Fundamentals and Applications of Metallocene Polyethylene

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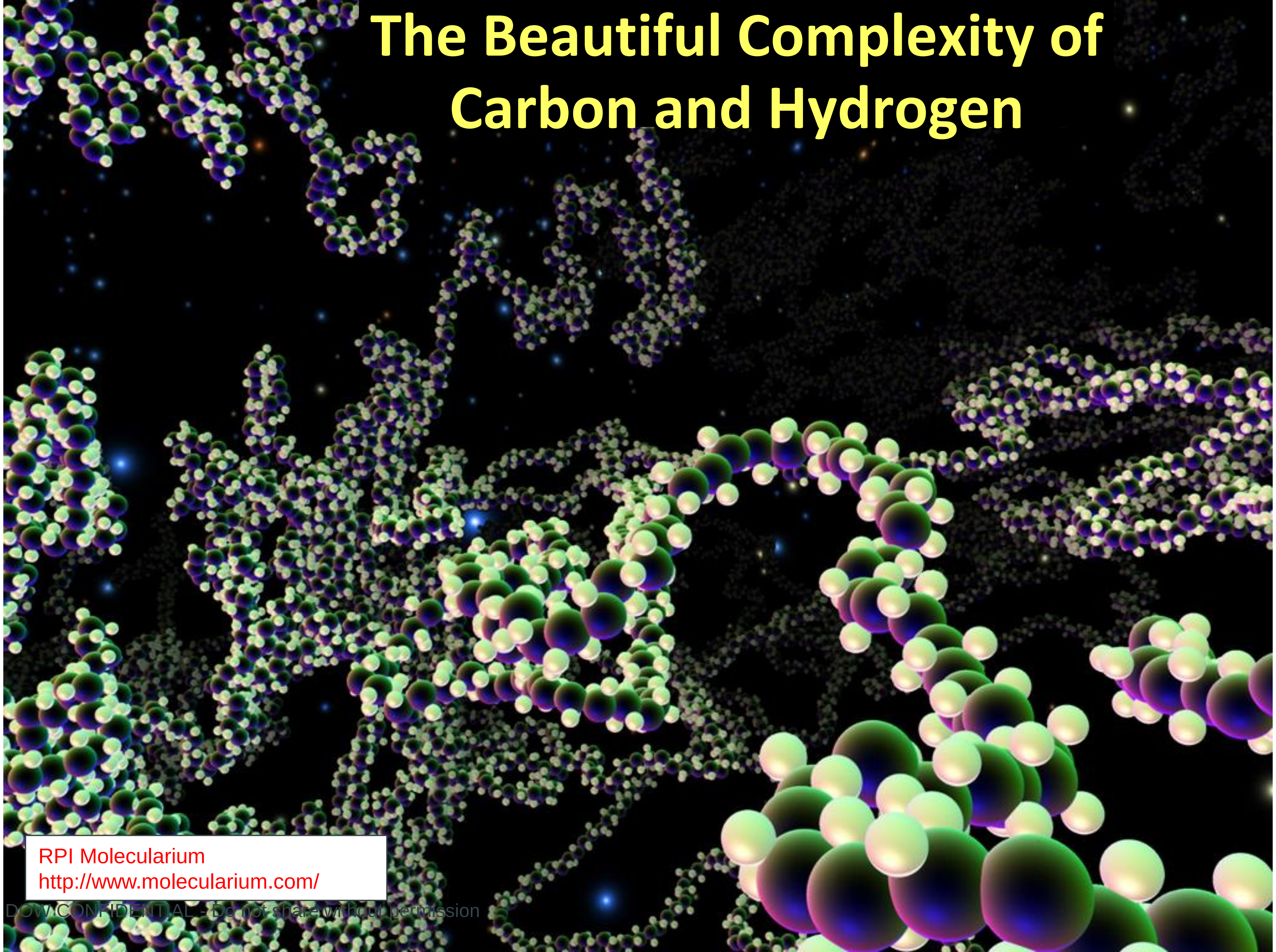
SPE Polyolefins Conference Tutorial, 2019

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
Metallocene &
Post-metallocene
(Single-site;
homogeneous)
POP/POE
mLLDPE

2006
Post-metallocene
catalyzed
Olefin Block
Copolymer
(OBC)

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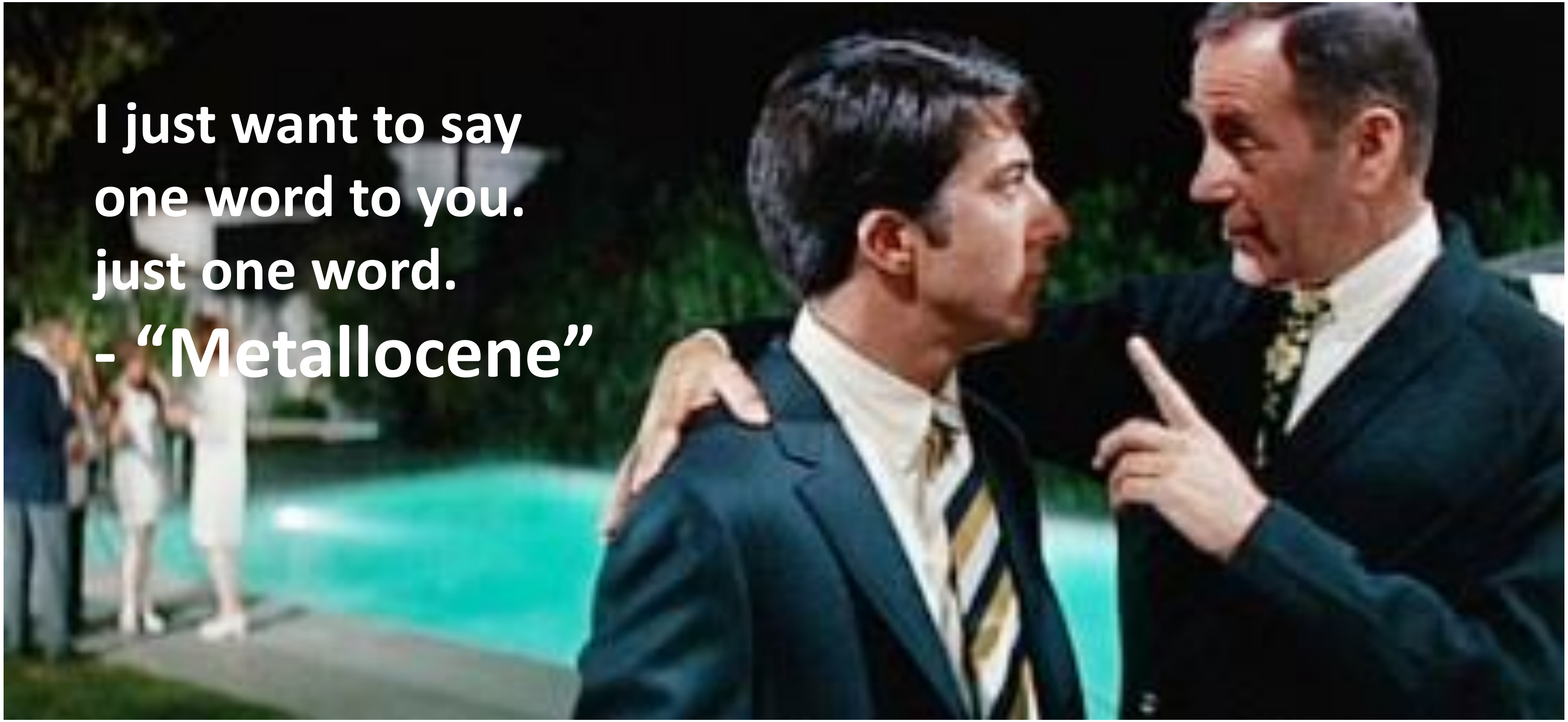

I just want to say
one word to you.
just one word.
- "Metallocene"

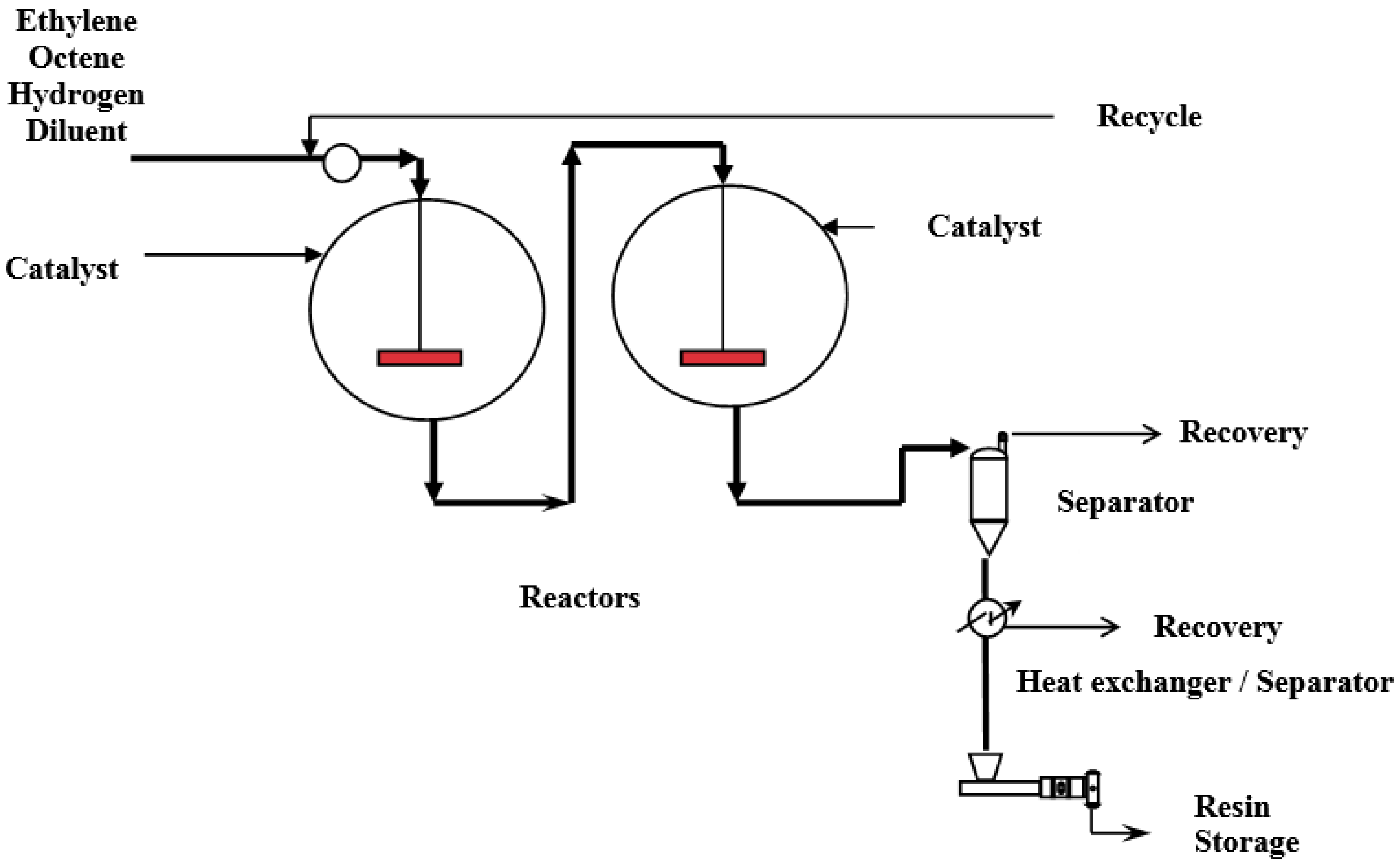
History of metallocene (homogeneous) polyethylene

- Metallocene 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



* Patel – "Chapter 2 - Polyethylene" – Multi-layer Flexible Packaging Book - Elsevier (2016)

