New Developments in Plexar®
Tie-Layer Adhesives

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Session: Extrusion Materials
Paper Number: 7680
New Developments in High-Performance Tie-Layers

Topics:

I. High-Clarity Barrier Films
   • New Developments
     • EVOH Applications
     • Nylon Skin Layer Application

II. High-performance tie-layer development for PS / HIPS Applications
   • Advantages of new development
   • Compare Theory to Experimental Results
   • Developed New Analytical Techniques
   • Correlation of Macro Scale Performance to Molecular Level
Global Trend: Increasing Demand for High-Clarity Barrier Films

• Consumer preference for retail display packages with excellent optics
  • Films with poor clarity detract from a quality image
• Intense competition in film-converting industry for distinguishing benefits
  • Clarity is a “must-have” feature
  • Low-clarity films are at a disadvantage
Transparency Loss in Barrier Coextrusions

Measurement: narrow angle scattering (NAS)

Phenomena
Coextruded barrier films with low optical transparency due to apparent instability at tie-barrier interface
- “Ground glass,” “graininess,” “orange peel” appearance

Cause
An uneven interface between tie layer and barrier layer, possibly caused by covalent bonding, that amplifies interfacial stresses that lead to nanometer scale distortions
Adhesion Versus Clarity in Standard Multi-layer Films With EVOH Barrier
Performance of New Tie-Layer Developments in Multilayer Films With EVOH Barrier

![Bar chart showing comparison of Standard-A, Tie-Clarity1, and Tie-Clarity-2 with 5X Adh (N/15 mm) and NAS values.](chart.png)
Key Attributes of New Developments

- LLDPE-based tie-layer: 1.1 MI, 0.92 density
- Specifically designed for EVOH blown film coextrusions where excellent optics and transparency are required
  - ✓ Good viscosity and shear stress matched of most blown film EVOH grades
  - ✓ Optimized anhydride content for adhesion and transparency
  - ✓ Unique structure and graft architecture
  - ✓ Ability to absorb and dissipate interfacial stresses
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   • Theory versus practice!

   — The effect of interfacial shear stress and elasticity ratio at the interface of nylon/tie multilayer film structures were found to be insufficient parameters to explain the optical properties measured experimentally
Attempt to Correlate Interfacial Elasticity Ratio with Clarity

![Graph showing correlation between Elasticity Ratio and Clarity for different materials.](image)
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   • Theory versus practice!
     — *Theory alone was inadequate in explaining experimental data*
     — It was predicted that such inadequacy was due to the neglect of *chemical interactions* at the Nylon/Tie interface
     — A new test was devised to rheologically probe the interaction at the nylon/tie interface
Rheological Probing of Nylon/Tie Interface: Increase in Elastic Modulus as a Function of Time
Effect of Outer Nylon Layer Thickness on Film Clarity

![Bar chart showing the effect of outer nylon layer thickness on film clarity. The chart compares the clarity of High Clarity Tie-A and Low Clarity Tie-B4 with two thicknesses of nylon: 20% PA and 10% PA. The chart indicates higher clarity with 20% PA compared to 10% PA.]
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   • Atomic Force Microscopy Study
     — A closer look at the interface
     — Additional parameters affecting clarity
Atomic Force Microscopy Images Showing Crystalline Morphology of Nylon
AFM Images Using High Clarity Tie Showing Continuous and Undisturbed Tie/Nylon Interface
AFM Images of Low Clarity Tie in Multilayer Nylon Film. Delamination at the Interface and Interlayer Mixing is Observed
Summary of High-Clarity Development

• The effect of adhesion on multi-layer film clarity was investigated
  – Analysis of current tie-layer grades show that higher adhesion typically leads to lower clarity
  – By carefully controlling the reaction kinetics and rheological characteristics of tie-layers, we were able to develop new adhesives that maintained high clarity and high adhesion at the same time
II- High-Performance Tie-Layer Development for PS/HIPS Applications

**Product characteristics**

- **LLDPE-based tie-layer adhesive**
- **Melt index = 3.30 g/10 min (D 1238)**
- **Density = 0.9335 g/cc (D 1505)**
- **Vicat softening point = 88.3°C (D 1525)**
Performance of New Tie-Layer Developments in PS/HIPS Applications

(A) Macro Scale Investigation

Adhesion Performance
- Heat Seal
- Sheet Co-Extrusion
- Effect of Temperature
- Thermoforming
- Optical Microscopy (Not Shown – Too big to be presented!!)
Effect of PS/HIPS Blends on Heat Seal Adhesion at 260°C
Adhesion Performance of New Tie-Layer in Co-Extruded Sheet Application

![Bar chart showing adhesion performance](chart.png)

<table>
<thead>
<tr>
<th>Tie-Layer</th>
<th>Adhesion (N/15 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref-1</td>
<td>5.1</td>
</tr>
<tr>
<td>Ref-2</td>
<td>9</td>
</tr>
<tr>
<td>Adh-PX</td>
<td>32</td>
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</tbody>
</table>
Effect of Temperature (50 °C) on Adhesion Performance in Co-Extruded Sheet Application

![Bar chart showing adhesion performance at 50 °C for different layers. The chart compares adhesion in N/15 mm for Ref-2 and Adh-PX layers, with data points at 3 and 5 minutes.]
Adhesion Performance of New Tie-Layer After Thermoforming

<table>
<thead>
<tr>
<th>Tie-Layer</th>
<th>Adhesion (N/15 mm)</th>
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</thead>
<tbody>
<tr>
<td>Side-Vertical</td>
<td>3.4</td>
</tr>
<tr>
<td>Side-Horizontal</td>
<td>3.8</td>
</tr>
<tr>
<td>Cup Rim</td>
<td>6</td>
</tr>
</tbody>
</table>
Performance of New Tie-Layer in PS/HIPS Applications

(B) Micro Scale Investigation

Atomic Force Microscopy
- A closer look at the interface
- Effect of Tie-Layer
- Effect of Thermoforming
- Molecular Orientation due to thermoforming
AFM Images of Low Performance Tie in PS Multilayer Sheet. Large Gap at Tie-PS Interface
AFM images of New Tie-Layer Exhibiting Excellent Adhesion with No Interfacial Delamination at Tie/PS Interface
AFM Images of Reference Tie in Thermoformed Cup: Vertical Gap at Tie/PS Interface
AFM Images of New Tie-Layer in Thermoformed PS Cup Exhibiting Excellent Adhesion in Presence of High Orientation
Technical Summary for PS/HIPS Applications

• 300% – 400% improved adhesion compared to references
• Optimized MI for sheet extrusion process
• LLDPE-based offer advantages over EVA-based adhesives
  – Low odor
  – Easy thermoform-ability
  – No Stringing
  – High temperature applications
• New tie-layer could have a cost/performance advantage upon down gauging
• Enhanced performance at high temperature
• Retained high performance after thermoforming
Conclusions

• Developed new tie-layer adhesives for high-performance applications:
  – High-clarity, multi-layer film application
    • Maintain high clarity and high adhesion at the same time
  – High-performance tie-layer development for PS/HIPS applications
    • Maintain high adhesion and container integrity after thermoforming
• Applied new analytical techniques in developing high-performance tie-layer adhesives that are targeted for specific applications
• Related performance on macro scale to micro / molecular level
Acknowledgments

Coauthors: Dr. Harry Mavridis and Dr. Francis Mirabella

The authors would like to thank Mr. Randy McIntosh, Mr. Michael Grubb, Mr. John Leurck, Mr. Daniel Riopell and Mr. William Shumake for their significant contribution and assistance.