Why Nucleators?

Polypropylene is a semi-crystalline polymer. Nucleating agents increase the crystallization rate and the overall percent crystallinity of the polymer. The faster crystallization rate allows for higher productivity in molding and extrusion processes. The overall percent crystallinity of the polymer improves the stiffness and heat deflection temperature.

By influencing the crystallization process, nucleating agents also affect the differential shrinkage of polypropylene. Since differential shrinkage is an important factor in part warpage, the selection of a nucleating agent can have a pronounced effect on the dimensional stability of a final part.

A new class of nucleating agents, described as "Hyper Nucleating Agents" are now commercially available. Hyper nucleating agents allow for the fastest processing in molding and extrusion processes, while providing the same physical property improvements as traditional nucleating agents. In addition, this new class promotes more isotropic shrinkage, which reduces the potential for part warpage. The first commercial example of a Hyper Nucleating agent is Hyperform® HPN-68L.

Classes of Nucleators:

The original nucleating agents used in polypropylene were aromatic carboxylic acid salts, with sodium benzoate the most commonly used even until today. Fillers, talc, and certain pigment colorants were also found to give a nucleation effect. These types of nucleating agents are referred to as conventional nucleating agents.

Beginning in the early 1980's, a newer advanced class of nucleating agents was introduced. These have since become widely used in copolymer resins that require additional modulus enhancement and faster crystallization. Most important among these advanced nucleating agents are the phosphate ester salts, pioneered by Asahi Denka of Japan. The phosphate...
ester salts, such as NA-11 and NA-21, are used predominantly for enhanced nucleation as compared to the conventional nucleating agents.

In 2002, Milliken Chemical introduced the first example of a **hyper nucleating agent** - Hyperform® HPN-68L. This represents a significant technological advance over the conventional and advanced nucleation technologies now in commercial use. Hyper nucleating agents **allow for the fastest processing speed in molding and extrusion processes**, while providing the same physical property improvements as traditional nucleating agents. In addition, this new class **promotes more isotropic shrinkage**, which reduces the potential for part warpage.

![Diagram showing isotropic shrinkage and crystallization temperature](image)

**Mode Action:**

All known nucleating additives are "heterogeneous" nucleators; that is, they present a heterogeneous surface to the PP melt during cooling that promotes polymer crystallization through epitaxial effects. During the cooling phase, a well-dispersed nucleating agent in molten PP, through this epitaxial or template-like effect, causes the formation of many more polymer crystals at a higher temperature as compared to the same resin without a nucleating agent. This process is shown pictorially in Figure 2.
Cycle Time Reduction:

Nucleating agents increase the temperature at which polypropylene begins to crystallize. The crystallization temperature of a polymer (denoted as "polymer Tc") is measured by differential scanning calorimetry (DSC). As shown in table 1, each of the nucleating agents increase the polymer Tc of the medium impact copolymer. The hyper nucleating agent, HPN-68L, gives a polymer Tc value that is 18°C higher than the control.

Increases in polymer Tc result in decreases in the cooling time required for part solidification. This improves the overall cycle time of a molding or extrusion process and increases productivity. Since Hyperform HPN-68L gives the highest polymer Tc, it would be expected to give the largest improvements in productivity.

See case studies on nucleating agents that correlate polymer crystallization temperature to processing speed:

<table>
<thead>
<tr>
<th>Class</th>
<th>Nucleating Agent</th>
<th>Polymer Tc (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (non-nucleated)</td>
<td>Resin --</td>
<td>108.8</td>
</tr>
<tr>
<td>Conventional Nucleator</td>
<td>Sodium Benzoate</td>
<td>116.2</td>
</tr>
<tr>
<td>Advanced Nucleator</td>
<td>Organophosphate Salt</td>
<td>125.3</td>
</tr>
<tr>
<td>Hyper Nucleator</td>
<td>Hyperform HPN-68L</td>
<td>126.8</td>
</tr>
</tbody>
</table>

Table 1: Polymer Tc results for nucleating agents in a medium impact copolymer (Cooling time = 20°C).
Nucleating agents can also be evaluated by determining the Isothermal Crystallization Half Time (ICHT) using DSC. This is the time that it takes a polypropylene sample to reach 50% of its crystallization when held at a constant temperature. This comparison was made at 145°C. The shorter the half time, the more powerful the nucleating agent. Hyper nucleating agents give fastest crystallization.

