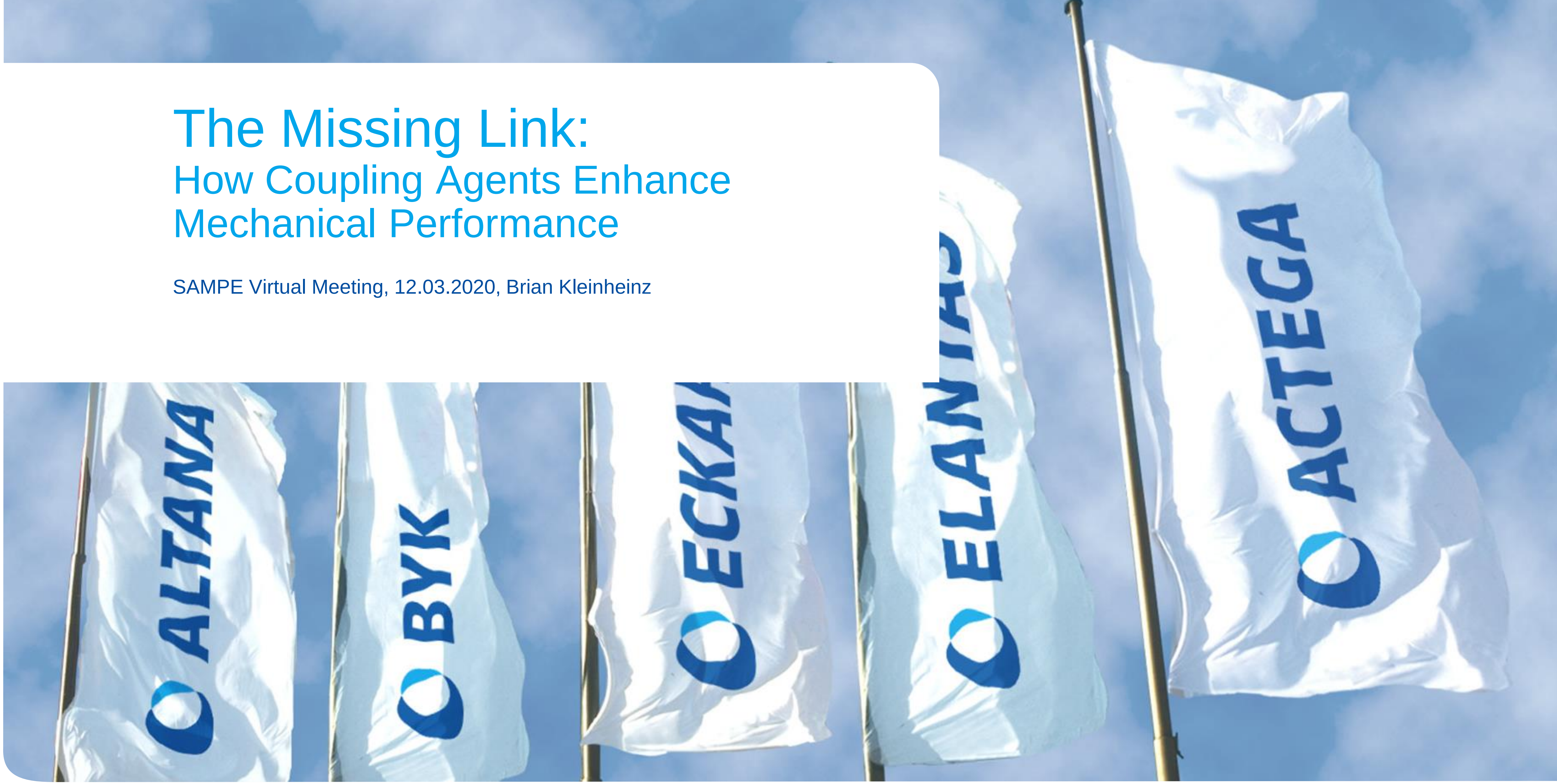
The Missing Link:
How Coupling Agents Enhance Mechanical Performance

SAMPE Virtual Meeting, 12.03.2020, Brian Kleinheinz



Outline

- Introduction to Coupling Agents
  - Performance-limiting interfaces
  - General structure and working mechanism
- Case Studies
  - Quartz-filled unsaturated polyester system (engineered stone)
  - Carbon-fiber vinyl ester SMC
  - Glass fiber amine-cured epoxy infusion

