Chemical, Physical and Mechanical Methods of Fiber-Matrix Adhesion and Interphase Characterization in Composites

Lawrence T. Drzal

Departments of Chemical Engineering

and Materials Science and Mechanics

Composite Materials and Structures Center

Michigan State University

East Lansing, MI 48824-1226

Tel. 517-353-5466 FAX 517-432-1634

drzal@egr.msu.edu

http://cmscsun.egr.msu.edu/cmsc/profiles/person.info/drzal.html

Electron Beam Curing Workshop at Oak Ridge National Laboratory

Outline...

- Introduction - Relation of Fiber-Matrix Interphase to Composite Properties
  - Examples of Fiber-Matrix Adhesion relationship to Composite Properties
  - Fiber-Matrix Adhesion is Related to the Interphase
- Adhesion Measurement Methods
  - Single fiber fragmentation test, Microdroplet Pull-off, Microindentation
- Adhesion and the Fiber-Matrix Interface/Interphase
  - Interface/Interphase Concept
- Interphase Characterization
  - Surface Energetics
  - Surface Chemistry
  - Reactivity with Polymeric Matrix
  - Surface Topography
  - Interphase Properties
  - Interphase Formation During Processing
- Design of an Optimum Interphase for Adhesion and Processability
  - Thermodynamics
  - Surface treatment, sizing or finish
  - Processability

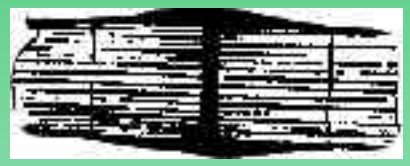
Why is Adhesion Important in Fiber Reinforced Composite Materials?

Properties of the Fibers and Matrix, Interfacial Shear Strengths and Failure Modes

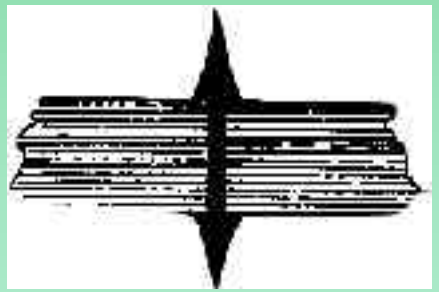
Material	Tensile Modulus (GPa)	Tensile Strength (GPa)	Intf. Shear Strength (Mpa)	Interfacial Failure Mechanisim
AU4	234.4	3.58	37.2	Poor Interfacial
AS4	234.4	3.58	68.3	Interfacial
AS4C	234.4	3.58	81.4	Strong Matrix
EPOXY	3.6	0.09	---	---

FAILURE MODES RESULTING FROM DIFFERENT ADHESION LEVELS

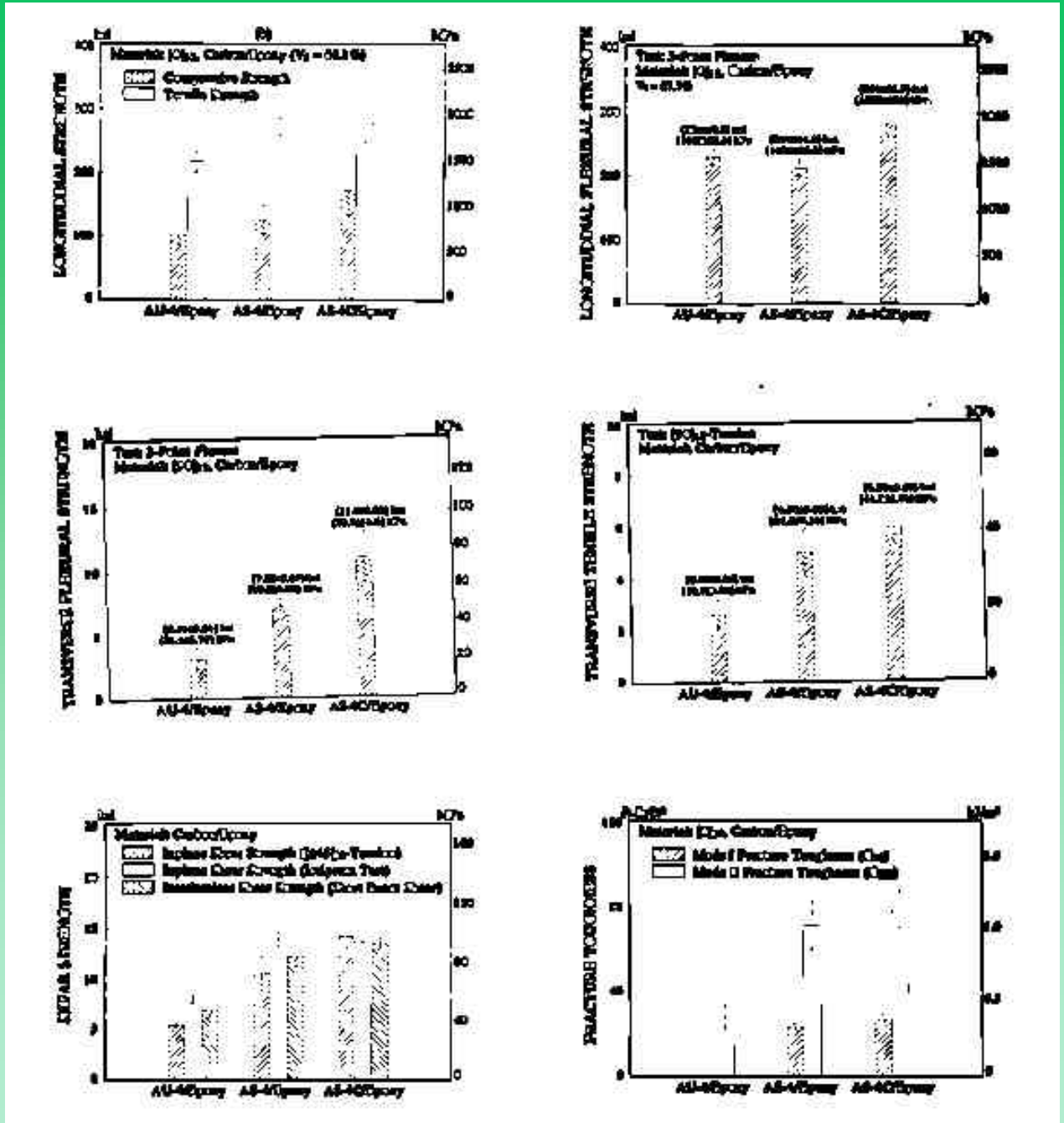
Frictional Debonding - Low Adhesion



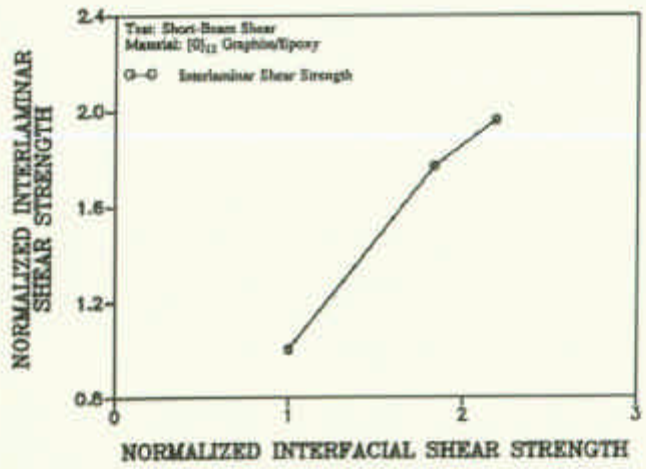
Interfacial Crack Growth - Intermediate Adhesion

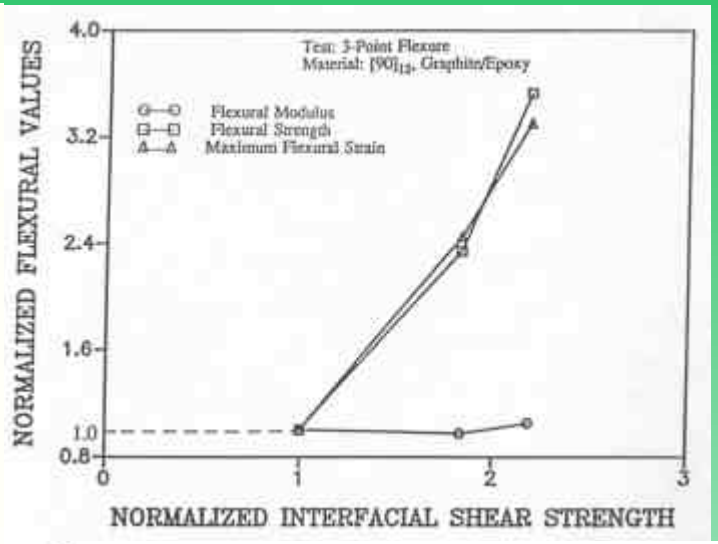


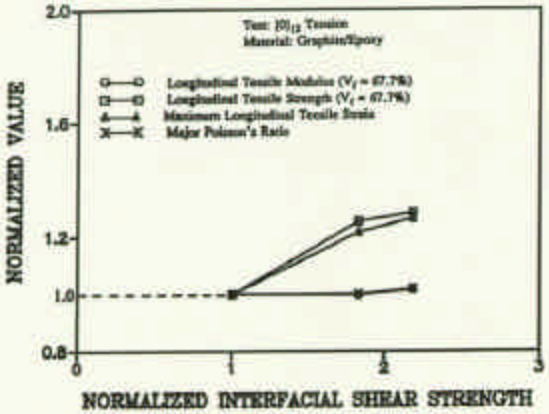
Matrix Crack Growth - Highest Adhesion

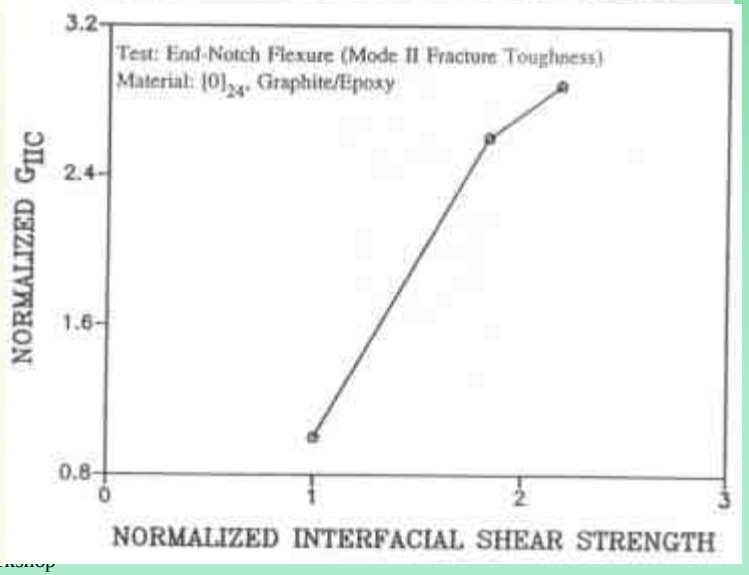


Fiber-Matrix Adhesion Effect on Composite Mechanical Properties









How is Adhesion Measured in Fiber Reinforced Composite Materials?

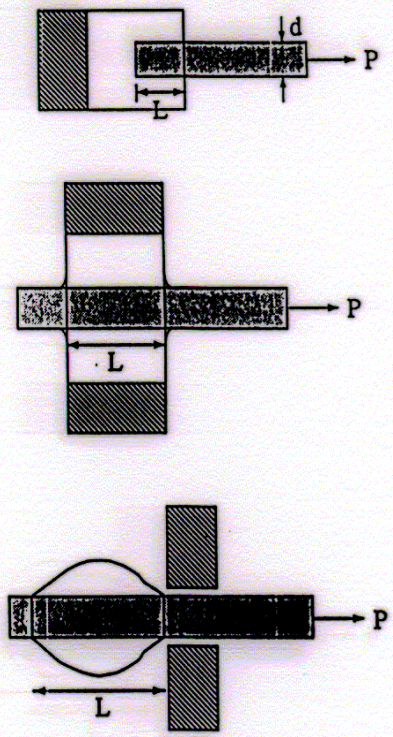
How are fiber-polymer adhesion and interface properties measured ?

