A NOVEL NUCLEATING AGENT FOR POLYETHYLENE

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Introduction

Polyolefins are the most widely consumed plastic materials in the world. Their wide ranging versatility and cost competitiveness has lead to continued growth in recent times. Polypropylene has been modified through the use of nucleation for a number of years. Nucleation, of which clarification is considered a subset, has led to improvements in optical properties, physical properties, warpage control, and processing speed of polypropylene across many different processing techniques (injection molding, blow molding and extrusion). Nucleation of polyethylene has been studied over the years but there has never been commercial adoption of nucleation as a technique for modifying polyethylene properties. This is generally owing to insufficient performance enhancement achievable through nucleators typically designed for polypropylene. This paper presents a new chemistry that shows breakthrough performance in polyethylene nucleation and describes interesting property enhancements realized through its use. This product, Hyperform® HPN-20E, was tested in various polyethylene resins against typical commercial and experimental nucleating agents. For clarity, these compounds are listed in Table 1 below along with the corresponding designation to be used in this paper:

<table>
<thead>
<tr>
<th>Tested Nucleator</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyperform® HPN-20E</td>
<td>N1</td>
</tr>
<tr>
<td>Hyperform® HPN-68L</td>
<td>N2</td>
</tr>
<tr>
<td>Millad® 3988</td>
<td>N3</td>
</tr>
<tr>
<td>ADK Stabilizer NA-11</td>
<td>N4</td>
</tr>
<tr>
<td>ADK Stabilizer NA-21</td>
<td>N5</td>
</tr>
<tr>
<td>Experimental Nucleator</td>
<td>N6</td>
</tr>
</tbody>
</table>
The Mechanism of Nucleation

When semi-crystalline polymers crystallize from the melt (typically during the cooling phase of a process), the lamellae organize from a primary nucleus to form complex macro-structures called spherulites. It is widely known that these spherulites continue to grow until they impinge on an adjacent spherulite at which point the growth ceases. The ultimate size of these spherulitic structures dictates a number of properties of the polymer, including optical and physical characteristics.

Additionally, for crystal growth to commence there is a primary process that has to occur called nucleation; this is basically the formation of a focal center around which the lamellae can organize themselves. This process is displayed in Figure 1. The secondary process of crystal growth follows nucleation and is characteristic for polyolefins.

![Figure 1: Schematic of the heterogeneous nucleation process](image)

The rate of secondary crystal growth and primary nucleation is strongly dependent on temperature, as well as the type of polymer being studied, as shown in Figure 2.

![Figure 2: Rate of nucleation and crystal growth as a function of temperature](image)
There are three phases of primary nucleation. The first is spontaneous nucleation which refers to homogeneous nucleation under the influence of super-cooling. The second is orientation-induced nucleation, which is a result of alignment of crystals (often due to process flow dynamics). This paper will deal with just the third phase; heterogeneous nucleation. This involves the addition of a foreign phase which presents a new surface on which crystal growth can occur. Typically, this foreign phase takes the form of a nucleating agent which has been designed to have a good epitaxial match with the growing polymer crystal. A detailed study and explanation of heterogeneous nucleation is beyond the scope of this paper and readers are encouraged to study the cited reference materials for a more complete and thorough treatment of the subject.¹

Polypropylene is recognized as a relatively easy material to nucleate. This is because the rate of crystallization is low enough to allow the nucleating agent to have a direct impact on the nucleation density. Conversely, polyethylene has an extremely fast rate of crystallization, rendering most nucleating agents as ineffective. This is probably the reason there has been such minimal commercial activity in the area of nucleating agents for polyethylene.

**A New Nucleating Chemistry for Polyethylene**

Successful nucleating agents increase the temperature at which a polyolefin begins to crystallize. This presents an immediate method for screening potential nucleation candidates for polyethylene. Clearly, there are other important factors to consider but as a starting point, a measurement of peak crystallization temperature ($T_c$) of a nucleated polyethylene is a strong indicator of nucleation effects. This can be measured by differential scanning calorimetry (DSC) using ASTM D-794-85. The following Figure shows this test performed on a 0.917g/cc density, 1.0 MI, Ziegler-Natta hexene LLDPE resin with a range of different commercial and experimental nucleating agents:

*Figure 3. Peak crystallization temperature ($T_c$) of known nucleating species in LLDPE*
This data shows that the new nucleating agent N-1 is able to raise the Tc of the LLDPE resin to its highest value, from 109ºC to 113ºC. It should also be noted that the comparison is versus “state of the art” nucleating chemistries for polypropylene and that a delta of just 1-2 ºC in Tc is typically an indicator of significant nucleation in polyethylene.

