High Thermal Conductivity Graphite Foam Reinforced Polymer Composites

by

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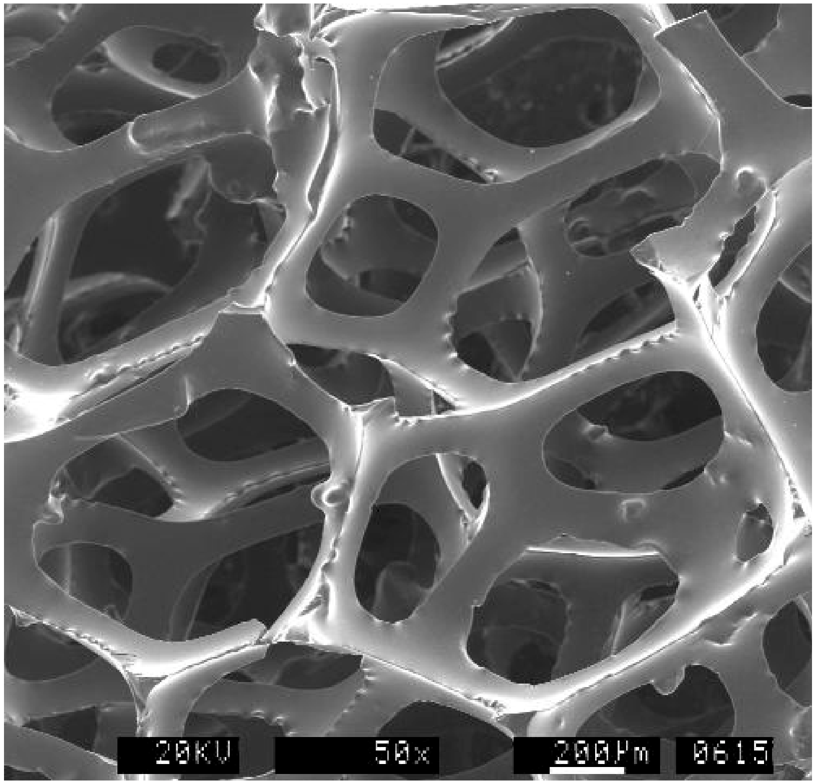
CIMTech
Carbon and Insulation
Materials Technology Group

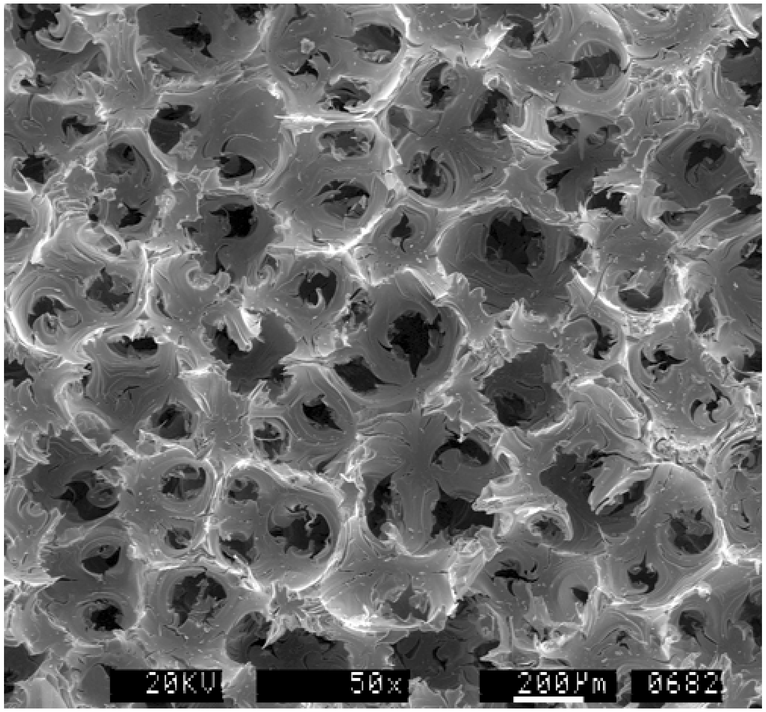
Typical Carbon Foams

- Made from amorphous carbons
- More recently made from pitches and mesophases
- 5-25% dense
- Thermal insulators
  - $\kappa < 10$ W/m·K
- Strengths similar to honeycomb materials
- Ability to absorb tremendous amounts of impact energy



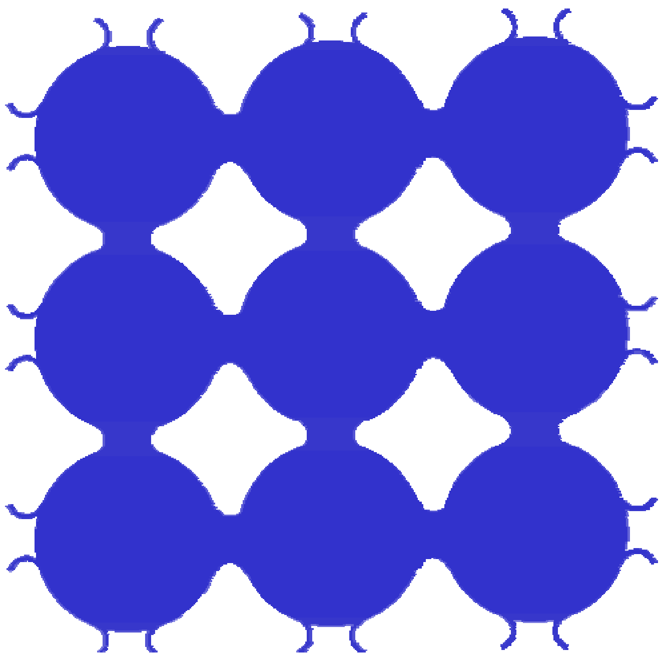
ORNL Mesophase-Derived Graphitic Foam

- Graphitic ligaments
  - Graphite-like properties (high κ, E, σ) along ligaments.
- Dimensionally stable, low CTE
- No out-gassing
- Open porosity
- Excellent thermal management material
  - Bulk conductivities greater than 150 W/m·K
  - Natural 3-D reinforcement for composites
  - Should yield composites with conductivities equivalent to aluminum

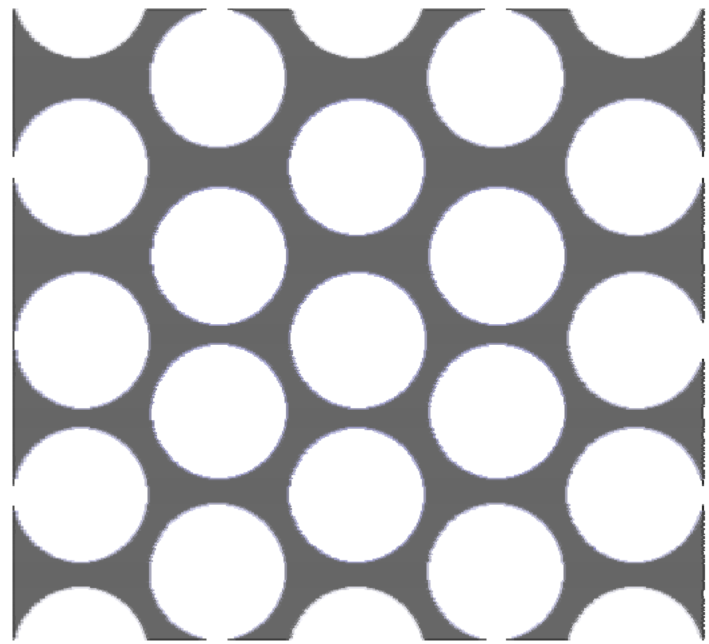


Unique Structure For a Composite

- Failure mechanisms not understood
- Thermal effects not understood
- Shrinkage upon cure might damage structure



Phase 1-Polymer



Phase 2-Foam

Materials Selection

- Selected various polymer candidates
  - Desired varying properties
    - Polycyanate resin, (RS-14)
      - Low viscosity, high toughness, high temperature stability, low shrinkage during cure
    - Epoxy, (Standard epoxy for mounting samples for polishing)
      - Low viscosity, excellent interfacial bonding to graphites, room temp cure
    - Polyester, (Bondo Fiberglass automotive grade resin)
      - Cheap (automotive uses), room temp cure, moderate viscosity
    - Phenolic, (Durite SC-1008, Borden Chemical)
      - Low viscosity, high temperature stability, can convert to carbon
    - SMJ Carbon (AFRL/PRSM), (proprietary pitch-type deposit)
      - High temperature applications, high thermal conductivity
    - Aluminum, (MMCC, Aluminum/Silicon alloy pressure cast method)
      - Tough, metallic, high thermal conductivity