- Composite Lamina Tests
  - Constituent geometry dependent *(e.g. V_f)*
  - Measure of static/dynamic strength, stiffness and/or toughness
  - Interface is subject to 'normal' processing
  - Lamina contains 'normal' defects
    - e.g. voids, inadequate tow or bundle wetout , poor fiber distribution
- Micro (Single Fiber) Tests
  - Isolate interface from lamina
  - Measure fiber-polymer adhesion
  - Observe interfacial failure mode
  - Use small amounts of material

Micro Tests

- Direct Micro Tests
  - single fiber pullout
  - single fiber fragmentation
  - single fiber indentation
  - single fiber compression
- Indirect Micro Tests
  - slice compression
  - ball compression
  - variable curvature
  - dynamic thermal methods
  - fiber bundle pullout

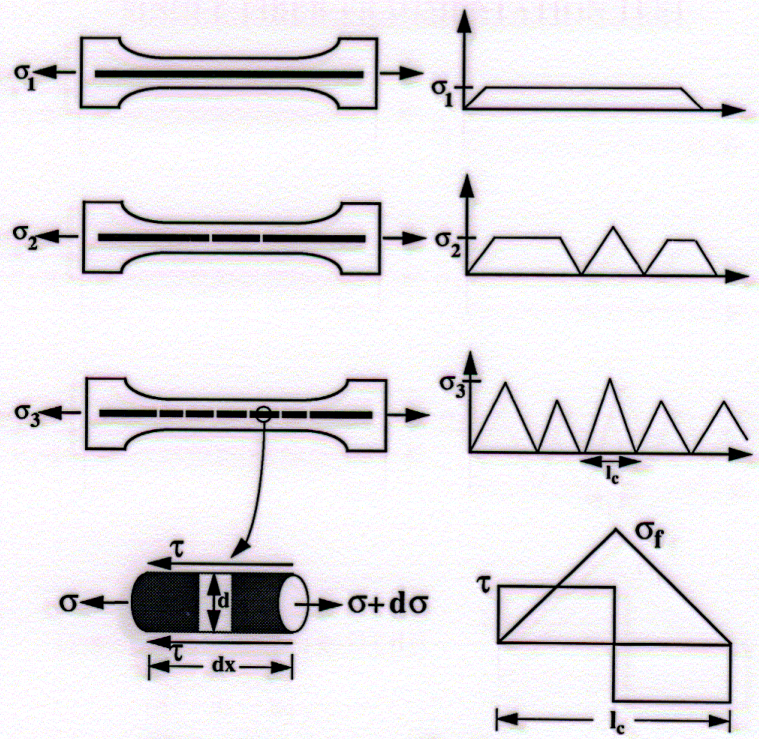
single fiber pullout



- advantages
  - any fiber/matrix combination
  - direct measurement of load at debonding and friction
- disadvantages
  - stress state different than composite
  - sample fixturing important
  - lacks failure mode info
  - 1 data point per specimen

single fiber is pulled-out of a block, disc or bead of polymer and the failure and frictional force are measured

SINGLE-FIBER-FRAGMENTATION TEST

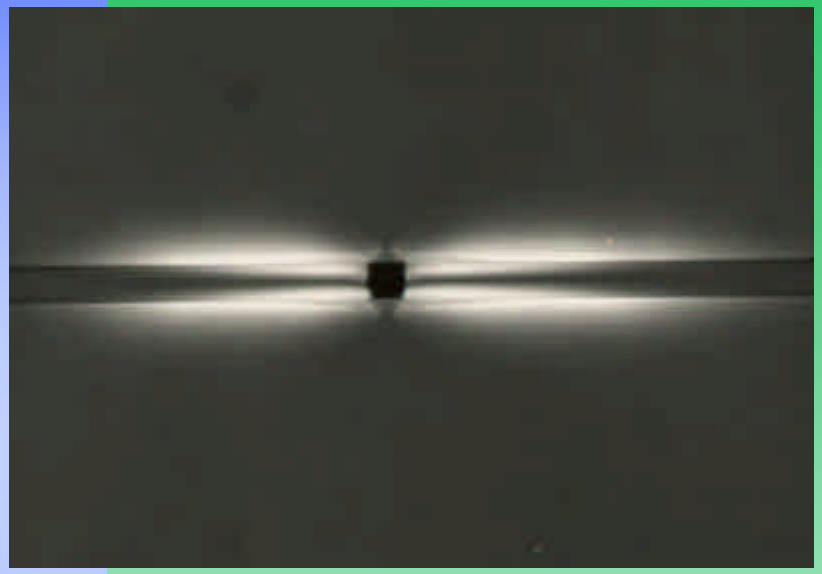


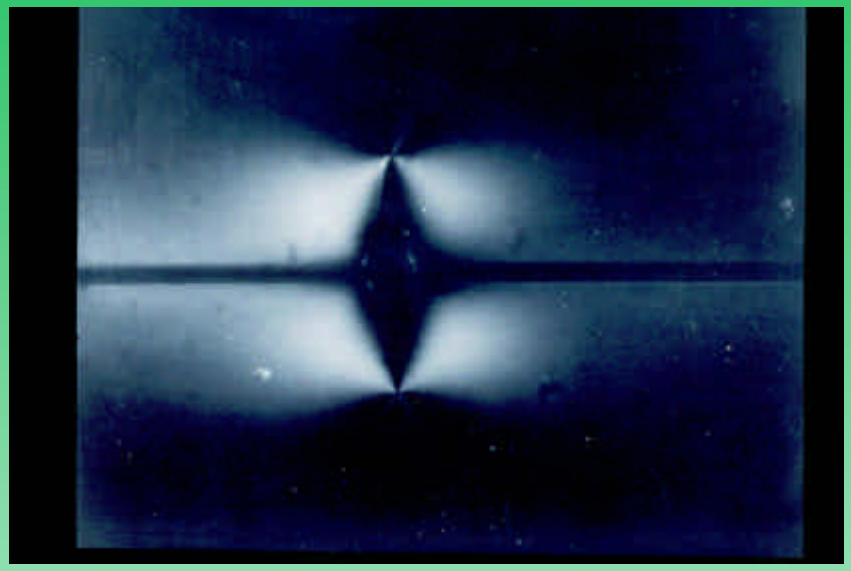
$$\frac{d\sigma}{dx} = \frac{4\tau}{d} \longrightarrow \tau = \frac{\sigma_f}{2}\left(\frac{d}{l_c}\right)$$

$\frac{l_c}{2} < l < l_c$ **Distribution in Critical Length**

$$\tau = \frac{\sigma_f}{2\beta}\Gamma\left(1 - \frac{1}{\alpha}\right)$$ **Weibull Distribution**

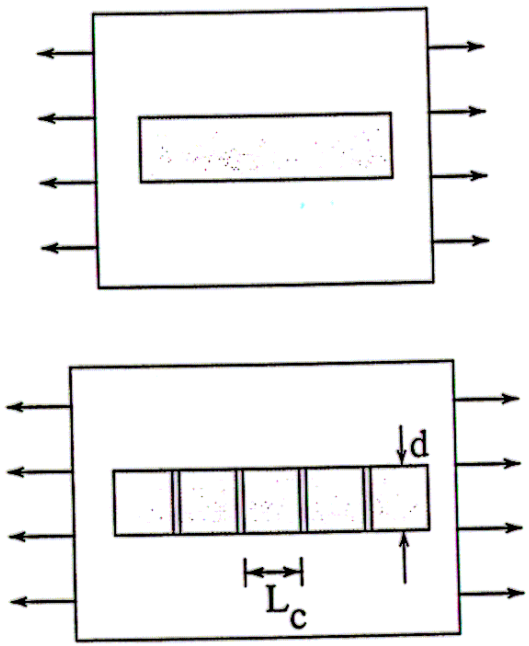
τ = Interfacial Shear Strength
d = Fiber Diameter
l_c = Fiber Critical Length
σ_f = Fiber Strength at l_c





Polarized Transmitted Light Micrographs at 70X of an E-Glass Fiber Break for a Water-Sized fiber (left) and Epoxy-Sized fiber (right) in a DER 383/DACH Epoxy Matrix

embedded fiber fragmentation



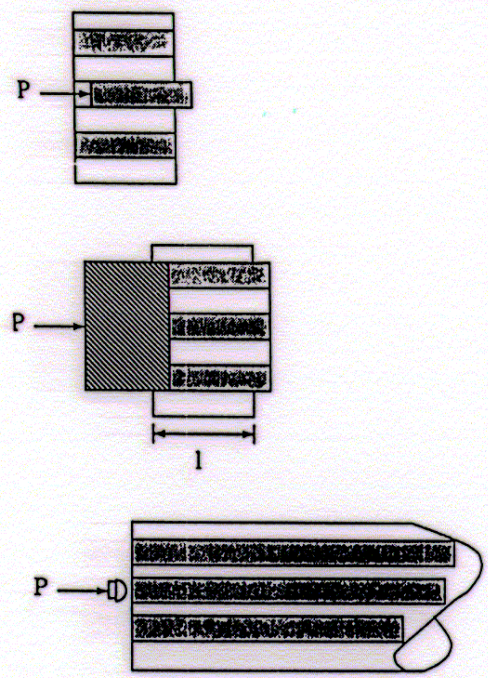
- advantages
  - stress similar to composite
  - direct obeservation of failure
  - many data points/specimen
  - sensitive to interphase
- disadvantges
  - isolated fiber
  - samples difficult to prepare
  - shear lag assumption
  - matrix strain >3X fiber strain
  - fiber strength/length data

coupon containing a single fiber encapsulated in the polymer matrix is loaded in tension and the fiber fractures into fragments of 'critical length' under shear loading

single fiber indentation

$\tau = f(P_{debonding})$

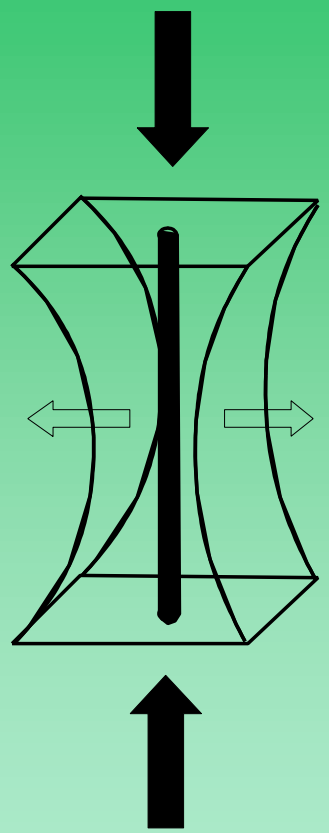
$$\tau = \frac{\sigma}{2}\left(\frac{G_m}{E_f}\right)^{1/2}\left(\frac{d}{T_m}\right)^{1/2}$$



- advantages
  - measurement on composite
  - force-displacement data
  - many data points/specimen
  - fast and automatable
- disadvantages
  - sample preparation artifacts
  - lacks failure information
  - requires material property assumptions

