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

Steve Bassetti
Global Marketing Director

Nagesh Potluri, Ph.D
Group Technology Director

Who We Are

Innovating a Sustainable Future

- Environmentally conscious
- Customer focused
- Family owned
- Global
- Professionally managed
- 70 years of experience

Global Headquarters – Cincinnati, OH

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

- <u>**Targeted Applications**</u>
  - Polyolefin Thermoplastics
  - Polyamide Thermoplastics
  - Thermosets
  - UD Tapes
  - Technical Textiles
  - Pre-Pregs

Typical Fiberglass Sizing Formulation

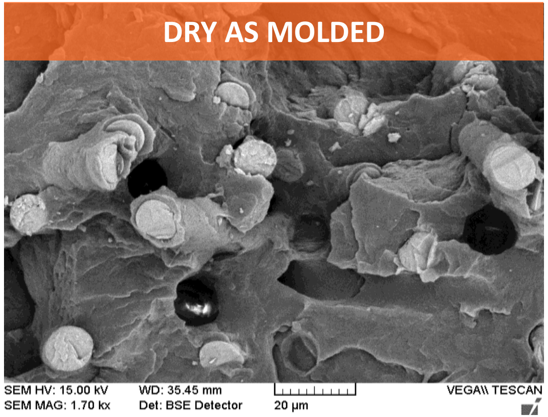
- 80-90% Film Former=**Major Component**
    - Facilitates fiber manufacturing
    - Protects and bonds filaments together
    - Compatibility/adhesion promoter
- 5-10% Silane Coupling Agent
    - Adhesion promoter
    - Wet strength
- 5-15% Size Modifiers
    - Lubricants, anti-stats, antioxidants
    - Wetting agents, processing aids

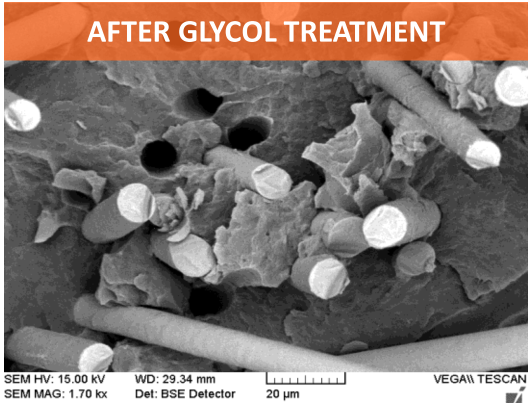
Focus on PA-66 Research

- **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.

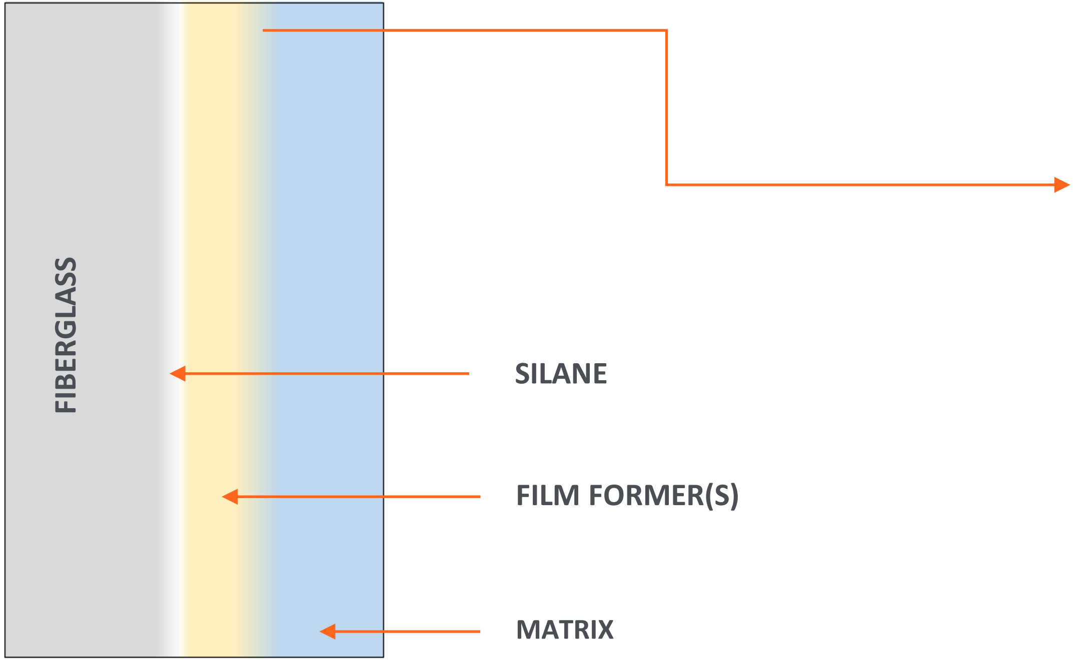
Problem statement: Interface Failure

- **What is happening?**
  - Failure at the interface of fiber and PA-66
  - Glycol is damaging the bonding
  - Better chemistry is needed