UNIPOL gas-phase process

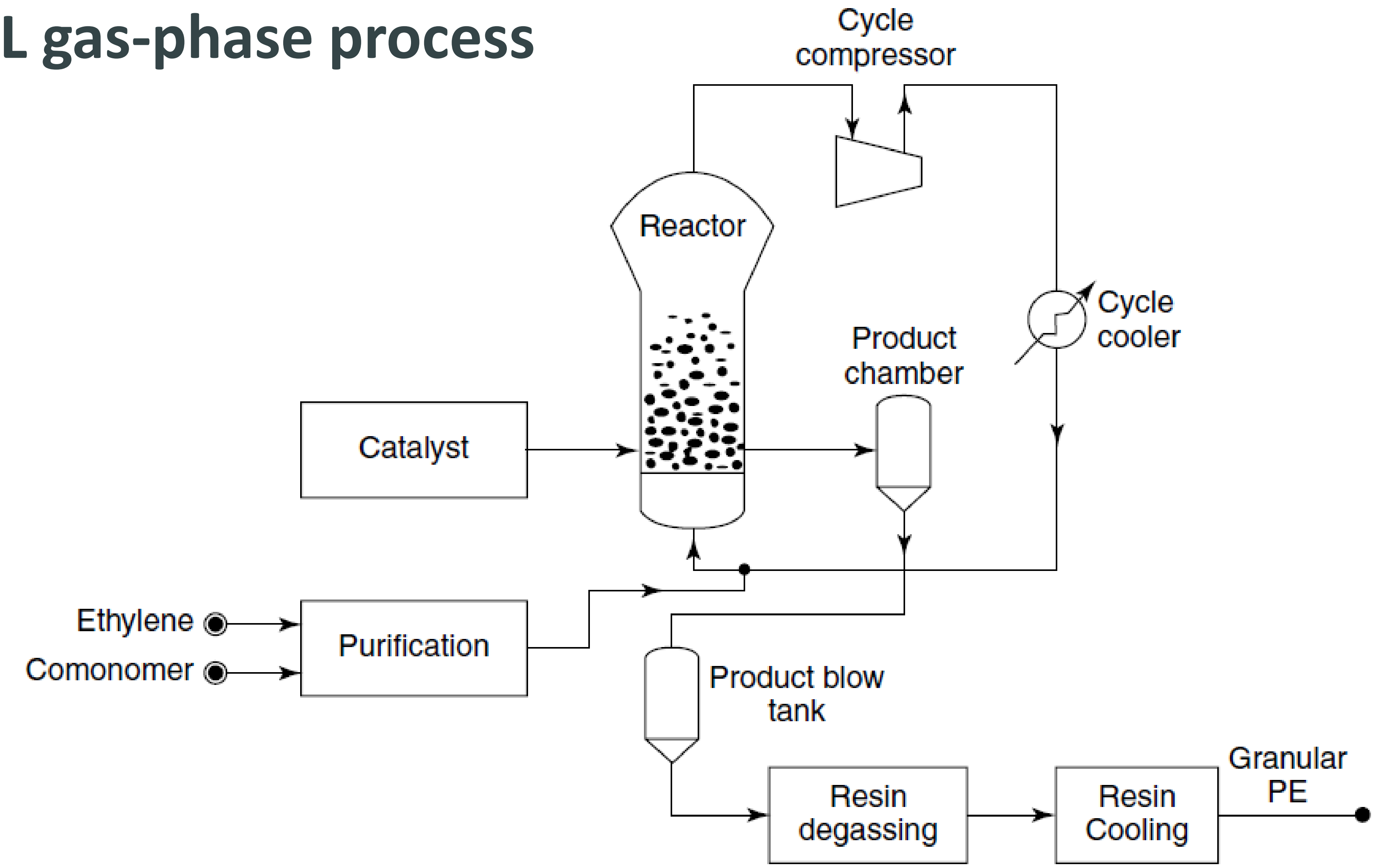


Fig. 20. Schematic of UNIPOL gas-phase polymerization process.

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

Slurry-phase process

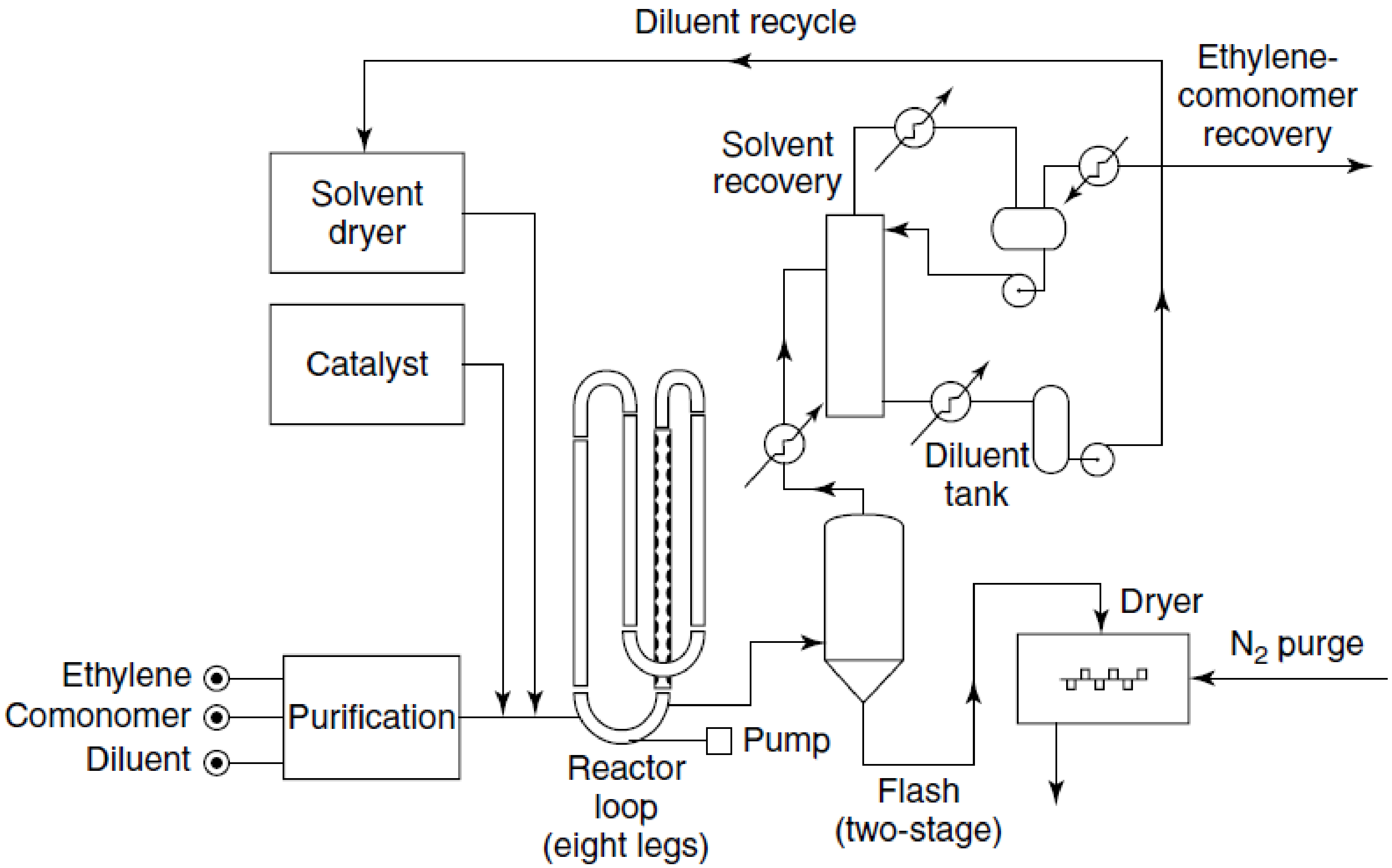


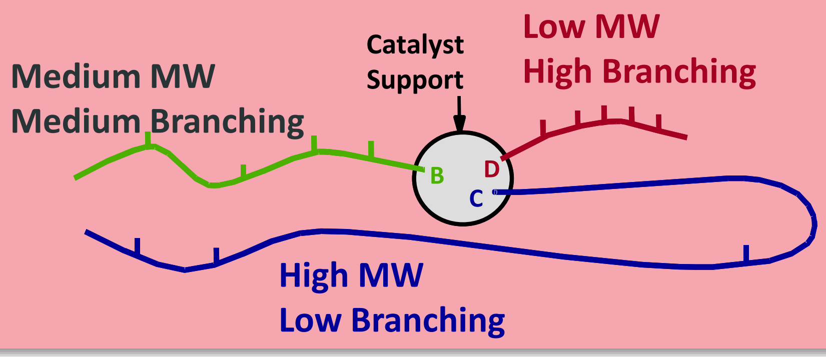
Fig. 22. Schematic of slurry-phase polymerization process.

* Simpson and Vaughan – "Ethylene Polymers, LLDPE" - Encyclopedia of Polymer Science and Technology

Multi-site vs. single-site catalysts

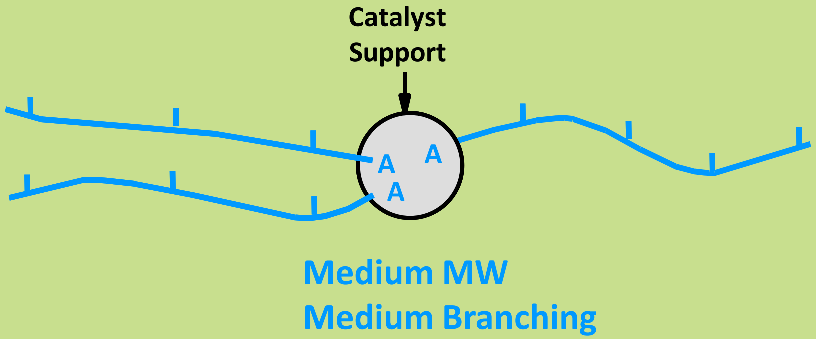
Ziegler-Natta and Chromium Catalysts (Multi-site)

- Different types of reaction sites on each catalyst particle (heterogeneous)
- Broad molecular weights and comonomer distributions



Metallocene Catalysts (Single-site)

- Single, consistent reaction sites (homogeneous)
- Narrow molecular weights and comonomer distribution

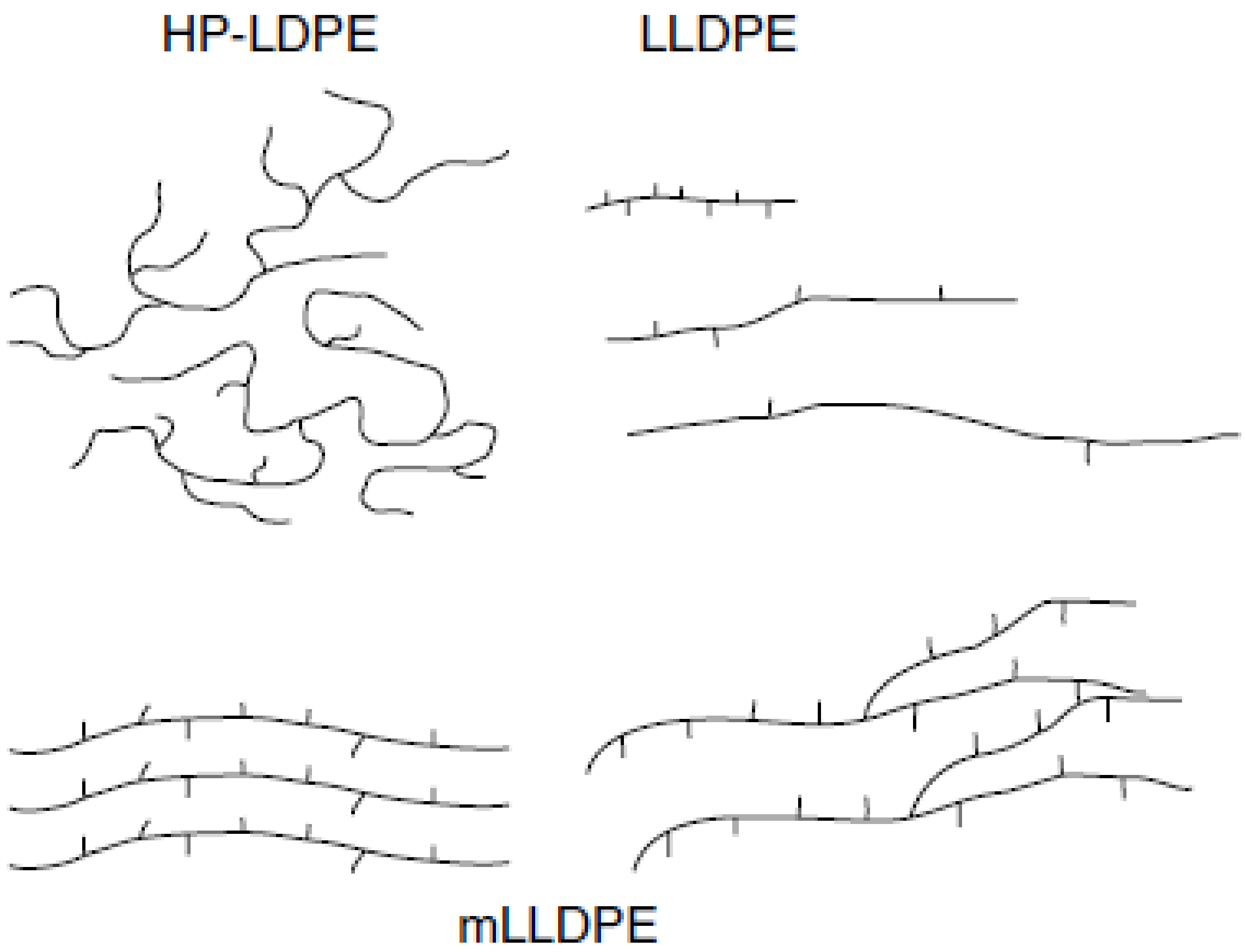


Traditional LLDPE/VLDPE are made using multi-Site catalyst (Z-N)

