Rapid Molding of Thermoplastic Composites

A Molding Process to Produce Thermoplastic Continuous Fiber Composite Parts in 5 to 10 Minutes.

Jim Mihalich
Cyclics Corp
The Missing Link – The Right Catalyst

• Different Catalysts Provide Cure Ranges from Seconds to Hours
• No Exotherm Allows Positive Rate Control Via Correct Catalyst Selection
• Melt Temperature Establishes Maximum Pot-Life and Infusion Time per Catalyst
• How to Balance a Fast Cure Rate with Infusion Time?
Catalyst Selection Criteria

- Commercially Available
- A Controllable Delay to Allow Infusion
- Fast Acting
- Liquid for Direct Metering to Resin Stream
- Produces High Molecular Weight and Acceptable Properties
## Polymerization Comparison of the Catalyst Candidates

<table>
<thead>
<tr>
<th>Molding Conditions</th>
<th>% Conversion</th>
<th>Molecular Weight Mw</th>
<th>D (Dispersity)</th>
<th>% Conversion</th>
<th>Molecular Weight Mw</th>
<th>D (Dispersity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaxis C204</td>
<td></td>
<td></td>
<td></td>
<td>Tyzor TE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>190°C 30 Minutes Air Cool</td>
<td>97</td>
<td>151,000</td>
<td>2.80</td>
<td>97</td>
<td>109,000</td>
<td>2.85</td>
</tr>
<tr>
<td>230°C 30 Minutes Air Cool</td>
<td>99</td>
<td>123,000</td>
<td>2.31</td>
<td>99</td>
<td>137,000</td>
<td>3.25</td>
</tr>
<tr>
<td>230°C 30 Minutes Quench Cool</td>
<td>99</td>
<td>122,000</td>
<td>2.47</td>
<td>97</td>
<td>154,000</td>
<td>3.55</td>
</tr>
</tbody>
</table>
# DSC Testing of the Catalyst Candidates

<table>
<thead>
<tr>
<th>Molding Conditions</th>
<th>190°C 30 Minutes Air Cool</th>
<th>230°C 30 Minutes Air Cool</th>
<th>230°C 30 Minutes Quench Cool</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystallinity</strong></td>
<td>45%</td>
<td>31%</td>
<td>33%</td>
</tr>
<tr>
<td><strong>Tg</strong></td>
<td>67</td>
<td>56</td>
<td>53</td>
</tr>
<tr>
<td><strong>Tm</strong></td>
<td>227</td>
<td>225</td>
<td>234</td>
</tr>
<tr>
<td><strong>Crystallinity</strong></td>
<td>47%</td>
<td>31%</td>
<td>39%</td>
</tr>
<tr>
<td><strong>Tg</strong></td>
<td>232</td>
<td>56</td>
<td>55</td>
</tr>
<tr>
<td><strong>Tm</strong></td>
<td></td>
<td>233</td>
<td>234</td>
</tr>
</tbody>
</table>
Rheometer Study

• Haake Parallel Plate Rheometer
• Screening to Compare Catalysts
• Explore Melt Temperatures
• Explore Mold Temperatures
• Two Minute Sample Preparation Minimum Time to Add and Mix Catalyst Limited Melt Temperature to 200°C Max
Viscosity Build of Two RTM Catalyst Candidates

- Rapid Reaction Rate
- High Viscosity and Weight
- Time to Infuse the Part

Seconds after Batch Catalyst Addition:
190C Melt Temp, 120 Secs -> 250C "Tool" Temp
Catalyst Selection for Process Trial

- Tyzor TE Meets or Exceeds All Needs
- **EXCEPT** It Is in 20% Isopropyl Alcohol
  - Isopropyl Alcohol would Add End Groups
    - Limits Molecular Weight Development
    - Flashes - Creates Voids at Infusion Temperatures
- Simple Fix - Replace Alcohol with a Polyol
  - Polyol used to Convert C204 to a Liquid
  - Changes Addition Level from 0.4% to ~1.0%
  - 0.5% “Soft Block” Should Have Minor Property Effect
Bench Scale Verification Set-Up

• Batch Resin Handling
  – Melting, Drying and Catalyzing
  – Gravity Feed into Open Tool

• Simple Sheet Steel Tool
  – Matched Top and Bottom
  – Lightweight to Facilitate Heat Transfer

• Heat Using Forced Air Oven

• Cooling on a Chilled Metal Plate and Fan
Resin Melting and Mixing Set-up

• Resin Melted Under Vacuum to Dry
• Catalyst Added and Mixed
• Two Minutes from Catalyst Addition to Addition of Resin Mix into Tool
Simple Tool Set-up with Weight in Forced Air Oven
Bench Scale Time-Line