Testing

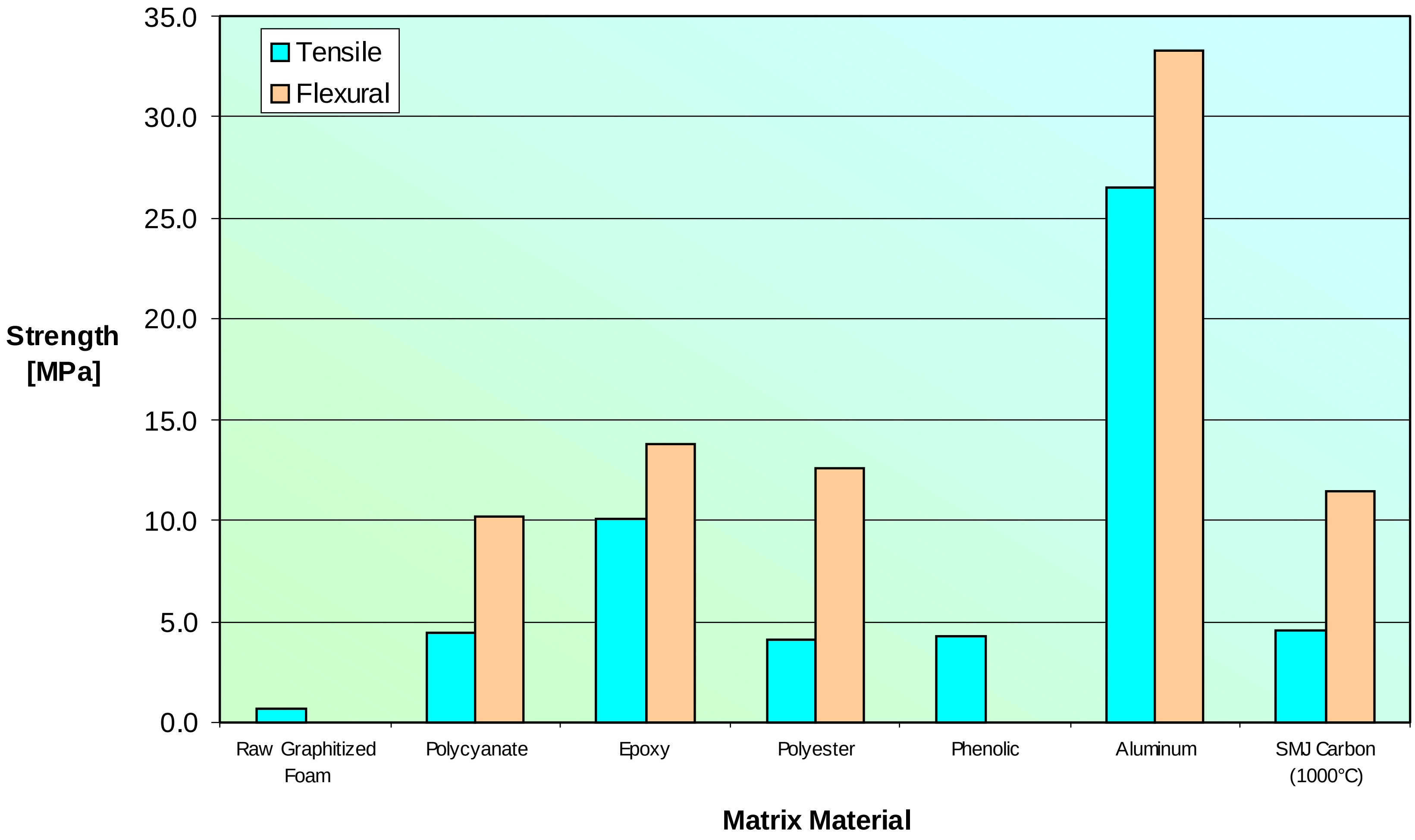
- Mechanical testing
  - Flexural Strength
    - → 4 point bend, specimens 0.2 x 0.5 x 4-in.
  - Tensile Strength
    - → specimens 0.2 x 0.5 x 4-in.
  - Compressive Strength
    - → specimens 0.5 x 0.5-in.
- Analysis
  - Thermal Conductivity
    - → specimens 0.5 x 0.5-in.
  - Fracture Surfaces (tensile)
    - → SEM

Flexural and Tensile Strength

Matrix	Density [g/cm^3]	% Dense	Tensile Strength MPa (Psi)	Flexural Strength MPa (Psi)
Raw Graphitized Foam	0.54		0.69 (100)	--
Polycyanate	1.37	88%	4.5 (653)	10.2 (1475)
Epoxy	1.31	84%	10.1 (1460)	13.7 (1990)
Polyester	1.33	85%	4.1 (595)	12.6 (1830)
Phenolic	1.00	64%	4.3 (624)	--
Aluminum	2.34	89%	26.5 (3850)	33.3 (4830)
SMJ Carbon (1000°C)	1.34	63%	4.6 (660)	11.5 (1660)

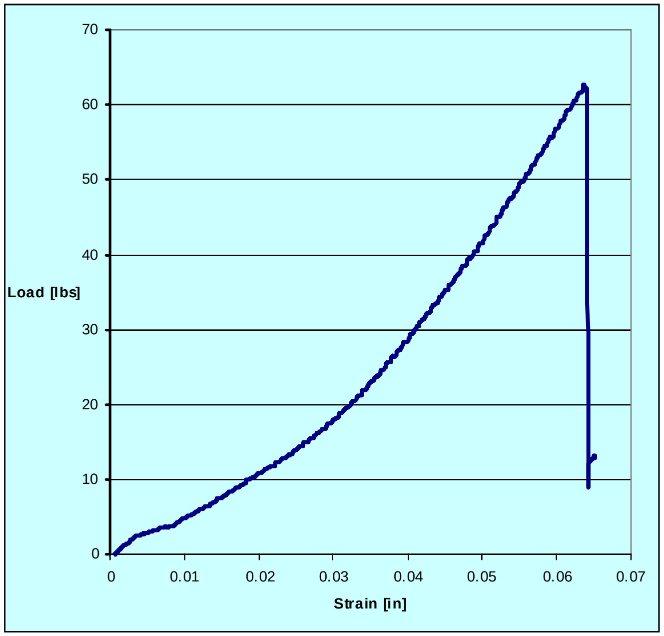
- Flexural strength greater than tensile strength indicates weibull effects and therefore strength is flaw limiting (expected).

Flexural and Tensile Strength

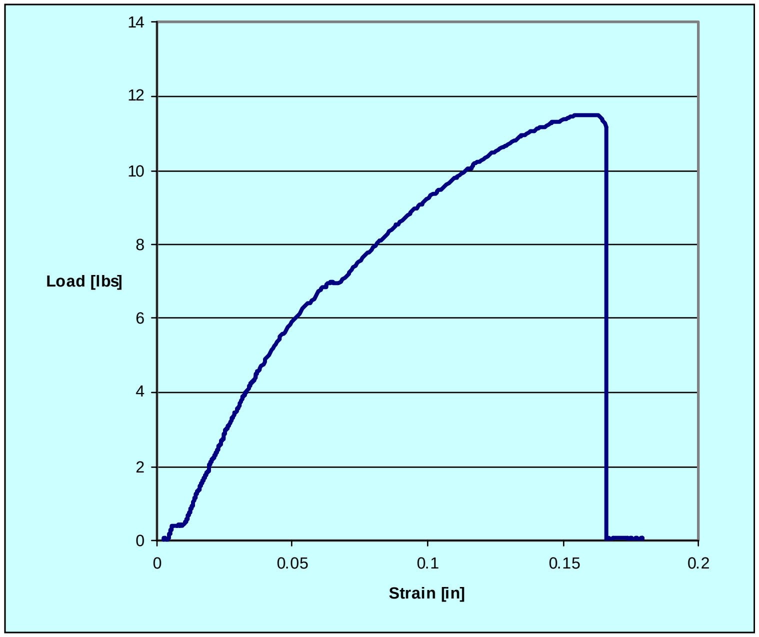


Stress-Strain Behavior

Tensile Test



Flexural Test



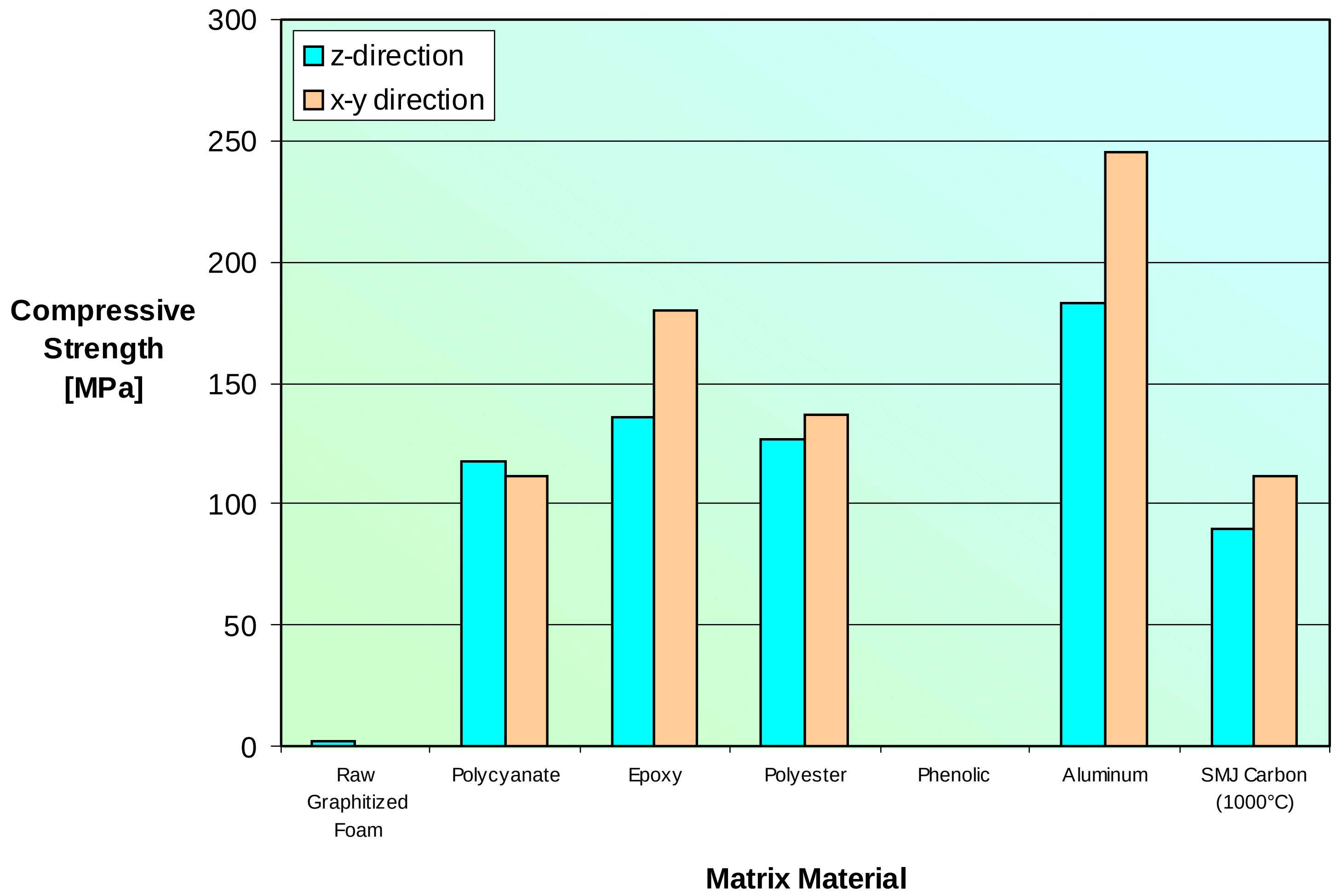
- Brittle fracture not usually seen in carbon/polymer composites