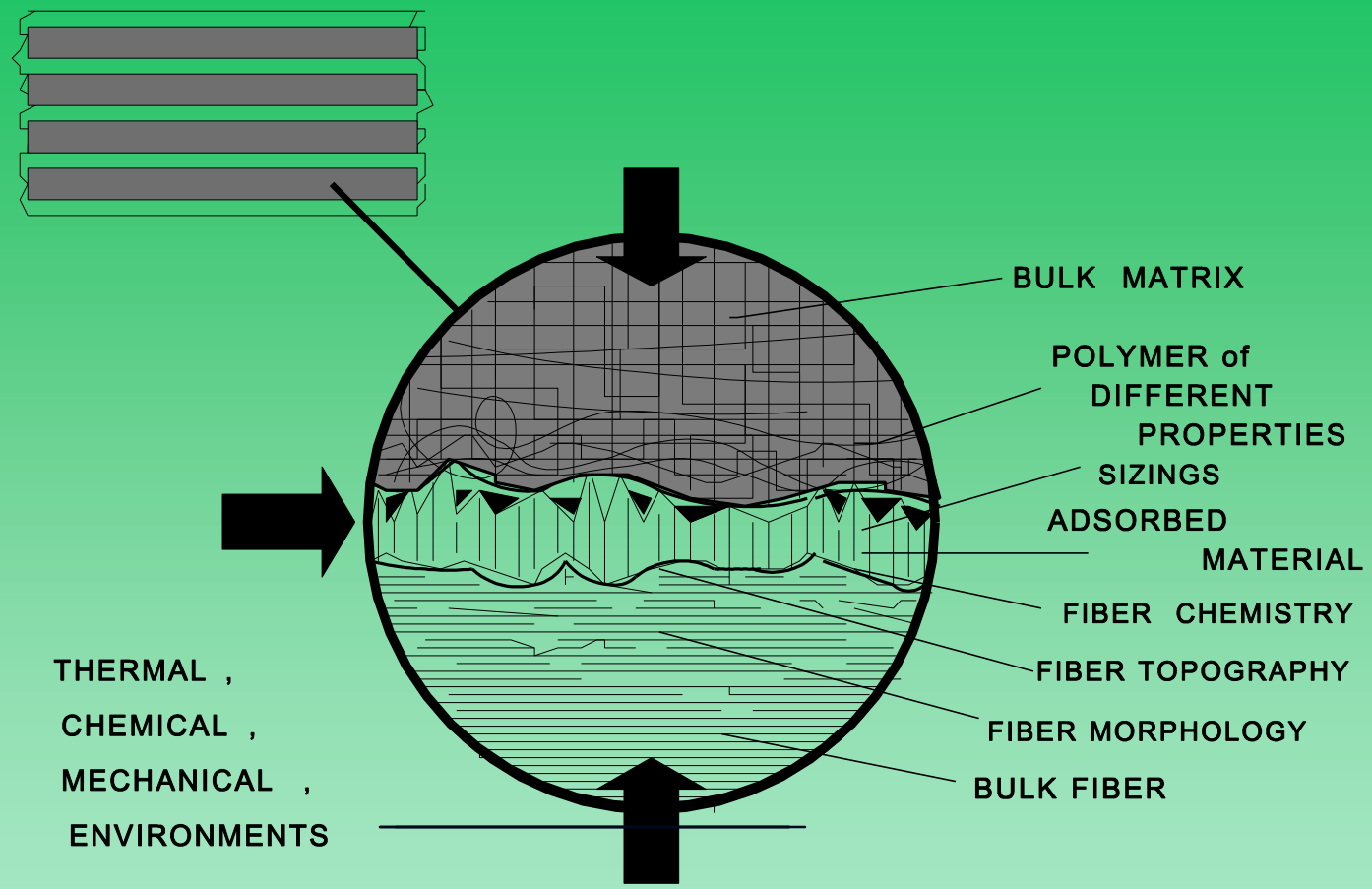
single fiber selected from a composite specimen is end loaded with an indentor and the force is applied to cause fiber-matrix interfacial failure is measured

Single Fiber Compression Test



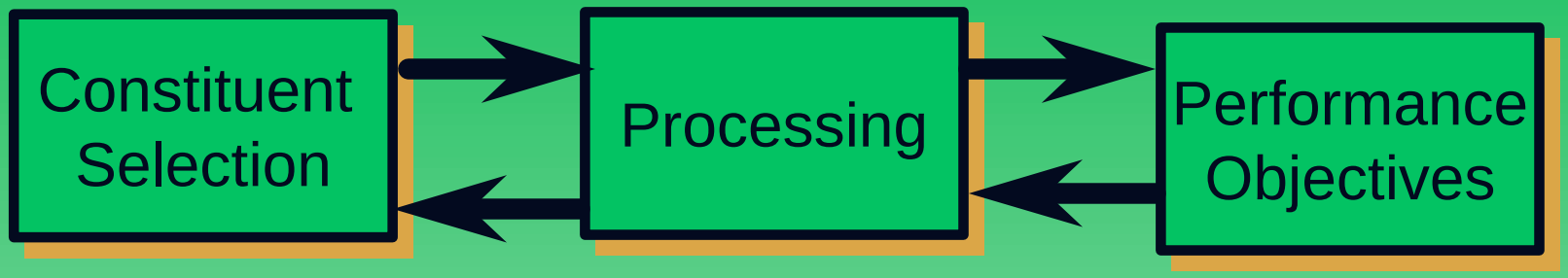
$$s_t = \frac{s_m(?_m - ?_f)E_f}{(1 - ?_m)E_f + (1 - ?_f - ?_f^2)E_m}$$

What is an INTERPHASE and How is it Characterized?



FIBER-MATRIX INTERPHASE

LTD, MSU, 1992



MATRIX
- thermoset
- thermoplastic
  - *amorphous*
  - *semicrystalline*

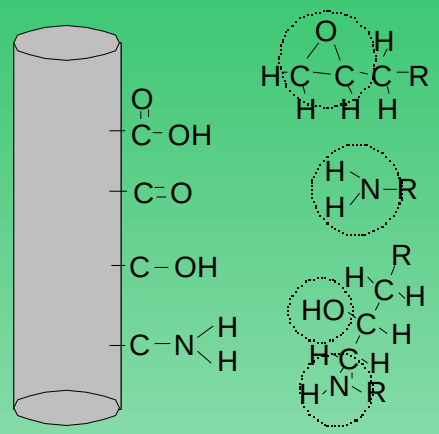
FIBER
- glass
- carbon
- polymeric
  - *aramid*
  - *polyethylene*
  - *liquid crystal polyester*

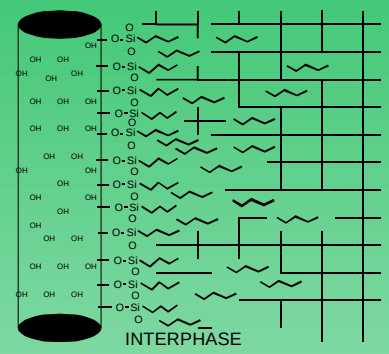
THERMAL
MICROWAVE
LIQUID
  MOLDING
REACTION
  INJECTION
  MOLDING
E-BEAM
UV LIGHT
GAMMA

ADHESION
STIFFNESS
STRENGTH
TOUGHNESS
DURABILITY
- fatigue
- temperature
- moisture
- impact

Reinforcing Fiber Surface Chemistry

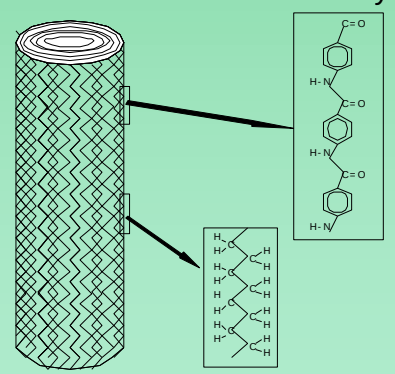
Carbon Fiber Surface Chemistry





Polymeric Reinforcing Fiber

Surface Chemistry

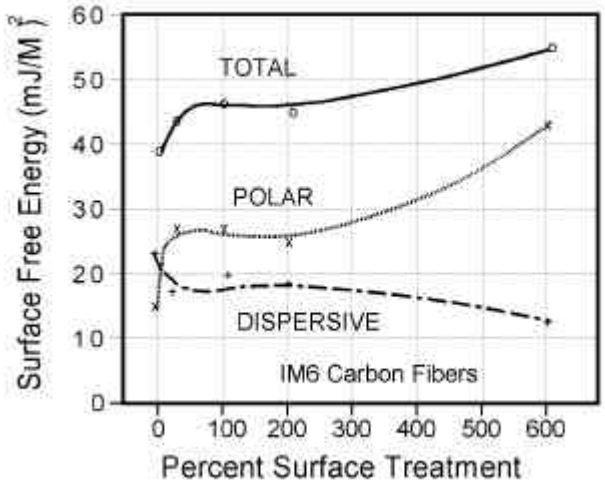


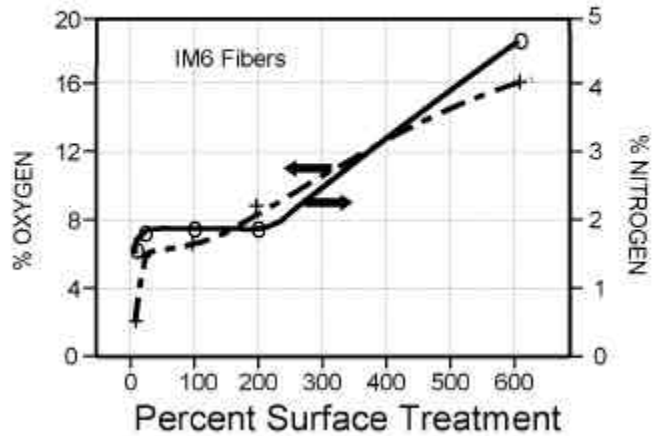
L. T. Drzal, Michigan State University
DOE Ebeam CRADA Workshop
April 20-22, 1999

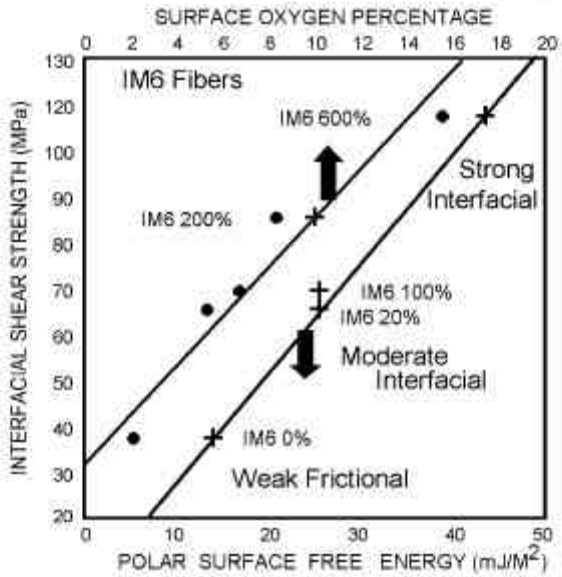
Interphase Characterization Tools

- Surface Energy
  - Contact Angle Inverse Gas Chromatography
- Surface Chemistry
  - Monofunctional Model Probes with Xray Photoelectron Spectroscopy (XPS or ESCA)
- Surface Topography
  - Scanning Probe Microscopy (AFM or STM)
- Interphase Modulus
  - Micro Indentation f(T)
- Interphase Fracture Toughness
  - Dynamic Microindentation, continuous indentation
- Interfacial Fracture Information
  - Fragmentation test, SEM +VCXPS of Composite Fracture Surface

Surface and Interfacial Thermodynamics

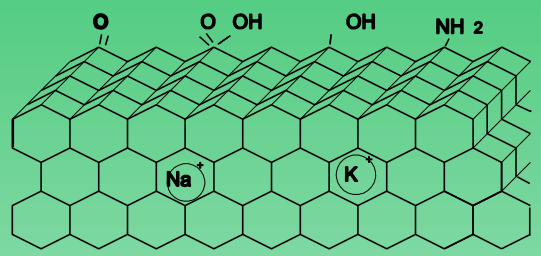




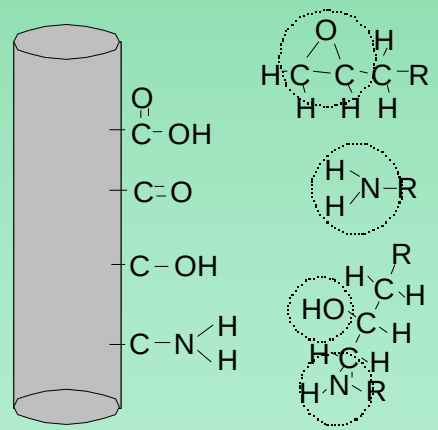


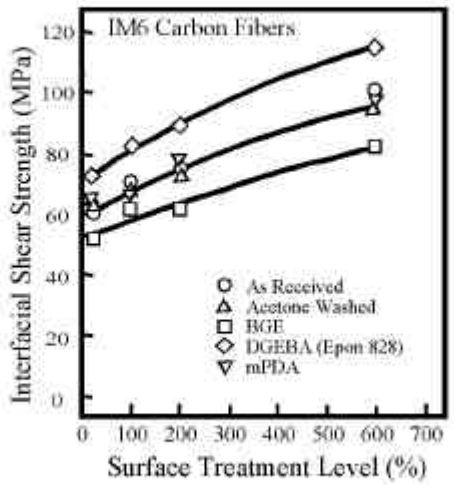
Chemical vs. Physical Bonding...