Figure 3: ICHT results for nucleating agents in a medium impact copolymer (ICHT Temperature = 145°C).

Hyper Nucleating Agents provide significant cycle time reductions in both injection and extrusion processes. This allows increased productivity which ultimately lowers manufacturing costs.

Figure 5 below shows typical % of productivity increase of various processes.
Warpage in polypropylene parts is due to the presence and interaction of many factors including polymer orientation and differential shrinkage, mold and part design, and processing conditions. **Nucleating Agents can affect the potential for warpage** by influencing the differential shrinkage of polypropylene. **The more isotropic the shrinkage, the less the chance for warpage in a molded part.**

**Dimensional Stability:**

Differential Shrinkage can be measured using an injection-molded rectangular part, gated on the shorter side (as shown in Figure 6). The shrinkage in the length and width directions is measured in each of three areas of the plaque: the gate area, the middle and the end of the plaque. The isotropic ratio is calculated by dividing the length shrinkage by the width shrinkage. The closer this value is to 1.0, the less potential for warpage.

As shown in Figure 7, Hyper Nucleating Agents promote more isotropic shrinkage in each of the three regions of the part as compared to the control resin and the other nucleating agents. This data predicts that a part made with a hyper nucleating agent should have less warpage than a part made from one of the other formulations.
The consistency of the isotropic shrinkage ratio across the part is also critical. Inconsistent differential shrinkage ratios are an indicator that warpage may occur with a particular resin. Unlike other commercial nucleating agents, resins containing hyper nucleating agents provide very consistent isotropic ratios across the part, which are close to 1.0. See Case Study on Dimensional Stability in DVD Cases.

**Figure 8**

Mechanical Performance enhancement
Stiffness
Flexural Modulus (stiffness) of polypropylene can be improved by the addition of nucleating agents. Typically, nucleating agents increase the stiffness of polypropylene by 10-15% over a non-nucleated control. Data in a 12 MFR HP and a 20 MFR Medium Impact Copolymer are shown in Figure 9.
Flexural Modulus: ASTM D790

Impact Resistance
The increase is stiffness due to the addition of nucleating agents is accompanied by a slight decrease in impact resistance. Gardner Impact data in a 20 MFR Medium Impact Copolymer is shown at 23°C and -30°C in Figure 10. Gardner Impact Resistance: ASTM D5420.

HDT Increase
Hyper nucleating agents increase heat deflection temperatures (HDT) approximately 20 - 25% over a non-nucleated PP and allow to significantly improve polymer resistance to distortion at elevated temperatures.
Case Study:

1, DVD Case

The shrinkage isotropy imparted by Hyper nucleating agents was studied on a commercial part using a DVD Case. This particular case is made from a homopolymer containing a low level of talc. The part is highly sensitive to warpage, as the disc tolerance is very tight. The circular area that houses the disc provides an ideal place to study differential shrinkage.

![Figure 13](image)

This figure shows a schematic for the part and the circular area in which the length dimension (D2) and the width dimension (D1) can be accurately measured. The ratio D2/D1 is the isotropic ratio. As with the lab study, a ratio of 1.0 is desired. (See Dimensional Stability)

Table 2 identifies the four formulations used for this study. Sample A is the base resin, which is nucleated with a low level of talc. Sample D is this base resin with the addition of a grey pigment via masterbatch. The other samples (B and C) contain the Hyper nucleating agent (HPN-68L), with and without grey pigment.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Nucleating Agent</th>
<th>Grey Masterbatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>B</td>
<td>Hyper</td>
<td>none</td>
</tr>
<tr>
<td>C</td>
<td>Hyper</td>
<td>1 %</td>
</tr>
<tr>
<td>D</td>
<td>none</td>
<td>1 %</td>
</tr>
</tbody>
</table>

Table 2: Formulations tested for isotropic shrinkage in a DVD Case.