Polyolefin Plastomers/Elastomers and mLLDPE are made using single-site (metallocene & post-metallocene) catalyst

DOW®

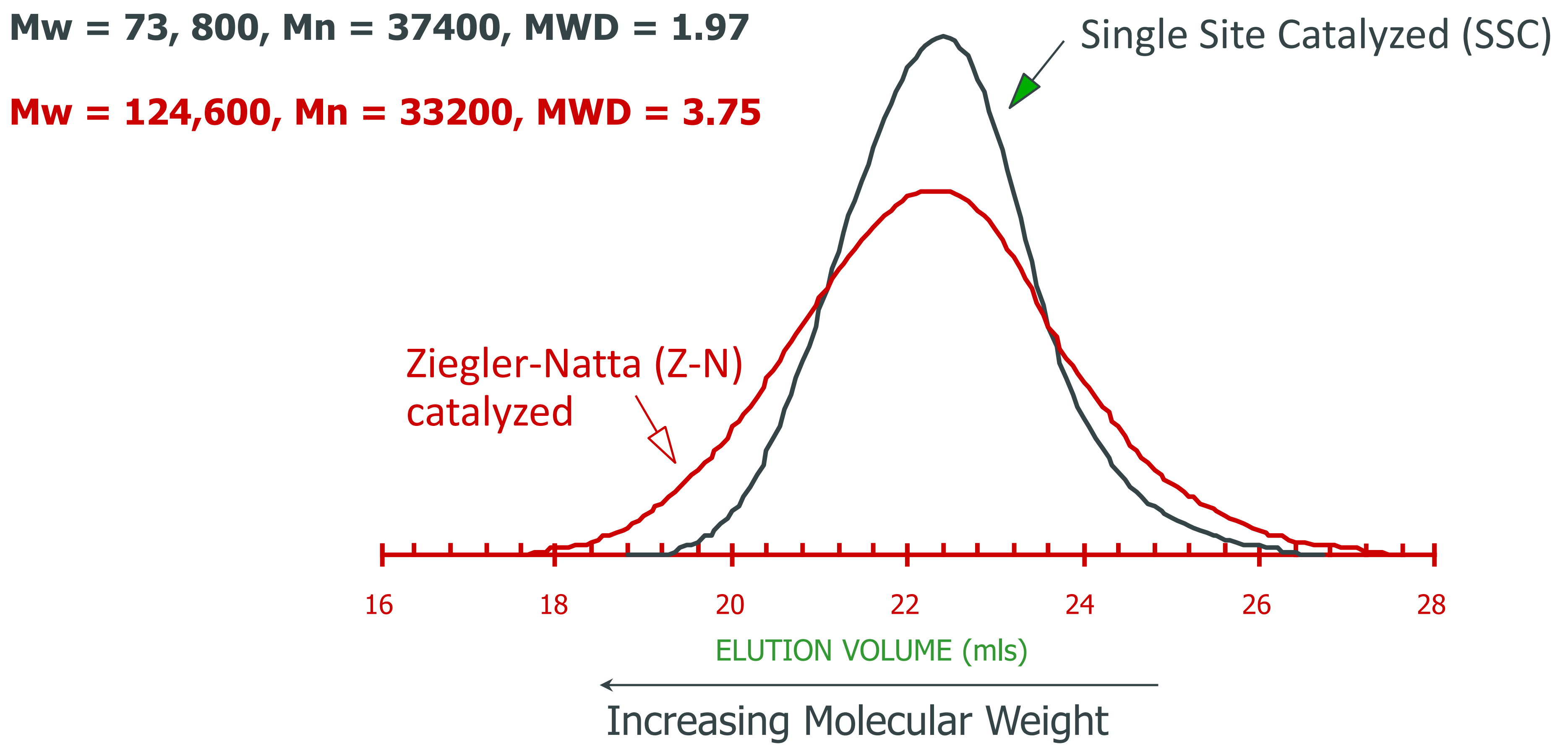
Structural differences between LDPE, Z-N LLDPE and Single-site catalyzed LLDPE*



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

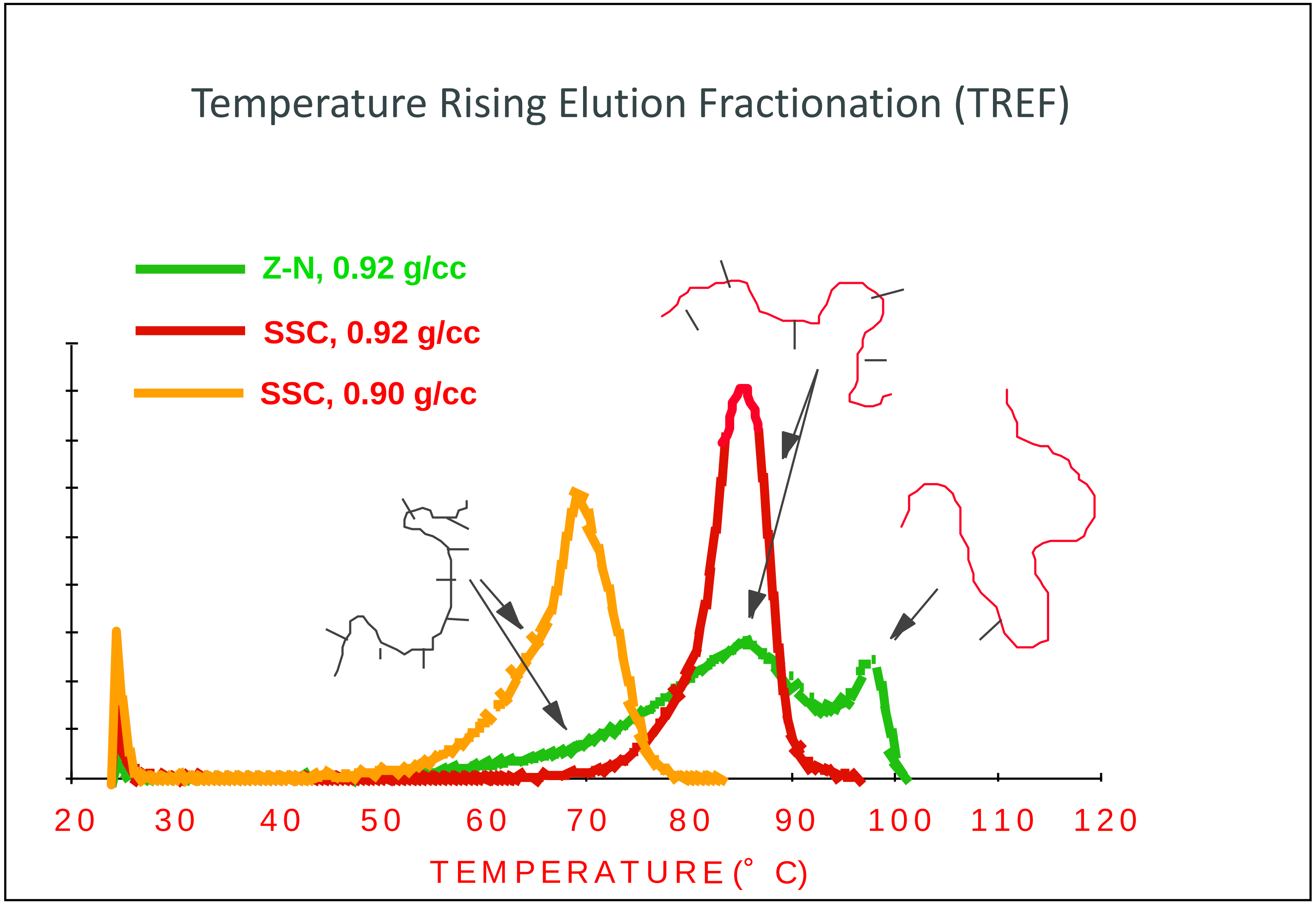
GPC Molecular Weight Distribution (MWD)

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

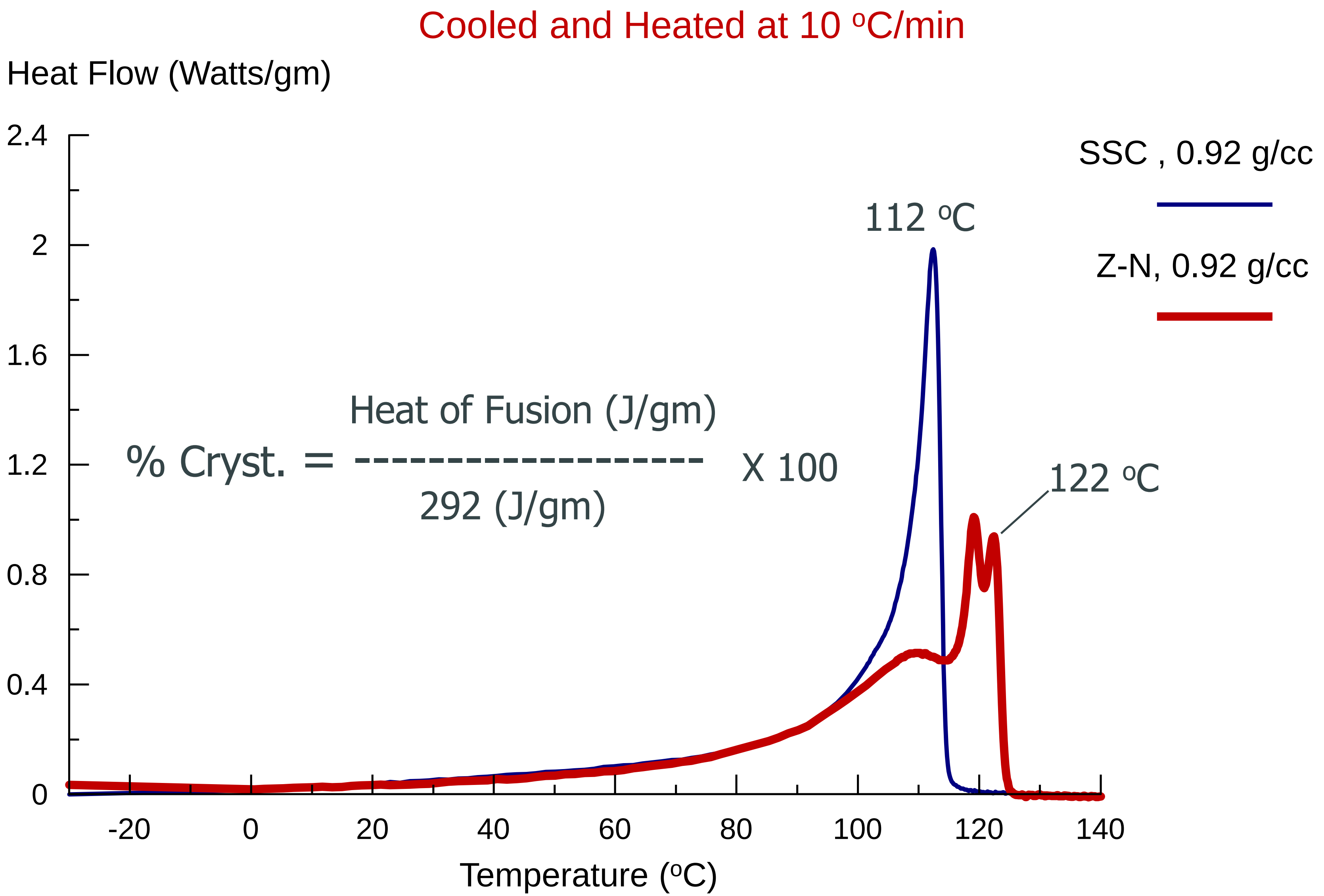


Short Chain Branching (Composition) Distribution

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



DSC Melting Endotherms



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

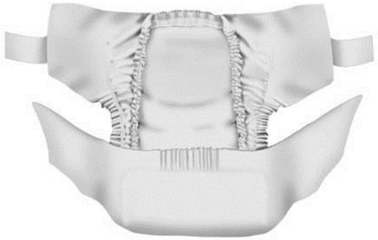
DOW®

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)