Compressive Strengths

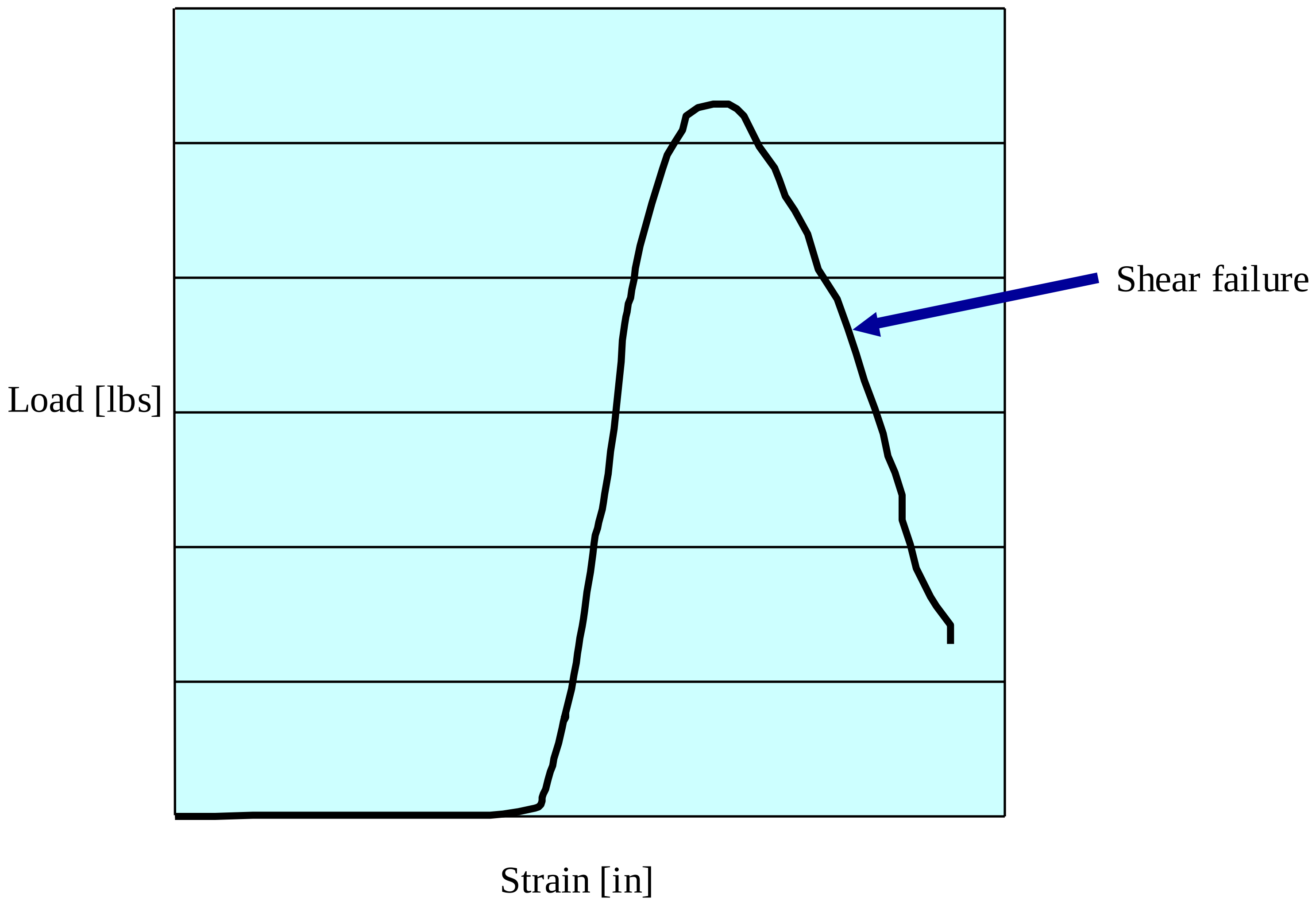
Matrix	Density [g/cm^3]	% Dense	Compressive Strength z-direction MPa (Psi)	x-y direction MPa (Psi)
Raw Graphitized Foam	0.54		2.1 (305)	
Polycyanate	1.37	88%	118 (17,100)	112 (16,200)
Epoxy	1.31	84%	136 (19,800)	180 (26,100)
Polyester	1.33	85%	127 (18,400)	137 (19,900)
Phenolic	1.00	64%		
Aluminum	2.34	89%	183 (26,500)	245 (36,500)
SMJ Carbon (1000°C)	1.34	63%	89 (13,000)	112 (16,200)

- Compressive strengths are dramatically higher than flexural and tensile strengths (typical carbon/polymer composites do not exhibit this large of a difference)

