

The background is a solid blue color with faint, light-colored sketches of chemical structures and a globe. The sketches include various molecular diagrams, some with arrows indicating processes or reactions, and a central globe with latitude and longitude lines.

Recent Advances in Polyethylene Nucleation

Darin L. Dotson, Ph.D

3rd Annual Petrochemical Conclave

Delhi, India

February 7, 2014

Milliken™

- I. Introduction to Milliken & Company
- II. Polyethylene (PE) Nucleation Fundamentals
 - I. Crystallization challenges
 - II. Crystallography of PE- Orientation Effects
- III. Commercial PE Nucleator History
- IV. Morphology of Hyperform® HPN-20E
 - I. Particle Orientation in Flow Fields
 - II. Orientation as Related to Barrier Enhancement
 - III. Orientation in Injection Molding
- V. New Developments in PE Nucleation

A Global Organization

Milliken

With application and development centers around the world, we have the ability to provide technical assistance long after the sale.

Wherever you are in the world, we are there to help.



Spartanburg, SC



Gent, Belgium



Pune, India



Shanghai, China



Singapore



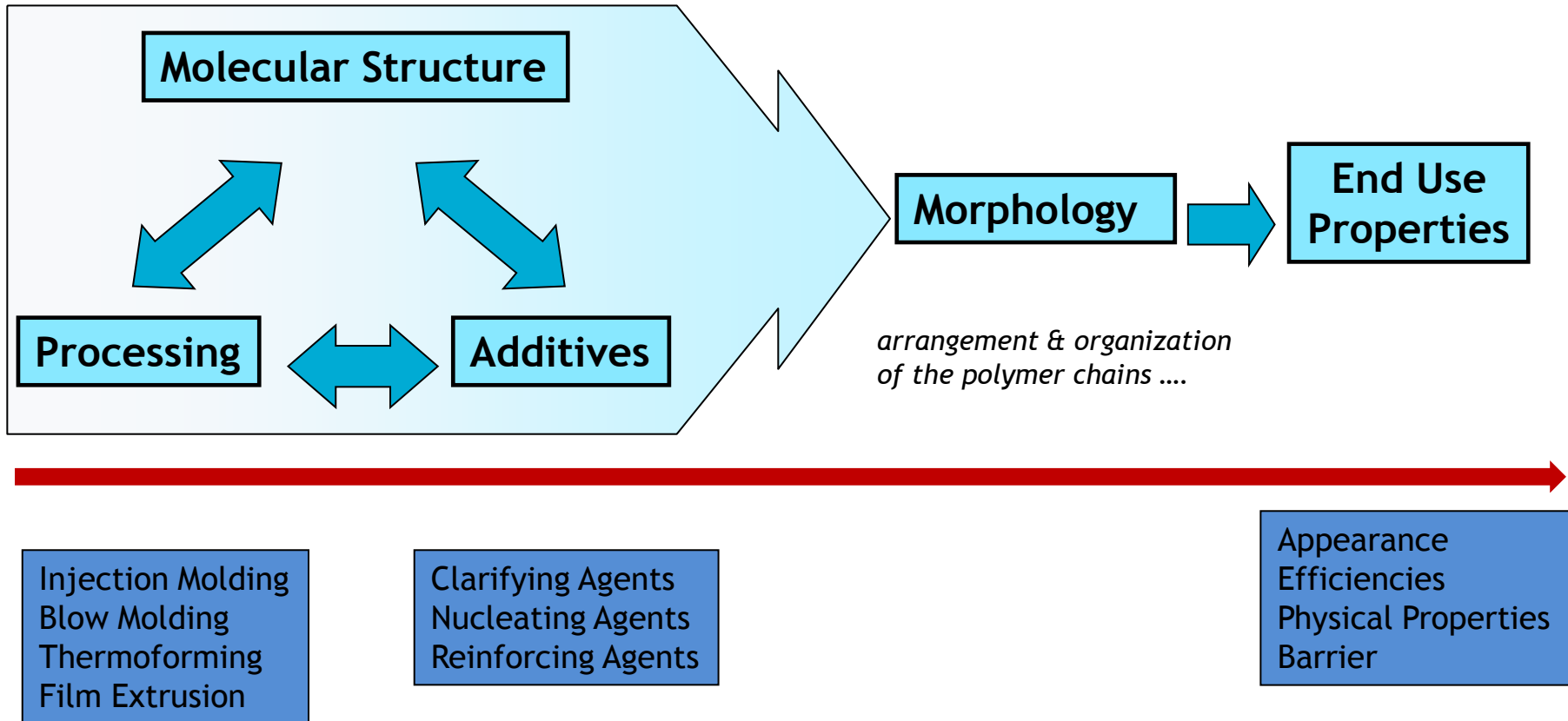
Sao Paulo, Brazil



-  HEADQUARTERS
-  APPLICATION & DEVELOPMENT CENTER
-  SALES OFFICE

Milliken Chemical's Core Competencies

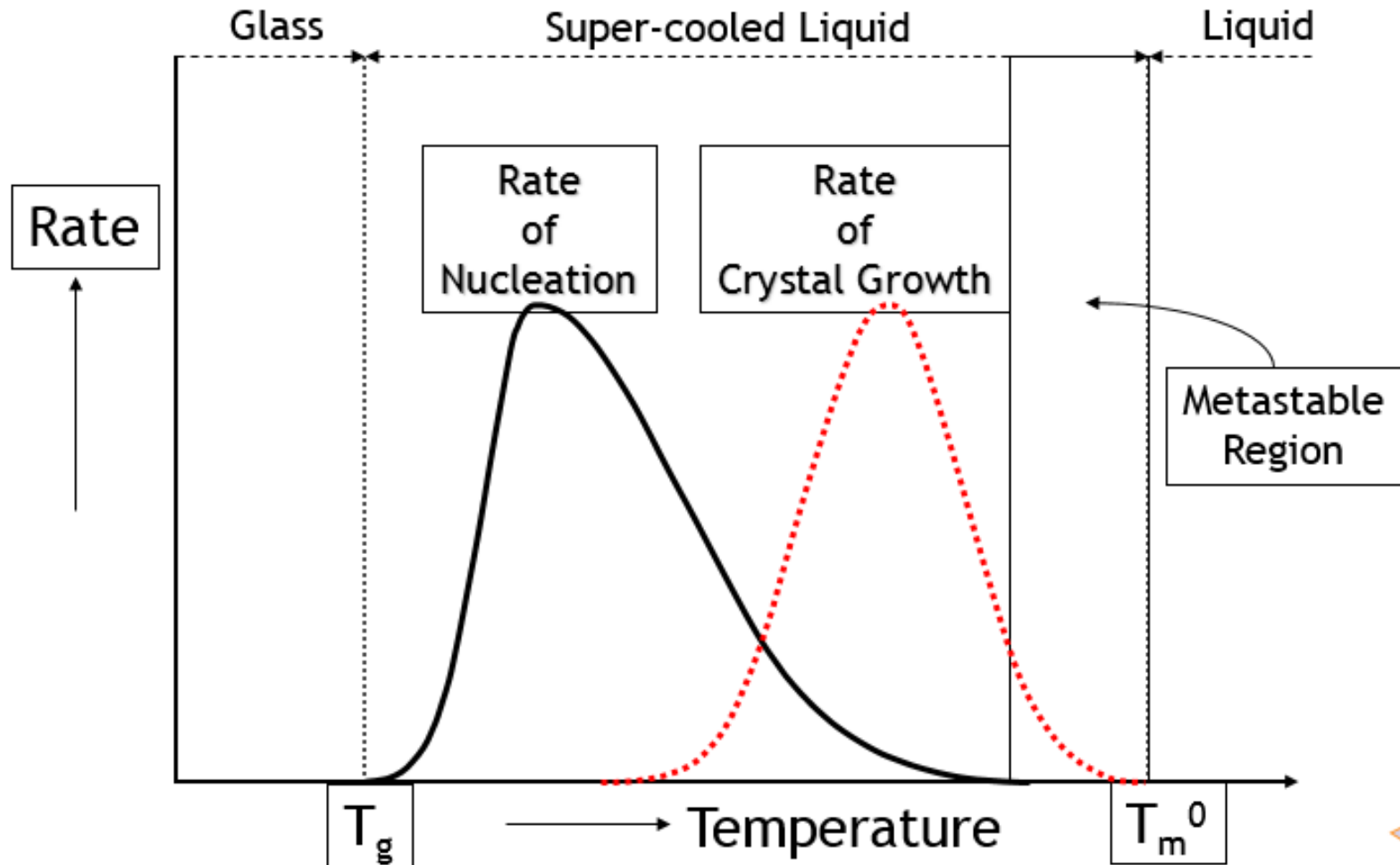
Morphology Modification of Polyolefins



PE Nucleation Challenges

Nucleation rate for Polyethylene

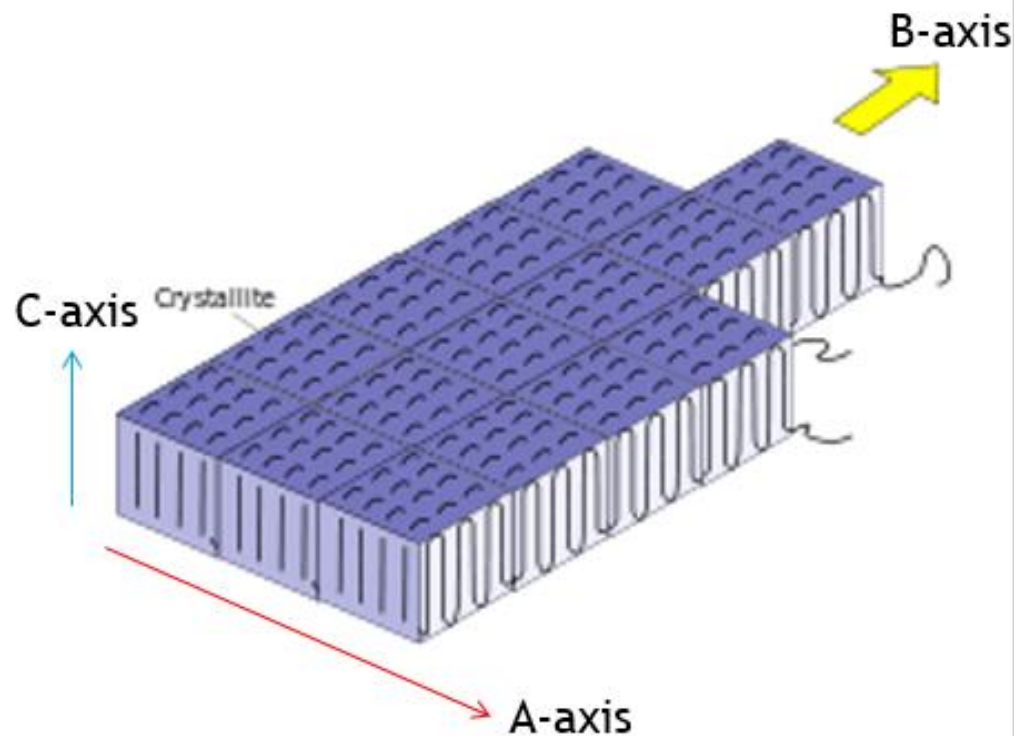
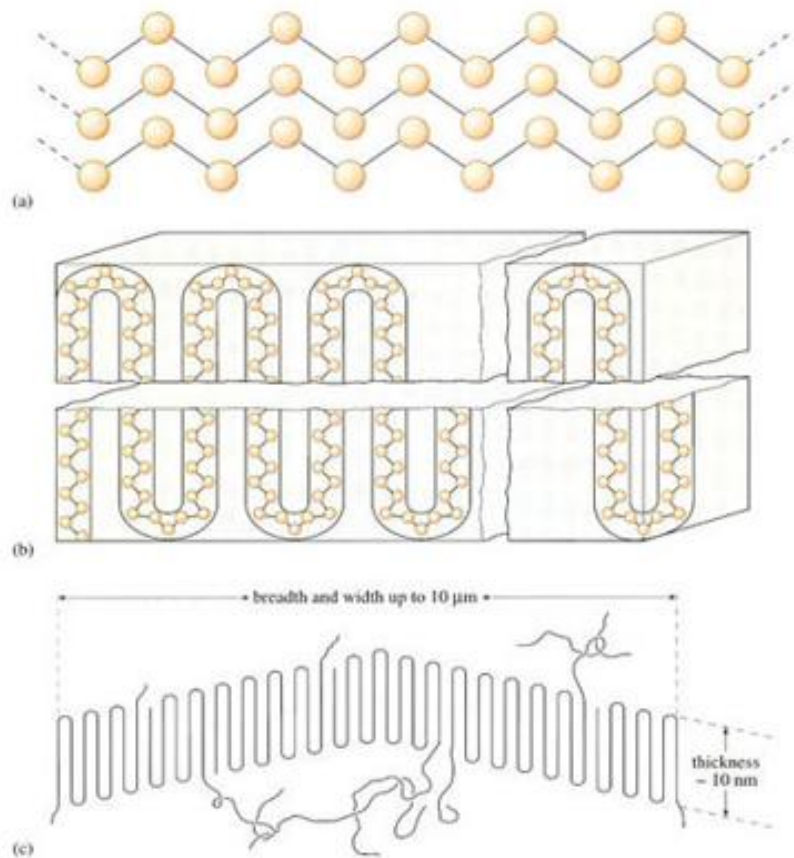
Milliken



