PEO-containing Copolymers as Polyurethane Soft Segments in the Development of High Performance Materials

by

LaShanda Teresa James-Korley

Bachelor of Chemical Engineering
Georgia Institute of Technology, Atlanta, GA, August 1999

Bachelor of Science, Chemistry and Engineering
Clark Atlanta University, Atlanta, GA, May 1999

SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING

AT THE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

JUNE 2005

©Massachusetts Institute of Technology. 2005. All rights reserved.

Signature of Author: __________________________
Department of Chemical Engineering/ Program in Polymer Science and Technology
May 12, 2005

Certified by: __________________________
Paula T. Hammond
Associate Professor of Chemical Engineering
Thesis Advisor

Certified by: __________________________
Gareth H. McKinley
Professor of Mechanical Engineering
Co-Thesis Advisor

Accepted by: __________________________
Daniel Blankschtein
Professor of Chemical Engineering
Chairman, Committee for Graduate Students
Abstract

Silk-inspired segmented polyurethanes containing flexible, hydrophilic segments with crystalline and liquid crystalline moieties were developed to mimic the hierarchical morphology of the continuous domain in and the superior mechanical properties of native spider silk. A series of polyurethane elastomers were designed with varying poly(ethylene oxide) (PEO)-containing soft segment lengths and hard segment contents. The incorporation of a hydrophobic poly(propylene oxide) (PPO) block and longer soft segment lengths (1900 g/mol) induced a higher degree of micro-phase segregation compared to PEO (1000 g/mol) soft segment polyurethanes of similar hard segment content. Segmented polyurethanes with longer PEO soft segment lengths (4600 g/mol) exhibited a lamellar morphology, which was driven by the high level of crystallinity in both the hard and soft domains. As the hard segment content (26 - 47 wt%) was increased, the crystallinity of the hard domains was enhanced, yielding a shift in the morphology of the continuous domain from soft segment continuous to hard segment continuous or an interconnected microstructure. The mechanical behavior of these systems was affected by the continuous domain morphology. Hysteresis and initial moduli increased, and extensibility decreased as the hard segment size was varied from 26 to 47 wt% in the PEO-PPO-PEO-containing polyurethanes. The pure PEO (1000 g/mol) soft segment polyurethane exhibited enhanced extensibility, tensile strength, and toughness compared to the PEO-PPO-PEO segmented polyurethanes, which was attributed to the presence of load-bearing crystallites.

Shearing of the highly ordered and hydrogen-bonded hard domains resulted in orientation of the hard blocks at a preferential angle (∆70°) to the stretch direction during tensile deformation. Strong alignment and strain-induced birefringence of the soft segment chains was identified in the pure PEO1000 soft segment polyurethane, which supported the observed mechanical behavior. An ordered mesophase was observed in the PEO-PPO-PEO soft segment polyurethane in which the soft block formed the continuous domain. The hard segments aligned ±30° to the elongation direction within the hard domain as a result of the hydrogen-bonded network structure.

Dramatic reductions (~16-fold decrease in toughness and ~6-fold decrease in extensibility) in mechanical properties were found in PEO-PPO-PEO soft segment polyurethane/Laponite nanocomposites. The soft segment mobility was restricted in these nanocomposites, diminishing the ability for strain-induced ordering and hindering slippage of the soft segment chains during deformation. Regions of exfoliated Laponite alternated with intercalated-and-flocculated clay regions. These findings were rationalized in terms of preferential attraction of the hydrophilic, PEO-based soft block to the hydrophilic Laponite discs, leading to the intercalated-and-flocculated structures. However, the Laponite particles also interact with the polar hard domains, which has been assigned to the observed exfoliation.

Poly(gamma-benzyl-L-glutamate) (PBLG)-PEO-PBLG copolymers were developed using custom-synthesized, diamine-terminated PEO1000. These copolymers exhibited both alpha-helix and beta-sheet conformations, depending on the PBLG block length. Only low molecular weight segmented polyurethanes were obtained using these liquid crystalline copolymers due to the possible low reactivity of the amine end-groups and cyclization within the PBLG block.
Acknowledgements

To God be all the glory and honor! His blessings of love, grace, strength, perseverance, and encouragement, and the gift of His Holy Spirit have sustained me throughout this doctoral program. Precious Lord, you are awesome! I praise God for my husband, Julius—a man of God, who has sacrificed so much to make this journey possible for me and encouraged me throughout this process. Julius, you share in this with me; I just hope that I am able to provide the support you need as you pursue your graduate education.

To Paula: You have been a wonderful research advisor and mentor, but also a friend, encourager, and champion, especially when I did not see the end in sight. Thanks so much for everything! Your achievements, professionally and personally, have been a reminder that by putting everything in perspective you can succeed! I also owe a debt of gratitude to my thesis committee members: Professor Gareth McKinley, Professor Robert Cohen, and Professor Anne Mayes. My graduate experience has been blessed by your support and encouragement. I would also like to express my thanks to Professor Edwin Thomas for his helpful discussions and career advice. I would like to say thank you to Dr. Thomas C. Ward at VA Tech for his sincere concern about my professional and personal growth. Thanks for believing in me and encouraging me along this journey! Special thanks also go out to Dr. Yaw Yeboah, a wonderful mentor who believed in me from the very beginning of my undergraduate studies at CAU and GA Tech.

I thank my parents, Jesse and Dasie James Jr., for instilling in me the confidence to pursue my dreams. To my sister, Perseco, thank you for taking every phone call and for all of your prayers! Much love to you Big Sis! Dean Staton, what I can say. Who knew that an encounter in the hallway would bring to me an angel on Earth. Your endless support for me and my family have made my time here at MIT joyful and blessed. I will miss you! To Dean Colbert and Barrie, thanks for all of your love and support. To my friends and church family, especially Pastor and Sandra Borders, Kara Dunn, Tamara Nall, and the Eutsays: God definitely answers prayers!

To the Hammond group, past and present, I say thank you! Mike Berg, Dean Delongchamp, Mark Johnson, and LaRuth McAfee: Thanks for everything! A special note of thanks goes to Monica Rixman and Shawna Liff for their friendship during the
whirlwinds in my time at MIT. I would also like to thank Jocelyn Nadeau and Brian Pate for their support and kindness as friends and collaborators.
# Table of Contents

**Chapter 1: Motivation and Background** .......................................................... 13  
1.1 Introduction ........................................................................................... 13  
1.2 Research Outline ...................................................................................... 14  
1.3 Background ................................................................................................ 14  
  1.3.1 Native Spider Silk.............................................................................. 14  
  1.3.2 Segmented Polyurethanes ............................................................... 21  
  1.3.3 Segmented Polyurethanes with Complex Soft Domain Architectures 24  
  1.3.4 Polyurethane Nanocomposites ........................................................... 26  
1.4 Conclusions .............................................................................................. 28  
1.5 References .................................................................................................. 28  

**Chapter 2: Materials Design** ........................................................................ 34  
2.1 Introduction .............................................................................................. 34  
2.2 Component Selection ................................................................................... 34  
  2.2.1 Soft Segment ....................................................................................... 35  
  2.2.2 Hard Segment ....................................................................................... 40  
  2.2.3 Nanofiller ............................................................................................. 41  
2.3 Conclusions .............................................................................................. 42  
2.4 References .................................................................................................. 43  

**Chapter 3: Semicrystalline PEO-containing Polyurethanes** ............................. 48  
3.1 Introduction .............................................................................................. 48  
3.2 Experimental ............................................................................................ 48  
3.3 Polymer Characterization ............................................................................ 52  
  3.3.1 Thermal Characterization .................................................................... 53  
  3.3.2 Morphological Characterization ......................................................... 57  
  3.3.3 Mechanical Behavior ........................................................................... 68  
3.4 Conclusions .............................................................................................. 72  
3.5 References .................................................................................................. 73
Chapter 4: Deformation-Induced Morphological Development in Semicrystalline
Segmented Polyurethanes

4.1 Introduction ................................................................. 77
4.2 Background .................................................................... 77
4.3 Experimental ............................................................... 85
4.4 In-situ SAXS Deformation .................................................. 86
  4.4.1 PU-1-33 ............................................................... 87
  4.4.2 PU-2-41 ............................................................... 92
4.5 In-situ WAXS Deformation.................................................. 94
  4.5.1 PU-1-33 ............................................................... 94
  4.5.2 PU-1-47 ............................................................... 98
  4.5.3 Effect of Temperature on the Tensile Deformation of PU-1-33 ........ 101
4.6 In-situ Optical Microscopy ............................................... 101
4.7 Conclusions ................................................................ 105
4.8 References .................................................................... 107

Chapter 5: PEO-Containing Polyurethane/Clay Nanocomposites

5.1 Introduction ................................................................. 109
5.2 Background .................................................................... 109
5.3 Experimental ............................................................... 111
5.4 Mechanical Behavior ...................................................... 114
5.5 Morphological Behavior .................................................. 118
5.6 Conclusions ................................................................ 128
5.7 References .................................................................... 128

Chapter 6: Liquid Crystalline PEO-containing Segmented Polyurethanes

6.1 Introduction ................................................................. 130
6.2 Experimental ............................................................... 130
6.3 Synthesis .................................................................... 132
  6.3.1 Diamine-terminated PEO ............................................ 133
  6.3.2 Gamma-Benzyl-L-Glutamate N-Carboxy Anhydride (BLG-NCA) ...... 135
  6.3.3 Poly(ethylene oxide)-poly(γ-benzyl-L-glutamate)-poly(ethylene oxide) (PEO-
  PBLG-PEO) ................................................................. 137
  6.3.4 PBLG-PEO-PBLG Soft Segment Polyurethanes ................. 139
6.3.5 Summary of Structural Characterization of PBLG-PEO-PBLG Copolymers and Polyurethanes .................................................................. 140

6.4 Morphological Behavior .................................................................................................................. 142
  6.4.1 Thermal Behavior ..................................................................................................................... 142
  6.4.2 PBLG-PEO-PBLG Conformation .............................................................................................. 144
  6.4.3 Small-Angle X-ray Scattering ................................................................................................. 145
  6.4.4 Optical Microscopy .................................................................................................................. 146

6.5 Conclusions ..................................................................................................................................... 148

6.6 References ...................................................................................................................................... 148

Chapter 7: Conclusions and Future Directions .................................................................................. 151

7.1 Summary ......................................................................................................................................... 151

7.2 Future Directions ............................................................................................................................. 153
  7.2.1 Semicrystalline Segmented Polyurethanes .............................................................................. 153
  7.2.2 PEO-containing Polyurethane/Laponite Nanocomposites ................................................. 154
  7.2.3 PBLG-PEO-PBLG Copolymers as Polyurethane Soft Segments ......................................... 154

7.3 References ...................................................................................................................................... 157
List of Figures

Figure 1.1: Amino Acid Composition of Spidroin 1 ................................................. 16
Figure 1.2: Energy-Minimization Model of Spider Silk .............................................. 18
Figure 1.3: Proposed Morphology Model of Spider Silk ............................................. 20
Figure 1.4: Two-Phase Microstructure of Segmented Copolymers ............................... 22
Figure 1.5: Deformation Model of Segmented Polyurethanes ...................................... 24
Figure 1.6: Segmented Polyurethanes with Ordered Regions within the Soft Domain .... 26
Figure 1.7: Surface Area to Volume Ratios for Various Nanofiller Sizes, Adapted ......... 27
Figure 2.1: Two-step Solution Synthetic Route High Molecular Weight Segmented
Polyurethanes ........................................................................................................... 35
Figure 2.2: Poly(ethylene oxide) (PEO)-containing Polyurethane Soft Segments ......... 36
Figure 2.3: PBLG-PEO-PBLG phase model .................................................................. 39
Figure 2.4: Hard Segment Chemical Structure ............................................................ 41
Figure 2.5: Schematic representation of Laponite ....................................................... 42
Figure 3.1: DSC Heating Scans of PEO-containing Semicrystalline Polyurethanes:
  Second Heating Cycle (y-axis shifted for clarity) .................................................. 56
Figure 3.2: Small-angle X-ray scattering Data for PEO-containing Semicrystalline
  Polyurethanes .......................................................................................................... 58
Figure 3.3: Possible Micro-phase Segregation Scenarios in Segmented Polyurethanes .. 61
Figure 3.4: Temperature-dependent SAXS patterns of PU-3-33 ................................. 62
Figure 3.5: Wide-angle X-ray Scattering Data of PEO-containing Semicrystalline
  Polyurethanes .......................................................................................................... 63
Figure 3.6: AFM Phase Images: a) PU-1-33, b) PU-1-43, and c) PU-1-47 ................. 65
Figure 3.7: Optical Micrographs of PEO-PPO-PEO containing Polyurethanes .......... 67
Figure 3.8: Morphological Model of Superstructure in Polyether-Polyurethanes ........ 68
Figure 3.9: Representative Stress-Behavior of PEO-containing Polyurethanes .......... 69
Figure 3.10: Representative Cyclic Loading of PU-1-43 ............................................... 70
Figure 3.11: Tan delta and Storage Modulus of Semicrystalline Polyurethanes .......... 72
Figure 4.1: Bonart Model for the Deformation Behavior of Paracrystalline Hard Segment
  Polyurethanes .......................................................................................................... 78
Figure 4.2: Schematic Model of FT-IR Dichroism Investigations of Paracrystalline and Crystalline Hard Segment Polyurethanes ........................................................................ 79
Figure 4.3: Schematic Model of the Orientation Mechanism of Spherulitic Polyurethaneureas under Deformation ................................................................. 80
Figure 4.4: Dominant Modes of Deformation Based on Shape and Structural Rigidity of the Hard Domains in Segmented Polyurethanes ................................................ 82
Figure 4.5: Summary of Deformation-Induced Structural Development in Segmented Polyurethaneureas for Soft Segment Continuous Morphologies ............................. 84
Figure 4.6: Cartoon of the Hard Domain Orientation Behavior that Induces the Scattering Patterns Typical in Segmented Polyurethanes ........................................... 87
Figure 4.7: Small-angle X-ray patterns of PU-1-33 as a Function of Strain. *Hard domains are represented by the black rectangles.* .................................................. 89
Figure 4.8: Azimuthal Plots of PU-1-33 ........................................................................................................ 90
Figure 4.9: Interdomain Spacing as a Function of Strain for PU-1-33 ...................................................... 91
Figure 4.10: Depiction of the Change in Interdomain Spacing with Increasing Strain for PU-1-33. *Hard domains are represented by the black rectangles.* .................. 92
Figure 4.11: In-situ SAXS Deformation of PU-2-41 ............................................................................... 93
Figure 4.12: Azimuthal Plot of PU-2-41 ..................................................................................................... 94
Figure 4.13: 2-D Wide-angle X-ray Scattering Patterns and Azimuthal Plots at 0% Strain (left) and 257% Strain (right) for PU-1-33. *Note: D (2θ = 19.6°), E (2θ = 21.3°), F (2θ = 23.6°), and α (2θ = 20.6°).* ......................................................... 96
Figure 4.14: Azimuthal Representation of the Hard Segment Reflections with Increasing Strain for PU-1-33 (Equator 180°) ......................................................................... 97
Figure 4.15: Pictorial Summary of the Wide-Angle X-ray Scattering Orientation Behavior for PU-1-33 (angle not drawn to scale) ......................................................... 98
Figure 4.16: 2-D Wide-Angle Scattering Patterns and Azimuthal Plots at 19% Strain (left) and 174% Strain (right) for PU-1-47. *Note: D (2θ = 19.6°), E (2θ = 21.3°), and F (2θ = 23.6°).* .................................................................................................................. 99
Figure 4.17: Azimuthal Representation of the Hard Segment Reflections in PU-1-47 with Increasing Strain ...................................................................................... 100
Figure 4.18: Wide-angle X-ray scattering patterns of PU-1-33 elongated to 175% strain at 23°C, 60°C, and 110°C (left to right) .............................................................. 101
Figure 4.19: Optical Micrographs of PU-1-33 under Cross-polarizers (5X magnification) as a Function of Strain ............................................................................... 103
Figure 4.20: Optical Micrographs of PU-2-41 under Cross-polarizers (5X Magnification) as a Function of Strain .............................................................................. 104
Figure 4.21: Optical Micrographs of PU-1-47 under Cross-polarizers (5X magnification) as a Function of Strain .............................................................................. 104
Figure 4.22: Summary of the In-situ Deformation Behavior of PU-1-33, PU-2-41, and PU-1-47 ........................................................................................................... 106
Figure 5.1: Polymer/Nanocomposite Morphologies ..................................................... 111
Figure 5.2: Comparison of the Stress-strain Behavior of PU-1-33 and 10 wt% Laponite Loaded PU-1-33 and PU-2-41 .............................................................. 115
Figure 5.3: Dynamic Mechanical Behavior of PU-1-33 Nanocomposites at 0 and 10 wt% Clay Loadings ......................................................................................... 117
Figure 5.4: DMA plot comparing 10 wt% PU-1-33/ and PU-2-41/Laponite Films ...... 118
Figure 5.5: TEM Images of 10wt% PU-1-33/Laponite Films. Top Image: Exfoliation and Phase Segregation, Bottom Image: Intercalated-and-flocculated Structures .......... 120
Figure 5.6: WAXD of 10wt% PU-1-33/Laponite Films ............................................... 122
Figure 5.7: SAXS patterns for the PEO-containing polyurethane nanocomposites ...... 123
Figure 5.8: Optical Micrographs of PEO-containing Polyurethane/Laponite Composites:
   a) PU-1-33, b) PU-1-33 & 10wt% Laponite, and c) PU-2-41 & 10wt% Laponite.
   Arrow points to grip ......................................................................................... 126
Figure 5.9: Schematic of Proposed PEO/Laponite Interaction in the PEO-containing Polyurethane/Laponite Clay Model ............................................................... 127
Figure 6.1: Synthetic Scheme for the Preparation of Diamine-terminated PEO1000 .... 133
Figure 6.2: Synthetic Route for the Preparation of BLG-NCA .................................. 135
Figure 6.3: Synthetic Route for the Polymerization of PBLG-PEO-PBLG .................. 137
Figure 6.4: Synthetic Scheme for the Development of Polyurethanes containing PBLG-PEO-PBLG Copolymers ................................................................. 139
Figure 6.5: FT-IR spectra of PBLG3-PEO1000-PBLG3 and PBLG5-PEO1000-PBLG5 ................................................................. 145

Figure 6.6: SAXS Patterns of Polyurethanes Containing PBLG-PEO1000-PBLG Copolymers ............................................................................................................................ 146

Figure 6.7: Polarized Optical Micrographs of a) PEO1000(NH₂)₂, b) PBLG₅-PEO1000-PBLG₅, and c) PBLG₅-PEO1000-PBLG₅ Polyurethane ................................................................. 147

Figure 7.1: Synthetic Scheme for the Design of PEO-PBLG-PEO copolymers .......... 156
## List of Tables

Table 1.1: Comparison of the Mechanical Properties of Spider Silk and Other Engineering Materials .................................................................................................................. 15

Table 3.1: Compositional Details for Semicrystalline Polyurethanes ........................................ 53
Table 3.2: Thermal Transitions of Semicrystalline PEO-containing Polyurethanes .............. 55
Table 3.3: Tensile Properties of PEO-containing Semicrystalline Polyurethanes ............. 69
Table 3.4: Hysteresis Percentages of PEO-containing Semicrystalline Polyurethanes .......... 70
Table 5.1: Tensile Properties of PU-1-33/ and PU-2-41/Laponite Films ..................... 115
Table 5.2: Thermal Properties of PU-1-33/Laponite Films ................................................. 124
Table 6.1: Structural Characterization of PBLG-PEO-PBLG Copolymers and Polyurethanes .................................................................................................................. 142
Chapter 1: Motivation and Background

1.1 Introduction

Knowledge of the superior combination of strength and extensibility of natural spider silk, especially the dragline silk of the golden orb weaver, *Nephilia clavipes*, has led to an overwhelming interest in the development of spider silk mimics over the last twenty years, spawning research thrusts in numerous industrial, academic, and military areas. Native spider silk consists of alternating hydrophilic, soft (amorphous, glycine-rich) and hydrophobic, hard (β-pleated sheets of alanine) blocks; a second level of order also exists within the glycine-rich, continuous domain. This “oriented” amorphous component has been attributed to the superior toughness of natural spider silk. Recombinant DNA technology, templated modular synthetic methods, and self-assembled, non-templated approaches have been applied to develop nano-structured biopolymers with high degrees of structural regularity as spider silk analogs, which contain amorphous soft blocks and β-pleated hard blocks 1-7. By focusing solely on block regularity, these approaches neglect the influence of partially oriented regions within the soft domain.

Thermoplastic elastomers, specifically multi-block copolymers such as segmented polyurethanes, provide a unique template for the design of synthetic materials with hierarchical structures within the continuous domain. In traditional segmented copolymers, the soft segments are above their glass transition temperature (T_g), creating a flexible, amorphous block, while the hard segments are below their T_g or melting temperature, forming a rigid or paracrystalline domain that “physically crosslinks” the continuous network of soft segments and acts as a reinforcing filler. These crosslinks are reversible at elevated temperatures and/or in appropriate solvents so that the material may be processed as a thermoplastic. However, soft segments may be chosen that contain ordered regions, which may reduce the ultimate elongation of the material, but contribute to the overall mechanical reinforcement.
This thesis focuses on the development of silk-inspired polyurethane elastomers, which incorporate hierarchical microstructure within the soft domain. The soft segment is designed to contain a rigid, orientable group, which can undergo strain during the deformation process. When incorporated as the polyurethane soft segment, aggregates of these crystalline or liquid crystalline groups contribute to the overall mechanical strength of these polymers by providing an additional load-bearing phase. Nanofillers, capable of specific and non-specific interactions with regions of the multi-block soft segment, may also enhance the toughness of these segmented polyurethanes. This research outlines the design, synthesis, and characterization of novel polyurethanes and polyurethane nanocomposites, which mimic the molecular architecture of native spider silk.

