Development of Ultra Low Density SMC

M. J. Sumner
Traditional New Product Development

Stage 1 • Idea Generation
Stage 2 • Idea Screening
Stage 3 • Business Analysis
Stage 4 • Product Development
Stage 5 • Test Marketing
Stage 6 • Commercialization
Customer Focused New Product Development

Stage 1
- Market Research

Stage 2
- Discovery Interviews
- Preference Interviews

Stage 3
- Side by Side Testing
- Product Objectives

Stage 4
- Business Analysis

Stage 5
- Product Development

Stage 6
- Commercialization

Unmeet product need definition: Tougher, lower density, e-coat capable, cost effective SMC

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Objectives for Ultra Low Density Class A SMC Development

• Improve the mechanical properties, or ‘toughness’, of our current 1.2 density SMC by a minimum of 20% or higher while:
  – Avoiding a major cost impact: < 20% increase
  – Maintaining surface quality: < 70 ALSA Value
  – Retaining processability

• Use the new “toughened” system as a platform to develop Class A systems of 1.1 and lower densities without sacrificing properties and avoiding a major cost impact
Outline

• Background
  • Experimental Approach to a “Toughened” 1.2 Density SMC
  • Initial Screening Results – Surface Quality
  • Mechanical Property Testing
    – Tensile
    – Flex
    – Drop Testing
      – Effect of Reactive Toughener
  • Effect of Curing Catalyst and Mold Temperature
    – Surface Quality and Mechanical Properties
• Ford E-coat Testing

• Approach to 1.1 Density Development
  – Mechanical Property and Surface Quality Measurements
  – Ford E-coat Testing

• Conclusions
• Future Work
Effect of Vinyl Esters on Surface Quality

<table>
<thead>
<tr>
<th>Vinyl Ester</th>
<th>VER:UPR Ratio</th>
<th>ALSA Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0:100</td>
<td>60</td>
</tr>
<tr>
<td>VER1</td>
<td>100:0</td>
<td>96</td>
</tr>
<tr>
<td>VER2</td>
<td>100:0</td>
<td>94</td>
</tr>
<tr>
<td>VER3</td>
<td>100:0</td>
<td>Unreadable</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>135</td>
</tr>
<tr>
<td>VER4</td>
<td>100:0</td>
<td>Unreadable</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>137</td>
</tr>
<tr>
<td>VER5</td>
<td>100:0</td>
<td>Unreadable</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>Unreadable</td>
</tr>
<tr>
<td></td>
<td>25:75</td>
<td>87</td>
</tr>
<tr>
<td>VER6</td>
<td>50:50</td>
<td>102</td>
</tr>
</tbody>
</table>

- VER1 and VER2 have similar surface quality when used as the sole base resin, however VER2 was selected for further development efforts due to superior mechanical properties.
- By selecting the appropriate low profile additive, is it possible to achieve Class A Surface quality using VER2 as the only base resin?
1.2 Density System Formulated with VER2 – LPA Screening

- Replaced the current primary low profile additive (LPA1) with a series of LPA’s of various chemical structures
- LPA1 is clearly the best choice for surface quality
- Next Step: Evaluate the effect of blending with the standard UPR on surface quality and mechanical properties
Effect of VER2 Concentration on Surface Quality

- Up to 50wt% of the UPR base resin can be replaced with VER2 without degrading surface quality.
Effect of VER2 Concentration on Mechanical Properties

- 25wt% VER2 in the resin blend improves properties by:
  - 20% for flex and tensile modulus
  - 15% flex strength and 30% for tensile strength

- 50wt% VER2 in the resin blend improves properties by:
  - 20% for flex and tensile modulus
  - 40% for flex and tensile strength
  - 20% for elongation