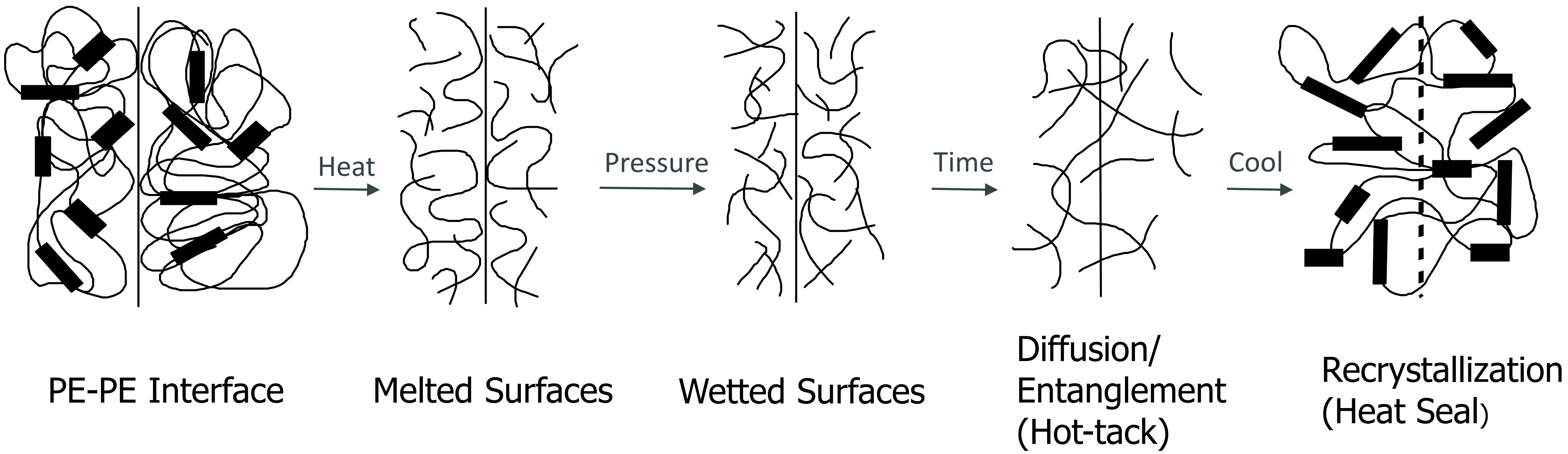
Key applications of Polyolefins Plastomers (POP) and Elastomers (POE)

- 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^{o}C impact application of PP)
- Hot melt adhesive (HMA)
- Molded soft goods
- Photovoltaic encapsulant Films
- Elastic laminates



AFFINITY™ High Performance Sealants

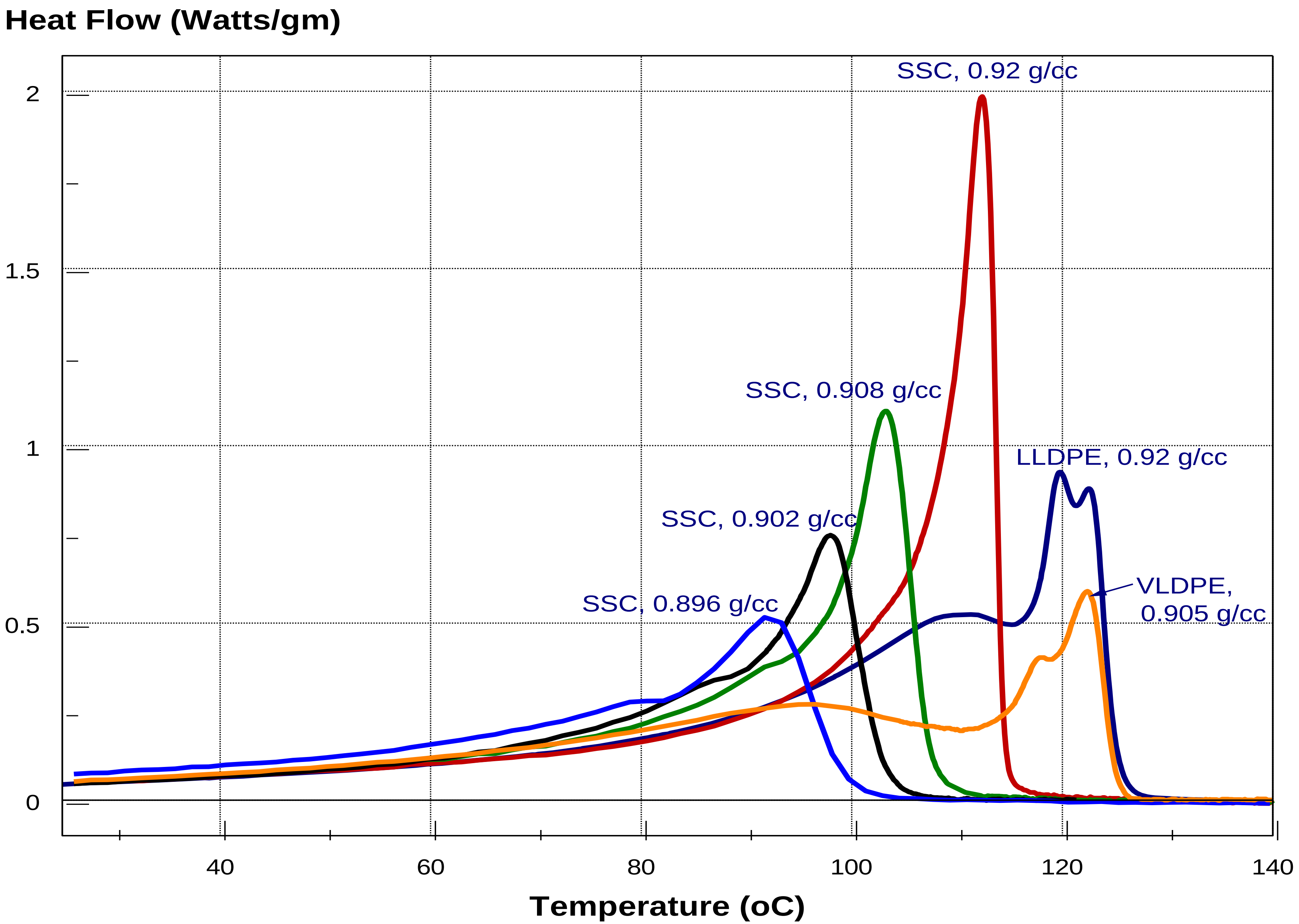
Sealants – Mechanism & performance requirements



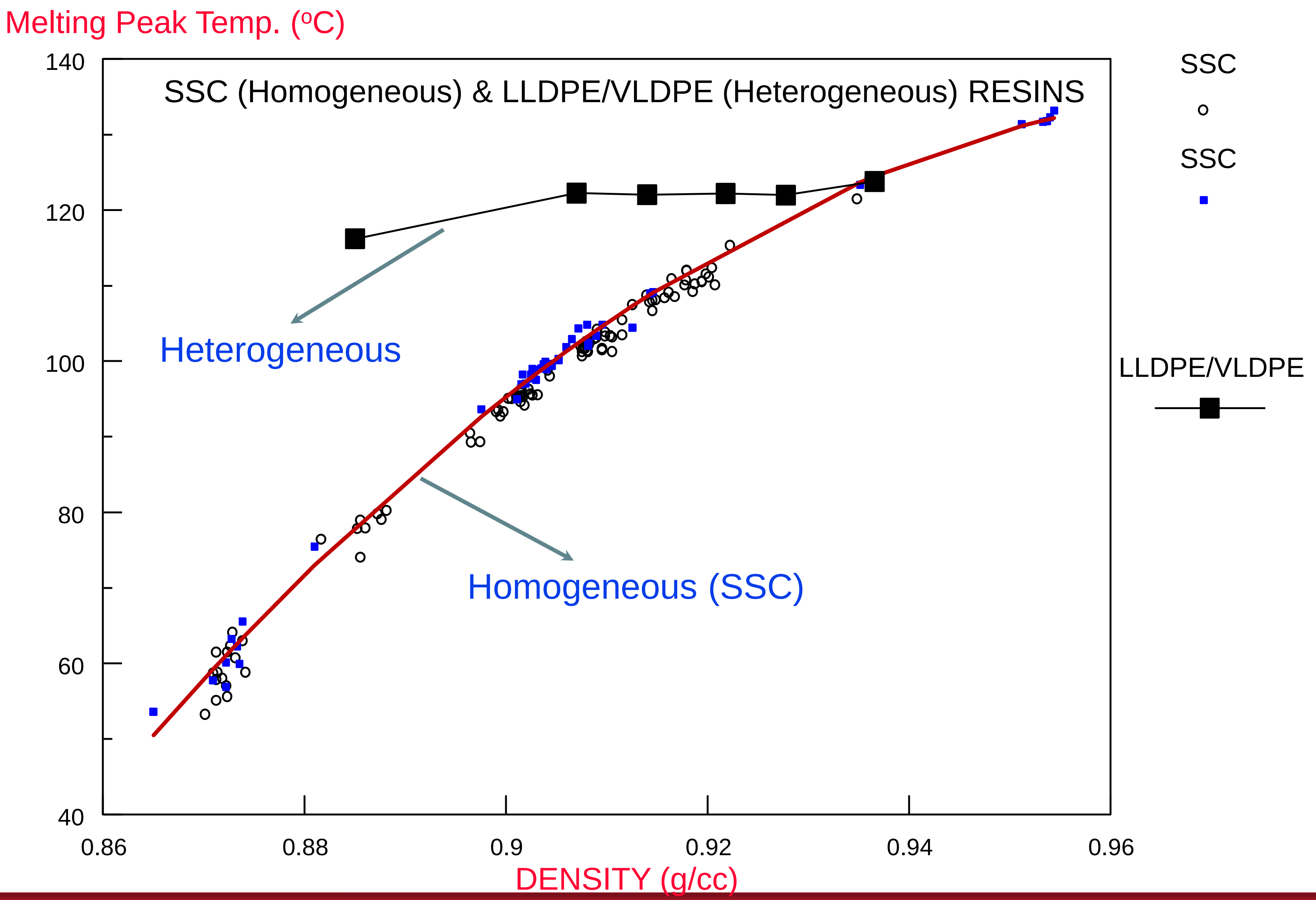
- ❑ Low seal initiation temperature (SIT)/High heat seal strength
- ❑ High hot-tack strength/Broad hot-tack window
- ❑ Good caulkability to give hermetic seals
- ❑ Excellent taste & odor properties

Stehling & Meka, JAPS, 51, 105 (1994)