The isotropy results are shown in Figure 14. Without the addition of a hyper nucleating agent, there is a great deal of anisotropy in the DVD case both with and without added pigment (Samples A and D). As hyper nucleating agents are added, however, the isotropic ratio gets very near to 1.0 (equal shrinkage in both directions), indicating a dimensionally stable part. The shrinkage data from the DVD case agrees well with the data from the laboratory test in plaques. (See Dimensional Stability)
2, Door Panel

An injection molding trial was run on a door panel to investigate improvements in cycle time and warpage due to nucleation. The base resin used to make the door panels is a 20 MFR impact copolymer. Both unfilled and filled (with 15% calcium carbonate) formulations with each of the nucleating agents were studied. The door panel has a 90-degree bend near the speaker grill that warps severely when the cooling time is too short (Figure 15). All of the formulations were molded under the same conditions, except that the mold cooling time was reduced until an off-quality part was made. By increasing the crystallization temperature of the resin with nucleating agents, the cooling time required to make an acceptable part decreases.

![Figure 15: Injection molded door panel.](image)
The yellow circle indicates the area of the panel that warps when cooling time is insufficient.

As shown in Figure 16, the addition of nucleating agents to both base resins (unfilled and calcium carbonate filled) allows an acceptable part to be made in less time. The degree to which the cycle time can be improved is related to the polymer crystallization temperature. The hyper nucleating agent gives the highest polymer Tc and the fastest cycle time. This increase with the hyper nucleating agent was 10% over that of the control for the unfilled ICP and 8% over the control for the filled system.
To investigate potential cycle time and warpage reductions with a hyper nucleating agent, an injection molding trial was run using a battery case. The limiting factor in terms of cycle reduction for this part is warpage in the end-walls of the case. When the cooling time was insufficient, the walls bow inwards.

Battery cases were molded from ICP formulations with and without a hyper nucleating agent. As shown in Table 3, the addition of a hyper nucleating agent to the polymer increased the polymer Tc by 11°C. The formulation containing HPN-68L produced essentially the same end-wall warpage as the non-nucleated materials, but with a 10s lower cycle. The reduction came completely from the mold cooling time. This 10s decrease equates to a 13% reduction in total cycle.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Polymer Tc</th>
<th>Total Cycle Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control ICP</td>
<td>113.3°C</td>
<td>75 s</td>
</tr>
<tr>
<td>ICP with Hyper</td>
<td>124.6°C</td>
<td>65 s</td>
</tr>
</tbody>
</table>

Table 3: Battery case injection molding trial results. The polymer crystallization temperatures were determined at a cooling rate of 20°C/min

The end-wall warpage was the limiting factor in these trials. Figure 17 shows a schematic of the battery case end. It depicts the warpage that can occur after molding. Figures 18 and 19 show the results of a detailed study on the effect of cooling time on the left and right end-wall warpage. At the same cycle, end-wall warpage in battery cases containing a Hyper nucleating agent was about 25% less than the end-wall warpage in battery cases containing no nucleating agent. This is another example of where the hyper nucleating agent, HPN-68L, decreases cycle time and limits warpage.
Figure 17: Schematic of the end-wall warpage of a battery case.

Figure 18: Battery case injection molding trial. Left end-wall warpage results.

Figure 19: Battery case injection molding trial. Left end-wall warpage results.
4, Pipe Fittings:

An injection molded trial was run on a pipe fitting for a laundry machine to show the effect of nucleating agents on cycle time and warpage. The base resin used for these trials was a 20% talc filled polypropylene. Formulations were run with and without a hyper nucleating agent. The two formulations were molded under the same conditions, except that the mold cooling time was reduced until an off-quality part was produced. When the cooling time was insufficient, a sink mark formed on this part around the gate area (Figure 20). By increasing the crystallization temperature of the resin with nucleating agents, the cooling time required to prevent the sink mark should decrease.

![Figure 20: Pipe Fitting:](image)

**(A)** Acceptable part.

**(B)** Unacceptable part - sink mark around gate area (yellow circle).

Table 4 shows the polymer Tc data and results from the molding trials. The addition of the hyper nucleating agent increases the crystallization temperature of the polypropylene. This allows the cooling time to be decreased, while maintaining part quality. The total cycle time for the base resin was 37 seconds. Adding the hyper nucleating agent to this base resin allows the total cycle time to be reduced to 30 seconds. This represents a 19% reduction in total cycle time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer Tc (°C)</th>
<th>Cycle Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc Filled PP</td>
<td>115.7</td>
<td>37</td>
</tr>
<tr>
<td>Talc Filled PP with Hyper Nucleating Agent</td>
<td>121.5</td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 4:** DSC and Cycle Time results for the pipe fitting part.

