HDPE blow molding applications
HDPE blow molding market overview
The HDPE blow molding market

HDPE in blow molding ≈ 11 MT in 2015, growing at ≈ 3.3% p.a.

Dominant markets are:
- Household industrial chemicals (HIC)
- Beverage bottles
- Industrial drums (large part)

Use of unimodal HDPE dominates globally; bimodal HDPE is more popular in Europe

Key bottle properties are:
- Environmental Stress Cracking Resistance (ESCR)
- Impact resistance
- Top load

Source: Townsend database
## Insights on key blow molding applications

<table>
<thead>
<tr>
<th>Applications</th>
<th>Household industrial chemicals (HIC)</th>
<th>Large part / industrial drums</th>
</tr>
</thead>
</table>
| **Applications**                  | • Water  
• Dairy  
• Juice                                                                                           | • Home and agricultural chemicals  
• Some food, caps and closures                                               |
| **Critical considerations**       | • Barrier and stiffness  
• Taste and odor  
• Contamination/defects                                                                               | • ESCR  
• Impact resistance                                                      |
| **Typical density for HDPE resin (g/cc)** | 0.960                                                                                                     | 0.940 – 0.955                                                          |
| **Typical MI for HDPE resin @ 190°C/2.16kg (g/10min)** | 0.3 – 0.7                                                                                                  | 0.2 – 0.5                                                               |
|                                  |                                                                                                          | < 0.1                                                                  |

**ESCR & impact resistance are key properties in segments like HIC and industrial drums**
Optimize ESCR and impact performance of the base HDPE resin with Vistamaxx™ performance polymers
Vistammaxx™ performance polymers

- Produced using proprietary metallocene catalyst technology
- Semi-crystalline copolymers of propylene and ethylene
- Tailored ethylene content (4-16 w%) to balance properties
- Vistamaxx 6102 was selected to bring ESCR and impact performance at low levels (5-10 wt%) in HDPE

<table>
<thead>
<tr>
<th>Properties</th>
<th>6102</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene content [wt%]</td>
<td>16</td>
</tr>
<tr>
<td>Based on EM test method</td>
<td></td>
</tr>
<tr>
<td>MI (@ 190°C/2.16kg) [g/10min]</td>
<td>1.4</td>
</tr>
<tr>
<td>Based on ASTM D1238</td>
<td></td>
</tr>
<tr>
<td>Density [g/cc]</td>
<td>0.862</td>
</tr>
<tr>
<td>Based on ASTM D1505</td>
<td></td>
</tr>
<tr>
<td>Flexural Modulus [MPa] 1% Secant</td>
<td>12.3</td>
</tr>
<tr>
<td>Based on ASTM D790</td>
<td></td>
</tr>
</tbody>
</table>

Data from tests performed by or on behalf of ExxonMobil. These typical properties are not to be construed as specifications.
Improved ESCR and impact resistance in HDPE blow molding

High ESCR performance
- Improves ESCR of standard HDPE resin
- Equals or outperforms ESCR of high performance Unimodal HDPE resin
- Substitution of high ESCR Unimodal HDPE at lower cost

Outstanding impact resistance
- Improves impact resistance of standard HDPE resin and outperforms high ESCR Unimodal HDPE resin
- Durability and less breakage of blow molded part

Excellent processability
- Little influence on MI of standard HDPE resin
- Reliable blow molding operation

Soft / squeezable bottle
- Reduction in density and flexural modulus makes it a softer part compared to standard HDPE resin
- Drawback is loss in stiffness, resulting in loss in top load of the final blow molded part

Testing on molded plaques
Data from tests performed by or on behalf of ExxonMobil
Case study:
Tailoring technical performance through Vistamaxx™ performance polymers addition
Methodology

Formulations:

- 100% Standard HDPE: ExxonMobil™ HYA 600 HDPE resin
- 100% High ESCR Unimodal HDPE: market reference
- 95% Standard HDPE + 5% Vistamaxx 6102
- 92% Standard HDPE + 8% Vistamaxx 6102
- 90% Standard HDPE + 10% Vistamaxx 6102
- 88% Standard HDPE + 12% Vistamaxx 6102

Evaluation of molded plaques

- ESCR
- Impact Resistance
- Flexural Modulus
Tailoring the ESCR performance of standard HDPE resin

Vistamxx 6102 at 8 wt% or higher in standard HDPE outperforms the ESCR performance of high ESCR Unimodal HDPE resin
Providing outstanding impact performance in standard HDPE resin

Vistamaxx 6102 significantly improves the impact performance of standard HDPE, outperforming the high ESCR Unimodal HDPE resin. Lower flexural modulus results in a softer / more squeezable part, but with reduction in top load performance.