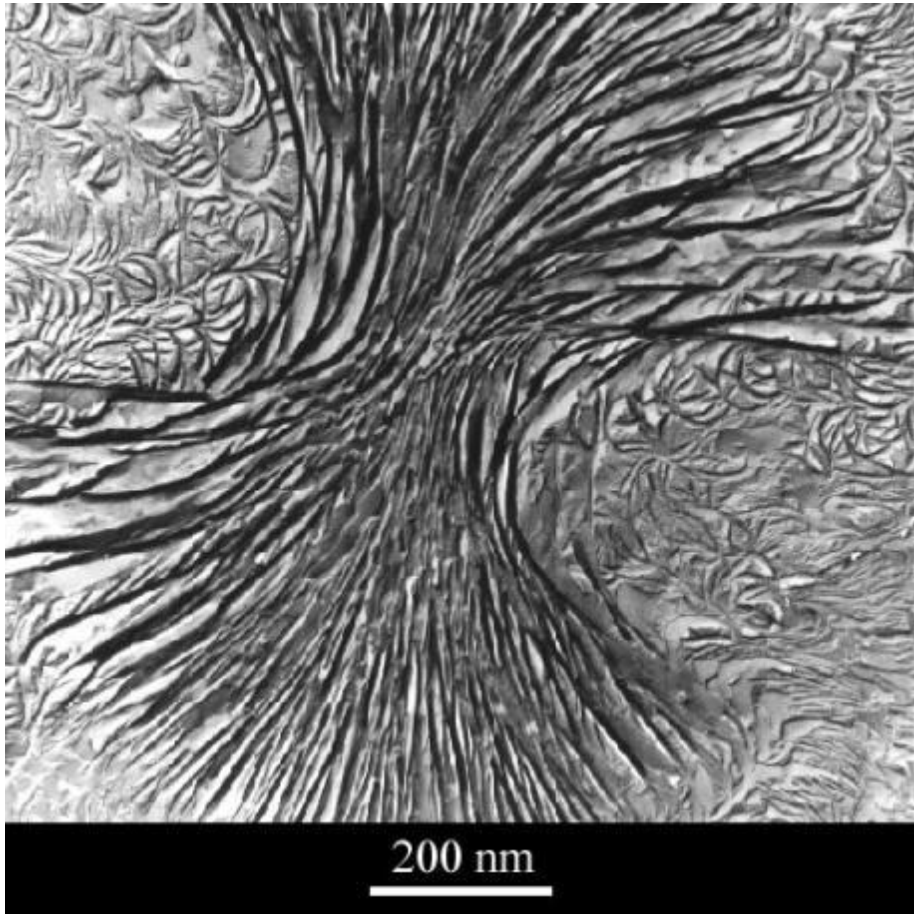
Rapid Lamellar Growth via Chain Folding

Milliken

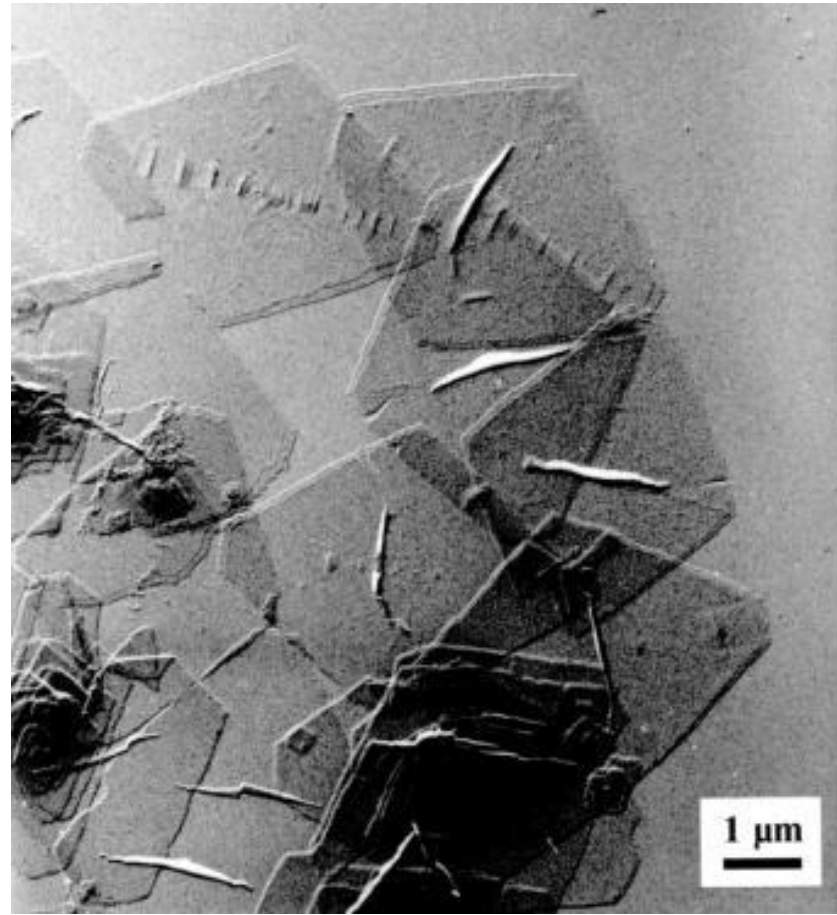
Planar Zig-Zag Conformation



Twisting occurs at larger distances, ~microns



Spherulite Consisting of Lamellar Sheets



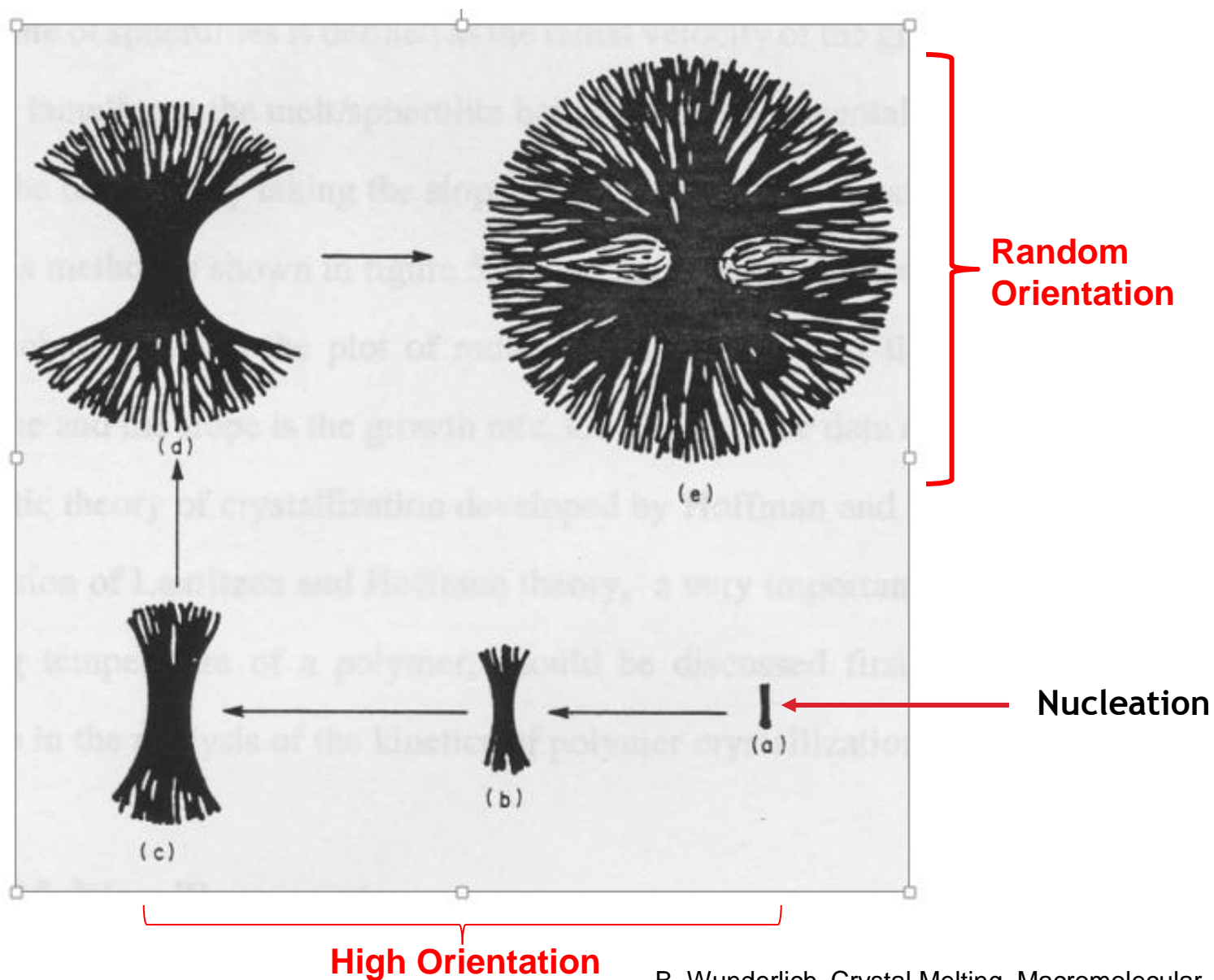
PE Single Crystals from Xylene

HDPE Spherulites

Milliken™



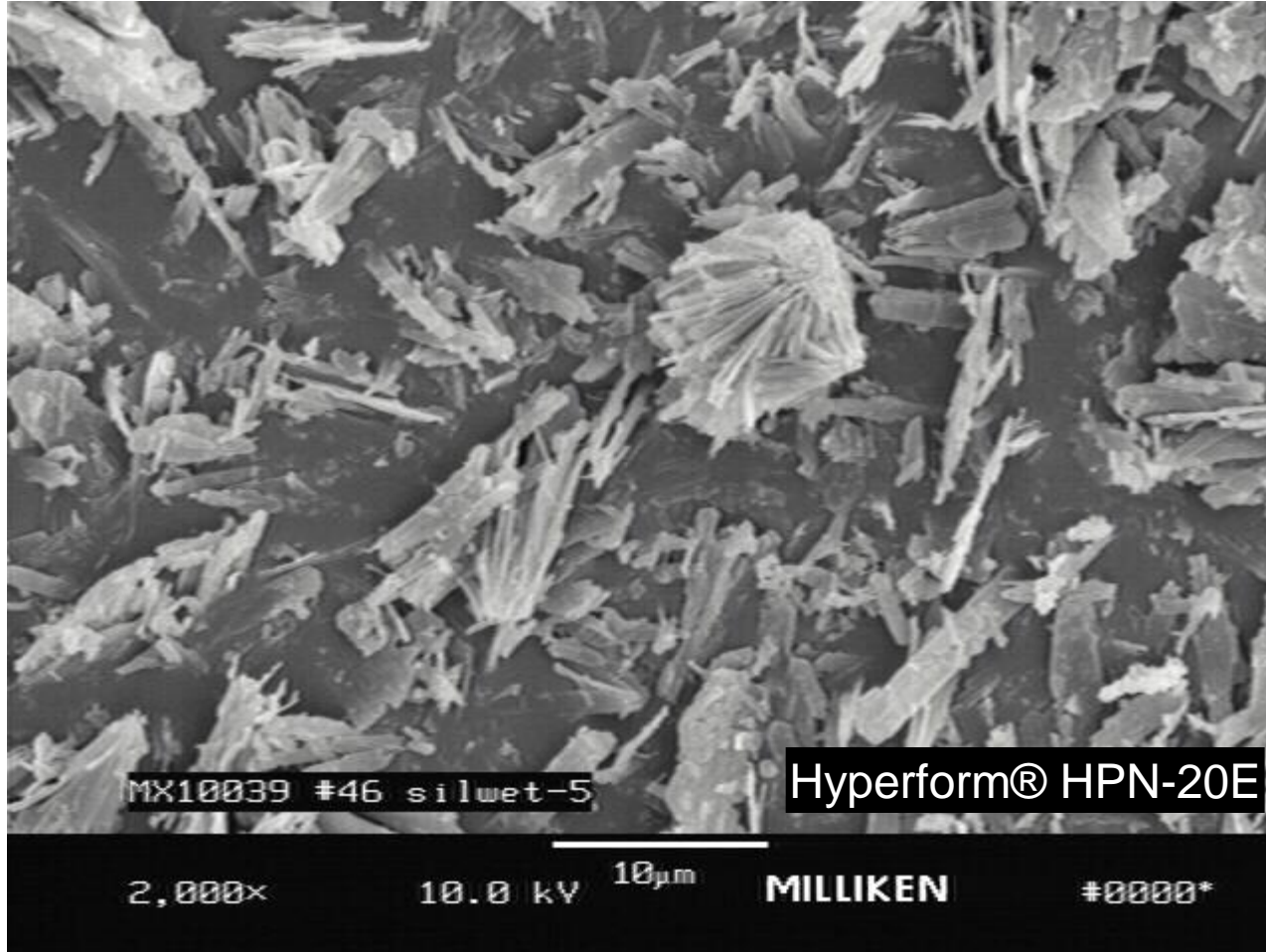
Spherulitic Development



Commercial PE Nucleation History

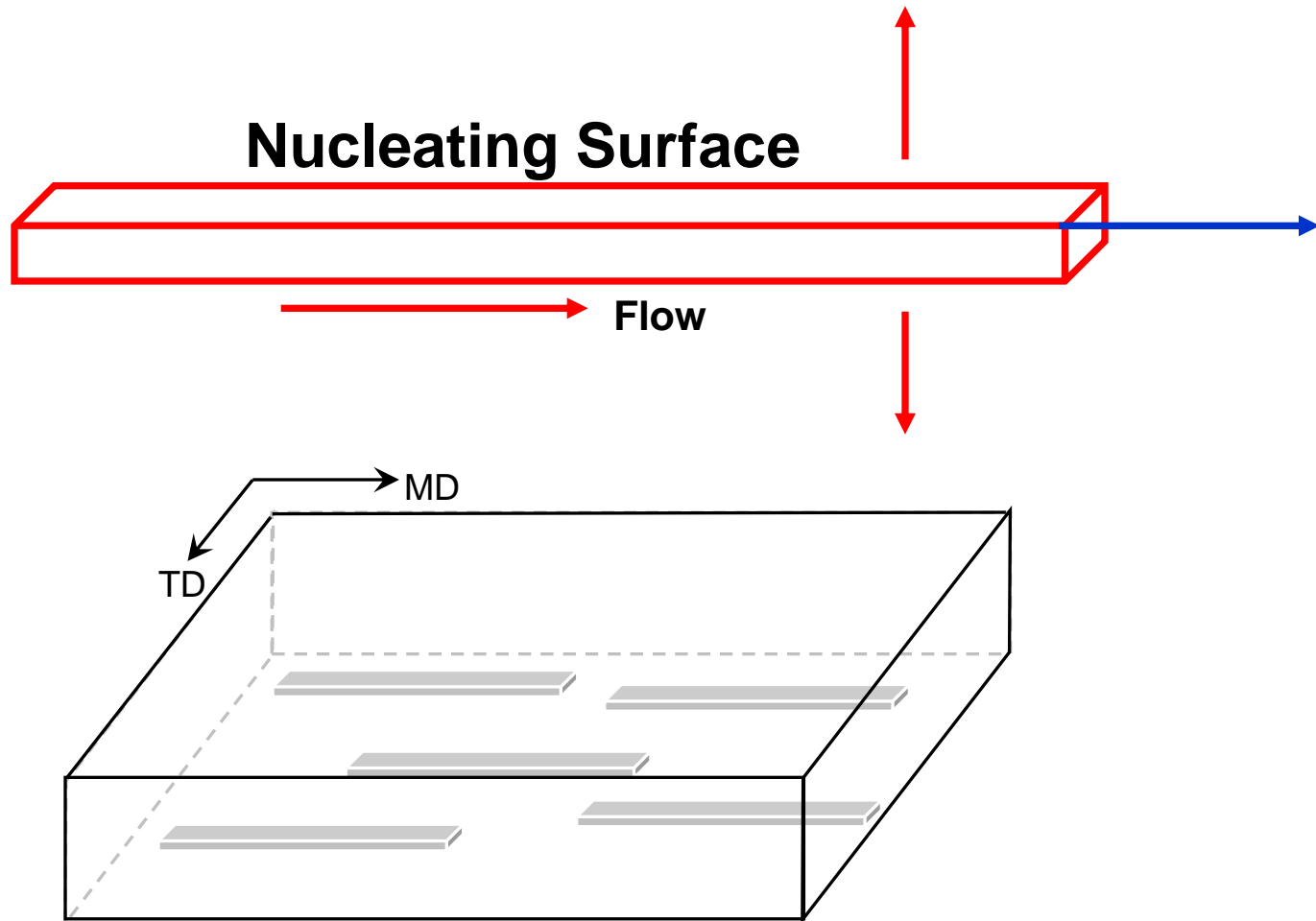
- The nucleation of polyethylene has never been commercially utilized until the launch of Hyperform® HPN-20E in 2006
- The nucleation effects of pigments and their contributions to shrinkage and warpage have been grudgingly “tolerated” over many years
- Hyperform HPN-20E is able to affect the crystal morphology (orientation and kinetics) of linear types of Polyethylene
 - This leads to a significant change in a range of properties (and balance of properties)
 - Can out-nucleate most common pigments to give consistent physicals
- The largest value attributes for HPN-20E today are:
 - Water vapor permeation reduction in HDPE blown films
 - Reduced cycle times and pigment leveling in caps/closures