Compressive Strengths



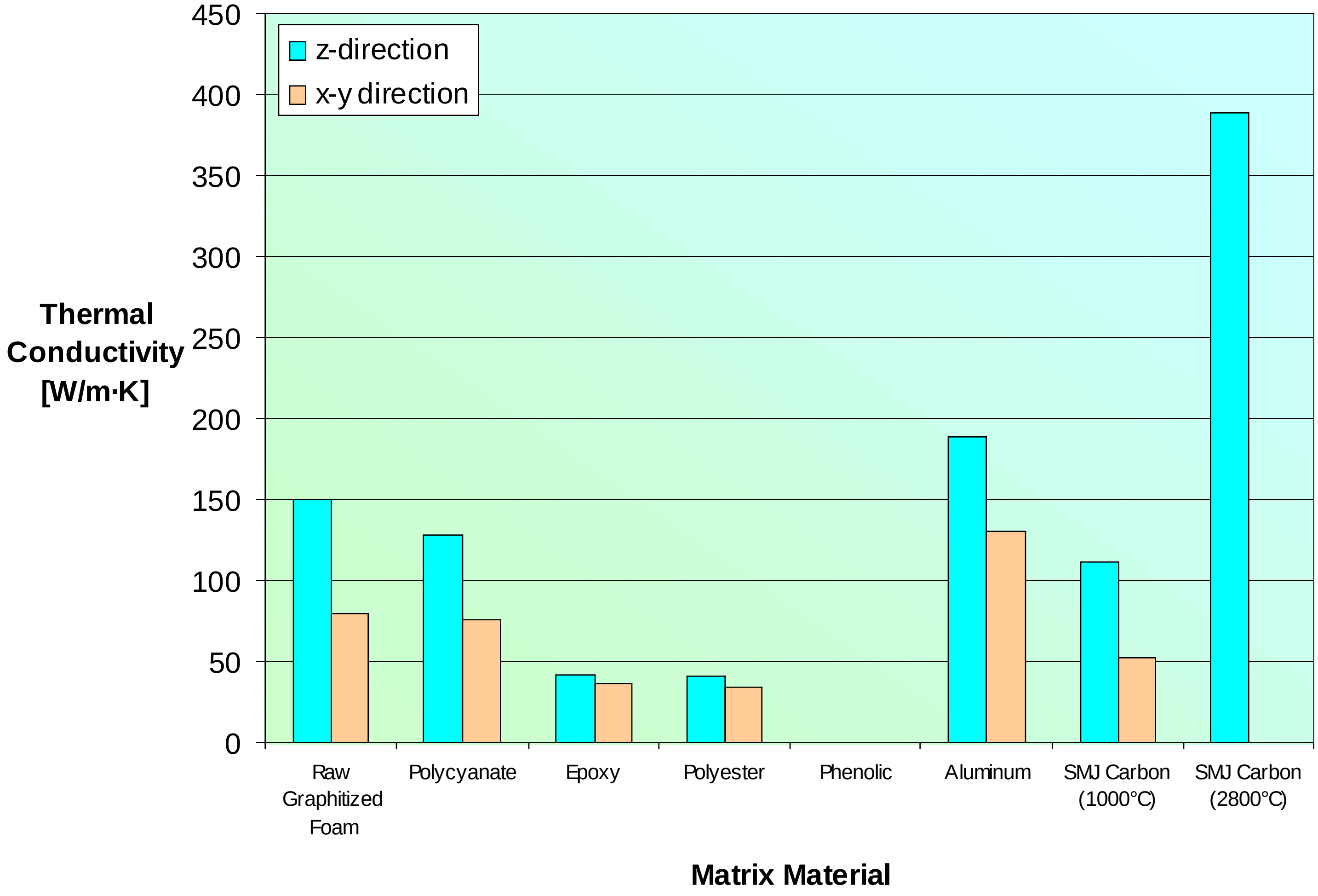
Stress-Strain Behavior - Compression



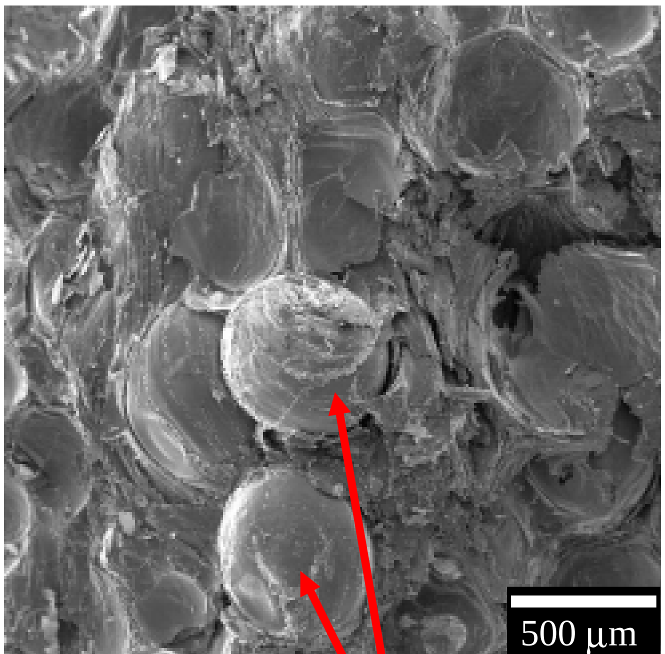
Thermal Conductivity

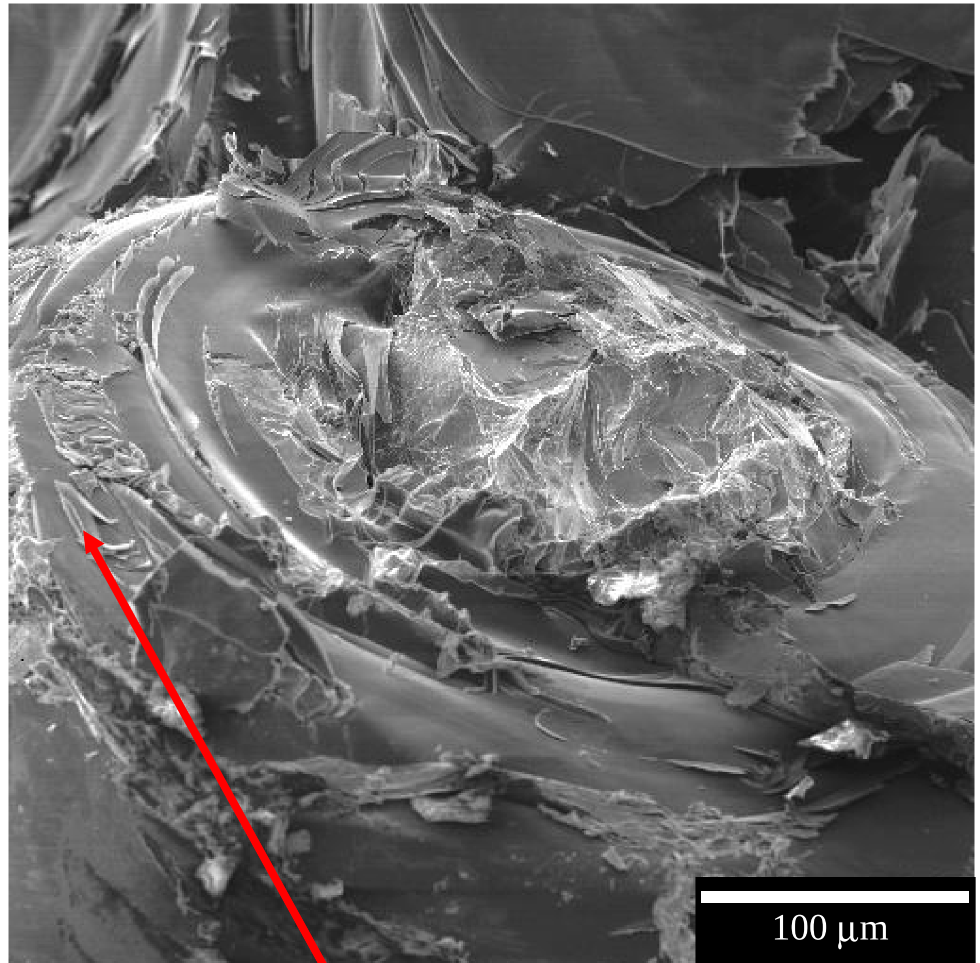
Matrix	Density [g/cm^3]	% Dense	Thermal Conductivity W/m·K z-direction	x-y direction
Raw Graphitized Foam	0.54		150	80
Polycyanate	1.37	88%	129	76
Epoxy	1.31	84%	42	36
Polyester	1.33	85%	40	34
Phenolic	1.00	64%		
Aluminum	2.34	89%	189	130
SMJ Carbon (1000°C)	1.34	63%	112	52
SMJ Carbon (2800°C)	1.29	58%	389	

Thermal Conductivity



Tensile Fracture Surface – Al/Foam





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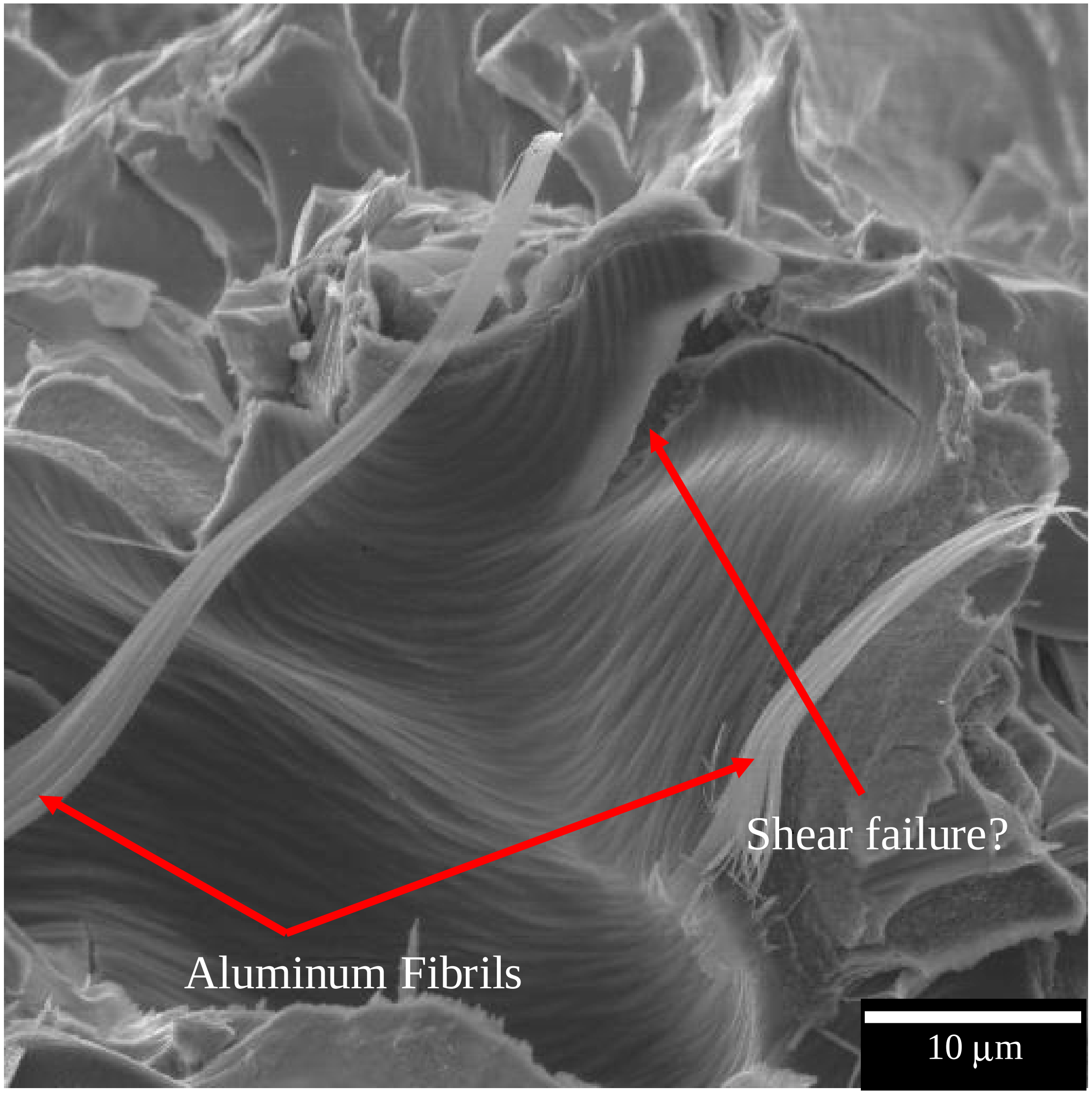

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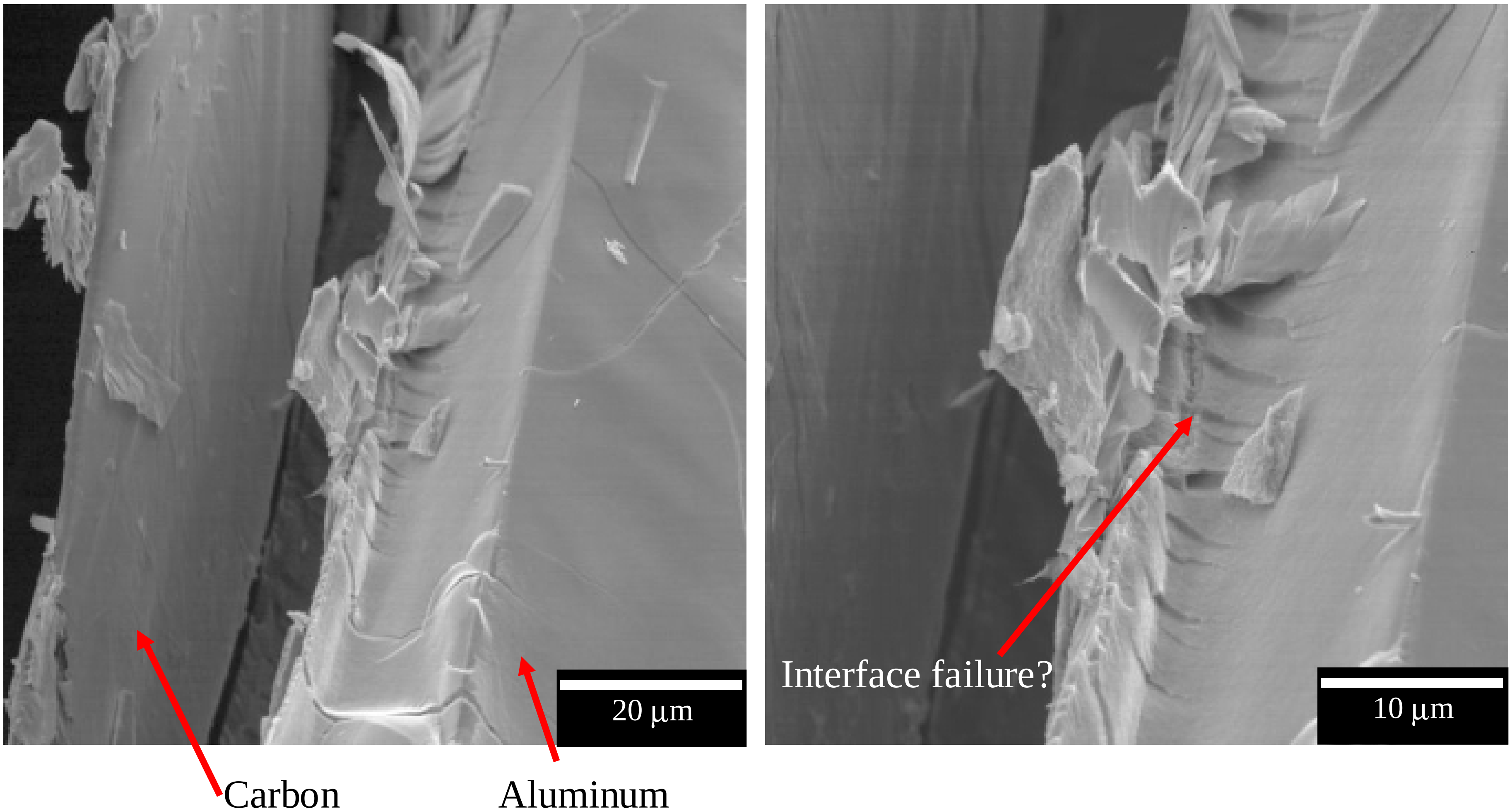
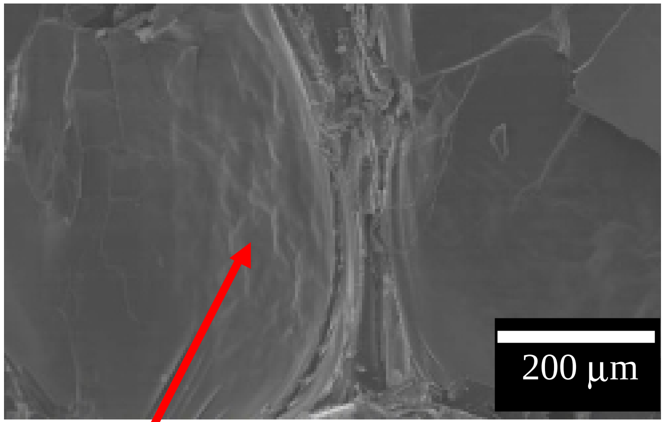
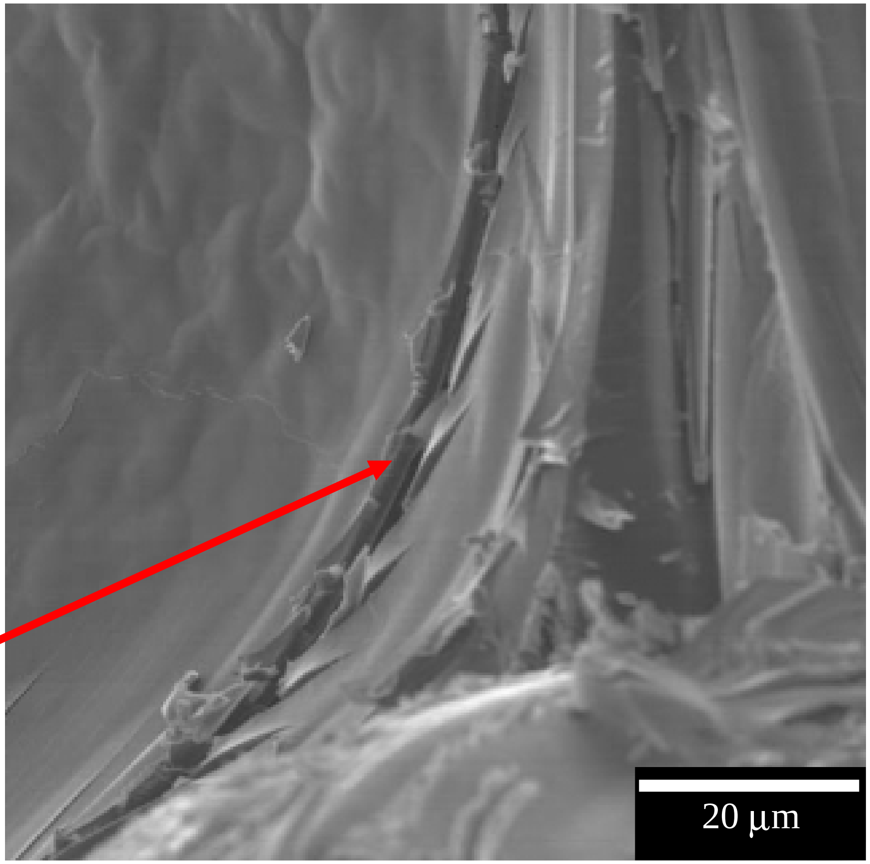


