RDECOM

Development of Melt Spun Polymer Nanofibers

US ARMY NATICK SOLDIER RD&E CENTER

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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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

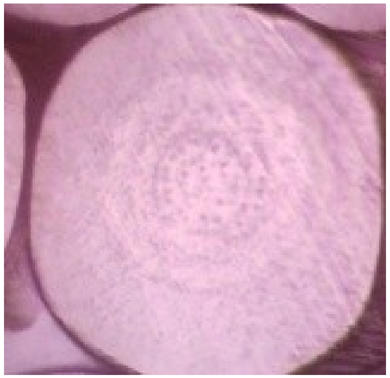
- **Objective:**
  - **Produce nanofibers (ultra fine) with a diameter of 100 nm or less by using a multi-component fiber spinning process that allows control of a number of variables (including critical aspects of confinement dimensions, thermal history and interfacial chemistry).**

- **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.**

"Islands-in-the-Sea" Cross Sectional View Optical & ESEM Microscopes

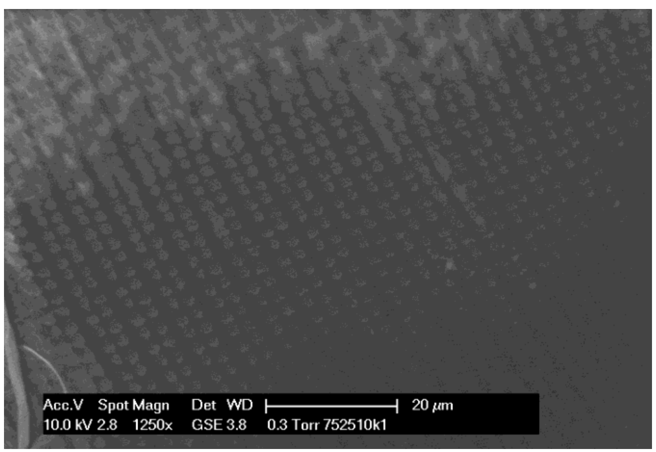
Free fall or undrawn fiber



