Development of Melt Spun Polymer Nanofibers

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Outline

• Introduction
  – Rationale
  – Fiber spinning and structure development
  – Nomenclature
• Fiber spinning setup and fiber size calculations
• Characterization
  – X-Ray Diffraction
  – Differential Scanning Calorimetry
    • Temperature Modulated - DSC
  – Atomic Force Microscopy
• Future work
  – Tri-component extruder – NRX-11
  – New Islands-in-the-Sea spin pack
Introduction

- **Objective:**
  - Produce nanofibers (ultra fine) with a diameter of 100 nm or less by using a multi-component fiber spinning process that allows control of a number of variables (including critical aspects of confinement dimensions, thermal history and interfacial chemistry).

- **Motivation:**
  - Large surface to volume
  - Unusual properties
    - “Confinement effects”
    - Size scale (potentially resulting in less defect sensitivity)

- **Applications:**
  - Confined polymer systems as implemented in melt-spun nanofibers have numerous potential applications in military systems, including clothing, shelters and airdrop equipment. Confinement effects may allow enhanced performance to be realized from commodity materials.
Free fall or undrawn fiber

2010 INS
10% PP / 90% PE

2010 INS
10% PP / 90% PLA

10,000 INS
25% PP / 75% PLA
ESEM Image

600 INS
10% PP / 90% PLA

1200 INS
30% PP / 70% PLA

ESEM Image courtesy of M. Auerbach, NSRDEC
Approximately 2000 PP nanofibers shown in a cross section of a single filament.

One quarter cross sectional view showing approximately 470 PP nanofiber “islands” surrounded by PLA “sea” material.

Spin packs are identified by the number of islands, 600, 2010, etc.

Images courtesy of Veeco Instruments.
Confinement

- Growth of crystals is limited by the “island” size

- Polymer molecules influenced by the surface as the island gets smaller

- Used PP with a polydispersity index (PDI) Mw/Mn approx. 3-3.5 and molecular weight of 180,000 (LyondellBasell Industries)

- Radius of gyration (Rg) 14nm

- Major axis = 49 nm
  - Theodoreau & Suter, “Shape of Unperturbed Linear Polymers: Polypropylene” Macromolecules 18, 1206-1214, 1985

- Jin et al. has found a size influence at 400 nm or less in multilayer extruded films
Confinement of Island Polymers

"Confining" sea polymer

100 nm

Polymer molecules
Previous Work

- Field is of growing interest and importance
- Many studies done on block copolymer systems
- Many studies on films and dispersed phases
- Few studies on fibers
- Few studies on melt-processed thermoplastics
- Few studies on homopolymers
- This study evaluates confinement effects produced in a “real world” process using commercial materials
Fiber Melt Spinning vs. Electrospinning

Schematic view of electrospinning process.
Picture taken from Nanotechweb.org

Schematic view of melt spinning process.
Picture taken from Structure Formation in Polymeric Fibers, D. Salem
Structure Development in Fiber Spinning

May or may not be present

Deformation of entanglement network

Deformation of crystallite network

Schematic model of the development of structure during high speed melt spinning of PET. (reference [124]).


• Fibers were spun at Hills, Inc., Melbourne FL
• 72 filaments (spinneret holes)
• Air quenched
• Spin finish applied
• Over denier & Godet rolls to winder
  – Leesona winder 500 – 2000 m/min
  – BarMag winder 1500 – 5500 m/min
    • 5500 m/min = Mach 0.26
• Directly to winder
• Use bi-component fiber spinning technology (Hills, Inc.,) to create confined small-scale domains
• High Islands-in-the-Sea (INS) fiber design (600 – 120,000)
• Polypropylene islands/Poly(lactic acid) sea
• Polypropylene islands/Polyethylene sea
• Bi-component fibers have been spun using PP as the confined polymer (island) and PLA or PE as the confinement phase (sea)
• Preliminary characterization of the fibers includes AFM, ESEM, DSC, and wide-angle X-ray diffraction
• Correlate morphology and properties as a function of confinement dimensions
Challenges

• How do we get down to 100 nm
  – Decrease the diameter island size by using low ratio islands, increased island count, and increased drawing

• Drawing
  – Increase the draw ratio to achieve lower deniers
    • In the melt by using a high speed (Oerlikon) Barmag winder (1500 – 5500 m/min)
    • Cold Draw
      – Processing over Godet rolls onto a (Leesona) filament yarn take-up winder (500 – 2000 m/min)

• Post Draw

• Maintaining Fiber Geometry
  – WAXD and DSC show distinct phases
## Diameter Calculations