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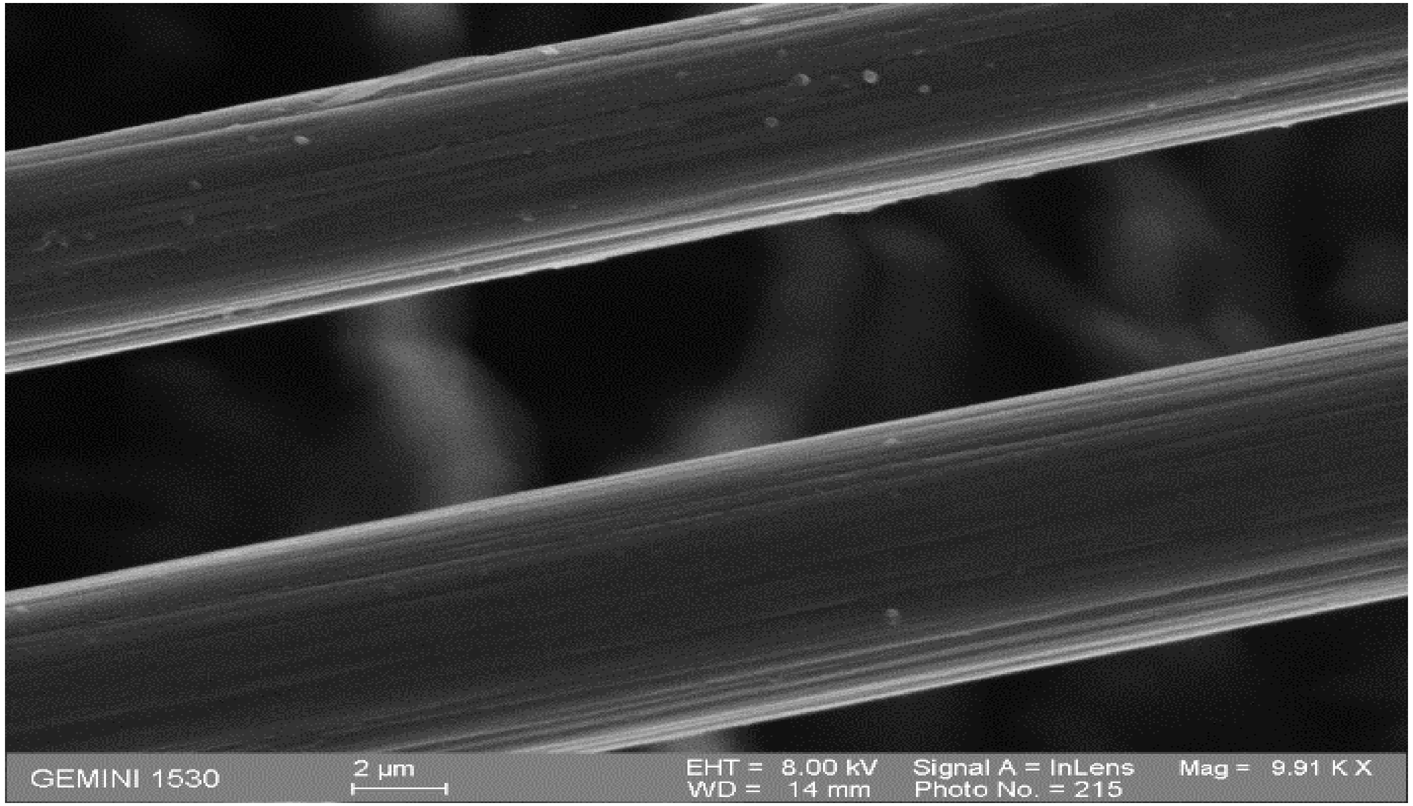
Introduction to Coupling Agents

Performance-limiting Interfaces

- Mechanical properties of a composite part depend in part on properties of the individual components
  - Matrix – unsaturated polyester, vinyl ester, epoxy, etc.
  - Fiber – glass, carbon
  - Filler – quartz, ATH, $CaCO_3$
- Individual properties can be improved, but failure frequently occurs at the resin/inorganic boundary

Performance-limiting Interfaces

- SEM image of a carbon-fiber composite after failure
- Fiber is intact, but no bond remains between resin and fiber
- Performance is limited not by strength of either resin or fiber, but by strength of bond between them



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General Structure and Working Mechanism

- Coupling Agents contain at least 2 functional groups
  - A reactive group that copolymerizes with the matrix during cure
  - A filler/fiber affinic group that adheres strongly to the inorganic reinforcement
- As each functional group is designed for a particular resin and reinforcement, there is no universal Coupling Agent

