Extrusion deposition additive manufacturing utilizing high glass transition temperature latent cured epoxy systems

Gary Gladysz  
*Dixie Chemical Company, USA*, gggladysz@dixiechemical.com

Christopher Hershey  
*Oak Ridge National Laboratory, USA*

John Lindahl  
*Oak Ridge National Laboratory, USA*

Karana Shah  
*Dixie Chemical Company, USA*

Alejandra Campanella  
*Dixie Chemical Company, USA*

See next page for additional authors

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Authors
Gary Gladysz, Christopher Hershey, John Lindahl, Karana Shah, Alejandrina Campanella, and Vlastimil Kunc

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Innovative Materials for Additive Manufacturing

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Large scale additive manufacturing utilizing high glass transition temperature latent cured epoxy systems


*Dixie Chemical Company  ** Manufacturing Demonstration Facility

Oak Ridge National Lab
Purpose: ORNL – Dixie CRADA

• Epoxy material solutions with anhydride curatives
  • excellent chemical properties
  • physical aging properties

• Printable on a large-scale printer

• Tooling requirement (in autoclave)
  • elevated temperature
  • pressure composite manufacturing process
  • Short production run
  • Product development
Benefits of latent cure

• Current solidification on part bed materials:
  • Melt process
  • Solidifies on part bed
    • Poor z-direction strength
    • Non-isotropic properties
    • Heating/cooling of part bed
  • High energy requirement to deposit

• New latent cure materials:
  • Thermoset epoxy-based composite
  • High Tg (150-220 C)
  • Deposit at ambient conditions
  • Does NOT solidify on part bed
    • Curing/x-linking occurs after part is built
    • Excellent Z-direction strength
    • Isotropic properties
  • 400% more energy efficient printing process
  • New design options for users
  • Creating custom, printable composite material formulations
Thermoplastic vs. thermoset printing

**Thermoplastic**

- **Rigidity**
- **Ideal Deposition Zone**
- **Solid Polymer**
- **Poor Bead Stability**

**Thermoset**

- **Ideal Deposition Zone**
- **Solid Polymer**
- **Heat (thermal) cure in oven**
- **Poor Bead Stability**

*Image credit: Oak Ridge National Laboratory*
Large scale printer

- MVP/ORNL developed
- Large-scale
- Composite materials
Target: Prototype Autoclave Tooling Requirements

- Cure cycle 177 C (350 °F) 690 kPa (100 psi)
- Dimensional tolerance ± 0.01 in. (.25mm)
- Vacuum
- 64 RMS surface roughness or better
- Low CTE
- Quasi-isotropic tool response
- Ketone resistant
- Low cost
- 10 parts minimum
Phase 1 results

Initially 4 resins & 4 anhydrides

<table>
<thead>
<tr>
<th>Resin</th>
<th>Anhydride curative</th>
<th>Tg (Tan Delta), °C</th>
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</thead>
<tbody>
<tr>
<td>Bis-A</td>
<td>ANH-1D</td>
<td>148</td>
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<tr>
<td>Cycloaliphatic</td>
<td>ANH-1D</td>
<td>220</td>
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<tr>
<td>Cycloaliphatic</td>
<td>ANH-2D</td>
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<tr>
<td>Cycloaliphatic</td>
<td>ANH-3D</td>
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<tr>
<td>Cycloaliphatic</td>
<td>ANH-4D</td>
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</table>

With nano clay

Dixie Chemical

OAK RIDGE National Laboratory
Materials

- **Resin**: Celloxide 2021P
- **Curative**: ANH-3D
- **Rheological modifier**: Garamite 7305 - Organophilic phyllosilicate

ANH-3D
NMA
MW = 185
Viscosity= 400 cps

Celloxide 2021P
Cycloaliphatic
MW = 252
Viscosity=350 cps
Formulation development

(a)

Clay in 2021P
- 12.5 wt%
- 14 wt%
- 15 wt%

(b)

Clay in ANH-3D
- 10 wt%
- 12.5 wt%
- 15 wt%
Phase 2: Scale-up to large scale

RAM® Print envelope dimensions
X = 4.9 m (16 ft)
Y = 2.4 m (8 ft)
Z = 1.1 m (3.5 ft)
Tasks

• Scale up formulations (optimize viscosity)
• Scale up mixing
• Optimize print parameters
• Optimize curing temperature profile
• Print aerospace tool
• Work with aerospace partner for in-autoclave trials
• Characterize important properties
Formulation development

![Graph showing storage modulus vs. stress for different samples with legends: 2021P/14.0% Clay, ANH-3D/10.9% Clay, 2021P/ANH-3D/12.3% Clay.]

- 5 layers to recover flat surface
- 1.5 inches
Mixing scale-up

- Hollow glass microspheres
- Latent curatives
- Epoxy resins
- Fibers
- Rheological modifiers

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Printing parameters – generic boat part
Aerospace tool

- Largest latent cure aerospace tool
- 36.3 kg (80 lb)
Characterization result

• Coefficient of thermal expansion (1/K)
  • $X = 52.44 \, \mu m/(m \, ^\circ C)$
  • $Y = 70.03 \, \mu m/(m \, ^\circ C)$
  • $Z = 54.90 \, \mu m/(m \, ^\circ C)$

• Flexure Properties
  • Strength = $99.2 \pm 6.9 \, MPa$
  • Modulus = $3.69 \pm 0.29 \, GPa$

• $T_g = 220 \, ^\circ C$
## Future Work

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Test Method</th>
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<tbody>
<tr>
<td>Color</td>
<td>Green</td>
<td>Visual</td>
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<tr>
<td>Glass Transition Temperature ($T_g$, °C)</td>
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<td>ASTM D4065</td>
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<tr>
<td>Coefficient of Thermal Expansion, °C⁻¹</td>
<td>X = 52.4</td>
<td>ASTM D2286</td>
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<tr>
<td></td>
<td>Y = 52.4</td>
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<td>Z = 54.9</td>
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<td>Flexural Strength, MPa</td>
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<td>Flexural modulus, GPa</td>
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<td>Density, kg/m³</td>
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<td>Hardness</td>
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<td>Compressive properties</td>
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<td>ASTM D695</td>
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<td>Tensile properties</td>
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</table>

- Work with aerospace partner
- 10 composite parts
- Check dimensions
Summary

- Cure cycle 177°C (350 °F) 690 kPa (100 psi)
- Dimensional tolerance ± 0.01 in. (.25mm)
- Vacuum
- 64 RMS surface roughness or better
- Low CTE
- Quasi-isotropic tool response
- Ketone resistant
- Low cost
- 10 parts minimum
Acknowledgements

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QUESTIONS?