### Drawn Fiber

<table>
<thead>
<tr>
<th>Polymer System</th>
<th>PP/PLA</th>
<th>PP/PLA</th>
<th>PP/PE</th>
<th>PP/PE</th>
<th>PP/PE</th>
<th>PP/PE</th>
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<tbody>
<tr>
<td>Godet</td>
<td>Barmag</td>
<td>Godet</td>
<td>Barmag</td>
<td>Post Drawn</td>
<td>Barmag</td>
<td>PD - Godet</td>
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<tr>
<td>Rolls</td>
<td>Winder</td>
<td>Rolls</td>
<td>Winder</td>
<td>Godet Rolls</td>
<td>PD - Godet</td>
<td></td>
</tr>
</tbody>
</table>

| Denier | 148 | 150 | 115 | 108 | 92 | 78 |
| DPF    | 2.06 | 2.08 | 1.60 | 1.50 | 1.28 | 1.08 |

| Island Diameter in Nanometers | 127 | 128 | 112 | 108 | 100 | 92 |

| Island Ratio | 10% |
| # of Islands | 2010 |
| # of Filaments | 72 |
| Island (PP) Density (solid) | 0.902 |
This view shows approximately 470 PP nanofibers

Mean Diameter 97 nm

Minimum Diameter 18 nm

Maximum Diameter for center cluster of nanofibers is 1636 nm

Image courtesy of Veeco Instruments
AFM cross sectional image of drawn single filament

Young's Modulus Map Analysis Based on DMT Model

Young's Modulus

Images courtesy of Veeco Instruments
PP homopolymer

WAXD shows a high degree of crystallinity and orientation in the PP fiber.

Godet Rolls
Leesona Winder
Speed 1600 mpm

Barmag Winder
Speed 3000 mpm
Wide-Angle X-ray Diffraction of Fibers
Intensity vs. Chi

Less oriented noted in PE fiber (sea)

PP Control
Godet Rolls
Leesona Winder
Speed 1600 mpm

10% PP / 90% PE

Godet Rolls
Leesona Winder
Speed 1700 mpm

PE Control
Godet Rolls
Leesona Winder
Speed 1500 mpm

Barmag Winder
Speed 3000 mpm

PP Control

PP / PE

UNCLASSIFIED TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.
Wide-Angle X-ray Diffraction of Fibers
Intensity vs. Chi

Amorphous PLA fiber (sea)

PP Control
Godet Rolls
Leesona Winder
Speed 1600 mpm

10% PP / 90% PLA

PLA Control
Godet Rolls
Leesona Winder
Speed 1400 mpm

Godet Rolls
Leesona Winder
Speed 500 mpm

UNCLASSIFIED  TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.
• A broad upward peak between 85°C and peaking near 100°C, corresponds to cold crystallization of PP
• The PP was partially prevented from crystallizing during processing
• Increasing island count appears to suppress the crystallization of the PLA
• Increase the draw – Increase the crystallinity of the PP

### Decreasing Island Spacing or Higher Island Count

<table>
<thead>
<tr>
<th>NO DRAW</th>
<th>DRAW</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 INS   Denier 3564  10% PP/90% PLA</td>
<td>1200 INS Denier 3620  10% PP/90% PLA</td>
</tr>
<tr>
<td>600 INS   Denier 936    10% PP/90% PLA</td>
<td>1200 INS Denier 511    10% PP/90% PLA</td>
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DSC Analysis

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### Data

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<tr>
<td>3564</td>
<td>NO DRAW</td>
</tr>
<tr>
<td>936</td>
<td>DRAW</td>
</tr>
</tbody>
</table>

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**Graphs:**

- **NO DRAW**
  - 64.83°C, 6.534μg
  - 96.17°C
- **DRAW**
  - 67.92°C, 1.336μg
  - 70.36°C, 2.495μg
  - 154.87°C, 56.71μg
  - 153.14°C
DSC Analysis

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**Sample:**

1200 INS    Denier 3620    10% PP/90% PLA

1200 INS    Denier 511    10% PP/90% PLA
Crystallization of PLA is suppressed in post-drawn INS fibers

<table>
<thead>
<tr>
<th>Denier</th>
<th>PP/PLA</th>
<th>Heat Flow Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>3564</td>
<td>10/90</td>
<td>Non-Reversing</td>
</tr>
<tr>
<td>3620</td>
<td>10/90</td>
<td>Reversing</td>
</tr>
<tr>
<td>936</td>
<td>10/90</td>
<td>Non-Reversing</td>
</tr>
<tr>
<td>511</td>
<td>10/90</td>
<td>Reversing</td>
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</tbody>
</table>
Summary

- Based on calculations the diameter readings appear to be in the nano scale range from 92 – 150 nm
- Based on AFM analysis we believe we have spun approximately 100 nm or smaller diameter fibers
- WAXD and DSC show distinct phases of the polymers used in processing are still present
- Increasing island count appears to suppress the crystallization of the PLA
- Increase the draw – Increase the crystallinity of the PP
- No unique properties seen yet, but testing still underway
Acknowledgements

Jim Brang
Hills Inc., Melbourne, FL for expertise in fiber spinning

Veeco Instruments
for their expertise in imaging fiber samples with AFM

Approved for Public Release – PAO #