/13/10, 60/10/30 and 49/21/30 were compounded using a single screw extruder. The compositions of the former two ternary blends were equivalent to those of (PEEK/PEI 85/15)/HX-1000 blends with weight ratios of 90/10 and 70/30, respectively. The composition of the third PEEK/PEI/HX-1000 blend corresponded to that of a (PEEK/PEI 70/30)/HX-1000 70/30 blend. Following compounding, the PEEK/PEI/HX-1000 blends were injection molded into plaques according to the specifications given in section 3.1.2. To investigate the effects of annealing on tribological performance, a number of injection molded plaques of the PEEK/PEI/HX-1000 60/10/30 blend were heat treated in a vacuum oven at 230 °C for 12
hours.

6.2.2 Dynamic Mechanical Thermal Analysis

DMTA was performed on each of the ternary PEEK/PEI/HX-1000 blends used as test materials in order assess the effects of thermally activated molecular relaxation processes on their mechanical behavior and tribological performance as well as to gain insight into their phase behavior.

Dynamic mechanical measurements were made across the temperature range from 20 °C to 250 °C using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer. The selected test configuration and operating mode were, respectively, single cantilever bending and fixed-frequency, constant-amplitude forced flexural oscillation. Mechanical loss factor (tan δ) and dynamic storage modulus were measured and recorded during thermoscans performed across the temperature range of interest. With the recorded data, relaxation spectra were generated for the test polymers. Further experimental details on DMTA testing can be found in Section 3.2.2.

6.2.3 X-ray Diffraction Measurements

Wide-angle x-ray diffraction (WAXD) was used to qualitatively investigate the development of crystallinity in the test polymers. WAXD scattering patterns for selected PEEK/PEI/HX-1000 samples were generated and recorded using a Philips PW-1840 diffractometer. A step scan interval of 2θ = 0.01° and a scanning speed of 0.02 (°2θ/s) were selected. In all cases CuKα1 radiation was used.
6.2.4 Microstructural Characterization

The microstructures of the PEEK/PEI/ HX-1000 blends were investigated by means of scanning electron microscopy (SEM). SEM was carried out on an International Scientific Instruments (ISI) SX-40 scanning electron microscope. SEM samples were prepared according to the procedures described in Section 3.2.3.

6.2.5 Tribological Evaluation

Tribological testing was carried out using a pin-on-disk apparatus (see Fig. 3.3). For each of the materials under study, a series of unlubricated sliding tests were conducted at selected temperatures in the range from 20 °C to 250 °C. For a complete description of experimental procedures, test setup and other important experimental details concerning tribological evaluation, refer to Section 3.2.1.

6.3 Results and Discussion

6.3.1 Dynamic Mechanical Thermal Analysis

Mechanical loss factor measurements for the as-molded PEEK/PEI/HX-1000 blends are shown in Figures 6.1(a). Regarding the temperatures at which the absolute maxima in tan δ (α peaks) occur in Figure 6.1(a) as glass transition temperatures (Tg), the Tg's of the PEEK/PEI/HX-1000 77/13/10, 60/10/30 and 49/21/30 blends were determined to be 153 °C, 152 °C and 168 °C, respectively. The location of the α peaks of the PEEK/PEI/HX-1000 77/13/10 and 60/10/30 blends is consistent with the formation of homogeneous PEEK/PEI 85/15 phases (see Fig. 4.1) in both ternary blends. The broad nature of the α peak of the PEEK/PEI/HX-1000 49/21/30 blend is attributable to the
Figure 6.1  Temperature dependence of the mechanical loss factor for: (a) as-molded PEEK/PEI/HX-1000 blends; (b) as-molded parent polymers.
overlapping of the glass transitions of a homogeneous PEEK/PEI 70/30 phase (see Fig. 4.1) and HX-1000 (see Fig. 6.1(b)). The shoulders on the high temperature side of the α peaks in the tan δ curves of the PEEK/PEI/HX-1000 77/13/10 and 60/10/30 blends, can be associated with the glass transition of the HX-1000 phase. The determination of whether or not PEI/HX-1000 phases were formed on the basis of the tan δ data obtained for the PEEK/PEI/HX-1000 blends was precluded by the poor resolution of the glass transitions of PEI and HX-1000 and the overlapping nature of the α peaks of the PEEK/PEI and HX-1000 phases.

The appreciable difference in intensity that existed between the glass transitions of PEEK and the PEEK/PEI/HX-1000 blends (notice the difference in height among the pertinent α peaks of tan δ in Fig. 6.1), suggested that PEEK was semicrystalline in the as-molded neat state and amorphous in the as-molded blended state—notice that PEEK is the only crystallizable phase in the PEEK/PEI/HX-1000 blends, and that the glass transitions of the latter blends correspond with the onset of major relaxations in PEEK-rich homogeneous PEEK/PEI phases.

WAXD scans performed on as-molded PEEK and PEEK/PEI/HX-1000 specimens, representative examples of which are shown in Figure 6.2, validated the foregoing observation. In fact, the peaks at 2θ ≈ 19°, 21°, 23° and 29° (PEEK crystalline reflections [80]) seen in the diffraction scan shown in Fig. 6.2(a) attest to the presence of a crystalline phase in as-molded PEEK. On the other hand, the broad WAXD intensity maxima (amorphous halos) characterizing the scans of the as-molded PEEK/PEI/HX-1000 blends (Figs. 6.2(b)–(d)) evidence the completely amorphous nature of these ternary mixtures [59, 60].

Plots showing the dependence upon temperature of the storage modulus of the PEEK/PEI/HX-1000 blends are presented in Figure 6.3. The following emerge as the
Figure 6.2  Typical WAXD scans for as-molded PEEK (a) and PEEK/PEI/HX-1000 blends (b)-(d).
Figure 6.3  Temperature dependence of the storage modulus for the as-molded PEEK/PEI/HX-1000 blends.
relevant observations to be made with respect to the results contained in the latter figure. First, as might have been anticipated, larger fractions of rigid HX-1000 (see Fig. 5.1(b)) resulted in stiffer (at temperatures below the T_g of HX-1000, naturally) PEEK/PEI/HX-1000 blends. Secondly, as a direct consequence of being amorphous in nature, the three as-molded PEEK/PEI/HX-1000 blends underwent abrupt drops in modulus (i.e., marked thermal softening) at their respective T_g's. Thirdly, in correspondence with its slightly higher T_g, the PEEK/PEI/HX-1000 49/21/30 blend exhibited a moderately better retention of modulus at elevated temperatures than the PEEK/PEI/HX-1000 77/13/10 and 60/10/30 blends. Fourth, and last, all three PEEK/PEI/HX-1000 blends were seen to experience a rise in modulus above their respective T_g's; this phenomenon evidenced the ability of the PEEK phase to cold-crystallize in the region above the glass transition [67].

As corroborated WAXD scans such as the ones shown in Figure 6.4, annealing induced PEEK crystallization (see Fig. 6.3(a)) in the PEEK/PEI/HX-1000 60/10/30 blend. This development had two main effects on the properties of the PEEK/PEI/HX-1000 60/10/30 blend (see Fig. 6.5). One was a substantial reduction in the intensity of the glass transition and the other, a 22 °C increase in T_g. Directly linked to these effects were a reduced ability to dissipate energy under dynamic deformation conditions and a moderate improvement in modulus retention at elevated temperatures.

### 6.3.2 Solid State Morphologies

Examination of PEEK/PEI/HX-1000 fracture surfaces by means of electron microscopy revealed that the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends possessed skin-core structures similar in appearance to those described in Chapter 5 (see Section 5.3.3) for HX-1000 and the PEEK/HX-1000 blends with TLCP weight percentages of 30
Figure 6.4  Typical WAXD scans for the as-molded (top) and annealed (bottom) PEEK/PEI/HX-1000 60/10/30 blends.
Figure 6.5  Temperature dependence of the mechanical loss factor (a) and storage modulus (b) for the as-molded and annealed PEEK/PEI/HX-1000 60/10/30 blends.
and above. By contrast, and probably due to its low TLCP content, the PEEK/PEI/HX-1000 77/13/10 blend did not exhibit a skin-core structure.

The inner morphologies of the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends were found to closely resemble that of the PEEK/HX-1000 70/30 blend (see Fig. 5.12). As in the case of the latter blend, the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends exhibited skin layers consisting of thin, densely packed sublayers possessing a high degree of orientational anisotropy along the axis coinciding with the mold fill direction. Moreover, the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 core layers did not appear to be characterized by the presence of sublayered structures or a distinct axis of orientational anisotropy.

SEM micrographs of representatives fracture surfaces of the PEEK/PEI/HX-1000 77/13/10, 60/10/30 and 49/21/30 are shown in Figures 6.6 and 6.7.

6.3.3 Friction and Wear Measurements

Plots showing the effects of sliding temperature on the steady state coefficient of friction and cumulative linear wear of the as-molded PEEK/PEI/HX-1000 77/13/10 blend are presented in Figure 6.8. For comparative purposes, the pertinent friction and wear curves of PEEK/PEI 85/15 (see Fig. 4.13), the binary isotropic matrix in this case, and HX-1000 (see Fig. 5.14), have also been plotted in Figure 6.8.