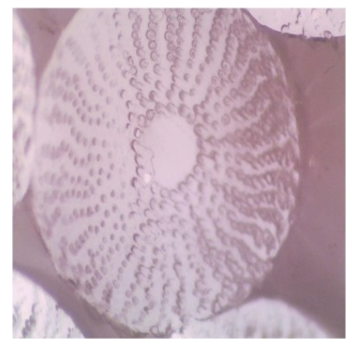
2010 INS
10% PP / 90% PE

2010 INS
10% PP / 90% PLA

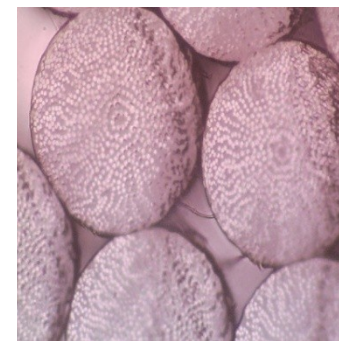
10,000 INS
25% PP /
75% PLA
ESEM Image



ESEM Image courtesy of M. Auerbach, NSRDEC

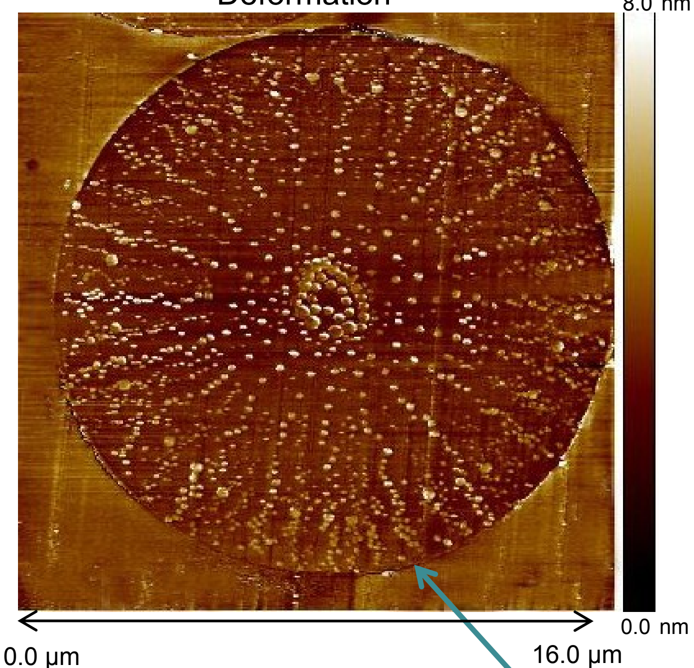


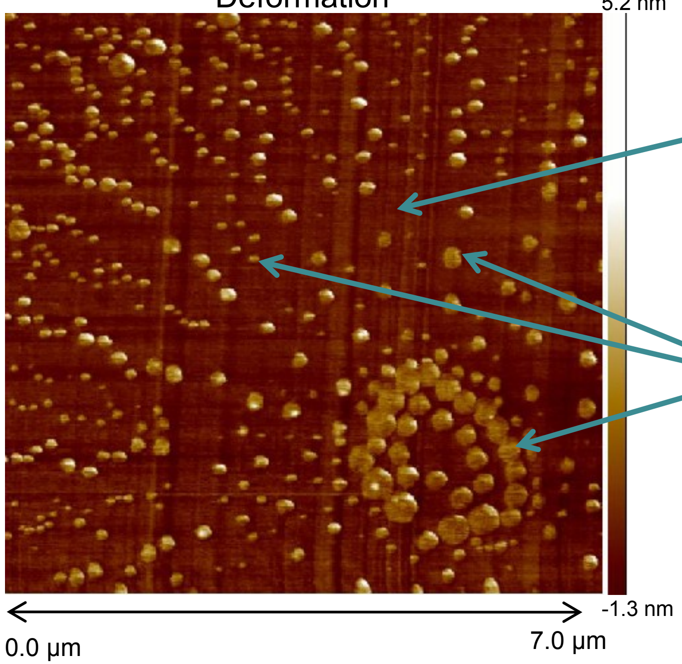
600 INS
10% PP /
90% PLA



1200 INS
30% PP /
70% PLA

"Islands-in-the-Sea" Cross Sectional View AFM Analysis





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

One Single Filament

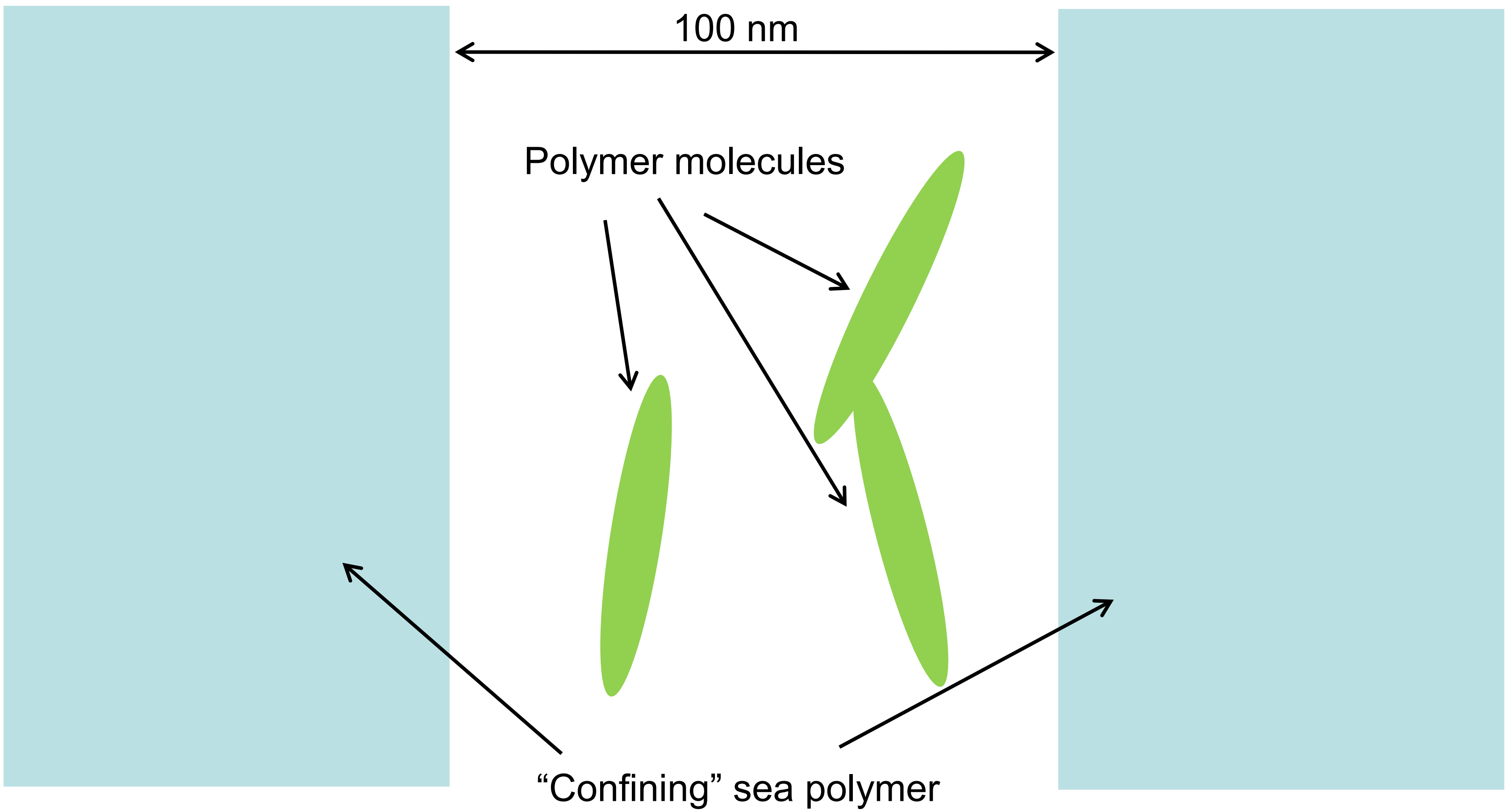
Spin packs are identified by the number of islands, 600, 2010, etc.

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
  - **Flory*, "Conformations of Macromolecules in Condensed Phases"*, pp.305-312, 1984**
- 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