1.2 Research Outline

The overall goal of this research is to investigate the role of soft domain ordering on the mechanical properties and morphological behavior of segmented polyurethanes in an effort to develop high performance materials. In Chapter 1, the motivation and background for this project will be introduced, which frames the design of these hierarchical silk-inspired materials (Chapter 2). Based on our three-pronged design strategy, the development of PEO-containing semicrystalline (Chapter 3) and liquid crystalline (Chapter 6) polyurethanes, and PEO-containing polyurethane nanocomposites (Chapter 5) will be discussed. Chapter 4 will detail the deformation-induced morphology of the semicrystalline PEO-based polyurethanes in an effort to understand their enhanced mechanical properties. Research conclusions and future directions are provided in Chapter 7.

1.3 Background

1.3.1 Native Spider Silk

A comparison of the mechanical properties of spider silk to other typical engineering materials is shown in Table 1.1. The combination of strength and extensibility gives spider silk its extreme toughness, leading to an investigation of the molecular architecture of native spider silk.
Table 1.1: Comparison of the Mechanical Properties of Spider Silk and Other Engineering Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Modulus (GPa)</th>
<th>Tensile Strength (GPa)</th>
<th>Extensibility (%)</th>
<th>Toughness (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dragline Silk</td>
<td>10</td>
<td>1.1</td>
<td>35</td>
<td>160</td>
</tr>
<tr>
<td>Viscid Silk</td>
<td>0.003</td>
<td>0.5</td>
<td>270</td>
<td>150</td>
</tr>
<tr>
<td>Synthetic Rubber</td>
<td>0.001</td>
<td>0.05</td>
<td>850</td>
<td>100</td>
</tr>
<tr>
<td>High Tensile Steel</td>
<td>200</td>
<td>1.5</td>
<td>0.8</td>
<td>6</td>
</tr>
<tr>
<td>Nylon Fiber</td>
<td>5</td>
<td>0.95</td>
<td>18</td>
<td>80</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>130</td>
<td>3.6</td>
<td>2.7</td>
<td>50</td>
</tr>
</tbody>
</table>

Lewis and Xu concluded that the silk of the *Nephilia clavipes* consists mainly of two proteins, designated as *Spidroin 1 & 2*. The amino acid representation of the primary component of dragline silk, *Spidroin 1*, is shown in Figure 1.1. In this amino acid sequence, hydrophilic glycine-rich soft regions alternate with hydrophobic alanine-rich hard regions, suggesting that the protein exists as a multi-block copolymer. The alanine-rich “hard” domains, which form β-pleated sheets (2 x 5 x 7 nm in size) via hydrogen bonding, are dispersed in flexible glycine-rich matrix. These alanine-rich segments aggregate to create physical crosslinks within the continuous, glycine-rich matrix, forming a thermoplastic elastomer. *Spidroin 2* contains a more random arrangement of alanine. These alanine residues are also interrupted by bulky proline-rich sequences, forming a more flexible, amorphous material.
The mechanical function of spider silk is intimately tied to its unique material properties. Two exceptional characteristics of native spider silk are its high degree of hysteresis\(^8\) (65\%) or the ratio of the energy dissipated to the energy absorbed and
supercontraction\textsuperscript{11} or the shrinkage of silk fibers when immersed in water. One of the most important uses of silk fiber is the capture of flying insects. This capture is made possible by absorption of the insect's kinetic energy and transformation into heat, preventing the prey from catapulting from the web and limiting the processes that cause fracture. Another less obvious feature of the silk fiber is supercontraction. This fiber contraction results in a dramatic decrease in its mechanical properties, most likely caused by the release of the extended conformations or "pre-stretch" developed during the spinning process as a result of hydration \textsuperscript{12}.

The morphological behavior of spider silk has been studied extensively using both computational and experimental methods. Termonia modeled the mechanical behavior of spider silk using an energy-minimization model on a fixed lattice \textsuperscript{8,12}. Figure 1.2 provides both a morphological and mathematical representation of the silk for a 15% volume fraction of β-pleated sheets. Based on the structural features noted in spider silk, this model included amorphous chains, β-pleated sheets, hydrogen bonds, and entanglements. The existence of a higher modulus layer adjacent to the crystallites, indicated by triple lines in the mathematical representation, was also included in this model.
The mechanical response of this two-phase semicrystalline network was obtained using physical estimates for the modulus of the hydrogen bonds, amorphous chains, crystallites, and the rubbery layer of high modulus. Additionally, the network is prestretched before hydrogen bonding is imposed to capture the stressed state of the dry silk. The stress-strain behavior predicted by this model is qualitatively consistent with experimental mechanical behavior, yielding a tensile strength of about 1 GPa and an elongation at break of 30% and predicting the supercontraction observed in natural spider silk.\textsuperscript{8,12}

Although this computational study has depicted qualitatively the mechanical behavior of spider silk, experimental investigations have added more detail to the domain structure of the traditional two-phase morphology of \textit{semicrystalline copolymers}. Using both small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD), Grubb and co-workers have concluded that two fractions exist within the amorphous phase in native spider silk: a partially oriented region and a fully isotropic portion.\textsuperscript{13,14} In these studies, the scattering patterns were described by a bimodal orientation.
distribution that accounted for the isotropic amorphous ring and an oriented non-crystalline phase.

Similarly, Simmons et al. have demonstrated in several solid-state nuclear magnetic resonance (NMR) studies that two separate oriented regions exist in native spider silk\(^{15,16}\). A best fit to the \(^2\text{H}\) NMR spectrum of silk fibers was obtained by two Gaussian distributions: one distribution that describes the highly oriented crystallites and another distribution that accounts for the weakly ordered crystalline region. The \(^{13}\text{C}\) cross polarization/magic angle sample spinning (CP/MAS) NMR spectra of silk fibers has revealed also that a portion of the fiber exhibits a relaxation time between that of an fully isotropic material and a purely crystalline material, but distinct from both. Based on these experimental findings, a widely accepted three-component morphology model has evolved\(^{16}\). Figure 1.3 gives a schematic of the proposed morphology of natural spider silk, in which highly oriented alanine-rich \(\beta\)-pleated sheets (~15%) and weakly ordered crystalline or "oriented" amorphous regions (~30%) are embedded in an amorphous, glycine-rich matrix (~55%). This unique morphology gives rise to the superior mechanical properties of dragline silk.
Figure 1.3: Proposed Morphology Model of Spider Silk\textsuperscript{16}
1.3.2 Segmented Polyurethanes

As suggested in the previous Section, the architecture of spider silk most closely resembles that of a thermoplastic elastomer, specifically a multi-block or segmented copolymer. The flexible design chemistry and extensive literature base of segmented polyurethanes contribute to their utility as the synthetic framework of materials with hierarchical ordering in the continuous domain.

Physically-crosslinked segmented polyurethanes were first reported by Schollenberger in 1958, describing an alternative to cross-linked polyurethane elastomers and launching a myriad of research investigations into the morphological and mechanical behavior as a function of soft and hard domain structure. Bonart and Clough et al. confirmed that, in these linear polyurethanes, the hard segments aggregate via hydrogen bonding of urethane linkages and/or paracrystallinity to form hard domains (100 – 200 Å) that physically crosslink the continuous, soft phase. These physical crosslinks, unlike chemical crosslinks, are reversible above the hard domain ordering transition and/or in polar solvents. The elastomeric nature of these linear multi-block polyurethanes has been attributed to the reinforcing effect of the nano-sized hard domains. Figure 1.4 illustrates a simplistic view of the morphology of segmented polyurethanes.
The polymerization method influences the microstructure regularity, and hence, the mechanical properties of these segmented polyurethanes. The one-shot method, in which the soft segment polyol, diisocyanate, and chain extender are mixed all at once, usually in bulk form, is the most commonly used polymerization method in industry, but lacks the control necessary for regularity of the block sequences. In the two-step method, usually in solution, the polyol or macrodiol is first reacted with a slight excess of the diisocyanate in a controlled, slow addition. This end-capped macrodiol is then chain-extended with a low molecular diol, such as 1,4-butanediol, and a stoichiometric amount of the diisocyanate to build high molecular weight polyurethane. The two-step solution polymerization method produces segmented polyurethanes with fewer side reactions and polydispersity indices (PDI) close to 2, as expected for step-growth polymerizations. Above a certain molecular weight, the mechanical properties of segmented polyurethanes are relatively constant.

The soft matrix is usually comprised of polyether or polyester diols or polyols, such as poly(tetramethylene oxide) (PTMO) and poly(ethylene adipate) glycol,
respectively, with a soft block molecular weight between 400 – 6000 g/mol\textsuperscript{21}. Polyether-based polyurethanes have exceptional hydrolytic stability and flexibility compared to polyester-based polyurethanes, which exhibit higher thermal stability, tensile strength, and modulus \textsuperscript{24,25}. The ether bond (C-O) bond in the polyether soft segments and the ester (CO-O) bond in the polyester are also capable of hydrogen bonding with the urethane linkages (NH-CO) in the hard domain, influencing the degree of micro-phase segregation; polyesters are generally stronger hydrogen bond acceptors than polyethers\textsuperscript{26}. These general observations are dependent upon the crystallinity or ordering of the soft segments, which is a function of molecular weight. As the polyol molecular weight decreases, the stiffness of the polyurethane increases, improving the tensile strength and tear strength of the materials \textsuperscript{21}.

Aromatic and aliphatic diisocyanates with diol chain-extenders are used as the polyurethane hard segments. 4,4'-methylene bisphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), which is a mixture of 2,4 and 2,6 isomers, are the most commonly used diisocyanates. The structural rigidity of these aromatic hard segments generally produce elastomers with high tensile strength and modulus and enhanced thermal stability \textsuperscript{21}. However, these aromatic units are susceptible to attack by ultraviolet radiation, causing degradation and yellowing without the use of stabilizers. Aliphatic diisocyanates, such as 1,6-hexamethylene diisocyanate (HDI), offer ultraviolet stability and resistance to hydrolytic degradation, but are less reactive than the aromatic hard segments \textsuperscript{21,26}. These aliphatic hard segments may impart more flexibility to the microstructure compared to aromatic hard segments, inducing a higher degree of phase separation based on kinetic arguments \textsuperscript{27,28}.

The mechanical behavior of segmented polyurethanes has been investigated extensively and is intimately linked to the composition of the hard and soft domain and their resulting morphology. Linear polyurethanes are generally characterized by high degree of extensibility, tensile strength and initial moduli and exhibit stress-softening and hysteresis under cyclic loading \textsuperscript{21,29}. Using infrared dichroism and small-angle X-ray scattering studies, the deformation behavior of multi-block polyurethanes was examined, reporting that strain-induced crystallization of the soft segments in the stretch direction occurs up to 200% elongation, shown as A in the model in Figure 1.5 \textsuperscript{19,26,29-32}. The hard
domains align perpendicular to the stretch direction as a result of the extended state of the soft segment. Above 200% elongation, the hard domains align in the stretch direction, disrupting the hydrogen-bonded hard domain aggregates and crystalline domains, which results in plastic deformation as observed by the large residual orientation of the hard domains after stress removal, which is depicted in B of the deformation model in Figure 1.5.

![Deformation Model of Segmented Polyurethanes](image)

**Figure 1.5: Deformation Model of Segmented Polyurethanes**

1.3.3 *Segmented Polyurethanes with Complex Soft Domain Architectures*

Previous studies have focused primarily on the effect of soft segment type and length, hard segment type and length, hard domain crystallinity, and the extent of micro-phase segregation on structure-function relationships in segmented polyurethanes. However, few investigations have targeted the role of soft segment ordering on the morphology and mechanical properties of segmented polyurethanes. In poly(ε-caprolactone) (PCL)-containing polyurethanes, PCL crystallites have been shown to contribute to the overall reinforcement of the continuous domain, enhancing the mechanical behavior of these systems. Chang and Wilkes considered the effect of
soft segment crystallinity on the morphology of segmented polyurethaneureas with amorphous hard domains and poly(ethylene oxide) (PEO) and/or poly(propylene oxide) (PPO) soft segments, determining that the PEO crystallinity dominates the superstructure at low hard segment contents and increases the modulus, but decreases the strain-at-break of these materials. Gunatillake et al. examined the role of soft segment paracrystallinity on the modulus and hardness of comacrodiols of polyethers [(CH₂)nO] of n>4.

A recent review of liquid crystalline (LC) polyurethanes highlighted the use of mesogenic hard segments and chain extenders in the development of novel segmented polyurethanes, which combine the processability, mechanical integrity, and design flexibility of multi-block polyurethanes and the electro-optical, mechano-optical, and magnetic properties of liquid crystals. In brief, the liquid crystalline (LC) phase is the partial ordering of a material between a solid and a liquid. These materials have the flow behavior of an isotropic liquid, but have molecular ordering between the isotropic liquid state and the true crystalline state (which possesses long-range, three-dimensional order). These rod-like molecules or mesogens may be incorporated directly into a polymer chain, forming a main-chain liquid crystal polymer, or attached as pendant groups, creating a side-chain liquid crystal polymer.

The development of novel segmented polyurethanes using side-chain LC poly(siloxane) soft segments is the only reported modification of the soft domain using liquid crystalline ordering groups to our knowledge. In these studies, Nair et al. reported the coupled deformation behavior of the smectic A layers and the paracrystalline hard domains, suggesting that the incorporation of liquid crystalline moieties within the soft block may provide additional energy-absorbing mechanisms. Figure 1.6 illustrates a morphological representation of segmented polyurethanes with complex ordering within the soft domain.
1.3.4 Polyurethane Nanocomposites

Thermoplastic polyurethane elastomers have benefited from the reinforcing effects of nano-sized fillers in contrast to micron-sized fillers, demonstrating marked improvements in mechanical (modulus, tensile strength, and ultimate elongation) and barrier properties and thermal stability. This drastic enhancement of material properties is a complex function of the increased surface area to volume (S/V) ratio, which promotes interactions between the polymer matrix and the nanofiller, molecular chain dynamics, and domain crystallinity. As the aspect ratio of the nanofiller increases (nanosilica < nanoclay < nanotubes), the exposed surface area increases (assuming sufficient dispersion), which magnifies the dependence of the enhanced material properties on the strength of the interface. A comparison of the surface area to volume ratios for three nanofiller geometries is shown in Figure 1.7.
The interfacial bond between the polyurethane matrix and the nanofiller may be strengthened by the use of compatibilizers. Through chemical modification of the filler surface, or exploitation of block polarity. By compatibilizing the polyurethane/filler interface, uniform nanofiller dispersion is achieved, maximizing contact between the segmented polyurethane and the reinforcing filler. This dispersed morphology generates the most desirable improvement in the properties of the polyurethane elastomer. The method of nanofiller dispersal has little effect on the enhancement of mechanical properties, if compatibility between the polyurethane and the nanofiller is maintained.

Various methods of nanofiller incorporation have been utilized in the development of polyurethane nanocomposites. One of the most widely used approaches to nanocomposite formulation is the in-situ polymerization or curing of the polyol or end-capped macrodiol, which was pre-mixed with the reinforcing agent. Melt compounding and solution processing are additional mechanisms of polyurethane nanocomposite preparation.

\[
\begin{align*}
\text{Surface Area} &= 4\pi r^2 \\
\text{Volume} &= \frac{4}{3}\pi r^3
\end{align*}
\]

\[
\frac{S}{V} = \frac{3}{r}
\]

\[
\frac{S}{V} = \frac{2}{t} + \frac{4}{l} = \frac{2}{r} + \frac{2}{l}
\]

**Figure 1.7: Surface Area to Volume Ratios for Various Nanofiller Sizes, Adapted**
1.4 Conclusions

This introductory chapter detailed the inspiration for this thesis research and offered background information relevant to designing materials, which emulate the desired properties of native spider silk. Insight into the molecular architecture, mechanical behavior, and microstructure of native spider silk was discussed. A literature review highlighted the well-established synthetic routes, design issues, and mechanical function of segmented polyurethanes. Previous investigations regarding the influence of ordering within the continuous domain on the mechanical behavior of polyurethane elastomeres were also discussed. Advances in and challenges associated with the design of high performance polyurethane nanocomposites were also reviewed. This motivational and background information will aid the development of silk-inspired polyurethanes contained partially oriented regions within the soft phase, which is the focus of Chapter 2.

1.5 References


Chapter 2: Materials Design

2.1 Introduction

Several design parameters must be considered in the development of high performance materials, which mimic the hierarchical morphology of native spider silk. As discussed in Chapter 1, natural spider silk exists as a multi-block copolymer, with alternating soft and hard blocks. The soft segments form a continuous domain, which is physically cross-linked through hydrogen bonding of the crystalline hard domains. However, the continuous, soft matrix also contains weakly ordered regions. This tri-component morphological model has been attributed to the superior toughness of natural spider silk. By controlling the relative amounts of amorphous and oriented regions within the soft domain, our goal is to develop multi-block copolymers with sufficient flexibility and increased initial moduli.

2.2 Component Selection

Segmented copolymers, such as polyesters, polyamides, and polyurethanes, exhibit the multi-block morphology of native spider silk. Segmented polyurethanes were chosen as the synthetic framework for the design of silk-inspired materials due to the extensive body of literature outlining their synthetic development and structure-property relationships\textsuperscript{124}, the flexibility and ease of block selection and incorporation, potential as composite materials, and the expertise and preliminary findings established in the Hammond laboratory\textsuperscript{25-27}. In order to mimic the unique morphology of native spider silk, these thermoplastic polyurethane elastomers are synthesized by a two-step solution polymerization, which allows for greater control of the average length of the soft and hard segments and, hence, a more well-defined microstructure\textsuperscript{28,29}. This synthetic method is detailed in Figure 2.1.
2.2.1 Soft Segment

The selection of a suitable soft segment for a thermoplastic elastomer with hierarchical ordering within the continuous matrix requires careful consideration of design parameters. The soft segment must possess a glass transition temperature below room temperature. Semicrystalline or liquid crystalline units are incorporated within the flexible matrix to introduce partial orientation within the soft domain. Additionally, the soft segment must be alcohol-terminated in order to react as a macrodiol in the
polyurethane and polyester chemistry. Finally, the soft segment and hard segment must be thermodynamically incompatible to promote phase separation. Figure 2.2 highlights the hierarchical polyurethane soft segments under investigation in this research. These soft segments will be discussed in detail below.

![Figure 2.2: Poly(ethylene oxide) (PEO)-containing Polyurethane Soft Segments](image)

2.2.1.1 Semicrystalline Soft Segment

Poly(ethylene oxide) (PEO) with hydroxyl-end groups is the most common semicrystalline polyether soft segment (SS) used in the synthesis of polyurethane elastomers. This polyether polyol may be synthesized by cationic or anionic ring opening of epoxide because of its high degree of ring strain. PEO is a water-soluble and biocompatible polymer, which makes it an attractive candidate to achieve benign
processing conditions, such as in native spider silk, to promote evaporating cooling, and to develop new biomaterials. Poly(ethylene oxide) is also highly polar; this polarity can be exploited in the design of nanocomposites. The glass transition temperature of PEO is well below room temperature, but, depending on its molecular weight, the melting temperature may vary from 30 - 60°C, which may moderate the extent of soft segment flexibility. By copolymerizing PEO with an amorphous component, the degree of order within the soft domain may be tuned, varying the material properties of the segmented polyurethane.

A variety of tri-block copolymers with different PEO (semi-crystalline) and amorphous poly(propylene oxide) (PPO) block sizes are commercially available, allowing for systematic control of the crystalline order within the soft segment without significant synthetic modification. Pluronics are manufactured via a two-step patented process. The PPO block is polymerized by the stoichiometric addition of propylene oxide to propylene glycol. Controlled addition of ethylene oxide to this hydrophobic block results in the desired tri-block structure, allowing for separate control of the PPO and PEO block lengths and ensuring a narrow polydispersity index (PDI) for the copolymer. The PPO segment may display specific interactions with treated-nanosilica surfaces and other hydrophobic surfaces, providing another mechanism to sequester preferentially the nanofillers within the soft domain and form polyurethane nanocomposites with enhanced mechanical properties similar to native silk.

Specifically, a hydroxyl-terminated PEO-PPO-PEO copolymer with a $T_m = 17°C$ was used as the candidate for the weakly oriented soft segment in the multi-block copolymers. The phase behavior and thermo-oxidative degradation profiles of PEO-PPO-PEO copolymers or Pluronics have been widely investigated for surfactant applications, providing insight into their long-term stability as polyurethane soft segments. Lan et al. developed polyurethane for biomaterial applications containing PEO-PPO-PEO soft segments with varying PEO block sizes and aliphatic hard segments, reporting that the PEO content favorably influenced the tensile properties and degree of phase segregation.

Pure poly(ethylene oxide) soft segments, with a molecular weight of 1000 g/mol ($T_m = 37°C$) and 4600 g/mol ($T_m = 58°C$), were also used for comparison studies.
2.2.1.2 Liquid Crystalline Soft Segment

The existence of a liquid crystalline phase has been attributed to the high degree of molecular order observed in the spinning dope of spider silk\textsuperscript{34}. Polypeptides, such as poly(\(\epsilon\)-lysine) and poly(\(\gamma\)-benzyl-\(\epsilon\)-glutamate) (PBLG), have been copolymerized with a variety of dissimilar blocks, such as PEO, PPO, polystyrene (PS), and polybutadiene (PB), to form rod-coil copolymers, which exhibit multiple levels of crystalline and liquid crystalline order\textsuperscript{35}.