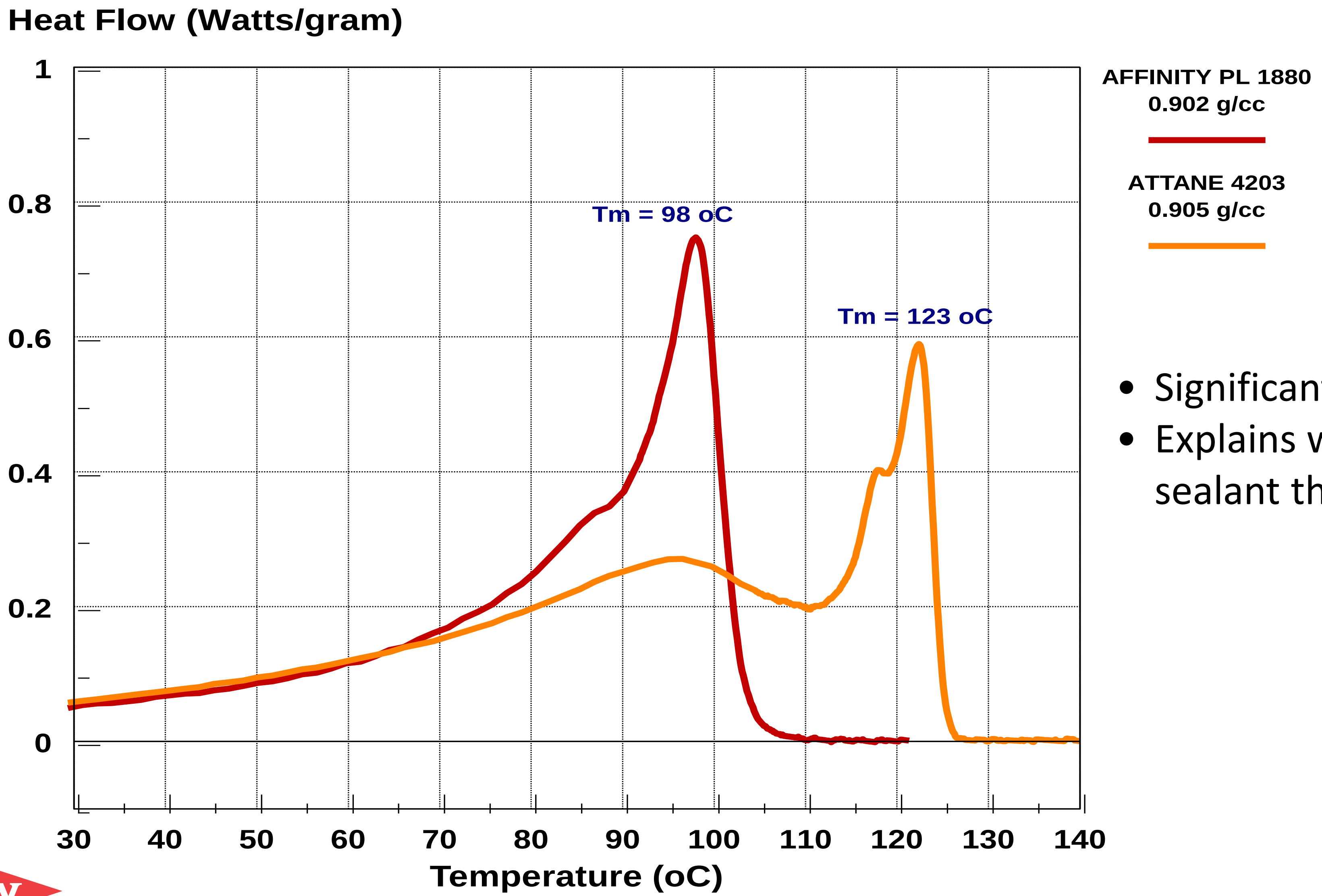
DSC Melting Endotherms



Melting Peak vs. Density

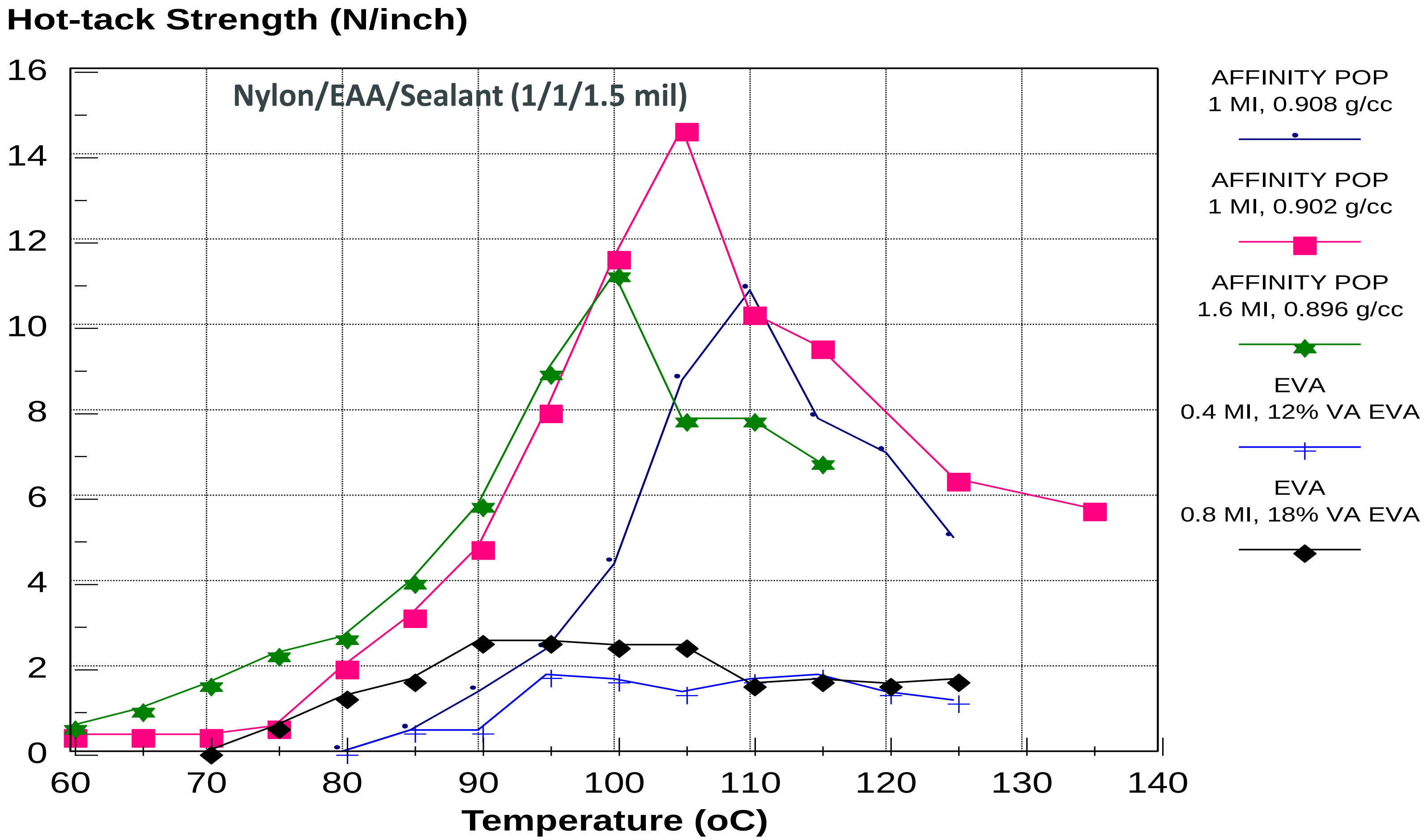


DSC of Homogeneous (AFFINITY™ POP) vs. Heterogeneous (ATTANE™ VLDPE) PE



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

Hot-tack strength of Plastomers vs. EVA



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 4. Blown Film[a] Mechanical Properties for LDPE, LLDPE, and mLLDPE

Property	ASTM Test method	LDPE	C_4 LLDPE	C_6 LLDPE	C_6 mLLDPE
Melt index I_2, g/10 min	D1238	1.0	1.0	1.0	1.0
Density, g/cm^3		0.919	0.918	0.917	0.917
Gauge, μm		25	25	20	20
Tensile strength, MPa[b]					
MD	D882	39	46	55	66
TD	D882	26	37	42	59
1% Secant modulus, MPa[b]					
MD	D882	200	201	207	173
TD	D882	220	234	228	175
Elmendorf tear, g					
MD	D1922	170	140	255	185
TD	D1922	55	400	580	280
Dart impact, g		80	100	160	>1000
Haze, %	D1003	8	12	15	12
Gloss, 45°	D2457		50	51	47

[a] 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.
[b] To convert MPa to psi, multiply by 145.

* Simpson and Vaughan – "Ethylene Polymers, LLDPE" - Encyclopedia of Polymer Science and Technology

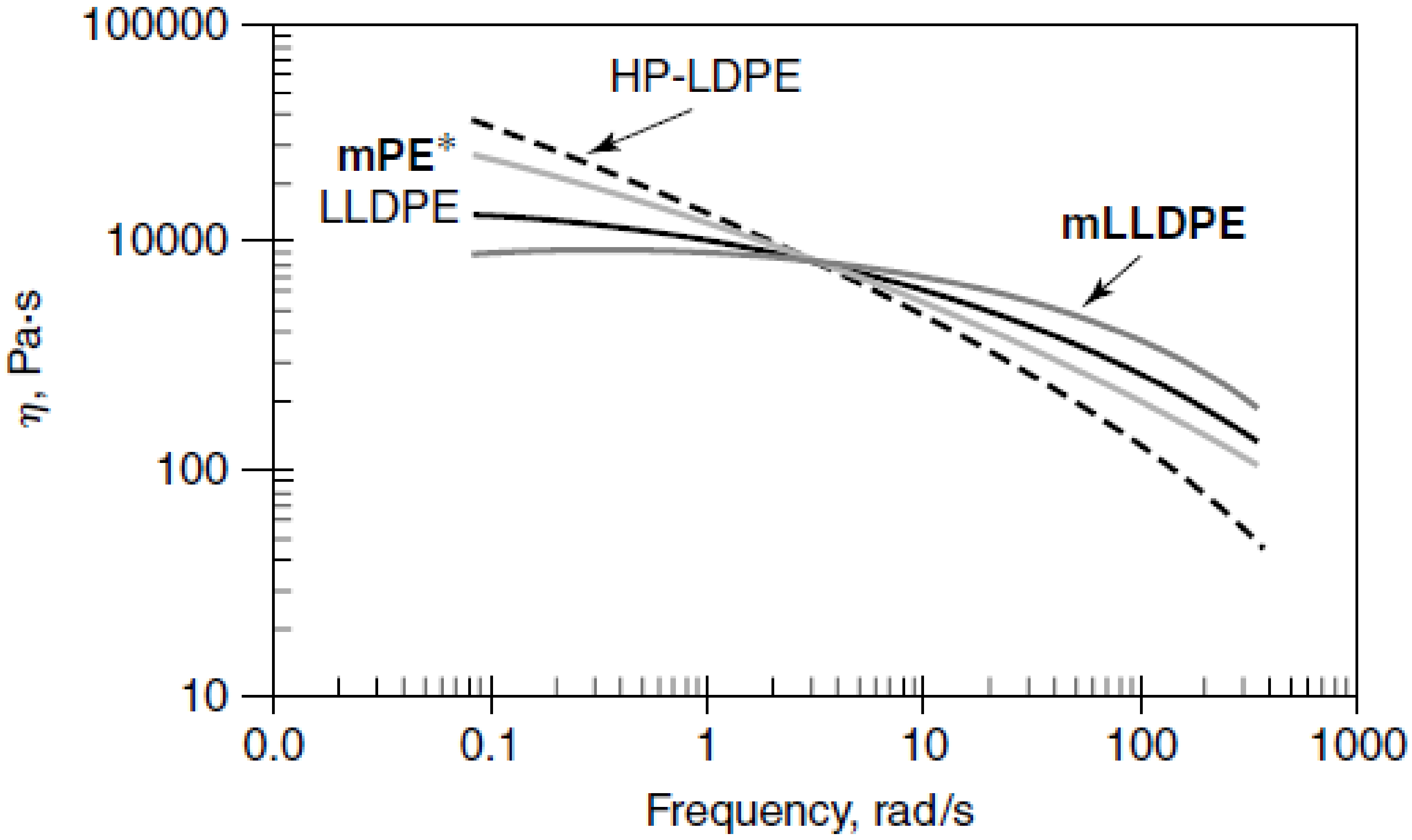
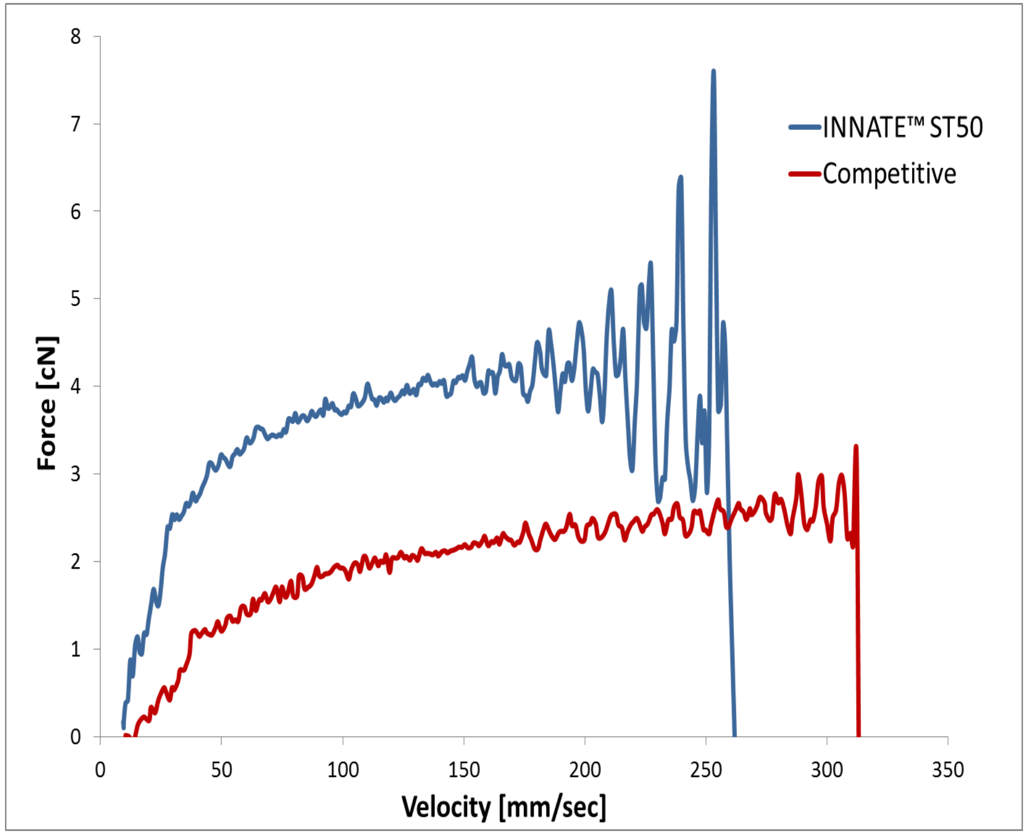


Fig. 23. Melt viscosity data for LDPE, LLDPE, and mLLDPE all normalized to1 g/10 min melt index. Also shown is new type of easy-processing metallocene-catalyzed polyethylene, mPE*. To convert Pa·s to P, multiply by 10.