DRY AS MOLDED


AFTER GLYCOL TREATMENT

Interface in a glass fiber composite

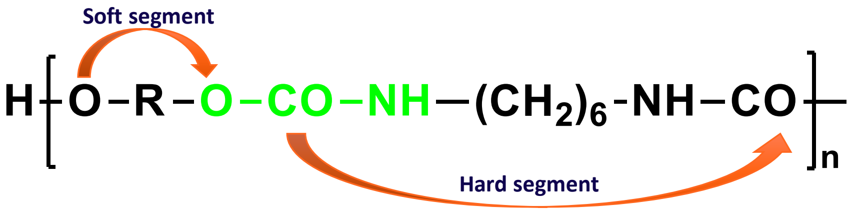


- Improve interaction between matrix and fiber through **SIZING**
- Introduction of **reactive chemistry**
- Glycol resistant film former(s)

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.

POLYURETHANE DISPERSION



$$H\left[O-R-O-CO-NH-(CH_2)_6-NH-CO\right]_n$$

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

	Film Former	Co-Film Former
M1	PUD-R	RP-1
M3	PUD	RP-1
M4	PUD-R1	RP-1
M5	PUD-R1	RP-1
M6	PUD	RP-2
M7	PUD-R	RP2

Incumbent Product

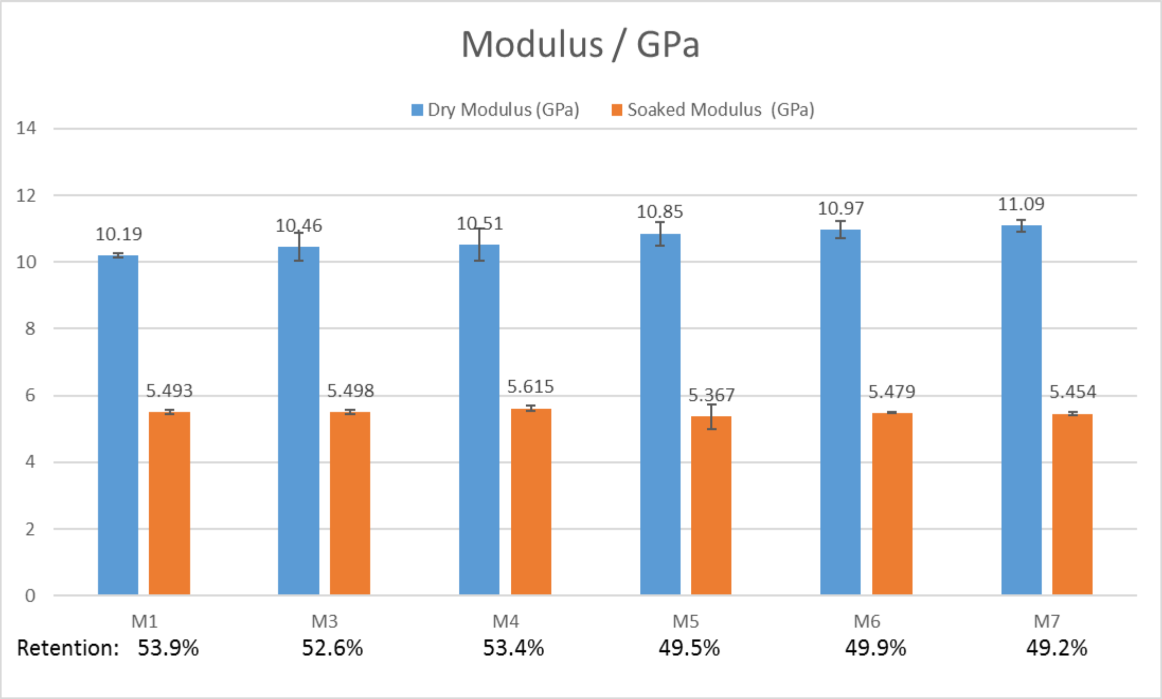
RP = Reactive polymer

PUD-R= Reactive PUDs

PUD= Conventional PUDs

