Next Generation Infusion Resin for Wind Turbine Blades - Fatigue Performance of a New High-Toughness Resin

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Background on Materia Inc.

- Privately held company with HQ in Pasadena, CA. Founded in 1998 to broadly commercialize Nobel Prize winning “green” catalyst technology for olefin metathesis.

- Materia’s core technology is a family of chemical catalysts which enable value-added products in chemicals, materials and pharmaceuticals. This technology is protected by over 350 patents and patent applications.

- We are team of highly skilled chemists, engineers and development professionals focused on applying this enabling catalyst technology in commercial markets.

- We are addressing significant opportunities in energy, products from renewables, and specialty chemicals. We have a proven record in application development, strategic partnerships and IP defense.

- Materia’s primary commercial focus is the development of our catalyst-enabled pDCPD thermoset resin for composite applications.
DCPD (Dicyclopentadiene)
- A monomer sourced from an abundant petrochemical stream
- Contains reactive olefin bonds suitable for Ring-opening Olefin Metathesis Polymerization (ROMP)
- Unlike conventional thermosets which use oligomers, ruthenium technology allows for curing of pure DCPD monomer yielding pDCPD with unique properties

Cross-linking/Cure controlled by
- Catalyst structure/ concentration
- Comonomers
- Additives
- Cure methodologies
Materia’s pDCPD

- A new category of “green” thermoset resins for composite applications.
- Thermoset system offering a novel combination of properties that are more “thermoplastic-like” and “fluoropolymer-like”
- Fit with VARTM and processes for Wind Blades.
- Tunable by formulation to match preferred processing conditions
Materia’s Poly-DCPD

A Game-Changing Thermoset Resin System

Ruthenium Catalyst
- 2005 Nobel Prize Winning Catalyst

Monomer (DCPD)
- By-product of petroleum industry

Proprietary Additives
- Custom adhesion promoters, impact modifiers, etc.
pDCPD Supply Chain

Crude Oil → Naptha Cracker → Crude DCPD

Materia’s Technology

Additives → Catalyst → Formulated DCPD → High Purity DCPD

Current Pilot Scale Capacity in Texas = 2000 MT (4.4 million lbs)

Fabricator → OEM
Historical Timeline of pDCPD

- **1980’s - Metton® (tungsten catalyst system) and Telene® (molybdenum catalyst system)**
  - Sensitivity of catalyst to air, moisture, and additives
  - Limited application primarily to RIM processing
  - Fast cure rate limits the ability to control “pot-life”
  - Unable to cure in the presence of reinforcements (composites)

- **1990’s- Grubbs catalysts (ruthenium) developed at Caltech**
  - Broad tolerance to air, moisture and additives
  - Expanded applications include those based on VARTM, RIM/RTM, Pultrusion, casting

- **2000’s - Materia develops complementary technology for composites**
  - Pot-life extenders provided more flexible processing options for large composite structures
  - Adhesion promoters delivered robust fiber binding for composite materials
  - Demonstrated scalability of 2nd Generation Grubbs catalysts
Properties of pDCPD Resin and Composites

- Neat Resin
- Glass composite static and fatigue properties
- Fracture toughness ($G_{Ic}$ & ply-drop)
Comparison of General Resin Properties

- pDCPD’s dominant features are high ductility/high strain with comparable modulus and strength.
- Other pDCPD attributes are low density (1.04), high Tg, and high water-resistance.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>pDCPD</th>
<th>Epoxy</th>
<th>UPR</th>
<th>Vinyl Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>MPa</td>
<td>58</td>
<td>55 - 65</td>
<td>40 - 55</td>
<td>60 - 75</td>
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<tr>
<td>Tensile Strain</td>
<td>%</td>
<td>5 - 6</td>
<td>3 - 4</td>
<td>1 - 2</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>GPa</td>
<td>2.5</td>
<td>2.9</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Tg</td>
<td>deg C</td>
<td>110 - 120</td>
<td>70 - 80</td>
<td>60 - 70</td>
<td>75 - 80</td>
</tr>
<tr>
<td>Water Absorption (7 days, 23 C)</td>
<td>%</td>
<td>&lt;1</td>
<td>4 - 5</td>
<td>4 - 5</td>
<td>2 - 4</td>
</tr>
<tr>
<td>Density</td>
<td>g/cc</td>
<td>1.04</td>
<td>1.15</td>
<td>1.15</td>
<td>1.14</td>
</tr>
<tr>
<td>Vol. Shrinkage</td>
<td>%</td>
<td>4 - 5</td>
<td>4 - 5</td>
<td>8 - 10</td>
<td>7 - 8</td>
</tr>
</tbody>
</table>