An additional screening tool for nucleation performance is a measurement of crystallization kinetics. This can be done by measuring the crystallization half time, referred to as t₁/₂ (again by interpreting the data output from a DSC), which is simply a measure of the time it takes for half the crystals to grow in a sample held at a given isothermal temperature. In the following test, the same resin was used as in Figure 3 and an isothermal temperature of 122.5ºC was chosen:

![Crystallization Half-Time at 122.5°C](image)

**Figure 4. Crystallization Half-time (t₁/₂) of Advanced Nucleating Agents in LLDPE**

Indeed, the data in this analysis is very compelling. The addition of nucleator N-1 results in dramatic reductions in crystallization half time versus both the control and another commonly employed polypropylene nucleating agent N-2 (a comprehensive study has been completed in this area against numerous known nucleating agents). In this study the crystallization half time is reduced from 57 minutes to 5.5 minutes, a nine-fold reduction. This is believed to be the first time such a dramatic effect on crystallization kinetics has been observed from the heterogeneous nucleation of a polyethylene.

HDPE resins have traditionally been difficult to nucleate due to the extremely high rate of crystallization inherent to these polymers. Figures 5 and 6 below show the nucleation performance of N-1 in a 1.0 MFR bimodal HDPE with regard to polymer Tc and crystallization half-time (t₁/₂):

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These figures show that although a $T_c$ increase of only 1 °C is observed, the speed of crystallization of HDPE is doubled, further demonstrating the efficiency of nucleator N-1.
Figure 7 below gives a more visual representation of the effect of nucleation in polyethylene. This test shows an image of a 40 micron compression molded plaque taken under hot stage microscopy. The polyethylene is a 0.952 g/cc HDPE which was heated to 200°C and then cooled at a controlled rate of 10°C per minute; the image is taken at the end of the test (after about 10 minutes and at a temperature of 100°C). The impact of the nucleating agent N-1 on the average spherulite size can clearly be seen.

![Nucleation of Different Types of Polyethylene](image.png)

**Figure 7. Hot Stage Microscopy Analysis of HDPE crystallization behavior**

**Nucleation of Different Types of Polyethylene**

A first step in an analysis to investigate the nucleation performance in polyethylene involves a study of a broad range of types of materials. The following table shows the materials employed in the remainder of the study unless otherwise stated:

<table>
<thead>
<tr>
<th>Resin grade</th>
<th>Density</th>
<th>MFI</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.917</td>
<td>1.0</td>
<td>Z-N hexene LLDPE</td>
</tr>
<tr>
<td>B</td>
<td>0.924</td>
<td>1.0</td>
<td>LDPE</td>
</tr>
<tr>
<td>C</td>
<td>0.918</td>
<td>1.0</td>
<td>Z-N butene LLDPE</td>
</tr>
<tr>
<td>D</td>
<td>0.958</td>
<td>0.95</td>
<td>HDPE</td>
</tr>
<tr>
<td>E</td>
<td>0.917</td>
<td>1.0</td>
<td>Metallocene LLDPE</td>
</tr>
<tr>
<td>F</td>
<td>0.920</td>
<td>1.0</td>
<td>Z-N octene LLDPE</td>
</tr>
</tbody>
</table>

*Table 1. List of polyethylene resins used in blown film trials*
An initial study by DSC of a representative LLDPE, mLLDPE and HDPE yielded the data in Figure 8. In conclusion, nucleating agent N-1 has successfully demonstrated effective nucleation of the LLDPE and HDPE polyethylene materials.

![Figure 8. Effect of Nucleator N-1 upon $T_c$ of different types of Polyethylene](image)

**Blown Film Trial Data - Results and Discussion**

Over 50% of the global consumption of polyethylene is for film applications and so it is a natural application choice in which to study the effects of nucleation. Within this area, processors employ cast and blown film processes to produce film structures for a variety of applications. The following experiments were conducted on traditional polyethylene blown film equipment (where there is an absence of quench cooling) to measure the effect of nucleation observed in the previous section upon a range of different film properties. A basic review of findings in 5 areas will be covered: optical, physical, processing, sealing and barrier properties.