* Simpson and Vaughan – "Ethylene Polymers, LLDPE" - Encyclopedia of Polymer Science and Technology

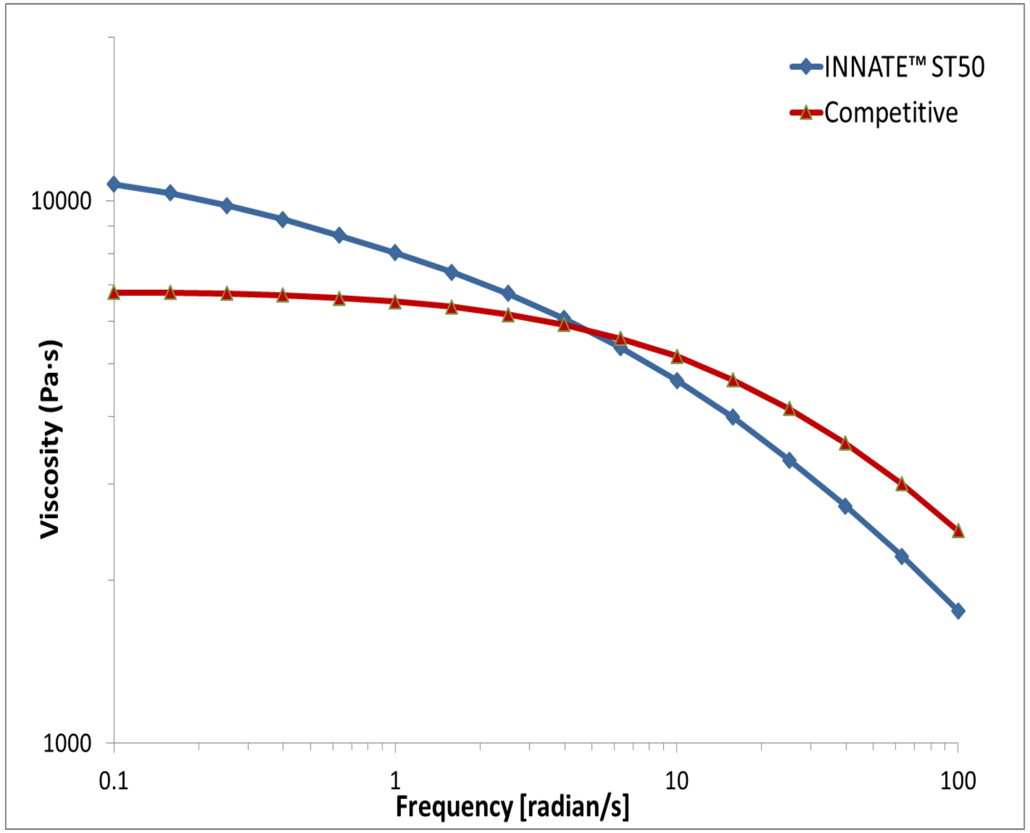
INNATE® - Improved Processability

Melt Strength



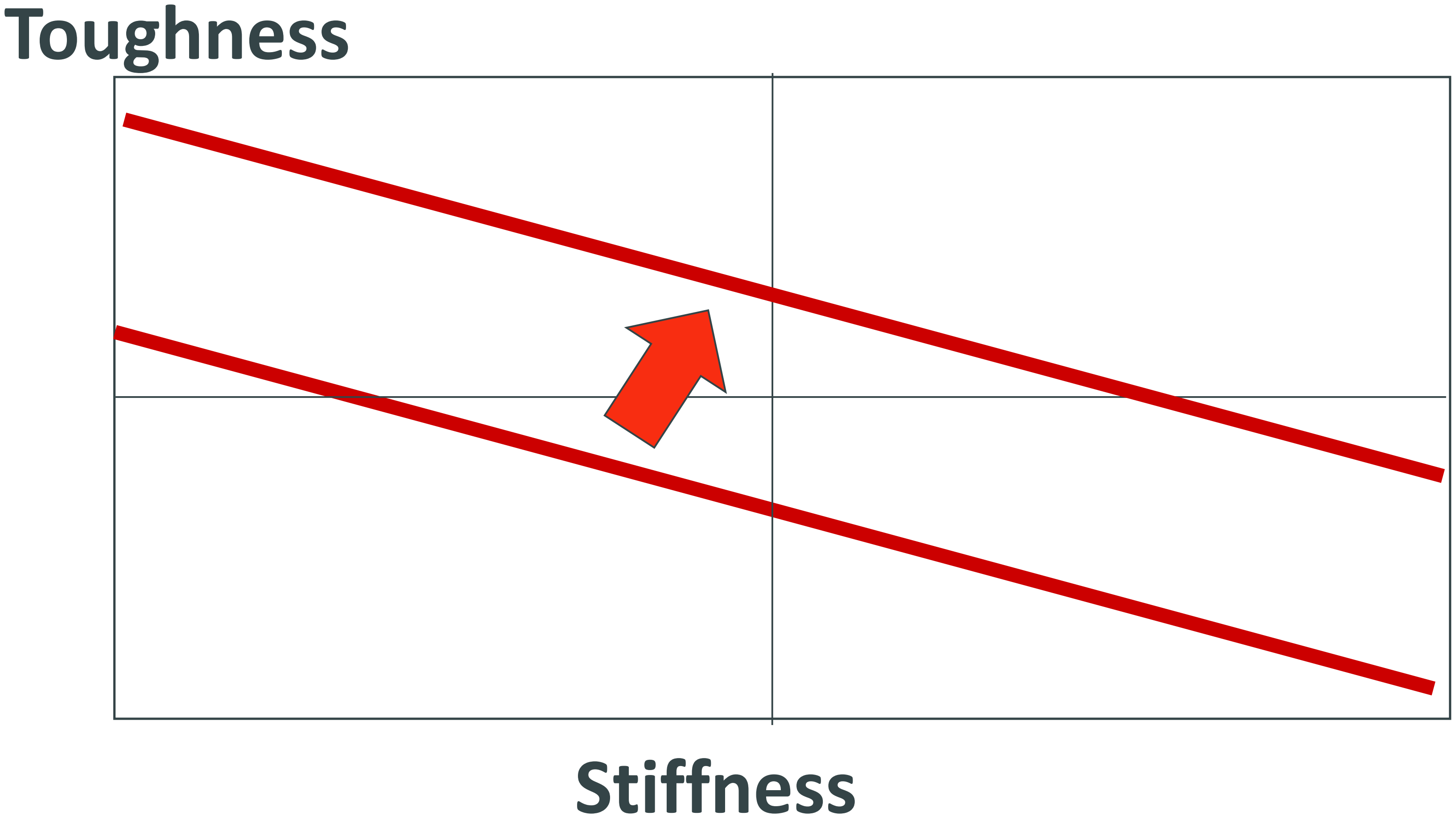
- Better melt strength for improved processability and output rates vs. competitive mLLDPE (1 MI, 0.918 d)

Viscosity



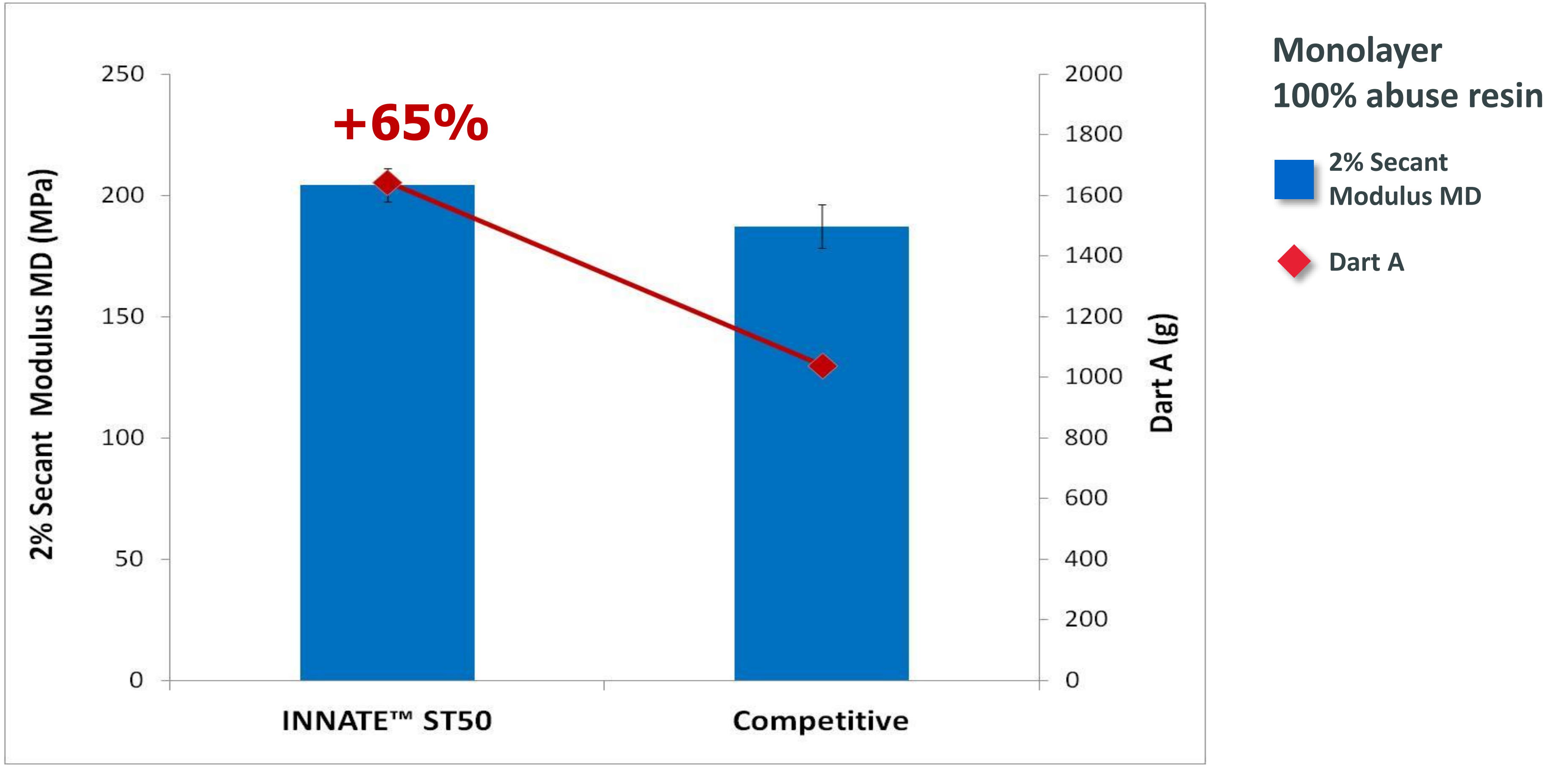
- More shear thinning for lower melt temperatures, amps & back pressures

Stiffness-toughness balance



INNATE® - Unprecedented Toughness Performance (1 mil film)

2% Secant Modulus MD and Dart A



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

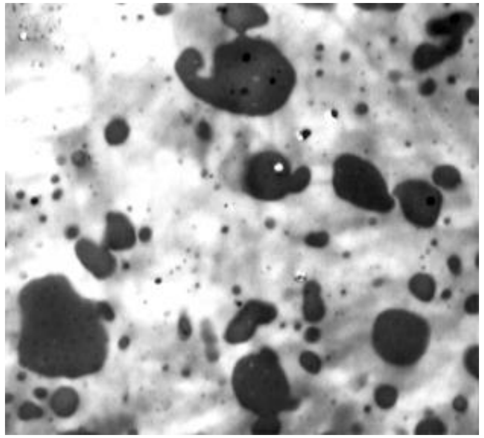
Soft TPO - Panel skins, Flooring, NVH

Impact modification of polypropylene (TPO) using ENGAGE POE

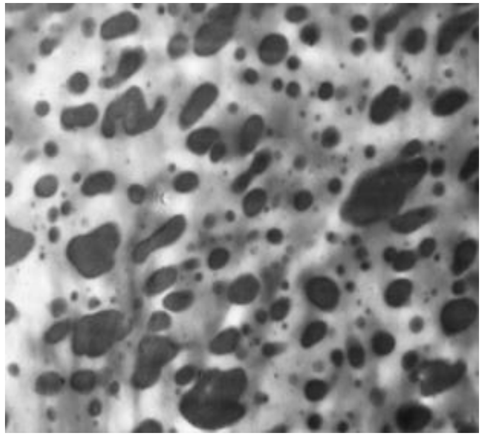
- Excellent dispersion in continuous compounding to make TPO (due to POE in free flowing pellet form)
- Excellent low temperature impact due to low glass transition temperature of POE (Tg ~ -55^{o}C by DSC)
- Excellent balance of stiffness and low temperature impact for TPO
- Displaced EPDM as modifier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

Society Benefit – Light weighting of cars for improved mileage efficiency.