MSU/DOE Database
## Static Properties of pDCPD Laminates

**Primary Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Units</th>
<th>pDCPD Laminate</th>
<th>Typical Epoxy Laminate*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Vol. %</td>
<td>—</td>
<td>%</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>0°, ISO 527-4</td>
<td>MPa</td>
<td>1020</td>
<td>700 - 1100</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>0°, ISO 527-4</td>
<td>GPa</td>
<td>39.2</td>
<td>41 - 43</td>
</tr>
<tr>
<td>Tensile Strain, at Max</td>
<td>0°, ISO 527-4</td>
<td>%</td>
<td>2.93</td>
<td>2.5 - 3.0</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0°, ISO 527-4</td>
<td>—</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>Compression Strength</td>
<td>0°, ISO 527-4</td>
<td>MPa</td>
<td>801</td>
<td>700 - 900</td>
</tr>
<tr>
<td>Compression Modulus</td>
<td>0°, ISO 527-4</td>
<td>GPa</td>
<td>45</td>
<td>43 - 49</td>
</tr>
<tr>
<td>Compression Strain, at Max</td>
<td>0°, ISO 527-4</td>
<td>%</td>
<td>1.85</td>
<td>1.8 - 1.9</td>
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<tr>
<td>Shear Strength</td>
<td>0°, ISO 14129</td>
<td>MPa</td>
<td>40.1</td>
<td>45 - 50</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>0°, ISO 14129</td>
<td>MPa</td>
<td>2.88</td>
<td>3.20 - 3.40</td>
</tr>
<tr>
<td>Shear Strain, at Max</td>
<td>0°, ISO 14129</td>
<td>%</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Lay-up: Unidirectional Saertex UD1200

Laminate Preparation: Vacuum infusion at Materia

Tested at IMA-Dresden

*Quoted by IMA-Dresden
Static Properties of pDCPD Laminates

- Although not important in current blade design methodologies, off-axis properties are telling for how a blade “wears” (performance and damage tolerance).
- Laminate cracking often initiates transversely beginning at strain levels of 0.5% (MSU). Materia pDCPD exhibits 3X the failure strain of epoxy.

## Off-Axis Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Units</th>
<th>pDCPD Laminate</th>
<th>Typical Epoxy Laminate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Vol. %</td>
<td>—</td>
<td>%</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>Tensile Strength 90°, ISO 527-4</td>
<td>MPa</td>
<td></td>
<td>72</td>
<td>50 - 65</td>
</tr>
<tr>
<td>Tensile Modulus 90°, ISO 527-4</td>
<td>GPa</td>
<td></td>
<td>11.2</td>
<td>10 - 14</td>
</tr>
<tr>
<td>Tensile Strain, at Max 90°, ISO 527-4</td>
<td>%</td>
<td></td>
<td>1.5</td>
<td>0.5 - 0.7</td>
</tr>
<tr>
<td>Tensile Strength +/-45°, ISO 527-4</td>
<td>MPa</td>
<td></td>
<td>105</td>
<td>110 - 120</td>
</tr>
<tr>
<td>Tensile Modulus +/-45°, ISO 527-4</td>
<td>GPa</td>
<td></td>
<td>10.3</td>
<td>11 - 13</td>
</tr>
<tr>
<td>Tensile Strain, at Max +/-45°, ISO 527-4</td>
<td>%</td>
<td></td>
<td>8.2</td>
<td>3 - 6</td>
</tr>
</tbody>
</table>

Lay-up: Unidirectional Saertex UD1200
Laminate Preparation: Vacuum infusion at Materia

*Tested at IMA-Dresden
Typical Tensile Stress-Strain Curves for pDCPD and Epoxy Multidirectional Laminates