Particle Morphology

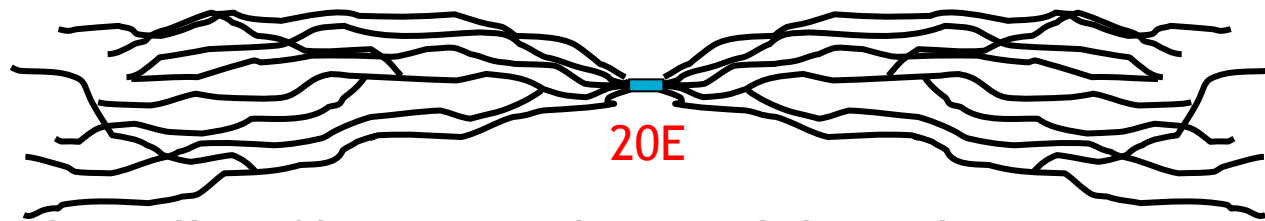
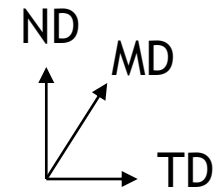
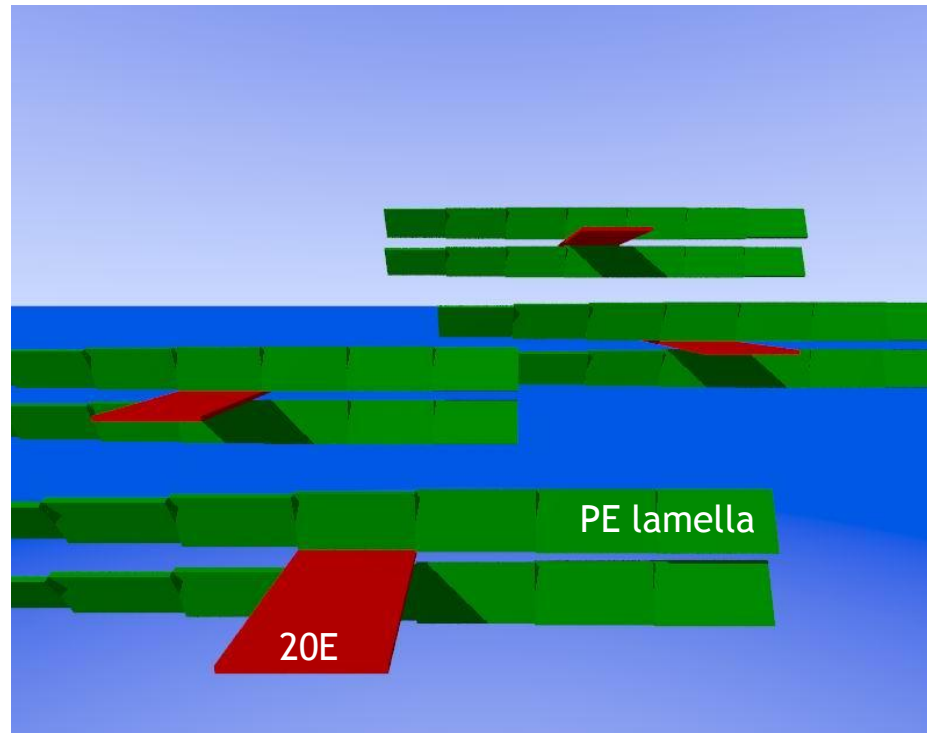


Nucleator Size Distribution: $d_{50} = 2.8$ microns, $d_{97} = 9$ microns

Nucleator Particle Shape Defines Performance- HPN-20E

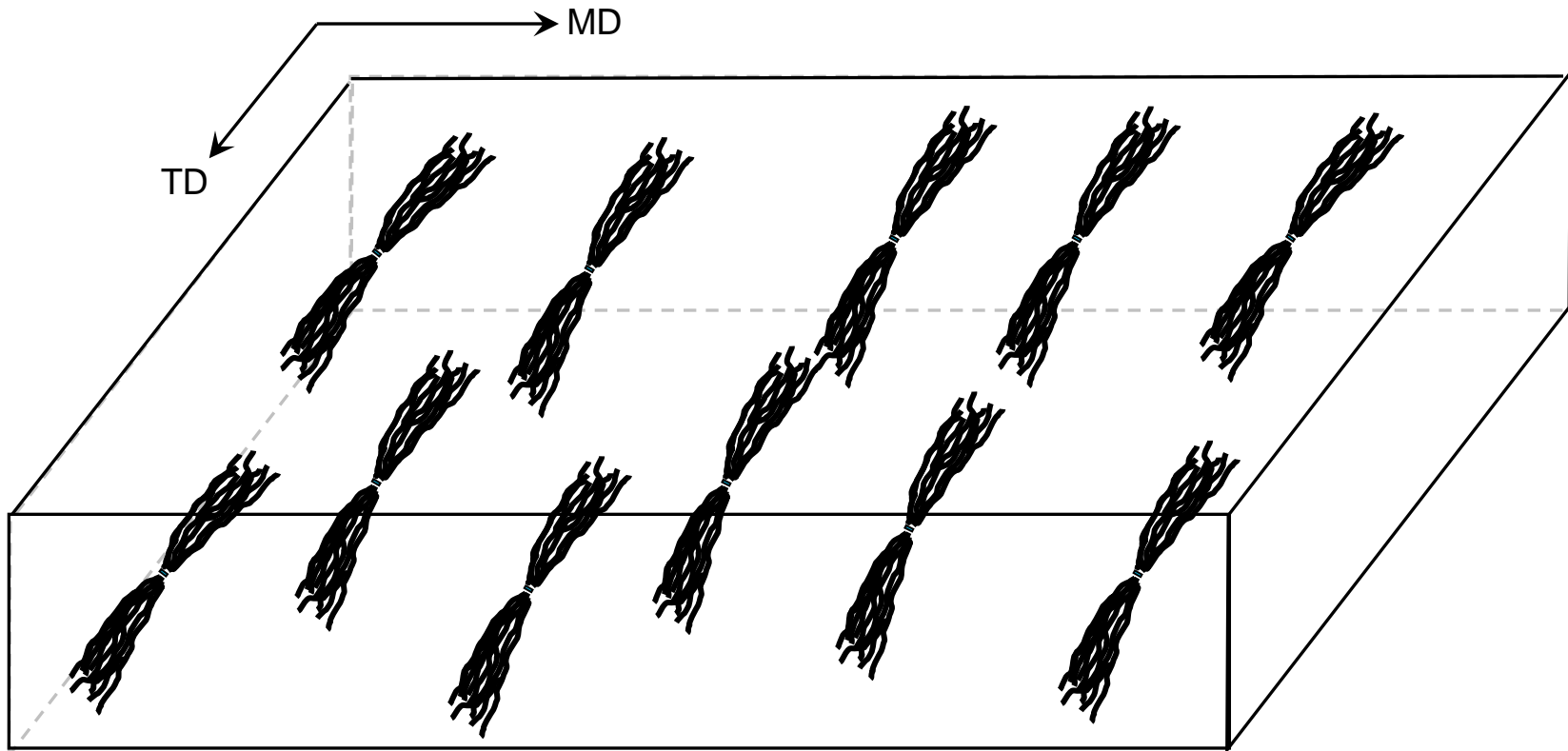


Improvements in water vapor barrier of HPN-20E nucleated HDPE blown film



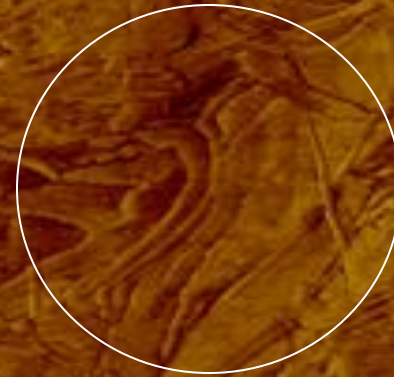
Crystalline Objects are Flat, not Spherical: A More Tortuous Path for Water Vapor

