STPC
Structural Thermoplastic Composites based on Reactive Polymerisation

Dany De Kock
Johns Manville

- Major fiber glass manufacturer in North America and Europe.
- Over 150 years of proud history; A Berkshire Hathaway company since 2001.
- Owned by Warren Buffet
- Leader in key markets
- 3 Divisions: Insulation, Roofing and Engineered Products

Johns Manville Engineered Products

- **Glass Fibers**
  - Glass fibers for composite reinforcement, glass nonwovens, and wallboard reinforcement

- **Nonwovens**
  - Glass and polyester nonwovens for roofing, flooring, filtration, and etc.
In-situ Polymerized Polyamide-6
Anionic Polymerization of Caprolactam

How does it work:

Raw materials:
- Caprolactam: Very low moisture content (typically < 200 ppm) Melting point ~69°C, water-like viscosity: 3.6 cP @ 110°C (vs. A typical epoxy resin viscosity ~1000 cP)
- Initiator (Catalyst C10): Metal caprolactamates, such as sodium caprolactamate
- Activator (C20): N-acyllactams such as caprolactam blocked isocyanates (in the sizing)

Challenges:
- Moisture sensitivity: Moisture deactivates polymerization initiator (catalyst)
- Fiber sizing compatibility: sizing chemicals may hinder/inhibit polymerization
Johns Manville Reactive Glass technology:

Glass fiber with surface-bonded activator group for the polymerization of caprolactam

- Polyamide-6 grows from glass surface: “Grafting from” approach
- Strong covalent bonding at fiber-matrix interface for efficient load transfer from resin matrix to reinforcing fibers
  - Improved mechanical properties, including flexural, tensile, and shear strengths
  - Improved aging performance

![Diagram showing standard glass fiber bonded with activator groups and glass fiber grafted with polyamide-6.](image-url)
Reactive Glass Benefits

Standard Non-Reactive Glass

Weak fiber-resin bonding; Failure at fiber/matrix interface

Johns Manville Reactive Glass

Strong fiber-resin bonding; Failure in resin matrix
Resin transfer molding (RTM)

Mold Carrier

Fabric layup

Courtesy of Fraunhofer ICT
Wet out with new fiber technology
RTM of Reactive PA-6

- Sizing development and properties done by high temperature RTM process for simplification
- **Reinforcement**: 6 layers of UD stitched fabric (0/90 layup), 50 vol.% glass
- **Injection pressure**: 10-15 bar for good resin impregnation / fiber wet-out
- **Fiber glass sizing**:
  - Sizing chemicals (lubricants, film former, etc.) optimized for excellent fiber wet-out
  - No hindrance on anionic polymerization of caprolactam
Grafting Polyamide-6 from Reactive Glass

Polyamide-6 covalently bonded to glass fibers
Charpy Impact

Reactive Glass (StarRov 886)

- Strong fiber-resin interface
  → effective load transfer from resin to glass
- No delamination, limited damage area

Non-reactive glass (StarRov 871)

- Weak fiber-resin interface
- Significant delamination, large damage area
RTM Reactive Glass Benefits

- Glass integrated with the polymer matrix through covalent bonding
- Significant improvements in composite properties – flexural strength, ILSS
- Interfacial strength tunable by adjusting the amount of activator on glass
- One component system (monomer/initiator) possible

Mechanical Property Improvement:
Reactive Glass vs. Non-reactive glass

- Inter-Lamella Shear Strength
- Tensile Strength
- Flexural Strength

Reactive Glass: Strong fiber-resin bonding
Development of a process for production of pultrusion profiles

- With partners under a AIF ZIM project (Germany)
- Results very promising
- High fiber content possible (> 80% by weight)
AP Nylon: Trade-offs

- **Anionic polymerization of caprolactam**
  - Moisture sensitivity
    - Can deactivate polymerization catalyst
    - Raw material moisture level must be very low (< 200 ppm)
    - Process: glass fabric & mold pre-drying

- **Resin chemistry**
  - Relatively high MW and low residual monomer (< 2%) achievable by optimizing amount of activator and catalyst in resin formulation
Prepreg STPC: Nylon-6

Key advantages of JM Nylon-6 prepreg technology:
• Fully impregnated and polymerized
• High glass content possible: >70%
• Thin prepregs can be wound to roll products
• Speed of production independent of fabric design & weight/m²
• Ready for compression molding to produce structural parts
• Suitable for overmolding
• Comparable cycle time to molding metal parts (<1 min)
Pioneering direct roving with reactive sizing designed for in-situ polymerized polyamides

**Product description:**
- Available in Currently 1200, 2400 Tex
  Different Tex on demand
- Filament Diameter 16µm
- Sizing Compatibility Polyamides

**Benefits:**
- Higher strength in in-situ polymerization
- Maximize glass-matrix bonding
- Improved mechanical properties
- Suitable for TP-RTM/RIM, TP-pultrusion, TP-winding
### JM Products for Polyamide Composites

#### Classic Products

<table>
<thead>
<tr>
<th>Product</th>
<th>Process</th>
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</thead>
<tbody>
<tr>
<td>ThermoFlow® 672</td>
<td>Extrusion Compounding</td>
</tr>
<tr>
<td>StarRov® LFT 890</td>
<td>LFT, DLFT, filament winding, organosheets</td>
</tr>
</tbody>
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#### New Product / Process for STPC

<table>
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<tbody>
<tr>
<td>StarRov® RXN 886</td>
<td>Caprolactam RTM/RIM</td>
</tr>
<tr>
<td>Caprolactam Prepreg</td>
<td>Caprolactam Pultrusion</td>
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- Reactive processing

#### Other Structural TP Processes

- Process development
- Composite property improvement

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Thank You

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