It is seen from Figure 6.8 that at sliding temperatures below the $T_g$ the tribological performance of the PEEK/PEI/HX-1000 77/13/10 blend was comparable to that of PEEK/PEI 85/15. At sliding temperatures in the vicinity of and above the $T_g$, however, an interesting phenomenon was seen to occur. While PEEK/PEI 85/15 and HX-1000, both amorphous in nature, underwent catastrophic tribological failure (gross loss of form
Figure 6.6 (a) PEEK/PEI/HX-1000 77/13/10 fracture surface; (b) skin-core structure of the PEEK/PEI/HX-1000 60/10/30 blend; (c) higher magnification view of PEEK/PEI/HX-1000 60/10/30 skin layer; (d) higher magnification view of PEEK/PEI/HX-1000 60/10/30 core layer.
Figure 6.7  Solid state morphology of the PEEK/PEI/HX-1000 49/21/30 blend: (a) Skin-core structure; (b) skin layer; (c) core layer.
Figure 6.8  Temperature dependence of the coefficient of friction (a) and cumulative linear wear (b) for the PEEK/PEI/HX-1000 77/13/10 blend. Bars show range of the data (PEEK/PEI 85/15 and HX-1000 friction and wear curves shown for comparison).
accompanied by seizure) at their respective $T_g$s, the PEEK/PEI/HX-1000 77/13/10 blend, also amorphous in nature, did not. In other words, the drastic deterioration of mechanical properties (the underlying cause of catastrophic tribological failure as seen in this study), or severe thermal softening, which characterizes the onset of the glass transition in amorphous polymers, was averted in the case of the PEEK/PEI/HX-1000 77/13/10 blend. It is apparent that the uncharacteristic behavior of the PEEK/PEI/HX-1000 77/13/10 blend at and above the $T_g$ derived from a synergistic interaction between the isotropic and liquid crystalline phases in the ternary blend. Such interaction has been rationalized as follows.

SEM examination of worn PEEK/PEI/HX-1000 77/13/10 surfaces (see Fig. 6.9 for representative examples) showed that a significant portion of the wear debris generated during sliding remained in the contact region and formed a layer of agglomerated, highly deformed material which covered the wear tracks. Preferential molecular orientation in the direction of sliding, and the presence of rigid liquid crystalline HX-1000, would appear to have imparted enough strength to the latter layer so it was able to effectively retard the process of damage to the surface layers underneath. As a direct consequence of this, the appropriate conditions (time and temperature) existed during the sliding of the PEEK/PEI/HX-1000 77/13/10 blend at temperatures above the $T_g$ for PEEK cold-crystallization to occur in the region beneath the contact interface. Mechanical property changes, such as increases in hardness and strength, arising from the phase transformation undergone by the PEEK phase are believed to have made the sliding of the PEEK/PEI/HX-1000 77/13/10 blend at and above the $T_g$ viable.

In reference to the issue of PEEK cold-crystallization during sliding, two observations ought to be made. First, recall that the ability of PEEK to cold-crystallize was made apparent by the DMTA results shown in Figure 6.2, as discussed in Section
Figure 6.9  SEM micrographs of PEEK/PEI/HX-1000 77/13/10 worn surfaces generated at 120 °C (top) and 205 °C (bottom). Arrows indicate sliding direction.
6.3.1. Secondly, WAXD scans performed on the sliding surfaces of PEEK/PEI/HX-1000 77/13/10 specimens before and after sliding experiments carried out at temperatures above the $T_g$ of the blend being evaluated (ca. 154 °C) confirmed the occurrence of PEEK cold-crystallization during tribological testing. Representative examples of the WAXD scans in question are shown in Figure 6.10.

Examination of the temperature dependence of the recovery parameter data (Fig. 6.11) in conjunction with profilometry traces of wear track cross-sections (see Fig. 6.12 for representative examples) indicated that viscoelastic and plastic plowing as well as material removal were the active wear modes during the sliding of the PEEK/PEI/HX-1000 77/13/10 blend. Of the three modes, viscoelastic plowing and removal of material were found to be predominant throughout the entire range of test temperatures; plastic plowing was, in most instances, minimal (notice the relative proportions of the cross-sectional areas of the wear groove and ridges of plastically deformed material on the sides of the wear tracks in Figure 6.12).

As corroborated by the results presented in Figures 6.11 and 6.12, at temperatures below the $T_g$ (ca.154 °C), the wear of the PEEK/PEI/HX-1000 77/13/10 blend was mild and viscoelastic plowing accounted for most of the frictional energy dissipated at the sliding surface. At temperatures in the vicinity of the $T_g$, and coupled to the onset of the glass transition, a noticeable change in the tribological behavior of the PEEK/PEI/HX-1000 77/13/10 blend was seen to occur. Such change was characterized by a pronounced intensification of the process of removal of material and a significant deterioration of the ability to undergo viscoelastic deformation during sliding. However, in the sliding regime above the glass transition, and apparently in connection the synergy described above, the latter situation was reversed; as sliding temperatures increased, viscoelastic plowing was seen to intensify substantially and removal of material became progressively less severe.
Figure 6.10 WAXD scans of PEEK/PEI/HX-1000 77/13/10 sliding surfaces taken before and after tribological evaluation at 180 °C (top) and 225 °C (bottom). For clarity, the "after" scans have been displaced upward by 1000 cps (counts per second).
Figure 6.11  Temperature dependence of the recovery parameter for the PEEK/PEI/HX-1000 77/13/10 blend. Bars show range of the data (PEEK/PEI 85/15 and HX-1000 data shown for comparison).
Figure 6.12  Profiles of wear tracks generated during the sliding of the PEEK/PEI/HX-1000 77/13/10 blend.
Worth noting at this point is that the hardening of the PEEK/PEI/HX-1000 77/13/10 surface layers due to PEEK cold-crystallization in combination with the protective action of a strong layer of agglomerated, highly deformed wear debris covering the wear track would explain the observed mitigation of the material removal process as well as the existence of a mostly viscoelastic state of deformation in the regions beneath the contact zone. As for the inverse relationship that existed between the severity of the process of removal of material and sliding temperature in the region above the $T_g$, the phenomenon can be explained as follows. As sliding temperatures rose above the $T_g$, the intense and highly directional strain field prevailing in the contact zone produced increasingly higher degrees of molecular orientation along the sliding direction in the layer of material covering the wear tracks (notice that molecular mobility is enhanced at and above the glass transition). As the degree of molecular orientation increased, the strength of the latter layer along the sliding direction improved. This, together with the hardening of the surface layers as a result of PEEK cold-crystallization, could have led to the increasing resistance to material removal seen during the sliding of the PEEK/PEI/HX-1000 77/13/10 blend above the glass transition region. Furthermore, the intensification of the viscoelastic plowing wear mode also seen in the latter sliding regime can be accounted for by noticing that rising temperatures above the $T_g$ must have rendered the material in the dissipation zone beneath the contact interface increasingly "rubbery."

Although instrumental in preventing the occurrence of catastrophic tribological failure at $T_g$ of the isotropic thermoplastic matrix, the incorporation of 10 wt% HX-1000 into PEEK/PEI 85/15 did not result in an in-situ composite with a high temperature tribological performance that could be categorized as outstanding. In fact, the friction and wear levels exhibited by TLCP-reinforced PEEK/PEI 85/15 at sliding temperatures above the $T_g$ were rather high. The fact that in terms of stability of mechanical properties at high
temperatures no substantial differences existed between the reinforcing HX-1000 and the isotropic PEEK/PEI 85/15 phases (notice the proximity of the Tgs of both phases), appeared to prevent the achievement of superior levels of tribological performance in the case of the PEEK/PEI/HX-1000 77/13/10 blend.

Friction and wear results from the sliding tests performed on the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends are shown in Figures 6.13 and 6.14, respectively. It is seen from these results that, in spite of their amorphous nature, the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends, did not undergo catastrophic tribological failure at the onset of their respective glass transitions. The same synergy that came into effect during the sliding of the as-molded PEEK/PEI/HX-1000 77/13/10 blend appeared to have led to the latter development. The fact that the formation of a layer of agglomerated, highly deformed wear debris covering the wear tracks (see Fig. 6.15) as well as PEEK cold-crystallization (see Figs. 6.16) were seen to occur during the sliding of the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends seemed to validate the foregoing observation.