Tensile Fracture Surface – Al/Foam

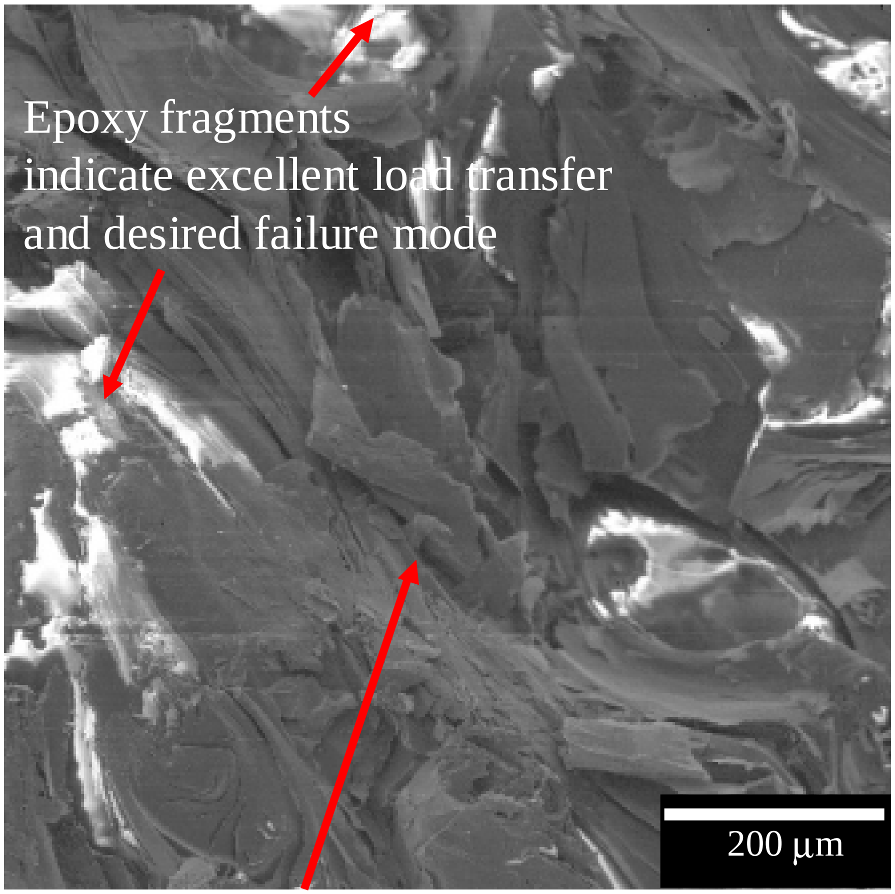


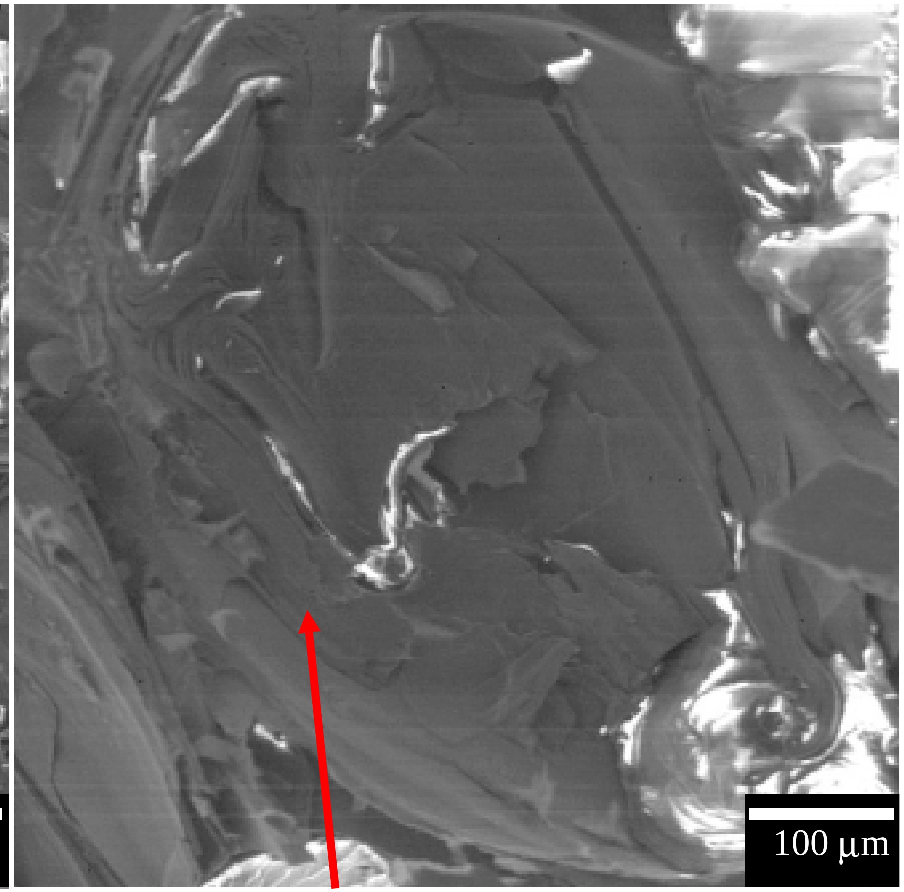
Deformation of cell wall indicates aluminum-carbide formation or good interface



Shear failure of cell wall indicates good load transfer

Tensile Fracture Surface – Epoxy/Foam



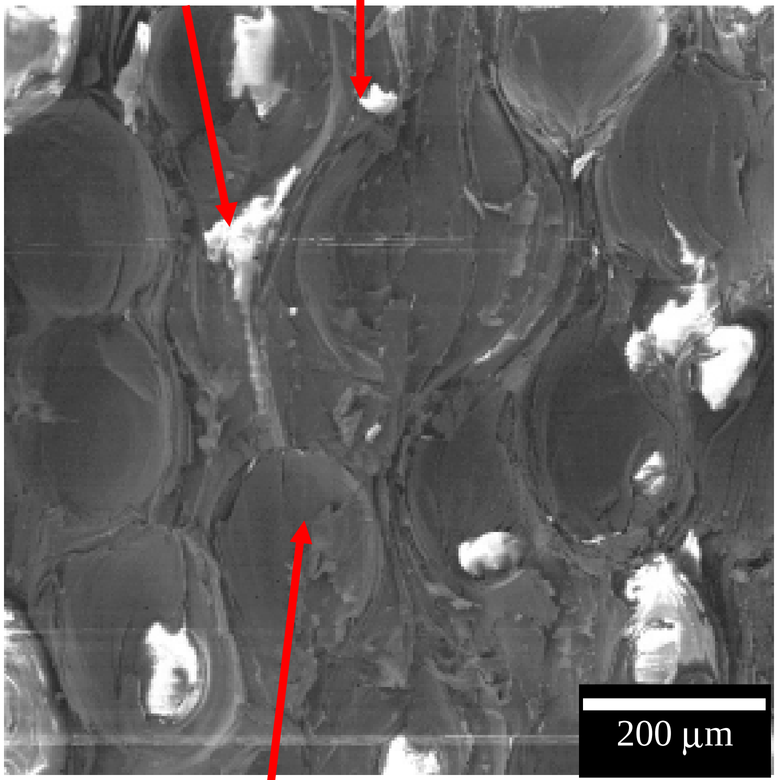


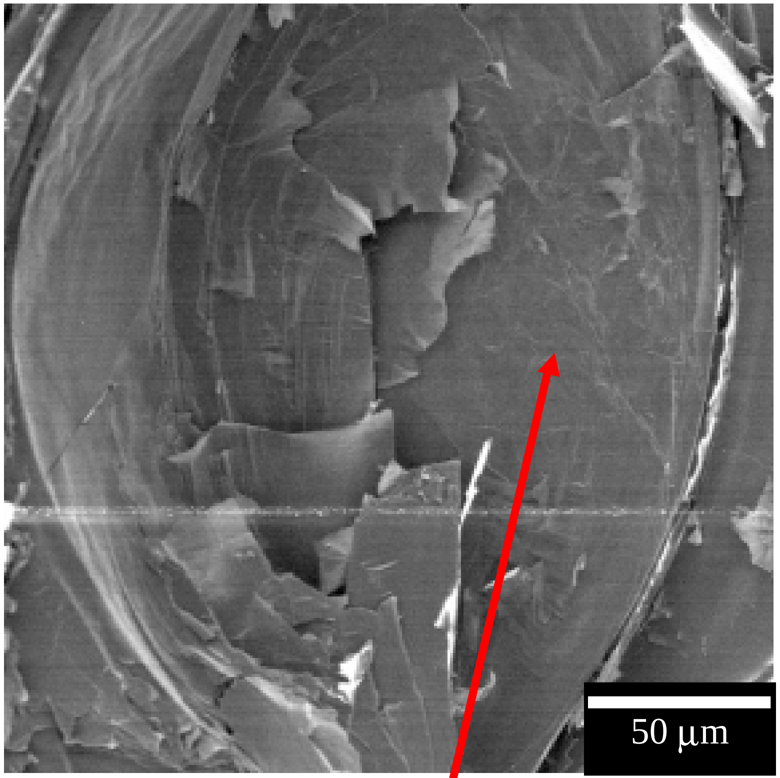
Fracture of cell wall
indicates excellent interface