Crystalline morphology of HDPE nucleated with HPN-20E



- Substantially Reduces TD Shrinkage
- All crystallinity is now “in-plane”

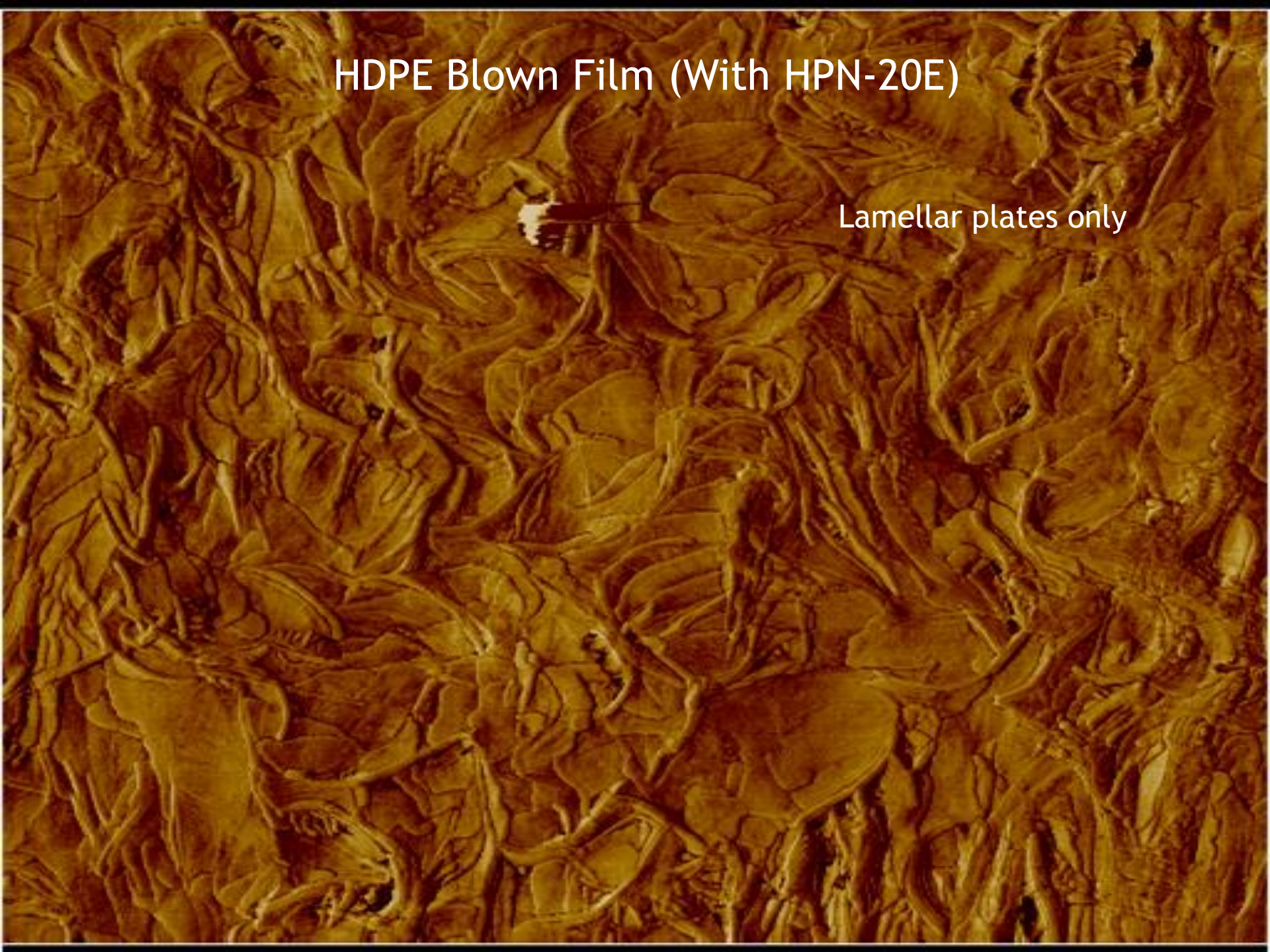
HDPE Control Blown Film



Stacked lamellar plates
(good for barrier)

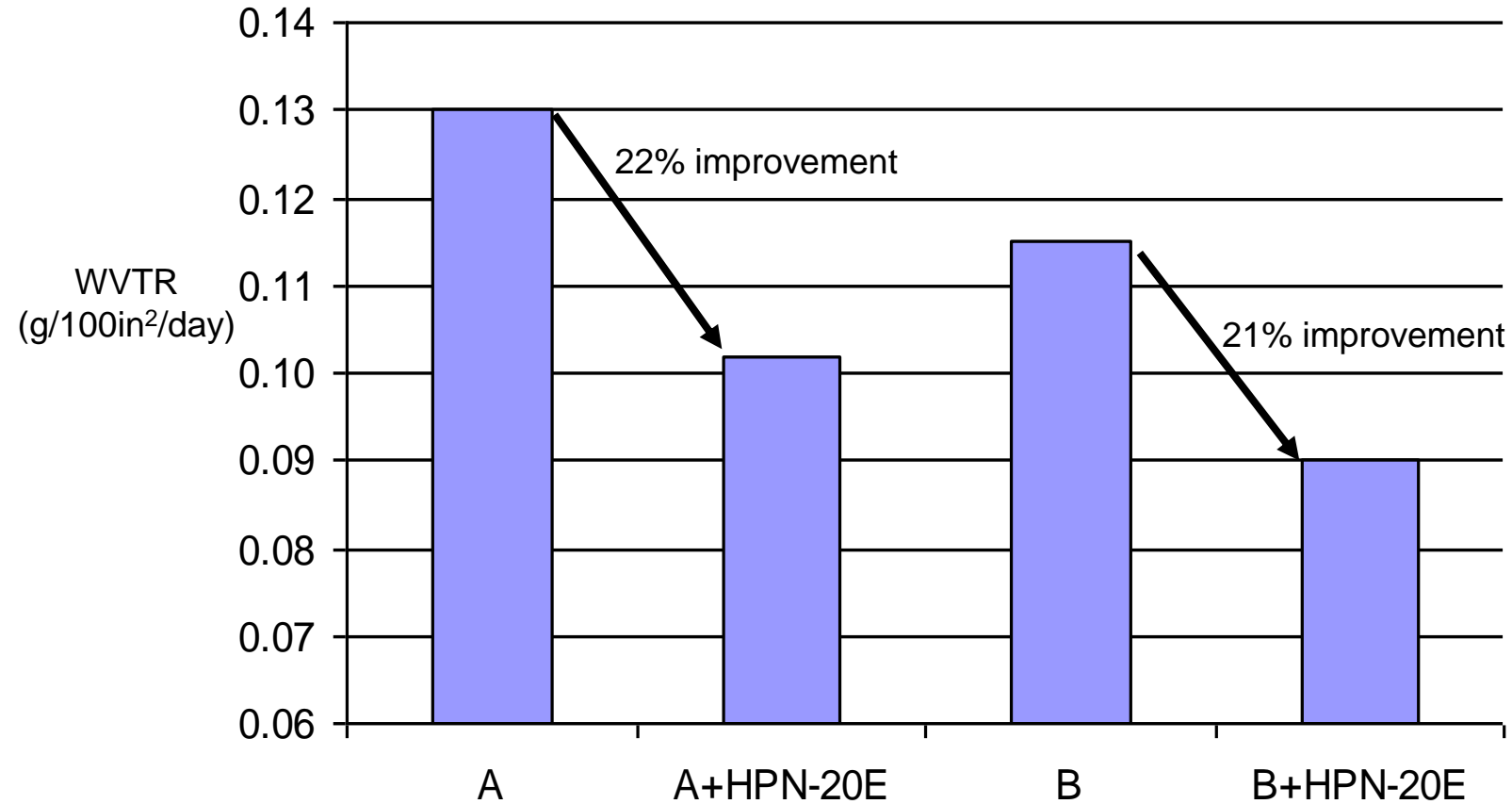
HDPE Blown Film (With HPN-20E)