**Blown Film Line Conditions and Details**

A Battenfeld-Gloucester production blown film line was used for the following trials. The line has 3 extruders although only one was in use for this monolayer trial (80mm extruder). The line has a 10” die and a 110mil die gap and for the purposes of this trial the blow up ratio (BUR) was held constant at 2.5. Additionally, the line had a chilled air ring and internal bubble cooling and was operated at 136kg/hour during the trial. All film samples were measured at a thickness of 1 mil. All nucleated samples were high intensity mixed in a Henschel blender prior to twin screw compounding.
1. Optical properties

The produced blown films were measured for optical properties using ASTM D1003 / D2457, shown below in Figure 9:

![Figure 9. Optical properties of different LLDPE resins with Nucleator N-1](image-url)

The positive effects on haze and gloss are consistently seen in butene and hexene comonomer LLDPE resins (haze reduction of 38-55%); optical enhancement of many octene comonomer LLDPE resins show inconsistent results when using nucleator N-1. Further studies are underway to better understand this phenomenon.

A more fundamental understanding of the mechanism by which N-1 is able to improve optical properties of LLDPE blown films was performed using atomic force microscopy (AFM). It is well known that the vast majority of film haze is caused by surface haze as opposed to internal haze (in thinner film sections). AFM analysis revealed that nucleation reduces the average surface haze seen in blown films via a reduction in surface roughness (Figure 10):
Further analysis of the optical properties of metallocene LLDPE films modified using N-1 showed some interesting performance (Figure 11) in both haze and gloss. It is hypothesized that the narrower molecular weight distribution of metallocene catalyzed resins form part of the explanation for the more pronounced effect on haze and gloss than is seen in Ziegler-Natta resins. The resultant mLLDPE films nucleated with N-1 exhibit outstanding haze and gloss properties.

**Effect of N-1 in mLLDPE**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Roughness-20um</th>
<th>Surface Roughness-5um</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE control</td>
<td>34.9 nm</td>
<td>20.7 nm</td>
</tr>
<tr>
<td>LLDPE plus N-1</td>
<td>20.5 nm</td>
<td>16.4 nm</td>
</tr>
</tbody>
</table>
2. Physical properties

It is important to note that the industry typically uses LDPE as a blend component in LLDPE blown film to enhance processing (bubble stability and output) and optics. Optical enhancement of LLDPE using LDPE can yield haze and gloss numbers close to and even slightly superior to those achieved with the nucleating agent. This is an established and practiced art in the field. There is a trade-off associated with employing LDPE as a blend component – there is usually a sharp drop in certain physical properties. Figure 12 attempts to study the effect on tear (both machine direction and transverse direction) and dart drop impact of different blends of LDPE and hexene Z-N LLDPE resins. This is directly compared to the same LLDPE resin incorporating N-1 (referenced against a control LLDPE with an additional compounding step owing to the fact that the nucleator was compounded as powder on pellet). It can be observed that the LDPE formulations have very distinct anisotropy in tear strength (severely diminished MD tear) and significantly reduced impact properties versus similar films made using the nucleating agent. This may present opportunities for reduction or even elimination of the LDPE blend component in certain instances which may be valuable to blown film producers for a variety of economic and technical reasons.

Figure 11. Optical properties of metalloocene LLDPE with Nucleator N-1
The addition of the nucleating agent to LLDPE resins also results in other related physical property enhancements. An increase in secant modulus has been observed under different trial conditions in the region of 10-15% in machine and transverse directions. Figure 13 shows this data (Trial 1 refers to the Battenfeld Gloucester trial). This can be important for attempts to downgauge the blown film or for improvements in downstream handling of films on conversion equipment.