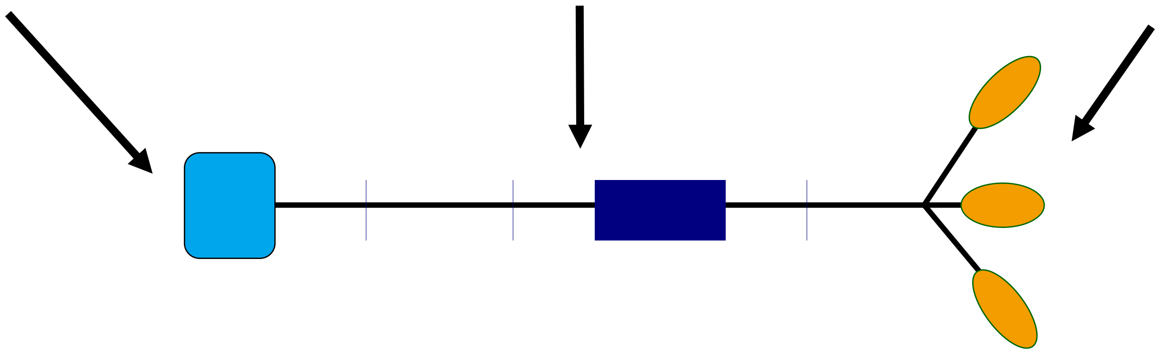
General Structure and Working Mechanism

- Each group is designed for a particular system

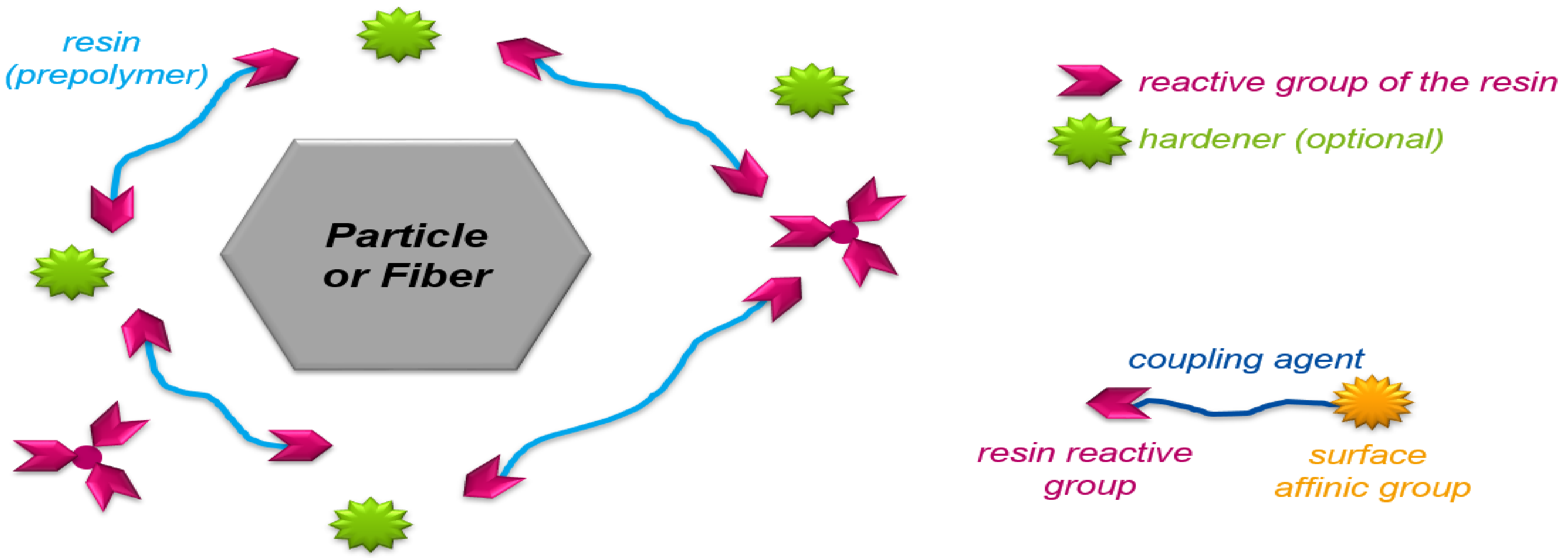
Resin reactive Group

Polymeric Resin Compatible Group

Substrate/Fiber Reactive Groups

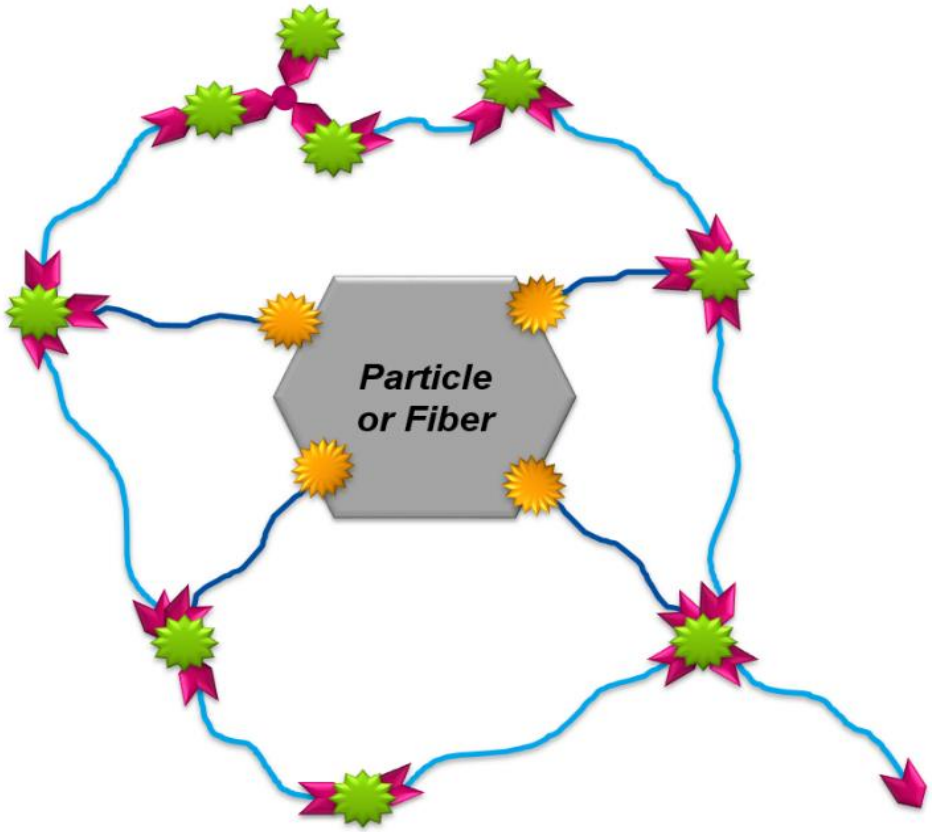


General Structure and Working Mechanism



Representation of system before curing

General Structure and Working Mechanism



Representation of system after curing

Case Studies

Case Study #1

Quartz-filled unsaturated polyester system

(engineered stone)