- Both concentrations had similar impact on % elongation: ~20% improvement

- HDT values on all samples were >200 °C
At 25wt% VER2, the improvement is marginal
50wt% VER2 increases impact resistance by an estimated 20%
Based upon overall properties, surface and mechanical, the 50:50 blend was identified as the best experimental candidate for additional development
Focused on further improvements related to impact resistance
Incorporation of a particular toughening agent improved performance by ~15%

Relative to the 100% UPR system (control), the toughening agent improved performance by ~40%
The toughening agent has no negative impact on mechanical properties
HDT remained unchanged as well: >200 °C for both samples
Initial surface quality measurements indicate the toughener may have a detrimental influence
Is this the result of a reduction in T_g?
Can the surface quality be improved by manipulating mold temperature and initiator type?
T<sub>g</sub> of 1.2 Density SMC

- T<sub>g</sub> of 1st LPA:
  - Arotran 720/722 (Control):
    - -27.60°C
  - 50:50 Resin Blend:
    - -24.31°C
  - 50:50 Resin Blend w/ 5wt% RT:
    - -25.44°C
  - Std. Density Class A:
    - -24.31°C

- T<sub>g</sub> of 2nd LPA:
  - Arotran 720/722 (Control):
    - 47.19°C
  - 50:50 Resin Blend:
    - 48.99°C
  - 50:50 Resin Blend w/ 5wt% RT:
    - 46.17°C
  - Std. Density Class A:
    - 48.99°C

- Mold Temperature:
  - Arotran 720/722 (Control):
    - 150.00°C: 6028MPa
  - 50:50 Resin Blend:
    - 150.00°C: 3103MPa
    - 165.60°C: 168.65°C
  - 50:50 Resin Blend w/ 5wt% RT:
    - 150.00°C: 3260MPa
    - 161.36°C: 2949MPa
  - Std. Density Class A:
    - 150.00°C: 6028MPa

- Storage Modulus (MPa) vs. Temperature (°C)

10000
1000
100
50
0
-50
-27.60°C
-24.31°C
-25.44°C
47.19°C
48.99°C
46.17°C
150.00°C
6028MPa
150.00°C
3103MPa
3260MPa
2949MPa
165.60°C
168.65°C
161.36°C
T<sub>g</sub> of Matrix
T<sub>g</sub> of 1st LPA
T<sub>g</sub> of 2nd LPA
Mold Temperature
150.00°C
3103MPa
3260MPa
2949MPa
165.60°C
168.65°C
161.36°C

1.0E5

Temperature (°C)
**Effect of Mold Temperature and Initiator System on Surface Quality**

<table>
<thead>
<tr>
<th>SMC</th>
<th>Initiator System</th>
<th>Mold Temperature</th>
<th>ALSA Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>TBPB/PDO</td>
<td>150 °C</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>TBPB/PDO</td>
<td>121 °C</td>
<td>84</td>
</tr>
<tr>
<td>50:50 Resin Blend</td>
<td>TBPB/PDO</td>
<td>150 °C</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>TBPB/PDO</td>
<td>121 °C</td>
<td>103</td>
</tr>
<tr>
<td>50:50 Resin Blend w/</td>
<td>TBPB/PDO</td>
<td>150 °C</td>
<td>97</td>
</tr>
<tr>
<td>Reactive Toughener</td>
<td>TBPB/PDO</td>
<td>121 °C</td>
<td>Unreadable</td>
</tr>
<tr>
<td></td>
<td><strong>Trig 141/TBPB</strong></td>
<td>150 °C</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td><strong>Trig 141/TBPB</strong></td>
<td>121 °C</td>
<td>67</td>
</tr>
</tbody>
</table>

- Selection of initiator system and mold temperature appear to have a substantial influence on surface quality.
- What effect, if any, do mold temperature and initiator system have on mechanical properties?
# Effect of Mold Temperature and Initiator System on Mechanical Properties