Surface Chemistry of Carbon Fibers



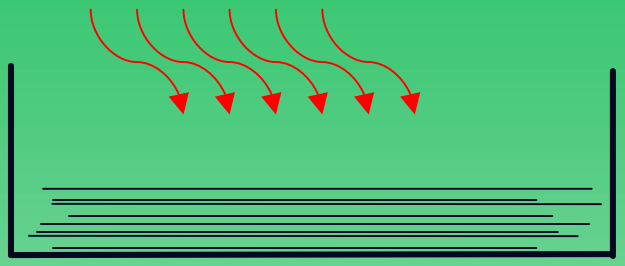
Carbon Fiber Surface Chemistry





Fiber-Matrix Chemical Bonding

Thermal or
E-Beam
10/100kGy

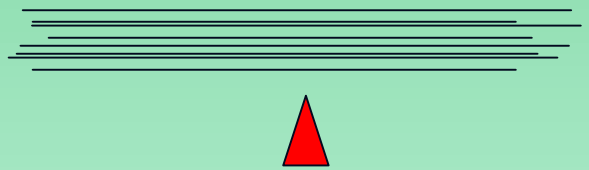


C-Fiber + Taxtix 123 or
OPPI/Acetone

1

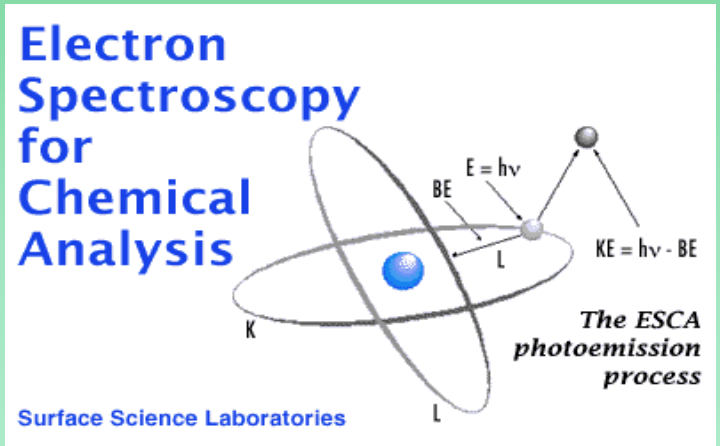
Acetone Reflux Wash 24 hours

2

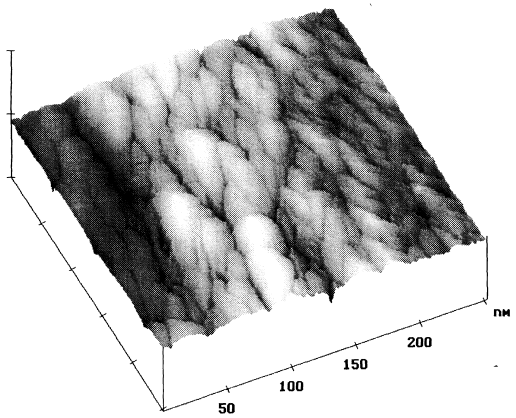


Dried for 3-4 h in air at 120°C

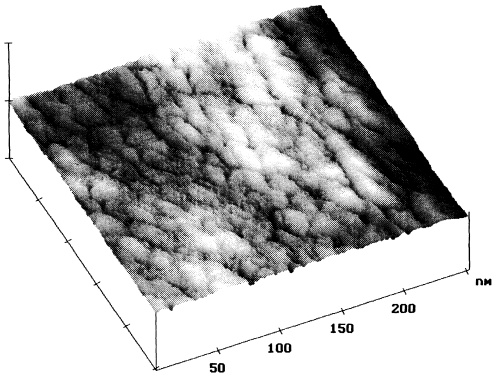
3



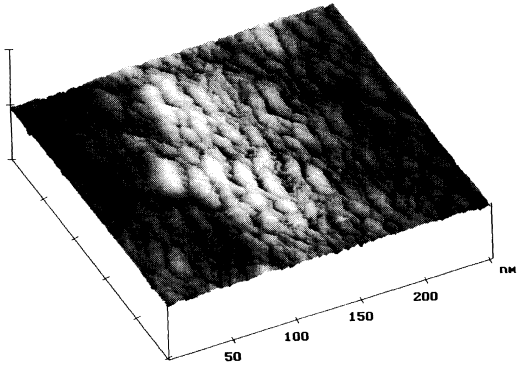
STM Analysis of Carbon Fiber Surface



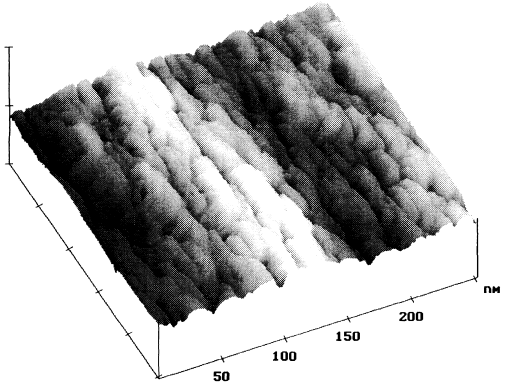
Carbon fiber IM-6 0%ST



