PUSHING the BOUNDARIES with NOVEL THERMOSET POLYOLEFIN COMPOSITES

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Materia, Inc., Pasadena, CA / Huntsville, TX

2019 SPE ACCE
• Background on Materia and its technology
• Composites for automotive: Materials and Processes
• Proxima Composite Resin performance
MATERIA AT A GLANCE

- Manufacturer of high-performance thermoset resins with unique performance properties
- Founded in 1998
- Applying Nobel-prize winning chemistry to materials
- World-class technical services and support
- Only resin system that utilizes Grubbs Catalyst® technology

We enable our global customer base to be more competitive in the market with...

- High Temperature Subsea Insulation and Buoyancy Products
- Tough, Downhole Tools for High Pressure and High Temperature
- High Speed and High Frequency Electronics
- Advanced Composites
PROXIMA® THERMOSET POLYOLEFINs

- Two-part liquid thermoset resin systems
- Based on dicyclopentadiene (DCPD) and a family of co-monomers
- Ring Opening Metathesis Polymerization enabled by Ru-based Grubbs Catalyst® technology
- Wide range of performance and processing capability
Proxima® Thermoset Polyolefin Resins combine high temperature stability with high impact toughness.
Proxima® composite resins enable significant formulation flexibility with controlled curing, from seconds to hours; enabling customers to optimize processing / molding.
SUCCESS IN HIGH TEMPERATURE SUBSEA INSULATION

WHY PROXIMA?
- Low Water Uptake, No Hydrolysis
- Flexibility allows low internal stress
- Low viscosity for easy / tunable processing

The in-field success of Thermoset Polyolefin Resins in Oil & Gas has been extended to Automotive

<table>
<thead>
<tr>
<th>Traditional Polymer Systems</th>
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<tbody>
<tr>
<td>Polypropylene</td>
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<tr>
<td>Polyurethane</td>
</tr>
<tr>
<td>Polystyrene</td>
</tr>
<tr>
<td>Vulcanized Rubber</td>
</tr>
<tr>
<td>Epoxy</td>
</tr>
</tbody>
</table>

Pipe-in-Pipe
COMPOSITES FOR AUTOMOTIVE: MATERIALS AND PROCESSES
TYPES OF FIBER-BASED COMPOSITES

Different industries define composites in various ways, and performance varies....

Fillers      Short Fiber           Long Fiber      Continuous Fiber


How to address the trade-off in Processability / throughput?
CompositesWorld has recently summarized the industry trends as follows:

Pre-2013: Direct use of “aerospace materials” for small volume auto

2013 (i-Series): Demonstration of HP-RTM for Structural parts / BIW

2016: Multi-materialism: steel, aluminum, CFRP, GFRP

BMW 7-series saves 130 kg

Optimizing Matrix/Fiber/Process to meet performance/cost (thermoplastic vs. thermoset, continuous vs. chopped fiber)

Current:

Aluminum saves 400 kg in 2012 Range Rover

Aluminum saves 300 kg in 2015 F-150

CFRTP saves 28 kg in 2019 GMC Sierra
Industry analysis (McKinsey, 2016) highlights weight savings and costs for various materials

Part Weight, % of Steel

Steel: 100%
HS steel: 80%
Aluminum: 60%
CFRP: 50%

Cost per Kg-saved over steel

HS steel: Low
GFRP: Moderate
Aluminum: Moderate
CFRP: High

Processing limitations account for 50% of CFRP Cost
Potential Remedies: fast-cure matrix, process optimization, automation

Fiber Length

- Continuous
- 10 - 50 mm
- 0.5 - 5 mm

Annual Production Capacity

Decreasing Properties

Processes for Fiber-Based Composites

- Autoclave
- RTM
- HP-RTM
- Liquid CM
- Pultrusion
- Thermoform Tape
- D-LFT/CM
- SMC
- Inj. Mold

MATERIAL
### PROCESSES FOR PARTS WITH SHAPE COMPLEXITY

<table>
<thead>
<tr>
<th>Process</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-RTM</td>
<td>• Requires low viscosity resin to achieve high FVF composites with fast cycle time (&lt;90 sec)</td>
</tr>
<tr>
<td>Wet Comp. Molding</td>
<td>• Allows injection pressure &lt; 140 psi which eliminates fiber movement</td>
</tr>
<tr>
<td>(LCM, DFCM)</td>
<td></td>
</tr>
<tr>
<td>Prepreg / UD Tape</td>
<td>• Automation demonstrated with increasing fiber placement speed</td>
</tr>
</tbody>
</table>
**Matrix Selection**

**Thermoplastics**
- **High Cost**: PEI, PES, PI, LCP, PEEK, PFA
- **Mid Cost**: PC, PETG, PA 4/6, 6/6, PA 11, 12, PBT, PA 6
- **Low Cost**: PMMA, ABS, ASA, PP / TPO, PE

**Thermosets**
- **High Cost**: BMI, PI, CE, UPR
- **Mid Cost**: Proxima, RTM PUR, RTM Epoxy, Vinyl Ester
- **Low Cost**: Novolac Epoxy, UPR, Phenolic

**Thermal / Mechanical**
- **High Cost**: Liquid Resin
- **Mid Cost**: Semisolid, Prepreg

*Plasticprop.com*
PROXIMA® vs. EPOXY

(Scale represents Proxima/Competition performance ratio)

- **Ultra-Low Viscosity**: 20x less viscous (7 cP at 25 °C)
- **Lightweight**: 10% lower density (1.04 g/mL)
- **Ultra-Tough**: 5x tougher ($K_{IC} = 2.8$ MPa·m$^{1/2}$)
- **Fast Heat Cure**: 50-75% faster cure profile
- **Cost Competitive**: Comparable to epoxies
Proxima® laminates absorb less water and retain properties better than market leading epoxy laminates.