It must be noted, however, that, in terms of protecting the sliding surface against disruption, the layers of agglomerated debris covering the wear tracks of the latter two blends were found to be appreciably less effective than those covering the PEEK/PEI/HX-1000 77/13/10 wear tracks. A factor leading to this situation appeared to be a restricted capacity to accommodate large deformations on the part of the layers formed during the sliding of the blends containing 30 wt% HX-1000. Supporting the latter statement was the fact that the layers covering the wear tracks of the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends were seen to deteriorate at a faster rate and to suffer more extensive damage than those covering the wear tracks of the PEEK/PEI/HX-1000 77/13/10 blend (see Figs. 6.10 and 6.15).
Figure 6.13  Temperature dependence of the coefficient of friction (a) and cumulative linear wear (b) for the as-molded and annealed PEEK/PEI/HX-1000 60/10/30 blends. Bars show range of the data (PEEK/PEI 85/15 and HX-1000 friction and wear curves shown for comparison).
Figure 6.14  Temperature dependence of the coefficient of friction (a) and cumulative linear wear (b) for the PEEK/PEI/HX-1000 49/21/30 blend. Bars show range of the data (PEEK/PEI 70/30 and HX-1000 friction and wear curves shown for comparison).
Figure 6.15 SEM micrographs of PEEK/PEI/HX-1000 60/10/30 (a-b) and 49/21/30 (c-d) worn surfaces generated at 120 °C (top) and 205 °C (bottom). Arrows indicate sliding direction.
Figure 6.16  Representative examples of WAXD scans of as-molded PEEK/PEI/HX-1000 60/10/30 (top) and 49/21/30 (bottom) sliding surfaces taken before and after tribological evaluation in the sliding regime above the glass transition. For clarity, the "after" scans have been displaced upward by approximately 1000 cps (counts per second).
Comparison of the results contained in Figures 6.8, 6.13 and 6.14 shows that the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends exhibited friction and wear performance levels that fell below that of their 77/13/10 counterpart. This outcome, it must be pointed out, seemed to be in direct correspondence with the different nature and intensity of the dissipative processes predominating at the sliding interfaces of the blends with 10 wt% and 30 wt% TLCP, as noted in the preceding paragraph.

Recovery parameter data and representative wear track profiles for the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends are shown in Figure 6.17 through 6.19. Examination of the results contained in the latter figures reveals that, as in the case of the as-molded PEEK/PEI/HX-1000 77/13/10 blend (see Figs. 6.11 and 6.12), viscoelastic and plastic plowing along with removal of material were the wear modes active during the sliding of the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends. Of the three wear modes, viscoelastic plowing and removal of material appeared to predominate over plastic plowing at all sliding temperature. Relative to the as-molded PEEK/PEI/HX-1000 77/13/10 blend, however, the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends showed a reduced ability to deform viscoelastically during sliding and, at the same time, underwent more extensive removal of material. As might have been expected, larger fractions of glassy, rigid phases (PEI and HX-1000) or, equivalently, lower PEEK weight percentages, rendered the tribological behavior of the as-molded PEEK/PEI/HX-1000 blends more brittle-like in nature.

The mechanism by which removal of material occurred during the sliding of the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends, was found to be the same as that observed for HX-1000 and the PEEK/HX-1000 blends with TLCP weight percentages of 30 and above. In other words, the mechanism in question involved the sequential disruption of surface layers (see Section 5.3.4.1 for a detailed description of this
Figure 6.17  Temperature dependence of the recovery parameter for the PEEK/PEI/HX-1000 60/10/30 (top) and 49/21/30 (bottom) blends. Bars show range of the data (PEEK/PEI 85/15, 70/30 and HX-1000 data shown for comparison).
Figure 6.18  Profiles of wear tracks generated during the sliding of the as-molded PEEK/PEI/HX-1000 60/10/30 blend.
Figure 6.19  Profiles of wear tracks generated during the sliding of the PEEK/PEI/HX-1000 49/21/30 blend.
mechanism). The activation of such material removal mechanism was in line with the fact that, as HX-1000 and the PEEK/HX-1000 blends with weight ratios of 70/30 and higher, the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends exhibited skin-core morphologies. Clear evidence of the activation of the mechanism of sequential disruption of surface layers during the sliding of the as-molded PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends can be found in the micrographs shown in Figures 6.15(b) and (d) (see also Figs. 5.18 and 5.20).

Annealing did not appear to have any major beneficial impact on the tribological behavior of the PEEK/PEI/HX-1000 60/10/30 blend. Hardening of the latter blend as a consequence of heat treatment resulted in both increased material losses and a reduced ability to undergo deformation (viscoelastic/plastic) during sliding. Evidence of the impact of annealing on the deformation characteristics of the PEEK/PEI/HX-1000 60/10/30 blend can be found in Figure 6.17 (top). Moreover, as can be inferred from the data in Figure 6.13, the friction and wear performance exhibited by the as-molded PEEK/PEI/HX-1000 60/10/30 blend was not greatly affected by heat treatment.

Finally, in Figure 6.20 the friction and wear results obtained for the two as-molded PEEK/PEI/HX-1000 blends with 30 wt% TLCP used in this study are compared against the corresponding results for the PEEK/HX-1000 70/30 blend (shown previously in Figure 5.24). Although all blends are seen to exhibit similar friction-temperature trends, it is apparent that a clear difference in wear performance existed, particularly at high temperatures, between the ternary and binary blends. At sliding temperatures above 150 °C the PEEK/PEI/HX-1000 60/10/30 and 49/21/30 blends underwent more pronounced wear than the PEEK/PEI 70/30. Such occurrence, i.e., the deterioration of the resistance to penetration and material removal—deriving from a degeneration of mechanical properties—
Figure 6.20  Temperature dependence of the cumulative linear wear (top) and coefficient of friction (bottom) for the as-molded PEEK/HX-1000 70/30, PEEK/PEI/HX-1000 60/10/30 and PEEK/PEI/HX-1000 49/21/30 blends. Bars show range of the data.
of the PEEK/PEI/HX-1000 blends, indicated that, at least at the concentration levels used (i.e., 10 and 21 wt%), and in spite of any interfacial activity it might have promoted between PEEK and HX-1000, PEI was, ultimately, not effective as a high temperature tribological performance enhancer for immiscible PEEK/HX-1000 blends.

6.4 Summary

The elevated temperature tribology of in-situ composite systems consisting of PEEK/PEI 85/15 and 70/30 isotropic thermoplastic matrices and the thermotropic liquid crystalline copolyester HX-1000 acting as the reinforcing phase was investigated. The specific tribological phenomena studied was unlubricated sliding. Friction and wear measurements were performed at selected temperatures within the range from 20 °C to 250 °C. Although individually both PEEK/PEI matrices and HX-1000 were seen to undergo catastrophic tribological failure at their respective glass transition temperatures (Tgs), the ternary PEEK/PEI/HX-1000 blends were able to maintain sliding at temperatures well in excess of the Tgs of their constituent phases. The combined effects of two phenomena appeared to have resulted in the synergistic behavior exhibited by the ternary PEEK/PEI/HX-1000 blends. One was the formation of a strong protective layer of agglomerated highly deformed wear debris covering the wear tracks; the other, PEEK cold-crystallization in the region beneath the contact interface. Despite the synergistic nature of the tribological behavior of the PEEK/PEI/HX-1000 blends in the sliding regime above the glass transition, the observed friction and wear levels above the Tg were high. This is attributable to the relatively low stability of mechanical properties at high temperatures (compared to those of the isotropic PEEK/PEI matrices) of the reinforcing HX-1000 phase. Viscoelastic and plastic plowing as well as removal of material were found to be the active
wear modes during the sliding of the PEEK/PEI/HX-1000 blends investigated. Of these
modes, viscoelastic plowing and removal of material were predominant; plastic plowing of
the sliding surfaces was, in all cases, moderate. A larger TLCP fraction in the
PEEK/PEI/HX-1000 blends led to more marked material losses and to a reduced ability to
undergo deformation during sliding, in other words, to a more brittle-like tribological
behavior. Annealing had the same effect on the PEEK/PEI/HX-1000 60/10/30; heat
treatment was inconsequential in terms of improving tribological performance.
Comparison of the wear behavior of the PEEK/PEI/HX-1000 60/10/30 and 49/21/30
blends with that of the PEEK/HX-1000 70/30 revealed that the blends containing PEI
exhibited lower levels of wear performance, in particular at high temperatures, than the
binary PEEK/HX-1000 blend. Thus, in spite of any interfacial activity it might have
promoted between immiscible PEEK and HX-1000, PEI did not appear to be effective as a
high temperature tribological performance enhancer for PEEK/HX-1000 blends.
CHAPTER 7

Conclusions

The dry sliding friction and wear behavior of injection molded in-situ composites based on binary PEEK/HX-1000 and ternary PEEK/PEI/HX-1000 blends has been investigated as a function of operating temperature. Below, the relevant conclusions emerging from the present investigation are summarized:

1. The incorporation of a thermotropic liquid crystalline polymer (TLCP) into an isotropic engineering thermoplastic resin appears to be a viable route to processability and elevated temperature property enhancement. Improvements in dynamic modulus and high temperature tribological performance as well as reductions in melt viscosity were seen to occur in connection with the incorporation of HX-1000, a thermotropic liquid crystalline copolyester, into PEEK. Within the temperature range from 20 °C to 200 °C, the addition of 10 to 80 wt% HX-1000 to PEEK led to storage modulus increases ranging from 10 to 370%. Shear viscosity (measured at 360 °C and 1000 s⁻¹) drops of 10% to about 90% corresponded with the addition of 10 wt% to 80 wt% HX-1000 to PEEK. The incorporation of 10 wt% and 30 wt% HX-1000 into PEEK led to reductions in cumulative linear wear and steady state coefficient of friction of approximately 8–35% and 6–30%, respectively, in the sliding regime above the glass transition region (i.e., at sliding temperatures above 150 °C).
2. In all the materials tested, the thermal activation of molecular relaxation processes associated with the glass transition had a distinct impact on tribological performance. HX-1000 and the PEEK/HX-1000 20/80 and 50/50 blends failed catastrophically at their respective glass transition temperatures (Tgs). In the case of PEEK, the PEEK/HX-1000 70/30 and 90/10 blends, and the ternary PEEK/PEI/HX-1000 blends the onset of the glass transition brought about increases in steady state coefficient of friction and cumulative linear wear ranging from 53% to 600%, and 20% to 190%, respectively.