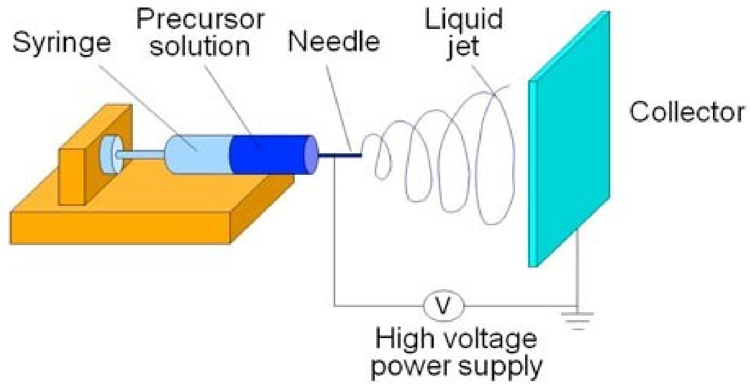
Confinement of Island Polymers



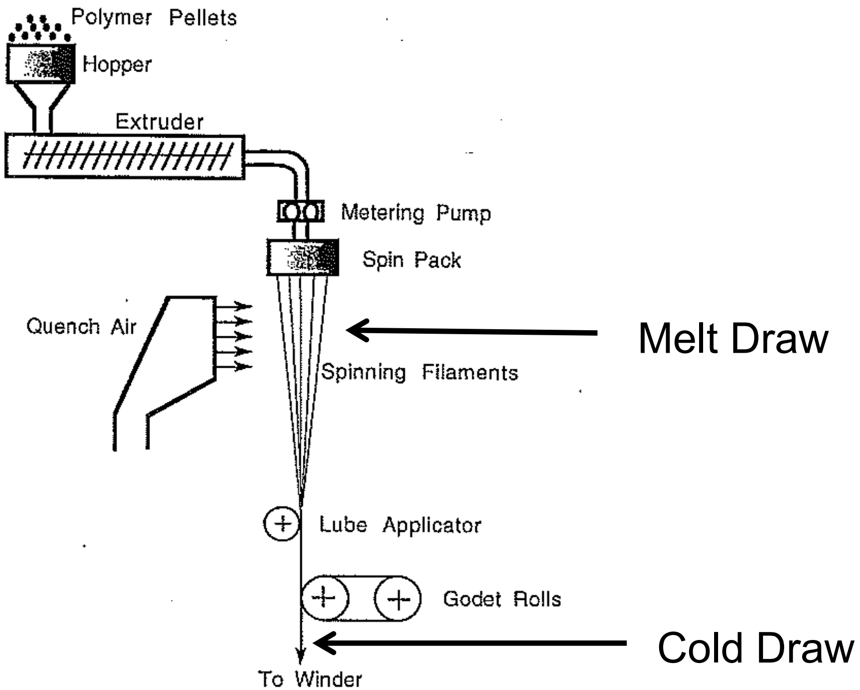
Previous Work

- 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

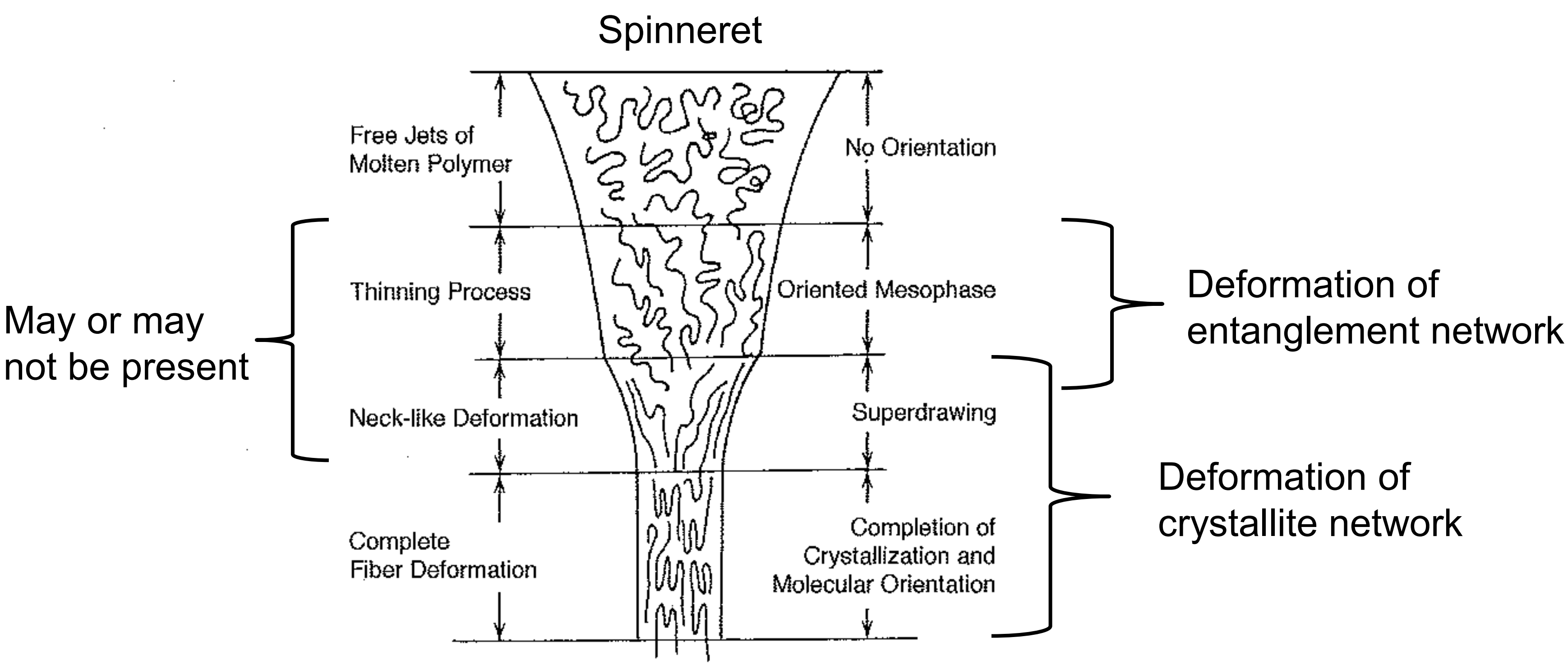


Schematic view of electrospinning process.
Picture taken from Nanotechweb.org



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

Structure Development in Fiber Spinnin



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

After Spruiell, J. E. Structure Formation during Melt Spining in Structure Formation in Polymeric Fibers, Salem, D. R. Ed. Hanser Munich 2000 p 59.