Due to its solubility characteristics and well-defined liquid crystalline behavior, PBLG, a hydrophobic, synthetic polypeptide, has been used to investigate self-assembly trends in rod-coil-rod block copolymers\textsuperscript{36-39}. Diamine-terminated PEO or PEO-PPO-PEO has been utilized as a macroinitiator for benzyl-L-glutamate N-carboxy anhydride (BLG-NCA), producing the desired tri-block or penta-block copolymer, which combines the desirable characteristics of PEO and hierarchical microstructure of PBLG\textsuperscript{40}. The incorporation of rod-coil copolymers as polyurethane soft segments offers an opportunity to explore further the complex deformation mechanisms of hierarchically designed, segmented polyurethanes. As shown in Figure 2.3, poly(\(\gamma\)-benzyl-\(\epsilon\)-glutamate)-poly(ethylene oxide)-poly(\(\gamma\)-benzyl-\(\epsilon\)-glutamate) (PBLG-PEO-PBLG) may exhibit crystallinity within the PEO block and may display both \(\alpha\)-helix and \(\beta\)-sheet secondary structures in the PBLG block, depending upon the PBLG volume fraction\textsuperscript{36}. The phase structures accessible in these triblock copolymers and PEO-PBLG-PEO copolymers make them ideal candidates for the investigation of soft segment ordering on the mechanical behavior of multi-block polyurethanes.
Several PEO or PEO-containing copolymers were considered as candidates for the middle block. As mentioned earlier, polyurethane soft segments vary between 500 – 5000 g/mol. In order to increase the PBLG volume fraction, and thus assess the liquid crystalline textures of the PBLG-PEO-PBLG triblock, the middle block must have a molecular weight below 2000 g/mol to balance these two criteria. Diamine-terminated PEO (molecular weight 2000 g/mol) is commercially available, but at a significant cost (~$250/g). Pluronics were also considered, but the amination process involves several tedious synthetic steps, each step requiring substantial purification. The most efficient method for purification involves repeated precipitation, which is not possible for PEO-PPO-PEO (1900 g/mol) due to its low melting point. Thus, PEO (1000 g/mol) was...
chosen for the middle block, allowing for purification via precipitation and fulfilling the molecular weight requirements.

2.2.2 Hard Segment

An aliphatic diisocyanate, 1,6-hexamethylene diisocyanate (HDI), chain-extended with 1,4-butanediol (BDO) will be incorporated as the polyurethane hard segment, as shown in Figure 2.4. HDI is a highly crystalline diisocyanate, which forms spherulitic structures under moderate annealing conditions (room temperature, on the order of minutes)\(^8,41,42\). Unlike 4,4'-methylenediphenyl diisocyanate (MDI) – BDO hard segments, HDI-BDO imparts flexibility to the hard domain, which promotes the rate and extent of micro-phase segregation and may moderate the plastic deformation behavior of the segmented polyurethane\(^8,41,42\). The use of an aliphatic diisocyanate, such as HDI, also circumvents issues related to thermal degradation and light instability usually associated with the aromatic hard domain\(^8,41,42\). In addition, the high degree of crystallinity in HDI lowers its susceptibility to hydrolytic attack. These findings support the decision to use HDI-BDO as the polyurethane hard segments.
2.2.3 Nanofiller

The introduction of nanofillers, such as nanosilica, nanotubes, and nanoclays, to the polyurethane matrix have been attributed to an enhancement of material properties, including reduced gas permeability, heat distortion temperature, and initial moduli, below a critical loading concentration \(^4^3\). In the PEO-containing polyurethane systems, the goal is to disperse these nanofillers within the ordered soft segment, constructing an additional level of deformational hierarchy in the continuous domain through disruption of the particle/soft segment interaction. As mentioned in Section 2.2.2.1, treated-nanosilica associates with the hydrophobic PPO via non-specific interactions \(^4^4\). For single phase, elastomeric polyurethanes, dramatic improvements in tensile strength and elongation-at-break are observed due to the nanosilica particles, which are similar in size to the polyurethane hard domains (10 - 20 nm), serving as additional reinforcing sites within the matrix \(^4^5\). However, the inefficiency of nanosilica dispersal (during polyurethane synthesis or mixing with polymer solution), the tendency for particle aggregation at high loadings, and weak dependence of the initial moduli on nanosilica loading may diminish their effectiveness \(^4^4, ^4^6\).
Carbon nanotubes have also been reported as fillers for thermoplastic polyurethane elastomers, which improve the shape-memory behavior by impacting strain-induced crystallization in the soft domain and enhancing the elastic moduli. However, the high cost of nanotube fabrication and the significant challenges associated with tube alignment and processing methods limit their large-scale viability as nanoreinforcers.

Natural and synthetic clays, such as Montmorillonite and Laponite, respectively, have served as reinforcing fillers for thermoplastic polyurethanes. Montmorillonite is a smectic, natural layered silicate with a high aspect ratio (~100), layer spacing, and non-uniform platelet size. While Montmorillonite has offered significant improvements in polyurethane material properties, the reduced gallery spacing, low heterogeneity, and strongly hydrophilic character of synthetic Laponite makes it an attractive alternative, especially for PEO-containing polyurethane/clay nanocomposites. This synthetic layered silicate has been reported to enhance the initial moduli without loss of tensile strength or elasticity using a novel solvent-exchange method for Laponite dispersal, which further supports the selection of Laponite for the formation of polyurethane nanocomposites. A representation of the Laponite clay is shown in Figure 2.5.

![Laponite Schematic](image)

**Figure 2.5: Schematic representation of Laponite, adapted from Fossum**

### 2.3 Conclusions

This chapter outlines the rational design of segmented polyurethanes with complex soft domain ordering that mimic the molecular architecture of natural spider silk. Semicrystalline and liquid crystalline PEO-containing copolymers will be used as polyurethane soft segments. The hard domain will be comprised of aliphatic, highly crystalline HDI, which has been shown to promote micro-phase segregation in PEO-
containing polyurethanes. Laponite, a hydrophilic, synthetic clay, will be dispersed in the polyurethane matrix as a reinforcing filler in candidate materials. These components will construct the development of high performance, segmented polyurethanes.

2.4 References


Chapter 3: Semicrystalline PEO-containing Polyurethanes

3.1 Introduction

While it has been suggested that crystalline soft segments may contribute to the overall mechanical reinforcement of the continuous domain, few investigations have targeted the role of soft domain ordering on the morphological and mechanical behavior of segmented polyurethanes. Inspired by the hierarchical continuous domain in native spider silk, this chapter details the synthesis, and mechanical and morphological characterization of segmented polyurethanes containing semicrystalline PEO and PEO copolymers.

3.2 Experimental

3.2.1 Materials

All materials were purchased from Sigma Aldrich Co. Dibutyltin dilaurate (DBTDL) was stored under dried nitrogen and used as received. Anhydrous N,N’-dimethylacetamide (DMAc), packaged in a Sure/Seal™ bottle, was used as received.

3.2.1.1 Soft Segment

Poly(ethylene oxide) (PEO) (1000 g/mol and 4600 g/mol) and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) were dehydrated and degassed under vacuum at 60°C for 3-4 hrs and stored under dried nitrogen.

3.2.1.2 Hard Segment

1,6-hexamethylene diisocyanate (HDI) was vacuum distilled and stored under dried nitrogen. 1,4-butanediol was distilled under reduced pressure and stored under dried nitrogen. The hard segment (HS) content was determined using the industry’s standard, which overestimates the diisocyanate contribution to the hard domain, but provides direct comparison for commercially available materials:
\[
\text{wt (\%)} \text{ HS} = \frac{(n+1)M_{\text{HDI}} + n * M_{\text{BDO}}}{(n+1)M_{\text{HDI}} + n * M_{\text{BDO}} + M_{\text{SS}}}
\]

\(n = \text{moles of BDO}\) 

\(M_i = \text{molecular weight}\)  

(Equation 1)

3.2.2 Synthesis

Figure 2.1. in Section 2.2, outlines the synthetic scheme for the synthesis of PEO-containing semi-crystalline polyurethanes. The synthetic procedure for PU-2-41 is detailed here as a representative example of the series.

3.2.2.1 PU-2-41

The segmented polyurethane was synthesized as shown in Figure 2.1. The polymerization was carried out in a glovebox in an effort to minimize any side reactions that may occur with water. An excess amount of HDI (2.58 g, 15.3 mmol) was dissolved in 5 mL of DMAc, added to the three-neck flask, and stirred. PEO (5.12 g, 5.12 mmol) and 5 drops of DBTDL were dissolved in 25 mL of DMAc and added to an addition funnel fitted to a three-neck flask. The PEO/catalyst solution was slowly (~1 hr) dripped into the HDI solution. The reaction mixture was then stirred at 65°C for three hours to form the macrodiol.

The endcapped macrodiol was chain extended to form a high molecular weight polymer. BDO (0.923 g, 10.2 mmol) was added to the reaction mixture and stirred at 85°C overnight; Fourier Transform Infrared Spectroscopy (FT-IR) confirmed the disappearance of the isocyanate peak (2260 cm\(^{-1}\)). The reaction mixture was precipitated into a large excess of warm distilled water. The resulting polyurethane was washed with methanol and dried under vacuum until constant weight. All polyurethane samples were stored in amber bottles at 2-8°C.

3.2.3 Instrumentation

3.2.3.1 Gel Permeation Chromatography

Molecular weights and molecular weight distributions of soluble polymers were determined relative to polyethylene oxide standards using a Waters Gel Permeation...
Chromatograph (GPC) equipped with two Styrogel columns and RI detector with DMAc at 60°C as the mobile phase.

3.2.3.2 Fourier Transform Infrared Spectroscopy

The polymerization was monitored by Fourier Transform Infrared Spectroscopy (FT-IR) with a Thermo Nicolet Nexus 870 spectrometer using a DTGS Kbr detector on West Georgia Laboratories poly(tetrafluoroethylene) (PTFE) IR cards.

3.2.3.3 Differential Scanning Calorimetry

The thermal phase behavior of these thermoplastic polyurethanes was investigated using a TA Instruments Q1000 Differential Scanning Calorimeter (DSC), operating at a heating rate of 10°C/min under nitrogen atmosphere. As-precipitated, unannealed polymer samples were subjected to two heating and cooling cycles between -90°C and 250°C. Transitions were recorded from the second heating and cooling scans using a linear extrapolation method ($T_m$) and the midpoint inflection method ($T_g$).

3.2.3.4 Small-angle and Wide-angle X-ray Scattering (SAXS and WAXS)

Small- and wide-angle X-ray scattering data was acquired at the X27C beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory or at the G1 beamline at the Cornell High-Energy Synchrotron Source (CHESS). The X27C X-ray wavelength, $\lambda$, was 1.366 Å, which was monochromatized from the bending magnet using a double-multilayer (silicon/tungsten) monochromator. The typical flux was $9 \times 10^{11}$ photons/s. The beam was collimated to a maximum spatial resolution of 100 nm using 3 pinholes. The relative X-ray intensity was measured before ($I_0$) and after ($I_1$) the sample by using proportional counters. The X-ray scattering was detected using a Fuji BAS 2500 Imaging Plate System, and SAXS and WAXS data were simultaneously measured. At the CHESS G1 beamline, $\lambda = 1.23$ Å, the beam was collimated to a horizontal divergence of 1 mrad via the wiggler 'K' factor and horizontal-focusing optics. This natural collimation was supplemented by use of two 1 mm slits and a third which functioned as a guard slit. The relative X-ray intensity was measured at positions (1) just before the sample, using a helium-filled proportional counter, and (2) upstream of the collimation slits, using a nitrogen-filled proportional counter. A MedOptics CCD
detector was used to measure the scattered radiation, with pixel size 47.19 μm/pixel and size 1024 x 1024 pixels.

A background pattern was collected for each sample environment, for a collection time equal to the sample collection time. A dark (blocked beam) pattern was measured for each collection time employed. The appropriate dark pattern was subtracted from each sample and background scattering pattern. Each sample pattern was then corrected using the following formula:

{Corrected Scattering Pattern} = {Sample Pattern} - T({Background Pattern}).

For the X27C data, the transmission ratio, T, was taken to be the ratio \( I_1\text{(sample)}/I_1\text{(background)} \) where \( I_1(x) \) was the measured beam intensity after the position of the sample or sample environment, as described above. For the G1 data, \( T \) was an arbitrary scaling factor taken to be 0.9. Data was reduced from 2D (intensity vs. \( \theta, \chi \)) to 1D (intensity vs. \( \theta \)) format by integrating over all values of \( \chi \), for each value of \( \theta \), where \( \theta \) is the scattering angle and \( \chi \) is the azimuthal angle. SAXS data has been expressed in terms of \( q \), where \( q = 4\pi\text{sin}(\theta)/\lambda \). The reduced data was normalized by \( I_1 \).

A Molecular Metrology SAXS equipped with CuK radiation (wavelength of 1.54 Å) and a two-dimensional, gas proportional multi-wire Gabriel detector was also used to obtain SAXS patterns. A hot stage assembly was used for temperature measurements. Background correction was applied as above.

3.2.3.5 Atomic Force Microscopy (AFM)

A Nanoscope D3100 with a Nanoscope IIIa controller and a Multimode Scanning Probe Microscopy were used to probe the nanostructured morphology of these polyurethane films using AFM. Phase images of the sample surfaces were collected in tapping mode using Veeco NanoProbe tips (130 μm, 280-361 kHz).

3.2.3.6 Optical Microscopy (OM)

The crystalline morphologies of the segmented polyurethanes were examined using a Carl Zeiss AxioScope 2MAT Polarizing Microscope under cross-polarizers.
3.2.3.7 Tensile Testing

The tensile properties of these segmented polyurethanes were determined using a Zwick/Roell Z010 with a 500 N load cell and convex jaw grips with aluminum and flat polyurethane faces to minimize tearing at the grips. Polyurethane films were solvent-cast from 5 or 7.5 g/mL solutions in DMAc into Teflon molds and allowed to dry for ~3 days at room temperature. After three days, the films were vacuum-dried at 60°C for ~1 hour prior to use. The samples were elongated to failure at 100% of the gauge length per minute. Tensile properties were the average of at least three specimens. Hysteresis experiments were performed by cycling the specimens between 0 -100 % and 100 % -0% strain three times, and then, elongating to failure.

3.3 Polymer Characterization

High molecular weight thermoplastic polyurethanes of varying hard segment sizes were synthesized. Table 3.1 details the molecular weight, soft segment type, and hard segment size (wt%) for these multi-block polymers. PEO-based polyurethanes with varying soft segment length were synthesized to study the effect, if any, of soft segment crystallinity on mechanical properties. PU-3-33 was insoluble in available GPC eluents so molecular weight information is unavailable. However, PU-3-33 can be solubilized by refluxing in DMAc at 130°C. An analog of the pure hard segment polymer, HDI-BDO, was also synthesized for comparison.
Table 3.1: Compositional Details for Semicrystalline Polyurethanes

<table>
<thead>
<tr>
<th>Polyurethane&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Soft Segment</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
<th>Hard Segment Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1-26</td>
<td>PEO-PPO-PEO</td>
<td>84,100</td>
<td>1.7</td>
<td>26</td>
</tr>
<tr>
<td>PU-1-33</td>
<td>PEO-PPO-PEO</td>
<td>111,000</td>
<td>1.7</td>
<td>33</td>
</tr>
<tr>
<td>PU-1-43</td>
<td>PEO-PPO-PEO</td>
<td>68,700</td>
<td>1.8</td>
<td>43</td>
</tr>
<tr>
<td>PU-1-47</td>
<td>PEO-PPO-PEO</td>
<td>103,000</td>
<td>1.8</td>
<td>47</td>
</tr>
<tr>
<td>PU-2-41</td>
<td>PEO 1000</td>
<td>111,000</td>
<td>2.5</td>
<td>41</td>
</tr>
<tr>
<td>PU-3-33</td>
<td>PEO 4600</td>
<td></td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>HDI-BDO</td>
<td>-</td>
<td>2,600</td>
<td>1.1</td>
<td>100</td>
</tr>
</tbody>
</table>

<sup>a</sup>PU-X-YY where PU denotes polyurethane, X denotes the soft segment type (1-PEO-PPO-PEO 1900 g/mol, 2-PEO 1000 g/mol, 3-PEO 4600 g/mol), and YY denotes the hard segment size (wt%) ($g$ BDO + $g$ HDI)/($g$ soft segment + $g$ BDO + $g$ HDI).<sup>b</sup> Pure hard segment

3.3.1 Thermal Characterization

Segmented polyurethanes display several thermal transitions, corresponding to the microstructure of the soft and hard domains. The soft block undergoes a low temperature glass transition, and, if ordered, a melting transition; the hard segments may display a glass transition and/or multiple ordering transitions. The soft segment glass transition and/or melting peak and the hard segment ordering peak of these polyurethanes with PEO and PEO-PPO-PEO soft segments were determined using DSC. As shown in Table 3.2 and in Figure 3.1, the soft segment glass transition of the PEO-PPO-PEO segmented polyurethanes is independent of hard segment content (26 – 47 wt%), showing a nominal increase in soft segment glass transition compared to the PEO-PPO-PEO copolymer $T_g$ - 69°C and indicating a relatively small amount of hard segment mixing within the soft domain. This behavior was similarly detailed by Sung et al. and O'Sickey et al. on poly(tetramethylene oxide) and poly(propylene oxide), respectively, for a comparable hard segment range<sup>1,2</sup>. Similarly, the glass transition of PU-2-41 and PU-3-33 is only slightly increased from that of pure PEO 1000 and pure PEO 4600. For the PEO polyurethane series, the presence of soft segment crystallites must also be considered in
the evaluation of soft segment $T_g$ since the mobility of the amorphous chains are restricted by neighboring crystallites\(^3\), which is addressed in the following paragraph.

Although pure PEO-PPO-PEO has a melting transition at 17°C, the PEO-PPO-PEO based polyurethanes do not exhibit any ordering within the soft domains. Soft segment crystallinity is observed in the segmented polyurethanes containing pure PEO soft segments. PU-2-41 shows a soft segment melting transition (11°C, 19 J/g), which is much lower than the homopolymer PEO (1000 g/mol) melting peak as determined using DSC (37°C). Thus, although PU-2-41 exhibits a soft segment $T_m$, these crystallites are quite small and ineffective in significantly raising the glass transition temperature. The higher molecular weight pure PEO soft segment (4600 g/mol) in PU-3-33 displays a more pronounced melting transition ($T_m = 41°C$) compared to PU-2-41, but this melting peak is still depressed from the homopolymer PEO melting transition (60°C). These results suggest that a certain degree of phase-mixing occurs between the hard and soft domains, which is commonly observed for polyether polyurethanes because hydrogen-bonding sites exits within both the hard and soft regions of the polymer and/or the crystallization may be constrained by domain confinement, inhibiting the growth of well-ordered crystallites\(^4\).
Table 3.2: Thermal Transitions of Semicrystalline PEO-containing Polyurethanes

<table>
<thead>
<tr>
<th>Soft Segment</th>
<th>Hard Segment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (°C)</td>
</tr>
<tr>
<td>PEO-PPO-PEO 1900</td>
<td>-69</td>
</tr>
<tr>
<td>PEO1000</td>
<td>-56</td>
</tr>
<tr>
<td>PEO4600</td>
<td>-59</td>
</tr>
<tr>
<td>PU-1-26</td>
<td>-62</td>
</tr>
<tr>
<td>PU-1-33</td>
<td>-61</td>
</tr>
<tr>
<td>PU-1-43</td>
<td>-62</td>
</tr>
<tr>
<td>PU-1-47</td>
<td>-63</td>
</tr>
<tr>
<td>PU-2-41</td>
<td>-50</td>
</tr>
<tr>
<td>PU-3-33</td>
<td>-52</td>
</tr>
<tr>
<td>HDI-BDO</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Glass transition temperature obtained from the 2nd heating curve; $^b$ Melting transition obtained from the 2nd heating curve; $^c$ Crystallization temperature obtained from the 2nd cooling curve; $^d$ $^e$ Enthalpy of fusion values are per gram of soft segment and hard segment, respectively.

The as-precipitated pure hard segment, HDI-BDO, exhibits a melting transition on the 2nd heating cycle of 165°C (46 J/g). MacKnight et al. and Li et al. reported values of 182°C (70 J/g) and 180°C (84 J/g), respectively, for pure HDI-BDO. Discrepancies between these literature values and our values are most likely due to variations in sequence length distribution and differences in thermal treatment by other researchers. Although not presented here, the 1st heating scans of the PEO and PEO-PPO-PEO polyurethanes display an annealing endotherm that shifts to higher temperatures as the hard segment composition increases. which has been associated with relaxation effects within the hard domains, specifically for MDI/BDO-based polyurethanes. As expected, the hard-domain melting peak increases as the hard segment content is increased, attaining a melting transition at 47 wt% hard segment that is equivalent to the pure hard domain for the PEO-PPO-PEO soft segment polyurethanes.
The hard-domain melting transitions for the PEO-PPO-PEO soft segment polyurethanes are higher than the pure PEO soft segment polyurethane at similar hard segment amounts. Comparison of PU-1-43 and PU-2-41, which possess a similar hard segment percentage, but different soft segment length and type, indicate a 20°C difference in hard domain melting point, and enthalpy of fusion of 64 versus 43 J/g, respectively. These observations may be the result of two phenomena. The incorporation of a longer soft segment (1900 g/mol versus 1000 g/mol) decreases the amount of exposed hard segment surface area per unit volume in the continuous domain (for a given molecular weight), inducing a higher degree of phase separation\textsuperscript{12}. Despite the differences in molecular weight between PU-1-43 and PU-2-41, the validity of this trend is quite probable. Chang and Wilkes investigated the effect of PPO and PEO content on the morphology of diamine-extended polyurethaneureas, reporting that the
PPO block promoted hard domain formation due to the hydrophobicity and incompatibility of PPO with the polar hard block\textsuperscript{13}. The PPO block in the PU-1-43 may also enhance hard domain aggregation compared to PU-2-41, which contains PEO homopolymer as a soft segment.

As the pure PEO soft segment length is increased from 1000 g/mol (PU-2-41) to 4600 g/mol (PU-3-33), we also expect enhanced incompatibility between the hard and soft segment, resulting in a higher degree of micro-phase segregation and implying purer hard and soft domains. If we compare PU-1-33 and PU-3-33, containing different PEO segment lengths, we observe enhanced micro-phase segregation in PU-3-33. It is noted that both materials exhibit a broad hard domain melting transition, but the melting peak of PU-3-33 is centered at that of the pure HDI-BDO (165°C). Coupled with the purity of the soft domain (T\textsubscript{m} = 41°C, 133 J/g), this observation suggests that PU-3-33 is quite phase-segregated. The broadness of the melting regime may be explained by the polydispersity of the hard segment sequence length. SAXS studies reinforce these observations, which will be discussed further during an examination of the morphology of PU-3-33.