Fracture of cell wall
indicates excellent load transfer

Tensile Fracture Surface – Polyester/Foam

Polyester fragments indicate excellent load transfer

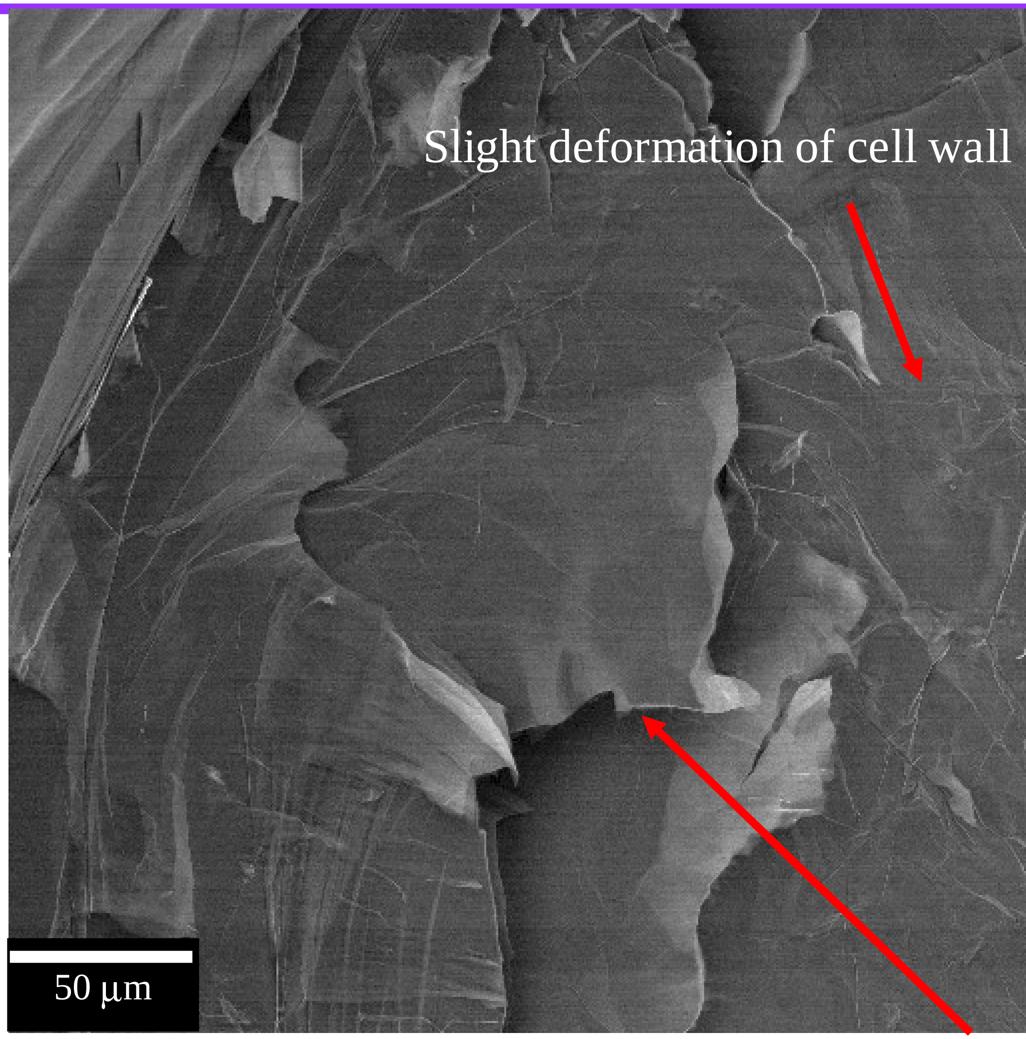




Slight deformation of cell wall indicates excellent interface

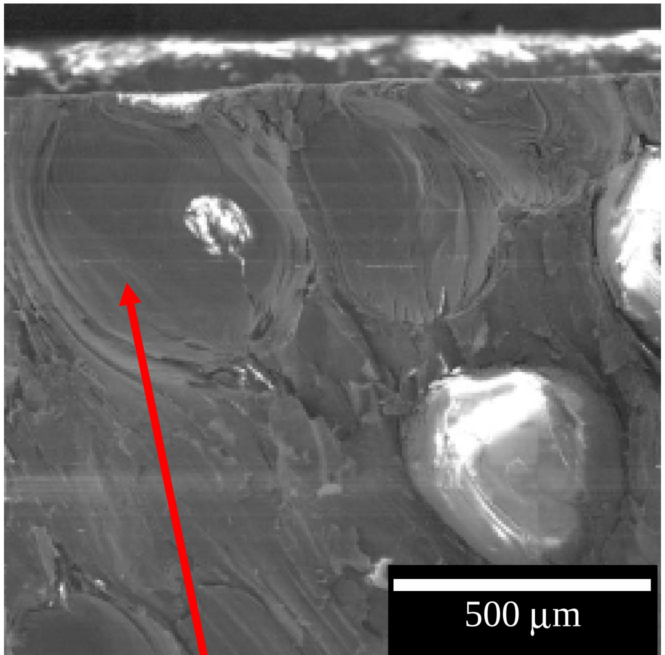
Slight fracture of cell wall indicates good load transfer

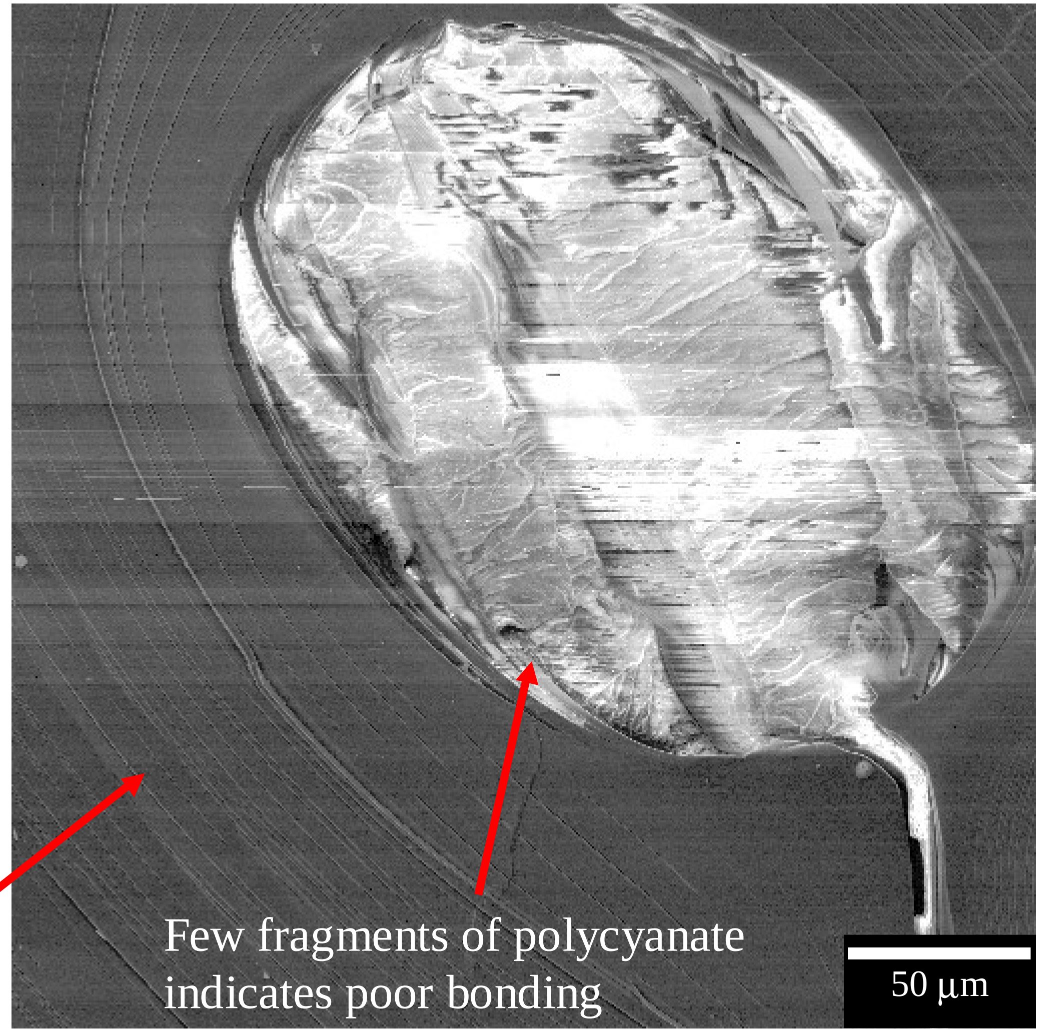
Tensile Fracture Surface – Polyester/Foam



