New Opportunities for Metallocene Polyethylene in Co-Extruded Blown Films

Richard W. Halle
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A new metallocene polyethylene (mPE) family (named Enable™ mPE) has been developed which exhibits the unique combination of LDPE-like processing and mPE film toughness. This new mPE family allows the converter to eliminate LDPE from many of his film formulations significantly improving film properties while maintaining efficient film production. This new mPE family also possesses shrink characteristics similar to fractional melt index LDPE. This unique attribute has led to the development of new high performance shrink films, which combine these mPEs with more traditional mPEs to obtain down-gauged shrink films with excellent toughness and high stiffness.

High clarity coex films (HCF) can also be made by utilizing these new mPEs as core layers with other mPEs. These films have exceptional clarity, heat sealing and toughness and can be utilized in a wide variety of packaging applications, such as lamination films and stand-up pouches.

Another application where the unique performance of these new mPEs is employed is in stiff, cast hand wrap film. These resins allow the converter to tailor the strain hardening behavior of his stretch film to achieve more effective stretch wrapping performance. These new mPEs' improved operational stability combined with their excellent film performance has been found to offer sustainability benefits in many applications.
New Opportunities for Metallocene Polyethylene in Co-Extruded Blown Films

Richard Halle
Senior Staff Engineer
Metallocene Polyethylenes - Review

- **Metallocene polyethylenes (mPE) have changed the shape of the PE film industry.**
  - Superior toughness as measured by dart drop impact strength and puncture resistance
  - Good clarity, superior heat sealing performance with high hot tack

- **Excellent mPE properties have led to package redesign and downgauging which has translated into source reduction.**

- **Several metallocene polyethylene families are produced today.**
  - Made using different metallocene catalysts & processes which generate unique sets of performance characteristics
  - Typically mPEs have narrow, uniform composition and/or molecular weight distributions.
  - Many names - Exceed™ mPE resin (hereafter mPE-1), mLLDPE, mVLDPE, Exact™ Plastomers, metallocenes

- **Some mPEs have proven to be processing challenges especially on older blown film lines.**
  - Narrow MWDs mean higher melt viscosities and greater extruder motor loads.
  - Low melt strength leads to poor bubble stability without LDPE addition, similar to conventional LLDPE.
  - But, adding LDPE to mPEs or LLDPEs to improve processing significantly degrades their film properties.
Types of Polyethylene - Composition and Branching

- The addition of α-olefins (such as butene-1, hexene-1, octene-1) to the polymer chain introduces short-chain branching (SCB)
  - Minimal effect on melt rheology
  - Significant effect on crystallization, solid state structure and resulting properties
- Long chain branching (LCB) occurs when branch length exceeds ~250 carbon atoms
  - Profound effects on melt rheology; shear and extensional viscosity
  - Little effect on crystallization
  - Significant effects on shear-induced crystallization and the development of orientation during film making process which can have significant effects on film properties

- Enable™ mPE resin (hereafter “New mPE”): New mPE family with easier processing and excellent toughness.
  - Molecular design combines Long Chain Branching (LCB) and a narrow Composition Distribution (CD).
  - Improved melt strength and greater shear thinning offer good bubble stability and greater extruder outputs vs. LLDPE blends.
  - Ability to replace LLDPE/LDPE blends with 100% new mPE offers improved film properties and the ability to downgauge.
New mPE Processing

**Flow Curve / 190°C**

- **New mPE-MD** (0.5 MI, 0.935 g/cm³)
- **New mPE** (1.0 MI, 0.920 g/cm³)
- **C4LLDPE** (1.0 MI, 0.918 g/cm³)
- **LDPE** (0.75 MI, 0.923 g/cm³)

**Typical during extrusion**

- Excellent shear thinning behavior
- High melt strength

**Melt Strength by Rheotens**

- **HP-LDPE**
- **New mPE**
- **Common LDPE** (operating range)
- **LLDPE**

**Maximum Output**

- **LD** (0.75 MI, 0.923 g/cm³)
- **New mPE** (1 MI, 0.920 g/cm³)
- **New mPE-MD** (0.5 MI, 0.935 g/cm³)
- **C4LL** (1 MI, 0.918 g/cm³)
Replacing LLDPE/LDPE blends with New mPE offers improved film properties, the ability to downgauge, and business simplification.
New mPE vs LLDPE/LDPE Blends