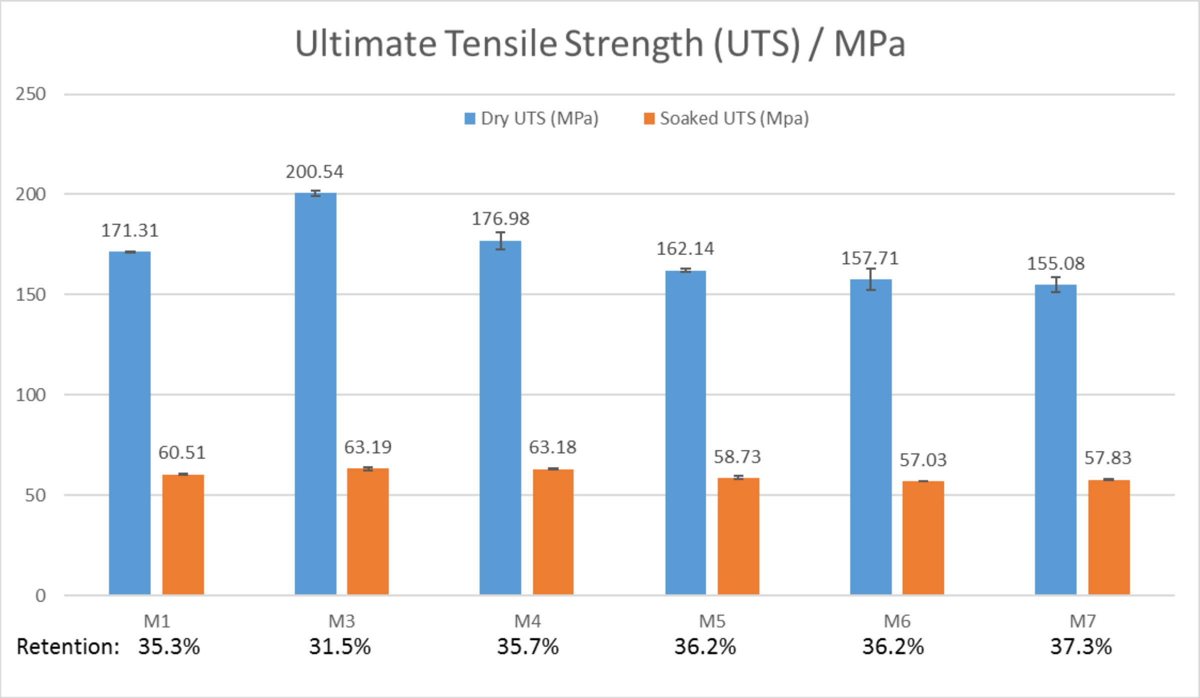
*** All sizing formulations had the same % of Amino propyl silanes**

Tensile Modulus of as molded (blue) and after Glycol soaking (orange)



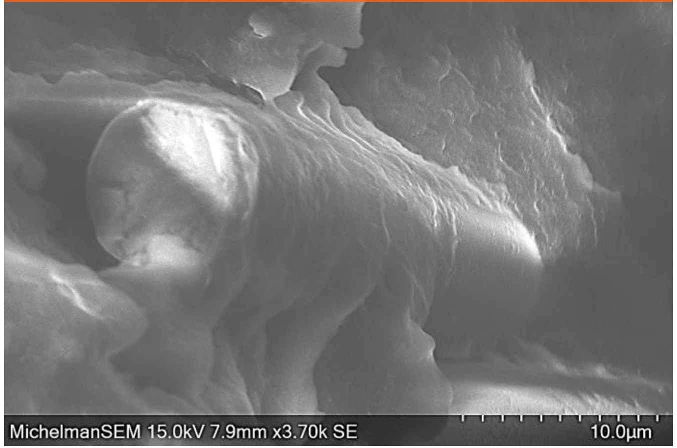
Retention: 53.9% 52.6% 53.4% 49.5% 49.9% 49.2%

Tensile Strength of as molded (blue) and after Glycol soaking (orange)



Improved interface

DRY AS MOLDED



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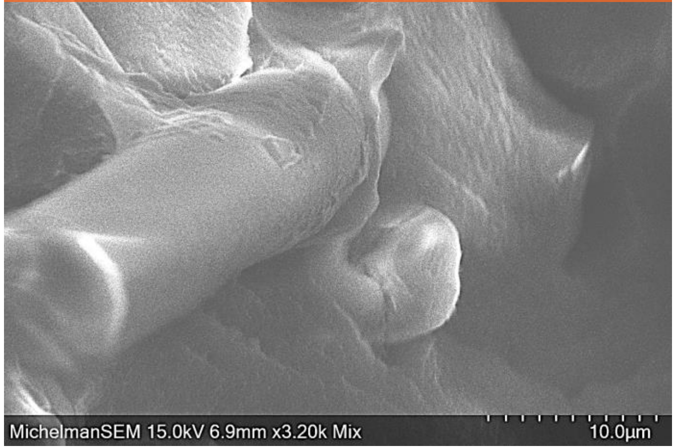

***Adhesion between matrix and fiber has improved**

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.

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Thank you!

Any questions?