Carbon fiber IM-6 20%ST

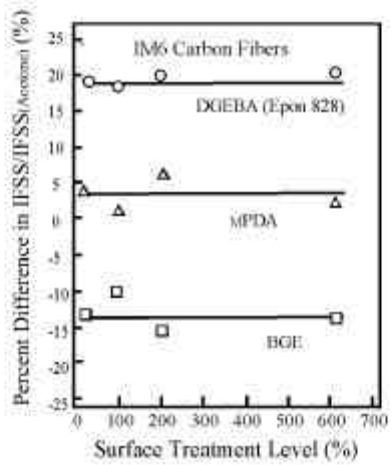


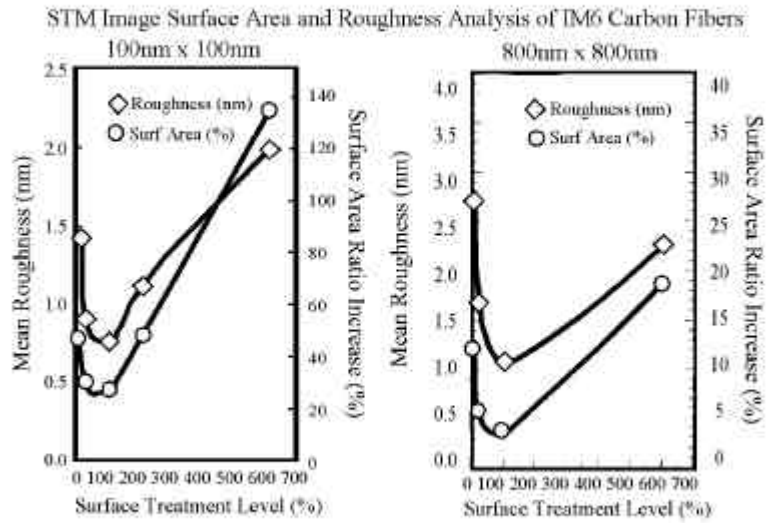
Carbon fiber IM-6 100%ST

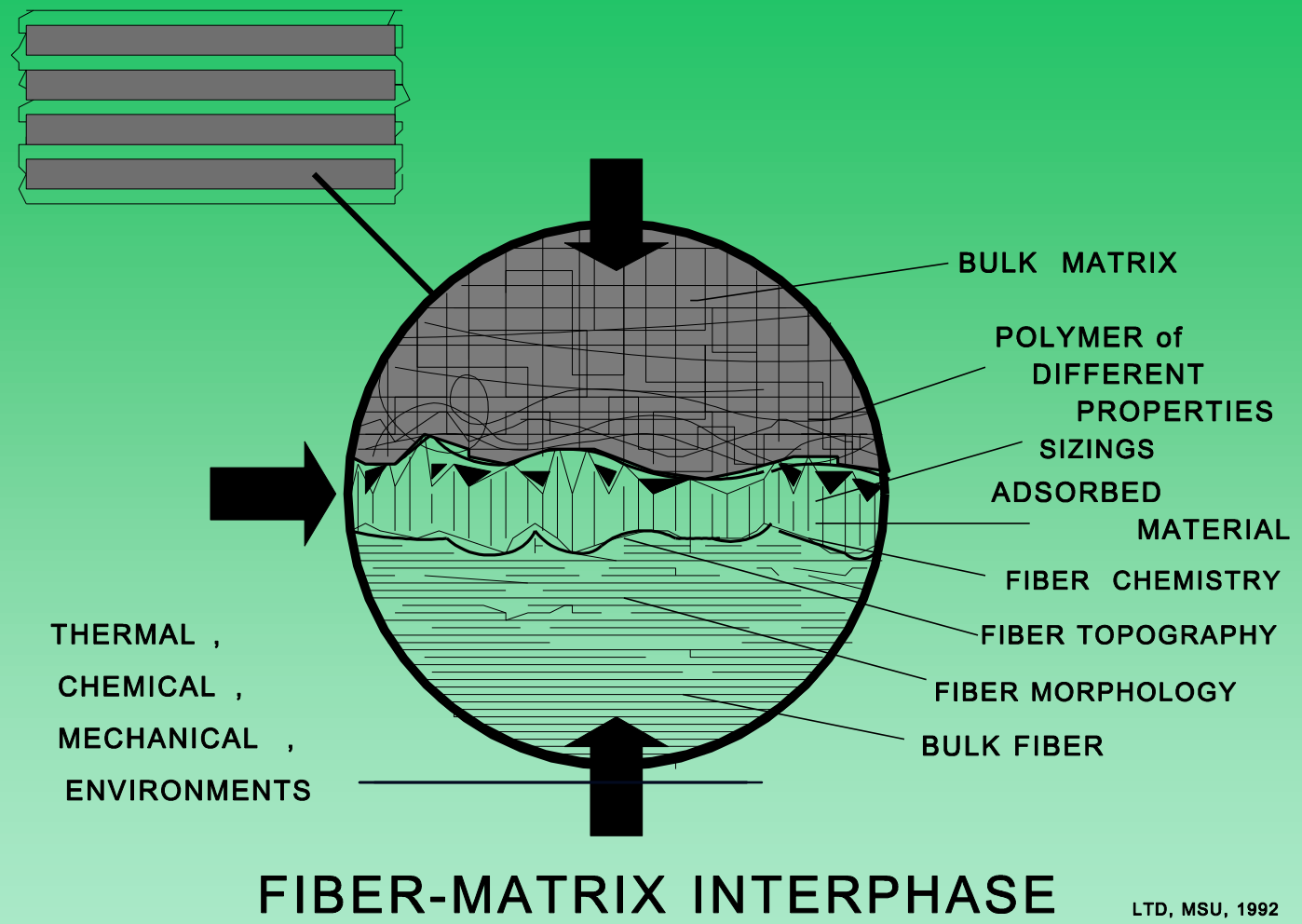


Carbon fiber IM-6 600%ST

Chemical vs. Physical Bonding

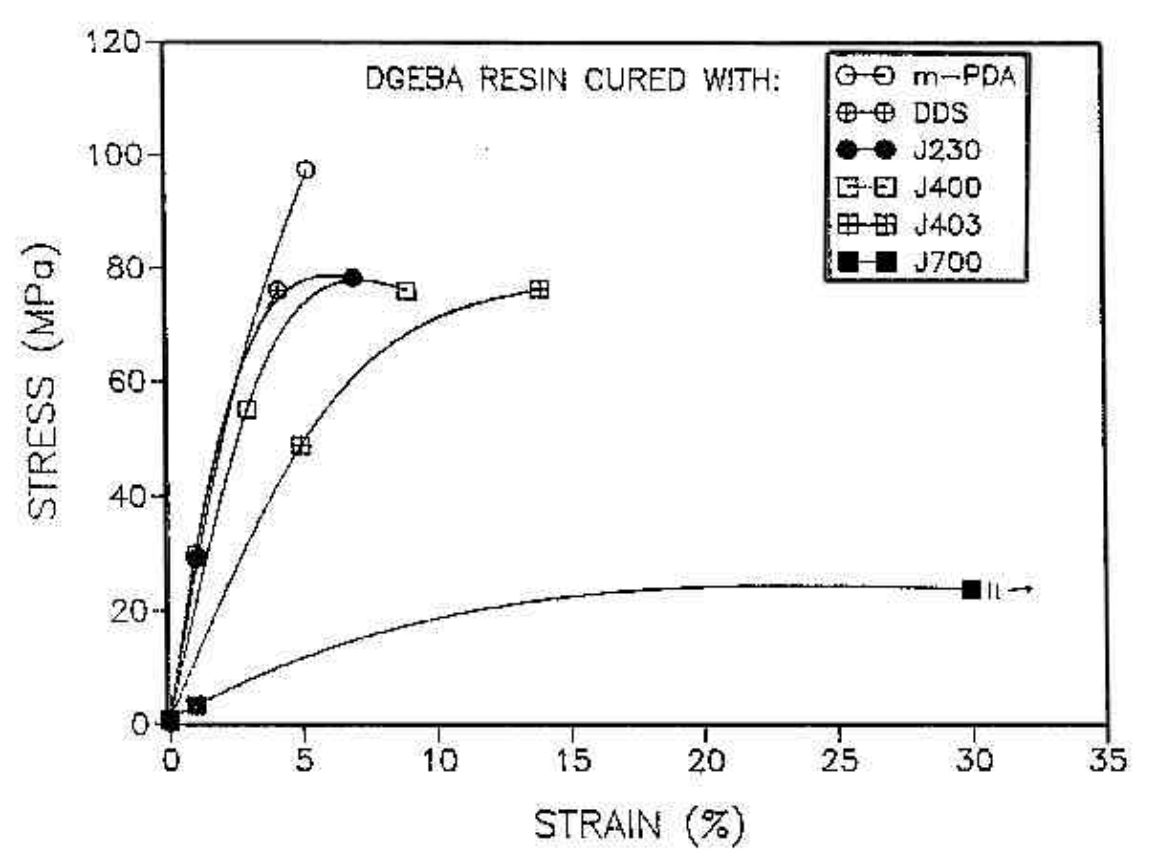




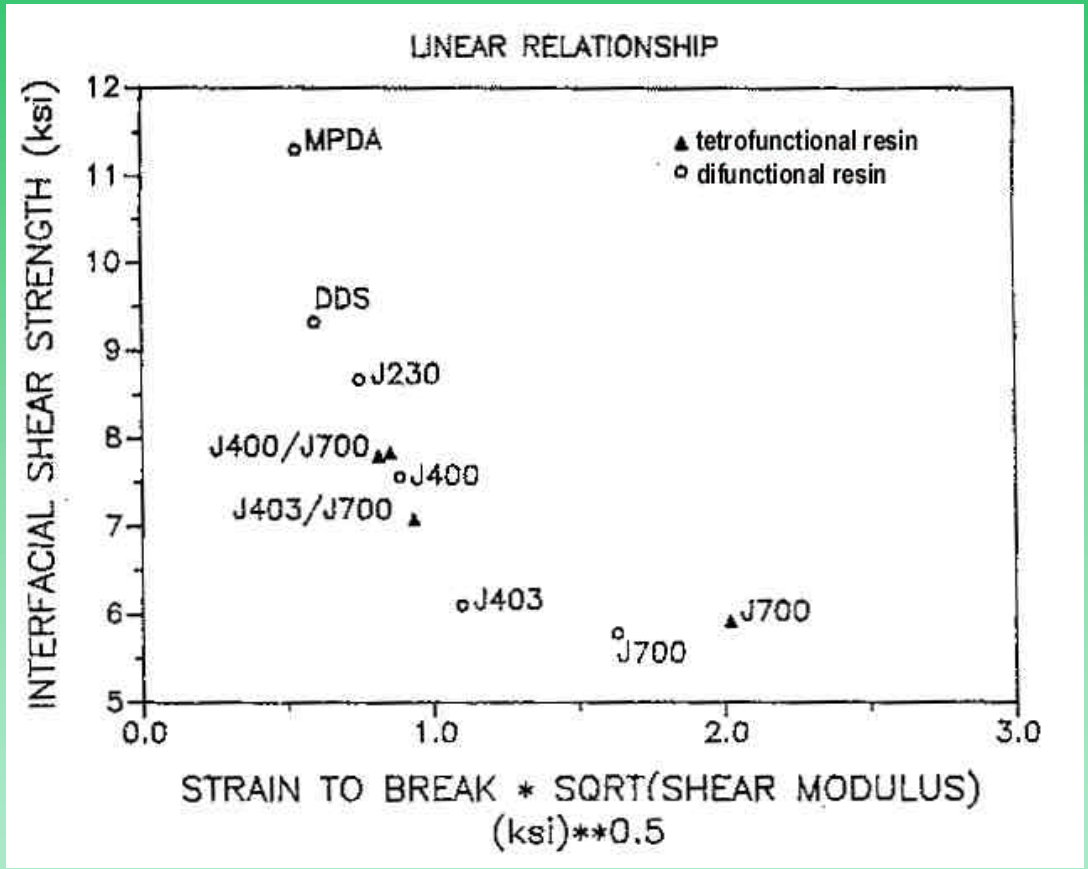


Matrix Contribution to Adhesion...

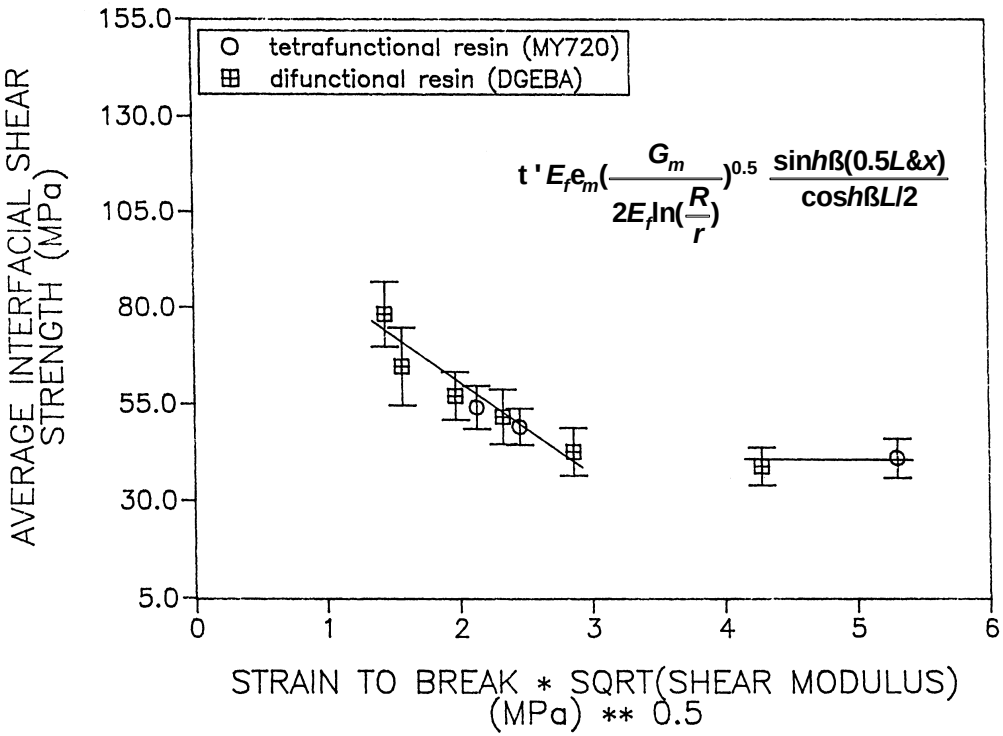
Dependency of Adhesion on Matrix Properties



Dependency of Adhesion on Matrix Properties



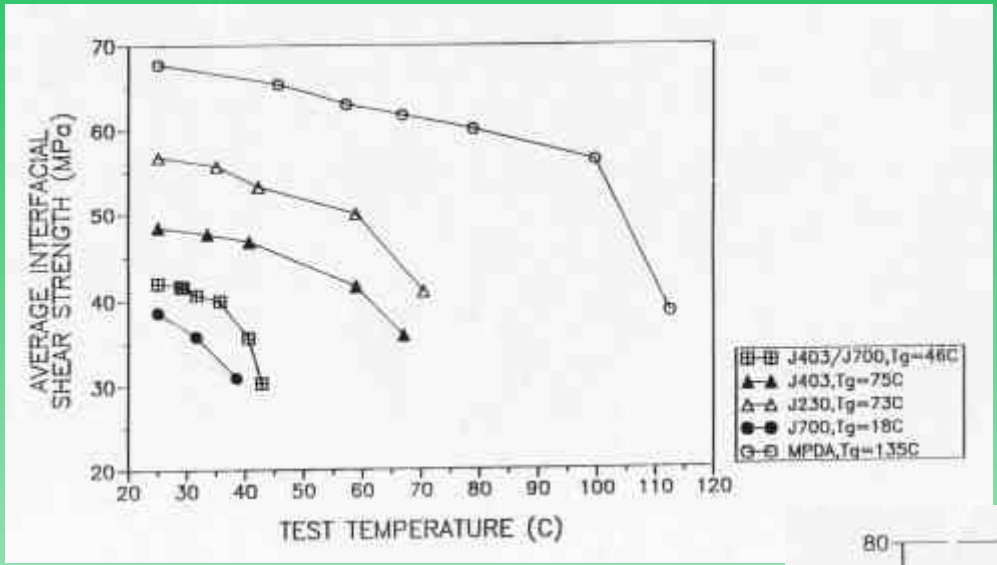
Dependency of Adhesion on Matrix Properties