Shear failure of cell wall
indicates excellent load transfer

Tensile Fracture Surface – Polycyanate/Foam



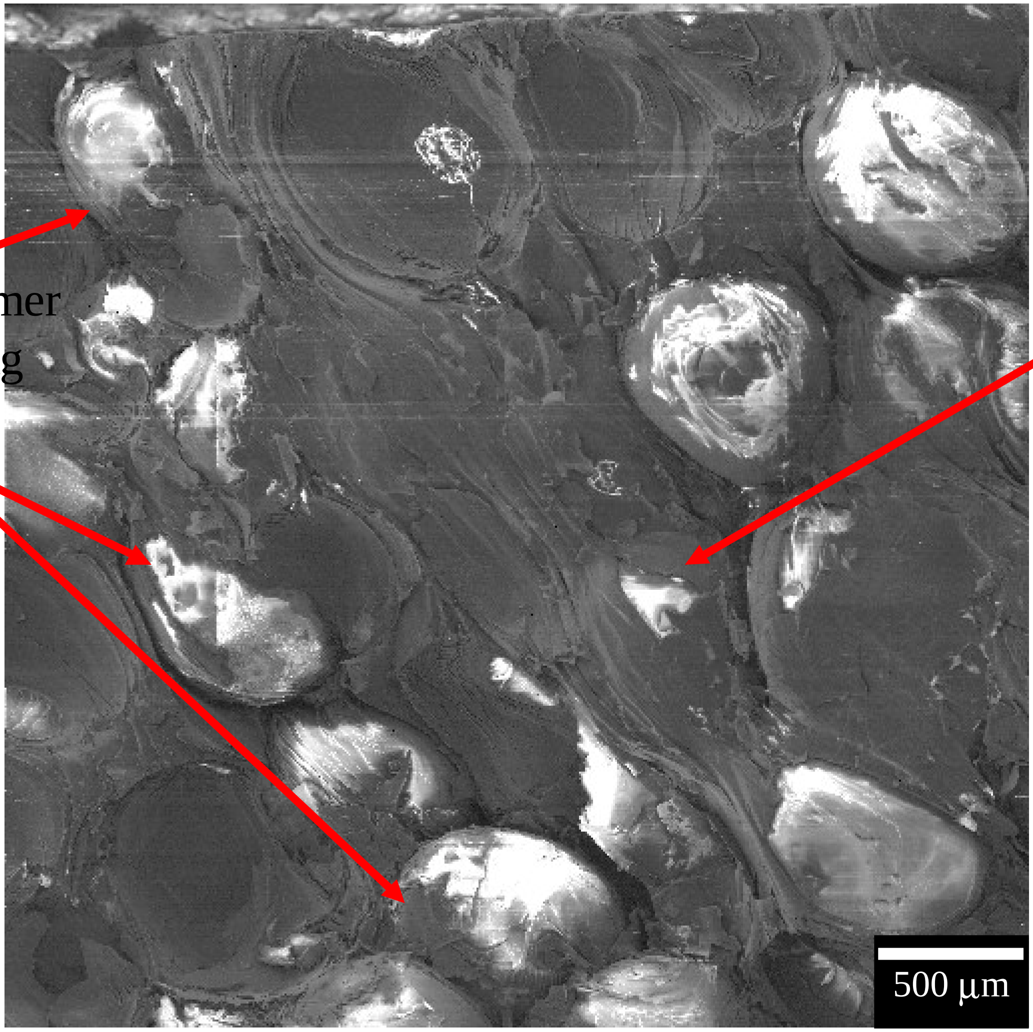


Smooth wall indicates poor interfacial bonding

Few fragments of polycyanate indicates poor bonding

Tensile Fracture Surface – Polycyanate/Foam

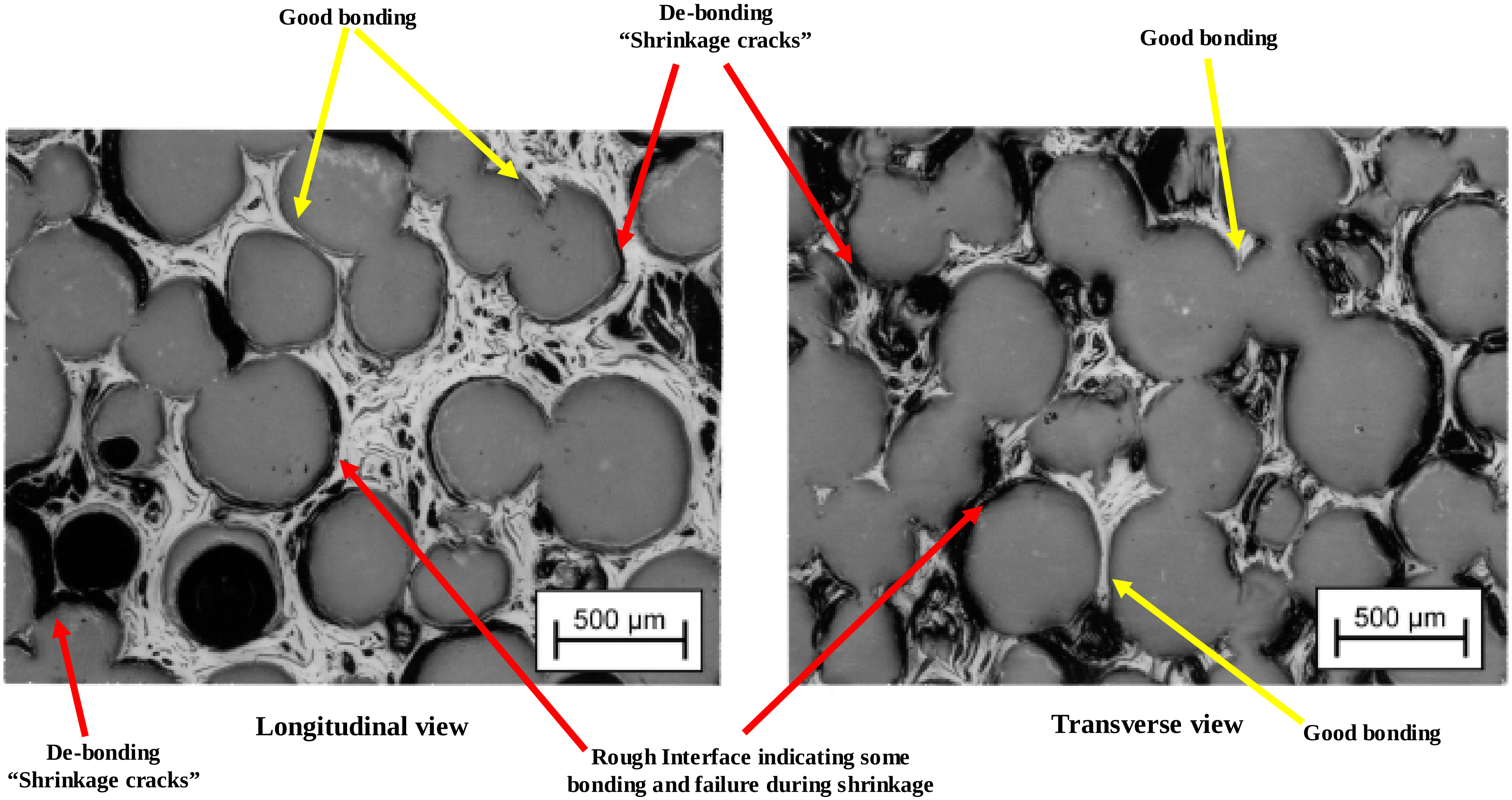
Bubbles of polymer are not deforming - poor interface



Broken cell wall shows polymer in next cell

Optical Analysis – Epoxy/Foam

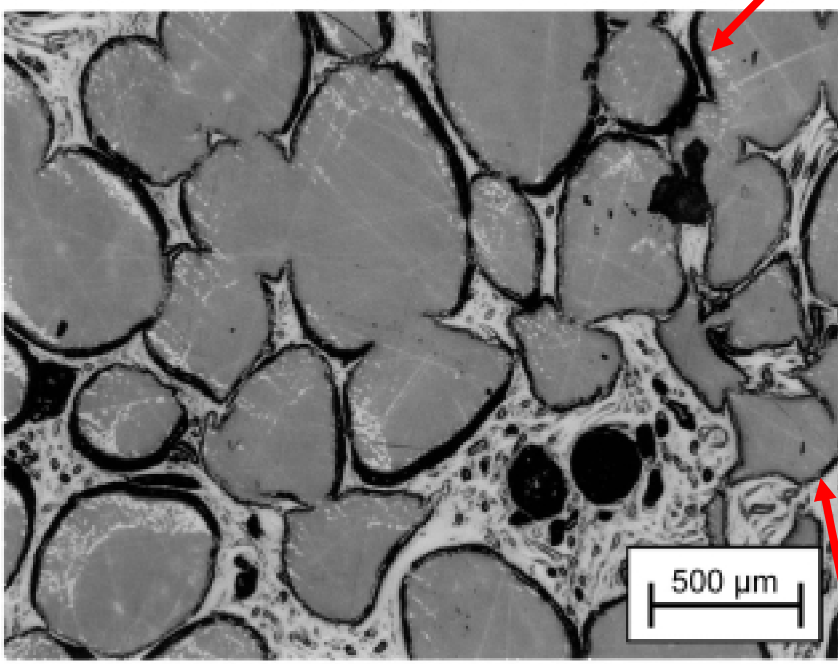
- Mostly good bonding with some de-bonding present



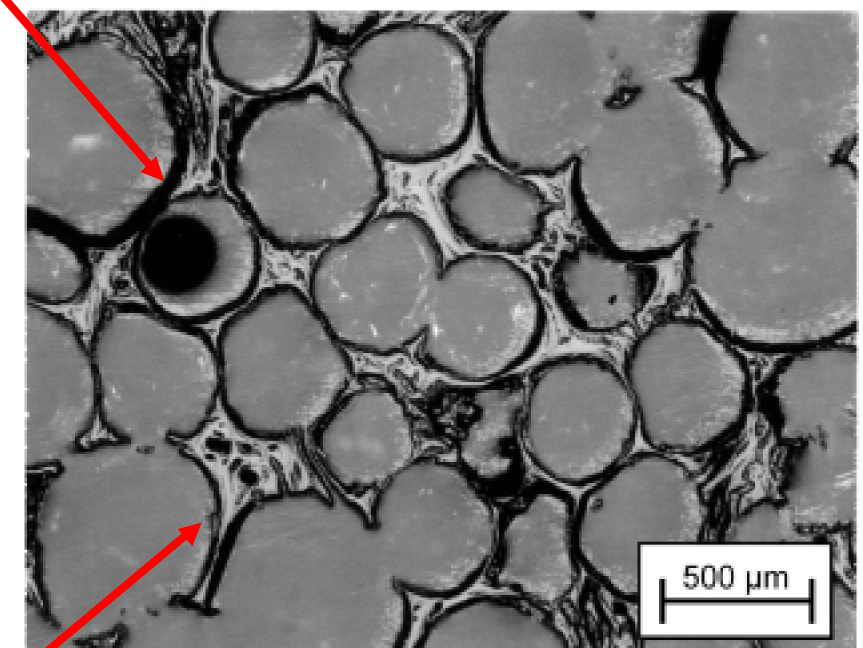
Optical Analysis – Polyester/Foam

- Mostly poor bonding with very little adhesion to foam

De-bonding
“Shrinkage cracks”



