Fundamentals and Applications of Metallocene Polyethylene

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Polyethylene – Simple yet complex

Polyethylene is composed of only carbon and hydrogen (with some exceptions), which can be combined in number of ways to make many different types of polyethylenes.
The Beautiful Complexity of Carbon and Hydrogen

RPI Molecularium
http://www.molecularium.com/
Polyethylene – Key innovations timeline

- **1939**: HP-LDPE
- **1955**: HDPE Z-N & Chrome
- **1978**: LLDPE Z-N (Multi-Site; heterogeneous)
- **1992**: Metalloocene & Post-metalloocene (Single-site; homogeneous) POP/POE mLLDPE
- **2006**: Post-metalloocene catalyzed Olefin Block Copolymer (OBC)
- **??**: NEXT BIG THING
I just want to say one word to you. just one word.
- “Metallocene”
History of metallocene (homogeneous) polyethylene

- Metalloocene catalyst for ethylene polymerization first described - 1957
- Elston (DuPont) homogeneous PE patent (US #3,645,992 – using V catalyst) – 1972
- Catalyst breakthrough by Prof. Walter Kaminsky and his group (MAO as an activator) to significantly improve catalyst efficiency - 1980
- Dow and ExxonMobil led commercialization of homogeneous PE using Substituted mono-cyclopentadienyl catalyst (Constrained Geometry Catalyst) and di-cyclopentadienyl (BisCp) catalyst, respectively – 1991-1993
  - Polyolefins Plastomers (POP) and Polyolefins Elastomers (POE)
- Dow, ExxonMobil and Chevron-Phillips led commercialization of metallocene/post-metallocene (single-site) catalyst based mLLDPE in late 1990’s.
Key processes to make single-site catalyzed polyethylenes

- Solution
- Gas Phase
- Slurry
Solution process - simplified

UNIPOL gas-phase process

**Fig. 20.** Schematic of UNIPOL gas-phase polymerization process.

* Simpson and Vaughan – “Ethylene Polymers, LLDPE” - Encyclopedia of Polymer Science and Technology
**Slurry-phase process**

![Diagram of Slurry-phase Polymerization Process]

**Fig. 22.** Schematic of slurry-phase polymerization process.

* Simpson and Vaughan – “Ethylene Polymers, LLDPE” - Encyclopedia of Polymer Science and Technology
**Multi-site vs. single-site catalysts**

**Ziegler-Natta and Chromium Catalysts (Multi-site)**
- Different types of reaction sites on each catalyst particle (heterogeneous)
- Broad molecular weights and comonomer distributions

**Metalloocene Catalysts (Single-site)**
- Single, consistent reaction sites (homogeneous)
- Narrow molecular weights and comonomer distribution

Traditional LLDPE/VLDPE are made using multi-Site catalyst (Z-N)
Polyolefin Plastomers/Elastomers and mLLDPE are made using single-site (metalloocene & post-metalloocene) catalyst
Structural differences between LDPE, Z-N LLDPE and Single-site catalyzed LLDPE*  

* Simpson and Vaughan – “Ethylene Polymers, LLDPE” - Encyclopedia of Polymer Science and Technology
GPC Molecular Weight Distribution (MWD)

*Homogeneous (single-site catalyzed)* vs. Heterogeneous (Z-N catalyzed)

Mw = 73,800, Mn = 37,400, MWD = 1.97

Mw = 124,600, Mn = 33,200, MWD = 3.75
Short Chain Branching (Composition) Distribution

*Homogeneous (single-site catalyzed) vs. Heterogeneous (Z-N catalyzed)*
DSC Melting Endotherms

Cooled and Heated at 10 °C/min

Heat Flow (Watts/gm)

Temperatures:
- 112 °C
- 122 °C

Heat of Fusion (J/gm): 292 (J/gm)

% Cryst. = \frac{\text{Heat of Fusion (J/gm)}}{X 100}

SSC, 0.92 g/cc
Z-N, 0.92 g/cc

Perkin-Elmer DSC-7
Why metallocene PE was a revolution?

- Ideal molecular structure (narrow MWD, narrow composition distribution)
- Low $T_m$ & hexane extractable for food packaging applications (sealant)
- High hot-tack vs. EVA (Sealant)
- Improved thermal/UV stability vs. EVA
- Ability to make ethylene copolymers ($C_4$-$C_8$) below 0.885 g/cc
- Ethylene-based elastomer in pellet form vs. EPDM bales
- Excellent dart impact and puncture vs. Z-N LLDPE
- Excellent optics vs. Z-N LLDPE
Polyolefin Plastomer (POP) and Elastomer (POE)

- POP - 0.910 g/cc to 0.885 g/cc
- POE - 0.885 g/cc to 0.857 g/cc

- Attributes of POP and POE
  - Better Optical Properties (Clarity, Haze & Gloss)
  - Lower $T_m$ and Heat Seal Temperature
  - Better Hot Tack (compared to EVA)
  - Very low modulus and Tg (POE)
  - Better Elastic Properties (POE)
Key applications of Polyolefins Plastomers (POP) and Elastomers (POE)