The development of the hard segment melting transition as a function of hard segment size also provides an interesting comparison to MDI/BDO hard segments. Figure 3.1 illustrates the 2\textsuperscript{nd} heating scans of these segmented polyurethanes. At the lower hard segment percentages (26 - 33%), a broad hard domain transition is observed. Increasing the hard segment content from 33% to 43% produces a multiple melting endotherm, which has been extensively investigated for MDI/BDO hard domains\textsuperscript{14-16}. A further increase in the hard segment composition (47%) leads to a sharper hard segment melting transition, as shown in Figure 3.1. The enthalpy of fusion values per gram of hard segment for these polyurethanes are tabulated in Table II. As revealed, the hard segment crystallinity increases as the hard segment composition is varied from 26 – 47%, which be further revealed in the WAXS analysis.

\textit{3.3.2 Morphological Characterization}

Morphological studies reconcile the structural and thermal characterization of these semicrystalline polyurethanes. Small-angle X-ray scattering data is presented in
Figure 3.2. We attribute the observed scattering peak to the average spacing between hard domains in the phase-separated films. The peak occurs at $q = 0.50 \text{ nm}^{-1}$ in most cases, which indicates a mean spacing between hard domains of 12 nm. In the case of PU-1-47, however, the SAXS peak is shifted to $q = 0.58 \text{ nm}^{-1}$, indicating a slightly smaller inter-domain spacing, $d$, of 11 nm. This correlates well with the AFM images (vide infra), which indicate a “meshed” structure for PU-1-47 with decreased spacing between hard domains; this effect is due to the denser packing of hard domains within the matrix. The insensitivity of the hard domain length to increasing hard segment content has been reported for a number of HDI-BDO polyurethanes; this behavior has been attributed to chain-folding of the lamellar morphology.$^{17}$

![Figure 3.2: Small-angle X-ray scattering Data for PEO-containing Semicrystalline Polyurethanes](image)
If we examine the SAXS pattern for PU-3-33, two prominent first and second order reflections are revealed, suggesting a high degree of phase segregation and supporting our DSC results. These reflections (q = 0.38 nm\(^{-1}\) and 0.76 nm\(^{-1}\)) correspond to a lamellar morphology; to our knowledge, higher order reflections have not been reported for segmented polyurethanes. In an effort to interpret further these surprising results, we considered the concept of micro-phase separation in the block copolymer literature\(^8\). For block copolymers comprised of blocks A and B, the order-disorder transition is defined by \(\chi_{\text{seg}}N=10.5\), where N is the sum of the molecular weights of block A and B and \(\chi_{\text{seg}}\), which is proportional to \((\delta_A - \delta_B)^2(T)^{0.5}\) (T is temperature and \(\delta_i\) is the solubility parameter), is the Flory interaction parameter. At fixed N, the order-disorder transition is proportional to the difference in solubility parameters for the individual blocks. If the block types, A and B, are fixed, the order-disorder transition, \(T_{\text{ODT}}\), is proportional to the total block length. Below the \(T_{\text{ODT}}\), the block copolymer is ordered; above the order-disorder transition, the block copolymer exists as a homogenous melt.

In segmented copolymers, such as polyurethanes, it is generally assumed that the copolymer segments exist as a homogenous melt above the melting point of the hard domains, implying that \(T_{\text{ODT}} \sim T_{\text{m,HS}}\). Hard domain aggregation or crystallinity has been understood to drive the micro-phase segregation. However, we must also consider the effect of N on the micro-phase separation behavior. In PU-3-33, both the soft segment length (and crystallinity) and the hard segment length are substantially increased compared to the other PEO-PPO-PEO or PEO soft segment polyurethanes. Thus, the order-disorder transition is shifted to higher temperatures, which may or may not correspond to the melting transition of the crystalline HDI-BDO hard domains.

Figure 3.3 outlines the possible scenarios for micro-phase segregation in segmented polyurethanes. In Scenario I, an order-disorder transition, \(T_{\text{ODT}}\), is observed distinctly from the melting transition, \(T_{\text{m,HS}}\), of the hard domains. Within kinetic constraints and potential phase-mixing, the micro-phase segregated morphology below the crystallization temperature of the soft segment consists of well-defined crystalline hard and soft domains driven by micro-phase segregation. In Scenario II, the \(T_{\text{ODT}}\) is equivalent to the \(T_{\text{m,HS}}\) so that the segmented polyurethane exists as a homogeneous melt above the clearing point of the crystalline hard domains. The crystallization of the hard
segments drives the micro-phase segregated morphology, but is hindered by the ability of the hard segment chains to diffuse from the melt to form spherulites, leading to more disordered crystalline domains as shown by the defects in comparison to the schematic for the final morphology in Scenario I. The free energy of mixing in Scenario II is lower than in Scenario II, which leads to a smaller $\chi_{seg}N$. Similar arguments have been explored for the morphologies developed in semicrystalline block copolymers, in which regions of confined, templated, and breakout crystallization were reported as a function of $\chi_{seg}N$ at the crystallization temperature normalized by the $\chi_{seg}N$ at the order-disorder transition\textsuperscript{6}. Liquid crystalline-ordering transitions have also been reported by our laboratory which induce order-disorder transitions and order-order transition in side-chain liquid crystalline-amorphous block copolymers\textsuperscript{19,20}. 
Figure 3.3: Possible Micro-phase Segregation Scenarios in Segmented Polyurethanes

A series of temperature-dependent SAXS experiments were performed to investigate the driving force for phase segregation in PU-3-33. Small-angle x-ray scattering patterns were obtained at 25°C, 60°C (above soft segment melting point), and 180°C (above hard domain melting point), as shown in Figure 3.4. Temperature control was ±15°C due to hot stage controller overshoot. Above the melting point of the soft segment, the scattering peak at q = 0.38 nm⁻¹ is still distinguishable, but the reflection at 0.76 nm⁻¹ has disappeared, suggesting that the strong tendency for soft segment crystallinity enhances the micro-phase segregation. At 180°C, which is 15°C above the
melting point of the hard domain, there is an absence of an ordering peak, which infers that PU-3-33 exists as a disordered melt, Scenario 2, given the instrumental error.

![Temperature-dependent SAXS patterns of PU-3-33](image)

**Figure 3.4: Temperature-dependent SAXS patterns of PU-3-33**

The wide-angle X-ray scattering data, presented in Figure 3.5, for this series of segmented polyurethanes reveals a series of prominent peaks in the region $\theta = 10 - 25^\circ$. All of the intensity maxima correlate well with the d-spacings we observe for a powder of the pure HDI-BDO, also presented in Figure 3.4. With increasing hard segment content, an obvious shift occurs in the intensity maxima. The maxima at $d = 4.1$ Å and especially $4.4$ Å become more well-defined compared to the peak at $d = 3.7$ Å, which may be attributed to a smaller contribution from the superposition of relatively disordered soft segment spacing. As the hard segment size increases, a more highly crystalline structure reduces the contribution from the disordered halo, resulting in the expression of a more
stable crystal form as substantiated by DSC. Indeed, the diffraction profiles may be fit quite well by superposing a broad pseudo-Voigt function at $d = 4.2 \, \text{Å}$ with a series of sharper pseudo-Voigts centered at the $d$-spacings of the pure hard segment$^{21}$. These peaks are resolved experimentally through in-situ tensile deformation experiments, which will be detailed in Chapter 4. The peak observed at $d = 2.8 \, \text{Å}$ for some samples is due to an impurity. WAXS patterns of PU-3-33 captured on the in-house instrumentation were not well-resolved, which was due to the instrument configuration, so PU-3-33 is not included. However, based on DSC, significant hard domain crystallinity is expected.

![Wide-angle X-ray Scattering Data of PEO-containing Semicrystalline Polyurethanes](image)

**Figure 3.5: Wide-angle X-ray Scattering Data of PEO-containing Semicrystalline Polyurethanes**

AFM has been increasingly used as an alternative to Transmission Electron Microscopy (TEM) for the visual interpretation of the nanostructure of segmented polyurethanes$^{22-24}$. The surface morphology of these multi-block polyurethanes was
imaged using tapping mode AFM. Figure 3.6 illustrates the captured morphologies. The high modulus hard domains and the low modulus soft blocks appear as light and dark regions, respectively. At lower hard segment content (33 wt%), the hard domains are randomly dispersed in a continuous soft domain, which is reflected in higher inter-domain spacings. As the hard block length increases, an interlocking hard segment morphology develops, decreasing the average distance between hard domains, but increasing in length, which is confirmed by the SAXS studies. The development of a hard domain continuous morphology upon increasing the hard segment size has been observed in other segmented polyurethanes. The influence of this shift from a continuous, soft matrix to a hard, interlocking morphology directly influences the mechanical behavior of these multi-block polyurethanes. The PEO soft segment polyurethanes displayed extremely rough surfaces, limiting their resolution via AFM.
Optical microscopy was also used to visualize the crystallinity of these segmented polyurethanes. As illustrated in Figure 3.7, PU-1-47 exhibits enhanced crystallinity compared to PU-1-26, which has been observed in WAXS. In these PEO-PPO-PEO soft segment polyurethanes, this observed crystallinity has been assigned to the HDI-BDO hard domains, which displays a spherulitic morphology that has been reported in other
HDI-BDO polyurethanes and HDI-BDO homopolymers\textsuperscript{25-27}. PU-3-33, which exhibits strong phase segregation and soft and hard segment crystallinity, is also shown in Figure 3.7 at two magnifications, 10X and 50X. The birefringence noted in these samples is quite remarkable, confirming the DSC results.

To further examine the spherulitic character of the hard domain, thin films of PU-1-33 were cast from a dilute solution (50 mg/mL) using spin coating. The samples were spin-coated, allowed to dry for 1 day, and dried under vacuum at 60°C for 1 hr to remove any residual solvent. Hard segment spherulites, approximately 50 μm in diameter, were detectable in the optical micrographs. These spherulitic structures are evidence of hard domain superstructure that have been noted for PEO/PPO random soft segment polyurethanureas\textsuperscript{13}. Chang and Wilkes proposed a morphological model for the hard domain superstructure; in which nucleation occurs and hard segment aggregation forms the radial arms of the spherulites. This model is shown in Figure 3.8.
Figure 3.7: Optical Micrographs of PEO-PPO-PEO containing Polyurethanes
3.3.3 Mechanical Behavior

The elongation-at-break, toughness, ultimate tensile strength, and initial modulus were obtained from tensile measurements for these segmented polyurethanes and compared to a commercial polyurethane, as outlined in Table 3.3. Elasthane, a commercial polyurethane containing MDI/BDO hard segments and poly(tetramethylene oxide) (PTMO) soft segments, was used for the comparison study. In these materials, the hard segments aggregate to form hard domains, which serve as reinforcing fillers, in a soft segment matrix. As the hard segment composition increases, a phase-inversion occurs, producing materials with inter-connected hard domains, which is evidenced in the AFM phase images. These higher-hard segment content materials exhibit limited extensibility, but increased initial modulus, as shown in Table 3.3 and in Figure 3.9. On further examination of the mechanical behavior of these PEO-containing polyurethanes, the high initial modulus (200 MPa) of PU-1-33 is also quite intriguing. At this hard segment fraction, an ideal balance between strength and extensibility must be fulfilled; the hard domains are truly serving as reinforcing fillers in a soft matrix.

Interestingly, the high hard segment percentage in PU-2-41 does not inhibit its extensibility, signifying an effect of soft segment crystallinity. Deformation studies (Chapter 4) will confirm this postulation. In fact, PU-2-41 displays excellent ultimate mechanical properties compared to the PEO-PPO-PEO systems and Elasthane. The limited solubility of PU-3-33 prevented sufficient film formation of this material for tensile testing.
Table 3.3. Tensile Properties of PEO-containing Semicrystalline Polyurethanes

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Elongation-at-break (%)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Initial Modulus (MPa)</th>
<th>Toughness (MJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1-26</td>
<td>587 ± 6.7</td>
<td>14.9 ± 1.2</td>
<td>72.5 ± 3.7</td>
<td>65.1 ± 9.0</td>
</tr>
<tr>
<td>PU-1-33</td>
<td>460 ± 3.9</td>
<td>18.1 ± 1.0</td>
<td>200 ± 8.1</td>
<td>59.2 ± 7.0</td>
</tr>
<tr>
<td>PU-1-43</td>
<td>447 ± 7.6</td>
<td>23.6 ± 1.2</td>
<td>156 ± 15</td>
<td>77.4 ± 14</td>
</tr>
<tr>
<td>PU-1-47</td>
<td>202 ± 2.7</td>
<td>18.2 ± 3.7</td>
<td>198 ± 30</td>
<td>31.6 ± 9.8</td>
</tr>
<tr>
<td>PU-2-41</td>
<td>711 ± 2.4</td>
<td>35.6 ± 0.31</td>
<td>209 ± 7.3</td>
<td>148 ± 5.4</td>
</tr>
<tr>
<td>Elasthane</td>
<td>390 ± 2.3</td>
<td>33.0 ± 3.8</td>
<td>31.4 ± 2.4</td>
<td>46.5 ± 5.4</td>
</tr>
</tbody>
</table>

Figure 3.9: Representative Stress-Behavior of PEO-containing Polyurethanes

The hysteresis behavior of the PEO-PPO-PEO soft segment polyurethanes was also determined. A representative cyclic testing representation for PU-1-43 is given in Figure 3.10. The percent hysteresis was calculated as the difference between the loading and unloading curves. As shown in Table 3.4, the hysteresis percentage increases with increasing hard segment content, which is a direct reflection of the two-phase...
morphology displayed in segmented copolymers\textsuperscript{12,28}. As shown in OM and WAXS, the crystallinity of the polyurethane increases as the hard segment percentage is increased from 26 – 47\%. AFM also provides evidence of an interconnected morphology develops upon increasing hard segment content. At low hard segment content (PU-1-26), the deformation mechanism involves extension of the soft segment chains; the hard segments are mixed within the continuous domain without significant aggregation so alignment and break-up of hard domain structure is not in operation, resulting in lower levels of hysteresis. As the hard segment is increased, elongation of the more crystalline, interconnected hard domains produces plastic deformation and disruption of the hydrogen-bonded and/or crystalline hard block structure, which is reflected in increasing amounts of hysteresis\textsuperscript{4,12,28,29}.

![Figure 3.10: Representative Cyclic Loading of PU-1-43](image)

Table 3.4: Hysteresis Percentages of PEO-containing Semicrystalline Polyurethanes

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Hysteresis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1-26</td>
<td>58</td>
</tr>
<tr>
<td>PU-1-33</td>
<td>69</td>
</tr>
<tr>
<td>PU-1-43</td>
<td>74</td>
</tr>
</tbody>
</table>
The dynamic mechanical behavior, illustrated in Figure 3.11, of these segmented polyurethanes was also investigated. The storage modulus, $E'$, provides information regarding the stiffness of the material, while $\tan \delta$ measures the degree of molecular motion. The glass transition temperature of the soft segment is defined as the $\alpha$ transition in the $\tan \delta$ curve. In the PEO-PPO-PEO soft segment polyurethanes, the $\tan \delta$ peak broadens due to restrictions on the soft segment flexibility imposed by the hard domains, but no appreciable change in peak position is observed as the hard segment content increases. PU-2-41 also displays a broad $\tan \delta$ transition, which reflects retardation of molecular mobility from both the hard domains and the soft segment crystallites.

The storage modulus also reflects the role of soft ordering on the viscoelastic properties. The soft segment crystallinity observed in PU-2-41 enhances the low-temperature stiffness of the polyurethane. As discussed, the crystalline regions of the soft domain serve as reinforcing fillers and contribute to the mechanical integrity of the polyurethane. Upon melting of the PEO crystallites, hard segment aggregates support the micro-phase segregated morphology, as reflected by similar plateau moduli for PU-2-41 and PU-1-47.
3.4 Conclusions

A series of high molecular weight PEO-PPO-PEO and PEO soft segment polyurethanes with HDI-BDO hard segments were developed. The PEO-PPO-PEO soft segments induced a higher degree of micro-phase segregation compared to PEO (1000 g/mol) soft segment, as revealed by insensitivity in soft segment glass transition to hard segment percentage. An increase in soft segment molecular weight and crystallinity also contributed to increased incompatibility between the hard and soft domains. As the hard segment content was increased, an increase in hard domain crystallinity was observed in WAXS, DSC, OM and AFM. The hard domain spacing decreased slightly with increasing hard segment in the PEO-PPO-PEO and PEO1000 polyurethanes. A lamellar
morphology was assigned to PU-3-33. By considering the effect of χN, the origin of the enhanced micro-phase segregation in PU-3-33 was investigated. Using temperature dependent SAXS, it was determined that the ToDT ≈ Tm,11S and that the strong tendency for soft segment crystallinity in PEO (4600 g/mol) impacted the micro-phase segregation behavior.

The surface morphology, as depicted by AFM, also provided evidence of a shift from a soft segment continuous matrix to a hard segment continuous or interconnected domain. This development in morphology influenced the mechanical behavior of these segmented polyurethanes. As the hard segment content was increased, the ultimate elongation decreased, while the hysteresis percentage, initial moduli, and tensile strength increased. These results have been rationalized in terms of the stiffness of the hydrogen-bonded and/or paracrystalline hard domains and the plastic deformation these structures. The combination of soft segment crystallinity and hard domain restrictions in PU-2-41 broadened the tan δ compared to the PEO-PPO-PEO soft segment polyurethanes. The presence of soft segment crystallites reinforced the polyurethane matrix in PU-2-41, which enhanced the low-temperature modulus of the material. The deformation behavior will be discussed in detail in Chapter 4.

3.5 References


Chapter 4: Deformation-Induced Morphological Development in Semicrystalline Segmented Polyurethanes

4.1 Introduction

The unique material properties of segmented polyurethanes are directly related to their hierarchical morphology. The response of this microstructure to deformation facilitates an understanding of its toughening mechanism. As discussed in Chapter 1, the hard segment aggregates or hard domains physically crosslink the continuous, soft domain, yielding an elastomeric network. By incorporating crystallizable PEO-containing copolymers as polyurethane soft segments, the purpose of this investigation was to determine the role and impact of the soft segment crystallites embedded in the continuous matrix on the deformation process. Additionally, the goal of this research was to explore the morphological development in PEO-PPO-PEO soft segment polyurethanes as the matrix shifts from soft segment continuous to an interconnected or hard segment continuous morphology.

4.2 Background

The deformation behavior of segmented polyurethanes has been studied extensively using a variety of experimental techniques. The vast number of soft and hard block lengths and types, and variations in polyurethane morphology complicate these investigations. Bonart investigated the response of physically-crosslinked polyurethane networks to deformation using small-angle and wide-angle X-ray scattering. Based on these studies, the tensile alignment of initially randomly oriented soft segment chains exerted a local torque force that orients the hard domains perpendicular to the direction up to 300% strain. Above 300% strain, the nature of the hard segment (crystalline or paracrystalline) strongly influenced the deformation behavior. For paracrystalline MDI-ethylene diamine or MDI-hydrazine hard segments, further elongation resulted in the reorientation and restructuring of the hard domains along the stretch direction as the stress is transferred from the strain-induced crystalline (PTMO) or paracrystalline (mixed polyesters) soft segments. In the crystalline MDI-BDO hard domains (~40 wt%
diisocyanate), the hard segments within the hard domains were found to orient along the equator up to 400% strain, which suggested that crystalline hard segments behave as inert fillers during deformation. Bonart also proposed that the hard segment reflections observed in diffraction patterns were due to the sterically-hindered lateral arrangement of hydrogen bonds between hard segments due to a pseudo crystalline lattice formation. A proposed model for the deformation behavior of a paracrystalline polyurethane elastomer subjected to 200% strain is given in Figure 4.1, but previously shown in Figure 1.5\textsuperscript{1}.

![Figure 4.1: Bonart Model for the Deformation Behavior of Paracrystalline Hard Segment Polyurethanes\textsuperscript{1}](image)

Fourier-transform infrared (FT-IR) dichroism has also been used to monitor the deformation behavior of segmented polyurethanes\textsuperscript{3-6}. The structural development of polyurethanes is assessed by examining the dichroic ratio or the ratio of the polarized infrared absorption bands (NH stretching vibration for the hard segments and the asymmetric CH\textsubscript{2} stretching vibration) parallel and perpendicular to the direction of tensile deformation. In these research studies, PTMO or polyester soft segment polyurethanes
containing 24 – 53 wt% MDI chain-extended with BDO, ethylene diamine, hydrazine, propylene diamine, or diaminodiphenylmethane were studied. Figure 4.2 summarizes the deformation model of paracrystalline and crystalline hard segments based on FT-IR dichroism studies. As in Bonart’s SAXS and WAXS investigations, the soft segments were found to always align parallel to the stretch direction, but the mechanism of hard segment orientation was dependent upon whether the hard domains were crystalline or paracrystalline. The hard segments within paracrystalline hard blocks exhibited positive orientation, aligning in the direction of stretch. The crystalline hard domains showed initial hard segment orientation transverse to the stretch direction; upon disruption of the hard segment crystallites, the hard segments aligned in the deformation direction. By raising the temperature or incorporating shorter soft segment lengths, the crystalline hard segments oriented in the direction of stretch for all strains.

![Figure 4.2: Schematic Model of FT-IR Dichroism Investigations of Paracrystalline and Crystalline Hard Segment Polyurethanes](image)

Kimura et al. probed further the deformation mechanisms in polyurethaneureas with crystalline hard domains. A model was proposed, as given in Figure 4.3, for the orientation of the hard segment crystallites. At low tensile strains, the long axis, which is
taken as the length of the lamellae, contributed to scattering at a tilt angle to the direction of elongation. As a result, hydrogen bonding between hard segments also produced alignment at a preferred angle to the deformation. At higher strains, the principal axis was along the length of the hard segment due to the disruption of the crystalline texture, forming nanofibrils and resulting in diffuse scattering along the equator. Nanofibrils are hard segment aggregates aligned in the stretch direction.

