Multicomponent Fiber Extrusion Technology Applied to Precursors

Carbon Fiber R&D Workshop
Hosted by Harper

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Presented By:
Timothy Robson

Hills, Inc.
7785 Ellis Road
W. Melbourne, FL 32904 USA
Overview

• Introduction to Hills, Inc
• WHAT are Bicomponent Fibers?
  • WHY?
    – Bico Markets
    – Cross Section review
    – Consumer & High-Value Examples
• HOW are Bico Fibers Made?
  – Production Methods
  – Technology
• Precursors
  – Bico Potential
  – Melt vs. Solution Spinning
  – Ideal precursor
Introduction to Hills, Inc.

Privately Held Company - Founded 1971

Number of Employees - >50

Business Focus - Development, Design, and Manufacture of Specialized, Technically Advanced, Synthetic Fiber Extrusion Equipment

Facilities
  Primary – Melbourne, Florida (USA)
  Satellite – Guangzhou (China)
  Contract – Pune (India) Vikas Technologies
Introduction to Hills, Inc.

Business Activities
- Main – Develop, Design, and Build Custom Fiber Extrusion Equipment
- Joint Research and Development (Industry, Government, Academia)
- Early and Small Scale Production of New Fiber and Nonwovens Products
- Ultra-Precision Manufacture of Large Photo Etched Parts
- Automation (Authorized Fanuc Robot Integrator)

Carbon Fiber Experience
- Just Starting!
WHAT are Bicomponent Fibers?

Two polymers in a single filament.

Also called:
- Multicomponent
- Composite fiber
- Dual layer
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Bicomponent Fiber Markets

**Major**: Hygiene
- Producers/Consumers: K/C, P&G (Pegas, PGI, Fitesa, etc.)
- PE/PP S/C spunbond

**Middle**: Wipes, fiberfill, filtration, roofing & carpet backing
- Producers: Freudenberg, Johns Manville, Colbond, Unitika, Kuraray, etc.
- Splittable/dissolvable (microfiber), S/S, S/C and mixed

**Small/Niche**: Specialized filtration, adsorbants, high-end leather, identification, CF precursor, etc.
- Producers: Too many to list!
- Unique bico, trico & quadco
Cross Section Review

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Sheath Core (<10% Sheath)

Uses:
- Surface Properties (Hygiene)
- Bonding
- Additives

Polymers:
- PP/PE
- PET/PE
- PET/CoPET
Sheath Core (concentric rings)

Use:
- Unique application where a client wanted particular optical properties

Polymers:
- Alternating coefficient of diffraction

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Sheath Core (metal core)

- Conductivity
- Polymers:
  - Various sheath and low-melt metal core
Sheath Core (meltblown)

Use:
- Various
- Charge maintenance

Polymers:
- Various olefins
Sheath Core (trilobal)

Use:
- Special for Carpet

Polymers:
- Anti-Stain or color in sheath
Side By Side (trilobal)

Uses:
• Self-bulking

Polymers:
• PP/PP (two different MFI)
• PET/PBT
• Any combination to induce differential strain or shrinkage
Side By Side (meltblown)

Uses:
- In-process splitable

Polymers:
- Various
Tipped (trilobal)

Uses:
• Bonding
• Bonding & Wicking

Polymers:
• PET/CoPET
• PET/PP
• Low-melt tips
Micro-Denier (Segment Pie)

Uses:
- Wipes
- Absorbants
- Other high-surface area apps

Polymers:
- Mostly PET/PA6
Micro-Denier (Hollow Segment)

Uses:
• Similar to previous but optimized for spunbond. Easy splitting with needle-punching or hydro entanglement

Polymers:
• Mostly PET/PA6
Micro-Denier (British Flag)

Uses:
• Wipes! Dusting clothes, mop heads, scrubbing sponges

Polymers:
• Mostly PET/PA6

VERY COMMON in consumer goods!
Micro-Denier (stripes)

Uses:
• Similar to segment pie but unique to glass wipes. Creates different hand and feel compared to segment pie.

