Dymalink® (9200 series) for Improved Melt Strength in Foam Applications

Description
Polypropylene (PP) is a semi crystalline polymer with a sharp melting point. Above their melting points most PP grades exhibit low melt strength or strain hardening behavior. This precludes the use of standard PP in applications where melt stretching or drawing are critical, such as foam molding, blow molding, thermoforming, or pipe extrusion.

Traditionally, to overcome the lack of melt strength, high-melt-strength polypropylene (HMS-PP) is added at levels between 10-50%. The HMS-PP products are based on the chemical incorporation of high levels of long-chain branches chemically linked to the polymer backbone. Other strategies have been proven efficient but introduce large amounts of low-molecular-weight byproducts into the polymer.

Introduction
Dymalink® 9200 is an acrylate functional zinc salt that reacts with aliphatic polymers to form a carbon-carbon covalent link. Due to the polar nature of the zinc salts, the ionic bonds tend to assemble into ionic clusters within the polymer matrix, promoting the formation of a dynamic network.
As illustrated in Figure 1, when the polymer is heated to temperatures greater than 170 °C, the ionic bond dissociates, but when subsequently cooled to <170 °C, the ionic bond reforms, yielding an ionic cross-link between the chains. At <170 °C, the ionic bond exhibits the ability to split along the hydrocarbon chain and re-form – this phenomenon is energy triggered. For instance, at low temperature the material will be cross-linked, whereas at high temperature (>170 °C), the ionic bonds are opened. Hence, the network generated by the ionic bonds is thermo-reversible. This leads to an unusually high melt strength behavior even at very low loadings.

**Experimental**

A neat homo-polypropylene with 3.0 melt index was compounded with 2500 ppm of an antioxidant package (AOX), 500 ppm Calcium stearate, and various levels of Dymalink in a 19 mm Brabender twin-screw extruder with the following temperature profile from inlet to die: 20 - 190 - 200 - 200 - 200 - 210 - 210 - 210 °C. The extruder die was fitted with a Rheotens 71.97 device comprising a 2 mm die, L/D 15, with the extruder pressure maintained at 85 bars in order to record melt strength.

Figure 2 shows that melt strength improvement is effective with percentages of Dymalink 9200 as low as 0.5%. Only a very minor increase in speed at breakage is observed when increasing the Dymalink dosing from 0.5% to 2%.
**Recommendation**

A temperature greater than 200 °C/390 °F (ideally 240 °C/465 °F) is required to have a good incorporation of the Dymalink 9200 into the polymer backbone. Under those conditions, the reaction is expected to be instantaneous due to the high reactivity of the acrylate group.

A masterbatch could be prepared but a low temperature is required to avoid the Dymalink reaction. In this case, it is recommended to compound the materials at a temperature lower than 170-180 °C (335-355 °F) and a low Dymalink concentration of <10% wt.

**Application**

**PHYSICAL FOAMING**

As a control, an extrusion grade of PP homopolymer with a 3.5 melt index and a loading of 0.5% talc was compounded with and without 1% Dymalink 9200 in a co-rotating twin-screw extruder (26 mm, L/D 44). For the foaming test, materials were processed on a single-screw extruder at 240 °C (465 °F) with a static mixer feeding CO₂ liquid at 74 bar (1100 psi). Compared to the control, the sample containing Dymalink 9200 exhibited a smooth surface appearance, indicating more homogeneous foaming, as seen in Figure 3.

The compound without Dymalink 9200 shows poor cell morphology with high open cell content, irregular sizes, and poor surface morphology, as seen in Figure 4. In contrast, the cell structure of the Dymalink 9200 sample is homogenous with good closed cell content.

![Figure 3: Extruded foam rods obtained without and with 1% of Dymalink® 9200.](image)

![Figure 4: Scanning electron microscope (SEM) picture of cell structure of foamed PP obtained without (left) and with (right) 1% of Dymalink 9200, 0.6 mL/min CO₂, 130 bar die pressure.](image)
CHEMICAL FOAMING
The chemical foaming study used a homopolymer PP with a 2.8 melt index, Dymalink 9200 and Safoam® PN-40E, an endothermic chemical foaming agent supplied by Reedy Chemical Foams. The Dymalink 9200 was added at 0.5% while the chemical foaming agent loadings used were 1.5% and 2%. Materials were blended and added at the feed throat of a single-screw extruder (30 mm, L/D 30). A decreasing temperature profile from 220 °C to 185 °C (430 °F to 365 °F) was used. Once again, compared to unmodified resin, the extruded material with Dymalink exhibited a smooth surface appearance with better foam morphology. Dymalink 9200 provided a homogenous cell structure with increased closed cell content. The foam without additive had lower closed cell content and cells with different sizes and shapes. Figure 5 shows cross-sections of PP foamed with 1.5% Safoam PN-40E. The image on the left contains no additive compared with the image on the right that contains 0.5% Dymalink 9200.

Dymalink 9200 reduced foam density to 0.50 g/cc with both 1.5% and 2% loadings of the chemical foaming agent. Additionally Dymalink 9200 reduced foam cell size to 125 µm and reduced density to 0.5 g/cc for both loadings of blowing agent. Table 1 shows foam cell nominal size, density and density reduction.

Table 1: Foam cell nominal size, density and density reduction of chemical foamed PP without and with Dymalink 9200

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dymalink 9200 (%)</th>
<th>Foam Cell Size (µm)</th>
<th>Density (g/cc)</th>
<th>Density Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base PP (No foam)</td>
<td>0</td>
<td>-</td>
<td>0.90</td>
<td>-</td>
</tr>
<tr>
<td>1.5% PN-40E</td>
<td>0</td>
<td>151</td>
<td>0.58</td>
<td>36%</td>
</tr>
<tr>
<td>1.5% PN-40E</td>
<td>0.5</td>
<td>125</td>
<td>0.50</td>
<td>44%</td>
</tr>
<tr>
<td>2% PN-40E</td>
<td>0</td>
<td>202</td>
<td>0.55</td>
<td>39%</td>
</tr>
<tr>
<td>2% PN-40E</td>
<td>0.5</td>
<td>125</td>
<td>0.50</td>
<td>44%</td>
</tr>
</tbody>
</table>

Figure 5: Light micrographs of cell structure of foamed PP with 1.5% Safoam® PN-40E, obtained without (left) and with (right) 0.5% of Dymalink 9200.
Summary
Addition of Dymalink 9200 to conventional PP improves the melt strength of the resin, allowing for more homogenous cell structure with high closed cell content. This allows a greater freedom to tailor compounds to specific end-use needs versus the use of conventional HMS-PP in foaming applications.

About TOTAL Cray Valley
TOTAL Cray Valley is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings, and other materials. TOTAL Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics, and other demanding applications.

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