Figure 4.3: Schematic Model of the Orientation Mechanism of Spherulitic Polyurethanes under Deformation

A SAXS investigation of the deformation behavior of the micro-phase segregated structure of segmented polyurethanes revealed two dominant response modes of the physically-crosslinked network to tensile strain. Segmented polyurethanes containing MDI hard segments chain-extended with BDO (37 wt% MDI) and toluene diisocyanate (TDI) hard segments chain-extended with either trimethylene glycol bis(p-aminobenzoate) (32 wt% TDI) or 1,1,1-trimethylolpropane (47 wt% TDI) were investigated by Desper and collaborators. From this study, a generalized model based on
shape and structural rigidity (hydrogen-bonding, crystallinity) of the hard domain response to deformation was presented. Hard segments with high degrees of structural integrity and cylindrical geometry (L/D >> 1) are subjected to a shearing mechanism due to the local torque applied by the aligning of soft segment chains, adopting a preferred tilt angle of the hard domains to applied stress and producing a four-point scattering pattern. This shearing mechanism induced lower levels of hysteresis behavior. In the case of hard domains with L/D~1 (cubic) and less ordered morphologies, the length of the hard block oriented perpendicular to the elongation, resulting in a two-point scattering pattern along the meridian. Higher levels of hysteresis dominated in the tensile mode of deformation. Figure 4.4 outlines the two modes of deformation reported by Desper and collaborators. Representative scattering patterns are also included for the two mechanisms.
Figure 4.4: Dominant Modes of Deformation Based on Shape and Structural Rigidity of the Hard Domains in Segmented Polyurethanes\textsuperscript{8,9}

Blundell \textit{et al.} conducted stress-strain studies of thermoplastic polyurethanes containing 42 wt\% hard segment\textsuperscript{9}. In the polyurethanes containing a lower percentage of aggregated hard segments (less structural rigidity), affine deformation occurred in the polyurethane network, which produced an elliptical pattern with scattering intensity on the meridian and similar to the findings of Desper and co-workers\textsuperscript{8}. For the interconnected (structurally rigid) hard domain morphologies, a slightly elliptical four-point pattern was observed due to structural reorganization, which is reminiscent of the...
shearing mechanism introduced by Desper and coworkers\textsuperscript{8}. The scattering patterns from the work of Blundell and collaborators are those shown in Figure 4.4.

Recent studies of the structural development of segmented polyurethanes using in-situ synchrotron simultaneous WAXS/SAXS, FT-IR dichroism, and AFM have complemented initial investigations, adding depth to the knowledge base of polyurethane deformation behavior\textsuperscript{10-13}. An excellent study of the deformation behavior of segmented polyurethaneureas was conducted by Yeh and coworkers\textsuperscript{10}. Yeh et al. concluded that disrupted hard domain lamellae and strain-induced aligned soft segments contribute to equatorial scattering in the low hard segmented (12 wt\%) polyurethane studied in their research, but the intensity may be decreased due to the lack of electron density contrast between the hard segment fibrils and the aligned soft segment chains and/or the decrease in coherent scattering due to the small size of the broken down lamellae\textsuperscript{10}. A pictorial summary of these findings is provided in Figure 4.5. Researchers also probed the contribution of various orientations (perpendicular, parallel, and at angle) of hard domain lamellae orientation on the initial mode of deformation for segmented polyurethanes containing 20 - 50 wt\% HS\textsuperscript{11}. Lamellae initially oriented perpendicular to the stretch direction produced an increase in the interdomain spacing under deformation, while those lamellae aligned parallel to the elongation undergo shearing under strain, which causes a decrease in the interdomain spacing. At higher hard segment contents, hard domain destruction occurred at lower strains. In addition, Lee et al. investigated the soft segment conformation using SAXS, concluding that the soft chains are only partially extended at high strains due to the hard domain lamellae break-up\textsuperscript{11}. Despite the issues related to surface area effects and reconciling differences in surface and bulk morphology, AFM has also shown promise as a metrology for visual examination of the anisotropy revealed in SAXS, WAXS, and FT-IR dichroism\textsuperscript{13}. 
The ordering behavior of the PEO-containing soft segments, the crystallinity of the hard domains, and the variation in morphology as a result of increasing hard segment concentration make the semicrystalline polyurethanes developed in Chapter 3 interesting and complex systems for further study via in-situ SAXS, WAXS, and OM deformation. Investigation of these PEO-based segmented polyurethanes will complement and extend...
the body of literature pertaining to the deformation of hierarchical segmented polyurethanes and aid in the design of future polyurethane materials with crystallizable moieties within the semicrystalline domain that will serve as load-bearing units.

4.3 Experimental

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering have been employed to examine the morphology of these samples, monitoring the evolution of soft segment ordering and hard domain crystallinity and domain structure as a function of applied strain. Optical microscopy also revealed the anisotropy that developed upon tensile deformation.

4.3.1 Instrumentation

4.3.1.1 Small-angle X-ray Scattering and Wide-angle X-ray Scattering

SAXS and WAXS data was acquired at the X27C beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory or at the G1 beamline at the Cornell High-Energy Synchrotron Source (CHESS). The X27C X-ray wavelength, \( \lambda \), was 1.366 Å, which was monochromatized from the bending magnet using a double-multilayer (silicon/tungsten) monochromator. The typical flux was \( 9 \times 10^{11} \) photons/s. The beam was collimated to a maximum spatial resolution of 100 nm using 3 pinholes. The relative X-ray intensity was measured before \( (I_0) \) and after \( (I_1) \) the sample by using proportional counters. The X-ray scattering was detected using a Fuji BAS 2500 Imaging Plate System, and SAXS and WAXS data were simultaneously measured. At the CHESS G1 beamline, \( \lambda = 1.23 \) Å, the beam was collimated to a horizontal divergence of 1 mrad via the wiggler 'K' factor and horizontal-focusing optics. This natural collimation was supplemented by use of two 1 mm slits and a third, which functioned as a guard slit. The relative X-ray intensity was measured at positions (1) just before the sample, using a helium-filled proportional counter, and (2) upstream of the collimation slits, using a nitrogen-filled proportional counter. A MedOptics CCD detector was used to measure the scattered radiation, with pixel size 47.19 μm/pixel and size 1024 x 1024 pixels.
A home-built stretcher was used to elongate continuously the ~0.1 mm thick samples at 25% of their initial length per minute. Scattering patterns were collected for one second in SAXS and 20 seconds in WAXS (time-averaged).

A background pattern was collected for each sample environment, for a collection time equal to the sample collection time. A dark (blocked beam) pattern was measured for each collection time employed. The appropriate dark pattern was subtracted from each sample and background scattering pattern. Each sample pattern was then corrected using the following formula:

\[
\text{Corrected Scattering Pattern} = \text{Sample Pattern} - T(\text{Background Pattern}).
\]

For the X27C data, the transmission ratio, T, was taken to be the ratio \(\frac{I_1(\text{sample})}{I_1(\text{background})}\) where \(I_1(x)\) was the measured beam intensity after the position of the sample or sample environment, as described above. For the G1 data, T was an arbitrary scaling factor taken to be 0.9. Data was reduced from 2D (intensity vs. \(2\theta, \chi\)) to 1D (intensity vs. \(2\theta\)) format by integrating over all values of \(\chi\), for each value of \(2\theta\), where \(2\theta\) is the scattering angle and \(\chi\) is the azimuthal angle. SAXS data has been expressed in terms of q, where \(q = \frac{4\pi\sin(\theta)}{\lambda}\). The reduced data was normalized by \(I_1\).

4.3.1.2 Optical Microscopy

A Carl Zeiss AxioScope 2MAT Polarizing Microscope equipped with a polarizer and retrofitted with a custom-built static stretcher was used to visualize the anisotropy (5X magnification) developed during deformation of the semicrystalline polyurethane films\textsuperscript{14}.

4.4 In-situ SAXS Deformation

The promising mechanical behavior of PU-1-33 and PU-2-41 warranted further study of their morphological development under tensile deformation. The ultimate elongations reported in this chapter differ from those reported in Chapter 3 due to variations in the stretching device, clamping configuration, and deformation rates, which influence the scattering analysis below.
To aid in the analysis of the SAXS and WAXS diffraction patterns, a cartoon of the deformation behavior is shown in Figure 4.6. In Figure 4.6, the long axis of the hard domain is perpendicular to individual hard segments, which are represented by the thin black lines. For illustration and clarity, the rectangular, open boxes surrounding the hard segments correspond to the hard domains. The hard domain orientation giving rise to two-point (meridional and equatorial) and four-point scattering patterns are shown in this representation.

Figure 4.6: Cartoon of the Hard Domain Orientation Behavior that Induces the Scattering Patterns Typical in Segmented Polyurethanes

4.4.1 PU-1-33

The small-angle interference patterns as a function of ensemble- and time-averaged strain along with depictions of the hard domain ordering for PU-1-33 are shown in Figure 4.7. The hard domains are represented by black rectangles, while the soft segment chains are omitted for clarity. Azimuthal plots of PU-1-33 at the static interdomain spacing are also given in Figure 4.8. As the sample is elongated, the isotropic static pattern, which denotes a random orientation of the hard domains, becomes
increasingly anisotropic. At 40% strain, the scattering intensity has shifted to the equator, implying that the hard segment lamellae are orienting in response to the tensile elongation. Further stretching of the sample between 80 – 160% induces a typical four-point pattern. This preferred tilt angle is due to the torque exerted by the alignment of the soft segment chains in the stretch direction upon deformation. By failure at 320% strain, a six-point pattern has developed. A large fraction of the hard block lamellae are still preferentially aligned at ± 70° from the stretch direction (90°), as shown in Figure 4.8. The super-imposed arcs on the meridian are due to the enhanced alignment (strain-induced crystallization or paracrystallinity) of the soft chains and hard segments within hard domains aligned parallel to the deformation. Similar scattering phenomena have been reported as a shearing mechanism by Desper et al., which has been attributed to the structural integrity of cylindrical-shaped hard segments aggregates. This behavior was observed in amine-extended polyurethaneureas, which exhibited enhanced microphase segregation compared to the diol-extended polyurethanes. Failure of the segmented polyurethane occurs before complete restructuring and reorganization of the hard domains in the direction of stretch, which should have resulted in a two-point scattering pattern on the meridian. A slight peak is barely discernable above the noise in the azimuthal plot in Figure 4.8 due to alignment of the hard segments. The slight ellipsoidal nature of the scattering patterns is a function of the anisotropy of the deformation and is consistent with the interference patterns of other segmented polyurethanes operating under the shearing mechanism; the smearing that occurs at low q values is most likely the result of void formation near strain-to-failure.
Figure 4.7: Small-angle X-ray patterns of PU-1-33 as a Function of Strain. Hard segments are represented by the black rectangles.
The change in interdomain spacing with deformation was also followed for PU-1-33 and detailed in Figure 4.9. As the randomly oriented hard domains are subjected to tensile deformation, the spacing between hard segment blocks increases from 13 nm to 14 nm up to 40% strain as the hard blocks respond to the alignment of the soft segment chains. Subsequent deformation up to 160% strain results in a decrease in the hard domain spacing to 12 nm as the hard domains adopt a preferential orientation under shear, and the randomness of the hard domain ordering is diminished. This interdomain spacing then increases again as the hard segment aggregates are disrupted, broken down to smaller widths, and partially aligned in the direction of stretch. A plateau value of 13 nm is reached as changes in morphology occur, which is stabilized by the load-bearing, ordered soft phase. Figure 4.10 depicts this change in hard domain morphology. In Figure 4.10, the hard domains are represented by black rectangles.
Figure 4.9: Interdomain Spacing as a Function of Strain for PU-1-33
4.4.2 PU-2-41

Small-angle X-ray static and ultimate elongation scattering patterns and azimuthal plots for PU-2-41, which contains a pure PEO soft segment, are shown in Figure 4.11 and 4.12, respectively. The static (0% strain) pattern denotes isotropic scattering due to the random orientation of the hard segment aggregates. Although the structural development was not followed as a function of intermediate deformations in this sample, the interference pattern at 320% strain reveals scattering lobes on the meridian and a broad halo at the equator. This scattering pattern is indicative of a certain degree of
orientation of the hard segments and the existence of oriented soft segment mesophase, all of which are aligning in the stretch direction. The ordered PEO phase alternating with oriented hard segments produces a more visible scattering contribution than in PU-1-33. These observations support the hypothesis that the higher toughness of PU-2-41, described in Chapter 3, is a consequence of load-bearing characteristics of the strain-induced PEO chains. The equatorial contribution has been attributed to the electron density contrast between the restructured hard blocks and contributions from the aligned soft segment chains\textsuperscript{10}. As in PU-1-33 at 320% strain, the azimuthal plots of PU-2-41 still show residual preferential orientation ($\pm 70^\circ$) of the hard segment stacks, but the intensity maxima are much less resolved, suggesting more complete alignment in the direction of deformation, as visually depicted in the scattering patterns. As in PU-1-33, this SAXS behavior depicts the shearing mechanism depicted by Desper\textit{ et al.} for hard domains with cylindrical domains with structural rigidity\textsuperscript{8}.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figures/saxs.png}
\caption{In-situ SAXS Deformation of PU-2-41}
\end{figure}
4.5 In-situ WAXS Deformation

Wide-angle X-ray diffraction was also employed to probe the structural development of the semicrystalline segmented polyurethanes with varying hard segment content under tensile deformation. Specifically, PU-1-33 (low hard segment content) and PU-1-47 (high hard segment content) were studied. Limited material quantities of PU-2-41 excluded this polyurethane from the investigation.

4.5.1 PU-1-33

Initially, only three wide-angle scattering peaks are observed in PU-1-33, as illustrated in Figure 4.13. These peaks are labeled D (2θ = 19.6°), E (2θ = 21.3°), and F (2θ = 23.6°), in Figure 4.13, and correspond to hard segment crystalline or paracrystalline spacings as determined by the diffraction pattern of pure HDI-BDO (Figure 3.5). Figure 4.13 details the orientation behavior of these peaks as a function of tensile deformation. For brevity, only the scattering patterns for lowest and highest elongations are included in
Figure 4.13. Azimuthal plots depict the scattering behavior at intermediate strains in Figure 4.14. As the sample is elongated (86% strain), an additional ordering contribution on the equator becomes apparent at $\theta = 20.6^\circ$ (4.2 Å). This spacing is a result of paracrystalline alignment of the PEO-PPO-PEO soft segment chains and becomes more pronounced with increasing strain. This assertion is reasonable for a soft segment continuous morphology as detailed for PU-1-33 in Chapter 3.15. Interpreting the development of the hard segment crystalline peaks with increasing elongation is complicated by the small separation of peaks D, E, and $\alpha$ and the broadness of the $\alpha$ peak, which is shown as a contribution to the azimuthal plots for each peak and necessitates examination of the scattering patterns for a baseline of peak orientation. Peak D (4.4 Å) aligns parallel the stretch direction and corresponds to a crystalline spacing along the HDI-BDO chain axis. Peak E (4.1 Å) initially aligns along the equator, but at higher strains, adopts a four-point arrangement at $\pm 30^\circ$, which is most likely due to spacings between the long axis of the spherulitic hard domain aggregates due to hydrogen-bonding, as shown in Figure 4.3.7. The equatorial scattering is assigned to peak F (3.8 Å), which increases with increasing strain and is due to spacing between extended fibrils of HDI-BDO chains. The view (Figure 4.7) of the orientation of the hard segments within the hard blocks as a result of deformation can now be extended. Again, the hard segments are represented by black rectangles, and the aligned soft segment chains are represented by black lines. Figure 4.15 summarizes the orientation of the hard segments within the hard blocks at 257% strain. These findings support our suggestion, based on the SAXS results, that complete disruption of the crystalline and hydrogen-bonded domains and reorganization of the hard segments has not occurred.
Figure 4.13: 2-D Wide-angle X-ray Scattering Patterns and Azimuthal Plots at 0% Strain (left) and 257% Strain (right) for PU-1-33. Note: $D (2\theta = 19.6^\circ)$, $E (2\theta = 21.3^\circ)$, $F (2\theta = 23.6^\circ)$, and $\alpha (2\theta = 20.6^\circ)$
Figure 4.14: Azimuthal Representation of the Hard Segment Reflections with Increasing Strain for PU-1-33 (Equator 180°)
4.5.2 PU-1-47

Unlike PU-1-33, only three hard segment scattering peaks are evident in the WAXS patterns for PU-1-47 with increasing strain due to its interconnected or hard segment continuous morphology, which resists alignment or paracrystallinity of the soft segment chains. As in PU-1-33, these peaks are labeled D ($\theta = 19.4^\circ$), E ($\theta = 21.3^\circ$), and F ($\theta = 23.6^\circ$) in Figure 4.16 as reflected in the pure HDI-BDO diffraction powder patterns. Although not shown, the static WAXS patterns indicated an absence of preferential alignment of the identified scattering peaks. At 19% strain, it is evident that D and E are beginning to orient on the meridian, which is parallel to the stretch direction. Peak F shows slight orientation along the equator. By 174% strain, which corresponds to the elongation-at-failure of PU-1-47 under these testing conditions, peak D shows strong alignment along the meridian, and peak F orients along the equator. However, peak E has now adopted four-point symmetry about the equator, showing diffraction peaks that are $\pm 30^\circ$ from the deformation direction as a result of shearing of the long axis of the crystalline lamellae. Figure 4.17 shows the development of the individual peaks at D, E, and F with increasing strain. The WAXS data reveal that D (4.4 Å) is a spacing along the polymer chain, and F (3.7 Å) is an interchain spacing between hard segment fibrils. Excluding the absence of an ordered soft segment phase upon deformation, the cartoon depicted for PU-1-33 in Figure 4.15 also applies for PU-1-47 at 174% strain.
Figure 4.16: 2-D Wide-Angle Scattering Patterns and Azimuthal Plots at 19% Strain (left) and 174% Strain (right) for PU-1-47. Note: $D (2\theta = 19.6^\circ)$, $E (2\theta = 21.3^\circ)$, and $F (2\theta = 23.6^\circ)$
Figure 4.17: Azimuthal Representation of the Hard Segment Reflections in PU-1-47 with Increasing Strain
4.5.3 Effect of Temperature on the Tensile Deformation of PU-1-33

The effect of temperature on the wide-angle deformation behavior was investigated for PU-1-33. Scattering patterns were collected at 23°C, 60°C, and 110°C for a film elongated to 175% strain, as reflected in Figure 4.18. If we examine the intensity and clarity of the hard segment reflections (D, E, and F) and soft segment mesophase contribution (α) as discussed in Section 4.5.1, it is evident that the diffraction pattern at 60°C exhibits more anisotropy than at 23°C or 110°C. At 60°C, the fluidity of the soft segment chains is enhanced, allowing for better alignment and structural reorganization of the hard segment crystallites in response to deformation. However, crystallization of the soft segments is destroyed. In contrast, 110°C is the approximate crystallization temperature (Table 3.2) of the hard segments, promoting the growth of the hard segment crystallites. However, the enhanced hard segment crystallinity may provide more resistance to orientation with increasing strain, which would explain the reduction in anisotropy compared to the scattering at 60°C.

![Figure 4.18: Wide-angle X-ray scattering patterns of PU-1-33 elongated to 175% strain at 23°C, 60°C, and 110°C (left to right)](image)

4.6 In-situ Optical Microscopy

Optical microscopy was also used to study the structural development of these PEO-containing segmented polyurethanes, especially the role of soft segment ordering.
Figures 4.19 and 4.20 illustrate the anisotropy that develops as a result of deformation in PU-1-33 and PU-2-41. In PU-1-33, a crystalline texture is evident in the static sample. Upon stretching, stress-whitening occurs as regions of stress-concentration develop. This stress is transferred by aligning the soft segment chains as evidenced by the strain-induced birefringence that develops between 100 - 150% strain, which given variations in strain-rate and experimental set-up are consistent with the WAXS deformation results. Hard segment crystallinity is also apparent at 0% strain in PU-2-41. However, PU-2-41 develops increased birefringence at much earlier strains (50%), suggesting the pure PEO crystallites offer a more effective load bearing mechanism and have an increased tendency to crystallize upon elongation. This observation also supports the higher tensile strength, strain-to-failure, and toughness in PU-2-41 compared to PU-1-33 and other PEO-PPO-PEO soft segment polyurethanes. Figure 4.21 details the structural development as the PU-1-47 film is elongated. As suggested by the in-situ WAXS data, strain-induced crystallization is not observed for PU-1-47 when deformed and imaged optically under cross-polarizers, implying that the dominant mode of stress transfer in a rigid continuous matrix is the break-up of the hard segment aggregates, leading to film rupture at lower deformations.
Figure 4.19: Optical Micrographs of PU-1-33 under Cross-polarizers (5X magnification) as a Function of Strain
Figure 4.20: Optical Micrographs of PU-2-41 under Cross-polarizers (5X Magnification) as a Function of Strain

Figure 4.21: Optical Micrographs of PU-1-47 under Cross-polarizers (5X magnification) as a Function of Strain
4.7 Conclusions

The crystalline HDI-BDO domains provide cohesiveness to the polyurethane network structure, which is illustrated in the preferential tilt (±70°) of the hard block lamellae to the direction of tensile deformation. As a result, the cylindrical HDI-BDO domains operate under the shearing mechanism in contrast to the MDI-BDO segments studied by Desper et al., which undergo affine tensile deformation of their microstructure. The pure PEO soft segment polyurethane, PU-2-41, appears to exhibit more pronounced strain-induced ordering of the soft segment chains compared to PU-1-33. Smearing at low scattering angles was interpreted as a result of void formation.

The WAXS data show the orientation behavior of the hard segment crystallites within the hard blocks. As the sample is elongated, D orients along the HDI-BDO chain in the stretch direction, E aligns at ±30° to the meridian and corresponds to an interchain spacing (hydrogen bond) between hard segments, and F arranges along the equator and is assigned to a crystalline spacing between hard segment chains. In PU-1-33, an additional broad scattering contribution arises due to the development of a PEO-PPO-PEO mesophase. Differences in domain morphology (soft segment matrix to hard segment matrix or interconnected matrix) dictate the stress-bearing role of the soft segment. By increasing the temperature of PU-1-33 at constant strain above the PEO-PPO-PEO melting temperature (60°C), but below the hard domain melting transition, a more pronounced orientation effect was observed in the diffraction patterns. The in-situ deformation behavior of PU-1-33, PU-2-41, and PU-1-47 is summarized in Figure 4.22.

