Crystallization Behavior and Film Properties of Nylon 66-rich Nylon 66/6 Copolymers

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Outline

- Introduction to nylon 66 and nylon 66 copolymers
- Background on nylon 66 copolymers
- Crystallization behavior of nylon 66 copolymers
- Film properties of nylon 66 copolymers
  - Monolayer blown films
  - Biaxially oriented films
- Laminate films containing nylon 66 copolymers
- Summary
Where are Nylons Used in Films

Food applications: 1B lbs./yr
Non-food applications: 0.3 B lbs./yr

Why nylon?
- Useful at food preparation temperatures.
- Gas barrier properties help preserve food and block odors during storage.
- High strength and toughness

Film Market by Nylon Type
- PA6-66 ~8%
- PA66 ~3%
- Specialty PA ~4%
- PA6 ~85%

- Nylon 6 – dominate material in polyamide films with the usage primarily in two processing technologies:
  - Biaxially oriented polyamide (BOPA)
  - Blown multi-layer films
- Nylon 66 – largely limited application space due to marginal processability

Source: PCI, “The Opportunity for Polyamide in Film Production”

Nylon end uses are highly concentrated in food packages primarily as a protective layer
Advantages and Disadvantages of Nylon 66 in Film

**Advantages**
- High melting point
- High strength
- High stiffness
- High toughness
- High puncture resistance
- Creep resistance
- Flex-crack resistance

**Disadvantages**
- High crystallization temperature
- Fast crystallization
- Poor aesthetics – limited clarity/gloss
Applications of Nylon66 in Film

Blends of Nylon 66 and Nylon 6 are used to enhance processing limitations in blown film

Ref: Nylon Plastics Handbook (M. Kohan 1995)
Nylon 66/6 Copolymer Melting Behavior

Effect of caprolactam level on copolymer melting point

Nylon 66 rich backbone enables a wider melting point range than Nylon 6 based copolymers

![Graph showing the melting points of Nylon 66/6 copolymers and Nylon 6/66 copolymers.](graph.png)
Thermal Behavior of Nylon 66 Rich Copolymers

Melting point depression follows Flory equation indicating random copolymers

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = \left( \frac{R}{\Delta H_u} \right) \ln X
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Caprolactam wt.%</th>
<th>Caprolactam mole %</th>
<th>RV</th>
<th>T_m (°C)</th>
<th>T_c (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>260</td>
<td>220</td>
</tr>
<tr>
<td>PA66_{94/6}</td>
<td>6.0</td>
<td>11.3</td>
<td>180</td>
<td>255</td>
<td>205</td>
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<tr>
<td>PA66_{99/610}</td>
<td>10.5</td>
<td>19.0</td>
<td>180/90</td>
<td>245</td>
<td>190</td>
</tr>
<tr>
<td>PA66_{64/616}</td>
<td>16.3</td>
<td>27.6</td>
<td>130/85</td>
<td>235</td>
<td>175</td>
</tr>
<tr>
<td>PA66_{77/623}</td>
<td>23.1</td>
<td>37.5</td>
<td>140/90</td>
<td>220</td>
<td>150</td>
</tr>
<tr>
<td>PA6</td>
<td>100</td>
<td>100</td>
<td>140/80</td>
<td>220</td>
<td>170</td>
</tr>
</tbody>
</table>
Half-time analysis yields useful data to support development of processing recommendation on existing equipment.

**Isothermal Crystallization Half-time DSC Thermogram**

**Test procedure:**
1. Heat the sample from 25°C to 305°C.
2. Holding for five minutes and then cooling at 200°C/min. to the target isothermal temperature.
3. Hold at the desired temperature until the recrystallization exotherm is complete.

**Data Analysis:**
1. The crystallization half-time \( t_{\frac{1}{2}} \) is the time when 50% of the recrystallization exotherm is complete.

For this sample \( t_{\frac{1}{2}} = 25.24 \text{ min} \ (1514 \text{ s}) \).
Crystallization Behavior of Nylon 66 copolymers

Reducing crystallization rate enables use of PA66 copolymers in classical film processing technologies such as blown film and biaxial oriented film.
Film Properties of Nylon 66 rich copolymers
1 mil monolayer blown films – Dart Drop and Elmendorf Tear

For both Dart Drop and Elmendorf Tear the PA66 Copolymer containing 23 wt.% caprolactam yields the highest values.