EPDM

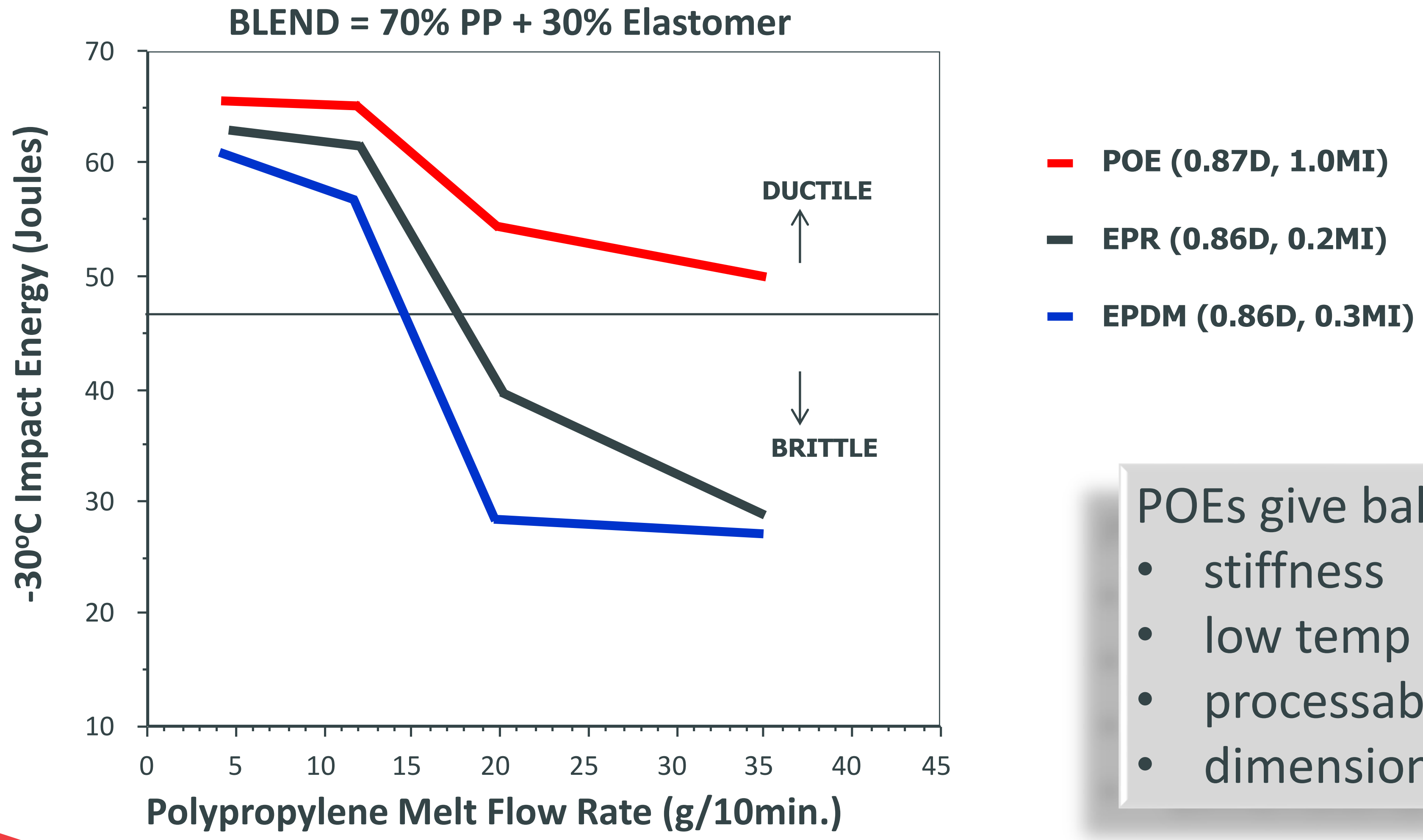


POE



(4.5 mm = 1µm)

Impact modification of polypropylene (TPO) using ENGAGE POE



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

DOW

Hot melt adhesives (HMA) based on AFFINITY GA

AFFINITY GA

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

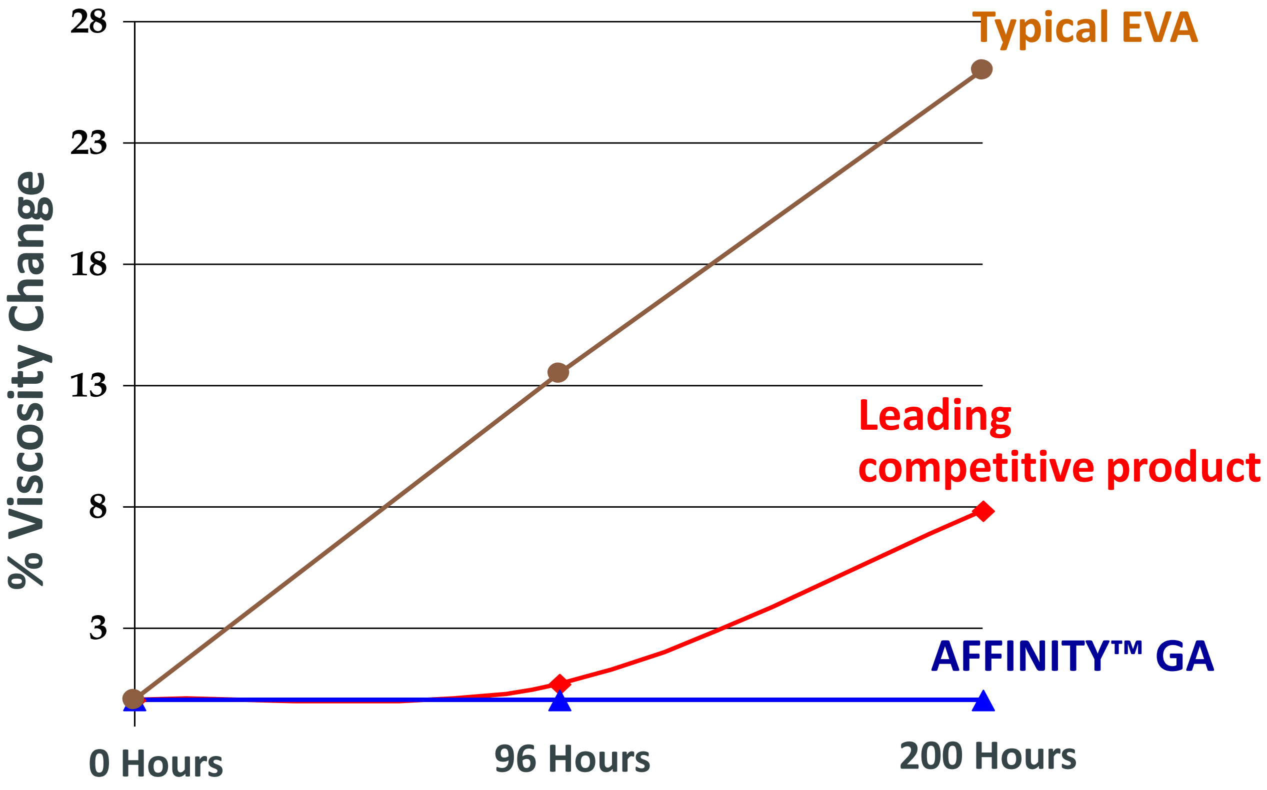
Application

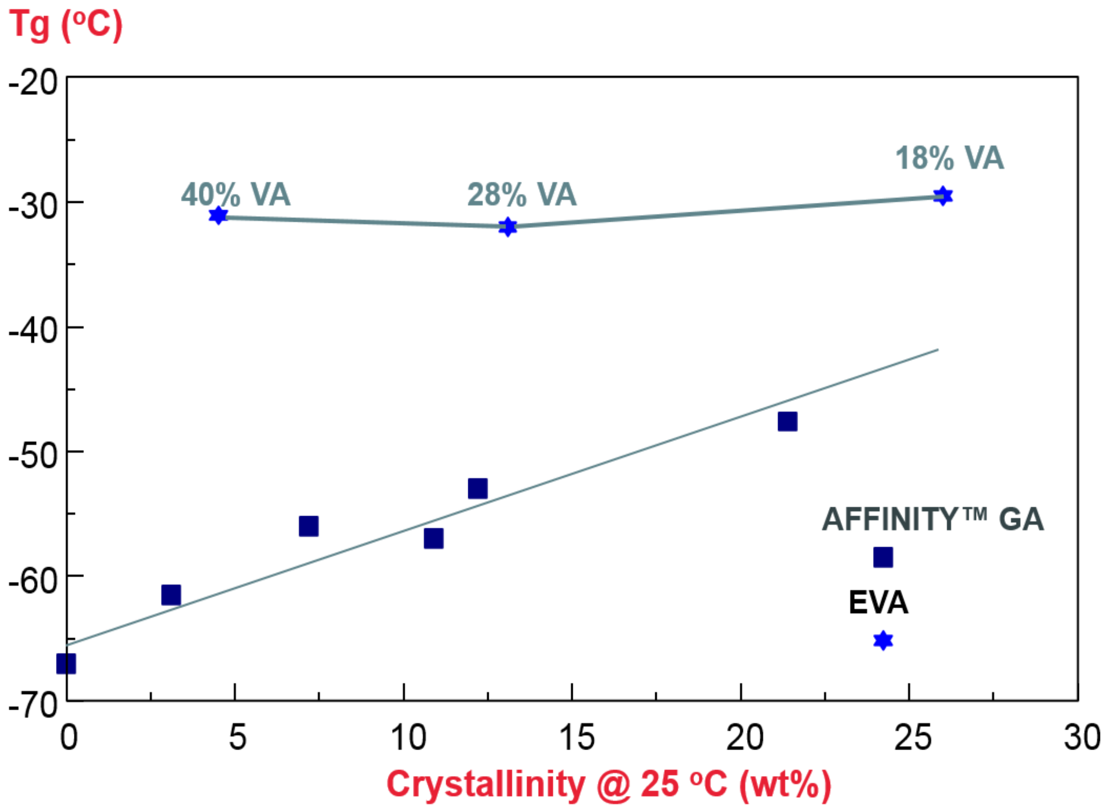
- Low odor / smoke from melt tanks
- Improved stability/reduce char in hoses/modules
- No angel hair/stringing
- Broad service temperature range (low Tg)
- Improved viscosity stability

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 -40ºC to 70ºC

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

Internal Costs (Maintenance Costs, Parts Costs, Line Downtime Costs, Cost of Low Mileage, Cost of Low Yield)

External Costs (Cost of Field Failures)