Quartz-filled Unsaturated Polyester

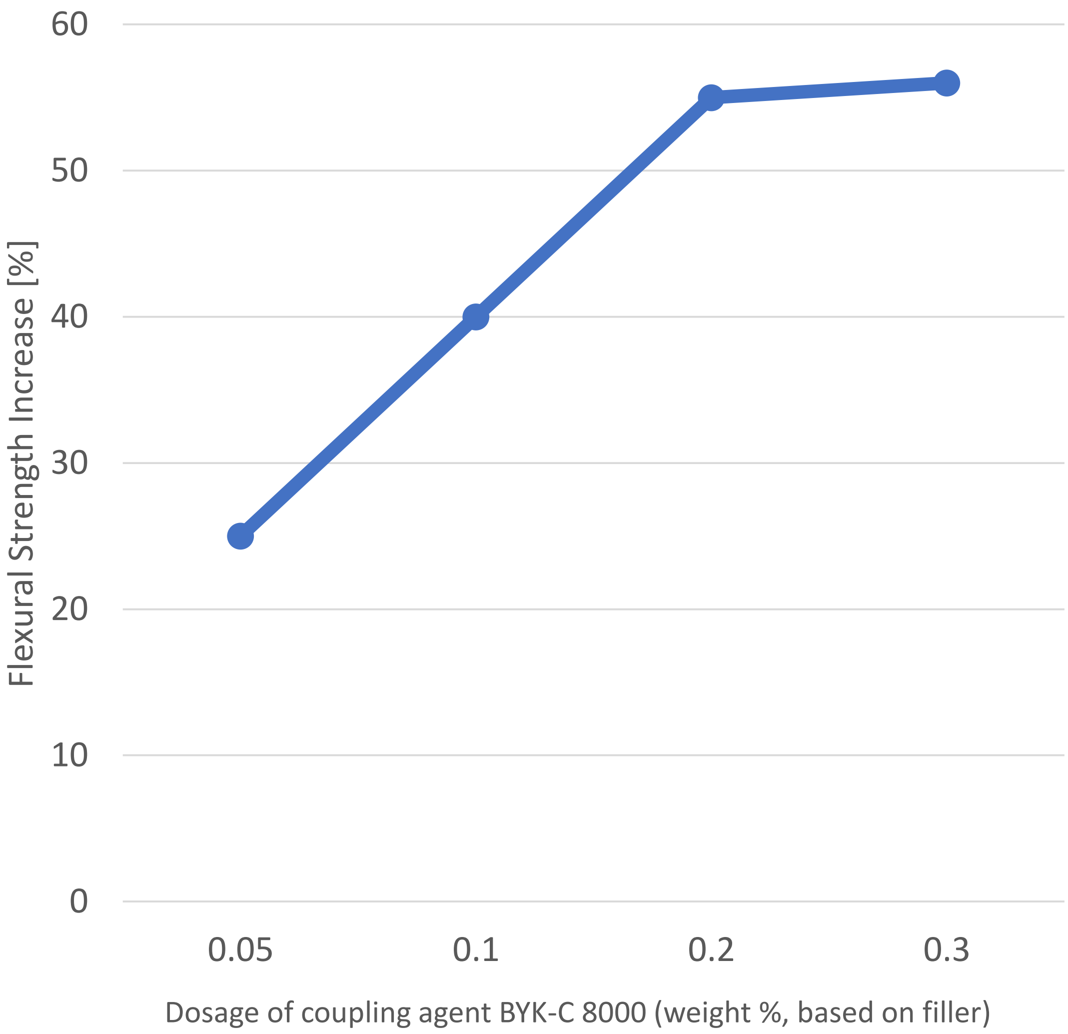
- Sample Preparation
  - All liquid components (save coupling agent) prepared as masterbatch
  - Coupling agent mixed in by hand
  - Curing initiator (peroxide) mixed in by hand
  - Filler (silica sand) added, system homogenized on dissolver for 90 s

Quartz-filled Unsaturated Polyester

- Sample Preparation
  - Sample poured into die (10 cm x 3.5 cm x 20.5 cm)
  - Cure 1 hour at room temperature
  - Post-cured overnight at 60 ^{o}C
  - Testing specimens cut according to DIN EN ISO 178

Quartz-filled Unsaturated Polyester

- Significant flexural strength increase (>50%) at relatively low dosage (0.2% on filler)
- Strength increases with dosage up to a saturation point (~0.3%)