Polarizing optical microscopy reveals differences in the structural development for PU-1-33 and PU-2-41, offering a comparison between the role of PEO-PPO-PEO and PEO soft segments. Strain-induced birefringence of the PEO chains in PU-2-41 occurs at lower strains compared to the PEO-PPO-PEO chains in PU-1-33; the chain alignment and crystallization serves as a load-bearing mechanism under deformation. This observation is consistent with the enhanced extensibility, tensile strength, and modulus of PU-2-41, which was reported in Chapter 3.
Figure 4.22. Summary of the In-situ Deformation Behavior of PU-1-33, PU-2-41, and PU-1-47
4.8 References


Chapter 5: PEO-Containing Polyurethane/Clay Nanocomposites

5.1 Introduction

The addition of nano-sized filler particles has provided significant enhancement of the material properties of segmented polyurethanes. As discussed in Section 2.2.2.3, Laponite, a hydrophilic, synthetic smectic clay, has shown extreme promise in the nanoreinforcement of segmented polyurethanes with polar blocks. Unlike previous methods to disperse organically-modified clay particles in a polyurethane matrix, the polar character of Laponite is exploited in a new solvent exchange method to develop exfoliated and/or intercalated clay/polyurethane systems. In the PEO-containing segmented polyurethanes, both the soft and hard blocks exhibit polar character, motivating the investigation of the nature of the polyurethane/clay interaction in these systems. In this chapter, the impact of Laponite loading on the mechanical properties of one of the most promising semicrystalline polyurethane candidate materials, PU-1-33 will be discussed. Due to limited material quantities, thorough analysis of PU-2-41 was not conducted; however, where relevant, partial morphological and mechanical information will be provided.

5.2 Background

As outlined in Section 1.3.4, dramatic improvements in the material properties of polymers are intimately related to the surface area-to-volume ratio of the nanofiller, which is a function of the level of dispersion in the polymer matrix. For polymer/clay nanocomposites, several thermodynamically stable morphologies are accessible. Figure 5.1 illustrates these various polymer/clay nanostructures. In Figure 5.1a, the clay platelets are miscible with the polymer, but the clay spacing is equivalent to its interlayer spacing. Upon increasing the strength of the polymer matrix/nanoclay interaction, the nanocomposite may exist as an intercalated, intercalated-and-flocculated, or an exfoliated (disordered or ordered) state. As shown in Figure 5.1b for intercalated nanocomposites, the polymer is inserted within the gallery spacing of the layered silicate, which expands
the layer height based on entropic-enthalphic interactions and is independent of clay loading$^2,3,6,7$. The intercalated-and-flocculated morphology, illustrated in Figure 5.1c, resembles the intercalated state, but include edge-edge interactions from the hydroxylated clay layers$^2$. In the exfoliated state (Figure 5.1d), the individual layers of clay are dispersed within the polymer matrix with an average spacing, which is dependent only upon clay content and maximizes the polymer-clay interactions and surface area-to-volume ratio, which may improve material properties. The basal spacing in a disordered exfoliated state is undetectable by WAXS, while the ordered exfoliated state exhibits a diffraction peak. Most polymer nanocomposites contain a mixture of exfoliated and intercalated regions within the polymer matrix$^7$. WAXS and transmission electron microscopy (TEM) are the primary tools employed for the determination of the nanocomposite morphology.

McKinley et al. have previously reported the exfoliation of Laponite in Elasthane, which is comprised of poly(tetramethylene oxide) as the soft segment and MDI-BDO as the hard segment (40 wt%)$^4$. TEM and WAXS confirm that the Laponite is fully exfoliated in the polyurethane matrix. In these Elasthane/Laponite nanocomposites, a dramatic 23-fold increase in initial modulus and a 4-fold increase in toughness (defined at 30% strain) are seen at 20 wt% clay loading without sacrificing extensibility or tensile strength. An increase in heat distortion temperature (HDT) and disappearance of hard domain melting transition with Laponite loading are also reported. These findings suggest that the clay discs are preferentially embedded within the hard domain.
5.3 Experimental

5.3.1 Materials

PU-1-33, which contains a PEO-PPO-PEO soft segment, and PU-2-41, which contains a pure PEO soft segment, were the HDI-BDO hard segment polyurethane elastomers used in this reinforcement study. The morphological and mechanical behavior of these materials were detailed in Chapters 3 and 4. Laponite RD, a discotic, smectic synthetic clay, was obtained from Southern Clay Products. N,N'-Dimethylacetamide (DMAc) was used as received from Sigma-Aldrich Company.
5.3.2 Novel Solvent-Exchange Method and Thin Film Casting

A novel approach for the dispersion of Laponite in the PU-1-33 and PU-2-41 matrices was employed4,5. In this method, Laponite was well-dispersed in deionized water (1 g / 100 mL) by stirring at room temperature over the course of a day. To that mixture, 100 – 200 g of DMAc was added and stirred for 24 hours. The water was removed from the DMAc/water/Laponite mixture via vacuum distillation at 75°C. The removal of water was monitored by measuring the mass loss, which was achieved once the loss in solution mass exceed that of the added water. This is a critical step due to the strong affinity of water and Laponite.

The PU-1-33 and PU-2-41 concentration in the segmented polyurethane/DMAc/Laponite mixture was varied between 1.6 wt %, and the amount of Laponite/DMAc dispersion added was adjusted to produce clay loading of 10 wt%. The solution mixtures were cast into Teflon molds. Thin films (80-100 μm) of the PU nanocomposites were obtained by controlled through N2 purge rate monitoring, slow evaporation of the DMAc at 60°C in an oven.

5.3.3 Instrumentation

5.3.3.1 Differential Scanning Calorimetry

The thermal phase behavior of these nanocomposites was examined using a TA Instruments Q1000 Differential Scanning Calorimeter (DSC), operating at a heating rate of 10°C/min under nitrogen atmosphere. Thin-film nanocomposites were subjected to two heating and cooling cycles between –90°C and 250°C. Thermal transitions of the prepared films were recorded from the first heating and cooling scans using a linear extrapolation method (Tm) and the midpoint inflection method (Tg).

5.3.3.2 Optical Microscopy

The long-range ordering of the crystalline soft and hard domains and the deformation-induced crystallinity of the PU-1-33/Laponite and PU-2-41/Laponite nanocomposites were investigated using a Carl Zeiss Axioskope 2MAT Polarizing Microscope equipped with a polarizer.
5.3.3.3 Wide-Angle X-ray Diffraction and Small-Angle X-ray Scattering

The clay dispersal mechanism in the thin-film nanocomposites was investigated using a Rigaku RU300 rotating anode X-ray generator with 185 mm diffractometer and a scintillation counter and a CuK source with a wavelength of 1.54 Å and a scan rate of 5° min⁻¹ and 0.5° sample interval.

A Molecular Metrology SAXS equipped with CuK radiation (wavelength of 1.54 Å) and a two-dimensional, gas proportional multi-wire Gabriel detector was also used to obtain SAXS patterns. A hot stage assembly was used for temperature measurements. Each sample pattern was then corrected using the following formula:

\[
\text{Corrected Scattering Pattern} = \text{Sample Pattern} - T(\text{Background Pattern}).
\]

The transmission ratio, T, was taken to be the ratio \(I_1(\text{sample})/I_1(\text{background})\) where \(I_1(x)\) was the measured beam intensity after the position of the sample or sample environment.

5.3.3.4 Tensile Testing

The tensile properties of these polyurethane nanocomposites were determined using a Zwick/Roell Z010 equipped with a 500 N load cell at a crosshead speed of 100% gauge length/minute. A convex aluminum and flat polyurethane jaw face was used to clamp the specimens at each end. A minimum of three samples was examined for statistical analysis.

5.3.3.5 Transmission Electron Microscopy

A RMC MT-X ultramicrotome with CR-X cryo attachment was used to section samples of 45 nm in thickness below room temperature. The diamond knife temperature was set at −95°C and the sample temperature set at −105°C. Films were transferred to copper grids. Unstained samples were observed with a JEOL 200CX electron microscope operating at 200kV.
5.3.3.6 Dynamic Mechanical Testing

The soft segment glass transition temperature ($T_g$) and the dissipation factor of the PU-1-33/Laponite composites were evaluated via dynamic mechanical analysis (DMA) using a TA Instruments Q800 series DMA over a temperature range of -100-250°C at a frequency of 1Hz, a ramp rate of 3°C min$^{-1}$, and an initial strain of ~0.2%.

5.4 Mechanical Behavior

Transparent thin-films were obtained from the slow evaporation of the PU-1-33/0 and 10wt% Laponite/DMAc and PU-2-41/10 wt% Laponite/DMAc mixtures. The tensile curves obtained for 0 and 10 wt% clay loading for PU-1-33 and PU-2-41 containing 10 wt% clay are shown in Figure 5.2. Unlike Elasthane/Laponite clay composites, at 10 wt% clay loading, the PU-1-33 nanocomposite displays a substantial reduction in toughness (~16-fold) and ultimate tensile strength (~3-fold) and elongation (~6-fold). However, the initial modulus, which is usually attributed to the hard domain rigidity, remains relatively constant at this Laponite loading. Dramatic reductions in ultimate tensile properties and toughness are also observed in PU-2-41 & 10 wt% Laponite when compared to the mechanical properties reported in Chapter 3. Several reasons for this decrease in material properties are possible, including inadequate dispersal of the Laponite discs and restriction of soft segment motion by the clay particles. Again, the initial modulus of PU-2-41 remains essentially unchanged in the nanocomposite. Table 5.1 summarizes the tensile properties of these nanocomposites.
Figure 5.2: Comparison of the Stress-strain Behavior of PU-1-33 and 10 wt% Laponite Loaded PU-1-33 and PU-2-41

Table 5.1: Tensile Properties of PU-1-33/ and PU-2-41/Laponite Films

<table>
<thead>
<tr>
<th></th>
<th>PU-1-33</th>
<th>PU-1-33 &amp; 10 wt% Laponite</th>
<th>PU-2-41 &amp; 10 wt% Laponite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Modulus (MPa)</td>
<td>181 ± 26</td>
<td>157 ± 3</td>
<td>161 ± 25</td>
</tr>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>16 ± 3</td>
<td>5 ± 4</td>
<td>5 ± 0.7</td>
</tr>
<tr>
<td>Ultimate Elongation (%)</td>
<td>3.85 ± 0.35</td>
<td>0.62 ± 0.21</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>Overall Toughness (MPa)</td>
<td>42.8 ± 9</td>
<td>2.7 ± 1.1</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>Toughness @ 30% strain (MPa)</td>
<td>1.60 ± 0.26</td>
<td>1.16 ± 0.04</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>
The dynamic mechanical behavior of these polyurethane nanocomposites was also explored. Figure 5.3 and Figure 5.4 display the thermo-mechanical results for these composites. As Laponite is added to the PU-1-33 matrix, the plateau modulus increases, suggesting a reinforcement effect which is most likely a result of clay-soft segment interactions. The heat distortion temperature, defined as the temperature at which the storage modulus ($E'$) equals 8 MPa, also increased (140°C to 160°C) upon Laponite loading, which has been reported for other filler-reinforced materials.$^2,^4,^5$ This increase in HDT is indicative of nanocomposites in which a portion of the clay particles resides within the hard domains. At 10wt% clay loading, the tan delta curve broadens, signifying a restriction of the mobility of the flexible chains, which will be discussed further during analysis of the DSC findings. These phenomena support our hypothesis that the Laponite particles are attracted to the polar PEO-containing segments.

In Figure 5.4, thermo-mechanical phenomena for PU-1-33 and PU-2-41 filled with 10wt% Laponite were compared. As discussed in Chapter 3, soft segment crystallinity improves the loss and storage modulus below the soft segment melting transition. This behavior is also observed in the PU-2-41 Laponite loaded films. Above $T_{m,ss}$, the moduli attain similar plateau values. The expansion of the tan $\delta$ peak is also observed in PU-2-41 containing 10wt% clay, which presumably is a result of mobility restrictions imposed by the soft segment crystallites, Laponite discs, and the hard domains.

The tensile properties are quite unexpected given the substantial improvements obtained for exfoliated Elasthane/Laponite films.$^4,^5$ The structural and morphological differences between Elasthane, PTMO/HDI-BDO polyurethanes, and the PEO-containing polyurethanes (PU-1-33 and PU-2-41) were examined to understand these results.
Figure 5.3: Dynamic Mechanical Behavior of PU-1-33 Nanocomposites at 0 and 10 wt% Clay Loadings
5.5 Morphological Behavior

As described previously, the fully-exfoliated morphology maximizes the surface-to-volume ratio between nanosized-Laponite platelets and the polyurethane matrix, yielding the vast improvement in mechanical properties. The first step in understanding the mechanism governing the reduction in extensibility and tensile strength for PEO-containing polyurethanes is assessing the morphological state of the slow-solvent evaporated thin films. TEM and WAXD provide direct evidence of the dispersed morphology.

The TEM image, shown in Figure 5.5, is taken from a 45 nm cross-section of a PU-1-33/10wt% Laponite film. The top TEM image in Figure 5.5 displays both exfoliation and intercalation of Laponite particles within the polyurethane matrix, while the bottom image in Figure 5.5 showcases an intercalated-and-flocculated structure.
Interestingly, these images also highlight an apparent phase-separated morphology, in which regions of exfoliated Laponite alternate with areas populated by intercalated and/or aggregated structures most likely the result of preferential attraction of Laponite discs to the continuous PEO-containing domain. The exfoliated areas are postulated to represent the hard domains. This proposed behavior will be addressed in following discussions, and similar observations of phase separation have been reported for PEO/montmorillonite systems above a certain PEO content.$^{8,9}$
Figure 5.5: TEM Images of 10wt% PU-1-33/Laponite Films. *Top Image*: Exfoliation and Phase Segregation, *Bottom Image*: Intercalated-and-flocculated Structures.
The WAXD spectra show reflections for the pure HDI-BDO hard segment and the PEO mesophase between 15 – 25°; understandably, these crystalline spacings are slightly different than those reported in Chapter 3 from the 2D detector at the CHESS and Brookhaven National Laboratory. For intercalated polymer nanocomposites, the pure Laponite RD (001) reflection should shift from \( \theta = 6.9^\circ \) \((d = 1.26 \text{ nm})\) to lower \( \theta \) (or higher \( d \)-spacings) to reflect the increase in gallery spacing due to the insertion of the polymer chain. However, in our PEO-containing polyurethane nanocomposites, a peak to the right (or lower \( d \)-spacings) of the pristine clay peak are observed in WAXD, shown in Figure 5.6, which implies platelet attraction. In contrast to other reported WAXD patterns for Laponite, the pristine Laponite used in this study exhibited an additional peak located at \( \theta \sim 4.5^\circ \). It is possible that a smearing of this peak into the 001 reflection results in the indistinguishable Laponite peak in our PU-1-33/10 wt% clay material. However, the scattering peak centered at \( \sim 10^\circ \) may be a higher order reflection induced by the sequestering of the clay particles within the continuous domain.

The small-angle X-ray scattering patterns were also obtained for these PEO-containing polyurethane/Laponite nanocomposites. As shown in Figure 5.7 and in Chapter 3, an interdomain spacing centered at \( \sim q = 0.5 \text{ nm}^{-1} \) is observed in the pure PU-1-33 and PU-2-41 material. The characteristic scattering peak disappears upon addition of 10 wt% Laponite to the polyurethane (PU-2-41 and PU-1-33) matrix. Based on DSC analysis (Table 5.2), a distinct hard domain and soft domain are observed in the nanocomposite films. Thus, the absence of a distinct SAXS peak is most likely the result of electron-density contrast matching between the soft and hard blocks due to the preferential attraction of the rigid clay particles to the PEO soft segments. If a fraction of the PEO chains are intercalated within the Laponite basal spacing, the pseudo electron density of the continuous domain is raised, limiting the perceived contrast between the soft and hard domains.
Figure 5.6: WAXD of 10wt% PU-1-33/Laponite Films
The thermal behavior of these clay nanocomposites is tabulated in Table 5.2. The first heating and cooling scans were examined to gather information regarding the as-cast morphology. The slow-cast PU-1-33 film exhibits similar thermal transitions observed in the 2nd heating and cooling scans obtained for the as-precipitated polymer. However, a hard domain glass transition is now observed, implying a certain level of segmental motion of the hard block. If the clay particles are dispersed within the soft domain as proposed, an increase in soft segment glass transition and melting point are expected. Upon addition of 10 wt% clay, the soft segment glass transition remains unchanged in our nanocomposites. Subtle changes in glass transition temperature are not always discernable in DSC; DMA, which shows a broadening of the tan δ or a breadth of segmental motion at higher temperatures, does provide evidence of reduced soft segment mobility, which supports this alignment effect reported by Gournis\textsuperscript{10}. WAXD also shows
a broad peak developing at $\sim 18^\circ$, which corresponds to a PEO mesophase with $d = 4.2$ Å as shown in Chapter 3. It may be that only a fraction of PEO resides in the Laponite galleries; the unbound soft segment dominates the thermal behavior of the nanocomposite due to the inaccessibility of the thermal dissociation temperature of the Laponite/clay interactions. The hard domain glass and melting transition are also identical to the pure PU-1-33 film, but the hard segment crystallization peak is shifted to a higher temperature, which reflects a higher degree of order within the hard domain. Although the slow-cast PU-2-41 was not available, similar trends are expected in this system.

<table>
<thead>
<tr>
<th></th>
<th>Soft Segment</th>
<th>Hard Segment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ ($^\circ$C)</td>
<td>$T_m$ ($^\circ$C)</td>
</tr>
<tr>
<td>PU-1-33</td>
<td>-62</td>
<td>-</td>
</tr>
<tr>
<td>PU-1-33 &amp; 10 wt % Laponite</td>
<td>-62</td>
<td>-</td>
</tr>
<tr>
<td>PU-2-41 &amp; 10 wt % Laponite</td>
<td>-54</td>
<td>0</td>
</tr>
</tbody>
</table>

$^{a}$Heating and Cooling; $^{b}$Glass transition temperature; $^{c}$Melting transition; $^{d}$Crystallization temperature; $^{e}$Enthalpy of fusion values are per gram of soft segment and hard segment, respectively; $^{f}$Glass transition temperature of the hard segment

The consequences of this observed alignment or restricted motion in the continuous domain are reflected in the poor tensile properties of the PEO-containing polyurethane/clay nanocomposites, which were evaluated further using optical microscopy under cross-polarizers. Figure 5.8 showcases the nanocomposite films, highlighting the deformed and undeformed regions of the films. Pure PU-1-33 shows brilliant birefringence due to chain alignment and orientation upon deformation of the films. In contrast, PU-1-33 and PU-2-41, both containing 10wt% Laponite, exhibit no birefringence in the deformed regions, which suggests that strain-induced crystallization is suppressed and the flexibility of the segmented polyurethane is inhibited. As a result, these polyurethane/clay nanocomposites fail to offer the improvement in mechanical properties detailed in other systems due to the unique, but inhibiting, interactions between PEO and Laponite.
Finnigan and co-workers have raised the notion of using differences in block polarity of segmented polyurethane to achieve exfoliated polyurethane/clay nanocomposites. In these polyurethane/clay nanocomposites, it is proposed that the polar hard segment hydrogen bonds to the clay surface, while the hydrophobic soft segment is not attracted to the silicate surface, pushing the silicate layers apart for entropic gain and forming intercalated and/or exfoliated morphologies. However, in our PEO-containing polyurethane/Laponite nanocomposites, it is believed that the PEO or PEO-PPO-PEO, due to its hydrophilicity and high polarity, are preferentially attracted to the hydrophilic Laponite platelets. In a poly(ethylene oxide)-b-polyisoprene (PEO-PI)/Laponite nanocomposite (<50 wt% clay), PEO intercalates the Laponite galleries in a planar conformation, while the hydrophobic PI block resides on the perimeter of the clay discs.

Based on our analysis of the mechanical and morphological behavior of these PEO-containing polyurethane nanocomposites and examination of other PEO and polyurethane nanocomposites, the following model is proposed for these systems. Both the polar hard domains and hydrophilic soft segments are capable of hydrogen bonding to the platelet surface, producing a complex array of polyurethane-clay interactions. At higher clay loadings, a portion of the hydrophilic PEO-containing soft segments are attracted to the face of the clay platelet, causing a complexation of the soft segments with the sodium ions in the gallery spacing and sequestering the majority of the nanoclay in an effort to satisfy the platelet-PEO attraction. This behavior should induce significant ordering of the Laponite platelets, which may explain the structural regularity proposed by the WAXD patterns. The PEO-clay attraction prevents the flexible chains from slipping past one another during deformation and suppresses strain-induced ordering in response to tensile elongation. Because of the planar conformation of the PEO, the majority of the hard segments are located outside of the Laponite nanofiller. The existence of a hard segment Tg after clay loading suggests that a majority of the hard domains are not preferentially interacting with the clay, which may factor into the increase in crystallization temperature. Figure 5.9 offers a schematic of the PEO/clay platelet interaction in the PEO-containing polyurethane nanocomposites.
Figure 5.8: Optical Micrographs of PEO-containing Polyurethane/Laponite Composites: a) PU-1-33, b) PU-1-33 & 10wt% Laponite, and c) PU-2-41 & 10wt% Laponite. Arrow points to grip
Figure 5.9: Schematic of Proposed PEO/Laponite Interaction in the PEO-containing Polyurethane/Laponite Clay Model
5.6 Conclusions

PEO-containing polyurethane/Laponite nanocomposites were developed using a novel solvent exchange process in an effort to enhance the material properties of the polyurethane matrix. The unexpected reduction in tensile properties obtained in these nanocomposite materials is a result of the proposed preferential attraction between the PEO soft segments and the Laponite platelets, restricting the mobility of the soft segments and affecting the ultimate tensile strength and elongation. Although the soft segment thermal properties remained essentially unchanged in the nanocomposites, the tan δ peak broadens at higher temperatures, reflecting multiples modes of segmental motion and signifying some reduction in mobility of the polyurethane/clay. The PEO segments appear to intercalate the Laponite galleries and to template ordering of the Laponite discs, which induces a higher order reflection in the WAXD patterns. Electron-density matching of the soft segment/clay and hard segment domains obscures the interdomain scattering peak that is characteristic of microphase-segregated polyurethanes, but DSC confirms that the nanocomposites are segregated into hard and soft domains. TEM reveals that regions of exfoliation (hard domain) and intercalation (soft block) exist within the polyurethane and point to a micro-phase segregated morphology. This proposed model for PEO and PEO-PPO-PEO soft segment polyurethanes suggests that the material properties of segmented polyurethane/clay nanocomposites may be tailored by selecting blocks with varying degrees of polarity and hydrophilicity.