- As a LLDPE/LDPE blend replacement, *New mPE* offers improved dart impact, MD tear, and tensile strength

- Melt temperatures reduced from 224 °C for the 75:25 blend to 202 °C at same melt index
  - Improved bubble stability has potential for increased output
Performance Enhancement of mPE Films

<table>
<thead>
<tr>
<th>Core Layer Composition</th>
<th>Melt Index (g/10mins)</th>
<th>Density (g/cm³)</th>
<th>mPE-1 / LDPE Film</th>
<th>Pure mPE Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>0.75</td>
<td>0.923</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>New mPE</td>
<td>0.5</td>
<td>0.920</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>mPE-1</td>
<td>1.0</td>
<td>0.918</td>
<td>80%</td>
<td>80%</td>
</tr>
</tbody>
</table>

mPE-1/New mPE blends offer significant property improvement versus mPE-1/LDPE formulations:

- Impact:
  - Significant improvement (up to 300%)
- MD tear:
  - Significant improvement (up to 300%)
- Tensile strength (MD and TD):
  - Significant improvement
- Hot tack:
  - Higher hot tack peak
  - Broader hot tack window
- Optical properties:
  - Similar clarity
  - Similar gloss
Coextruded PE Films for Enhanced Performance

**Advantages of coex vs monolayer blends**

- Meet specific performance requirement
  - Barrier properties
  - High strength, tear
  - Improved sealability
  - Better stiffness/toughness balance
  - High gloss surfaces for printing
- Reduce cost
  - Reduce amount of expensive polymers
  - Down-gauge with same properties
- Reduce number of process steps
  - Reduce need for lamination
- Reduce waste
  - Incorporate recycle layers

*Photos used are representative of potential product applications only*
Classic High Clarity Coex Films

Combining core layer of ZN-LLDPE with skins of LDPE improves overall film performance

OUTSIDE LAYER:
Surface properties
Gloss
Printability

MIDDLE / BULK LAYER:
Strength

INSIDE LAYER:
Sealing

Common perception: “High Clarity LDPE grades required to make a High Clarity Film”

Introduction mPE resins in the mid 90’s formed the basis for development of high strength clarity coex films and other coex innovations

LDPE Meltindex (g/10 min)

Haze (%)

Improved opticals
ExxonMobil’s High Clarity, High Stiffness Technology

Monolayer mPE-1 Film

100% mPE-1 Film
25 µm

Rough surface = Poor optical properties

HCF (high clarity, high stiffness) Technology

30 µm
A : 100% mPE-1
B : 60% mPE-1
40%HDPE
C : 100% mPE-1

mPE HCF Technology delivers excellent opticals together with high stiffness
mPE HCF Films Translate into Improved Packaging

**Good optical properties**

- Critical for point-of-sale merchandising
- High clarity/low haze for see-through packaging
- High gloss for sharp reverse printing

**Higher stiffness while maintaining toughness**

- Easier handling film on packaging lines
  - Increases packaging speed
  - Easier to cut
  - Less drape over the edges
- Stiff films increase package appeal – more “body” to provide “luxury” feeling
- Downgauging leads to **more sustainable flexible films**
Clear, Stiff HCF Coex Films based on New mPE

New mPE Coex

- New mPE-1
  - 0.920 g/cc, 1.0 MI
- New mPE-2
  - 0.927 g/cc, 0.5 MI
- New mPE-1
  - 50 micron, 1.4 mm die gap, 2.8 BUR