Polymers:
• PET/PA6

Source: http://www.eftfibers.com/prod_k-spec.php
Micro-Denier (Islands)

Uses:
• Filtration
• Synthetic leather
• High-tenacity filament

Polymers:
• PA6 or PET islands, PLA, EVOH, ESPET sea
Nano-Denier (600 islands)
Nano-Denier (2010 islands)

Islands – PA6  Sea – EVOH  Number Islands - 2010
Fiber Size – 4 DPF  Island Diameter – 250 nm

Image made by NC State University Analytical Instrumentations Lab (AIF) under a project sponsored by 3F, LLC and the National Science Foundation (NSF)
Nano-Denier (10,000 islands)

Image made by NC State University Analytical Instrumentations Lab (AIF) under a project sponsored by 3F, LLC and the national Science Foundation (NSF)
Other (winged)

BEFORE washing/extraction

AFTER washing/extraction

Source: Allasso Industries
Other (shaped islands)
Consumer Goods Examples

- Target
- Bed, Bath & Beyond
- K-mart
- Etc.
High-Value Example #1

Chromatography Substrate

Function: Uses high-surface area properties of bico fiber which is “functionalized” to adsorb proteins.

Replaces a very expensive glass product.

Polymers: Various

Source: US patent application 2012/0029176 A1 (EMD Millipore)
High-Value Example #2

**Synthetic Leather**

Function: Uses INS fiber with special “sea” polymer. **Does not require inorganic solvents.**

Replaces toluene extraction process.

Polymers: PA6/special polymer (water soluble)

High-Value Example #2 cont’d

**CLARINO PROCESS**

Current Process uses DMF and Toluene to extract the fibers:

- Spinning
- Non-woven Sheet
- PU Dipping
- Coagulation
- Sea Polymer Extracted by Solvent
- Substrate
- Dyeing/Coating

DMF ➔ Toluene

**TIRRENINA PROCESS**

New process eliminates all solvents by using hot water to extract fibers:

- Spinning
- Non-woven Sheet
- PU-Em Dipping
- Drying
- Sea Polymer Extracted by Water
- Substrate
- Dyeing/Coating (Non-solvent PU)

Source: http://www.tirrenina.com/
### High-Value Example #3

**Identification (Logo) Fibers**

**Function:** Uses resolution of high-island count INS to form logos in very small-scale (~Ø20micron).

**Polymers:** Various
Tricomponent (segmented pie)
Tricomponent (segmented pie)
Tricomponent (islands in the sheath)
HOW Are Bico Fibers Made?

Production Methods
Melt-Spinning (99%)
• Spunbond
• Filament
• Staple
• Meltblown

Solution Spinning (1%)
• Wet, gel, etc.

Bonding
(Calender, TAB, Needle, Hydro, Chemical, etc.)

Winder
Compaction
Roll

Aspirator
Spinbeam

Polymer (& handling)

Bico Spunbond Process

Extruder
Filter
Pump
Pack
Quench
Aspirator
Compaction Roll

Fibers
Forming Belt

Tension Roll

Height Adjustable Platform

Height Adjustable

Guide Roll

Bonding
(Calender, TAB, Needle, Hydro, Chemical, etc.)
Bicomponent Filament Process

- Polymer Hopper
- Metering Pump
- Spinhead
- Quench Air
- Extruder
- Polymer pipe
- Pack
- Relax Rolls
- Post-interlace
- Feed Rolls
- Pre-interlace
- Draw Rolls
- Automatic Winder
- Finish Application
Bicomponent Meltblown Process

- Polymer Hopper
- Spinbeam
- Polymeric Hopper
- Bicomponent Meltblown Process
- Tension Roll
- Forming Belt
- Exruder
- Filter
- Pump
- Die
- Height Adjustable Platform
- Winder
- Guide Roll
- Tension Roll
Bico Solution Spinning Process

- Metering Pump
- Dope vessel
- Feed Rolls
- Pack
- Coagulation
- Rinse
- Draw
- Heated Rolls
- Finish Application
1.7M MB Machine
NANO & BICO Capable
Multi-component Fiber Technology

- Proprietary pack designs
- Low & equal polymer residence time
- Polymer temperature separation
- High hole densities (usually same as homo)
- Unlimited spinneret size and geometry
- Exceptional Flexibility
  - Most any polymer types and ratios
  - All Fiber cross sections
**Bicomponent Pack (Hills)**

| ~25 MM | Top          |
| ~25 MM | Filter Plate |
| ~25 MM | Distribution Plates |
| ~5 MM  | Spinneret     |
| ~25 MM |              |

- **Internal Cross Section**
  - Distribution/Metering Plate Design
  - Viscosity Match/Mismatch of A & B polymers
  - Interfacial Tension Difference Between A & B polymers

- **External Cross Section**
  - Spinneret Orifice Design
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Temperature Separation Equipment
USP 7,252,493
Why Bico Precursors?