5.7 References


Chapter 6: Liquid Crystalline PEO-containing Segmented Polyurethanes

6.1 Introduction

The implementation of PBLG-PEO-PBLG copolymers as polyurethane soft segments will allow us to harness the wealth of information regarding their thermal, morphological, and mechanical behavior to develop materials, which mimic the molecular architecture of natural silk and that display a variety of material properties. Chapter 6 will detail the synthesis of PBLG-PEO-PBLG copolymers and their structural and morphological behavior. The design of segmented polyurethanes containing these liquid crystalline copolymers will also be discussed, providing insight for the future development of these silk-inspired materials.

6.2 Experimental

6.2.1 Materials

All materials were purchased from Sigma Aldrich Co. Purification procedures are included in the synthetic descriptions.

6.2.2 Instrumentation

6.2.2.1 $^1$H Nuclear Magnetic Resonance (NMR)

A Varian Mercury 300 MHz NMR spectrometer with an Oxford Instruments Ltd. superconducting magnet or a Bruker 400 MHz NMR spectrometer equipped with a SpectroSpin superconducting magnet was used to confirm chemical structures and to obtain the block sizes and overall molecular weights of the PBLG-PEO-PBLG tri-blocks.

6.2.2.2 Gel Permeation Chromatography (GPC)

Molecular weights and molecular weight distributions of soluble polymers were determined relative to polystyrene (PS) standards using a Waters Gel Permeation Chromatograph (GPC) equipped with two Styrogel columns and RI detector with
tetrahydrofuran (THF) as the mobile phase. Molecular weight characterization of the polyurethaneureas was conducted using DMAc as the mobile phase with PEO standards.

6.2.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The chemical structure of diamine-terminated PEO was monitored by Fourier Transform Infrared Spectroscopy (FT-IR) with a Thermo Nicolet Nexus 870 spectrometer using a DTGS Kbr detector on West Georgia Laboratories poly(tetrafluoroethylene) (PTFE) IR cards or on FT-IR grade potassium bromide (KBr) pellets.

6.2.2.4 Differential Scanning Calorimetry (DSC)

The thermal phase behavior of these thermoplastic polyurethanes was investigated using a TA Instruments Q1000 Differential Scanning Calorimeter (DSC), operating at a heating rate of 10°C/min under nitrogen atmosphere. As-precipitated, unannealed polymer samples were subjected to two heating and cooling cycles between −90°C and 250°C. Transitions were recorded from the second heating and cooling scans using a linear extrapolation method (Tm) and the midpoint inflection method (Tg).

6.2.2.5 Optical Microscopy (OM)

A Carl Zeiss Axioscope 2MAT Polarizing Microscope equipped with a polarizer was used to visualize the crystalline and liquid crystalline textures of the copolymers and polyurethanes. The copolymers and polyurethanes were cast from 5 w/v% solutions from DMAc or dichloromethane onto glass slides for imaging.

6.2.2.6 Small-angle X-ray Scattering

A Molecular Metrology SAXS equipped with CuK radiation (wavelength of 1.54 Å) and a two-dimensional, gas proportional multi-wire Gabriel detector was also used to obtain SAXS patterns. A background pattern was collected for each sample environment, for a collection time equal to the sample collection time. A dark (blocked beam) pattern was measured for each collection time employed. The appropriate dark pattern was subtracted from each sample and background scattering pattern. Each sample pattern was then corrected using the following method:
\{\text{Corrected Scattering Pattern}\} = \{\text{Sample Pattern}\} - T(\{\text{Background Pattern}\}).

The transmission ratio, $T$, was taken to be the ratio $I_1(\text{sample})/I_1(\text{background})$ where $I_1(x)$ was the measured beam intensity after the position of the sample or sample environment, as described above.

6.3 Synthesis

6.3.1 Diamine-terminated PEO

The synthesis of PBLG-PEO-PBLG polyurethane soft segments requires the use of diamine-terminated PEO as the macroinitiator. Commercially available diamine-terminated PEO (2000 g/mol and higher) presents a significant synthetic cost, averaging $175$ per gram. Coupled with the requirement of compacting the PBLG blocks with a total soft segment molecular weight of less than 5000 g/mol copolymer, it was necessary to synthesize diamine-terminated PEO1000. However, a small amount of diamine-terminated PEO2000 was purchased for comparison studies.

A literature review yielded several synthetic routes for the development of the amine-terminated PEO\textsuperscript{1-6}. Dihydroxy-terminated poly(ethylene oxide) is usually first converted to a PEO-dichloride or PEO-ditosylate using thionyl chloride or tosyl chloride, respectively. At this juncture, three schemes for conversion to diamine-terminated PEO are possible\textsuperscript{7}:

1) In the Hofmann method, PEO-dichloride or PEO-ditosylate may be reacted with aqueous ammonia at high temperatures and pressures followed by conversion to the diamine by alkylation; secondary amines may be formed in this reaction as a byproduct.

2) The Gabriel synthesis involves the reaction of the PEO-dichloride or PEO-ditosylate with sodium azide at high temperature with catalytic reduction to the primary amine.

3) Primary diamine-terminated PEO may also be obtained by reacting the PEO-dichloride or PEO-ditosylate with potassium pthalimide and subsequent hydrazinolysis.
Although hydrazine hydrate warrants significant safety precautions due to its toxicity and flammability hazards, the use of sodium azide and aqueous ammonia at high temperatures and/or pressures was deemed more dangerous. Thus, Scheme 3 was chosen for the development of the PEO macroinitiator, as shown in Figure 6.1.

**Figure 6.1: Synthetic Scheme for the Preparation of Diamine-terminated PEO1000**

6.3.1.1 Poly(ethylene oxide) Ditosylate (PEO1000-OT₄)

Poly(ethylene oxide) (MW = 1000; 50 g; 0.05 mol), PEO1000, was dried overnight by stirring under vacuum at 100 °C in a 500 mL Schlenk flask. After allowing the PEG1000 to cool to room temperature, the flask was placed under argon and dry toluene (200 mL) was added via cannula. To this stirring solution, n-butyl lithium (2.5 M in hexanes; 45 mL; 0.11 mol) was slowly added via syringe. An orange polymeric material immediately precipitated out of solution, but mostly went back in within a few minutes of stirring. About 50 mL of toluene was added to dissolve the remaining precipitate. A solution of tosyl chloride (28.6 g; 0.15 mol) in toluene (60 mL) was added slowly with vigorous stirring, and the reaction mixture was stirred under argon overnight. The reaction mixture was concentrated under reduced pressure to give a light yellow solid. The crude mixture was taken up in dichloromethane (1000 mL) and passed...
through Celite to remove undissolved material. The filtrate was concentrated to give a yellow oil. The oil was dissolved in a minimal amount of dichloromethane and precipitated from an excess of cold ether (-40°C; 1000 mL). The light yellow solid was filtered then dried overnight under vacuum (45.1 g). The solid was redissolved in ethanol (~300 mL) and placed in a -40°C freezer. The precipitate was collected by filtration and dried under reduced pressure to give PEO1000-TOS as a white solid in 58% yield (37.5 g): $^1$H-NMR (300 MHz; CDCl$_3$) $\delta$ 2.45 (s, 6H), 3.58-3.76 (m, 124H), 4.15 (t, 4H), 7.33-7.36 (m, 4H), 7.78-7.82 (m, 4H). GPC(PS standards, THF): $M_n$=1628 g/mol, $M_w$=1743 g/mol, PDI = 1.07.

6.1.1.2 Poly(ethylene oxide) Diphthalimide (PEO1000-Phthal$_2$)

A 1.0 L 2-neck round bottom flask was fitted with a reflux condenser and purged with argon. A solution of PEO1000-TOS$_2$ (33.6 g; 0.026 mol) in dimethyl formamide (DMF) (100 mL) was added to the flask via syringe followed by another 100 mL of DMF. Potassium phthalimide (69.3 g; 0.374 mol) was added under an active purge of argon. Another 200 mL of DMF was added to the flask to dissolve the potassium phthalimide, and the reaction mixture was heated to 160°C for 16 hours. The reaction mixture was cooled to room temperature and the precipitate was filtered off. The filtrate was concentrated under reduced pressure with heating. The resulting orange oil was dissolved in a minimal amount of dichloromethane and precipitated from cold ether (-40°C). The yellow waxy solid was collected by filtration, resubjected to the precipitation conditions, and then dried under reduced pressure to give PEO1000-Phthal$_2$ as a light yellow waxy solid in 63% yield (20.6 g): $^1$H-NMR (300 MHz; CDCl$_3$) $\delta$ 3.57-3.63 (m, 74H), 3.72 (t, 4H), 3.91 (t, 4H), 7.69-7.72 (m, 4H), 7.80-7.85, 4H). GPC(PS standards, THF): $M_n$=1747 g/mol, $M_w$=1896 g/mol, PDI = 1.08.

6.1.1.3 Poly(ethylene oxide) Diamine (PEO1000-(NH$_2$)$_2$)

A 500 mL 2-neck round bottom flask was equipped with a stir bar and fitted with a reflux condenser attached to an argon inlet. The flask was charged with PEO1000-Phthal$_2$ (20.9 g; 0.017 mol) dissolved in 200 mL of absolute ethanol. The solution was brought to reflux under argon, hydrazine hydrate (5.96 g; 0.119 mol) was added, and the reaction mixture was refluxed overnight under argon. Upon cooling to room temperature,
the reaction mixture was acidified with dilute $\text{HCl}_{(\text{aq})}$. The insoluble material was removed by filtration, and the solution was treated with 2.0 M $\text{KOH}_{(\text{aq})}$ until it was basic. The solution was extracted three times with dichloromethane. The organic extracts were combined, dried over magnesium sulfate ($\text{MgSO}_4$), filtered, and concentrated under reduced pressure. The residue was taken up in a minimal amount of dichloromethane and precipitated into cold ether ($-40^\circ\text{C}$). The fluffy light yellow solid was collected by filtration, reprecipitated, and then dried under reduced pressure to give $\text{PEO}_{1000}-(\text{NH}_2)_2$ as an off-white solid in 72% yield (12.3 g): $^1\text{H}-\text{NMR}$ ($300 \text{ MHz}$; $\text{CDCl}_3$) $\delta$ 2.96 (t, 4H), 3.65 (s, 103H). GPC (PS standards, THF): $M_n=1616 \text{ g/mol}$, $M_w=1527 \text{ g/mol}$, PDI=1.06.

6.1.2 Gamma-Benzyl-L-Glutamate N-Carboxy Anhydride (BLG-NCA)

Synthetic procedures for BLG-NCA are well-documented, differing primarily in the recovery steps. The use of triphosgene, a solid phase alternative to gaseous phosgene, significantly improves the safety hazards associated with this reaction. Two methods were employed in the synthesis of BLG-NCA; both will be detailed below and are shown in Figure 6.2.

![Figure 6.2: Synthetic Route for the Preparation of BLG-NCA](image)

Scheme 1: The synthetic procedure of Poche et al. was followed.

A vacuum dried three-neck 250 mL flask was fitted with a reflux condenser and glass stoppers, equipped with a stir bar, and connected to a nitrogen inlet and purge. $\gamma$-benzyl-L-glutamic acid ester (2 g; 0.0084 mol) was suspended in 60 mL of dry ethyl acetate and heated to reflux ($90^\circ\text{C}$). One-third molar equivalent of triphosgene (0.83 g; 0.0028 mol) of triphosgene was added to the reaction mixture via a funnel. The reaction mixture did not turn clear after refluxing for five hours so approximately 0.15 g of
additional triphosgene was added. After two hours, the reaction mixture was still cloudy so another 0.10 g of triphosgene was added and allowed to reflux overnight. The solution was cooled to room temperature, and the stoppered flask was further cooled to −40°C.

The following recovery steps were conducted quickly to minimize exposure to air. The cooled reaction mixture was transferred to a 125 mL separatory funnel and washed with cold (°C) deionized water to yield an acidic aqueous layer. The ethyl acetate layer was then washed with a 0.5 weight per volume percent solution of sodium bicarbonate in water (100 mL) to yield a slightly basic aqueous layer. The ethyl acetate layer was then treated with anhydrous magnesium sulfate until dry (no clumping observed). This slurry was filtered to obtain the product solution, which was concentrated to about 20 mL using a rotary evaporator. Recrystallization was induced by adding 20 mL of n-hexane to the concentrated solution and allowing to sit in the −40°C freezer for five hours. White BLG-NCA crystals were collected by filtration and dried under reduced pressure. The resulting crystals were reprecipitated three times, yielding 1.7 g (61 % yield). BLG-NCA was stored in the −40°C freezer for no more than three days prior to use. 

\[
\begin{align*}
\text{H-NMR (400 MHz; } & \text{CDCl}_3) \delta 2.10-2.33 (\text{m, 2H, } \gamma-\text{CH}_2), 2.60-2.62 (\text{t, 2H, } \gamma-\text{CH}_2), 4.37-4.40 (\text{t, 1H, } \alpha-\text{CH}_2), 5.15 (\text{s, 2H, benzylic CH}_2), 6.20 (\text{s, 1H, N-H}), 7.35-7.37 (\text{s, 5H, aromatic H}). \\
T_m &= 85 - 86°C.
\end{align*}
\]

Scheme 2: The procedure of Goodman was followed.

A vacuum dried three-neck 250 mL flask was fitted with a reflux condenser and glass stoppers, equipped with a stir bar, and connected to a nitrogen inlet and purge. γ-benzyl-L-glutamic acid ester (10.6 g; 0.045 mol) was suspended in 133 mL of dry THF. One-third molar equivalent of triphosgene (4.4 g; 0.0028 mol) of triphosgene in 41 mL of THF was added to the reaction mixture. The reaction mixture was heated to reflux (50°C). After three hours, the reaction mixture was mostly clear except for a small amount of γ-benzyl-L-glutamic acid ester so a small amount of triphosgene was added and the reflux temperature was adjusted to 60°C. The reaction mixture was still not clear after an additional hour so remaining undissolved γ-benzyl-L-glutamic acid ester was filtered, and the reaction mixture concentrated via a tertiary trap. The concentrated mixture was added to cold hexane (-40°C) and allowed to sit in the −40°C freezer.
overnight. White BLG-NCA crystals were collected by filtration and dried under reduced pressure, yielding 11.0 g (73%). $T_m = 81 - 83 \, ^\circ C$. $^1$H-NMR (400 MHz; CDCl$_3$) δ 2.08-2.36 (m, 2H, $\beta$-CH$_2$), 2.61-2.64 (t, 2H, $\gamma$-CH$_2$), 4.36-4.40 (t, 1H, $\alpha$-CH$_2$), 5.16 (s, 2H, benzylic CH$_2$), 6.11 (s, 1H, N-H), 7.35-7.38 (s, 5H, aromatic H).

Both Scheme I and Scheme II provide similar yields and narrow melting points, but Scheme I requires tedious recovery steps and, at times, rephosgenation. Thus, Scheme II is recommended. Although the melting points obtained were lower than literature values (92 – 93 $^\circ$C and 96 – 97$^\circ$C)\textsuperscript{11}, these differences may be attributed to the method of melting point determination. The most important indicator of sample purity is the narrowness of the melting transition.

6.1.3 **Poly(ethylene oxide)-poly(γ-benzyl-L-glutamate)-poly(ethylene oxide)** (*PEO-PBLG-PEO*)

Two synthetic routes were followed in the design of PBLG-PEO-PBLG copolymers; both are described in the following paragraphs. Figure 6.3 summarizes these schemes.

![Scheme I and Scheme II](image)

**Figure 6.3: Synthetic Route for the Polymerization of PBLG-PEO-PBLG\textsuperscript{13-14}**
Scheme I: The following method was adopted from Floudas\textsuperscript{12}

In a glovebox, BLG-NCA (2.74 g; 0.01 mol) was dissolved in 9 mL of anhydrous DMF and transferred to a three-neck flask. Previously vacuum dried (PEO1000-NH\textsubscript{2} (0.00084 g; 0.00084 mol) was dissolved in 8.4 mL of DMF and then transferred to the flask containing the BLG-NCA solution. The reaction was allowed to proceed at room temperature for \~48 hours.

DMF was removed under reduced pressure, and the resulting product was dissolved in a minimal amount of dichloromethane. This product solution was precipitated in cold ether (-40°C), yielding a gummy, yellowish material after vacuum filtration. The material was subsequently redissolved in dichloromethane, and the recovery steps were repeated twice, achieving a final yield of 1.46 g (53%). \textsuperscript{1}H-NMR (400 MHz; CD\textsubscript{2}Cl\textsubscript{2}) δ 2.02-2.28 (m, 40H, \(\gamma\)-CH\textsubscript{2}), 3.52-3.68 (m, 103H, CH\textsubscript{2}CH\textsubscript{2}O), \(\alpha\)-CH\textsubscript{2} (unresolved under CH\textsubscript{2}CH\textsubscript{2}O peak), 5.02-5.10 (m, 20H, benzylic H), 7.26-7.34 (m, 50H, aromatic H), DP = 6, \(M_n\) (NMR) = 2314 g/mol.

Scheme II: The following method was adapted from Tanaka et al.\textsuperscript{13}

PEO1000-NH\textsubscript{2} (3.1 g; 0.0031 mol) was dried by azeotropic distillation (130°C) in toluene using a Dean-Stark trap fitted to a Schlenk flask containing a stir bar for two hours. The toluene was removed by rotary evaporation. Freshly prepared BLG-NCA (4.9 g; 0.037 mol) was added to the Schlenk flask. Then, dry dichloromethane (100 mL) and anhydrous DMF (25 mL) were added to the reaction vessel. A reflux condenser was fitted to the single port, and the reaction was allowed to proceed at 40°C for 24 hours. A solid white powder (impurity) was observed after the reaction, which was collected by filtration.

The collected filtrate was concentrated by rotary evaporation and precipitated in ethanol, yielding a yellowish, resin like material. The precipitate was washed with ethanol four times to yield a slightly yellow, gum-like product, which was dried overnite at 50 mTorr (6.9 g; 86%). \textsuperscript{1}H-NMR (400 MHz; CD\textsubscript{2}Cl\textsubscript{2}) δ 2.18-2.46 (m, 24 H, \(\beta\)-and \(\gamma\)-CH\textsubscript{2}), 3.43-3.67 (m, 103 H, CH\textsubscript{2}CH\textsubscript{2}O), \(\alpha\)-CH\textsubscript{2} (unresolved under CH\textsubscript{2}CH\textsubscript{2}O peak), 5.08-5.11 (m, 12 H, benzylic H), 7.33-7.34 (m, 30 H, aromatic H), DP = 10, \(M_n\) (NMR) = 3379 g/mol.
6.1.4 PBLG-PEO-PBLG Soft Segment Polyurethanes

Figure 6.4 details the synthetic route chosen for the polymerization of segmented polyurethanes containing PBLG-PEO-PBLG soft segments.

![Synthetic Scheme for the Development of Polyurethanes containing PBLG-PEO-PBLG Copolymers](image)

This synthetic procedure was conducted in a glovebox and followed a route similar to the two-step solution polymerization scheme outlined in Chapter 3 for semicrystalline polyurethanes. However, the end-capping step of this route may be carried out at room temperature due to the enhanced reactivity of the amine end-groups of PBLG-PEO-PBLG compared to hydroxyl end-groups. Technically, the resulting polymers from using amine-terminated PBLG-PEO-PBLG copolymers are polyurethaneureas instead of polyurethanes.

PBLG-PEO1000-PBLG (DP = 10 (3379 g/mol); 0.58g; 1 mol) was vacuum dried at 50°C for 5 hrs. A three-neck flask fitted with an addition funnel was used. PBLG-PEO1000-PBLG was dissolved in 17 mL of DMAc and transferred to the addition funnel.
along with 3 drops of DBTDL. HDI (0.14 g; 138 μL) and 5 mL DMAc were added to the three-neck flask. The soft segment solution was slowly (~1 hr) dripped into the HDI/DMAc solution. The reaction was allowed to proceed for three hours at room temperature; FT-IR confirmed the formation of urea bonds. After the end-capping step, BDO (0.062 g; 4 mol; 55 μL) was added, and the reaction proceeded overnight at 85°C. The disappearance of the isocyanate peak was confirmed by FT-IR. The reaction mixture was precipitated into an excess of warm (~70°C) water to reveal a glassy, brown precipitate, which was collected by filtration. The collected precipitate was vacuum dried until constant weight (0.21g; 27%). GPC(PEO standards, DMAc): \( M_n = 5569 \text{ g/mol}, M_w = 10426 \text{ g/mol}, PDI = 1.87. \)

6.1.5 Summary of Structural Characterization of PBLG-PEO-PBLG Copolymers and Polyurethanes

Amine-terminated PEO was synthesized using a three-step scheme, involving the tosylation of diol-terminated PEO, the conversion to diphthalimide-capped PEO, and reduction of the phthalimide units to amine end-groups. The overall conversion was affected by the use of a low molecular weight PEO (1000 g/mol) as the starting material since PEO1000 is difficult to purify by precipitation. NMR, and GPC and FT-IR (not shown) confirm that the end-group conversion did not affect the PEO structure. While the degree of amination was not determined using titration methods, FT-IR supports our assumption of almost complete conversion of the hydroxyl-end groups to amine end groups as indicated by the characteristic double peak due to amine (-NH2) absorption. This diamine-terminated PEO1000 exhibits a melting transition at 39°C (149 J/g), a crystallization peak at 17°C (141 J/g), and a glass transition temperature of -55°C, which are comparable to the values obtained for hydroxyl-terminated PEO1000 (Table 3.2).