3. A stability of mechanical properties at high temperatures which was not significantly better than that of PEEK was found to be the factor effectively limiting the potential of HX-1000 as a high temperature mechanical property and tribological performance enhancer for PEEK. In effect, the fact that marked thermal softening of amorphous HX-1000 occurs at only about 30 °C above the Tg of PEEK rendered all the observed improvements in high temperature tribological performance modest and confined to the relatively narrow temperature range extending from the Tg of PEEK (ca. 150 °C) to about 200 °C. In principle, the utilization of a TLCP reinforcing phase with superior retention of mechanical properties at elevated temperatures, namely a semicrystalline TLCP, could lead to the development of PEEK-based in-situ composites with superior high temperature tribological performance.

4. In spite of its potential as a PEEK–HX-1000 compatibilizer, PEI (which is mutually miscible with PEEK and HX-1000) did not appear to be instrumental in enhancing the elevated temperature tribological performance of immiscible blends of PEEK and HX-
1000. PEEK/PEI/HX-1000 blends with TLCP concentrations of 10 and 30 wt% exhibited lower levels of wear performance, particularly at high temperatures (i.e., above 150 °C, the Tg of PEEK), than binary PEEK/HX-1000 with equal TLCP weight fractions.

5. Skin-core morphologies were observed in all the blends with TLCP weight percentages of 30 and above. In general, the skin layers were composed of a series of sublayers in which a high degree of molecular orientation along the mold fill direction (i.e., the direction of flow during injection molding) was apparent. By contrast, the core layers were not found to exhibit either a sublayered structure or an axis of orientational anisotropy. By harnessing the inherent anisotropy of in-situ composites, superior levels of tribological performance could be potentially achieved. For instance, sliding in a direction parallel to the axis of anisotropy of the skin layers of molded in-situ composites could lead to lower coefficients of friction (since energy dissipated in plastic reorientation of molecules is markedly reduced) and, good interfacial strength provided, to superior wear resistance (since strength along polymer chain axis is high). It seems appropriate to point out here that preliminary results from reciprocating (unidirectional) sliding tests performed, along and across the mold fill direction (MFD), on injection molded samples of PEEK/HX-1000 50/50—a blend exhibiting a skin-core morphology—appeared to support the foregoing notion. In fact, both a lower steady state coefficient of friction (see Fig. 7.1) and minimal damage (wear) to the sliding surface (see Fig. 7.2) resulted when the sliding direction coincided with the MFD or, equivalently, the axis of anisotropy of the PEEK/HX-1000 50/50 skin layers.

6. The relationship between structure, properties and tribological performance in
Figure 7.1 Friction trends observed during the reciprocating sliding of the PEEK/HX-1000 50/50 blend.
Figure 7.2  Electron micrographs of worn surfaces generated during the reciprocating sliding of the PEEK/HX-1000 50/50 blend: (a) SD perpendicular to the MFD; (b) SD parallel to the MFD (SD: sliding direction; MFD: mold fill direction). Arrows indicate sliding direction.
thermoplastic-based in-situ composites is very complex in nature. An in-depth understanding of this relationship is crucial to the exploitation of the full potential of the latter composites as performance tribomaterials. Presently, such level of understanding does not exist; therefore, further research on the matter is needed.
References


56. Sabol, E. A., "The Development of a Dual Extrusion Blending Process and Composites Based on Thermotropic Liquid Crystalline Polymers and


    (1985).

76. Jones, J. W. and N.S. Eiss, "Effect of Chemical Structure on the Friction and Wear 


78. Hornbogen, E. and K. Schäfer, "Friction and Wear of Thermoplastic Polymers," in 
    *Fundamentals of Friction and Wear of Materials*, D. A. Rigney (Ed.), A.S.M, Ohio, 


80. Blundell, D. J. and B. N. Osborn, "The Morphology of Poly(aryl-ether-ether- 

    Functions for Polyethylene Films Prepared by Unidirectional and Oriented 

82. Wilchinsky, Z. W., "Determination of Orientation of the Crystalline and Amorphous 
    (1968).

83. Cakmak, M., J. E. Spruiell and J. L. White, "Basic Study of Orientation in 

84. Muir, M. C., and R. S. Porter, "Processing Rheology of Liquid Crystalline 

    Gedde, "Microstructure in Injection Molded Samples of Liquid Crystalline 
    Poly(P-Hydroxy-Benzoic Acid-Co-Ethyylene Terephthalate)," *Polym. Eng. Sci.*, 28, 

86. Ostberg, G. M. K. and J. C. Seferis, "Annealing Effects on the Crystallinity of

Appendix A

Numerical Friction and Wear Data for PEEK, PEI and HX-1000
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$h_1^c$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>70.57</td>
<td>82.79</td>
<td>76.68</td>
<td>2.50</td>
<td>3.50</td>
<td>3.00</td>
<td>0.236</td>
<td>0.201</td>
<td>0.219</td>
</tr>
<tr>
<td>60</td>
<td>101.18</td>
<td>80.02</td>
<td>90.60</td>
<td>4.50</td>
<td>6.50</td>
<td>5.50</td>
<td>0.172</td>
<td>0.218</td>
<td>0.195</td>
</tr>
<tr>
<td>90</td>
<td>105.95</td>
<td>112.71</td>
<td>109.33</td>
<td>5.00</td>
<td>6.00</td>
<td>5.50</td>
<td>0.155</td>
<td>0.153</td>
<td>0.154</td>
</tr>
<tr>
<td>120</td>
<td>101.23</td>
<td>138.62</td>
<td>120.03</td>
<td>10.50</td>
<td>11.00</td>
<td>10.75</td>
<td>0.124</td>
<td>0.115</td>
<td>0.120</td>
</tr>
<tr>
<td>140</td>
<td>110.63</td>
<td>110.82</td>
<td>110.73</td>
<td>14.00</td>
<td>12.60</td>
<td>13.25</td>
<td>0.119</td>
<td>0.155</td>
<td>0.137</td>
</tr>
<tr>
<td>152</td>
<td>183.61</td>
<td>129.43</td>
<td>156.52</td>
<td>32.00</td>
<td>17.50</td>
<td>24.75</td>
<td>0.377</td>
<td>0.276</td>
<td>0.327</td>
</tr>
<tr>
<td>180</td>
<td>287.15</td>
<td>273.02</td>
<td>280.09</td>
<td>10.50</td>
<td>12.50</td>
<td>11.50</td>
<td>0.454</td>
<td>0.496</td>
<td>0.475</td>
</tr>
<tr>
<td>200</td>
<td>268.30</td>
<td>279.06</td>
<td>273.68</td>
<td>17.00</td>
<td>18.00</td>
<td>17.50</td>
<td>0.503</td>
<td>0.480</td>
<td>0.492</td>
</tr>
<tr>
<td>225</td>
<td>331.88</td>
<td>294.23</td>
<td>313.06</td>
<td>24.00</td>
<td>25.00</td>
<td>24.50</td>
<td>0.463</td>
<td>0.519</td>
<td>0.491</td>
</tr>
</tbody>
</table>

$^a$h: Cumulative linear wear at 3000 sliding cycles, in μm  
$^b$H: Total linear wear, in μm  
$^c$μ: Steady state coefficient of friction
Table A.2 Sliding Friction and Wear Data for PEI

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_{1^c}$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>339.60</td>
<td>350.67</td>
<td>345.14</td>
<td>335.00</td>
<td>326.00</td>
<td>330.50</td>
<td>0.430</td>
<td>0.357</td>
<td>0.394</td>
</tr>
<tr>
<td>50</td>
<td>326.87</td>
<td>345.11</td>
<td>335.99</td>
<td>290.00</td>
<td>306.00</td>
<td>299.00</td>
<td>0.512</td>
<td>0.399</td>
<td>0.456</td>
</tr>
<tr>
<td>90</td>
<td>320.85</td>
<td>310.03</td>
<td>315.44</td>
<td>305.00</td>
<td>256.00</td>
<td>280.50</td>
<td>0.450</td>
<td>0.421</td>
<td>0.436</td>
</tr>
<tr>
<td>105</td>
<td>69.39</td>
<td>93.18</td>
<td>81.29</td>
<td>12.00</td>
<td>15.00</td>
<td>13.50</td>
<td>0.181</td>
<td>0.157</td>
<td>0.169</td>
</tr>
<tr>
<td>120</td>
<td>76.20</td>
<td>105.26</td>
<td>91.73</td>
<td>18.50</td>
<td>17.00</td>
<td>17.75</td>
<td>0.252</td>
<td>0.210</td>
<td>0.231</td>
</tr>
<tr>
<td>140</td>
<td>80.17</td>
<td>88.88</td>
<td>84.53</td>
<td>15.00</td>
<td>18.00</td>
<td>16.50</td>
<td>0.209</td>
<td>0.112</td>
<td>0.161</td>
</tr>
<tr>
<td>160</td>
<td>80.23</td>
<td>110.54</td>
<td>95.39</td>
<td>14.00</td>
<td>18.00</td>
<td>16.00</td>
<td>0.160</td>
<td>0.289</td>
<td>0.225</td>
</tr>
<tr>
<td>180</td>
<td>99.71</td>
<td>120.58</td>
<td>110.15</td>
<td>13.00</td>
<td>16.00</td>
<td>14.50</td>
<td>0.287</td>
<td>0.255</td>
<td>0.271</td>
</tr>
<tr>
<td>213</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
</tr>
</tbody>
</table>

