Structural Thermoplastic Composites from Reactive Resin Systems

New Fiber Sizing Developments for Optimized Properties

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STPC Introduction

- Structure thermoplastic composites (STPC) - Key part of Johns Manville innovation strategy
- Structural molding processes currently dominated by thermoset resins
- Thermoplastics:
  - Recyclable, moldable, easy to postform, impact and delamination resistant
  - High melt viscosity prevents use in molding processes for large structural parts

- New technology development needed for STPC
  - **Need:** Property advantage of thermoplastics + Processing advantage of thermosets
  - **Solution:** Reactive glass to enable in-situ polymerization of low viscosity monomer to form thermoplastic polymers
JM Products for Polyamide Composites

Commercially Available

<table>
<thead>
<tr>
<th>Product</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThermoFlow®</td>
<td>Caprolactam</td>
</tr>
<tr>
<td>StarRov® 672</td>
<td>RTM/RIM</td>
</tr>
<tr>
<td>StarRov® 871</td>
<td>Pultrusion</td>
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<tr>
<td>LFT, RTM,</td>
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<tr>
<td>Pultrusion,</td>
<td></td>
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<tr>
<td>Cast PA</td>
<td></td>
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<tr>
<td>Woven Multi-Axials</td>
<td></td>
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<tr>
<td>TP-RTM/RIM</td>
<td></td>
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<tr>
<td>TP Pultrusion</td>
<td></td>
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<tr>
<td>Other Structural TP Processes</td>
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</tbody>
</table>

• Process development
• Composite property improvement
Maturity versus Complexity of TP-Processes

Maturity

G-LFT  GMT  D-LFT

“local” reinforcement

Complexity

TP-Pultrusion  TP-RTM/RIM
<table>
<thead>
<tr>
<th>Process</th>
<th>VARTM</th>
<th>RTM</th>
<th>S-RIM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Injection</td>
<td>≤1 bar</td>
<td>≤ 5 bar</td>
<td>≤ 50 bar</td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tooling</td>
<td>Single sided tool</td>
<td>Double sided tool</td>
<td>Double sided steel tool</td>
</tr>
<tr>
<td>Injection Unit</td>
<td>Mixing vessel</td>
<td>Pressure vessel, most cases no mixing head</td>
<td>Separate tanks for each component, mixing head</td>
</tr>
<tr>
<td>Typical Fiber Volume Content</td>
<td>40%</td>
<td>40 %</td>
<td>55%</td>
</tr>
</tbody>
</table>
Reactive Thermoplastic
VARTM/RTM/S-RIM

- Similar to the thermoset process

- In-situ polymerization of monomers or oligomers creates a thermoplastic resin that can be melted, post-shaped, welded, ...

- Low viscosity is required

- Possible resin systems: PA, TPU, CBT (Cyclics)
- Structural Reaction-Injection-Molding (S-RIM)
  - Use of prepared glass fiber wovens

Courtesy of Fraunhofer ICT
• Weight/performance:
  ▸ Excellent

• Design flexibility:
  ▸ Limited to preforming capability, flow length and flow behavior of the resin

• Processing:
  ▸ Reaction can be sensitive to moisture and fiber sizing

• Recycling:
  ▸ Production fabric scrap during preforming step depends on preforming method
    ■ Can be used as reinforcement in other processes (e.g. compounding)
  ▸ Part recycling: Can be used in other processes
Liquid Molding Processes

Materials used for liquid molding processes
- Reactive Polyamide
- Cyclic esters - CBT (Cyclics®)
- Isoplast® – Thermoplastic Polyurethane

Requirement for these materials
- Viscosity lower than 3000 mPa.s (cP) (better lower than 1000 mPa.s (cP))
- Viscosity influences achievable fiber content
Reactive Polyamide-6

- Reactive polyamide-6: most widely used / low cost option
- Most experience: Polyamide-6 casting without fiber reinforcement
- RTM/RIM processes: well-known but limited use

- Typical raw material for reactive polyamide-6 process:
  - Caprolactam
    AP-Quality (for anionic polymerization), water content < 200 ppm
  - Catalyst
    Sodium-Caprolactam used in concentration of app. 1.2-3.0%
  - Activator
    Caprolactam blocked isocyanate or similar materials used in concentration of app. 1.0-2.5%
**Anionic Polymerization of Caprolactam**

Sodium Caprolactam + Activator → Polyamide-6

Caprolactam + Polyamide-6
Reactive Thermoplastic Molding Issues

- Incomplete polymerization caused by
  - Moisture
  - Chemicals in fiber sizing
    - Most thermoplastic compatible sizings not developed for these processes
    - Compatible sizing availability in the form of fabric very limited
  - Oxygen (in the case of anionic polymerization)
  - Tooling materials
  - Materials used in processing equipment in contact with the monomers
AP Nylon: Trade-offs

