Recent Advances in PP and PE Nucleation

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Outline

I. Introduction to Milliken & Company

II. Properties of Good Nucleating Agents
   I. Creating Value with Nucleation
   II. Crystalline Morphology of PP and PE

III. Commercial PP Clarifying Agents

IV. Commercial PE Nucleating Agents
   I. Hyperform ® HPN-20E
   II. Hyperform ® HPN 210 M

V. Summary and Conclusions
Milliken - 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

arrangement & organization of the polymer chains ....

Injection Molding
Blow Molding
Thermoforming
Film Extrusion

Clarifying Agents
Nucleating Agents
Reinforcing Agents

Appearance
Efficiencies
Physical Properties
Barrier
An Effective Nucleating Agent:

- Increases significantly the crystallization rate of PP or PE under real-world processing conditions, and in the presence of:
  
  A. Other nucleants such as pigments, other added nucleators
  
  B. Self-nucleating species created under conditions of strain (shish-kebabs during high strain or shear)

- Creates a specific crystalline orientation that gives beneficial physical properties in fabricated parts, creating value upstream and downstream

- A clarifying agent does the above but with a level of dispersion and higher nucleation density not possible with insoluble additives
Nucleation of PP and PE - Creating Value

Material properties affected by nucleation

- Increased Tc
- Altered Shrinkage*
- Increased Stiffness
- Increased HDT
- Better opticals

* Not all nucleators improve shrinkage isotropy

Optimizing cost structure & Improving part quality

- Higher productivity
- Material savings & Better quality
- Reduced cooling time
- Reduced Scrap & warpage
- Down gauging
- Better T resistance
- Transparency

These are all orientation effects!!!
PE and PP Crystal Spherulites

Polyethylene (slow cooling rate)

Polyethylene (isothermal 123°C)

Polypropylene (slow cooling rate)

Polyethylene with nucleating agent
PP Spherulitic Morphology

Random Orientation!!

PE Spherulitic Morphology

Random Orientation!!

*with permission from Julien Giboz, Univ. of Savoie
• Crystals grow starting from a nucleus. If there is no nucleus, the crystal cannot start growing.

• During the formation of the nucleus (nucleation), the nucleus must reach a certain size $R_0$ before it can start growing. Below size $R_0$ the nucleus is unstable.

Creation of new surface takes energy

The bulk phase of the nucleus starts to form. Crystallization enthalpy is released and helps surface formation

The released energy exceeds the energy needed for surface formation. Crystal growth begins
PP Clarifying Agents
Generations of sorbitol acetal-based clarifying agents

1G
Millad® 3905
1982-Present

2G
Millad® 3940
1988-Present

3G
Millad® 3988
1993-Present

Next Gen
Millad® NX8000
2009-Present

1,3;2,4-bisbenzylidenedesorbitol
1,3;2,4-bis(4-methylbenzylidene)sorbitol
1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol
1,2,3-desoxy-4,6,5,7-bis(4-propylbenzylidene)nonitol
Model for sorbitol acetal-based clarifying agents in PP

- Strong local PP crystallite orientation
- No bulk PP crystallite orientation due to random orientation of Millad fiber network
- No spherulites can form - too small!!
- Light scattering is minimized

**Millad® NX™ 8000 Case Study**

**The Value of Clarity in Personal Care Packaging**

<table>
<thead>
<tr>
<th>Application</th>
<th>Packaging</th>
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<tbody>
<tr>
<td>Process</td>
<td>EBM</td>
</tr>
<tr>
<td>Region</td>
<td>US</td>
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<tr>
<td>Material Replaced</td>
<td>PET</td>
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**Drivers for material replacement:**

- Anti-slippery design for customer experience improvement
- Better squeezability

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Millad® NX™ 8000 Case Study

The Value of Clarity in Food Storage

**Application**
- Food Storage

**Process**
- IM

**Region**
- China

**Material Replaced**
- PP upgrade

**Drivers for material replacement:**
- Crystal clear for premium product
- Fresh looking
PE Nucleating Agents
Milliken Commercial PE Nucleators

