Selecting the proper polyamide for multilayer food packaging films: process and performance considerations

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Polyamides are so useful for numerous reasons

- **High Mechanical Strength**
  - *Fishing line, Rope, Bristles*

- **Easily co-extruded**
  - *Multilayer structures with dissimilar polymers possible*

- **Heat & Chemical Resistance**
  - *Roasting bags, Intake manifolds*

- **Thermoformable**
  - *High residual corner thickness*

- **Barrier**
  - *Barrier mulch film*

- **Abrasion Resistance**
  - *Weed trimmer, wire jacketing*
Major variables in addition to final properties considered when selecting the proper polyamide
Key polyamide intrinsic factors

Intrinsic

Process

Structural
Polymer construction and resulting crystal chain direction greatly influences properties
Most polyamides used in flexible packaging are semi-crystalline polymers.

amorphous:  
PC, PMMA, PS, ...

semicrystalline:  
PA6, PA66, PBT, ...

E-modulus vs. temperature
Flexible packaging’s polyamide crystallinity spectrum

- Decreasing crystallinity / higher transparency / less haze
- Increased softness / higher flexibility / better thermoforming
- Higher blow up ratio
- Lower melting point / lower processing temperature / higher frost line
- Fewer wrinkles during blown film collapse process
- Increased shrinkage from orientation process
- Increasing puncture resistance @ constant force
- Higher tear strength / Lower tensile strength

(Polyamide 66)  (Polyamide 6)  (Polyamide 6/66)
Intrinsic crystallinity comparison

DSC melting endotherm of a **semicrystalline polymer**

(Polyamide 6/66)  
$T_m$: 180 to 200°C  
$T_c$: 110 to 145°C

(Polyamide 6)  
$T_m$: 220°C  
$T_c$: 170°C

(Polyamide 66)  
$T_m$: 260°C  
$T_c$: 218°C
PA crystallinity differences show in various ways including less hazy film

PA 6/66 (haze 3.0)  
Very low crystallinity PA6/66 (Ultramid® C37LC) (haze 0.45)

Blown Film 150μm / BUR 1:2 / ASTM D-1003
Mechanical properties as a function of MW & nucleation

PA6 Tensile Strength vs MW & Nucleation

PA6 Tensile Elongation vs MW & Nucleation
Key polyamide process factors

Intrinsic

Process

Structural
Production process vs cooling rate & PA6 crystallinity

Production Process Vs Cooling Rate (°C/min)

Cast Film
250 - 800

Blown Film
20 – 80

Water Quench
1000 - 3000
Cooling rate influences final properties by way of morphological differences

- Polarized light micrographs of Ultramid® B40 PA6 cast film with / without nucleating agent

<table>
<thead>
<tr>
<th></th>
<th>Neat &amp; Slowly Cooled</th>
<th>Nucleated &amp; Slowly Cooled</th>
<th>Neat/Nucleated &amp; Rapidly Cooled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.128</td>
<td>1.126</td>
<td>1.110</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>% 38</td>
<td>% 32</td>
<td>% 20</td>
</tr>
<tr>
<td>Thermoforming</td>
<td>µm 12</td>
<td>µm 10</td>
<td>µm 18</td>
</tr>
<tr>
<td>(residual wall</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>thickness)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haze</td>
<td>% 2.8</td>
<td>% 11</td>
<td>% 0.4</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Process Mechanical Comparison</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>tensile strength (MO)</td>
</tr>
<tr>
<td>tensile strength (TO)</td>
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<tr>
<td>elongation/break (MO)</td>
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<tr>
<td>elongation break (TD)</td>
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<tr>
<td>puncture resistance – F</td>
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<tr>
<td>puncture resistance – W</td>
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<tr>
<td>OTR</td>
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<td>WVTR</td>
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Water Cool (1): (15C) 12umPA6/6umTie/18umPE/6umTie/40umPA6/10umTie/75umPE (170um)
Cast: (20C chill roll) 12umPA6/6umTie/18umPE/6umTie/40umPA6/10umTie/75umPE (170um)
Blown: Air 12C; IBC -5C 10umPA6.66/8umTie/15umPE/8umTie/25umPA6.66/10umTie/65umPE (140um)
Higher orientation is possible with low crystallinity copolyamides

<table>
<thead>
<tr>
<th>Tape stretch ratio at max. machine force</th>
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<tbody>
<tr>
<td>PA6/66</td>
</tr>
<tr>
<td>Low crystallinity PA6/66 (Ultramid C37LC)</td>
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Key polyamide structural factors

Intrinsic

Process

Structural
Structure thickness distribution and symmetry dramatically vary between applications.

75um - 225um

Sealant Layer

PA commonly 25-40% of overall structure

Common PA/EVOH/PA combination for barrier

Moisture barrier

Abrasion/Heat resistant

Printability
Blown film curl as a function of asymmetry

1. Directly after die
   >220°C
   all components molten

2. PA frostline
   180-140°C
   PA solidifies+shrinks
   PE soft → shrinks

3. PE frostline
   120-80°C
   PE solidifies+shrinks
   PA rigid → can not shrink/PE
   → curl to PE side
Lower crystallization temperature dramatically reduces curl for asymmetric blown films

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.) LDPE</td>
<td>64</td>
</tr>
<tr>
<td>B.) Tie</td>
<td>18</td>
</tr>
<tr>
<td>C.) Polyamide</td>
<td>25</td>
</tr>
<tr>
<td>D.) Tie</td>
<td>18</td>
</tr>
<tr>
<td>E.) LDPE</td>
<td>30</td>
</tr>
<tr>
<td>F.) Tie</td>
<td>18</td>
</tr>
<tr>
<td>G.) Polyamide</td>
<td>25</td>
</tr>
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Very low crystallinity
PA6/66
(Ultramid C37LC)
Polyamide viscosity selection

Viscosity match PE-PA for good layer distribution:

- **Ultramid® B36LN + PE (MI=2.5-4)**
- **Ultramid® B40LN + PE (MI=0.7-2)**

The graph shows the viscosity vs. shear rate for different polyamides and polyethylene:

- **LDPE MI 3.6 220°C**
- **PA6 RV 3.6 250°C**

The MI range and extrusion range are indicated on the graph.
Example of PE/PA viscosity mismatch in cast film process
Summary

- Choose **polyamide chemistry** based on crystallinity level to achieve final properties under desired process conditions.
- **Higher MW** provides higher mechanical properties.
- If process conditions allow, **nucleating agents** produce consistently crystalline layers.
- Rate of **melt cooling** significantly alters the morphology of PA6 yielding very different properties.
- **Orientation and thermoforming** require low crystallinity which can be built into the polyamide and/or reduced by the film production process.
- **Matching PA viscosity** to adjoining layers is important.
- **Structure asymmetry** is possible even for critical flat applications but requires use of very low crystallinity grades of polyamides such as Ultramid C37LC.
PA grade selection: A place to start

**Cast Film**
- PA6 RV 3.3 to 4.0 depending on viscosity matching and throughput requirements
- Nucleation recommended for stiffer, dimensionally stable top webs. Requires higher chill roll temperature
- PA6/66 can be blended for deeper draw thermoforming webs

**Blown Film**
- PA6 RV 3.6 to 4.0 depending on viscosity matching and throughput requirements
- Nucleation provides smaller, more consistent crystals but may increase curl if structure is not balanced
- PA6/66 can be blended or substituted for thick and asymmetric films or clearer thermoforming films

**Water Quench**
- PA6 RV 3.6 to 4.0 depending on viscosity matching requirements
- PA6/66 can be blended or substituted for thick and/or highly oriented films
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