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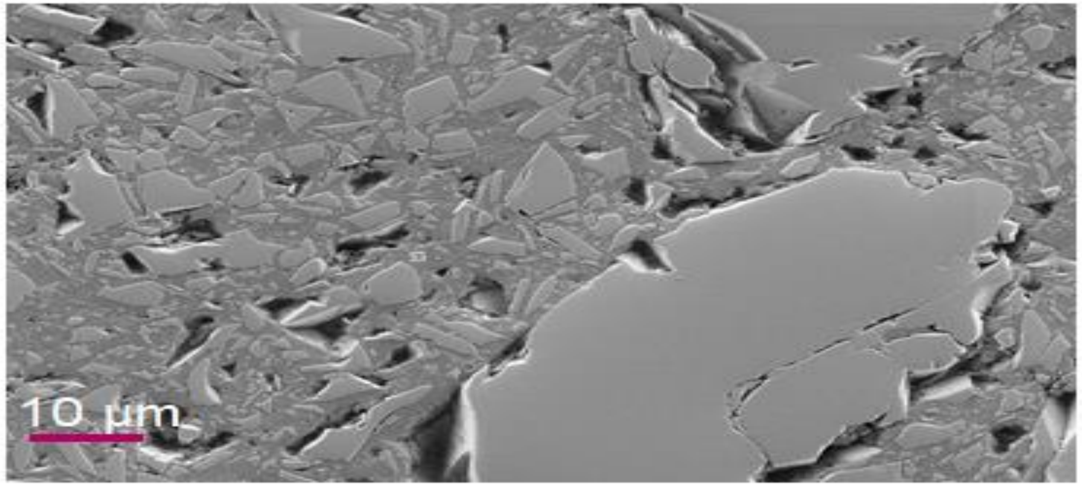
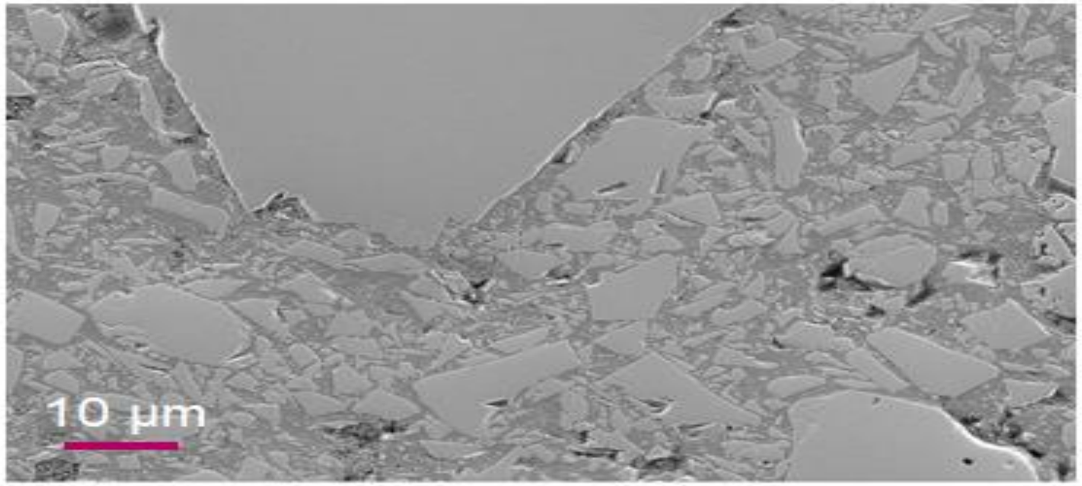
Quartz-filled Unsaturated Polyester



without BYK-C 8000



with BYK-C 8000

- SEM images after exposure of the system to hot water
- The sample with coupling agent shows minimal cavities reflecting the improved bond between resin and filler
- In addition to increased mechanical properties, this also provides increased water and corrosion resistance

Case Study #2

Carbon-fiber vinyl ester SMC

Carbon-fiber vinyl ester SMC

- Sample Preparation
  - Coupling agent can be added to the system in any of 3 ways:
    - To the resin ahead of time by the resin manufacturer or compounder
    - To the mix during the SMC compounding
    - Directly to the fiber as a novel "Second Sizing" procedure
  - SMC is compounded, stored for at least 1 day at 35 ^{o}C
  - Panels molded, then cut for tensile and flexural testing according to DIN EN ISO 527-5 and DIN EN ISO 14125

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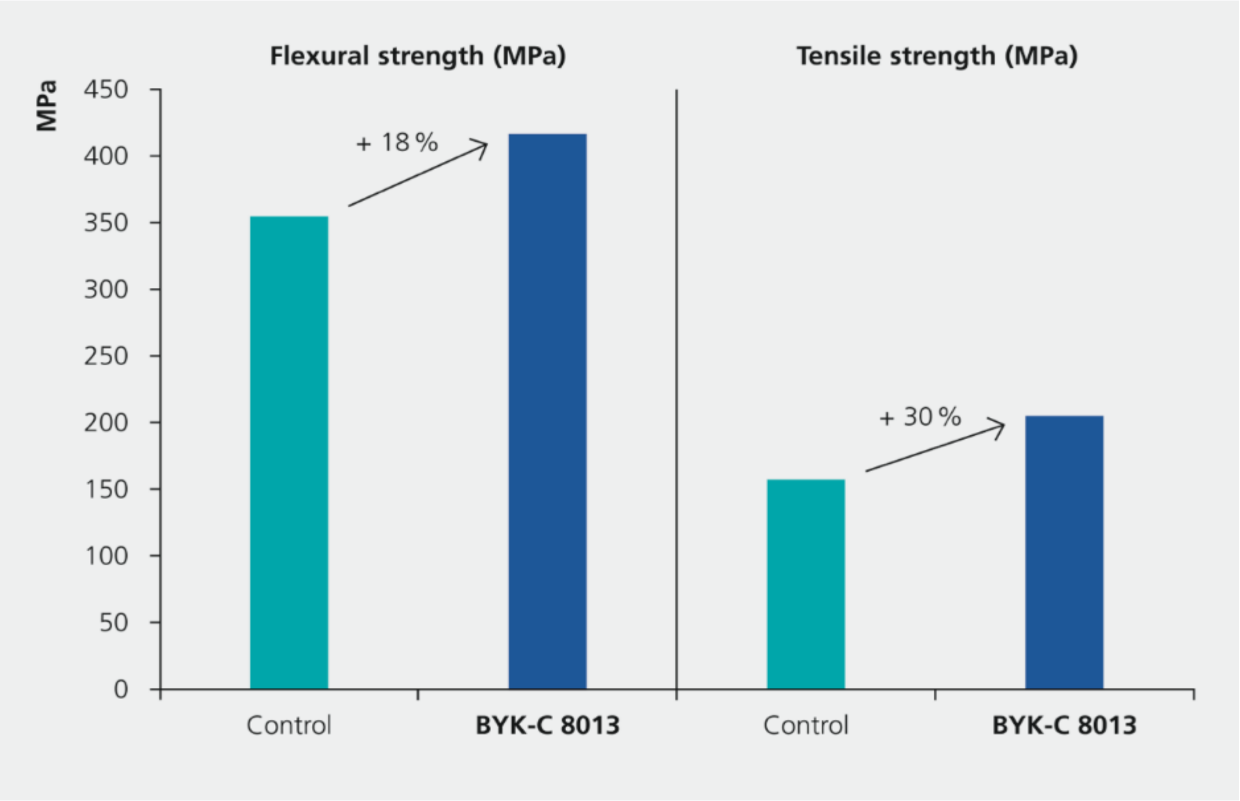
Carbon-fiber vinyl ester SMC