*a* $h$: Cumulative linear wear at 3000 sliding cycles, in μm

*b* $H$: Total linear wear, in μm

*c* $\mu$: Steady state coefficient of friction

*d* CF: Catastrophic Failure
Table A.3  Sliding Friction and Wear Data for HX-1000

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>157.72</td>
<td>108.25</td>
<td>132.99</td>
<td>74.00</td>
<td>66.00</td>
<td>70.00</td>
<td>0.350</td>
<td>0.350</td>
<td>0.350</td>
</tr>
<tr>
<td>50</td>
<td>164.71</td>
<td>150.63</td>
<td>157.67</td>
<td>84.00</td>
<td>68.00</td>
<td>76.00</td>
<td>0.370</td>
<td>0.350</td>
<td>0.360</td>
</tr>
<tr>
<td>80</td>
<td>193.00</td>
<td>176.52</td>
<td>184.76</td>
<td>78.00</td>
<td>81.00</td>
<td>79.50</td>
<td>0.380</td>
<td>0.380</td>
<td>0.380</td>
</tr>
<tr>
<td>110</td>
<td>178.88</td>
<td>178.88</td>
<td>178.88</td>
<td>76.00</td>
<td>88.00</td>
<td>82.00</td>
<td>0.360</td>
<td>0.340</td>
<td>0.350</td>
</tr>
<tr>
<td>140</td>
<td>240.10</td>
<td>218.18</td>
<td>229.14</td>
<td>152.00</td>
<td>107.00</td>
<td>129.50</td>
<td>0.410</td>
<td>0.400</td>
<td>0.405</td>
</tr>
<tr>
<td>160</td>
<td>287.15</td>
<td>268.35</td>
<td>277.75</td>
<td>150.00</td>
<td>162.00</td>
<td>156.00</td>
<td>0.400</td>
<td>0.410</td>
<td>0.405</td>
</tr>
<tr>
<td>180</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
</tr>
</tbody>
</table>

$^a$h: Cumulative linear wear at 3000 sliding cycles, in $\mu$m  
$^b$H: Total linear wear, in $\mu$m  
$^c$µ: Steady state coefficient of friction  
$^d$CF: Catastrophic Failure
Appendix B

Numerical Friction and Wear Data for PEEK/PEI Blends
Table B.1 Sliding Friction and Wear Data for PEEK/PEI 85/15

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>127.90</td>
<td>135.68</td>
<td>131.79</td>
<td>4.00</td>
<td>3.00</td>
<td>3.50</td>
<td>0.163</td>
<td>0.122</td>
<td>0.143</td>
</tr>
<tr>
<td>40</td>
<td>225.43</td>
<td>151.23</td>
<td>188.33</td>
<td>5.00</td>
<td>3.00</td>
<td>4.00</td>
<td>0.149</td>
<td>0.152</td>
<td>0.151</td>
</tr>
<tr>
<td>60</td>
<td>121.37</td>
<td>145.67</td>
<td>133.52</td>
<td>7.00</td>
<td>5.00</td>
<td>6.00</td>
<td>0.104</td>
<td>0.169</td>
<td>0.137</td>
</tr>
<tr>
<td>80</td>
<td>138.73</td>
<td>110.35</td>
<td>124.54</td>
<td>6.00</td>
<td>4.00</td>
<td>5.00</td>
<td>0.091</td>
<td>0.134</td>
<td>0.113</td>
</tr>
<tr>
<td>100</td>
<td>149.56</td>
<td>131.29</td>
<td>140.43</td>
<td>4.00</td>
<td>5.00</td>
<td>4.50</td>
<td>0.087</td>
<td>0.145</td>
<td>0.116</td>
</tr>
<tr>
<td>130</td>
<td>186.45</td>
<td>165.98</td>
<td>176.22</td>
<td>10.00</td>
<td>8.50</td>
<td>9.25</td>
<td>0.258</td>
<td>0.313</td>
<td>0.286</td>
</tr>
<tr>
<td>152</td>
<td>143.03</td>
<td>189.43</td>
<td>166.23</td>
<td>20.00</td>
<td>21.00</td>
<td>20.50</td>
<td>0.257</td>
<td>0.325</td>
<td>0.291</td>
</tr>
<tr>
<td>160</td>
<td>262.27</td>
<td>301.25</td>
<td>281.76</td>
<td>86.00</td>
<td>90.00</td>
<td>88.00</td>
<td>0.376</td>
<td>0.428</td>
<td>0.402</td>
</tr>
<tr>
<td>175</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
</tr>
</tbody>
</table>

$^a$h: Cumulative linear wear at 3000 sliding cycles, in μm
$^b$H: Total linear wear, in μm
$^c$μ: Steady state coefficient of friction
$^d$CF: Catastrophic Failure
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>108.00</td>
<td>118.04</td>
<td>113.02</td>
<td>23.50</td>
<td>14.00</td>
<td>18.75</td>
<td>0.330</td>
<td>0.290</td>
<td>0.310</td>
</tr>
<tr>
<td>40</td>
<td>108.19</td>
<td>128.28</td>
<td>118.24</td>
<td>7.00</td>
<td>5.00</td>
<td>6.00</td>
<td>0.149</td>
<td>0.257</td>
<td>0.203</td>
</tr>
<tr>
<td>60</td>
<td>136.55</td>
<td>114.93</td>
<td>125.74</td>
<td>6.50</td>
<td>6.50</td>
<td>6.50</td>
<td>0.173</td>
<td>0.110</td>
<td>0.142</td>
</tr>
<tr>
<td>80</td>
<td>110.24</td>
<td>124.07</td>
<td>117.16</td>
<td>5.00</td>
<td>4.00</td>
<td>4.50</td>
<td>0.149</td>
<td>0.196</td>
<td>0.173</td>
</tr>
<tr>
<td>100</td>
<td>117.06</td>
<td>131.51</td>
<td>124.29</td>
<td>4.50</td>
<td>6.00</td>
<td>5.25</td>
<td>0.175</td>
<td>0.213</td>
<td>0.194</td>
</tr>
<tr>
<td>120</td>
<td>133.92</td>
<td>119.78</td>
<td>126.85</td>
<td>6.00</td>
<td>5.00</td>
<td>5.50</td>
<td>0.149</td>
<td>0.108</td>
<td>0.129</td>
</tr>
<tr>
<td>140</td>
<td>144.00</td>
<td>161.26</td>
<td>152.63</td>
<td>5.50</td>
<td>6.00</td>
<td>5.75</td>
<td>0.120</td>
<td>0.135</td>
<td>0.128</td>
</tr>
<tr>
<td>159</td>
<td>238.23</td>
<td>354.27</td>
<td>296.25</td>
<td>36.00</td>
<td>40.00</td>
<td>38.00</td>
<td>0.305</td>
<td>0.390</td>
<td>0.348</td>
</tr>
<tr>
<td>170</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
</tr>
</tbody>
</table>