- **Sealants**
  - Excellent hot-tack strength (VFFS) and low seal temperatures for faster packaging line speeds

- **Breathable food packaging**
  - fresh cut produce (high OTR)

- **Impact modification of polypropylene**
  - Elastomers @ ~ 0.87 g/cc (low temp., ~ -30°C impact application of PP)

- **Hot melt adhesive (HMA)**

- **Molded soft goods**

- **Photovoltaic encapsulant Films**

- **Elastic laminates**
AFFINITY™ High Performance Sealants
Sealants – Mechanism & performance requirements

- Low seal initiation temperature (SIT)/High heat seal strength
- High hot-tack strength/Broad hot-tack window
- Good caulkability to give hermetic seals
- Excellent taste & odor properties

Stehling & Meka, JAPS, 51, 105 (1994)
DSC Melting Endotherms

Heat Flow (Watts/gm)

SSC, 0.92 g/cc
SSC, 0.902 g/cc
SSC, 0.908 g/cc
SSC, 0.896 g/cc
LLDPE, 0.92 g/cc
VLDPE, 0.905 g/cc

Temperature (oC)
Melting Peak vs. Density

Melting Peak Temp. (°C)

SSC (Homogeneous) & LLDPE/VLDPE (Heterogeneous) RESINS

Heterogeneous

Homogeneous (SSC)

DENSITY (g/cc)
DSC of Homogeneous (AFFINITY™ POP) vs. Heterogeneous (ATTANE™ VLDPE) PE

- Significantly lower $T_m$ at similar density
- Explains why Plastomer is a better sealant than Z-N VLDPE

AFFINITY PL 1880
0.902 g/cc

ATTANE 4203
0.905 g/cc

$T_m = 98 \, ^\circ C$

$T_m = 123 \, ^\circ C$

Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow
Plastomers have excellent hot-tack strength compared to EVA, i.e. for VFFS applications. Enables improved package integrity and efficiency.
Keys to commercial success

- Compelling value propositions across the value chain

  - Co-packers/Brand Owners: Faster packaging line speeds (reduced pkg cost)

  - Brand Owners: Improved organoleptics and improved package integrity. Ability to make large/heavy package due to improved hot-tack strength
mLLDPE For Packaging Applications
What’s Driving Today’s Packaging Market?

**Brand Owners**
- More sustainable packaging
- Lighter weight
- On-the-go lifestyles
- Single-serve packaging
- Cost-effective

**Converters**
- Down-gauging
- Tougher films
- Processability
- Reduced Equipment Fouling

**OEMs**
- Faster running equipment
- Efficiencies
<table>
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<tr>
<th>Property</th>
<th>ASTM Test method</th>
<th>LDPE</th>
<th>C₄ LLDPE</th>
<th>C₆ LLDPE</th>
<th>C₆ mLLDPE</th>
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<td>Melt index $I_2$, g/10 min</td>
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<td>Density, g/cm³</td>
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<td>0.919</td>
<td>0.918</td>
<td>0.917</td>
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<td>Gauge, μm</td>
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<td>25</td>
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<td>Tensile strength, MPa&lt;sup&gt;b&lt;/sup&gt;</td>
<td>D882</td>
<td>39</td>
<td>46</td>
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<tr>
<td>MD</td>
<td>D882</td>
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<td>D882</td>
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<td>201</td>
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<td>1% Secant modulus, MPa&lt;sup&gt;b&lt;/sup&gt;</td>
<td>D882</td>
<td>220</td>
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<tr>
<td>TD</td>
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<td>&gt;1000</td>
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<td>Gloss, 45°</td>
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<sup>a</sup>Films made at 1.8-kg/cm die circumference/h [10 lb/(hr-in.)] output rate, 2.5:1 BUR. 1.5-mm (60-mil) die gap used for LLDPE and mLLDPE, 0.76-mm (30-mil) die gap used for LDPE.

<sup>b</sup>To convert MPa to psi, multiply by 145.

* Simpson and Vaughan – “Ethylene Polymers, LLDPE” - Encyclopedia of Polymer Science and Technology
Fig. 23. Melt viscosity data for LDPE, LLDPE, and mLLDPE all normalized to 1 g/10 min melt index. Also shown is new type of easy-processing metallocene-catalyzed polyethylene, mPE*. To convert Pa·s to P, multiply by 10.

* Simpson and Vaughan – “Ethylene Polymers, LLDPE” - Encyclopedia of Polymer Science and Technology
INNATE® - Improved Processability

- Better melt strength for improved processability and output rates vs. competitive mLLDPE (1 MI, 0.918 d)
- More shear thinning for lower melt temperatures, amps & back pressures
Stiffness-toughness balance

Toughness

Stiffness
INNATE® - Unprecedented Toughness Performance (1 mil film)

INNATE™ ST50 (0.85 MI, 0.918 d) delivers significantly higher dart performance at similar modulus vs. competitive mLLDPE grade (1 MI, 0.918 d).
ENGAGE™ Polyolefin Elastomer (POE) for Impact Modification of Polypropylene (TPO)
Impact modification of polypropylene (TPO) using ENGAGE POE