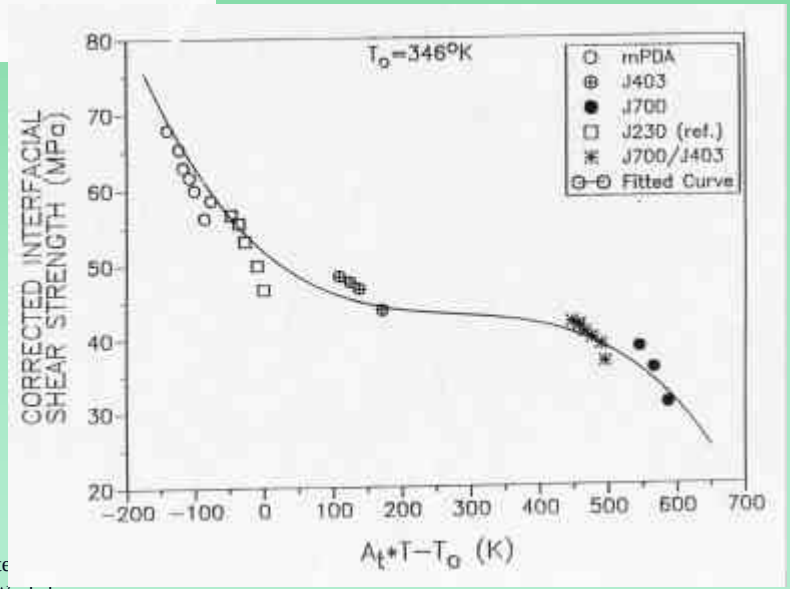


Cox's Equation

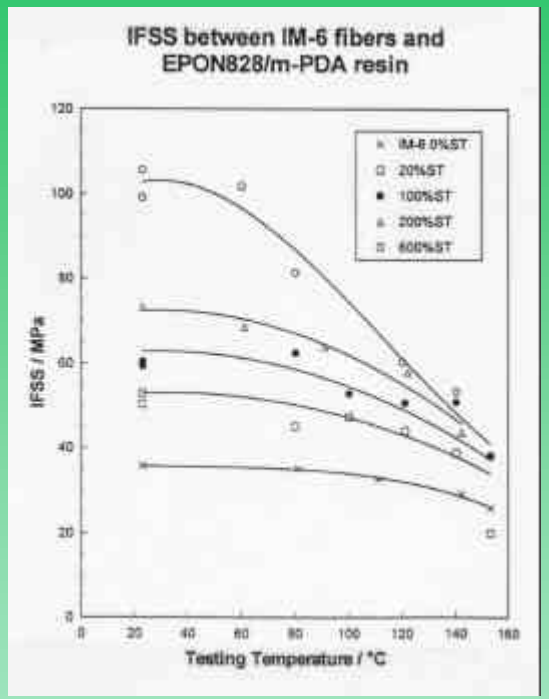
$$t' E_f e_m \left(\frac{G_m}{2E_f \ln\left(\frac{R}{r}\right)} \right)^{0.5} \frac{\sinh ß(0.5L \& x)}{\cosh ßL/2}$$

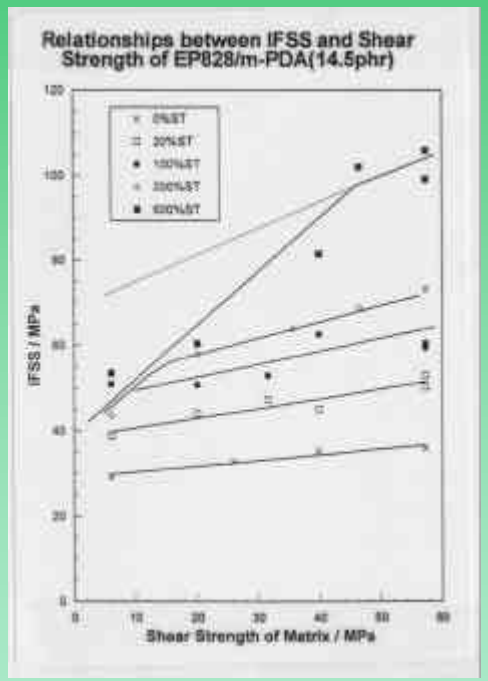
Adhesion Scaling Based on Matrix Properties...

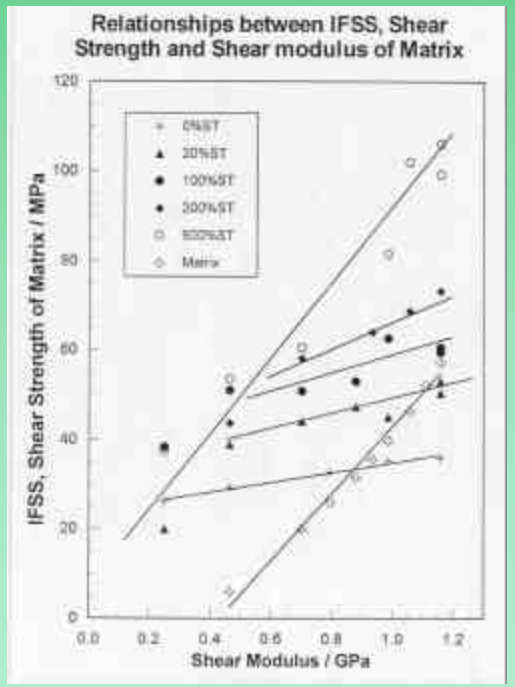




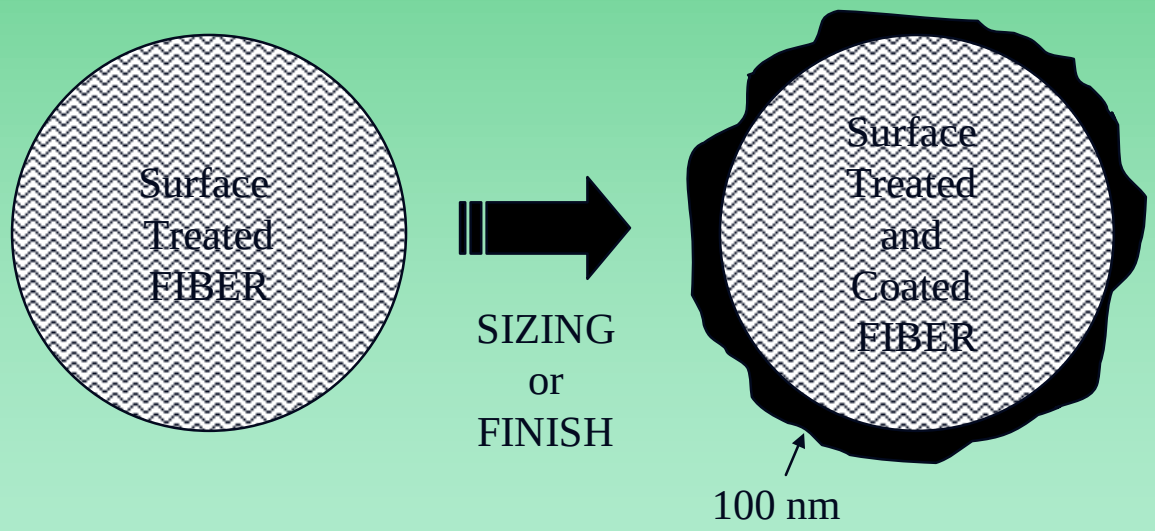
Upper Bound on Adhesion ...



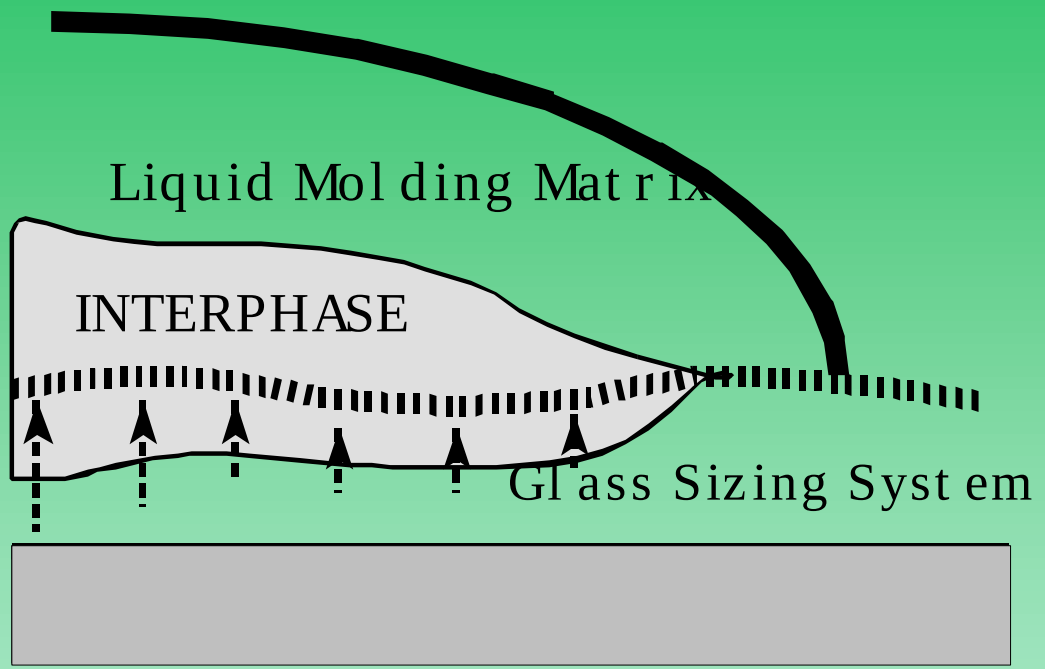




What is a Sizing/Finish and How Does it Affect Fiber-Matrix Adhesion?