• Time 0 Minutes
  – Tool in Pre-Heated in Oven, Resin Pre-Melted
  – Fiber Added to Tool
  – Catalyst Mixed into Resin – Clock Started

• Time 1 Minute
  – Resin Removed from Mixing Vessel and Charged into Tool

• Time 2 Minute
  – Resin Charge Complete, Tool and Oven Door Closed

• Time 6 Minute
  – Tool Removed from Oven & Cooled with Forced Air / Cold Plate

• Time 7 Minute
  – Part Removed and Tool Replaced in Oven

• Time 14 Minute / 0 Minute Cycle 2
  – Tool Re-Heated to Molding Temperature
Bench Scale Verification Results

- De-Mold to De-Mold in 14 Minutes
- Cure Temperature 230°C – Low Side
- 87 - 91% Conversion – Acceptable
- 104,000 - 115,000 Mw – Good
- Physical Properties Not Checked
  – Thickness Variation Due to Inexpensive Mold
  – Surface Voids Due to Manual Infusion
  – Good Fiber Wet-Out (When Properly Infused)
Round 2 – Faster Re-Heating of the Tool

• Replace Forced Air Oven with Compression Press
• Test Re-Heat Rate Prior to Molding
• Targeting 4 to 5 Minute Time-in-Press
  – Heat up Plus Cure Time
Compression Tool

- 2 pieces of ½ inch 13” x 13” Aluminum Stock
- 5.6 kg
- Re-Heat Rate in 275C Press Suggest 4-5 Minute Time in Press is Possible
Temperature Recovery for Compression Tool

- Mold Temp
- Lower Platten
- Upper Platten
Resulting Process

**Time**
- 0:00 - Resin Melted - Press / Tool Preheated - Catalyst Added to Resin
- 1:30 – Pre-Dried Fiber and Resin Added to Mold
- 2:00 - Mold (Resin and Fiber) Added to Press
- 7:00 – Mold Removed from Press and Cooled
- 8:00 - Catalyst Added to 2\textsuperscript{nd} Batch of Resin
- 9:00 – Part Removed from Mold
- 10:00 - Fiber and Resin Added to Mold
- 10:30 – Mold Added to Press
- 15:30 – Mold Removed From Press and Cooled
- 17:30 – 2\textsuperscript{nd} Part Removed from Mold

**Two Parts Produced in 16 Minutes of Mold Time**
Resulting Parts

• Very Good Polymerization
  – Part 1 - 97% Conversion- Mw 112,000 - D 3.0
  – Part 2 - 94% Conversion- Mw 145,000 - D 4.0

Time – Temperature was Sufficient

• Poor Infusion
  – Dry Corners in Both Parts
  – Large Number of Surface Pits

Gravity Driven Infusion Not Adequate

Too Much Time -Temperature Between Catalyst Add and Resin Add
Basic Process Starting Point

• Load Fiber into Tool at 150C
• Concurrently, Melt Resin at 190C
• Begin Heating Tool when Fiber is Loaded
• Begin Infusion when Tool Reaches 190C
• Add Catalyst to Resin in Venturi or Static Mixer Built into Tool
• Hold Tool at Temperature 230 - 250C for 3 to 5 Minutes to Cure
• Rapidly Cool Tool to 150C to Remove Part
Thermal Management “Must Haves”

• Resin Melt Temperature 185C to 250C
• Cure Temperature 230C to 275C
• Hold Time for Cure Depends on Catalyst & Resin Temperature After Catalyst Addition
  – Resin Melt Temperature During Infusion
  – Heat-up Rate
  – Cool-Down Rate
• Rapid Cooling Yields Tougher Parts
Projected cPBT RTM Mold Temperature Profile
Equipment Desires

- Dry and Melt the Resin In-Line
- Meter / Mix the Catalyst in the Tool
  - 100:1 Catalyst Let-Down Ratio
  - In Tool Mixing Minimizes Clean-outs
  - Sprues Become Static or Venturi Mixers
- Pull Vacuum to Assist Infusion
- Rapidly Thermal Cycle the Tool
  - < 160C to > 230C
Opportunities to Reduce Cycle Time

• Increase Resin Melt Temperature > 190°C
• Raise Tool Loading and Unloading Temperature to 170°C (max)
• Reduce Tool Mass to Speed Heat Rate and Cooling Rate
• Increase Catalyst (+/- 25% in Loading)
• Increase Hold/Cure Temperature > 250°C

10 Minutes is Viable, 5 Minutes is the Goal