Advances in Micro- and Nano Layer Multiplying Coextrusion Toward Next Generation Novel Commercial Products

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I. Introduction/Review of layer multiplying coextrusion
II. 2D coextrusion toward high modulus products
III. Nanolayer confinement for barrier enhancement
IV. Scale-up studies: nanolayered lenses & capacitors

**Enabling Technology: Multilayer Coextrusion Processing**

- Multilayer coextrusion is an established, scalable processing technique commercialized developed in the 1960s.

- Continuous process for micro- to nanometer thick layers

- Layered materials exhibit change from material bulk properties
  - Optical
  - Mechanical
  - Transport
  - Electrical
  - Adhesive
  - Rheological

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1. R. Harder, (1965), U.S. Patent 3,195,865
Micro- and nanolayered technology patents applications have significantly increased following increased availability of commercial feed block and multiplier technology.
Commercial polymer coextrusion combines polymer streams from separate extruders in a custom designed multilayered feed block

- Designated number of layers
- Rheologically matched flow channels
U.S. multilayered feed block manufacturers include Cloeren and Nordson
• Capabilities: 2 to 1000+ layers.

**Advantages (Precision):**
• Highly uniform layering
• High production throughput

**Limitations (Flexibility):**
• Single number of layers per feed block
  • Second possible in advanced designs
• Design is material/composition specific.
• Complex designs or 1000+ layers require significant capital costs
Bridging the Development Gap: Microlayered Commercialization

PolymerPlus was founded to fill an unmet need in evaluating and maturing new microlayer and nanolayer technologies for commercial applications.

- Develop & License Multilayered IP
- Optimize, manufacture, and integrate 1st generation products
- Translate to Market

A. Universities

B. Internal IRAD

C. 3rd Parties Companies

- Investigating commercial product formulations @ R&D or pilot scales
- Establishing raw material and technology supply chains
- Serve as a technology development & LRIP production partner
PolymerPlus Technology Platform: Micro- and Nanolayer Coextrusion

Extruder B

Melt Pump B

ATBTA Feed block

Extruder T

Melt Pump T

Layer Multipliers

Surface Layer Extruder

Exit Die

Number of layers = $2^{n+2} + 1$

where $n = \text{number of multipliers}$

Thousands of layers
PolymerPlus Facility: Layer Multilayering Coextrusion

PolymerPlus processing facilities:
- Custom cast film nanolayer lines
- R&D or Pilot Scale

<table>
<thead>
<tr>
<th>Nanolayering Line</th>
<th>Rate</th>
<th># Layers</th>
<th># Materials</th>
<th>Skin Layers</th>
<th>Film Thickness</th>
<th>Film Width</th>
<th>Max. Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;D</td>
<td>1 - 8 lb/hr</td>
<td>1 - 4,097</td>
<td>3</td>
<td>Yes</td>
<td>3 - 500 micron</td>
<td>20&quot;</td>
<td>325 C</td>
</tr>
<tr>
<td>Pilot</td>
<td>5 - 80 lb/hr</td>
<td>1 - 4,097</td>
<td>3</td>
<td>Yes</td>
<td>3 - 500 micron</td>
<td>20 – 40”*</td>
<td>400 C</td>
</tr>
</tbody>
</table>

**R&D Line:**
¾” Extruders
Melt Pumps

**Pilot Line:**
1” – 1 ¼” Extruders
Melt Pumps
Capabilities:
- Max speed of 150 fpm
- Take-off: 42” chill roll, Several crown rolls
- In-line thickness gauge

Extrusions Rates:
- R&D: 10 – 40 lb/hr
- Full Capacity: 300 lb./day
Mechanical nature of the sequential multilayer coextrusion process requires similar polymer viscosities for uniform layering.

**Ideal Viscosity Match**
- Polystyrene
- Polypropylene

**Processing Window**
- High Viscosity
  - High Elasticity
- Low Viscosity
  - Low Elasticity

**Off-Set Temperature Match**
- Polycarbonate
- Polymethylmethacrylate

**Processing Window**
- High Viscosity
  - High Elasticity
- Low Viscosity
  - Low Elasticity

**PP/PS coextrusion at viscosity match temperature**
- \( T_{PS} = T_{PP} = 260 \, ^\circ C \)

**Off-set extrusion temperatures required for viscosity match**
- \( T_{PC} = 225 \, ^\circ C \)
- \( T_{PMMA} = 210 \, ^\circ C \)
Layer Multiplying System Capabilities

Sequential multiplication coextrusion process has successfully fabricated films and sheets ranging from 2 to 64,000 layers.