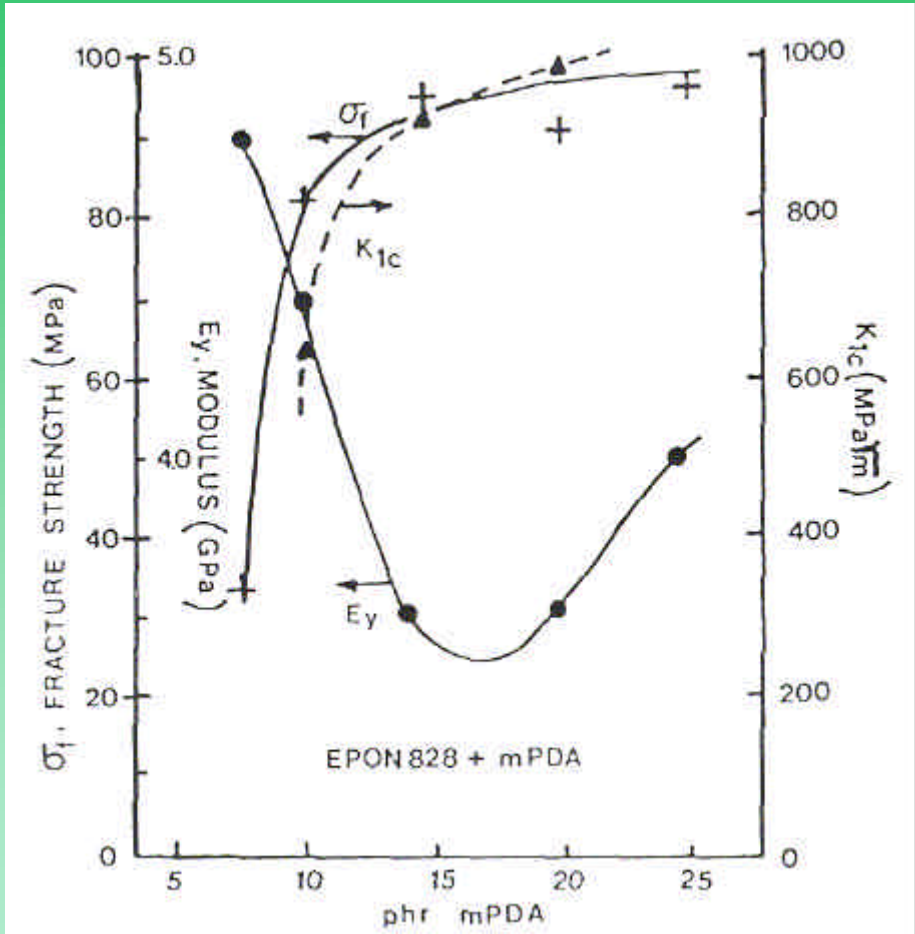


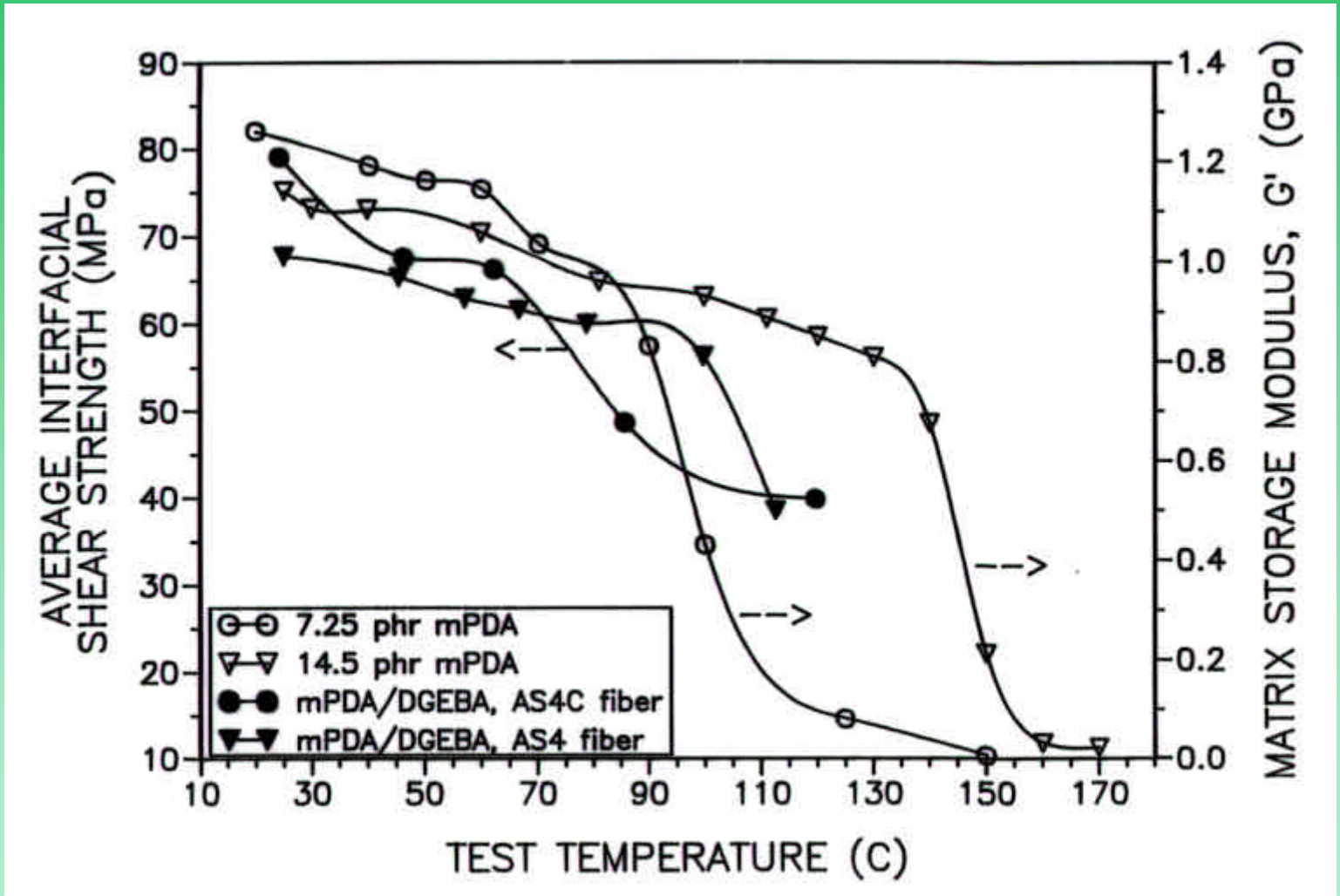
Interphase Formation During Processing



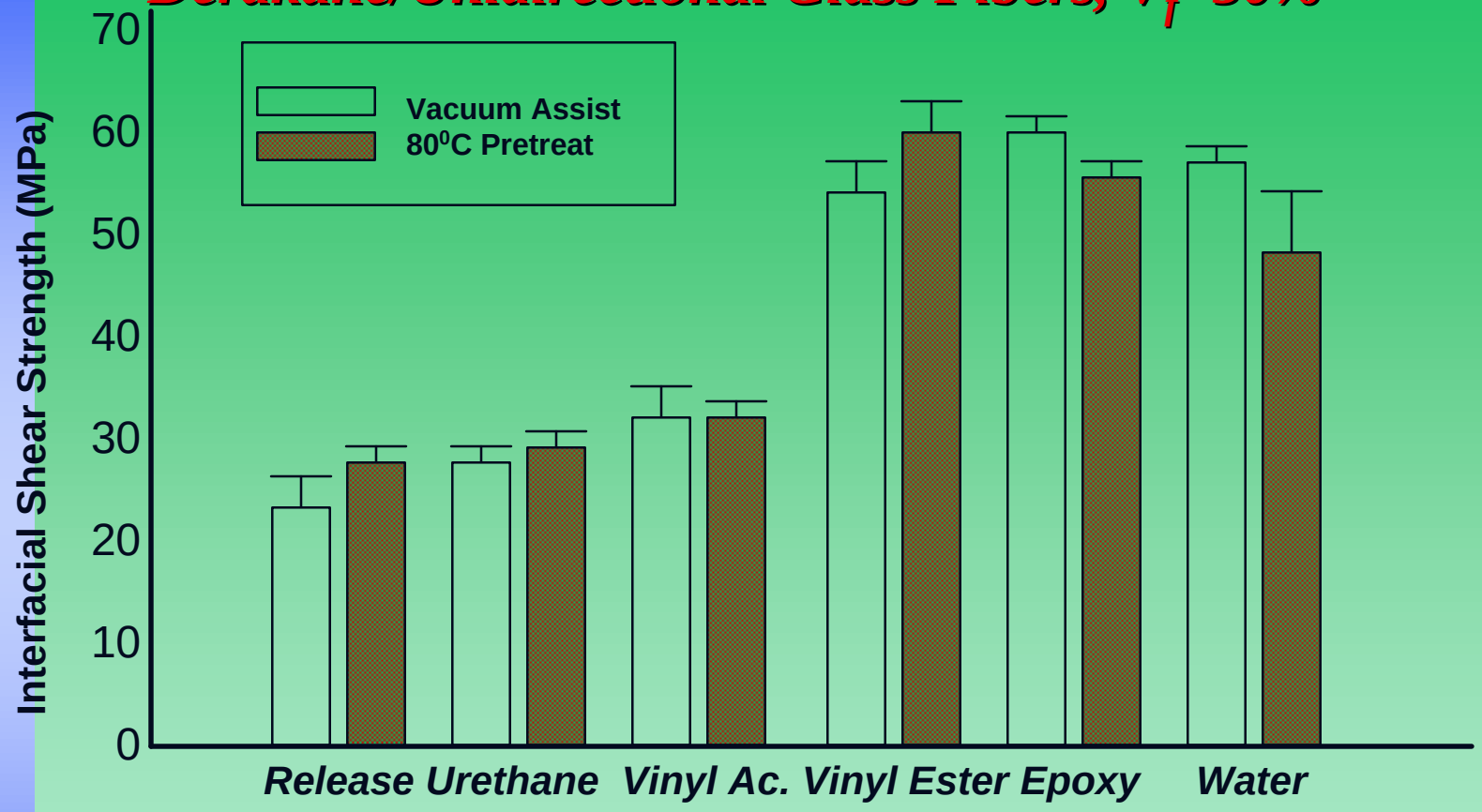
Time Dependent Formation of the Interphase Between the Fiber Sizing and Liquid Matrix

Modulus, Strength and Toughness of an Aromatic Amine Cured Epoxy an a Function of Stoichiometry



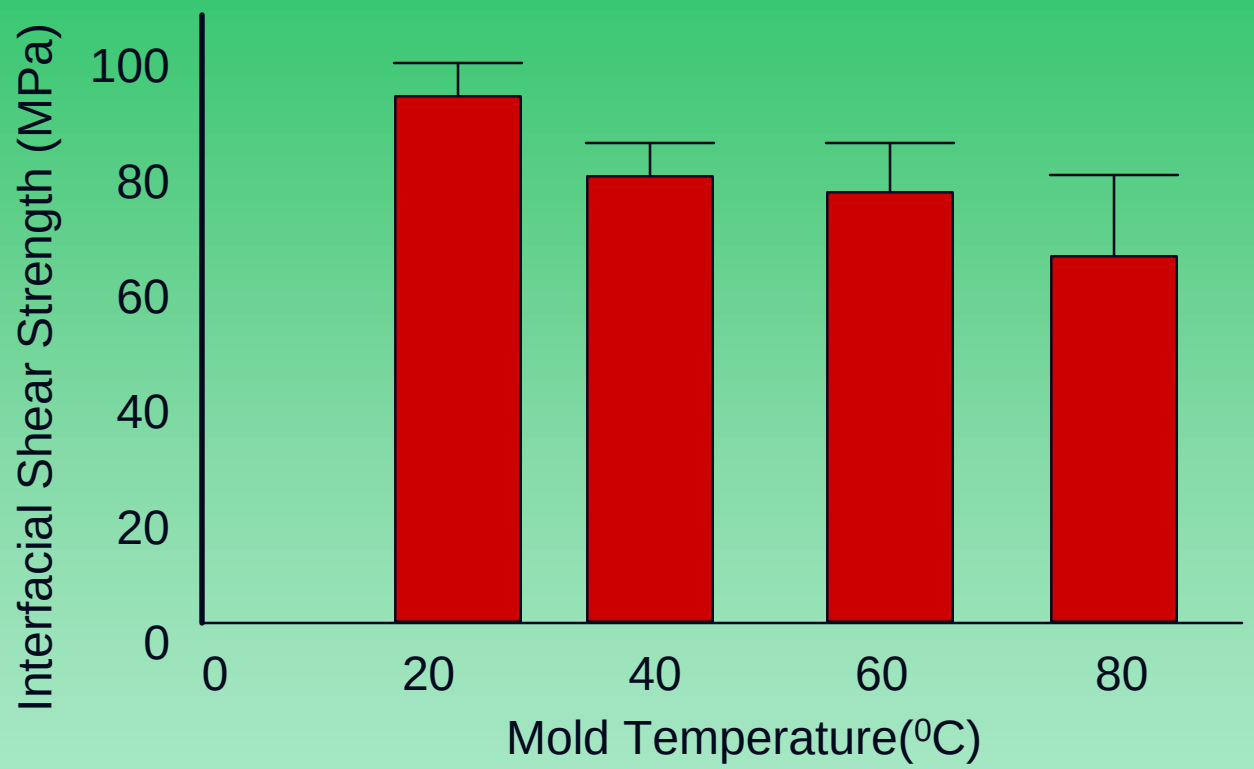

AVERAGE INTERFACIAL SHEAR STRENGTH (MPa)
MATRIX STORAGE MODULUS, G' (GPa)
TEST TEMPERATURE (C)
7.25 phr mPDA
14.5 phr mPDA
mPDA/DGEBA, AS4C fiber
mPDA/DGEBA, AS4 fiber
<--
-->
-->
90
80
70
60
50
40
30
20
10
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
10
30
50
70
90
110
130
150
170

Short Beam Shear Strength Comparison Derakane/Unidirectional Glass Fibers, V_f=50%

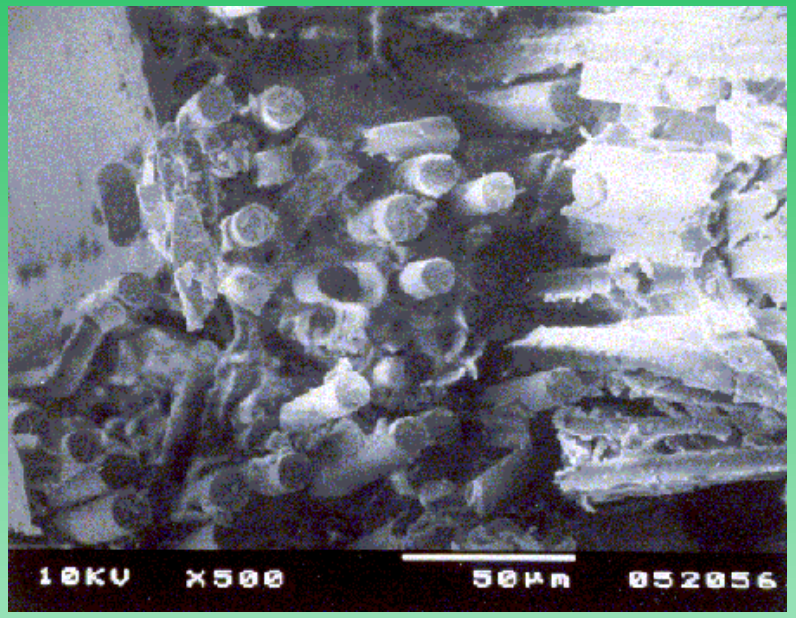


Short Beam Shear Strength Comparison Between Derakane/Unidirectional Glass Fiber Composites with 50% Fiber Volume Fraction for Vacuum and Heat Pretreat Processing Cycles.