124. Shimazu, J. et al in High Speed Fiber Spinning, Ziabicki, A. & Kawai, H. Eds. Wiley, New York 1985 p. 429.

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Processing

- 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

Approach / Polymers

- 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

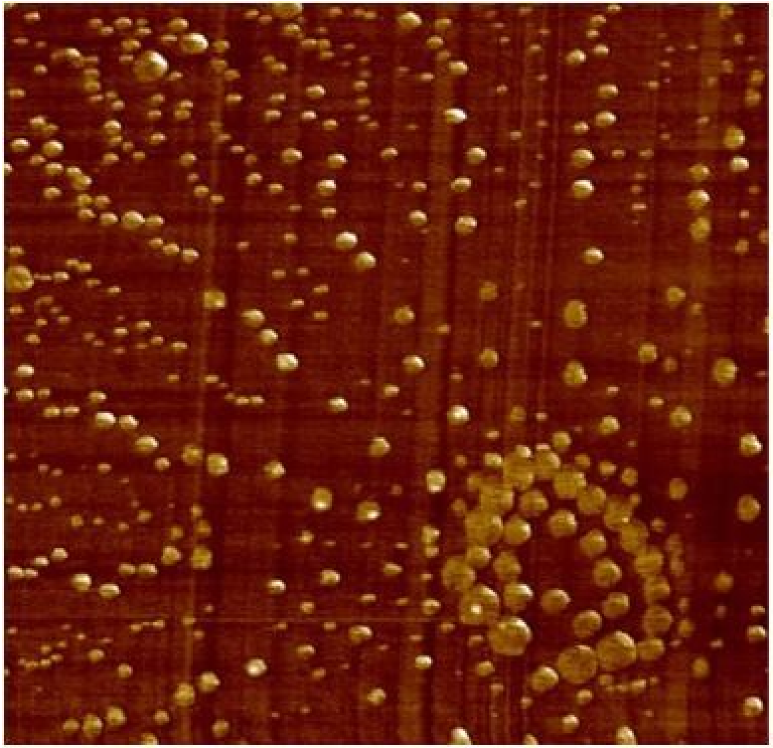
Drawn Fiber

Polymer System	PP/PLA	PP/PLA	PP/PE	PP/PE	PP/PE	PP/PE
	Godet	Barmag	Godet	Barmag	Post Drawn	Barmag
	Rolls	Winder	Rolls	Winder	Godet Rolls	PD - Godet
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

Diameter Calculations using AFM Analysis

PP nanofibers diameter distribution



This view shows approximately 470 PP nanofibers

Mean Diameter 97 nm

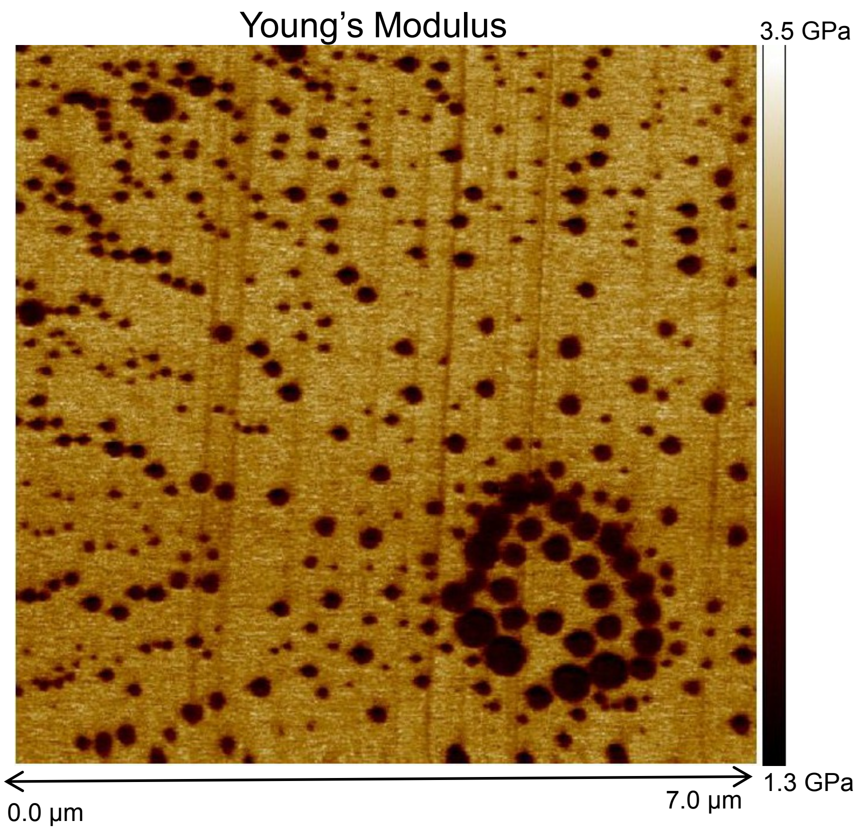
Minimum Diameter 18 nm

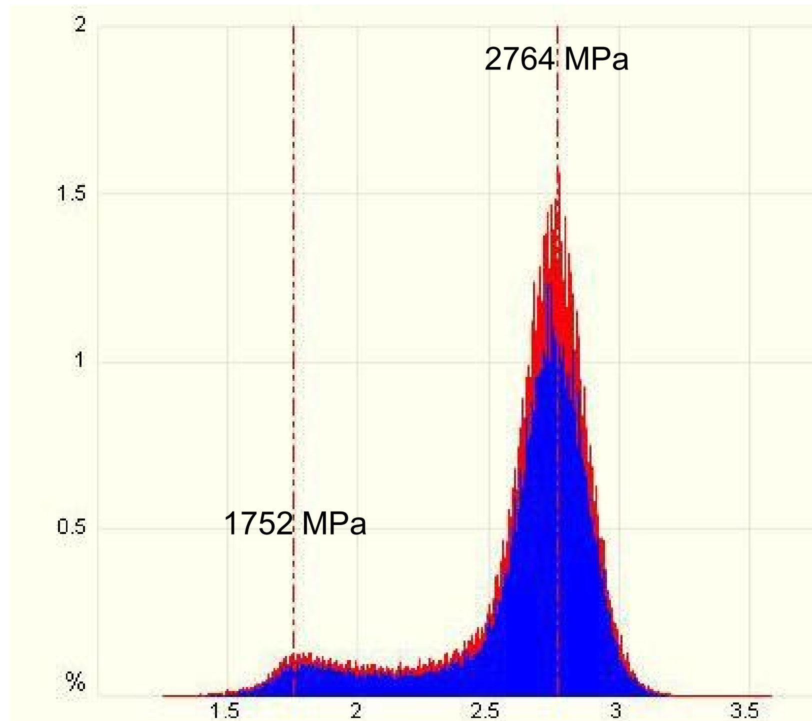
Maximum Diameter for center cluster of nanofibers is 1636 nm