New mPE
New mPE High Clarity Coex Film

New mPE Monolayer

New mPE-1

New mPE-1 ➔ 0.920 g/cc, 1.0 MI
50 micron, 1.0 mm die gap, 2.5 BUR

New mPE Coex

New mPE-1

New mPE-2

New mPE-1

New mPE-1 ➔ 0.927 g/cc, 0.5 MI
50 micron, 1.4 mm die gap, 2.8 BUR

0.927 density New mPE in the core improves optical performance with a substantial increase in stiffness
New mPE-MD is an excellent choice for high clarity coex due to its low internal haze level. Clarity, tear and impact resistance can be tailored by choice of mPE in skin layers.
Enhanced Coextruded Collation Shrink Films

Snug fit around the product
- Efficient/controlled shrinkage
- ‘Bull's-eye’ as handle
- Stiffness

Optical properties
- Low haze, good contact or ‘see-through’ clarity
- High gloss for printing

Packaging line performance
- Seal consistency
- Efficient shrinkage rate
- Low coefficient of friction

Downgauging potential
- Sustainable packaging
- Source reduction
- Unit cost reduction

Package integrity
- Tensile properties
- High holding force
- No hole formation

Unique molecular structure of New mPE imparts shrink performance similar to frac-melt LDPE Coex films provide added degrees of freedom in shrink film design
New mPE Coex Shrink Films

Compared to New mPE resin-based mono film, New mPE & mPE-1 resin-based coex film offers:
- Outstanding film optics
- Improved impact resistance and TD tear
- Improved stiffness and holding force ⇒ downgauging

Compared to LD based coex films, New mPE & mPE-1 resin-based coex films offer:
- Significantly improved film toughness, puncture/impact resistance ⇒ downgauging
- Higher TD tear ⇒ improved bulls-eye pick-up
- Equivalent shrink performance
New mPE Coex Shrink Films Tailored to Customer Requirements

Shrink Properties:

<table>
<thead>
<tr>
<th></th>
<th>Higher LDPE content</th>
<th>Higher HDPE content in core</th>
<th>Higher HDPE content in skin</th>
<th>Layer Distribution 1-2-1 to 1-4-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrink Speed</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>➤</td>
</tr>
<tr>
<td>% Shrink MD</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
</tr>
<tr>
<td>% Shrink TD</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>➤</td>
</tr>
<tr>
<td>Plastic Force</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>➤</td>
</tr>
<tr>
<td>Holding Force</td>
<td>➤</td>
<td>↑</td>
<td>↑</td>
<td>➤</td>
</tr>
<tr>
<td>Shrink Temperature</td>
<td>No change</td>
<td>Higher Temperature</td>
<td>Lower Temperature</td>
<td>No change</td>
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</tbody>
</table>

Optical & Mechanical Properties:

<table>
<thead>
<tr>
<th></th>
<th>Higher LDPE content</th>
<th>Higher HDPE content in core</th>
<th>Higher HDPE content in skin</th>
<th>Layer Distribution 1-2-1 to 1-4-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haze / Gloss</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
</tr>
<tr>
<td>Clarity</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>↓</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
</tr>
<tr>
<td>Stiffness</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>➤</td>
</tr>
<tr>
<td>MD Tear</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>➤</td>
</tr>
<tr>
<td>TD Tear</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
</tr>
<tr>
<td>Dart Impact</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
<td>➤</td>
</tr>
<tr>
<td>Puncture Resistance</td>
<td>➤</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
</tbody>
</table>

↑ = Higher  ➤ = No Change  ↓ = Lower
Drivers

- Globally traded products drive the need to reduce film weight
  - Lower logistics costs and sustainability credits
- Hand wrap segment growth driven by local distribution networks
  - ~80% of Asia Market is hand wrap, ~40% of NA and Europe Market is hand wrap
- Advanced multi-layer cast film lines and enhanced mPE have led to improved stretch films
  - Value via downgauging and/or improved performance
  - Premium market ‘shares’ value of downgauged films

Trends

- Enhanced coextrusion capability becomes critical to follow downgauging trend
  - Allows tailoring of more internal layers to get required performance balance
  - Surface layers are designed for cling, optics, abrasion resistance, etc.
- Film producers are focusing on new higher performance films
  - Enhanced machine films targeted at 15-17 µm
  - New stiff handwrap films targeted at 12 µm and below
Improved Cast Hand Wrap - ‘Stiff’ CHW Concept