Tests on molded plaques:
Notched Izod Impact Resistance based on ISO 180/1A
Flexural Modulus based on ISO 178
Conclusions
# Vistamaxx polymers in HDPE blow molding

<table>
<thead>
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<th>Delivered attributes</th>
<th>Derived benefits</th>
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<tr>
<td><strong>Environmental stress cracking resistance (ESCR)</strong></td>
<td>• Improved ESCR of standard HDPE to match or outperform ESCR for high ESCR Unimodal HDPE</td>
</tr>
<tr>
<td></td>
<td>• Substitution of specialty HDPE at lower cost</td>
</tr>
<tr>
<td><strong>Impact resistance</strong></td>
<td>• Tailoring impact resistance of standard HDPE, outperforming high ESCR Unimodal HDPE</td>
</tr>
<tr>
<td></td>
<td>• Durability and less breakage of blow molded parts</td>
</tr>
<tr>
<td><strong>Excellent processability</strong></td>
<td>• Minor changes versus processing of standard HDPE</td>
</tr>
<tr>
<td></td>
<td>• Reliable blow molding operation</td>
</tr>
<tr>
<td><strong>Softness</strong></td>
<td>• Soft and squeezable blow molded part</td>
</tr>
<tr>
<td></td>
<td>• Drawback is loss in top load resistance</td>
</tr>
</tbody>
</table>
## Test methods

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test based on</th>
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</thead>
<tbody>
<tr>
<td>Density (23°C)</td>
<td>ISO 1183</td>
</tr>
<tr>
<td>MI (190°C/2.16kg)</td>
<td>ISO 1133</td>
</tr>
<tr>
<td>Tensile Modulus (5 mm/min)</td>
<td>ISO 527-2</td>
</tr>
<tr>
<td>Flexural Modulus (1% secant)</td>
<td>ISO 178</td>
</tr>
<tr>
<td>Hardness (15 sec)</td>
<td>ISO 868</td>
</tr>
<tr>
<td>Tensile stress at yield (50 mm/min)</td>
<td>ISO 527-2</td>
</tr>
<tr>
<td>Elongation at yield (50 mm/min)</td>
<td>ISO 527-2</td>
</tr>
<tr>
<td>Notched Izod Impact at Room Temperature</td>
<td>ISO 180/1A</td>
</tr>
<tr>
<td>Vicat (10N)</td>
<td>ISO 306 / A50</td>
</tr>
<tr>
<td>ESCR @ 50°C (10% Igepal)</td>
<td>ASTM D1693, cond B</td>
</tr>
<tr>
<td>Top load</td>
<td>ASTM D2658</td>
</tr>
</tbody>
</table>
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Back-up
ESCR on blow molded bottles

ESCR MEZ068 (Based on ASTM D 1693, condition B) - 10% Igepal - 50°C on bottle samples; specimen prepared per protocol below

No samples broken after 672 hours: blow molded bottles exhibited low stress
Top load on blow molded bottles

Addition of Vistamaxx 6102 in standard HDPE resin affects the top load performance of the final bottle.
What is Environmental Stress Cracking?

- Slow crack growth phenomenon defined as the surface-initiated failure of polyaxially stressed polymers in the presence of surface-active substances via surface micro-cracks
- Physical phenomenon; not chemical degradation
- Environment accelerates the stress cracking process but does not affect the macroscopic brittle-crack fracture mechanism, Figure 1.
- Tie molecules can be used to explain polymer microstructural variables on ESCR, such as molecular weight (MW), co-monomer type, and short chain branching frequency.

Figure 1. Schematic of brittle failure (ESC) of tie molecules in the amorphous region of polyethylene
ESCR testing

Test standard
• Testing was conducted according to Internal test method,
• MEZ 068 Environmental Stress Crack Resistance (revision 4: 29/04/10)
  (based on ASTM D-1693, Environmental Stress - Cracking of Ethylene Plastics)

Test protocol
• Sample plaques compression molded from each blend in a Collin vertical press (based on ASTM D-4073)
• Sample preparation between 2 and 4 days prior to testing
• Test reagent prepared 1 day before testing initiated
• Bath heating initiated 1 day before testing
• 10 test specimens cut from molded plaque using ASTM D1693 cutter within 25 hours of molding
• Specimen conditioning for a minimum of 40 hours at 23 °C
• Specimen notching using a CEAST notcher jig (max 100 notches per notch blade)
• Racks of 10 test specimens bent into test jig, placed in test tube, filled with test solution and placed in heated bath and monitored over the test period
• The time to crack failure (hours) of each specimen was recorded
• Test is complete when all 5 and /or all 10 specimens had failed
• Reagents: 10% solution of Igepal CO-630 and high purity de-ionized water

Testing
• Testing commenced within 40 to 96 hours after conditioning had begun
• The time to crack failure (hours) of each specimen was recorded
• Test temperatures: 10% Igepal solution – 50 °C
• Test was complete after 336 hours; plus reporting of $F_{50}$ was achieved
ESCR testing

- Testing was conducted using an internal EMCC test method MEZ 068, based upon ASTM D 1693. Originally, ASTM D1693 specified that 100% *Igepal®* was to be used for all conditions but the test period to failure was too long. A more aggressive 10% by volume *Igepal®* solution was substituted in order to cause more rapid failure. The latest revision of ASTM D1693 reflects this.

- *Presence of a Notch* The fact that a sample or a piece of pipe is notched allows the crack propagation to start earlier, because of the introduction of a critical defect. Brittle failures are typically facilitated due to the state of stresses and strains generated in the sample by a notch. Therefore, the way the notch is milled, especially its geometry (notch length and notch tip radius) may affect the times to failure. This factor is as important as the stress, temperature and the surface active agent.

- When considering ESCR, it is important for the resin customer to compare "apples to apples. “ Find out test conditions such as temperature, surfactant used, bottle type and weight, among other variables. For best comparison, the polymers in question should be subjected to side by- side testing, using the same equipment, operator and environment. These conditions minimize much of the test variation and give the fairest comparison.