Lamellar plates only

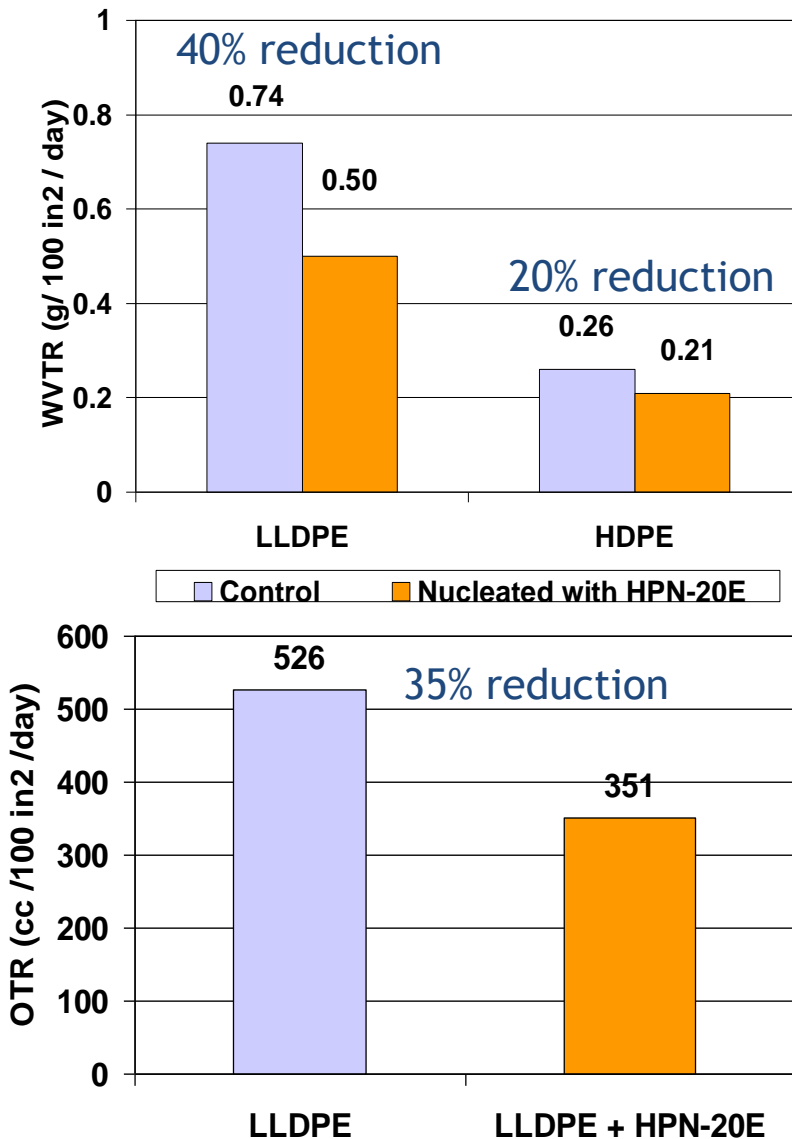


Barrier Data: Film Thickness = 2 mils / 50 μ m

Typical commercial grades today ~ 50% WVTR Reduction!



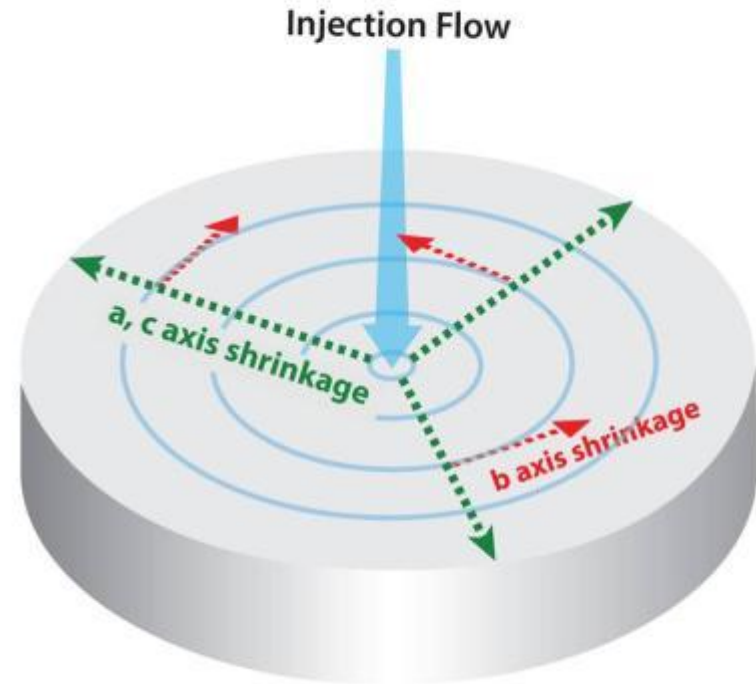
Barrier Property Enhancement (Moisture & Oxygen)



Enhanced moisture barrier allows for downgauging in the cereal liner / cracker market - a key driver in the quest for more sustainable packaging

Hyperform HPN-20E[®] in PE injection molding: Radial, Center-Gated Parts Ideal for HPN-20E

- In a circular center gated part the flow lines are equal in all directions
- The shrinkage of the b-axis is located in the transverse direction and is also the lowest
- The shrinkage of the a,c-axis in the machine direction is higher and very different from the b-axis shrinkage
- Due to the equal flow lines in all directions, the unequal shrinkage behaviour is not important as it is the same in all directions