Image courtesy of Veeco Instruments

Young's Modulus Map Analysis Based on DMT Model

AFM cross sectional image of drawn single filament



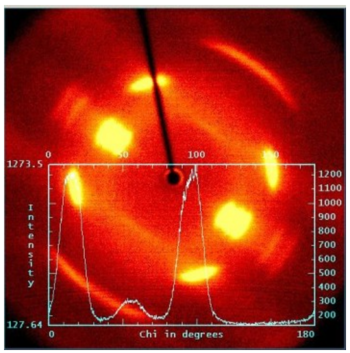


Images courtesy of Veeco Instruments

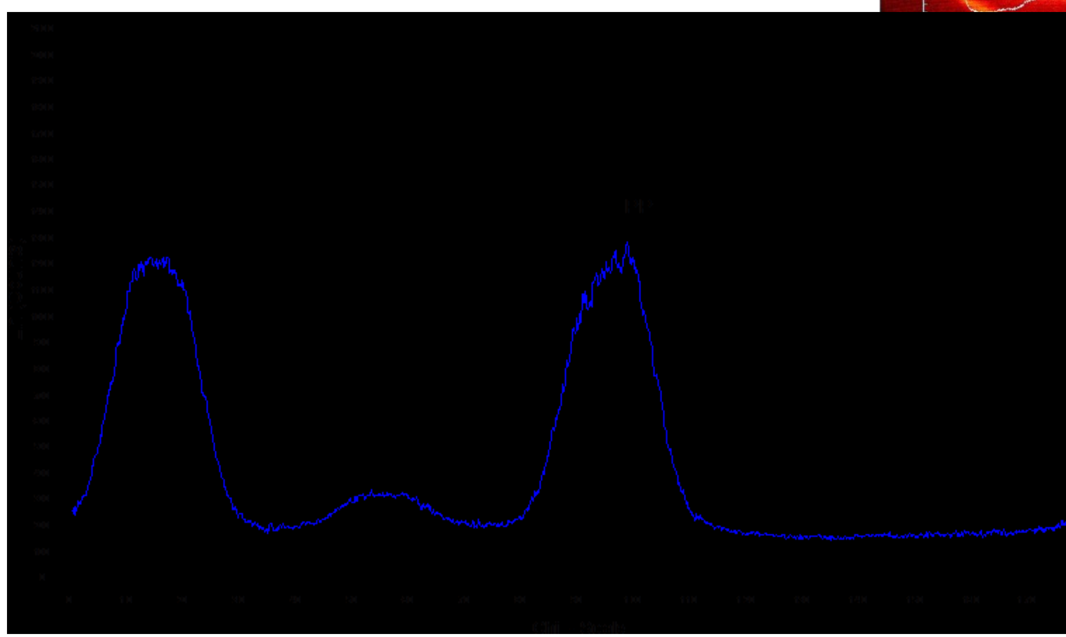
Wide-Angle X-ray Diffraction of Fibers Intensity vs. Chi

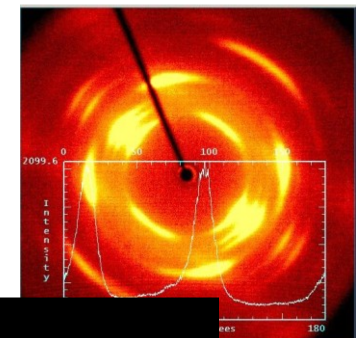
PP homopolymer

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



Godet Rolls
Leesona Winder
Speed 1600 mpm





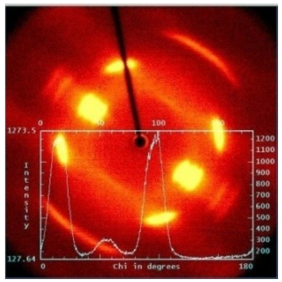
Winder
00 mpm

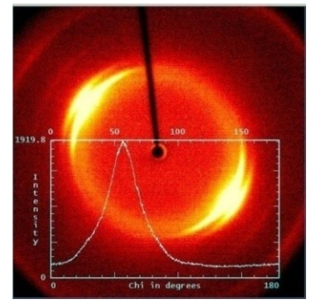
Wide-Angle X-ray Diffraction of Fibers
Intensity vs. Chi

Less oriented noted in PE fiber (sea)

PP Control

Godet Rolls
Leesona Winder
Speed 1600 mpm

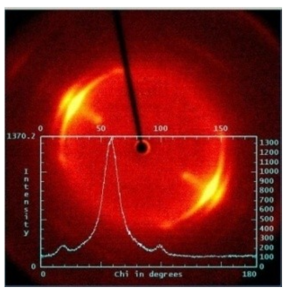




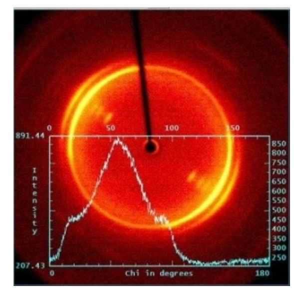
PE Control

Godet Rolls
Leesona Winder
Speed 1500 mpm

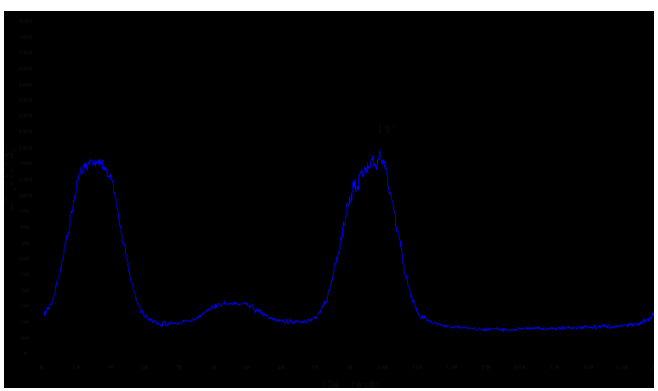
Godet Rolls
Leesona Winder
Speed 1700 mpm