DSC experiments run at a cooling rate of 20°C/min.

5, Garden Furniture:
The ability of hyper nucleating agents to reduce cycle time was studied using a single component lawn chair. This part was molded using a homopolymer/impact copolymer blend. A hyper nucleated formulation was compared to the non-nucleated control.

Figure 21

The injection molding cycle for this chair is 82 seconds when using the non-nucleated control. The largest part of this cycle is the mold cooling time, or the actual amount of time the polymer must remain in the mold and obtain enough crystallinity to demold. In this evaluation, the addition of the Hyperform nucleating agent to the formulation allowed for a 42% reduction in cooling time.

Figure 22

In terms of the total cycle, the hyper nucleating agent provided a 16% reduction in cycle time as compared to the control. The increase in polymer crystallization temperature with a hyper nucleating agent allows the part to be removed from the mold faster.

If we then annualize this productivity, assuming a 365-day molding campaign, then 72,000 more chairs would be produced. This productivity increase can be obtained with no additional capital expenditures.
6. Closures:

Nucleated resins were tested in both injection molded (IM) closures and extrusion compression molded (ECM) closures. In both cases, impressive productivity gains were realized with the addition of a hyper nucleating agent.

IM Closures

In the injection molding trials, 28mm closures were produced on a 16 cavity mold using a 4 MFR homopolymer. Three formulations containing nucleating agents from each class were compared to a non-nucleated control. In terms of productivity, the Hyper nucleating agent increased productivity 12% over the control, with 7100 parts per hour being produced. The advanced nucleating agent produced only 6500 parts per hour. 12% may not sound like a large increase, but consider the improvement on an annualized basis: If this machine, with 16 cavities, ran nonstop for 365 days, then 1.7 million more parts would be produced than with advanced nucleator - and this improvement is obtained without any additional capital expenditures.

![Figure 23](image)

ECM Closures

Extrusion Compression Molding trials were run on a SACMI CCM-001 32 Cavity machine using a 7 MFR Impact Copolymer. Asian one-piece hot fill caps were produced at a punch temperature of 20°C. In these evaluations, a conventional nucleating agent was compared to a hyper nucleating agent. As shown in the following chart, the formulation containing the hyper nucleating agent allowed quality closures to be made at a rate of 600 caps/min, while the conventional nucleating agent only allowed for a maximum rate of 450 caps/min. This
represents a 33% increase in molding productivity. Figure 25 shows two caps made from each formulation at a production rate of 600 caps/min.

Figure 24

![Figure 24](image)

Figure 25

![Figure 25](image)

Hyper Nucleating Agents with Pigments:

Commercial pigments are known to nucleate polypropylene to different degrees. This inconsistency in nucleation makes it difficult to produce identical parts containing different pigments. Processing conditions must be adjusted to account for differences in crystallization speed and differential shrinkage. Certain pigments, particularly blue and green phthalocyanines, are known to cause warpage issues due to anisotropic shrinkage properties.

Hyper nucleating agents can be added to these pigment formulations to level out the effect of crystallization temperature and differential shrinkage. As shown the figure below, the addition of a hyper nucleating agent (HPN-68L) to various pigmented formulations makes the crystallization temperature and shrinkage performance of the pigments much more consistent.
Hyper Nucleating Agents with Fillers:

Hyper nucleating agents are compatible with filled PP systems, including talc, calcium carbonate and glass filled polypropylene. While the filler provides the greatest contribution to the increase in flexural modulus with these systems, Hyper nucleating agents still bring significant increases in other key performance areas such as polymer crystallization temperature, isothermal crystallization half-time, isotropic shrinkage and HDT enhancement. These attributes translate into benefits such as productivity gains in molding and extrusion processes and reduced potential for warpage in actual parts.

See two case studies in this report:
Pipe fittings with 20% talc
Automobile Door Panels with 15% calcium carbonate.