- The strain hardening behavior for New mPE-based Cast Hand Wrap (CHW) structures results in “resistance to stretching”
- CHW made from conventional LLDPE exhibits low resistance to stretching and elongate easily

Unique Stress/Strain relationship yields improved holding force / toughness

- Stiffness, as described by secant modulus, is the slope of the tangent on the tensile curve measured at 1% elongation
- An increase in LLDPE density leads to an increase in secant modulus
- The use of a higher modulus LL can give rise to a stiffer feel, but does NOT provide the stretching resistance associated with strain hardening
New mPE – 3 Layer Formulations

New mPE provides the improved stiffness needed for downgauged cast hand wrap (MD Tensile and Stretch Force) and less neck-in during wrapping.

New mPE delivers a step change in tear performance and excellent puncture at 20% downgauging.

Excellent New mPE optics (after stretch) yields good cling performance, aesthetics, and bar code reading.

Significant value created to share between supplier, converter, and end user.

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**New mPE in skin layer (25% of total)**

<table>
<thead>
<tr>
<th>Layers</th>
<th>MI (g/10min)</th>
<th>Density (g/cm³)</th>
<th>New mPE Coextruded 3 layer 12 µ film</th>
<th>Reference Coextruded 3 layer 15 µ film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer Distribution (%)</td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>C4 LLDPE</td>
<td>2.0</td>
<td>0.918</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>New mPE</td>
<td>1.0</td>
<td>0.920</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

8% Vistamaxx added to layer C for cling
New mPE – 5 Layer HAO Formulations

**New mPE**

**in sub-skin layers**

<table>
<thead>
<tr>
<th>Layers</th>
<th>MI (g/10min)</th>
<th>Density (g/cm3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6LLDPE</td>
<td>3.2</td>
<td>0.918</td>
</tr>
<tr>
<td>C6LLDPE</td>
<td>2</td>
<td>0.918</td>
</tr>
<tr>
<td>New mPE</td>
<td>0.5</td>
<td>0.920</td>
</tr>
</tbody>
</table>

**New mPE in subskins 24% of total film**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>20</td>
<td>30</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>

**Reference Coextruded 5 layer 12μ film**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>20</td>
<td>30</td>
<td>20</td>
<td>15</td>
</tr>
</tbody>
</table>

**New mPE in sub-skin layers** – New mPE 40% in subskin – New mPE 60% in subskin – Reference

- New mPE delivers superior stiffness vs the HAO control
- More effective wrapping – less neck-in - fewer wraps per load
- Film stiffness / toughness / processing balance is tunable by adjusting the New mPE grade and amount in subskin and core layer
- End use performance is improved via enhanced stretch resistance / higher holding force
### New mPE Coex Films - Value-in-Use Summary

<table>
<thead>
<tr>
<th>Delivered Attributes</th>
<th>Derived Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>• <strong>Downgauging</strong></td>
<td>➔ Sustainability</td>
</tr>
<tr>
<td></td>
<td>➔ Lower per impression cost</td>
</tr>
<tr>
<td></td>
<td>➔ Raw material savings</td>
</tr>
<tr>
<td></td>
<td>➔ Lower logistics costs (transportation)</td>
</tr>
<tr>
<td>• <strong>Improved toughness / stiffness / sealing</strong></td>
<td>➔ More efficient packaging operation</td>
</tr>
<tr>
<td></td>
<td>➔ Less risk of damage in transit</td>
</tr>
<tr>
<td></td>
<td>➔ Securely held loads</td>
</tr>
<tr>
<td>• <strong>Greatly enhanced film optical properties</strong></td>
<td>➔ Improved package appearance</td>
</tr>
<tr>
<td></td>
<td>➔ Excellent see-through clarity</td>
</tr>
<tr>
<td></td>
<td>➔ High print quality</td>
</tr>
</tbody>
</table>

*Utilizing mPE resins in coextruded films leads to improved film structures which maximize value both to the converter and his customers.*
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Data contained in all graphs and figures are from tests performed by or on behalf of ExxonMobil Chemical