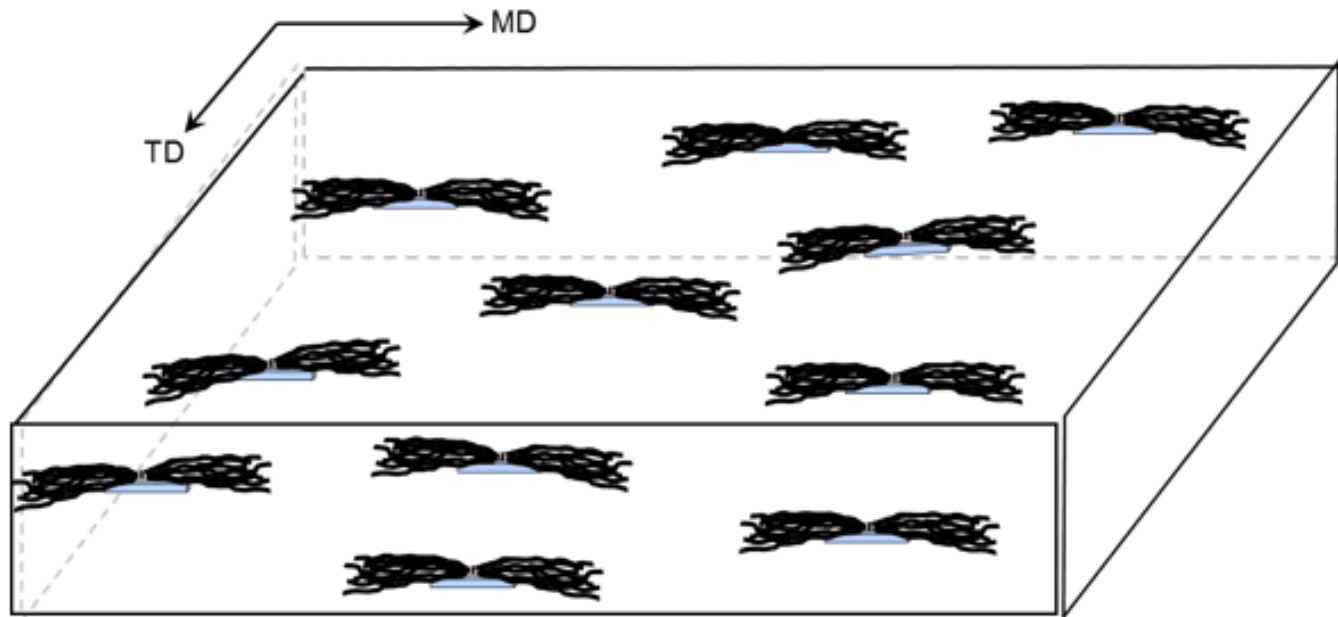
Caps, closures, EBM

- Reduced diameter shrinkage = larger parts
- Faster cooling allows shrinking back to specifications
- 10-20% cycle time reductions typical

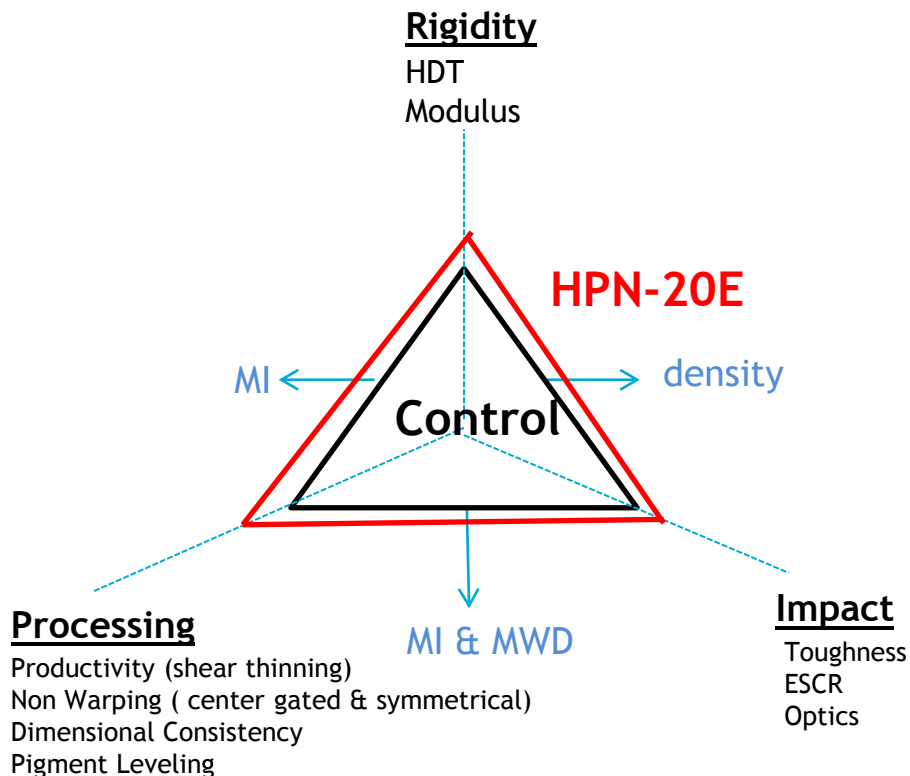
New Developments in PE Nucleation

A New Orientation Discovered!

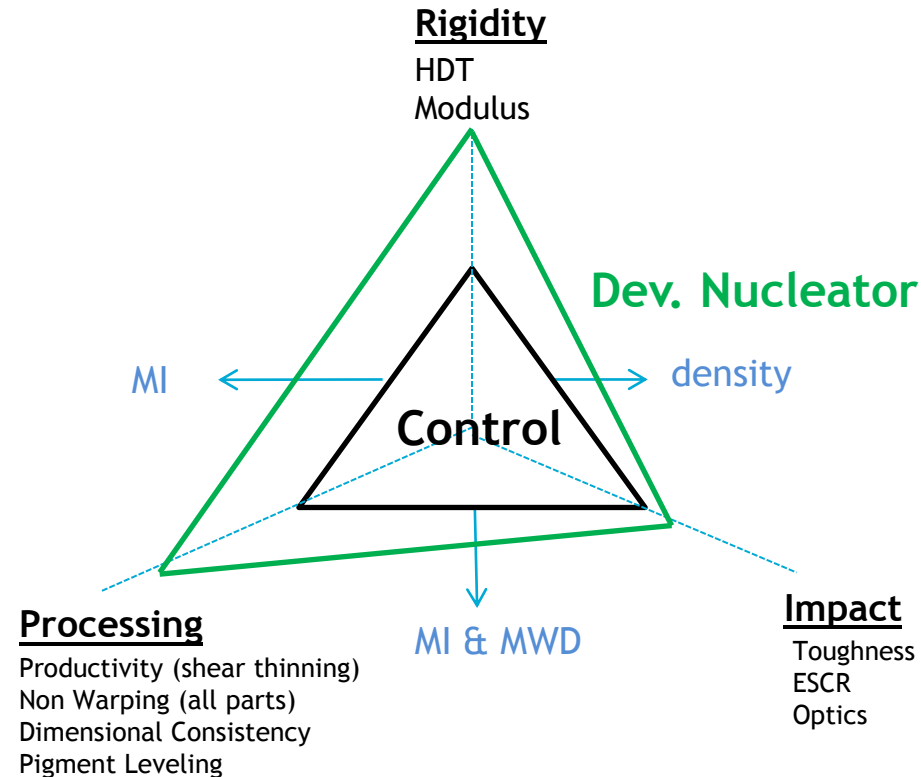
MD Lamellar Growth



Performance Triangles in Rigids



HPN-20E moderately increases HDT, transverse ESCR, improved dimensional stability in radial parts, effectively levels pigment nucleation



Dev. nucleator dramatically increases HDT, flexural modulus, improved dimensional stability in large injection molded parts, levels pigments, no adverse effect on impact resistance

A Breakthrough Orientation...

- For the first time, PE lamellae are capable of growing in the flow (machine) direction of PE articles. A new material!
- Unique property sets are observed (exceptional modulus, directionally low shrinkage, excellent dimensional stability, and very high HDT's)
- This additive is entirely developmental at this point- internal evaluations are underway

Application Benefits from Nucleation and Conclusions



- Milliken has commercialized the first nucleating agent for polyethylene (Hyperform® HPN-20E), and continued to develop additives for PE that induce new morphological changes to PE articles.
- These complementary orientations are expected to elicit new and valuable properties in the following applications:
 1. PE pipe
 2. PE caps and closures (IM and ECM)
 3. Blown films (HDPE)
 4. EBM articles (bottles, drums)
 5. Rotomolding
 6. Fibers (nonwovens and monofilament)
 7. Thermoformed PE sheet and articles
 8. Extruded tubes
 9. Cast films
 10. PP material replacement

Thank you!

Any Questions?

Contact Info:

Darin L. Dotson, Ph.D.
Milliken Chemical, M-401
920 Milliken Road
Spartanburg, SC 29303
864-503-1190 (office)
864-542-6304 (cell)