- Chopped fiber SMC, Coupling Agent dosage 5% on resin
- Flexural strength increased by 18%
- Tensile strength increased by 30%



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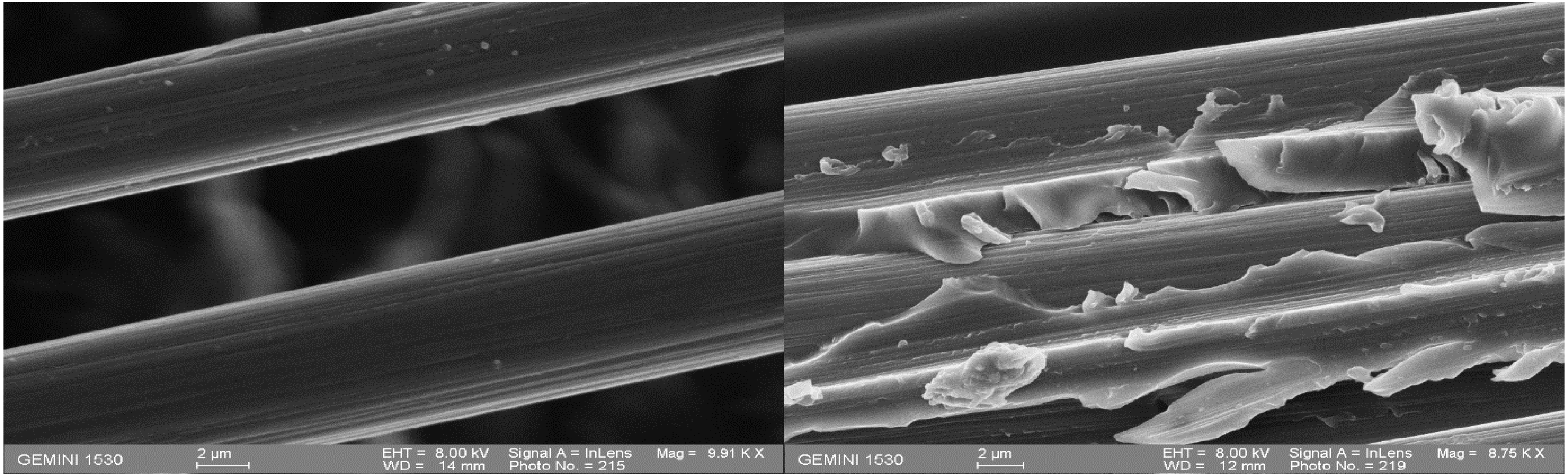
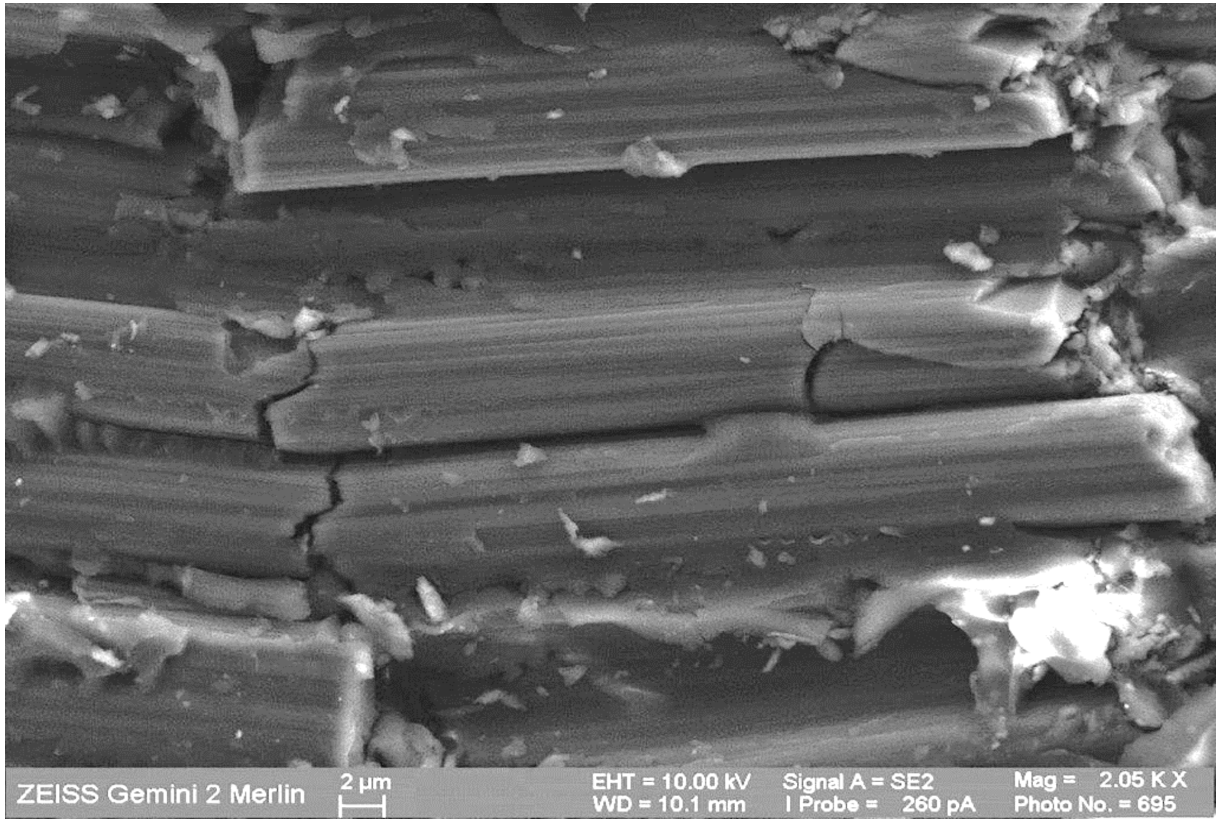
Carbon-fiber vinyl ester SMC