- **Anionic polymerization of caprolactam**
  - Moisture sensitivity
    - Moisture deactivates polymerization catalyst
    - Raw material moisture level must be very low
      - AP-grade caprolactam (moisture < 200 ppm), suitable for anionic polymerization of caprolactam, available from multiple suppliers
    - Process: glass fabric & mold pre-drying

- **Resin chemistry**
  - Balance polymer molecular weight and residual monomer
  - Increasing activator/catalyst can lower residual monomer; but leads to lower molecular weight
  - High MW and low residual monomer (< 2%) achieved by optimizing the amount of activator and catalyst
**Highlights**

- **JM Reactive Glass development**
  - StarRov® RXN 886 glass designed for anionic polymerization of caprolactam
    - Improved fiber wet-out
    - Excellent coupling between glass fiber and polyamide-6
  - Demonstrated performance improvement from reactive StarRov® RXN 886 glass

- **RTM technology development**
  - RTM technology development at Johns Manville Technical Center, enabling in-house evaluation of new sizing technologies
  - In-house knowledge available for customer support

- **TP Pultrusion:**
  - Ongoing development in multi-partner project
RTM Composite Properties

- Mechanical properties of AP nylon composites comparable to PU/Epoxy composites
- Excellent impact resistance of AP nylon composites

Impact test

AP Nylon

Impact tip: hemispherical, 0.5” diameter
RTM Technology Development

- **Resin impregnation:** Common problems
  - Fabric: Bundles of fibers tied by stitches → high injection pressure needed for resin penetration
  - Glass sizing: Some sizing additives cause difficulty in resin impregnation and fiber wet-out
  ⇒ Optimized sizing formulation and fabric design necessary

- **Moisture control:** AP-Nylon grade resin raw materials, fabric drying, N₂ protection

- **Molding capability:** Flat plaque and contour shape capability
Reactive Glass

- Glass fiber with surface-bonded activating group for the polymerization of caprolactam
  - Polyamide grow from glass surface
  - Maximal fiber-matrix bonding
    - Enhanced mechanical properties
    - Reduced thermal stress around fibers
- Resin very low viscosity prior to polymerization
  - Fast resin infusion / fiber wetting

**Reactive Glass**

- Strong fiber-resin bonding
  - Failure in resin matrix

**Non-Reactive Glass**

- Weak fiber-resin bonding
  - Failure at matrix/fiber interface
Reactive Glass Benefits

Improvements

• Glass integrated with the polymer matrix, not a filler
• Excellent fiber wet-out $\rightarrow$ very good adhesion
• Significant improvements in composite properties – flexural strength, ILSS
• One component system possible

Composite Performance Improvement:
Reactive Glass vs. Non-reactive glass
Improved Coupling
At Fiber Matrix Interface
Profile Pultrusion

Development of a process for production of pultrusion profiles

- Ongoing with partners under a AIF ZIM project
- First results very promising
- High fiber content possible (> 80% by weight)
Direct glass roving manufactured and designed for TP-RTM, LFT-pultrusion, organo sheet laminates

**Product description:**
- Available in 1200 Tex and 2400 Tex
- Filament Diameter 16µm
- Sizing content 0.4%
- Sizing Compatability Polyamides

**Benefits:**
- Good surface aesthetics
- Low fuzz
- Optimum and fast wet-out
- Excellent mechanical properties
- Optimum for weaving
Pioneering direct roving with reactive sizing manufactured and designed for in-situ polyamide polymerization

TP-RTM, LFT-pultrusion

Product description:
- Available in 1200, 2400 and 4800 Tex
- Filament Diameter 16µm and 23µm
- Sizing content 0.4 - 0.9%
- Sizing Compatbility Polyamides

Benefits:
- Higher strength in in-situ polymerization
- Maximize glass-matrix bonding
- Improved impact properties
- Suitable for TP-RTM/RIM, TP-pultrusion, TP-winding
Potential Applications and Composite Processes

- All **thermoset** processes and applications can be used
  - Final composite material will be a fiber reinforced **thermoplastic** that can be welded and post-shaped as well as easy recycled.
  - Anionically polymerized polyamide-6 has superior properties over standard polyamide-6 due to higher molecular weight.
- Pultrusion: complex profiles
- RTM/RIM: large, structural parts with woven fabric reinforcement
- Discontinuous and continuous fiber reinforced sheets for thermoforming applications
- Standard processes (compounding and profile extrusion) also possible
Thank You