**TYPICAL HARD TPO**

- 65-85% Polypropylene (h-PP, ICP, R-TPO)
- 15-35% Elastomer
- Talc up to about 30%
- Performance Additives (UV, AO, Scratch&Mar, etc.)
- Generally Injection Molded

**TYPICAL SOFT TPO**

- Over 50% Elastomer
- Polypropylene & Other Additives (Cost/Performance)
- Both Molded and Extruded

Fascia / Claddings

Interiors / Consoles

Soft TPO - Panel skins, Flooring, NVH
Impact modification of polypropylene (TPO) using ENGAGE POE

- Excellent dispersion in continuous compounding to make TPO (due to POE in free flowing pellet form)
- Excellent low temperature impact due to low glass transition temperature of POE (Tg ~ -55°C by DSC)
- Excellent balance of stiffness and low temperature impact for TPO
- Displaced EPDM as modifier of choice for Automotive TPOs
- Many uses in durable applications

**Society Benefit** – Light weighting of cars for improved mileage efficiency.
Impact modification of polypropylene (TPO) using ENGAGE POE

**BLEND = 70% PP + 30% Elastomer**

- **Polypropylene Melt Flow Rate (g/10min.)**
- **-30°C Impact Energy (Joules)**

**POEs give balance of**
- stiffness
- low temp toughness
- processability
- dimensional stability
Keys to commercial success

- Compelling value propositions across the value chain
  - Compounders: Ease of compounding using ENGAGE POE (pellets) vs. EPDM (bales/crumbs)
  - Molders: Improved processability
  - OEM: Improved stiffness/toughness balance for lightweighting.
AFFINITY™ GA for Hot Melt Adhesives (HMA)
Typical formulation for hot melt adhesive (HMA)

- **Polymer ~35%**
  - Strength
  - Low Temp Performance

- **Tackifier ~45%**
  - Lowers Viscosity
  - Increase and Broaden Tg

- **Wax ~25%**
  - Lowers Viscosity
  - Fast Set-up Time
Hot melt adhesives (HMA) based on AFFINITY GA

Hot melt adhesives based on AFFINITY™ GA offer *improved adhesive performance, application, and total cost (vs. EVA based).*

**Application**
- Low odor / smoke from melt tanks
- Improved stability/reduce char in hoses/modules
- No angel hair/stringing
- Broad service temperature range (low Tg)
- Improved viscosity stability

**Lower Total Cost**
- Improved overall mileage as compared with EVA (lower density)
- Lower overall maintenance cost.
- Reduced downtime due to much less nozzle plugging.
AFFINITY™ GA vs EVA – Viscosity stability & glass transition temperature

- Long pot life, No char/odor
- Broad service temperature range – from -40°C to 70°C
Hot melt adhesive – Total system cost

Adhesive Price / lb

- Maintenance Costs
- Parts Costs
- Line Downtime Costs
- Cost of Low Mileage
- Cost of Low Yield
- Cost of Field Failures

HMA based on AFFINITY GA - Total Cost Savings of 30 - 50% vs. HMA based on EVA
Keys to commercial success

- Technical: Polarity does not matter for adhesion to paper (adhesion via mechanical interlocking)

- Partnership with HMA supplier to accelerate development and commercialization

- Reduced total system cost of HMA for various applications
INFUSE™ Olefin Block Copolymer (OBC)
Random vs. Block copolymer structures

Random Copolymers

- Adding more comonomer lowers the polymer’s density and crystallinity while increasing flexibility.
- However, the melt temperature, crystallization temperature, and heat resistance also drop as density is lowered.

Block Copolymers

- OBCs use same raw materials arranged into alternating “soft” and “hard” blocks.
- The soft blocks deliver flexibility and the hard blocks deliver heat resistance.
- The customer gets flexibility similar to random copolymers (e.g. ENGAGE™ POEs) but with improved heat resistance, elastic recovery, compression set, and cycle times.
Catalytic block technology

Catalyst 1

Readily incorporates available comonomer: “soft” ethylene-octene copolymer

Chain Shuttling Agent

“CSA”

Hard/Soft multi-block copolymer!

Catalyst 2

Incorporates little of the available comonomer: “hard” high density PE

Dow Shuttling System

- Coupled, reversible chain transfer between 2 different catalysts
- High catalyst efficiency
- Compatible with a wide variety of monomers
INFUSE OBCs exhibit unique properties versus polyolefin elastomers (POE) including:

- Outstanding flexibility-high temperature resistance balance
- Fast set-up in processing (shorter cycle time)
- Excellent elastic recovery properties
- Good compression set performance at room and elevated temperatures
- Improved abrasion resistance
Elastic performance of OBC elastomers

0.865 g/cc OBC has comparable elastic properties as SEBS
Dynamic set after testing @ 40°C - EVA, POE and OBC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dynamic set (1 min after test)</th>
<th>Dynamic set (1 wk after test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA</td>
<td>51.6%</td>
<td>51.6%</td>
</tr>
<tr>
<td>OBC</td>
<td>56.1%</td>
<td>11.0%</td>
</tr>
<tr>
<td>POE</td>
<td>56.7%</td>
<td>51.8%</td>
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</tbody>
</table>

100K cycles