Hyperform® HPN-20E
• Launched in 2006 as the first commercial PE nucleator
• Primary value propositions:
  A. Decreased WVTR in LLDPE and HDPE films and rigid
  B. Enhanced optics of blown films
  C. Reduced radial shrinkage enabling cycle time reductions
     in EBM and radial part injection molding (IM)
  D. Pigment leveling

Hyperform® HPN 210 M
• Launched in September 2014 as a second-generation PE nucleator
• Primary value propositions:
  A. Enhanced dimensional stability to HDPE injection-molded parts
  B. Maximum PE stiffness and low shrinkage to closely match that of PP
  C. Cycle time reductions in HDPE injection molding through reduced
     warpage
  D. Pigment leveling
• Selected as one of the top 100 inventions in the world for 2015
Particle Morphologies by SEM
Particle Alignments in Polymer Flow

20E, 210 M
Commercial Nucleator HPN-20E

TD Lamellar Growth

Substantially Reduces TD Shrinkage
Orientation Effects
Barrier and Physical Properties in Film

- 25 - 50% lower transmission rates in HDPE and LLDPE (H₂O and O₂)
- Higher MD and TD modulus with slight to no loss in tear and impact properties

Lumicene® M6012EP mHDPE

58% Reduction WVTR

3.0 mil LLDPE Film
27% Average Reduction WVTR
HDPE Blown Film
Grease barrier for HPN-20E

Rate of Grease penetration of flexible blown film (ASTM 119-82; accelerated method)

<table>
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<tr>
<th>Type</th>
<th>Density</th>
<th>MI</th>
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<tbody>
<tr>
<td>HDPE</td>
<td>0.960</td>
<td>0.95</td>
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</table>

HPN-20E increases the time to fail with > 50%.
The Value of Nucleation in Flexible Packaging

- **Application**: Bag in box films for dry food packaging

- **Process**: Blown

- **Hyperform® selected because**:
  - Up to 50% reduction in WVTR in HDPE
  - Enables down gauging or extended shelf life
  - Improves gloss and clarity
The Value of Nucleation in Flexible Packaging

**Application**
- Cosmetic or food tubes

**Process**
- Co-extrusion or lamination

**Hyperform® HPN-20E for PE**

**Coextruded Tube**
- HPN-20E in both layers (50/50 HD/LD & 100% LD)
- Lowered haze 19%, WVTR 36% and OTR 33%

**Laminated Tube**
- HPN-20E in printing and sealing layers:
  - Enabled 30% reduction of EVOH in barrier layer
  - Improved optics 40% and stiffness 12%, overall
Commercial Nucleator Hyperform ® HPN 210 M

MD Lamellar Growth

Substantially Reduces MD Shrinkage
End-Gated Part Flow - ASTM Flex Bar

Before Nucleation (Melt State)

After Nucleation (PE Crystal Growth)

Maximum Stiffness

Flow Direction

210 M Particles

PE Crystal Growth (Minimal Shrinkage)
In the lamellar growth direction, there is minimal volumetric shrinkage

HPN 210 M gives HDPE the stiffness and shrinkage properties of HPP!!

ASTM Flex Bar Comparison - End Gated

210M
HDPE
Flex. 1420 MPa
HDT 94°

LYB Profax 6301 Control
HPP
Flex. 1351 MPa
HDT 92°

Nova 19G Control
HDPE
Flex. 980 MPa
HDT 60°
IM² Pallets using Regrind - Warpage and Modulus

- The use of 210 M resulted in much less surface buckling and better fit with base
- The weldability of the top/bottom pallet pieces was improved with 210 M
- No loss of impact when dropped from over 9 feet
- Modulus of pallet was increased 25% with 210 M
Effective Nucleation of PP and PE can deliver value in:

• Dramatically clearer parts which can allow inter-material replacements between PP and higher cost thermoplastics

• In PE, Better Barrier, Optics, and Modulus
  – 25-50% reduced transmission rates in LLDPE and HDPE
  – Lower haze, higher gloss and contact clarity
  – HDPE with the same stiffness and low shrinkage of HPP

• Sustainability
  – Down gauge
  – Extend shelf life
  – Enable recyclable pouches

• Cost Savings
  – Expand material options
  – Increase machine throughputs
Thank you!

Any Questions?

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