• Small fibers: $< \Phi 250 \text{nm}$ possible
• Islands-in-the-Sea (continuous tow)
• Meltblowing (nonwoven mat)
• Unique internal shapes:
Why Bico Precursors?

• Unique combinations (alter coagulation rate in solvent spinning)
• Additives (CNTs, etc.) in core or islands
• Oxidizing agent on sheath
• Two different precursors in single filament
• Controlled porosity/density

Source (photos): Kumar, FUNCTIONAL POLYMER - POLYMER/CARBON NANOTUBE BI-COMPONENT FIBERS
Solution Vs. Melt Spinning

**Melt-Spinning**
(Filament, Staple, Spunbond, Meltblown)

- Polymers: Commercially available grades, known chemistry and behavior.
- Pack Pressure: >1000psi
- Temp: 220-400°C
- Viscosity: 500-2000 poise (peanut butter-like)

**Solution Spinning**
(Wet, Dry, Short Gap, Gel, etc.)

- Polymers: Customized dopes (~30% in solution)
- Pack Pressure: < 100psi
- Temp: <100°C
- Viscosity: 1cP-100 Poise (water-like)
**Solution Vs. Melt Spinning**

Highly graphitic. Accelerated stabilization is a challenge; high carbon yield but very expensive CF.

**Pitch:**
- Isotropic Liquid Pitch
- Liquid Crystals (mesophase)

**PAN:**
- 68% C Content
- 45-50% Yield
- Monomer: $800-$2200/MT
- Solution spun fiber: $1.5 - $3/lb

**PE:**
- 86% C Content
- 65-80% Yield
- Melt-spun fiber: $0.50 - $0.60/lb

*Zhang and Sun, JAPS, 1996; Hexcel report to DOE on LCCF, 2004*

Slide courtesy of Amit Naskar, Oak Ridge National Laboratory
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<tr>
<th>Polymer</th>
<th>Process</th>
<th># filaments</th>
<th>Spinning speed</th>
<th>Draw</th>
<th>Wind m/min</th>
<th>Ø (µm)</th>
<th>kg/hr</th>
<th>Carbon yield (%)</th>
<th>CF yield (KG)</th>
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</thead>
<tbody>
<tr>
<td>PAN</td>
<td>Solution</td>
<td>1500</td>
<td>50m/min</td>
<td>3x - 10x</td>
<td>500</td>
<td>10</td>
<td>14.1</td>
<td>50%</td>
<td>7.1</td>
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<tr>
<td>PE</td>
<td>Filament</td>
<td>1000</td>
<td>500m/min</td>
<td>3x-5x</td>
<td>1500</td>
<td>12</td>
<td>31.2</td>
<td>80%</td>
<td>25.0</td>
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<tr>
<td>Lignin</td>
<td>Filament</td>
<td>1000</td>
<td>1500 min</td>
<td></td>
<td>1500</td>
<td>12</td>
<td>31.2</td>
<td>60%</td>
<td>18.7</td>
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<tr>
<td>Lignin</td>
<td>Meltblown</td>
<td>50/inch</td>
<td>3000 N/A</td>
<td></td>
<td>3000</td>
<td>10</td>
<td>26.0</td>
<td>60%</td>
<td>15.6</td>
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# Solution Vs. Melt Spinning

**Melt-Spinning Pros**
- Variety of methods from tows to nonwoven mats
- Very round filaments, low variability
- No voids
- No solvents, extraction, effluent
- Minimizes floor space
- Existing capacity in North America
- High throughput/low cost (commoditized)

**Melt-spinning Cons**
- No existing polymers match properties of gel-spun PAN
“Ideal” Precursor

- **Polymer:** Commercially available thermoplastic
- **Process:** Melt spinnable
  - Filament
  - Meltblown
- **Properties:** Tailorable through multicomponent spinning
  - Modulus
  - Tensile
  - Density
  - Etc.
Thank You!

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