TT-TPI-EP = Araldite LY1564/XB3485

MSU/DOE Database for Composite Materials
pDCPD ductility translates into higher shear resistance

Measured on ±45 Deg Laminates
(ISO 14129 / ASTM 3518)

EP-1=
Hexion RIMR 135/
RIMH 136

Shear Modulus
(calculated between 0.15 - 0.55%)

pDCPD: 2.68 GPa
EP-1: 2.63 GPa
Fatigue Properties of pDCPD Laminates
Tension Fatigue Testing, R=0.1

pDCPD shows equivalent performance vs. epoxy laminates at high fiber volume fraction

Epoxy Resins
- SP Prime 20LV /
  Slow Hardener. 51%
- Vantico/Huntsman
  TDT 177-155, 56%
- Vantico/Huntsman
  TDT 177-155, 48%
- Huntsman Araldite
  LY1564/XB3485, 53%
- Vantico/Huntsman
  TDT 177-155, 61%

MSU/DOE Database for Composite Materials
pDCPD composites outperform the best epoxy laminates from the MSU/DOE database in strain at N > 1 Million

QQ1 = Vantico/Huntsman TDT 177-155; TT-TPI-EP = Araldite LY1564/XB3485

MSU/DOE Database for Composite Materials
Additional Testing Completed

- Adhesives
- Core Materials
- Coating Systems
- Environmental testing
Interlaminar Fracture Toughness of pDCPD Composites: $G_{IC}$ and Damage Growth at Ply-Drops
Pre-mature cracking/failures of blades can be caused by:

- Regions of thickness transition (ply-drops)
- Process defects (wrinkles, dry regions, resin-rich regions)
- Traditional fatigue coupons contain no defects, making estimation of defect-tolerance difficult
- Special tests can probe defect tolerance and may enable new blade designs through better prediction of failures
Measurement of IL Fracture Toughness

Mode I Opening

Mode I Delamination
Modified ASTM D5528
Treatment per Reed and Crews

Film Insert

Laminate

Mode II Shear

Mixed Mode Delamination
Modified ASTM D6671
Treatment per Reed and Crews
Comparison of $G_{IC}$ Fracture Toughness

- **pDCPD** shows better crack resistance vs. Epoxy
  - pDCPD: $G_{IC} = 1700 \text{ J/m}^2$
  - Epoxy: $G_{IC} = 330 \text{ J/m}^2$

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**ASTM D5528**
Double Cantilever Beam Treatment per Reed and Crews

$$G_{IC} = \frac{12P_c^2}{b^2h^3E_{11}} \left( a_0^2 + \frac{2a_0}{\lambda} + \frac{1}{\lambda^2} + \frac{h^2E_{11}}{10G_{13}} \right)$$

$$\lambda = \frac{1}{h} \sqrt{\frac{6E_{22}}{E_{11}}}$$
MSU has developed a test method for studying the effect of a ply drop in transition zones.
Effect of Load on Damage Growth

With decreasing loads, a ductile resin shows larger differences in damage growth (R=-1)

### Resin Type

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Product Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-1</td>
<td>Hexion RIMR 135/ RIMH 1366</td>
</tr>
<tr>
<td>pDCPD</td>
<td>Materia EXP-1166/ EXP-1122C</td>
</tr>
</tbody>
</table>

**R = -1**
Variable Max Loads
pDCPD laminate shows dramatically slower crack growth, especially with lower loads at high cycles.

Fatigue Tests of Ply-Drop Specimens

<table>
<thead>
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<th>Resin Type</th>
<th>Product Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-1</td>
<td>Hexion RIMR 135/</td>
</tr>
<tr>
<td></td>
<td>RIMH 1366</td>
</tr>
<tr>
<td>pDCPD</td>
<td>Materia EXP-1166/</td>
</tr>
<tr>
<td></td>
<td>EXP-1122C</td>
</tr>
</tbody>
</table>

R = -1, Max Loads = 22 kN
Effect of Static Tensile Load (Ply-Drop)

Compared to Epoxy, pDCPD requires significantly higher tensile load to grow a crack of equal length.
Summary of pDCPD Performance vs. Epoxy

- pDCPD’s general resin properties exhibit high ductility with 12% lower weight and superior moisture resistance.

