Preliminary Studies on the Effect of Polymeric Film Formers and Cross Linking Chemistries on the Water-Glycol Resistance of PA-Glass Fibre Composites.

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Who We Are

Innovating a Sustainable Future

• Environmentally conscious
• Customer focused
• Family owned
• Global
• Professionally managed
• 70 years of experience
Our Vision: The Interface Experts

• Industrial Manufacturing Group Mission
  
  • To become the **Interface Adhesion Experts** delivering new solutions to the Composites Value Chain through new and differentiated technology, proven and validated with industry-standard equipment, testing, and data.

  • To optimize the interface adhesion between Fibers and Polymers across **all types** of composites, whether Thermoplastic or Thermoset.
Complete Composites Portfolio

- **Michelman** develops film formers and surface treatments to serve **ALL** fiber types:
  - Glass
  - Carbon
  - Basalt
  - Natural
  - Synthetic

- **Targeted Applications**
  - Polyolefin Thermoplastics
  - Polyamide Thermoplastics
  - Thermosets
  - UD Tapes
  - Technical Textiles
  - Pre-Pregs
Typical Fiberglass Sizing Formulation

- 80-90% Film Former = **Major Component**
  - Facilitates fiber manufacturing
  - Protects and bonds filaments together
  - Compatibility/adhesion promoter

- 5-10% Silane Coupling Agent
  - Adhesion promoter
  - Wet strength

- 5-15% Size Modifiers
  - Lubricants, anti-stats, antioxidants
  - Wetting agents, processing aids
Focus on PA-66 Research

• **High Temperature Thermoplastics** continue to remain “hot” and “in-demand” technology in several applications
  
  • Metal replacement in automotive industry
  
  • Longer lifetime of oil and gas assets
  
  • Air intake manifolds, rocker covers, radiator end tanks, electrical connectors and others.

• **Polyamides** are generally used for their excellent balance of oil resistance, thermal stability, mechanical strength, and other desirable properties.
What is happening?

- Failure at the interface of fiber and PA-66
- Glycol is damaging the bonding
- Better chemistry is needed
Interface in a glass fiber composite

- Improve interaction between matrix and fiber through **SIZING**
- Introduction of **reactive chemistry**
- Glycol resistant film former(s)

Diagram:
- FIBERGLASS
- SILANE
- FILM FORMER(S)
- MATRIX

**SPE ACCE 2019**
Film Formers for PA-66

- Polyurethane polymers in form of dispersions (PUD) are used for many polyamide applications.
- For PA-66 glycol resistance is most effective by using a combination of film formers.
- Michelman designs PUD’s by adjusting building blocks. (PUD1, PUD2)
- Copolymers of reactive polymers are used as co-film formers to boost glycol resistance in PA-66.
Materials and Methods

- **E-Glass** – Leibniz-Institut für Polymerforschung Dresden
- **Fiberglass Sizings*** - Michelman
- **Resin** – PA 66 Ultramid A27 E
- **Extrusion and Molding** - Leibniz-Institut für Polymerforschung Dresden
- **Tensile Testing ISO 527A (DAM and After glycol)** - Michelman
- **Glycol Resistance Test** - Michelman
- **SEM Images** – Michelman
# Michelman Sizing Chemistries

<table>
<thead>
<tr>
<th>Film Former</th>
<th>Co-Film Former</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>PUD-R</td>
</tr>
<tr>
<td>M3</td>
<td>PUD</td>
</tr>
<tr>
<td>M4</td>
<td>PUD-R1</td>
</tr>
<tr>
<td>M5</td>
<td>PUD-R1</td>
</tr>
<tr>
<td>M6</td>
<td>PUD</td>
</tr>
<tr>
<td>M7</td>
<td>PUD-R</td>
</tr>
</tbody>
</table>

*All sizing formulations had the same % of Amino propyl silanes*
Tensile Modulus of as molded (blue) and after Glycol soaking (orange)
Tensile Strength of as molded (blue) and after Glycol soaking (orange)

![Bar Chart]

**Ultimate Tensile Strength (UTS) / MPa**

<table>
<thead>
<tr>
<th>Retention</th>
<th>M1</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>M7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60.51</td>
<td>63.19</td>
<td>63.18</td>
<td>58.73</td>
<td>57.03</td>
<td>57.83</td>
</tr>
<tr>
<td>M1 Retention</td>
<td>35.3%</td>
<td>31.5%</td>
<td>35.7%</td>
<td>36.2%</td>
<td>36.2%</td>
<td>37.3%</td>
</tr>
</tbody>
</table>
Improved interface

*Adhesion between matrix and fiber has improved*
Composites Collaboration Center

- Polymer Design
  - Polymer Synthesis
  - Polymer Characterization

- Emulsion Development
  - Emulsion Development
  - Dispersion Technology
  - Particle Size Management

- Fiber Sizing Application
  - Sizing Capability
  - Fiber Sizing Application

- Polymer Conversion
  - Compounding
  - Extrusion

- Test Part Manufacture
  - Injection Molding
  - Thermoforming

- Composite Testing
  - Mechanical Performance
  - Aging Studies
  - Hydrolysis /Glycol Resistance
  - Fractography
Conclusions

• Our results indicate retention of 35-37% in tensile strength and 49-53% in Tensile modulus.

• PUDs in combination with reactive polymers have resulted in performance equivalent to current incumbent solutions (M1).

• Although we currently don’t have a winning candidate, this study has provided us an understanding of current state of art of film formers that resist glycolysis.

• In working with our partners, we are building a better understanding of structure/property relationships between fibers and matrices.

• The knowledge gained through this work will help us in designing next generation film formers and co-film formers for improving glycol resistance.
Future Work

- Interfacial Shear Strength is a unique and valuable test method to determine fiber/matrix interaction.

- Work is underway to establish a correlation between single fiber pull out and bulk mechanical properties

- Additional work will continue to improve our understanding of the fiber/matrix interactions, specifically as they relate to glycol resistance.

- We will continue to explore the relationships between Silanes, film formers, and reactive polymers with the goal to optimize the entire sizing system.

- This work is an ongoing effort, with several variables that will be systematically studied.
Thank you!

Any questions?