Longitudinal view



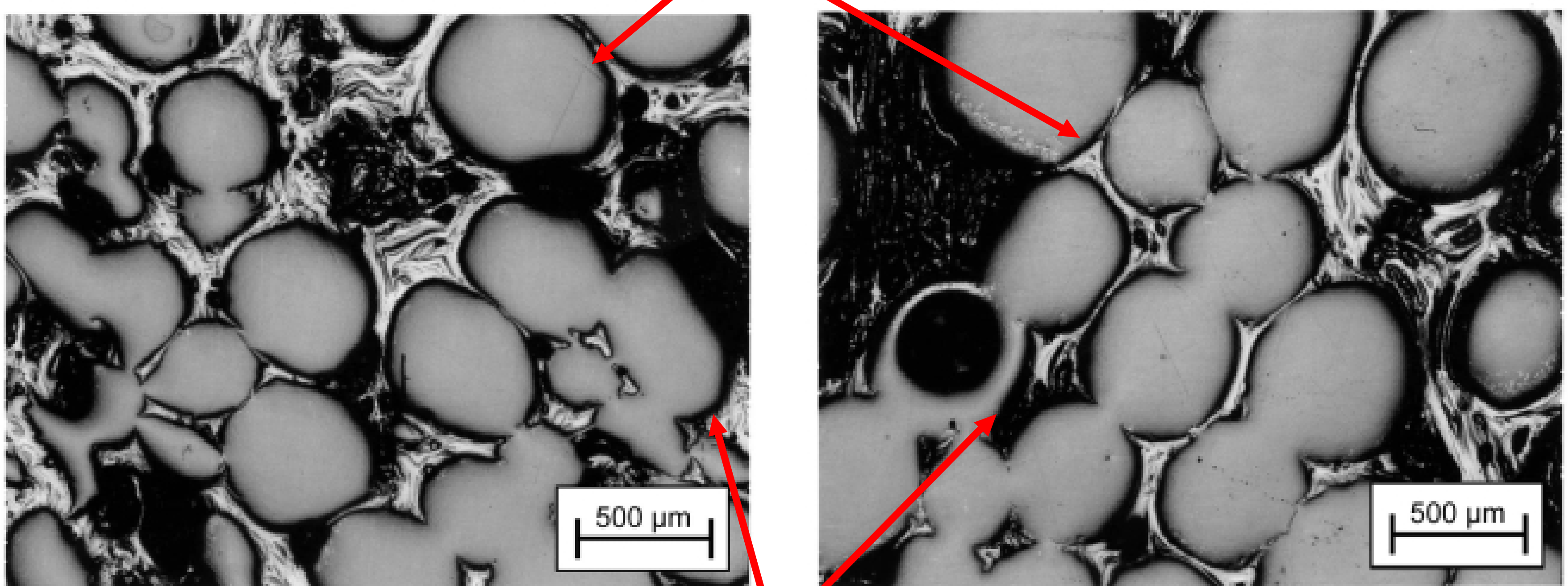
Transverse view

Rough Interface indicating some bonding and failure during shrinkage

Optical Analysis – Polycyanate/Foam

- Mostly poor bonding with very little adhesion to foam

De-bonding
“Shrinkage cracks”

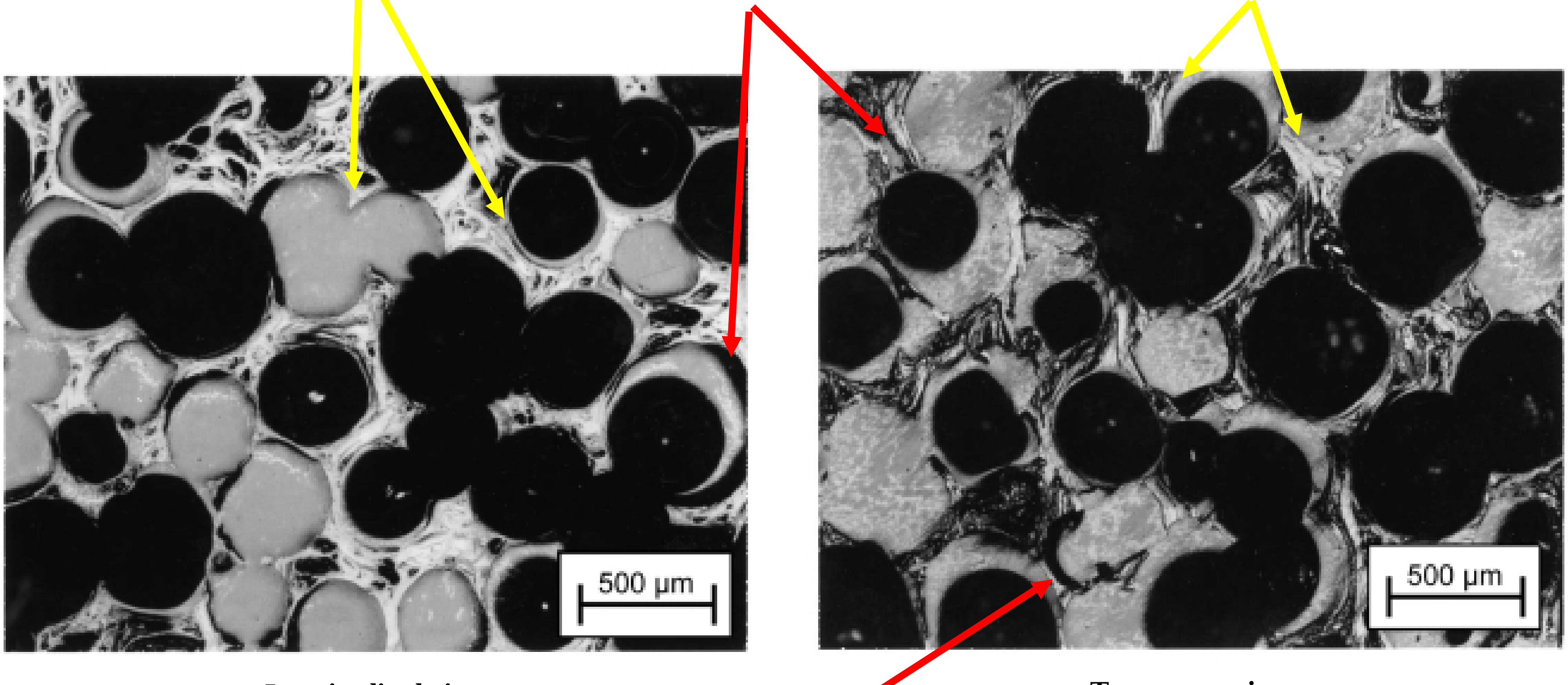


Longitudinal view **Transverse view**

Clean Interface indicating little bonding
and now failure during shrinkage

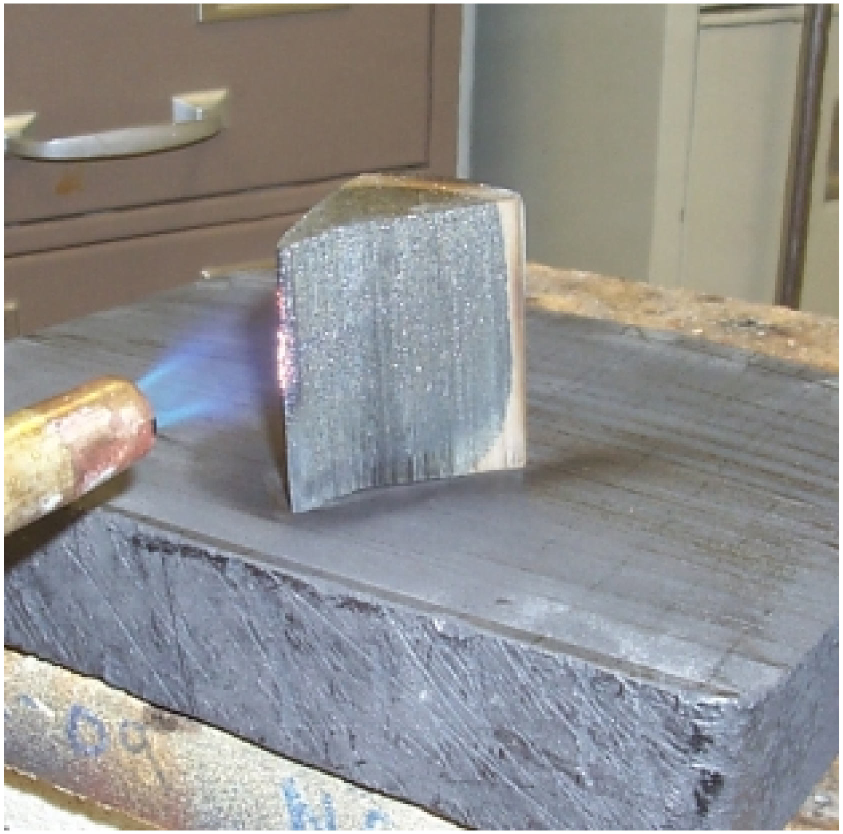
Optical Analysis – Phenolic/Foam

- Mostly good bonding with some de-bonding/shrinkage cracks.



Longitudinal view **Transverse view**

Thermal Stability – Polycyanate/Foam



Foam/Polycyanate
after 50 sec

Conclusions - Mechanical

- Wetting and adhesion is a key factor!
- Epoxy and phenolic resins seem to exhibit best interfacial bond while polycyanate and polyester exhibit a weak interface.
  - Epoxies typically bond better to carbons
  - Used as a sizing agent with carbon fibers
- Shrinkage during processing (cure or cooling) is causing samples with weak interface to pull away from foam leaving two non-connected continuous phases.
- Unique co-continuous structure may be leading to very dramatic differences in flexural/tensile strengths and compressive strengths.

Conclusions - Thermal

- A lower thermal conductivity in some samples may be due to the damage of cell structure due to the shrinkage of the matrix with good bonding present, thereby damaging structure.
- It is unsure if the interface is affecting thermal conductivity directly through heat transfer or indirectly through failure mechanisms.

- Obviously, there are more questions than answers.

Conclusions

- It was noticed that the samples which were densified in a series of cycles (phenolic and SMJ carbon) did not densify as well (64%) as the samples densified in one cycle (polyester, epoxy, polycyanate) (85%).
- Yet they experienced very similar tensile and flexural strengths.
- The process of only laying down a small layer allows the polymer to shrink around the ligaments rather than pull away as the polymer cures and/or cools.
- Building up these layers to a denser composite may result in better reinforcement of the foams than a “one-shot” densification.

Conclusions

- This was tried with a polyimide (LaRC-SI) which is soluble in a solvent by Engineered Ceramics, Inc.
- The polymer is applied, dried, cured with as many as 8 cycles needed to densify the sample.
- After achieving densifications comparable to the polycyanates the flexural strength was reported to be 80 MPa, compared to 10 MPa for the samples densified in one cycle.

- Perhaps, this is the best method to densify carbon foams for structural reinforcement.

Future

- Study interfacial bonding
  - Sizing agents (epoxies and other polymers)
  - Surface treatments (oxidation)

- GOAL
  - Show relationship between enhanced interfacial bond and tensile/flexural/compressive properties.
  - Determine if interfacial bond will affect thermal conductivity directly.
  - Develop fundamental understanding of failure mechanisms of this unique co-continuous two-phase system.

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