Wide range of commercial and developmental polymer materials micro- and/or nanolayered via layer multiplication process.

- Polyolefins (PE, PP, COC)
- Nylons
- PET
- EVOH
- Polyolefins (Polyethylene, Polypropylene, Copolyester)
- Styrene
- Acrylics
- Polycarbonates
- Fluoropolymers
- Polysulfone
- Cellulose
- BioPolymers
- TPUs
- Filled Systems
- Elastomers
- LCPs
- Block Copolymers
I. Introduction/Review of layer multiplying coextrusion

II. 2D coextrusion toward high modulus products

III. Nanolayer confinement for barrier enhancement

IV. Scale-up studies: nanolayered lenses & capacitors

2D Coextrusion Design: Micro/Nano Fiber-Film

Description of Stages - I to IV
Cross section of HDPE/LDPE layers

HDPE

LDPE

Feed-block

- Stage I: Turning the layers around
- Stage II: Vertical layer multiplication
- Stage III: Adding the ‘cap’ layer
- Stage IV: Vertical layers/cap layers multiplication

Introduce Surface Layer
Estimated PA6/PP Fiber Sizes

Fiber Size Depends on:
- Film composition (50/50)
- Width of the film (2 in)
- Thickness of the film (0.1 mm)

Effect of Multiplication on Estimated Fiber Size in Extruded Fiber-Film

<table>
<thead>
<tr>
<th>System</th>
<th>HDPE/LDPE # of Layers</th>
<th>HDPE or LDPE fiber size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>512 x 32</td>
<td>98 x 2.8</td>
</tr>
<tr>
<td></td>
<td>2098 x 32</td>
<td>24 x 2.8</td>
</tr>
<tr>
<td></td>
<td>4096 x 32</td>
<td>12 x 2.8</td>
</tr>
<tr>
<td></td>
<td>8192 x 32</td>
<td>6 x 2.8</td>
</tr>
<tr>
<td></td>
<td>16384 x 32</td>
<td>3 x 2.8</td>
</tr>
</tbody>
</table>

- Highway to Nano-fibers
  - More multiplication of vertical/horizontal layers
  - Uniaxial stretching of the fiber-films to nano/sub-micron scales
Orientation of the Fibrous Tapes

DSC for the PP/PA6 Fibrous Tapes

- $T_{m,PP} = 162^\circ C$
- $T_{m,PA6} = 218^\circ C$
- $T_{g,PS} = 102^\circ C$
- $T_{Orientation}$

PP & PA6 crystal orientation resembles that of orientated/drawn fibers

As-extruded

Oriented, DR = 4.5x
Leading Edge: Mechanically Enhanced Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Modulus (Secant 2 %) (GPa)</th>
<th>Avg</th>
<th>Stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marlex HDPE Control</td>
<td>-</td>
<td>1.2</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Engage LDPE Control</td>
<td>-</td>
<td>0.01</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>Pellet Blend</td>
<td>50/50</td>
<td>1.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>&quot;1D&quot; 17 Layer</td>
<td>50/50</td>
<td>1.15</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>&quot;2D&quot; 2048 x 32 Layer</td>
<td>50/50</td>
<td>3.8</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

2D layered structures promotes higher orientation/stiffness in HDPE
- 3X improved over natural HDPE
- Improvement over blends & 1D layers
Target Applications for Coextruded Layered Fibers
Military & Consumer

Ultimate goal of 2D layered fiber technology is to compete with high strength solution cast fibers
• Goal: UHMWHDPE (Spectra): tensile modulus = 60-100 GPA
• Standard Extrusion HDPE : modulus = 1 GPA
• Current 2D as-extruded films: modulus = 3.8 GPA

Development Roadmap:
1. Reduce extruded fiber thickness
   – Current fibers 7x4 micron = 3.8 GPA
   – Future fibers 0.8 x 0.8 micron = ?
2. Ultra-draw extruded fiber tapes
   – Current in-line extrusion ~ 2x
   – Ultra draw in tape/fiber system ~ 10X

Applications: UHMWHDPE alternative in helmets and impact resistant equipment
Layer Multiplying Coextrusion: Discussion Topics and Technology Case Studies

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Gas Barrier Enhanced Nanolayered Films

- Microlayer coextrusion is an industrially accepted polymer processing technique allowing for potential scale-up of this technology.

