### New Microlayer and Nanolayer Polymer Composites

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The highlights of this period are centered around the development of polymer nanolayer systems by a novel continuous coextrusion method. Nanolayers ranging in thickness between 5 nm to 500 nm have been manufactured using inexpensive polymeric materials such as polystyrene, polyethylene, acrylonitrile copolymers, polypropylene, polyethylene, polycarbonate and polymethylmethacrylate. Two and three component systems have been made from various combinations of these polymers.

In particular, the morphology of polypropylene has been drastically changed from a routine spherulitic form structure to a discoidal meso-form structure by just decreasing the layer thickness to nano dimensions. High density polyethylene has been totally changed to a “shish-kabab” structure due to the fact that the nano-layer thickness is less than the radius of gyration of the polymer macromolecule. When oriented, this novel crystalline morphology appeared as extended chain fibrillar crystals imbedded in polystyrene acting as the continuous phase in a nanocomposite structure.

Recently, we have started to develop nano-systems with anisotropic electrical and mechanical properties. Also, gradient and vertical layer structures are being considered. In the last few weeks we have actually succeeded in creating a vertical composite with highly anisotropic mechanical properties composed of polystyrene and a styrene-butadiene block copolymer.
1. Publications:


Oral Presentations:


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2. list of PI’s, students, and postdocs supported under the grant

Undergraduate Students
S. Norek, A. Hasan, A. Shah, M. Dennison

Graduate Students
C. Mueller, T. Ebeling, T. Schuman, J.A. Kerns

Postdoctoral Research Associates
S. Nazarenko, E.V. Stepanov, L. Flandin

3. awards and honors from the past year

Michael Dennison won the best poster prize at the 1999 National Engineers Week for his poster on *Microlayer Gradient Structures with Concentrated Filler Particles.*
4. description of interactions with ARL scientists during past year
   
   - Alex Hsieh - ballistics
   - Jo Ann Ratto - biodegradation

5. list of significant technology transfer activities with industry or Army labs during past year

6. short summary of most notable accomplishments, breakthroughs, and technology transfer events during the past year under the program

   See attached

7. 1-2 view graphs that highlight recent accomplishments (Powerpoint slides)

   See attached
Novel Nanolayered Films

PP/PS Microlayered System

<table>
<thead>
<tr>
<th>Composition PP/PS</th>
<th>Film Thickness (mils)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td><strong>Calculated PP Layer Thickness (nm)</strong></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>--</td>
</tr>
<tr>
<td>90/10</td>
<td>50</td>
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<td>80/20</td>
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<td>50/50</td>
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<tr>
<td>20/80</td>
<td>9</td>
</tr>
<tr>
<td>10/90</td>
<td>5</td>
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Microlayering is a unique method for achieving films where the layer thickness can be controlled from the micro to the nanoscale. As the film thickness is decreased, limitation on the crystal growth in the third dimension occurs at different hierarchical scales.
As PP layer thickness decreases, constraint on the spherulitic level occurs, and two-dimensional spherulites (discoids) are obtained. Orientation of this nanolayered film would decrease PP layer thickness an order of magnitude, causing mixing of the components on the molecular scale.
Novel Molecular Composite

**HDPE/PS Microlayered System**

<table>
<thead>
<tr>
<th>System</th>
<th>Nanolayer 4096 Layers</th>
<th>Microlayer 128 Layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition HDPE/PS</td>
<td>Film Thickness (mils)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 2</td>
<td>10 2</td>
</tr>
<tr>
<td></td>
<td>Calculated HDPE Layer Thickness (nm) (µm)</td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>--  --</td>
<td>-- --</td>
</tr>
<tr>
<td>30/70</td>
<td>37  7</td>
<td>1.2 0.20</td>
</tr>
<tr>
<td>20/80</td>
<td>25  5</td>
<td>1.30 0.16</td>
</tr>
<tr>
<td>10/90</td>
<td>12  3</td>
<td>0.40 0.08</td>
</tr>
<tr>
<td>5/95</td>
<td>6  1</td>
<td>0.20 0.04</td>
</tr>
<tr>
<td>0/100</td>
<td>--  --</td>
<td>-- --</td>
</tr>
</tbody>
</table>

There is great scientific interest in ultrathin layers, where the layer thickness is decreased to the scale of a few nanometers and is comparable with the radius of gyration of the polymer molecules.
**Optical Microscope**  
**Atomic Force Microscope**

HDPE/PS, 5/95, 4096 Layers, 2 mil thick

This novel crystalline morphology of nanolayers appeared as extended-chain fibrillar crystals. Orientation of such system at high temperature will create a fiber reinforced molecular composite.
Anisotropic Electrical Properties

Microlayers having highly anisotropic electrical properties were created

In-plane and cross-plane resistivity of the microlayers differed by ten orders of magnitude

- A non-conductive system of nickel in polyethylene was microlayered using a low amount of filler

- After annealing the samples in the melt, interdiffusion of the layers created a moving boundary, subsequently concentrating the particles to a point above the percolation threshold.
Optical micrographs of filled-unfilled PE microlayers annealed in the melt for 0, 5, 600, 3000, and 10000 minutes

Electrical behavior of unfilled-filled and filled-filled microlayers superimposed on resistivity versus volume fraction for nickel platelets

- These anisotropic conductive systems have application in EMI shielding, electronic switching, solid-state batteries, and ESD protection.

- Concentrating systems can extend to a wide range of filler types, particularly those that exhibit poor processability at high loading.
Gradient Microlayer Structures

Microlayered films that exhibit a gradient in layer thickness can be achieved with new multiplier design.

This can be accomplished by increasing the B/A ratio in each subsequent multiplier, as illustrated.

Current multiplier

<table>
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Cutting Edge

Gradient multiplier

A ≠ B

With 6 multiplier die elements, layer thicknesses would differ by a factor of 50

This geometry can be tailored to create films having novel transport properties, or unique optical, electrical, and mechanical properties.
Vertical Microlayers

Turning the existing multipliers by 90 degrees will lead to the creation of vertical layers

Decreasing layer thicknesses to the nanoscale may lead to morphologies that emulate lamellar block copolymer systems

This structure can exhibit highly anisotropic mechanical properties, as exemplified in the PS/Kraton 512 layer system shown here.