Outline

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

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.
Milliken Chemical’s Core Competencies

Morphology Modification of Polyolefins

- Molecular Structure
- Processing
- Additives
- Morphology
  - End Use Properties

- Injection Molding
- Blow Molding
- Thermoforming
- Film Extrusion

- Clarifying Agents
- Nucleating Agents
- Reinforcing Agents

Appearance
Efficiencies
Physical Properties
Barrier

arrangement & organization of the polymer chains ....
PE Nucleation Challenges
Nucleation rate for Polyethylene

Rate

Glass
Super-cooled Liquid
Liquid

Rate of Nucleation
Rate of Crystal Growth

Metastable Region

$T_g$

$T_{m^0}$

Temperature
Rapid Lamellar Growth via Chain Folding

Planar Zig-Zag Conformation

Twisting occurs at larger distances, ~microns
Lamellae vs. Single Crystal Morphologies

Spherulite Consisting of Lamellar Sheets

PE Single Crystals from Xylene
Acknowledgements to prof. Bernard Lotz (Institute Charles Sadron, Strasbourg)
Spherulitic Development

Random Orientation

Nucleation

High Orientation

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

Nucleating Surface

Flow

MD

TD

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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 / 50µm

Typical commercial grades today ~ 50% WVTR Reduction!

- WVTR (g/100in²/day)
  - 22% improvement
  - 21% improvement

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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.
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.

- 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 Rigid Polymers

**Rigidity**
- HDT
- Modulus

**HPN-20E**
- MI & MWD
- Density

**Control**
- MI & MWD

**Impact**
- MI
- Toughness
- ESCR
- Optics

**Processing**
- Productivity (shear thinning)
- Non Warping (center gated & symmetrical)
- Dimensional Consistency
- Pigment Leveling

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?
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