- Applications for gas barrier and toughness enhanced polymer systems
  - Food and beverage packaging (longer self-life, reduced failure)
  - Health care applications – i.e. intravenous or blood packaging
  - Flexible displays and OLED applications
Gas Transport Model in Layered Polymer Systems

Layered structures offer optimized configuration of materials to minimize gas permeability in multiphasic systems.

Permeability Blend films:

\[ P_{film} = \Phi_A P_A + \Phi_B P_B \]

Permeability of Layered films:

\[ P_{film} = \frac{1}{\left(\frac{\Phi_A}{P_A} + \frac{\Phi_B}{P_B}\right)} \]

- \( P \), permeability; \( \phi \), volume fraction
Oxygen Barrier Enhancement
Confined Crystallization in Multilayer Films

Microlayers
PEO Layer 1-10 μm

Nanolayers
PEO Layer 10-100 nm
Effect of Layer Thickness on Gas Barrier

**P(O_2) of 50/50 Films**

- **Test condition:** 23°C, dry

**Calculated P(O_2) of PEO Layer***

- *Calculated from series model*

\[
P_{PEO} = \phi_{PEO} \left( \frac{1}{P_{Film}} - \frac{1}{P_{EAA}} \right)^{-1}
\]

Oxygen barrier of PEO layer improved 130X with decreasing layer thickness.
Aligned PEO Lamellae as Gas Barrier

125nm PEO layer

25nm PEO layer

PEO Stacked Lamellar Crystals

PEO Single Crystal
Estimation of Aspect Ratio of PEO Lamellae

For PEO 20nm layers, the aspect ratio from was estimated as high as 120. PEO “single crystal” lateral dimension can be more than 2 µm.

Cussler Model

\[ P = P_m \left[1 + \frac{\alpha^2 \phi_c^2 \cos^2 \theta}{4(1 - \phi_c)}\right]^{-1} \]

Parameters:
- \( P \), permeability of EAA/PEO layered film
- \( P_m \), permeability of EAA as matrix
- \( \phi_c \), volume fraction of PEO crystals
- \( \cos^2 \theta = 0 \) for perpendicular orientation

Aspect ratio \( \alpha = \frac{L}{W} \)

*Cussler, E. L.; Hughes, S. E.; Ward, W. J., III; Aris, R. J Membr Sci, 1988, 38, 161–174*
Effect of Layer Confinement on Lamellar Morphology

Crystalline layer thickness

- 20 μm
- 1 μm
- 100 nm
- 20 nm

3D spherulites 2D spherulites Stacked in-plane lamellae Single crystals

Ref:
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Multilayered Polymer Optics Technologies

- Synthetic Copies of Biological GRIN
- Micro- & Nanolayer Coextrusion
- Non-Imaging Optics
- Bragg Crystals
- Composite Systems
- Imaging lens implants, models
- Non-Imaging Optics
- Reflective Optics
- UV-Vis Imaging NVG Optics
- Flat prisms, Beam Shaping Reflective Optics
- All plastic laser NLO films/sheet Optical Data Storage
- Reflectors Filters Low-cost Gradient Layer films

Lightweight, Custom Optics with Improved Imaging and Light Collection
Nanolayered polymer GRIN optics technology has demonstrated a capability to reduce Vis-SWIR optical system mass/volume derived by replacing glass or homogenous plastic optic(s) and reducing the required optical element count.

These advances were enabled by leveraging:

- Activating subsurface lens material optical power (focus & chromatic) through adding gradient index profiles
- Increased design freedom (design to variable RI profile shape/magnitude – axial, spherical, “radial”)
- Flexible manufacturing technology capable of achieving a wide variety of GRIN profiles & final lens diameter/geometry
Nanolayer Films with Tailored Refractive Index

Metricon Film Refractometer Scan @ 633 nm: Layered PMMA/SAN17 Films

Layered films < \(\lambda/4\) act as total interphase media:

\[ n_{\text{composite}} \approx \phi_A n_A + \phi_B n_B \]

Where:

\[ \phi_A = \frac{d_A}{d_A + d_B} \]
\[ \phi_B = \frac{d_B}{d_A + d_B} \]
Enabling Technology: Nanolayered Films of Variable Refractive Index