- SEM images of samples after failure with and without Coupling Agent
- Sample without Coupling Agent (left) shows no resin adhesion to fibers
- Sample with Coupling Agent (right) shows significant residual resin bound to fibers

Carbon-fiber vinyl ester SMC

- Extremely strong adhesion between fiber and matrix
- Material failure as a result of fiber fracture rather than adhesive failure
- Composite approaching ultimate strength of fiber



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Case Study #3

Glass fiber amine-cured epoxy infusion

Glass fiber amine-cured epoxy infusion

- Sample preparation
  - 4 layers unidirectional glass mat, 380 mm^2 x 380 mm^2
  - Orientation 90°/0°, 0°/90 // 90°/0°, 0°/90
  - Distance frame (2.5 mm) is used to set the fiber volume/weight content
  - Coupling agent added ahead of time to either epoxy or hardener

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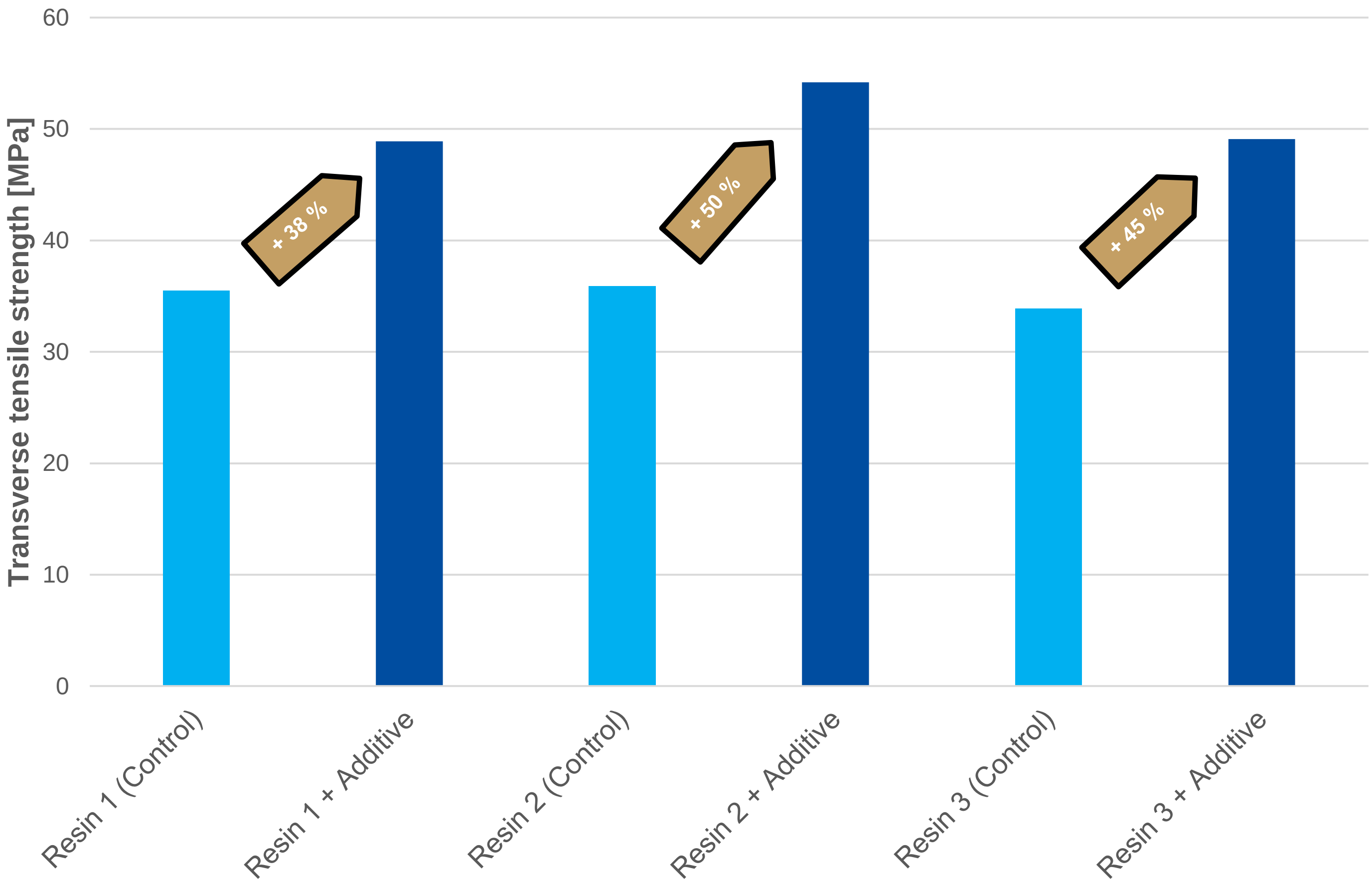
Glass fiber amine-cured epoxy infusion