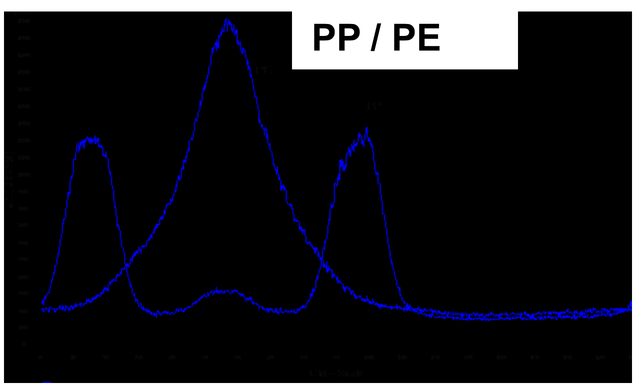
10% PP / 90% PE

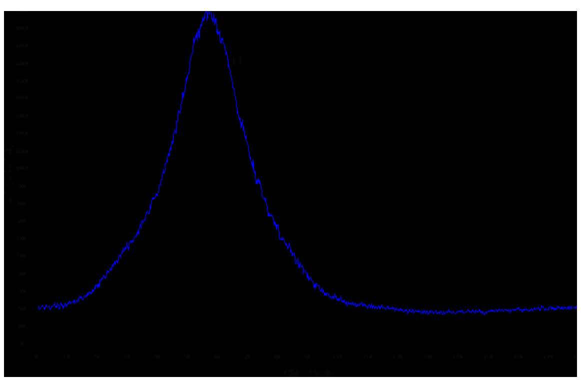


Barmag Winder
Speed 3000 mpm



PP / PE





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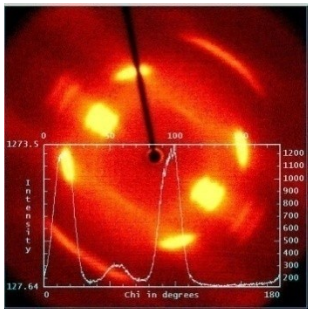
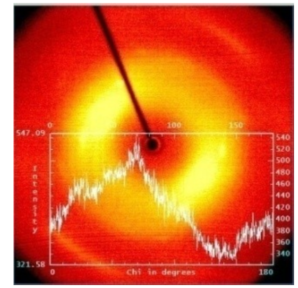
Wide-Angle X-ray Diffraction of Fibers
Intensity vs. Chi

Amorphous PLA fiber (sea)

PP Control

Godet Rolls
Leesona Winder
Speed 1600 mpm

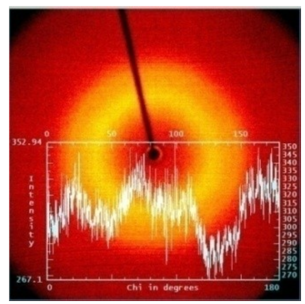




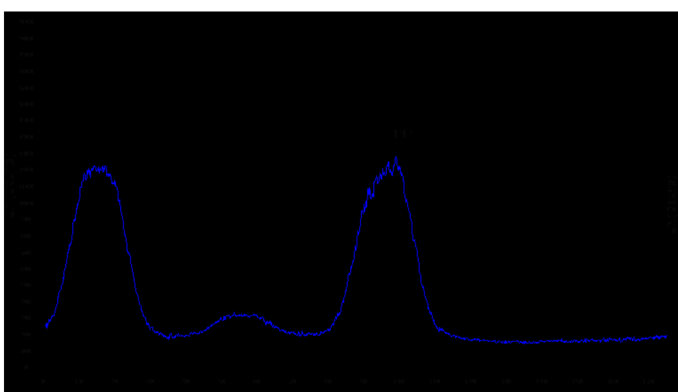
PLA Control

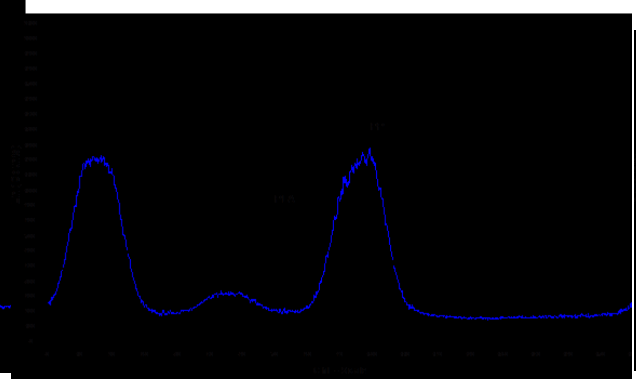
Godet Rolls
Leesona Winder
Speed 1400 mpm

10% PP / 90% PLA



Godet Rolls
Leesona Winder
Speed 500 mpm





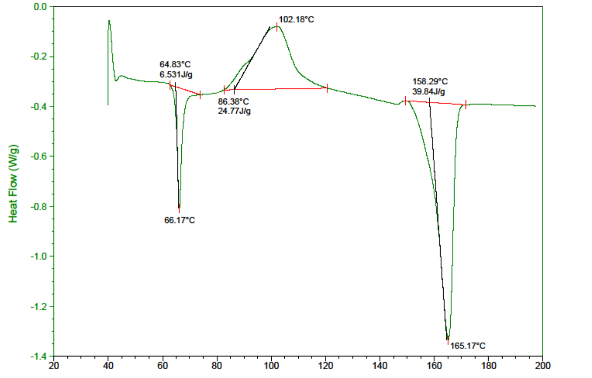
DSC Analysis

- A broad upward peak between 85C and peaking near 100C, 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

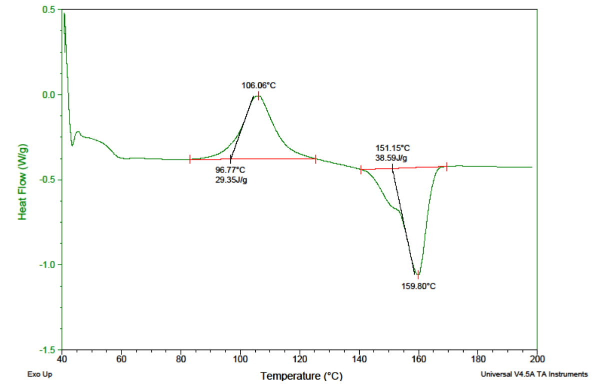
Decreasing Island Spacing or Higher Island Count →