![Figure 12. Comparison of physical properties (tear and impact) of blending LL/LDPE versus nucleating LLDPE with Nucleator N-1](image)

![Figure 13. Effect on nucleation on secant modulus of LLDPE film](image)
3. Processing Benefits

As discussed previously, nucleation of LLDPE increases the temperature at which the polymer begins to crystallize. This effect can be measured in the laboratory but also becomes apparent upon conducting trials on a film line. This is seen through a drop in the Frost Line Height (FLH) of LLDPE during the blown film process (due to faster crystallization kinetics); this presents opportunities to increase extruder throughput and hence line speed. Trials have typically yielded line speed increases from 5-20% but clearly this is heavily dependent on other features of the line setup. Nonetheless, the drop in frost line height and change in bubble shape can be seen in Figure 14. Additionally, qualitative observations have shown that thickness variation and overall film consistency are often improved through nucleation, probably as a result of more uniform crystallization behavior.

![LLDPE Control](image1.png) ![LLDPE + 1000ppm N-1](image2.png)

*Figure 14. Photographs of blown film bubble showing drop in frost line height (FLH) due to nucleation effects*

4. Sealing properties

A critical parameter in many film applications is seal performance. This can be characterized through two different methods; ultimate seal strength and hot tack strength. These properties have varying degrees of importance depending on the application and downstream conversion process. Ultimate seal strength is measured against ASTM F 88-05 and involves creation of a seal at a given temperature, pressure and dwell time followed by the measurement of the tensile strength (to initial failure) once the film has cooled to ambient temperature.
Hot tack strength is measured against ASTM F 1921-98 and is more a measure of seal strength at the moment it has just been formed (before cooling). This is typically very important in Vertical, Form, Fill and Seal (VFFS) applications where a seal is formed and is subjected to load before it has completely cooled. Enhancements in hot tack performance can be particularly beneficial to VFFS packaging lines as it potentially allows for faster throughputs and/or less leaking packages.

Figure 15 shows the initial study of the ultimate seal strength of Resin A against a nucleated version of the same. It can be concluded that nucleation appears to show no positive or negative effects on the ultimate seal strength of the LLDPE resin. Further work is planned to investigate the effect of nucleation on the seal performance of blended film systems.

Figure 15. Ultimate seal strength of polyethylene film constructions

Figure 16 shows the results of hot tack tests performed on resin A with and without the nucleating agent. Further work is underway, but there is a consistent trend in performance enhancement with the presence of the nucleating agent. Higher hot tack strength is obtained at a given sealing temperature, reduced hot tack seal initiation temperature is observed and a broader hot tack curve results. These three parameters are all very important potential advancements in hot tack performance.

Figure 16. Effect of nucleation on hot tack curves of LLDPE films
5. Barrier properties

Flexible packaging has seen outstanding growth as a packaging medium for food in recent times. With the advent of co-extrusion and new lamination techniques, there is now a wide and varied array of different structures being employed to meet the ever increasing barrier demands of the different foods being packaged. Polyethylene resins are not typically used for their oxygen or moisture vapor barrier; however, there are certain applications where HDPE is used for its balance of mechanical and barrier properties and excellent cost competitiveness. A particularly large market segment where HDPE moisture vapor barrier performance is important is in the area of cereal liners and dry food packaging. Additionally, LLDPE moisture vapor barrier performance can be important in silage films and industrial liners (for packaging hygroscopic products).

Figure 17 shows the results of Moisture Vapor Transmission Rate testing (MVTR) and Oxygen Transmission Rate testing (OTR) for the LLDPE and HDPE resins (note in this study, a 0.45MI, 0.958g/cc HDPE barrier grade was employed). Reductions in MVTR are typically reduced by approximately 40% (LLDPE) and 10-20% (HDPE) when adding nucleator N-1. Oxygen transmission rate reductions (OTR) also follow the same trend.

![Figure 17. WVTR and OTR measurements for LLDPE and HDPE films](image)

**Conclusions**

Nucleator N-1 is a new chemistry that successfully nucleates certain types of polyethylene. Analytical work has observed the elevated crystallization temperature and reduced crystallization half-time associated with nucleation performance in a polyolefin. Additionally, surface roughness modifications (via AFM) and changes in the crystallization behavior (DSC) have also been observed. A series of polyethylene resins were nucleated with the new chemistry, run on a production scale blown film line and the resultant films measured for changes in optical, physical, sealing and barrier properties. The nucleating agent is able to positively impact these different properties which may present future industrial opportunities. Further work is planned to further quantify, optimize and understand polyethylene property modification using nucleation.
References

5. Cantor, K., Blown Film Extrusion, An Introduction, 2006