<table>
<thead>
<tr>
<th>SMC</th>
<th>Initiator System</th>
<th>Mold Temp</th>
<th>Tensile</th>
<th>Flex</th>
<th>$T_g(\degree C)$</th>
<th>Drop Dart (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Str. (MPa)</td>
<td>Mod. (MPa)</td>
<td>% E</td>
<td>Str. (MPa)</td>
</tr>
<tr>
<td>Control</td>
<td>TBPB/PDO</td>
<td>150 °C</td>
<td>57.3</td>
<td>7439</td>
<td>0.96</td>
<td>103.5</td>
</tr>
<tr>
<td></td>
<td>TBPB/PDO</td>
<td>121 °C</td>
<td>47.1</td>
<td>5681</td>
<td>1.14</td>
<td>119.0</td>
</tr>
<tr>
<td>50:50 Resin Blend</td>
<td>TBPB/PDO</td>
<td>150 °C</td>
<td>82.1</td>
<td>8115</td>
<td>1.41</td>
<td>165.1</td>
</tr>
<tr>
<td></td>
<td>TBPB/PDO</td>
<td>121 °C</td>
<td>77.3</td>
<td>6902</td>
<td>1.54</td>
<td>139.0</td>
</tr>
<tr>
<td>50:50 Resin Blend w/ Reactive Toughener</td>
<td>TBPB/PDO</td>
<td>150 °C</td>
<td>77.0</td>
<td>7391</td>
<td>1.39</td>
<td>170.3</td>
</tr>
<tr>
<td></td>
<td>TBPB/PDO</td>
<td>121 °C</td>
<td>76.9</td>
<td>7295</td>
<td>1.42</td>
<td>127.0</td>
</tr>
<tr>
<td></td>
<td>Trig 141/TBPB</td>
<td>150 °C</td>
<td>84.8</td>
<td>7922</td>
<td>1.35</td>
<td>161.6</td>
</tr>
<tr>
<td></td>
<td>Trig 141/TBPB</td>
<td>121 °C</td>
<td>84.8</td>
<td>7295</td>
<td>1.62</td>
<td>183.6</td>
</tr>
</tbody>
</table>
Ford E-coat Test Protocol

- Used the method in section 3.2.11 of the Ford WSS-M3D188-A engineering material specification
  - Panels are dried at 75 °C for 2 hours and then allowed to cool for 1 hour at room temperature
  - Samples are exposed to 100 °F @ 100% humidity for 10 days
  - IR lamps are used to heat the surface of the panel to ~ 200 °C in ~16 mins
  - Samples are held at ~ 200 °C for ~15 mins

- Our labs did not have an IR lamp capable of heating at the desired rate
- Identified a Blue M oven capable of generating a heating rate similar to the Ford IR oven
  - Oven reached ~ 200 °C in about 20 mins vs. ~ 16 mins for the Ford IR oven
  - Samples were cooled to room temperature by simply turning the oven off and opening the doors to allow for rapid cooling
Ford E-coat Test: Data Summary

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Absorption %</th>
<th># of Blisters</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:50 Resin Blend</td>
<td>~2.25</td>
<td>0</td>
</tr>
<tr>
<td>50:50 Resin Blend with Reactive Toughener</td>
<td>~2.25</td>
<td>0</td>
</tr>
</tbody>
</table>

*Passing requires no blistering*
Technical Approaches for 1.1 and Lower Density Class A SMC

- Using the toughened 1.2 system as a base for formulating, the following options are being explored:

<table>
<thead>
<tr>
<th>Option</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Increase low density filler concentration</td>
<td>• Simple adjustment to the formula</td>
<td>• High A-paste viscosity which can lead to inadequate fiber wetout</td>
</tr>
<tr>
<td></td>
<td>• Possible to maintain resin concentration</td>
<td>• Possible surface quality erosion</td>
</tr>
<tr>
<td></td>
<td>• No change in glass content</td>
<td>• Can add significant cost</td>
</tr>
<tr>
<td>2. Improve resin adhesion to glass fibers</td>
<td>• Potentially allows for reduced glass content which will reduce</td>
<td>• A more “structural” type glass can erode surface quality</td>
</tr>
<tr>
<td></td>
<td>density, but maintain properties</td>
<td>• Glass surface treatment: Identifying the right additive is not a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>trivial exercise – can be very time consuming and add cost</td>
</tr>
<tr>
<td>3. Replace a portion of the glass fiber with</td>
<td>• Formulation adjustment is possibly minimized</td>
<td>• Carbon fiber tows can difficult to wetout which can erode</td>
</tr>
<tr>
<td>carbon fiber</td>
<td>• At a minimum, properties should remain the same as the density is</td>
<td>surface quality</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>• Adds significant cost</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Another fiber type adds processing complexity</td>
</tr>
</tbody>
</table>
For every 0.1 density reduction through higher microsphere concentration, the A-paste viscosity essentially doubles.

As expected, simply increasing the microsphere concentration to achieve the desired density results in an A-paste viscosity that does not process well.

However, through optimizing styrene concentration and careful selection of the right formulation components, a processable 1.1 density formulation was developed.
### Mechanical Properties and Surface Quality Comparison of 1.1 and 1.2 Density Class A SMC

<table>
<thead>
<tr>
<th>SMC</th>
<th>Density</th>
<th>Microsphere Type</th>
<th>Tensile</th>
<th>Flex</th>
<th>ALSA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Str. (MPa)</td>
<td>Mod. (MPa)</td>
<td>% E</td>
</tr>
<tr>
<td>Toughened System</td>
<td>1.2</td>
<td>1</td>
<td>91.9</td>
<td>9694</td>
<td>1.43</td>
</tr>
<tr>
<td>Experimental 1</td>
<td>1.1</td>
<td>1</td>
<td>75.5</td>
<td>7688</td>
<td>1.35</td>
</tr>
<tr>
<td>Experimental 2</td>
<td>1.1</td>
<td>2</td>
<td>84.8</td>
<td>7950</td>
<td>1.47</td>
</tr>
</tbody>
</table>

- The microsphere type appears to have a significant impact on strength values in the 1.1 density system
  - Type 2 microsphere did lower the A-paste viscosity which may have resulted in better glass wetout
  - Interaction between the microsphere surface and the matrix may have influenced properties as well
- Increasing the microsphere concentration to achieve a 1.1 density did not compromise surface appearance
Ford E-coat Test on 1.1 Density Class A System

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Absorption %</th>
<th># of Blisters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Data to come</td>
<td></td>
</tr>
</tbody>
</table>

*Passing requires no blistering*
Conclusions

• A vinyl ester-UPR blend, Arotran 771, has been identified that is capable of producing a ‘tougher’ Class A 1.2 density SMC.

• Relative to our current 1.2 system, the blend improves certain mechanical properties by 40% without a major compromise in surface quality.

• The impact resistance of the blend can be further enhanced through the use of a particular reactive toughener without a reduction in mechanical properties.

• The detrimental effect of the reactive toughener on surface quality can be overcome through proper manipulation of mold conditions and initiator selection.

• Based upon the toughened 1.2 density platform, a new 1.1 Class A SMC system has been developed.

• The new 1.1 density system has mechanical properties and surface quality approximately equivalent to its 1.2 predecessor.
Future Work

• Optimizing the 1.1 density system to meet the Ford e-coat requirement
• Explores approaches to 1.0 density Class A development
  – New low viscosity resins to accommodate higher concentrations of low density filler
    • Need to provide similar fiber wetout properties as existing resins and be shrink controllable through the use of low profile additives (LPA’s)
  – Improve adhesion to glass
    • Develop chemistries that would, in-situ, manipulate the glass surface to provide better adhesion
    • Theoretically, would allow for lower glass content without a major sacrifice in mechanical properties or surface quality
  – Carbon and glass fiber hybrid systems
    • Find an optimal blend of these reinforcements that meets density and mechanical property requirements
    • Possibly avoids substantial manipulation of existing formulas