Key technology breakthrough is the large scale processing of nanolayered polymer films with a single, compositionally dependent refractive index.
From Films to Optics

Through a series of stacking and thermoforming steps, PolymerPlus can create a platform of optics with a wide variety of refractive index distribution shapes.
SWAP and Off-Axis Performance: SWIR PVS-14 GRIN Eye Piece

Representative Commercial Glass Eye Piece Design:
- 6 lenses
- 81 gram lens weight

GRIN/Plastic Eye Piece Design:
- 4 lenses (GRIN d=28 mm, Δn=0.08)
- 11 gram lens weight

- GRIN improved off-axis system performance as compared to Glass eye piece.
- GRIN/plastic eye performed to military specification MIL-PRF-49427B(CR) at RT.
- GRIN demonstrated a 24% weight savings in final eye piece (includes housing)
GRIN technology spun out into Peak Nano (TX based company) for scale-up

- Strategic investment/partnership with L3 Technologies
- 50K pilot GRIN lens manufacturing line in Ohio Q2 2020
- 1st generation product is wide field of view binocular
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**Why it works**

**Resin A**
High Dielectric constant  
Low Breakdown Strength

**Resin B**
Low Dielectric constant  
High Breakdown Strength

**COEXTRUSION**

- Synergistic combination - high dielectric strength and high breakdown strength
- High energy density
- Reduces losses

Solid state polymer film capacitors

**Nanolayer Dielectric Film**
Multilayer Film Capacitors: Value Statement

MLF Dielectric Advantages

• 2x dielectric constant (40% smaller capacitors)
• 70 °C increase in usage temperature
• Improved Breakdown Strength
• Scalable manufacturing
• Drop-in product to BOPP capacitor supply chain

Nanolayered film capacitors enable product enhancement over state-of-art BOPP polymer capacitors:

• Higher energy density
• Increased temperatures

40% smaller capacitors
Reduced device cooling/smaller electrical system

Coextrusion

Dielectric Multilayer Films

Reduced size Capacitors

EVs, Pulse power, Power Grid applications
## Customer Needs and Our Solution

Customers require higher energy density, higher temperature, and inexpensive capacitor film materials!

- Current materials, BOPP and Mylar, are low cost, but require significant improvement in energy density and high temperature use.
- Multilayer films use commercial polymers to achieve higher energy density and high temperature use!
- Target markets: electric vehicles, pulsed power (lasers), grid storage

<table>
<thead>
<tr>
<th>Plastic Film Capacitors</th>
<th>Market ($, Million)</th>
<th>Properties</th>
<th>Limitations</th>
<th>Advantages</th>
</tr>
</thead>
</table>
| BOPP                    | 1200                | • Dielectric Constant: 2.2  
• Max Use Temp: 85 °C | • Limited Use temperature  
• Low Dielectric Constant  
• Bulky Capacitors | Low cost, low loss, very thin |
| Mylar                   | 900                 | • Dielectric Constant: 3.1  
• Max Use Temp: 105 °C | • Very Expensive  
• Only small size capacitors | Low cost, very thin |
| Others (PPS, PEN, PTFE) | 200                 | • Dielectric Constant: 1-3  
• Use Temp: Up to 150 °C | • Currently scaling production | High temperature, low loss |
| PolymerPlus Multilayer Film | Great Opportunity | • Dielectric Constant: 4-6  
• Max Use Temp: 150 °C | | • High Energy Density,  
• High Temperature,  
• Compact capacitors |
Multilayer Film
“Drop In” Supply Chain Replacement

Film Manufacturing – PolymerPlus

Polymer Resins → Nanolayer Film Coextrusion → Defect-free Film Winding

Capacitor Fabrication - Partners

Film Metallization and Slitting → Film Winding and End-capping → Capacitor Testing

MLF
2.4 lb.
BOPP
4.6 lb.
PolymerPlus conducted an internally funded commercial pilot line nanolayered dielectric film trial at a 3rd party U.S. manufacturer.