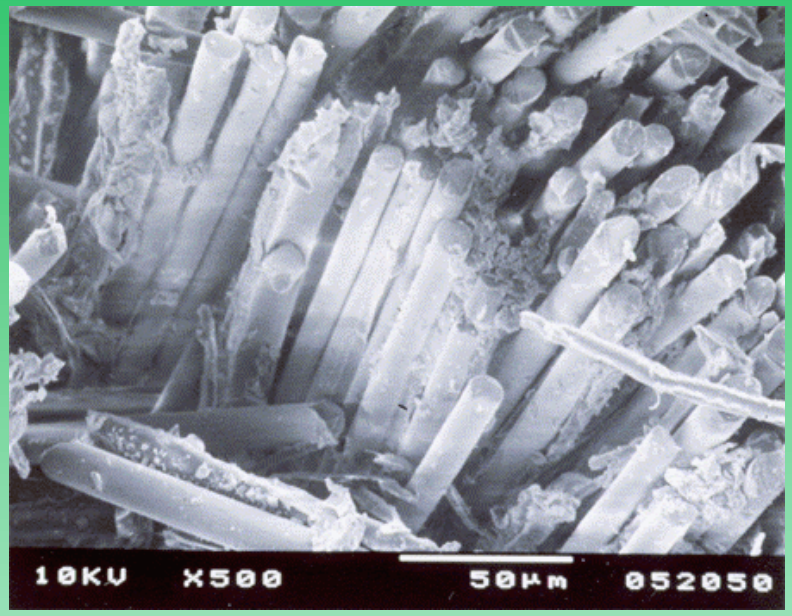
Interfacial Shear Strength vs. Temperature
Derakane/Glass Fiber, Measured Using ITS



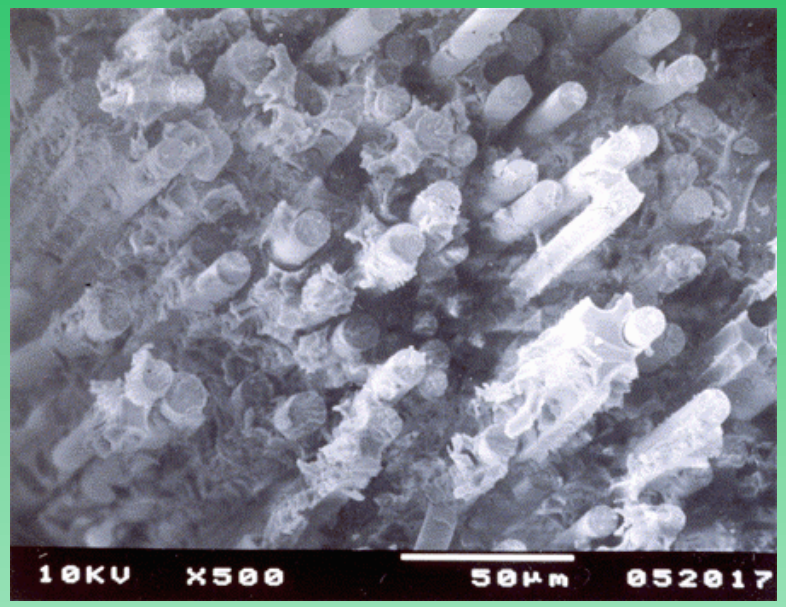
Interfacial Shear Strength of Derakane/Glass Fiber (with Soluble Polyester Sizing) Composites Processed with Vacuum Assist vs. Mold Temperature



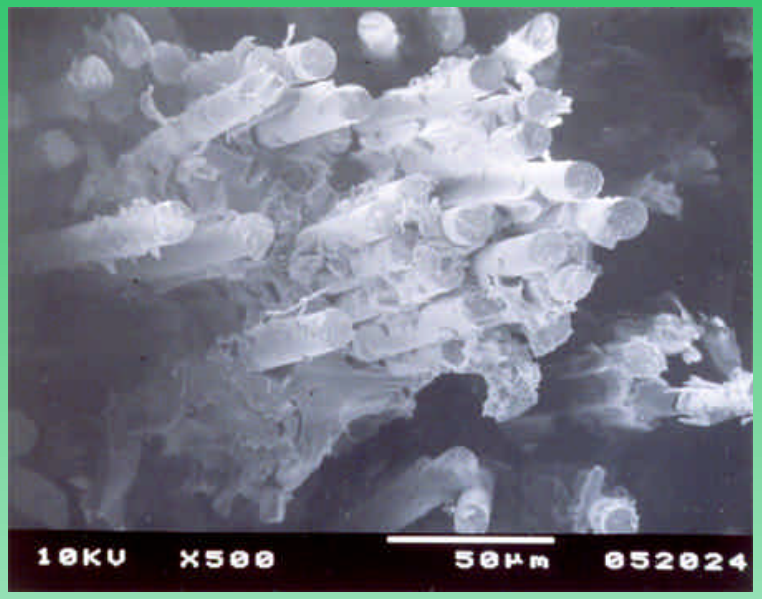
Tensile Fracture surface of insoluble polyurethane sized fiber (#2) composites



Tensile Fracture surface of semi-soluble polyvinyl acetate sized fiber (#3) composites



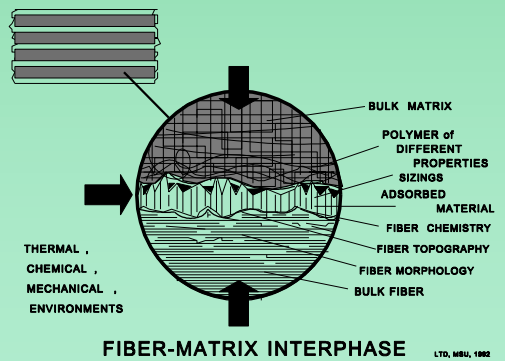
Tensile fracture surface of soluble polyester sized fiber (#4) composite



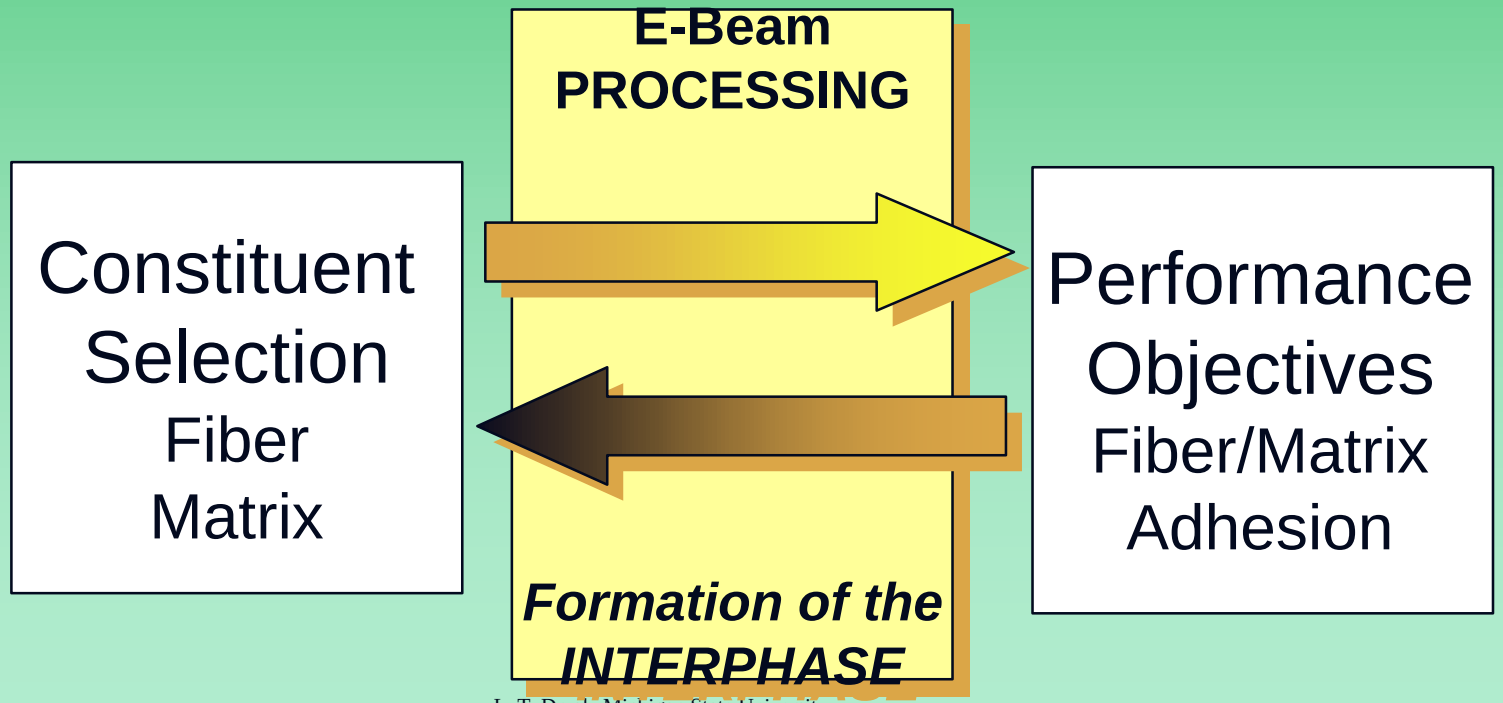
Tensile fracture surface of soluble epoxy sized fiber (#5) composite

Contributing Factors to Formation of the Interphase and Adhesion ...

- Fiber surface morphology and mechanical properties
- Fiber surface chemistry
- Fiber surface topography
- Fiber surface energetics
- Fiber surface-matrix interfacial energetics
- Fiber surface-matrix chemical interactions in the Interphase
- Polymer matrix chemistry
- Polymer matrix mechanical properties
- Polymer matrix molecular weight
- Polymer matrix transcrystallinity



Designing an Interphase for Optimum Adhesion and Processability



What are the Chemical, Physical and Mechanical properties of a Optimally Designed INTERPHASE?

- thermodynamic wetting of the fiber by the matrix
- combination of physical and chemical bonding between fiber surface and matrix
- interphase matrix properties must insure
  - effective stress transfer
  - high strength
  - high toughness
  - high durability

What Should a Surface Treatment do to a Reinforcement to Improve Adhesion?

- Remove the ‘native’ surface
  - reduces surface defects that reduce strength
- Increase surface energy
  - combination of cleaning, functionalization
- Increase microtopography
  - pores and asperities increase mechanical interlocking
- Functionalize surface
  - increase chemical reaction between the fiber surface and the matrix in the appropriate processing window

What Should a Surface Sizing or Finish do to Improve Adhesion?

- Sizing or finish should be *soluble* in the liquid matrix under the processing conditions
- Sufficient time should be allowed for the sizing or finish for complete *dissolution* in the matrix
- Effect of sizing or finish must not adversely affect the matrix reaction kinetics and/or cured matrix properties