Effects of water aging of GFRP at 60 °C on SBS and $T_g$ were compared.

TOUGH COMPOSITES USING A TOUGH POLYMER

Laminates produced with Proxima® resins resulted in 48% less damage than epoxy laminates.

**Epoxy**

Damage zone of Proxima® laminate is 48% smaller than that of the epoxy laminate

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>METHOD (ASTM)</th>
<th>UNIT</th>
<th>ACR 4100</th>
<th>INFUSION EPOXY</th>
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<tbody>
<tr>
<td>Fracture Toughness, $K_{IC}$</td>
<td>D5045</td>
<td>MPa-m$^{1/2}$</td>
<td>2.6</td>
<td>0.5</td>
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<tr>
<td>Interlaminar Fracture Toughness, $G_{IC}$</td>
<td>D5528$^{1,2}$</td>
<td>J/m$^2$</td>
<td>1,700</td>
<td>330</td>
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<tr>
<td>Damage after impact$^3$</td>
<td>D7136-07</td>
<td>mm$^2$</td>
<td>403</td>
<td>779</td>
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</tbody>
</table>

1 Data treatment per Reeder and Crews (NASA) for fracture toughness at crack initiation
2 Laminates prepared by VARTM of 1200 gsm unidirectional glass fabric and cured at 120 °C for 2h
3 Tested by Delsen Testing Laboratories
PROXIMA® INTERLAMINAR FRACTURE TOUGHNESS (G_{IC})

- Compared to epoxy infusion resins, Proxima shows **very high crack resistance**
  Interlaminar Fracture toughness at crack initiation:
  - Proxima: \( G_{1c} = 1700 \, \text{J/m}^2 \)
  - Epoxy: \( G_{1c} = 330 \, \text{J/m}^2 \)

- Proxima laminates exhibit a ductile failure mode similar to thermoplastic resins

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ASTM D5528, data treatment per Reeder and Crews (NASA)
Proxima glass fiber laminates provide high fracture-toughness which translates to improved fatigue performance and off-axis properties.

**Tension-Tension Fatigue R=0.1 (Triaxial Glass NCF laminate)**

Graph showing the comparison between Epoxy and Proxima in terms of stress and cycles to failure.
THICK CF SECTIONS VIA INFUSION

- 130 plies
  Fabric: Saertex U-C-603gsm, Zoltek Panex 35, 50K Carbon Tow
- 500mm x 500mm x 76mm
- FVF = 0.62
- Void-free
## UPDATE ON CF LAMINATE TEST RESULTS

<table>
<thead>
<tr>
<th>Test Performed</th>
<th>Test Method</th>
<th>Mean Value</th>
<th>95/5 C.V.</th>
<th>Units</th>
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<tbody>
<tr>
<td>0° Tensile Strength</td>
<td>ISO 527</td>
<td>1651</td>
<td>1371</td>
<td>MPa</td>
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<tr>
<td>0° Tensile Modulus</td>
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<td>112</td>
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<td>GPa</td>
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<td>GPa</td>
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<td>923</td>
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<tr>
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<td>GPa</td>
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<tr>
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<tr>
<td>90° Compression Modulus</td>
<td>ASTM D 6641</td>
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<td>Shear Strength at Failure</td>
<td>ISO 14129</td>
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<tr>
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<td>GPa</td>
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<tr>
<td>Short Beam ILSS</td>
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<td>58</td>
<td>MPa</td>
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</tbody>
</table>

Saertex U-C-603 (603 gsm based on Panex 35 tow)
FVF (4-ply) = 0.55
* Zwick-IMA HCCF fixture used (6 breaks), showing COV for Comp. Strength = 0.10
BUILDING A PATH TO FAST CYCLE COMPOSITES

**VARTM**
- Benchmark setting (ILSS, Tg, ...)
- Confirm laminate construction

**LP-RTM – Screening**
- Carbon Fiber NCF 45 psi, Inj. Pressure 110 – 140 °C tool
- FVF > 0.50 >90% vs. ILSS control for 90 to 120 sec

**HP-RTM**
- Validate predictions of screening
- On-going efforts
FUTURE DEVELOPMENTS: LEVERAGING TOUGHNESS

- Range of Tg and ductility by moving beyond DCPD
- Stepping beyond DCPD while maintaining hot / wet performance
CONCLUSIONS

• Materia sees composites materials as being tailored to designer’s needs and the Proxima® portfolio will be extended in collaboration with customers

• Proxima resins provide a new path to high toughness / low defect parts

• Materia continues to partner with OEMs in Automotive, Wind, and Oil & Gas to qualify resins for continuous GF and CF composite parts

• Engaging fabricators / molders across multiple processes is critical to meet demand for complex molded parts, pultruded profiles and FW pressure vessels

Next Steps:

• Developing a better understanding of Auto Industry needs for next 1-3 years
• Defining a framework for collaboration and material qualification