Film samples conditioned at 23°C ± 3°C and 50% RH ± 5% for at least 40 hrs prior to testing.
BOPA Film manufacture of Nylon 66 rich copolymers

40% lower initial stretch force

Higher elongation at break

PA66 rich copolymers can be manufactured using existing Nylon 6 BOPA assets and conditions
Majority of Film properties do not varying significantly with Nylon type except for Puncture Resistance

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>PA6</th>
<th>PA66&lt;sub&gt;90/610&lt;/sub&gt;</th>
<th>PA66&lt;sub&gt;84/616&lt;/sub&gt;</th>
<th>PA66&lt;sub&gt;77/623&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretch Ratio</td>
<td></td>
<td>3 x 3</td>
<td>3 x 4.7</td>
<td>3.5 x 4.1</td>
<td>4 x 4</td>
</tr>
<tr>
<td>Thickness</td>
<td>µm</td>
<td>14.3</td>
<td>17.9</td>
<td>16.1</td>
<td>13.5</td>
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<tr>
<td>Tensile Strength</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>MPa</td>
<td>265</td>
<td>270</td>
<td>300</td>
<td>287</td>
</tr>
<tr>
<td>TD</td>
<td>MPa</td>
<td>258</td>
<td>324</td>
<td>320</td>
<td>258</td>
</tr>
<tr>
<td>Elongation</td>
<td>%</td>
<td>100</td>
<td>100</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>TD</td>
<td>%</td>
<td>90</td>
<td>70</td>
<td>110</td>
<td>80</td>
</tr>
<tr>
<td>Barrier Properties @ 23°C and 50% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ Transmission Rate</td>
<td>cc/day-atm</td>
<td>55</td>
<td>61</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td>Puncture, 1.6mm pin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Puncture Resistance (Normalized)</td>
<td>N/mm</td>
<td>1910</td>
<td>2670</td>
<td>2320</td>
<td>2280</td>
</tr>
<tr>
<td>Optical Properties</td>
<td>%</td>
<td>92.0</td>
<td>92.2</td>
<td>92.3</td>
<td>92</td>
</tr>
<tr>
<td>Transmission</td>
<td>%</td>
<td>96.3</td>
<td>99.7</td>
<td>99.4</td>
<td>97.9</td>
</tr>
<tr>
<td>Clarity</td>
<td>%</td>
<td>3.0</td>
<td>1.1</td>
<td>2.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Haze</td>
<td>%</td>
<td>&lt; 2.0</td>
<td>&lt; 1.5</td>
<td>&lt; 1.0</td>
<td>&lt; 5.0</td>
</tr>
<tr>
<td>Shrinkage @ 160°C, 5 min</td>
<td>%</td>
<td>&lt; 1.5</td>
<td>&lt; 1.5</td>
<td>&lt; 1.0</td>
<td>&lt; 2.0</td>
</tr>
</tbody>
</table>

Effect of Nylon type on BOPA Film Properties

Results from Sequential Stretching biaxial film line
Benefits of Puncture Improvement

Toughness vs. Thickness

End user choice:

- Delivering unmet toughness requirements in new and existing applications compared to PA6 based BOPA film
- Same performance as PA6 based BOPA film but using thinner film

BOPA Film made from Nylon 66 copolymers provide unique performance compared to Nylon 6 based BOPA
Application Development Strategy
Exploring translation of monolayer film properties to BOPA Film laminates

4 Ply Plastic Film Construction

| BOPET film | Reverse printing | Adhesive | Aluminium Foil | Adhesive | BOPA film | Adhesive | LLDPE film |

Partner Development Model: (Pull through activation)

Ascend → BOPA Film Producer → Bag Manufacturer → Ascend

Film Suppliers

Ascend 25kg pellet bags are made from a 4 ply structure containing 15 micron PA6 based BOPA Film
Comparison of BOPA Film Type on Laminate Puncture

15 micron BOPA film in an 180 micron Al foil laminate

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Energy to Break (J)</th>
<th>Force to Break (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66$<em>{77}$/6$</em>{23}$</td>
<td>0.20</td>
<td>60</td>
</tr>
<tr>
<td>PA66$<em>{84}$/6$</em>{16}$</td>
<td>0.25</td>
<td>70</td>
</tr>
<tr>
<td>Control Bag</td>
<td>0.15</td>
<td>60</td>
</tr>
</tbody>
</table>

Testing Speed = 25 mm/in
Testing Pin = 1.6 mm radius

Laminates with Nylon 66 copolymers BOPA film show 5-30% improvement in Slow Rate Puncture Tests vs the Control
Enhancing Puncture Resistance
15 micron BOPA film in an 180 micron Al foil laminate

### Monolayer Film

- 100% of structure is Nylon
- 20% improvement in puncture force

### Foil-based Laminate Film

- ~10% of structure is Nylon
  - 35% improvement in puncture force
  - 45% improvement in puncture

Higher film puncture resistance translates to increased puncture in laminate structures.
Summary

• Nylon 66 rich copolymers are a preferred option for addressing processing limitations of Nylon 66 compared to Nylon 66/Nylon 6 blends

• Nylon 66 copolymers containing caprolactam can be engineered to provide tailored processing characteristics

• Monolayer blown films of Nylon 66 copolymers yield tear and dart drop property advantages over Nylon 6 films

• Nylon 66 copolymer based BOPA Films exhibited superior puncture performance than Nylon 6 BOPA films while maintaining most other film properties

• Al foil laminate containing Nylon 66 copolymer BOPA Film gave 35-45% increase over the Control Bag laminate containing Nylon 6 BOPA Film
Acknowledgements

Tricia Bowen
Zach Carben
John Tria
Mike Goodin
Lisa Goldstein
Ed Nerlich
Steve Manning
Questions?