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

Keys to commercial success

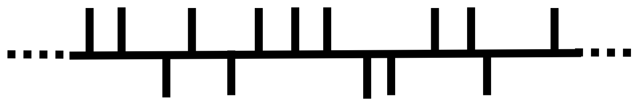
- Technical: Polarity does not matter for adhesion to paper (adhesion via mechanical interlocking)
- Partnership with HMA supplier to accelerate development and commercialization
- Reduced total system cost of HMA for various applications

INFUSE™ Olefin Block Copolymer (OBC)

Random vs. Block copolymer structures

Random Copolymers

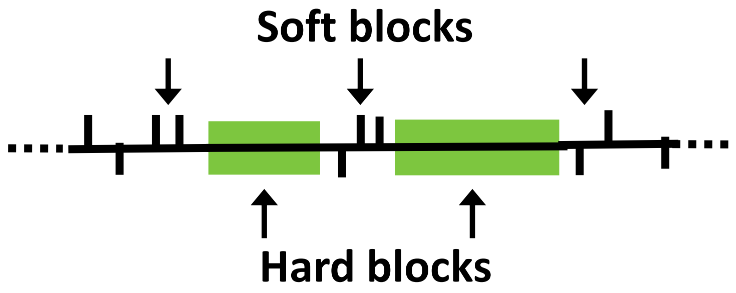
Less comonomer and higher density



More comonomer and lower density

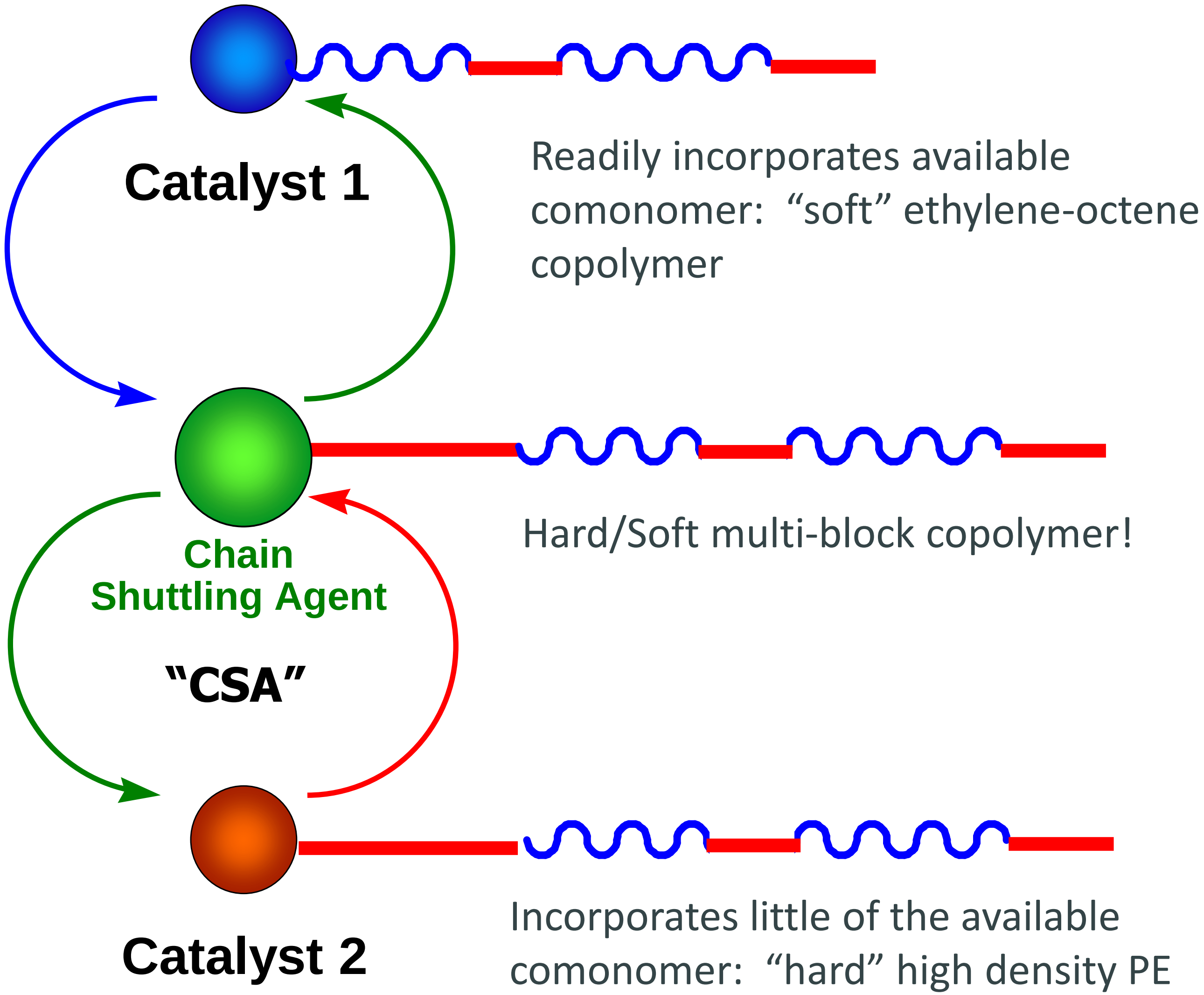
- Adding more comonomer lowers the polymer's density and crystallinity while increasing flexibility.
- However, the melt temperature, crystallization temperature, and heat resistance also drop as density is lowered.

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



Dow Shuttling System

- Coupled, reversible chain transfer between 2 different catalysts
- High catalyst efficiency
- Compatible with a wide variety of monomers

INFUSE™
OLEFIN BLOCK COPOLYMERS

Unique attributes of INFUSE™ olefin block copolymer (OBC)

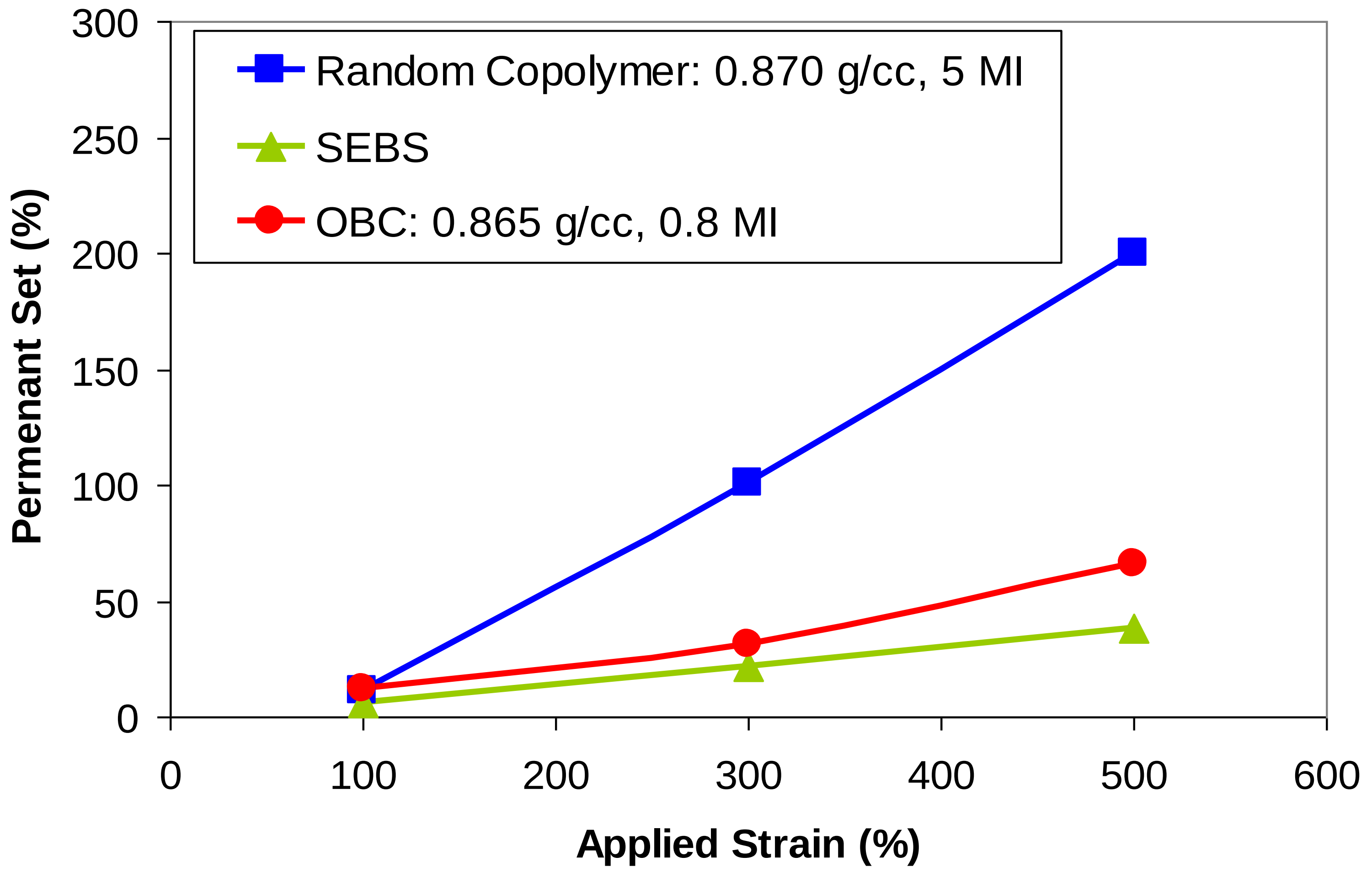
INFUSE OBCs exhibit unique properties versus polyolefin elastomers (POE) including:

- ❑ 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

INFUSE™ OLEFIN BLOCK COPOLYMERS

DOW®

Elastic performance of OBC elastomers



0.865 g/cc OBC has comparable elastic properties as SEBS

INFUSE™ OLEFIN BLOCK COPOLYMERS

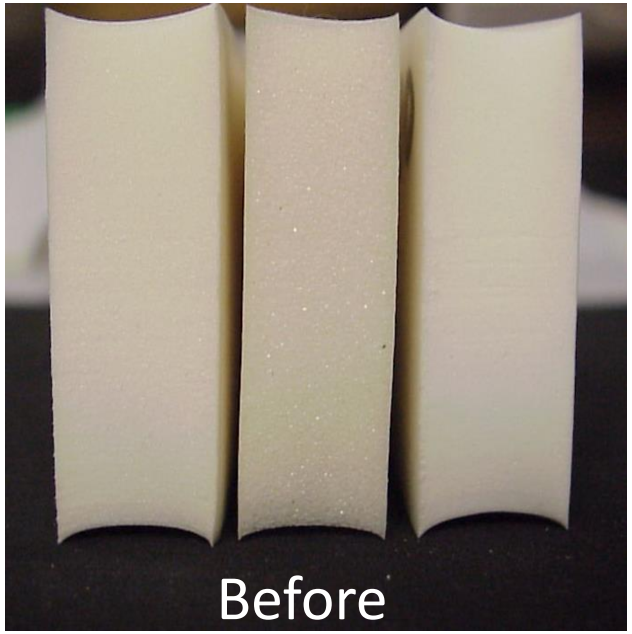
DOW®

Dynamic set after testing @ 40ºC - EVA, POE and OBC

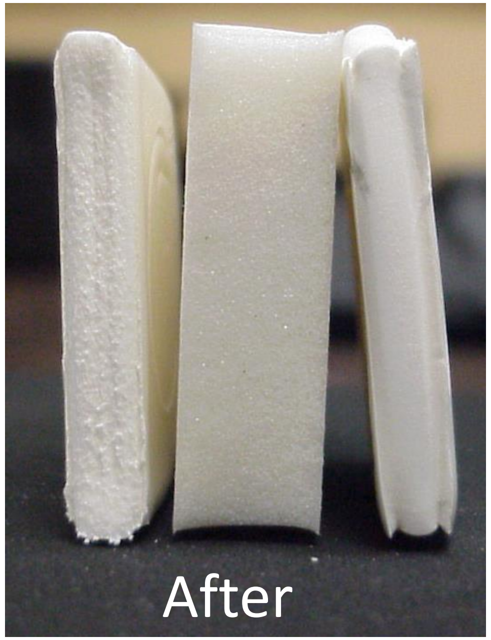
Sample	Dynamic set (1 min after test)	Dynamic set (1 wk after test)
EVA	51.6%	51.6%
OBC	56.1%	11.0%
POE	56.7%	51.8%

100K cycles

EVA OBC POE



EVA OBC POE



спасибо 谢谢

GRACIAS

THANK YOU

ありがとうございました MERCI

DANKE धन्यवाद

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