NO DRAW

600 INS Denier 3564 10% PP/90% PLA

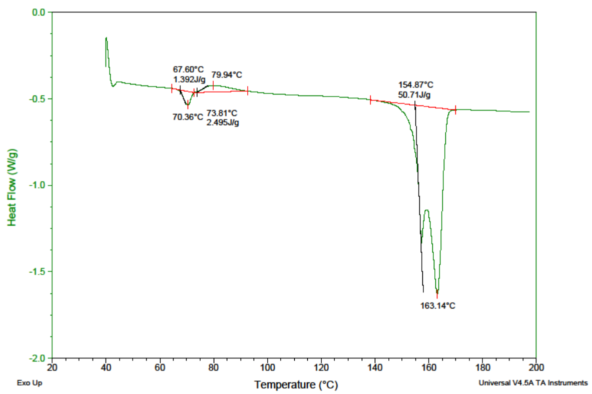


1200 INS Denier 3620 10% PP/90% PLA

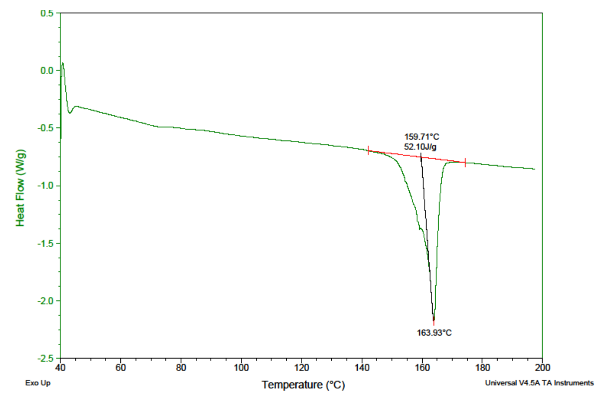


DRAW

600 INS Denier 936 10% PP/90% PLA



1200 INS Denier 511 10% PP/90% PLA



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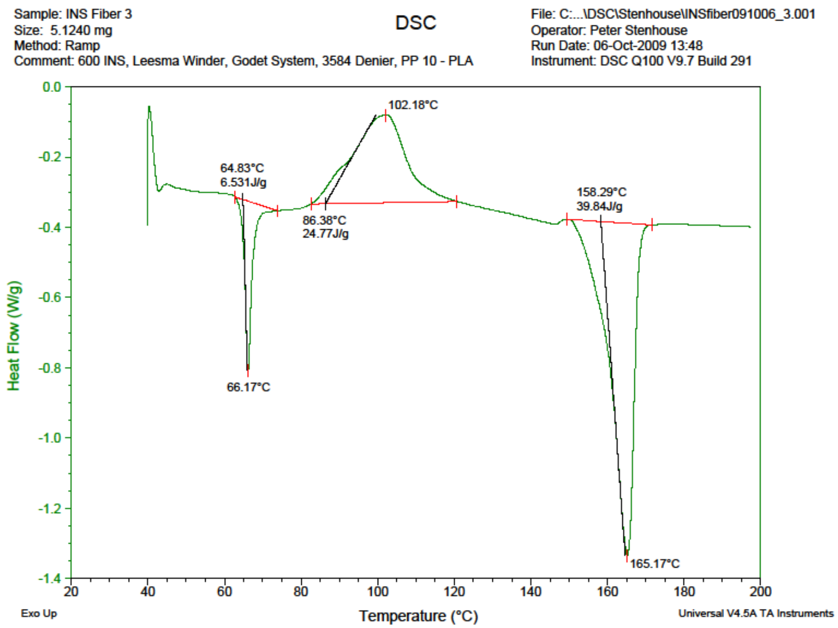
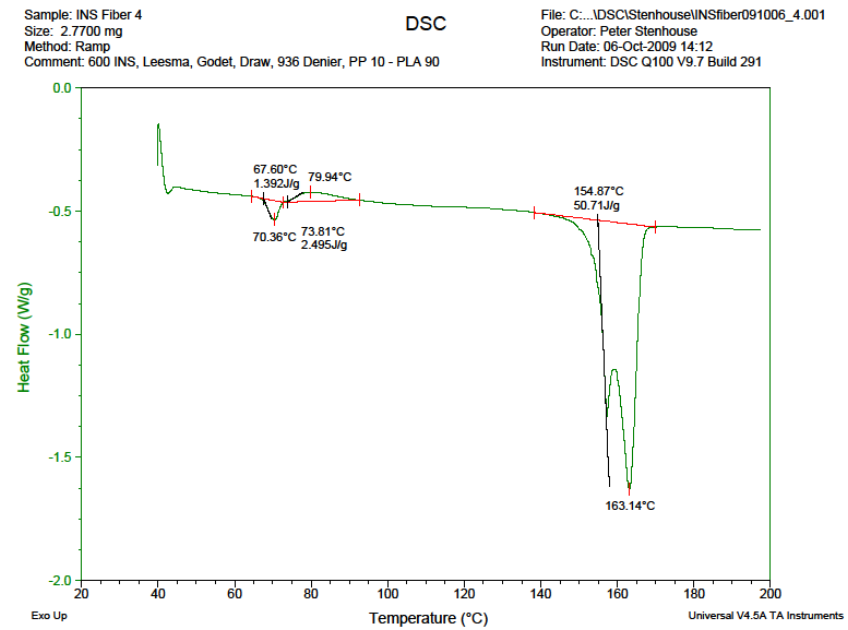