### PolymerPlus Multilayered Dielectric Films Mfg Capability

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PolymerPlus Pilot Line</th>
<th>Commercial Pilot Line</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Pilot Line Upgrade Dec. 2016</strong></td>
<td><strong>- June 2016</strong></td>
</tr>
<tr>
<td>Maximum Production Rate</td>
<td>&lt; 50 lb/h</td>
<td>300 lb/h</td>
</tr>
<tr>
<td>Film Width</td>
<td>12” - 36”</td>
<td>12” – 54”</td>
</tr>
<tr>
<td>Thickness, µm</td>
<td>4- 20 + up to 2.2 µm</td>
<td>&gt; 12 + 0.5 µm</td>
</tr>
<tr>
<td>Film Rate, sq. ft/h</td>
<td>2,000 – 4,000</td>
<td>6,000 - 12,000</td>
</tr>
<tr>
<td>Estimated Production, lb/shift</td>
<td>75-150</td>
<td>200 - 1,200</td>
</tr>
</tbody>
</table>

Produced 300 lb film for PolymerPlus.
Multilayered Capacitor Performance at Elevated Temperatures

<table>
<thead>
<tr>
<th>Capacitor Prototype</th>
<th>Size</th>
<th>Dissipation Factor (%)</th>
<th>Capacitance Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PolymerPlus MLF Capacitors</strong></td>
<td>37 µF</td>
<td>1.0-1.2 (RT-160 °C)</td>
<td>&lt; 1 (25 -180 °C)</td>
</tr>
<tr>
<td>1.1 µF</td>
<td>0.6-1.2 (RT-160 °C)</td>
<td>&lt; 1 (25 -160 °C)</td>
<td></td>
</tr>
<tr>
<td><strong>BOPP Capacitors</strong></td>
<td>1.5 µF</td>
<td>0.02- 0.1%</td>
<td>3 (25 -100 °C)</td>
</tr>
<tr>
<td><strong>PET Capacitors</strong></td>
<td>1.5 µF</td>
<td>0.5%</td>
<td>15 (-25 -125 °C)</td>
</tr>
</tbody>
</table>

- Capacitance was stable after capacitor drying and clearing at 1000 VDC.
- Over 25 to 160°C, capacitance changed only slightly (~1%)
  - BOPP capacitance change from 25 – 100 C (high temp failure) is 3%
## MLF Capacitor Development

<table>
<thead>
<tr>
<th>Event</th>
<th>Year</th>
<th>Activities</th>
<th>Achievements</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWRU Concept/ONR Program</td>
<td>2005-2010</td>
<td>Film development and Analysis, Patents</td>
<td>Materials Research</td>
</tr>
<tr>
<td><strong>PolymerPlus</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ONR SBIR Phase I</td>
<td>2012</td>
<td>High Temperature Film</td>
<td>Film Samples</td>
</tr>
<tr>
<td>NSF PFI with CWRU</td>
<td>2013</td>
<td>Technology advancement</td>
<td>0.4 – 1 µF</td>
</tr>
<tr>
<td>ONR SBIR Phase II</td>
<td>2014</td>
<td>First Prototypes</td>
<td>1- 37 µF</td>
</tr>
<tr>
<td>ONR Special Topics</td>
<td>2015</td>
<td>Film production, New Materials</td>
<td>Film Rolls</td>
</tr>
<tr>
<td>DARPA-LLNL</td>
<td>2015</td>
<td>Capacitor Prototypes</td>
<td>600 pF/HV</td>
</tr>
<tr>
<td>Commercial Trial</td>
<td>2016</td>
<td>Demonstrated Scalability</td>
<td>300 lb. Film</td>
</tr>
<tr>
<td>DOE-EERE</td>
<td>2015/2016</td>
<td>Prototypes, Thin Films, New Materials</td>
<td>100µF (Target: 1 mF)</td>
</tr>
<tr>
<td>ONR SBIR Phase II</td>
<td>2016</td>
<td>Capacitor Prototypes</td>
<td>200 µF</td>
</tr>
<tr>
<td>Internal Development</td>
<td>2016-17</td>
<td>40” Film Die, 42” Take-off unit</td>
<td>32” wide film</td>
</tr>
</tbody>
</table>
Summary

- Micro- and nanolayer coextrusion represent the next, near term, advancement in commercial polymer film processing for advanced technologies.
  - Commercially relevant scale processes available internationally

- Micro- and nanoscale coextrusion access a realm of material interactions not available to conventional layer processing.

- Property enhancement can be seen in technology examples/literature across multiple property spectrums:
  - Optical
  - Electrical
  - Adhesion
  - Transport
  - Mechanical
  - Dispersion

- Layering multiplying coextrusion processing techniques have been successfully demonstrated at various processing scales both in-house and through 3rd party processing trials for optics and dielectric films.
Gov’t & DoD Program Funding
Acknowledgments