$^a$h: Cumulative linear wear at 3000 sliding cycles, in μm
$^b$H: Total linear wear, in μm
$^c$μ: Steady state coefficient of friction
$^d$CF: Catastrophic Failure
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>93.87</td>
<td>100.71</td>
<td>97.29</td>
<td>15.00</td>
<td>10.00</td>
<td>12.50</td>
<td>0.276</td>
<td>0.264</td>
<td>0.270</td>
</tr>
<tr>
<td>48</td>
<td>126.12</td>
<td>116.69</td>
<td>122.41</td>
<td>11.00</td>
<td>13.00</td>
<td>12.00</td>
<td>0.099</td>
<td>0.247</td>
<td>0.173</td>
</tr>
<tr>
<td>71</td>
<td>107.51</td>
<td>117.89</td>
<td>112.70</td>
<td>8.00</td>
<td>7.00</td>
<td>7.50</td>
<td>0.096</td>
<td>0.087</td>
<td>0.092</td>
</tr>
<tr>
<td>94</td>
<td>121.28</td>
<td>107.50</td>
<td>114.39</td>
<td>6.00</td>
<td>8.00</td>
<td>7.00</td>
<td>0.125</td>
<td>0.091</td>
<td>0.109</td>
</tr>
<tr>
<td>117</td>
<td>105.25</td>
<td>100.66</td>
<td>102.96</td>
<td>9.00</td>
<td>12.00</td>
<td>10.50</td>
<td>0.260</td>
<td>0.089</td>
<td>0.175</td>
</tr>
<tr>
<td>140</td>
<td>125.87</td>
<td>128.12</td>
<td>127.00</td>
<td>7.00</td>
<td>9.00</td>
<td>8.00</td>
<td>0.121</td>
<td>0.220</td>
<td>0.171</td>
</tr>
<tr>
<td>163</td>
<td>130.42</td>
<td>139.61</td>
<td>135.02</td>
<td>9.00</td>
<td>10.00</td>
<td>9.50</td>
<td>0.234</td>
<td>0.175</td>
<td>0.205</td>
</tr>
<tr>
<td>186</td>
<td>224.24</td>
<td>343.27</td>
<td>283.76</td>
<td>32.00</td>
<td>40.00</td>
<td>36.00</td>
<td>0.493</td>
<td>0.477</td>
<td>0.485</td>
</tr>
<tr>
<td>209</td>
<td>315.81</td>
<td>494.26</td>
<td>405.04</td>
<td>62.00</td>
<td>60.00</td>
<td>61.00</td>
<td>0.597</td>
<td>0.672</td>
<td>0.635</td>
</tr>
<tr>
<td>232</td>
<td>750.06</td>
<td>741.67</td>
<td>745.87</td>
<td>78.00</td>
<td>81.00</td>
<td>79.50</td>
<td>0.573</td>
<td>0.602</td>
<td>0.588</td>
</tr>
</tbody>
</table>

$^a$ $h$: Cumulative linear wear at 3000 sliding cycles, in $\mu$m  
$^b$ $H$: Total linear wear, in $\mu$m  
$^c$ $\mu$: Steady state coefficient of friction
<table>
<thead>
<tr>
<th>$T [, ^\circ C]$</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>310.00</td>
<td>290.66</td>
<td>300.33</td>
<td>270.00</td>
<td>245.00</td>
<td>257.50</td>
<td>0.426</td>
<td>0.401</td>
<td>0.414</td>
</tr>
<tr>
<td>45</td>
<td>314.00</td>
<td>330.58</td>
<td>322.29</td>
<td>260.00</td>
<td>240.00</td>
<td>250.00</td>
<td>0.459</td>
<td>0.386</td>
<td>0.423</td>
</tr>
<tr>
<td>70</td>
<td>80.20</td>
<td>105.70</td>
<td>92.95</td>
<td>6.00</td>
<td>9.00</td>
<td>7.50</td>
<td>0.108</td>
<td>0.150</td>
<td>0.129</td>
</tr>
<tr>
<td>100</td>
<td>84.52</td>
<td>95.40</td>
<td>89.96</td>
<td>4.50</td>
<td>5.50</td>
<td>5.00</td>
<td>0.098</td>
<td>0.097</td>
<td>0.098</td>
</tr>
<tr>
<td>120</td>
<td>106.23</td>
<td>117.55</td>
<td>111.89</td>
<td>4.00</td>
<td>6.00</td>
<td>5.00</td>
<td>0.154</td>
<td>0.102</td>
<td>0.128</td>
</tr>
<tr>
<td>150</td>
<td>91.00</td>
<td>112.36</td>
<td>101.68</td>
<td>6.00</td>
<td>7.00</td>
<td>6.50</td>
<td>0.166</td>
<td>0.136</td>
<td>0.151</td>
</tr>
<tr>
<td>165</td>
<td>112.71</td>
<td>159.73</td>
<td>136.22</td>
<td>38.00</td>
<td>23.50</td>
<td>30.75</td>
<td>0.330</td>
<td>0.281</td>
<td>0.306</td>
</tr>
<tr>
<td>178</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
</tr>
</tbody>
</table>

*a* $h$: Cumulative linear wear at 3000 sliding cycles, in $\mu$m  
*b* $H$: Total linear wear, in $\mu$m  
$c$ $\mu$: Steady state coefficient of friction  
*d* $CF$: Catastrophic Failure
Appendix C

Numerical Friction and Wear Data for PEEK/HX-1000 Blends
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>79.94</td>
<td>98.72</td>
<td>89.33</td>
<td>6.50</td>
<td>2.50</td>
<td>4.50</td>
<td>0.294</td>
<td>0.153</td>
<td>0.224</td>
</tr>
<tr>
<td>50</td>
<td>110.27</td>
<td>94.38</td>
<td>102.33</td>
<td>5.00</td>
<td>4.50</td>
<td>4.75</td>
<td>0.156</td>
<td>0.135</td>
<td>0.146</td>
</tr>
<tr>
<td>80</td>
<td>98.72</td>
<td>103.53</td>
<td>101.13</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>0.136</td>
<td>0.136</td>
<td>0.136</td>
</tr>
<tr>
<td>100</td>
<td>105.94</td>
<td>105.94</td>
<td>105.94</td>
<td>8.50</td>
<td>8.50</td>
<td>8.50</td>
<td>0.277</td>
<td>0.153</td>
<td>0.215</td>
</tr>
<tr>
<td>130</td>
<td>127.13</td>
<td>145.43</td>
<td>136.28</td>
<td>10.50</td>
<td>11.50</td>
<td>11.00</td>
<td>0.135</td>
<td>0.270</td>
<td>0.203</td>
</tr>
<tr>
<td>155</td>
<td>141.09</td>
<td>162.28</td>
<td>151.69</td>
<td>21.00</td>
<td>33.00</td>
<td>27.00</td>
<td>0.331</td>
<td>0.319</td>
<td>0.325</td>
</tr>
<tr>
<td>180</td>
<td>366.94</td>
<td>176.25</td>
<td>271.60</td>
<td>15.00</td>
<td>10.00</td>
<td>12.50</td>
<td>0.233</td>
<td>0.146</td>
<td>0.190</td>
</tr>
<tr>
<td>200</td>
<td>225.85</td>
<td>207.07</td>
<td>216.46</td>
<td>20.00</td>
<td>30.50</td>
<td>25.25</td>
<td>0.455</td>
<td>0.413</td>
<td>0.434</td>
</tr>
<tr>
<td>225</td>
<td>235.00</td>
<td>173.84</td>
<td>204.42</td>
<td>34.00</td>
<td>29.00</td>
<td>31.50</td>
<td>0.437</td>
<td>0.433</td>
<td>0.435</td>
</tr>
</tbody>
</table>

$^{a}h$: Cumulative linear wear at 3000 sliding cycles, in μm

$^{b}H$: Total linear wear, in μm

$^{c}\mu$: Steady state coefficient of friction
<table>
<thead>
<tr>
<th>T [ °C ]</th>
<th>( h_1 )</th>
<th>( h_2 )</th>
<th>( h_{ave} )</th>
<th>( H_1 )</th>
<th>( H_2 )</th>
<th>( H_{ave} )</th>
<th>( \mu_1 )</th>
<th>( \mu_2 )</th>
<th>( \mu_{ave} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>94.15</td>
<td>138.67</td>
<td>116.51</td>
<td>21.00</td>
<td>19.00</td>
<td>20.00</td>
<td>0.271</td>
<td>0.263</td>
<td>0.267</td>
</tr>
<tr>
<td>50</td>
<td>103.56</td>
<td>99.51</td>
<td>101.56</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>0.252</td>
<td>0.231</td>
<td>0.242</td>
</tr>
<tr>
<td>80</td>
<td>152.99</td>
<td>113.75</td>
<td>133.37</td>
<td>17.00</td>
<td>8.00</td>
<td>12.50</td>
<td>0.246</td>
<td>0.165</td>
<td>0.206</td>
</tr>
<tr>
<td>100</td>
<td>122.39</td>
<td>98.85</td>
<td>110.62</td>
<td>29.00</td>
<td>11.00</td>
<td>20.00</td>
<td>0.340</td>
<td>0.120</td>
<td>0.230</td>
</tr>
<tr>
<td>130</td>
<td>105.91</td>
<td>103.48</td>
<td>105.91</td>
<td>33.00</td>
<td>27.50</td>
<td>30.25</td>
<td>0.276</td>
<td>0.228</td>
<td>0.252</td>
</tr>
<tr>
<td>155</td>
<td>148.28</td>
<td>129.48</td>
<td>138.87</td>
<td>45.00</td>
<td>56.00</td>
<td>50.50</td>
<td>0.480</td>
<td>0.289</td>
<td>0.385</td>
</tr>
<tr>
<td>180</td>
<td>183.59</td>
<td>200.09</td>
<td>191.84</td>
<td>52.00</td>
<td>51.00</td>
<td>51.50</td>
<td>0.486</td>
<td>0.390</td>
<td>0.438</td>
</tr>
<tr>
<td>200</td>
<td>178.88</td>
<td>256.55</td>
<td>217.71</td>
<td>64.00</td>
<td>74.00</td>
<td>69.00</td>
<td>0.408</td>
<td>0.456</td>
<td>0.432</td>
</tr>
<tr>
<td>225</td>
<td>343.63</td>
<td>341.85</td>
<td>342.74</td>
<td>74.00</td>
<td>84.00</td>
<td>79.00</td>
<td>0.569</td>
<td>0.532</td>
<td>0.551</td>
</tr>
</tbody>
</table>