- pDCPD static laminate properties match the performance level of epoxy while exhibiting superior off-axis strength and strain.

- pDCPD fatigue laminate properties are comparable to epoxy in tension-tension while exhibiting superior compressive fatigue performance.

- pDCPD is 5 times higher in Mode I fracture toughness ($G_{IC}$).

- pDCPD has significantly higher delamination resistance and structural integrity as exhibited ply-drop fatigue.

**pDCPD enables a superior level of structural integrity of laminates through high resistance to crack initiation, crack growth and overall delamination.**
Processing Characteristics
pDCPD Composites: Choice of Glass Sizing Treatments

- Viscosity of pDCPD = 15 cP (23°C) enables a step-change for VARTM!
  - Dramatically faster infusion rates / times.
  - No need to pre-heat resin to enhance infusion
  - Reduced use of vacuum consumables / infusion aids
  - One-shot thick sections (root areas)
  - Low void content -> high quality laminates (monolithic & cored structures)
  - Truly “enabling” for carbon infusion
  - Higher fiber volume fractions are possible (0.58 – 0.60)
Viscosity Profile of pDCPD Resin

- Significant viscosity advantage versus traditional infusion resins allows for 10X faster infusion rates
- Longer pot-life formulations are possible (> 3 hrs)
**Effect of Viscosity on Infusion**

**Infusion of Thin Glass Fiber Laminate**  
(380 x 200 x 4 mm)

<table>
<thead>
<tr>
<th>Resin</th>
<th>Material</th>
<th>Infusion Media</th>
<th>Size</th>
<th>Resin Viscosity</th>
<th>Infusion Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCPD</td>
<td>Glass</td>
<td>Yes</td>
<td>380 x 200 x 4</td>
<td>20</td>
<td>0.25</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Glass</td>
<td>Yes</td>
<td>380 x 200 x 4</td>
<td>300</td>
<td>7</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Glass</td>
<td>Yes</td>
<td>380 x 200 x 4</td>
<td>120</td>
<td>2</td>
</tr>
</tbody>
</table>

**No Infusion Media**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Material</th>
<th>Infusion Media</th>
<th>Size</th>
<th>Resin Viscosity</th>
<th>Infusion Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCPD</td>
<td>Glass</td>
<td>No</td>
<td>380 x 200 x 4</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>DCPD</td>
<td>Glass</td>
<td>No</td>
<td>500 x 75 x 50</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>DCPD</td>
<td>Carbon</td>
<td>No</td>
<td>500 x 75 x 50</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

**Infusion of Thick Glass Fiber Laminate**  
(500 x 75 x 50 mm)

**Infusion of Thick Carbon Fiber Laminate**  
(500 x 75 x 50 mm)
Carbon Footprint
Greener (Epoxy vs Poly-DCPD)

- **Naphtha C4 - C10**
  - Steam Cracker
  - Benzene
  - Propylene
  - 1. Chlorine
  - 2. Peroxide
  - Epichlorohydrin

- **C5 Stream**
  - 1. Allow CPD dimerization
  - 2. Distill off unreacted C5
  - Crude DCPD
  - Distill
  - Resin-Grade DCPD

- **Formulating**
  - Acid
  - Base
  - Bis-Phenol A
  - Amine Curing Agent

- **Epoxy Resin**
  - Acetone
  - Phenol

Inherently lower production costs and environmental footprint
Greener (Carbon Footprint Analysis)

**Total Product Life Cycle Emissions**
*(kg CO2-e)*

- **Resin-Grade DCPD**
- **Epoxy**

**Analysis Performed by Sustainability A to Z**
Value Drivers – pDCPD

1. Mechanical Performance
   Comparable mechanical performance to epoxy
   Improved damage tolerance and laminate structural integrity

2. Lower Density
   Lower weight of laminates / blades

3. Processing advantages
   Faster infusion rates
   Shorter cure cycle times
   Less vacuum consumables

4. Lower Cost
   Lower initial purchase price versus epoxy
   Additional – 10% density reduction (purchase less resin)

5. Laminate Quality
   Lower void content in laminates / fewer dry regions
   Higher fiber volume fractions

6. Greener technology
   Lower carbon footprint by 50%