NO DRAW

600 INS Denier 936 10% PP/90% PLA



DRAW

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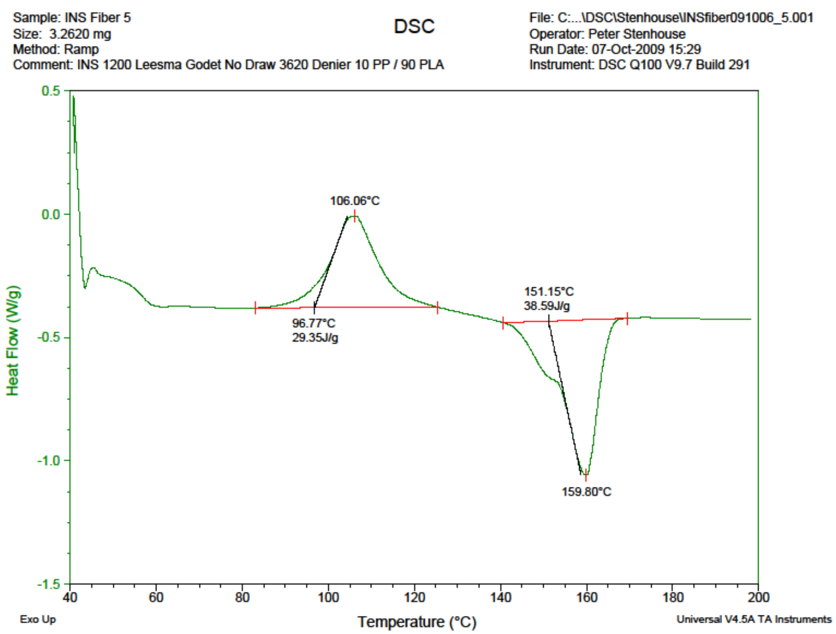
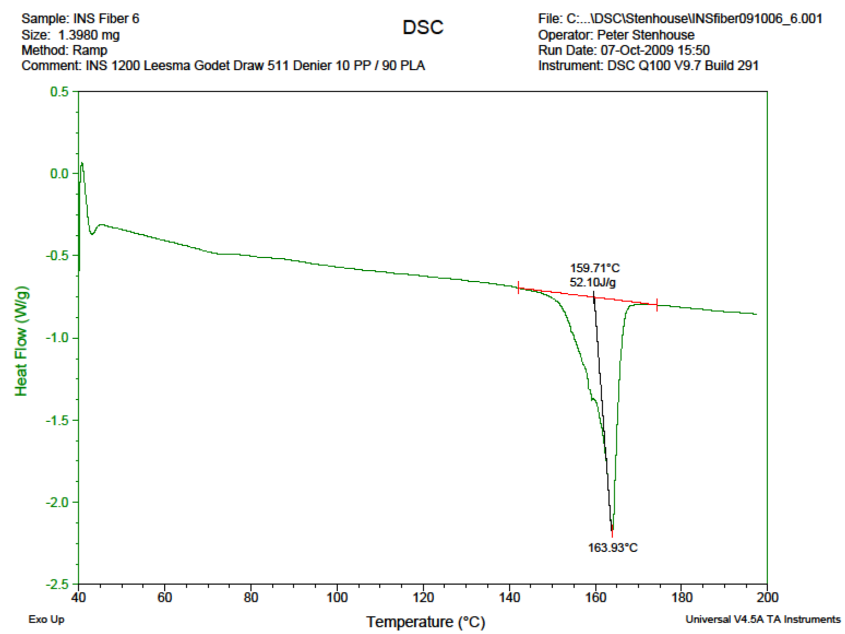


NO DRAW

1200 INS Denier 511 10% PP/90% PLA



DRAW

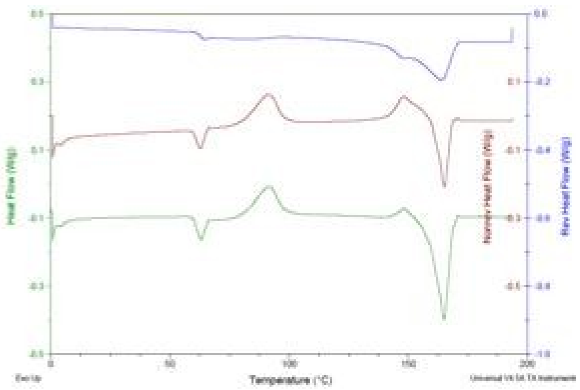
Modulated DSC Analysis

____HEAT FLOW ___NONREVERSING HEAT FLOW ___REVERSING HEAT FLOW

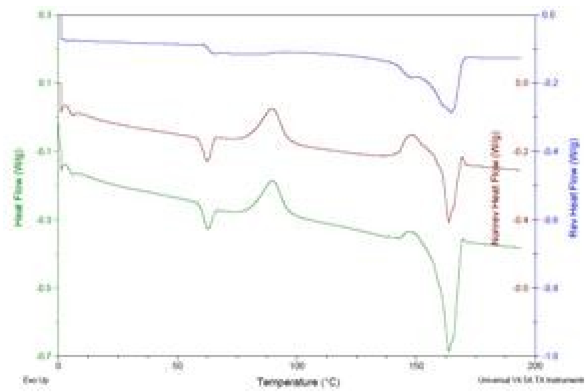
Crystallization of PLA is suppressed in post-drawn INS fibers

NO DRAW

600 INS Denier 3564 10% PP/90% PLA



1200 INS Denier 3620 10% PP/90% PLA



DRAW

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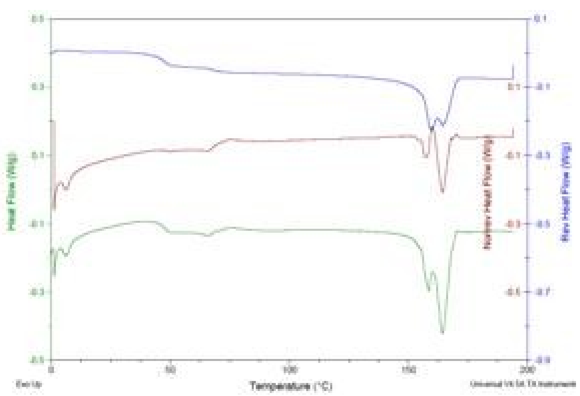

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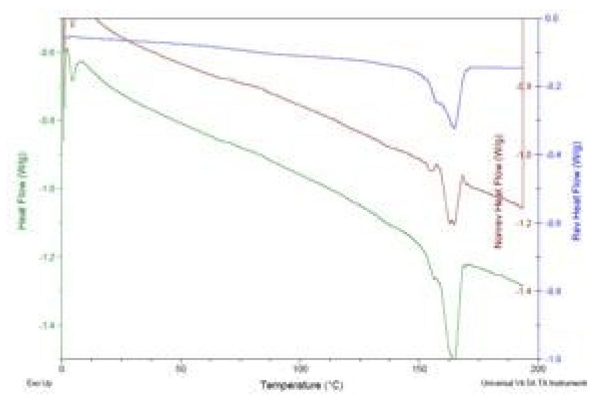

Summary

- 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 #