\( h_1 \): Cumulative linear wear at 3000 sliding cycles, in \( \mu m \)

\( H_1 \): Total linear wear, in \( \mu m \)

\( \mu \): Steady state coefficient of friction.
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$\bar{h}_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$\bar{H}_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$\mu_2$</th>
<th>$\bar{\mu}_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>98.66</td>
<td>122.17</td>
<td>110.52</td>
<td>21.00</td>
<td>28.50</td>
<td>24.75</td>
<td>0.237</td>
<td>0.217</td>
<td>0.227</td>
</tr>
<tr>
<td>50</td>
<td>115.30</td>
<td>121.00</td>
<td>118.15</td>
<td>24.00</td>
<td>22.00</td>
<td>23.00</td>
<td>0.234</td>
<td>0.232</td>
<td>0.233</td>
</tr>
<tr>
<td>80</td>
<td>129.47</td>
<td>129.43</td>
<td>129.45</td>
<td>21.00</td>
<td>28.00</td>
<td>24.50</td>
<td>0.201</td>
<td>0.246</td>
<td>0.224</td>
</tr>
<tr>
<td>100</td>
<td>112.99</td>
<td>115.12</td>
<td>114.06</td>
<td>29.00</td>
<td>32.00</td>
<td>30.50</td>
<td>0.225</td>
<td>0.231</td>
<td>0.228</td>
</tr>
<tr>
<td>130</td>
<td>131.84</td>
<td>130.61</td>
<td>131.23</td>
<td>40.00</td>
<td>52.50</td>
<td>46.25</td>
<td>0.274</td>
<td>0.279</td>
<td>0.277</td>
</tr>
<tr>
<td>165</td>
<td>157.72</td>
<td>138.87</td>
<td>148.30</td>
<td>41.00</td>
<td>46.00</td>
<td>43.50</td>
<td>0.287</td>
<td>0.297</td>
<td>0.292</td>
</tr>
<tr>
<td>180</td>
<td>203.49</td>
<td>202.40</td>
<td>202.95</td>
<td>56.00</td>
<td>38.00</td>
<td>47.00</td>
<td>0.343</td>
<td>0.334</td>
<td>0.339</td>
</tr>
<tr>
<td>200</td>
<td>242.41</td>
<td>230.01</td>
<td>236.21</td>
<td>84.00</td>
<td>83.50</td>
<td>83.75</td>
<td>0.393</td>
<td>0.411</td>
<td>0.402</td>
</tr>
<tr>
<td>225</td>
<td>237.13</td>
<td>350.68</td>
<td>293.91</td>
<td>85.50</td>
<td>146.00</td>
<td>115.75</td>
<td>0.406</td>
<td>0.478</td>
<td>0.442</td>
</tr>
</tbody>
</table>

$^a$h: Cumulative linear wear at 3000 sliding cycles, in μm

$^b$H: Total linear wear, in μm

$^c$μ: Steady state coefficient of friction
Table C.4 Sliding Friction and Wear Data for PEEK/HX-1000 50/50

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>94.05</td>
<td>106.34</td>
<td>99.70</td>
<td>24.00</td>
<td>25.50</td>
<td>24.75</td>
<td>0.247</td>
<td>0.259</td>
<td>0.253</td>
</tr>
<tr>
<td>50</td>
<td>122.27</td>
<td>126.55</td>
<td>124.41</td>
<td>30.00</td>
<td>30.00</td>
<td>30.00</td>
<td>0.244</td>
<td>0.227</td>
<td>0.236</td>
</tr>
<tr>
<td>80</td>
<td>110.52</td>
<td>129.30</td>
<td>119.91</td>
<td>51.00</td>
<td>49.00</td>
<td>50.00</td>
<td>0.273</td>
<td>0.269</td>
<td>0.271</td>
</tr>
<tr>
<td>100</td>
<td>150.48</td>
<td>137.49</td>
<td>143.09</td>
<td>46.00</td>
<td>46.00</td>
<td>46.00</td>
<td>0.285</td>
<td>0.310</td>
<td>0.298</td>
</tr>
<tr>
<td>130</td>
<td>162.23</td>
<td>176.74</td>
<td>169.43</td>
<td>55.00</td>
<td>57.00</td>
<td>56.00</td>
<td>0.297</td>
<td>0.303</td>
<td>0.300</td>
</tr>
<tr>
<td>155</td>
<td>199.84</td>
<td>185.78</td>
<td>192.81</td>
<td>67.00</td>
<td>100.00</td>
<td>83.50</td>
<td>0.308</td>
<td>0.332</td>
<td>0.320</td>
</tr>
<tr>
<td>180</td>
<td>258.64</td>
<td>244.53</td>
<td>251.59</td>
<td>130.00</td>
<td>104.00</td>
<td>117.00</td>
<td>0.412</td>
<td>0.359</td>
<td>0.386</td>
</tr>
<tr>
<td>200</td>
<td>467.87</td>
<td>524.02</td>
<td>495.95</td>
<td>435.00</td>
<td>480.00</td>
<td>457.50</td>
<td>0.490</td>
<td>0.436</td>
<td>0.463</td>
</tr>
<tr>
<td>225</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
</tr>
</tbody>
</table>

$^a$h: Cumulative linear wear at 3000 sliding cycles, in μm
$^b$H: Total linear wear, in μm
$^c$μ: Steady state coefficient of friction
$^d$CF: Catastrophic Failure
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>96.41</td>
<td>110.87</td>
<td>103.64</td>
<td>41.00</td>
<td>40.00</td>
<td>40.50</td>
<td>0.258</td>
<td>0.273</td>
<td>0.266</td>
</tr>
<tr>
<td>50</td>
<td>122.27</td>
<td>148.17</td>
<td>135.22</td>
<td>47.00</td>
<td>40.00</td>
<td>43.50</td>
<td>0.259</td>
<td>0.289</td>
<td>0.274</td>
</tr>
<tr>
<td>80</td>
<td>141.05</td>
<td>128.36</td>
<td>134.71</td>
<td>44.00</td>
<td>42.00</td>
<td>43.00</td>
<td>0.293</td>
<td>0.272</td>
<td>0.283</td>
</tr>
<tr>
<td>100</td>
<td>164.59</td>
<td>141.09</td>
<td>152.84</td>
<td>66.00</td>
<td>68.00</td>
<td>67.00</td>
<td>0.298</td>
<td>0.301</td>
<td>0.300</td>
</tr>
<tr>
<td>130</td>
<td>171.82</td>
<td>189.08</td>
<td>180.35</td>
<td>82.00</td>
<td>81.50</td>
<td>81.75</td>
<td>0.306</td>
<td>0.325</td>
<td>0.316</td>
</tr>
<tr>
<td>155</td>
<td>268.03</td>
<td>470.23</td>
<td>369.13</td>
<td>105.00</td>
<td>168.00</td>
<td>136.50</td>
<td>0.353</td>
<td>0.347</td>
<td>0.350</td>
</tr>
<tr>
<td>180</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
<td>CF</td>
</tr>
</tbody>
</table>

$h$: Cumulative linear wear at 3000 sliding cycles, in $\mu$m
$H$: Total linear wear, in $\mu$m
$\mu$: Steady state coefficient of friction
$CF$: Catastrophic Failure
Appendix D

Numerical Friction and Wear Data for PEEK/PE1/HX-1000 Blends
Table D.1 Sliding Friction and Wear Data for PEEK/PEI/HX-1000 77/13/10

<table>
<thead>
<tr>
<th>$T , [^\circ C]$</th>
<th>$h_1$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>69.28</td>
<td>98.77</td>
<td>94.06</td>
<td>1.25</td>
<td>3.25</td>
<td>2.25</td>
<td>0.120</td>
<td>0.290</td>
<td>0.205</td>
</tr>
<tr>
<td>50</td>
<td>134.02</td>
<td>103.44</td>
<td>118.73</td>
<td>1.55</td>
<td>1.40</td>
<td>1.48</td>
<td>0.090</td>
<td>0.080</td>
<td>0.085</td>
</tr>
<tr>
<td>80</td>
<td>98.77</td>
<td>129.30</td>
<td>114.04</td>
<td>1.50</td>
<td>1.60</td>
<td>1.55</td>
<td>0.100</td>
<td>0.090</td>
<td>0.095</td>
</tr>
<tr>
<td>120</td>
<td>124.63</td>
<td>129.43</td>
<td>125.53</td>
<td>6.50</td>
<td>10.00</td>
<td>8.25</td>
<td>0.060</td>
<td>0.140</td>
<td>0.100</td>
</tr>
<tr>
<td>155</td>
<td>131.70</td>
<td>131.66</td>
<td>131.68</td>
<td>56.00</td>
<td>76.00</td>
<td>66.00</td>
<td>0.350</td>
<td>0.460</td>
<td>0.405</td>
</tr>
<tr>
<td>180</td>
<td>246.89</td>
<td>207.02</td>
<td>228.96</td>
<td>140.00</td>
<td>120.00</td>
<td>130.00</td>
<td>0.420</td>
<td>0.390</td>
<td>0.405</td>
</tr>
<tr>
<td>205</td>
<td>308.00</td>
<td>204.56</td>
<td>256.28</td>
<td>84.00</td>
<td>68.00</td>
<td>71.00</td>
<td>0.490</td>
<td>0.460</td>
<td>0.475</td>
</tr>
<tr>
<td>225</td>
<td>531.39</td>
<td>376.19</td>
<td>453.79</td>
<td>76.00</td>
<td>69.00</td>
<td>72.50</td>
<td>0.430</td>
<td>0.410</td>
<td>0.420</td>
</tr>
</tbody>
</table>