PBLG-PEO-PEO copolymers were synthesized by the initiation of BLG-NCA using diamine-terminated PEO as the macroinitiator, assuming that the pseudo-living mechanism is nucleophilic addition to the carbonyl group residing next to the α-carbon of BLG-NCA. A variety of PBLG block sizes were obtained by varying the ratio of BLG-NCA to PEO(NH2)2. The PBLG block sizes (x=y in Figure 6.3) and the copolymer molecular weights were calculated by comparing the ratio of the PEO methylene groups (δ ~3.5 ppm) to the aromatic protons (δ ~7.3 ppm). GPC traces of the copolymers
revealed broad, single peaks, which suggest a distribution of PBLG block lengths were obtained. Commercially available PEO2000(NH$_2$)$_2$ was also used to initiate BLG-NCA, yielding a copolymer with a degree of polymerization of 60, which was much higher than the target of 20. Since $DP \sim [M]/[I]$, this situation is most likely a result of a lower concentration of initiator or initiator end-groups than measured, which increases the DP. NMR analysis of PEO2000(NH$_2$)$_2$ confirmed that this material contains a significant number of impurities, lowering the actual initiator concentration used in the DP calculations.

Segmented polyurethanes containing PBLG-PEO-PBLG copolymers were synthesized using a modified version of the two-step synthesis outlined for PEO or PEO-PPO-PEO soft segment polyurethanes. However, the degree of polymerization of these polyurethanes was limited, as suggested by the low molecular weights obtained and the poor film-forming properties of these materials. The low molecular weight of the segmented polyurethane is most likely due to the low end-group reactivity of the PBLG-PEO-PBLG copolymers and possible end-group cyclization, which would decrease the amine-functionality. According to Fontaine et al., PBLG oligomers synthesized at approximately room temperature for short reaction times ($\leq 1$hr) exhibited amine end-group concentrations close to the theoretical value (no significant cyclization of the PBLG blocks) with minimal loss in yield. These observations suggest that the synthetic conditions for the copolymers with short PBLG block lengths must be optimized. Table 6.1 summarizes the structural information regarding the PBLG-PEO-PBLG copolymers and polyurethanes.
Table 6.1: Structural Characterization of PBLG-PEO-PBLG Copolymers and Polyurethanes

<table>
<thead>
<tr>
<th>PEO MW (g/mol)</th>
<th>PBLG DP</th>
<th>PBLG-PEO-PBLG MW(^a) (g/mol)</th>
<th>Polyurethane M(_b)(^b) (g/mol)</th>
<th>Hard Segment Content (wt%)</th>
<th>Volume Fraction of PBLG(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>10</td>
<td>3379</td>
<td>10426</td>
<td>26</td>
<td>0.26</td>
</tr>
<tr>
<td>2000</td>
<td>6</td>
<td>2314</td>
<td>5231</td>
<td>34</td>
<td>0.17</td>
</tr>
<tr>
<td>2000</td>
<td>60</td>
<td>15340</td>
<td>-</td>
<td>-</td>
<td>0.51</td>
</tr>
</tbody>
</table>

\(^a\) Molecular weight determined using \(^1\)H-NMR; \(^b\) Molecular weight determined using GPC (PEO standards, DMAC (70°C)); \(^c\) Taken from Floudas et al. (ref)

\[
f_{PBLG} = \left( \frac{N_{n, PBLG}}{N_{n, PBLG} + N_{n, PEO}} \right)^{0.5};
\]

\[
N_{n, PEO} = N_{n, PEO} \left( \frac{\rho_{PBLG}}{\rho_{PEO}} \right)^{0.5};
\]

\[
\begin{align*}
\rho_{PEO} &= 1.12 \frac{g}{cm^3}; \\
\rho_{PBLG} &= 1.278 \frac{g}{cm^3} (\alpha - \text{helix})
\end{align*}
\]

6.2 Morphological Behavior

6.2.1 Thermal Behavior

As suggested in Chapter 2, PBLG-PEO-PBLG copolymers show promise as polyurethane soft segments for high performance applications. The utility of these copolymers are linked to the various secondary structures (\(\alpha\)-helix and \(\beta\)-pleated sheets) available as energy-absorbing mechanisms. Morphological studies of these PBLG copolymers will enable the determination of the conformation of the PEO and PBLG blocks, the extent of micro-phase segregation, and the thermal behavior. These investigations will be limited to the PBLG copolymers based on PEO1000(NH\(_2\))\(_2\).

The thermal properties of these liquid crystalline PEO-containing copolymers and polyurethanes were determined using DSC. PBLG\(_3\)-PEO1000-PBLG\(_3\) exhibits two low temperature glass transitions, -61°C and -22°C. Assuming that a mixture of tri-block and di-block results from the copolymer synthesis and given the small block lengths, it is likely that these thermal transitions correspond to the \(T_g\) of the PEO when attached to various PBLG block sizes. The absence of a PEO melting transition suggests that these systems are not micro-phase separated, which contradicts the assertion of micro-phase segregation for copolymers containing less than 0.26 volume fraction of PBLG, as reported by Floudas and coworkers\(^{12}\). However, their studies indicated that large
undercoolings were necessary for PEO crystallization, which is difficult for our copolymers due to the low melting transition of PEO1000.

Upon incorporation of the PBLG\textsubscript{3}-PEO1000-PBLG\textsubscript{3} as the polyurethane soft segment, the 1\textsuperscript{st} heating cycle of the as-precipitated polyurethane (34 wt% HS) also shows two low temperature glass transitions. However, the second glass transition has shifted from -22°C to -3°C, suggesting that the HDI-BDO hard segments have limited the flexibility of the PEO chains. A broad, hard domain melting transition occurs at 139°C (22 J/g of HS). An annealing endotherm is also evident at 56°C. During the 2\textsuperscript{nd} heating cycle, the hard domain melting transition is replaced by a glass transition at 94°C, implying that the PBLG ordering has inhibited hard domain crystallization. The second low temperature \( T_g \) returns to an approximate copolymer glass transition value (-16°C), which supports the supposition that, upon erasing the original thermal history, the PBLG copolymer morphology influences the molecular architecture of the segmented polyurethane.

The thermal behavior of PBLG\textsubscript{5}-PEO1000-PBLG\textsubscript{5} was also examined. A single low temperature PEO glass transition (-19°C) is observed in these copolymers during the first heating, which implies that copolymer is composed mostly of tri-block material with the motion of the PEO chains hindered by the increase in PBLG block length. Above this \( T_g \), a glass transition is observed at 50°C, which is attributed to the PBLG block and depends on block length\textsuperscript{13}. An endothermic transition exists at 95°C, corresponding to the PBLG helical transformation (7\textsubscript{2} to 18\textsubscript{5})\textsuperscript{13}. Although this transformation is not observed upon cooling, the second heating cycles reproduces this endothermic peak as a weak, broad transition and at a lower temperature (81°C). The glass transition above room temperature has disappeared in the 2\textsuperscript{nd} heating curve, and the PEO \( T_g \) has shifted to slightly higher temperatures (-16°C). As in PBLG\textsubscript{3}-PEO1000-PBLG\textsubscript{3}, micro-phase segregation is not distinguished.

The polyurethane (26 wt% HS) containing PBLG\textsubscript{5}-PEO1000-PBLG\textsubscript{5} as the soft segment exhibits four thermal transitions during the 1\textsuperscript{st} heating cycle. The PEO glass transition has shifted by 10°C to -9°C in the segmented polyurethane. The PBLG \( T_g \) has been lowered (39°C), which is mostly like the result of the interfacial mixing with the rigid hard domains. Two pronounced hard domain melting transitions are noted, 157°C
(55 J/g of HS) and 224°C (35 J/g of HS), suggesting a high degree of association within the hard block. Yet, only a single low temperature glass transition (-9°C) is detected during the 2^{nd} heating cycle, which implies that phase-mixing has occurred. It appears that, at a higher volume fraction of PBLG, the rigid hard domains and helical PBLG units retard motion and suppress hard domain association at higher temperatures.

6.2.2 PBLG-PEO-PBLG Conformation

FT-IR studies of copolymers films can provide information regarding the conformation of PBLG and PEO in these materials. Poly(γ-benzyl-L-glutamate) may exist as an α-helix or as β-sheet, depending on stabilization of the secondary structure. The presence of amide absorption bands at 1650 and 1550 cm\(^{-1}\) correspond to the α-helical conformation, while infrared absorption at 1630 and 1530 cm\(^{-1}\) indicate a β-sheet conformation\(^{13}\). The α-helical structure of PEO is observed at 950 and 850 cm\(^{-1}\).\(^{16}\)

The FT-IR spectra for PBLG\(_3\)-PEO-PBLG\(_3\) and PBLG\(_5\)-PEO-PBLG\(_5\) are given in Figure 6.5. The PBLG block in PBLG\(_3\)-PEO-PBLG\(_3\) displays a mixture of α-helical and β-sheet conformations, as indicated by the shouldered peak in Figure 6.5. The PEO 7\(_2\) helix is also observed in this copolymer, suggesting that the absence of PEO crystallization in DSC may due to inadequate cooling rates. In PBLG\(_5\)-PEO-PBLG\(_5\), only the α-helical secondary structure is evident, indicating that destabilization of the β-sheet conformation and disruption of PEO crystallinity occur with an increase in PBLG block size.
6.2.3 Small-Angle X-ray Scattering

The extent of micro-phase segregation in these polyurethanes containing PBLG-PEO1000-PBLG copolymers was studied using small-angle X-ray scattering, as shown in Figure 6.6. The characteristic scattering peak due to micro-phase segregation of soft and hard blocks is absent in the PBLG$_3$-PEO1000-PBLG$_3$ soft segment polyurethane, which is not surprising given its low molecular weight and weak hard domain enthalpy of fusion. In the PBLG$_5$-PEO1000-PBLG$_5$ soft segment polyurethane, a slight shoulder is evident in the scattering pattern at $q = 0.16$ nm$^{-1}$, corresponding to d-spacing of 39 nm. This Bragg spacing is much larger than the inter-domain spacing (~10 nm) reported for PU-1-33, which contains a similar hard segment content. The origin of this scattering
peak is unknown, but may be a consequence of the hierarchical microstructure of PBLG₅-PEO1000-PBLG₅ polyurethane, as highlighted by thermal analysis.

![Graph showing SAXS Patterns of Polyurethanes Containing PBLG-PEO1000-PBLG Copolymers](image)

**Figure 6.6: SAXS Patterns of Polyurethanes Containing PBLG-PEO1000-PBLG Copolymers**

6.2.4 Optical Microscopy

Polarizing optical microscopy was used to evaluate the crystalline and liquid crystalline textures in these PBLG-PEO-PBLG copolymers and polyurethanes. In Figure 6.7, polarized optical micrographs are shown for a) PEO1000(NH₂)₂, b) PBLG₅-PEO1000-PBLG₅, and c) PBLG₅-PEO1000-PBLG₅ polyurethane. The polarized OM image (Figure 6.7a) of the diamine-terminated PEO1000 shows strong birefringence due to the spherulitic crystalline texture of PEO1000. The copolymerization of PEO1000(NH₂)₂ with PBLG yields a polyurethane soft segment exhibiting overall texture, but the PEO crystallinity has been suppressed, as revealed in Figure 6.7b and supported by DSC results. The resulting polyurethane (Figure 6.7c) shows birefringent behavior due to the spherulitic HDI-BDO hard domains.
Figure 6.7: Polarized Optical Micrographs of a) PEO1000(NH$_2$)$_2$, b) PBLG$_5$-PEO1000-PBLG$_5$, and c) PBLG$_5$-PEO1000-PBLG$_5$ Polyurethane
6.3 Conclusions

PBLG-PEO-PBLG copolymers with overall PBLG block sizes of 6 and 10 were developed using diamine-terminated PEO1000, which was custom synthesized due to high commercial costs and design issues. The small PBLG block sizes were necessary to satisfy the molecular weight constraints set forth in Chapter 2. Due to the low degree of polymerization of PBLG, the range of secondary structures reported for higher molecular weight PBLG-PEO-PBLG tri-blocks were not attained, as evidenced by SAXS and OM investigations. However, the resulting morphologies provided crucial information for the future design of PBLG-based polyurethane soft segments, which will focus on precise control of block length, preservation of end-group functionality, and separation of the rigid PBLG units from the crystalline HDI-BDO domains.

Low MW polyurethanes with varying degrees of phase-mixing were obtained using these PBLG-PEO-PBLG copolymers. The polyurethanes displayed poor film properties and lacked the micro-phase segregation characteristic of segmented polyurethane elastomers. However, the PBLG5-PEO-PBLG5 soft segment polyurethane did exhibit a weak scattering shoulder (d = 39 nm), which may be attributed to hierarchy within the soft block.

6.4 References


Chapter 7: Conclusions and Future Directions

7.1 Summary

The hierarchical microstructure responsible for the superior material properties of native spider silk motivated the development of segmented polyurethanes with soft segments containing multiple levels of order. This thesis details the design, synthesis, and characterization of these silk-inspired thermoplastic polyurethane elastomers.

Semicrystalline and liquid crystalline PEO-containing polyurethane soft segments were incorporated into polyurethanes with crystalline HDI-BDO hard segments. A series of high molecular weight PEO (1000 and 4600 g/mol) and PEO-PPO-PEO (1900 g/mol) soft segment polyurethanes with varying hard segment contents were synthesized using a two-step solution polymerization method. Due to an increase in soft segment length and the influence of the PPO middle block, the PEO-PPO-PEO soft segment induced a higher degree of phase separation than the PEO (1000 g/mol) soft segment. The presence of soft segment crystallinity (PEO 1000 g/mol) was shown to improve the storage modulus of the segmented polyurethanes below the T_m of the soft block. At a higher PEO (4600 g/mol) soft segment length, a lamellar, micro-phase segregated morphology was evident via SAXS, which prompted an investigation of the influence of \( \chi N \) on the morphological behavior. Temperature-dependent SAXS studies concluded that the soft segment crystallinity was the driving force for micro-phase segregation. The solubility of the PEO4600 soft segment polyurethane was limited due to its highly crystalline hard and soft domain. As the hard segment content was increased, the degree of hard domain ordering was enhanced, which was observed using DSC, WAXS, OM, and AFM. AFM also revealed that the morphology of the segmented polyurethanes shifts from soft segment continuous to interconnected and/or hard domain continuous with increasing hard segment size. This change in matrix morphology with increasing HS content directly impacted the mechanical behavior of these polyurethane elastomers, resulting in diminished ultimate elongation and higher hysteresis values, but enhanced initial moduli and tensile strengths.
The deformation behavior of these semicrystalline polyurethane elastomers was also investigated using SAXS, WAXS, and OM. As a consequence of shearing of the rigid, crystalline HDI-BDO blocks, the hard domains adopt a preferential alignment (±70° to the stretch direction) under tensile deformation. The hard segments within the hard blocks aligned ±30° to the meridian to maximize the hydrogen bonding between chains. A scattering contribution from the PEO-containing copolymer mesophase was observed in the low hard segment content polyurethane (33 wt% HS), which was postulated to result from differences in domain morphology (soft segment continuous versus hard domain matrix or interconnected domains). In comparison to the PEO-PPO-PEO soft segment polyurethane, the PEO1000-based segmented polyurethane exhibited better alignment and/or paracrystallinity of the soft segment chains, improving the mechanical response under deformation as reflected in a higher initial modulus, and increased extensibility and tensile strength. In-situ optical microscopy experiments offered visual evidence of the role of the soft segment in the deformation of these semicrystalline segmented polyurethanes, showing that strain-induced birefringence occurred at lower elongations for the pure PEO1000 soft segment polyurethane. It was also shown that the higher hard segment polyurethane (47 wt% HS) showed an absence of soft segment chain alignment under deformation. These observed differences emphasize that the alignment and crystallinity of the PEO-containing soft segment chains serve as a load-bearing mechanism in response to tensile deformation.

In an effort to improve the material properties of a PEO-PPO-PEO soft segment polyurethane containing 33 wt% HS, a novel solvent exchange method was employed to disperse 10 wt% Laponite within the polyurethane matrix. It was shown that the addition of clay discs to the polyurethane resulted in dramatic reductions in tensile strength and ultimate extensibility, while the initial modulus remained relatively unchanged. This unexpected mechanical behavior was a result of the preferential attraction of the clay particles to the PEO-rich soft domain. A micro-phase segregated morphology of the PEO-containing polyurethane/Laponite nanocomposite is evident in DSC studies and suggested by the TEM analysis. It was postulated that the exfoliation occurs within the hard domains, while the PEO-based soft segments intercalate the Laponite galleries.
Several synthetic strategies were employed to develop PBLG-PEO-PBLG copolymers (PBLG DP = 6 & 10) using custom synthesized, diamine-terminated PEO1000. While the small PBLG block lengths required by the materials design criteria (<5000 g/mol soft segment) limited detection of the PBLG secondary structures, usually reported for higher molecular weight PBLG-PEO-PBLG tri-blocks, these copolymers were incorporated as polyurethane soft segments using two-step solution polymerization, yielding low molecular weight materials. At higher PBLG block lengths, superstructure was observed in SAXS and DSC, which was assigned to a certain degree of hierarchy within the soft segment copolymer.

7.2 Future Directions

This thesis work reports several findings that warrant future exploration for the design of segmented polyurethanes, which mimic the hierarchical morphology of native spider silk.

7.2.1 Semicrystalline Segmented Polyurethanes

The pure PEO (1000 and 4600 g/mol) soft segment polyurethanes exhibited interesting morphological and mechanical behavior and supported our position that the soft segment crystallites provide a reinforcing effect within the polyurethane matrix, but the small batch sizes and/or limited solubility hindered complete characterization of these materials. Future studies would involve developing a series of segmented polyurethanes with various PEO block lengths (low PDI) as a function of hard segment size and probing the role and impact of increasing soft segment crystallinity on mechanical properties (i.e. strain-induced crystallization) upon tensile deformation using in-situ WAXS and OM. In-situ relaxation experiments would yield information about the extent of plastic deformation and allow correlation of the hysteresis levels calculated from cyclic mechanical data. It would also be ideal to optimize the deformation conditions (strain rate, clamping configuration) for SAXS and WAXS to reproduce the observed mechanical behavior (i.e. ultimate elongation) in tensile studies, revealing a more complete picture of the hard domain restructuring upon elongation and providing more conclusive crystalline peak assignments for the hard and soft blocks. Examination of the longer hard and soft block length polyurethanes will allow further study of the influence
of \chi N on the micro-phase separated morphology, which has been extensively probed for block copolymers, but not for segmented copolymers, such as polyurethanes, polyesters, and polyamides.

### 7.2.2 PEO-containing Polyurethane/Laponite Nanocomposites

With the existing series of segmented polyurethanes, it would be intriguing to determine the material properties as a function of the amount of Laponite added to the polyurethane matrix. In this way, the partitioning of the clay particles can be examined using DSC and TEM. Additionally, it is clear that the mechanical reinforcement (or lack thereof) achieved in the polyurethane nanocomposites is not only dependent upon block polarity and hydrophilicity, but is also influenced by the matrix morphology (hard versus soft domain continuous). Therefore, analysis of the mechanical behavior of low and high hard segment content polyurethanes will offer further insight into the dominant reinforcing mechanisms in these polyurethane elastomers. Despite the reduction in material properties reported for the PEO-PPO-PEO polyurethane/Laponite nanocomposite investigated in this work, the concept of preferential attraction of the clay particles to either the hard or soft block offers unique opportunities to tailor the material properties by varying block polarity and hydrophilicity.

### 7.2.3 PBLG-PEO-PBLG Copolymers as Polyurethane Soft Segments

Only low molecular weight polyurethane elastomers were obtained using the PBLG-PEO-PBLG copolymers synthesized in this thesis research, which was postulated as a consequence of the low amine-end group functionality due to end-group cyclization. By lowering the reaction temperature and decreasing the reaction time without compromising yield, close to theoretical amine functionality has been reported for PBLG-PEO-PBLG oligomers, which is a starting point for the future design of the copolymers. Further consideration of the design of liquid crystalline PEO-containing polyurethane soft segments has led to conceptual development of PEO-PBLG-PEO copolymers. By confining the liquid crystalline character to the middle block, the crystalline nature of the hard segment and soft segment are decoupled by a soft PEO block (n < 25) and lower overall DP are necessary for observation of \(\alpha\)-helical and \(\beta\)-sheet liquid crystalline
textures. The synthetic scheme for the development of these PEO-PBLG-PEO copolymers is given in Figure 7.1.
1) PBLG Synthesis

\[
\text{PBLG} + \text{H}_2\text{N}--\text{CH}_2\text{CH}_2--\text{NH}_2 \quad \rightarrow \quad \text{20°C, \< 1 hr, \text{N}_2} \quad \text{9/1 (v/v): DCM/DMF}
\]

2) PEO Endcapping

\[
\text{HO} \left( \text{CH}_2\text{O} \right)_n \text{H} + 2 \text{OCN} - \text{CH}_2\text{CH}_2 - \text{NCO} \quad \rightarrow \quad \text{65°C, 3-5 hrs, \text{N}_2} \quad \text{DBTDL, CH}_2\text{Cl}_2, \text{precipitate in ether}
\]

3) PEO-PBLG-PEO Synthesis

\[
\text{A} + \text{B} \quad \rightarrow \quad \text{RT, 18 hrs, \text{N}_2} \quad \text{CH}_2\text{Cl}_2, \text{precipitate in ether}
\]

Figure 7.1: Synthetic Scheme for the Design of PEO-PBLG-PEO copolymers
As shown in Figure 7.1, the PBLG block is initiated by a highly reactive, small molecule diamine, such as ethylene diamine, allowing for precise control of the PBLG block length under reaction conditions shown to preserve end-group functionality. Reacting the diamine-terminated PBLG with a low PDI diisocyanate-terminated PEO block creates the tri-block copolymer (diisocyanate-terminated). Depending on the PBLG block length and conformation, the reactivity of the amine end-groups on the PBLG may be diminished. In this case, it may be more beneficial to exploit the relatively fast reaction kinetics between amines and diisocyanates by end-capping the PBLG block instead of the PEO with the diisocyanate. Then, the PBLG with diisocyanate functionality is reacted with rigorously dry PEO to form diol-terminated PEO-PBLG-PEO. The main advantage of the synthetic route outlined in Figure 7.1 is that the resulting tri-block copolymer can be directly chain-extended to form the segmented polyurethane.

7.3 References


DISCLAIMER OF QUALITY

Due to the condition of the original material, there are unavoidable flaws in this reproduction. We have made every effort possible to provide you with the best copy available. If you are dissatisfied with this product and find it unusable, please contact Document Services as soon as possible.

Thank you.

Some pages in the original document contain color pictures or graphics that will not scan or reproduce well.