- Sample preparation
  - Epoxy / hardener mixed on dissolver for 10 minutes
  - Resin infused, held 1 hour at room temperature
  - Mold placed in oven, cured 8 hr at 40 ^{o}C
  - After demolding, panel is post-cured 8 hr at 80 ^{o}C
  - Samples cut for testing according to DIN EN ISO 527-5B

Glass fiber amine-cured epoxy infusion

- 3 different epoxy systems tested
- Improvement in transverse tensile strength ranging from 38% to 50%



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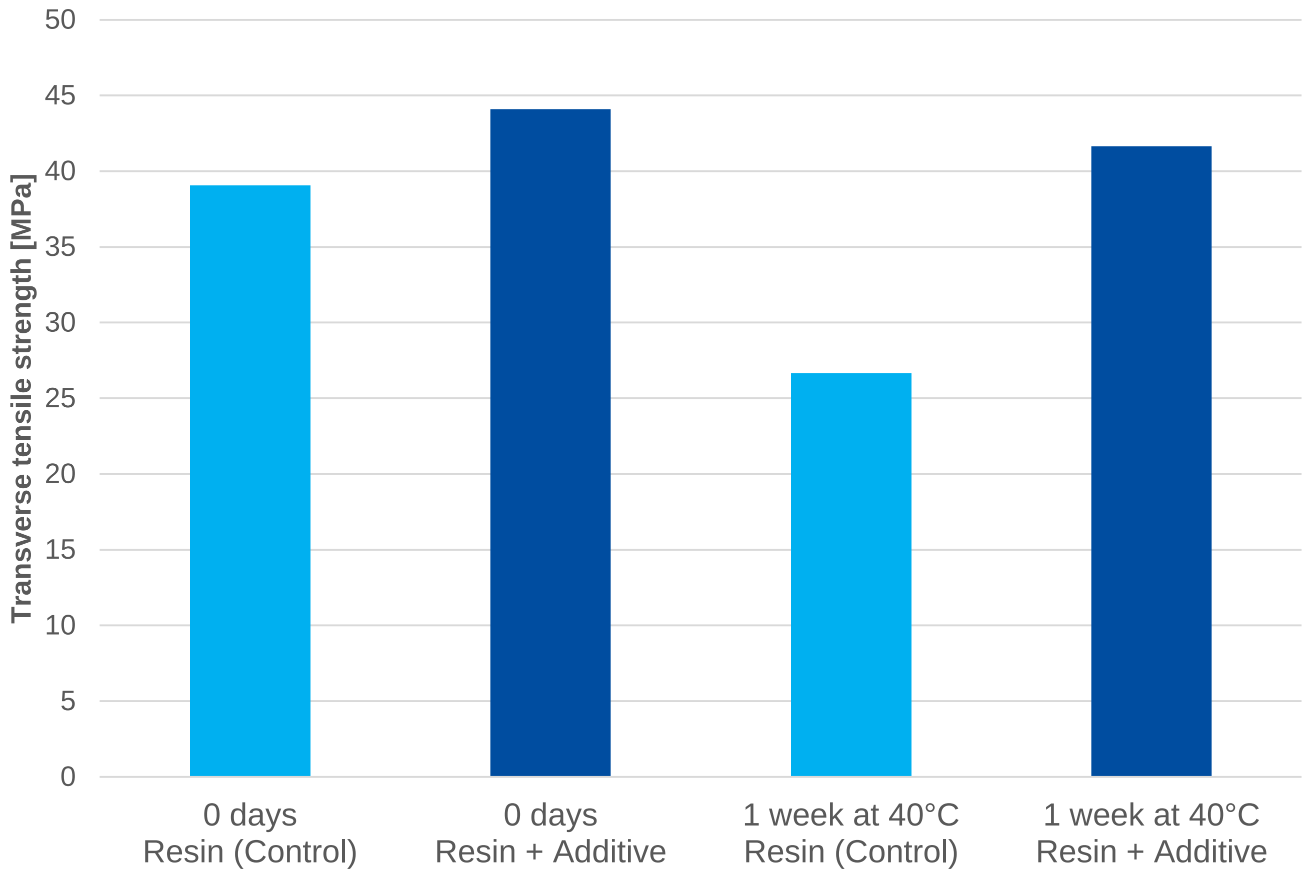
Glass fiber amine-cured epoxy infusion

- Glass fiber sizings deteriorate with age
- Coupling Agents can compensate for this affect
- Minimal drop in performance after elevated temperature aging of glass



Summary

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- Mechanical performance in composite materials can be limited by the strength of the bond between matrix and filler / fiber
- Coupling agents serve as a bridge between matrix and filler / fiber, strengthening this bond and enhancing overall performance

Summary

Coupling agents are tailored to specific resins and fibers / fillers

Mechanism	*Resin Systems*	*SiO_2*	*ATH, $CaCO_3$*	*Glass Fiber*	*Carbon Fiber*
Radical Curing	UP, VE	**BYK-C 8000**	BYK-C 8002	**BYK-C 8003**	**BYK-C 8013** **BYK-C 8014**
	Acrylate	BYK-C 8000	**BYK-C 8002**	BYK-C 8003	BYK-C 8013
Polyaddition	Epoxy	**BYK-C 8001**		**BYK-C 8001**	

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Summary

- Coupling agents can provide many benefits
  - Increased mechanical properties
  - Greater design freedom (weight reduction, material selection)
  - Better water and corrosion resistance (cast systems)
  - Ease of use - incorporation at many stages of the manufacturing process
  - Compensation for aged glass to maintain high performance

Acknowledgements

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Thank you for your attention.