$^a$h: Cumulative linear wear at 3000 sliding cycles, in $\mu$m
$^b$H: Total linear wear, in $\mu$m
$^c$\mu: Steady state coefficient of friction
### Table D.2 Sliding Friction and Wear Data for PEEK/PEI/HX-1000 60/10/30

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>h₁[^a]</th>
<th>h₂</th>
<th>hₐve</th>
<th>H₁[^b]</th>
<th>H₂</th>
<th>Hₐve</th>
<th>μ₁[^c]</th>
<th>μ₂</th>
<th>μₐve</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>141.09</td>
<td>151.94</td>
<td>146.52</td>
<td>33.00</td>
<td>35.50</td>
<td>34.25</td>
<td>0.247</td>
<td>0.259</td>
<td>0.253</td>
</tr>
<tr>
<td>80</td>
<td>152.64</td>
<td>143.69</td>
<td>148.26</td>
<td>37.00</td>
<td>32.50</td>
<td>34.75</td>
<td>0.235</td>
<td>0.212</td>
<td>0.224</td>
</tr>
<tr>
<td>80</td>
<td>225.75</td>
<td>136.37</td>
<td>181.06</td>
<td>12.50</td>
<td>19.00</td>
<td>15.75</td>
<td>0.165</td>
<td>0.169</td>
<td>0.167</td>
</tr>
<tr>
<td>120</td>
<td>152.64</td>
<td>177.65</td>
<td>165.25</td>
<td>29.00</td>
<td>30.00</td>
<td>29.50</td>
<td>0.244</td>
<td>0.229</td>
<td>0.237</td>
</tr>
<tr>
<td>155</td>
<td>204.61</td>
<td>222.97</td>
<td>213.79</td>
<td>51.50</td>
<td>57.00</td>
<td>54.25</td>
<td>0.310</td>
<td>0.289</td>
<td>0.300</td>
</tr>
<tr>
<td>180</td>
<td>230.42</td>
<td>522.00</td>
<td>376.21</td>
<td>90.00</td>
<td>161.00</td>
<td>125.50</td>
<td>0.373</td>
<td>0.396</td>
<td>0.385</td>
</tr>
<tr>
<td>205</td>
<td>425.59</td>
<td>483.71</td>
<td>454.85</td>
<td>190.00</td>
<td>175.50</td>
<td>182.75</td>
<td>0.464</td>
<td>0.504</td>
<td>0.484</td>
</tr>
<tr>
<td>225</td>
<td>529.75</td>
<td>620.71</td>
<td>574.73</td>
<td>381.00</td>
<td>357.50</td>
<td>374.25</td>
<td>0.499</td>
<td>0.546</td>
<td>0.523</td>
</tr>
</tbody>
</table>

[^a]: Cumulative linear wear at 3000 sliding cycles, in μm
[^b]: Total linear wear, in μm
[^c]: Steady state coefficient of friction
Table D.3  Sliding Friction and Wear Data for Annealed PEEK/PEI/HX-1000 60/10/30

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1^a$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1^b$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1^c$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>134.02</td>
<td>120.79</td>
<td>127.41</td>
<td>44.00</td>
<td>48.00</td>
<td>46.00</td>
<td>0.241</td>
<td>0.237</td>
<td>0.239</td>
</tr>
<tr>
<td>50</td>
<td>129.30</td>
<td>122.24</td>
<td>125.77</td>
<td>47.00</td>
<td>42.50</td>
<td>44.75</td>
<td>0.245</td>
<td>0.240</td>
<td>0.243</td>
</tr>
<tr>
<td>80</td>
<td>117.55</td>
<td>131.66</td>
<td>124.61</td>
<td>23.00</td>
<td>50.00</td>
<td>36.50</td>
<td>0.241</td>
<td>0.254</td>
<td>0.248</td>
</tr>
<tr>
<td>120</td>
<td>120.30</td>
<td>145.27</td>
<td>197.29</td>
<td>47.00</td>
<td>54.50</td>
<td>50.75</td>
<td>0.272</td>
<td>0.286</td>
<td>0.280</td>
</tr>
<tr>
<td>155</td>
<td>174.03</td>
<td>182.35</td>
<td>178.19</td>
<td>48.00</td>
<td>52.50</td>
<td>50.25</td>
<td>0.285</td>
<td>0.264</td>
<td>0.275</td>
</tr>
<tr>
<td>160</td>
<td>176.34</td>
<td>251.61</td>
<td>213.99</td>
<td>101.00</td>
<td>114.00</td>
<td>107.50</td>
<td>0.341</td>
<td>0.358</td>
<td>0.350</td>
</tr>
<tr>
<td>205</td>
<td>352.69</td>
<td>293.93</td>
<td>323.31</td>
<td>228.00</td>
<td>252.50</td>
<td>240.25</td>
<td>0.418</td>
<td>0.402</td>
<td>0.410</td>
</tr>
<tr>
<td>225</td>
<td>754.78</td>
<td>717.17</td>
<td>735.98</td>
<td>494.00</td>
<td>595.00</td>
<td>544.50</td>
<td>0.546</td>
<td>0.539</td>
<td>0.543</td>
</tr>
</tbody>
</table>

\(^a\text{h: Cumulative linear wear at 3000 sliding cycles, in } \mu\text{m}\)

\(^b\text{H: Total linear wear, in } \mu\text{m}\)

\(^c\text{\(\mu\): Steady state coefficient of friction}\)
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>$h_1$</th>
<th>$h_2$</th>
<th>$h_{ave}$</th>
<th>$H_1$</th>
<th>$H_2$</th>
<th>$H_{ave}$</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$\mu_{ave}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>101.13</td>
<td>107.20</td>
<td>104.17</td>
<td>40.00</td>
<td>43.00</td>
<td>41.50</td>
<td>0.253</td>
<td>0.268</td>
<td>0.261</td>
</tr>
<tr>
<td>50</td>
<td>145.77</td>
<td>163.26</td>
<td>154.62</td>
<td>38.00</td>
<td>40.50</td>
<td>39.25</td>
<td>0.261</td>
<td>0.232</td>
<td>0.247</td>
</tr>
<tr>
<td>80</td>
<td>150.48</td>
<td>148.17</td>
<td>149.33</td>
<td>50.00</td>
<td>40.00</td>
<td>45.00</td>
<td>0.289</td>
<td>0.266</td>
<td>0.278</td>
</tr>
<tr>
<td>120</td>
<td>169.31</td>
<td>153.23</td>
<td>161.27</td>
<td>60.00</td>
<td>52.00</td>
<td>56.00</td>
<td>0.289</td>
<td>0.272</td>
<td>0.281</td>
</tr>
<tr>
<td>155</td>
<td>162.23</td>
<td>168.91</td>
<td>165.57</td>
<td>50.00</td>
<td>55.50</td>
<td>52.75</td>
<td>0.320</td>
<td>0.347</td>
<td>0.334</td>
</tr>
<tr>
<td>180</td>
<td>336.58</td>
<td>282.19</td>
<td>310.39</td>
<td>250.00</td>
<td>206.00</td>
<td>227.50</td>
<td>0.531</td>
<td>0.473</td>
<td>0.502</td>
</tr>
<tr>
<td>205</td>
<td>376.24</td>
<td>408.86</td>
<td>392.55</td>
<td>250.00</td>
<td>212.00</td>
<td>231.00</td>
<td>0.514</td>
<td>0.479</td>
<td>0.497</td>
</tr>
<tr>
<td>225</td>
<td>599.58</td>
<td>509.00</td>
<td>554.29</td>
<td>445.00</td>
<td>383.00</td>
<td>414.00</td>
<td>0.624</td>
<td>0.485</td>
<td>0.555</td>
</tr>
</tbody>
</table>

*a* $h$: Cumulative linear wear at 3000 sliding cycles, in µm  
*b* $H$: Total linear wear, in µm  
*c* $\mu$: Steady state coefficient of friction
Vita

Jorge Hanchi studied engineering at the Polytechnic University (ESPOL) in Ecuador, where he was born. He graduated as a mechanical engineer in 1986. In the Spring of 1991 he received a M.S. degree in mechanical engineering from the University of Minnesota, Twin Cities. While at Minnesota, he conducted research in the areas of acoustic phenomena in tribology and development of sensors for manufacturing process control. In the Fall of 1991 he transferred to Virginia Tech and began work towards a Ph.D. degree in mechanical engineering. Under the supervision of Professor Norman Eiss, Jr., he carried out research on the elucidation of fundamental aspects of the tribological behavior of thermoplastic-based in-situ composites. He completed his Ph.D. degree in May of 1995.