FIBER-RESIN INTERACTIONS AND INTERPHASE FORMATION IN THERMOSETTING COMPOSITE SYSTEMS° °

Giuseppe R. Palmese

University of Delaware Center for Composite Materials

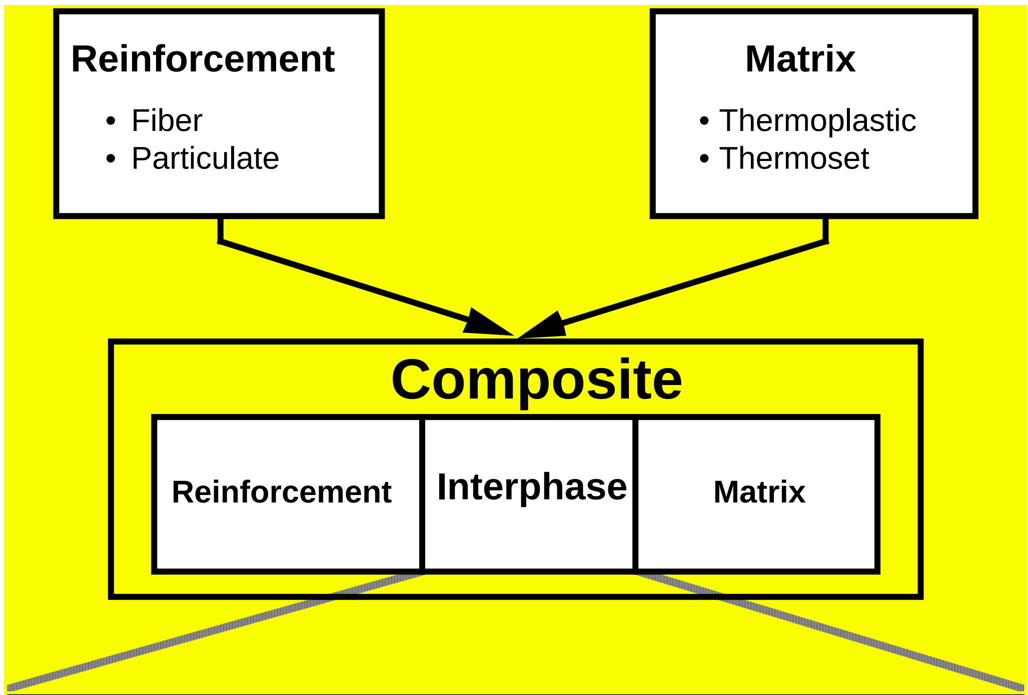
EB Workshop • Oak Ridge, Tennessee • April 20-21, 1999

OUTLINE

- Background
  - Interphase
- Epoxy-Amine-Carbon Systems
- Vinyl-Ester
  - Glass
  - Carbon
- E-Beam Systems
  - Free Radical
  - Cationic

University of Delaware Center for Composite Materials

THE INTERPHASE IN COMPOSITE MATERIALS



Interphase: A region which develops between the constituents of a composite and possesses neither the properties of the reinforcement nor those of the neat matrix.

CONTROL VARIABLES THAT INFLUENCE COMPOSITE BEHAVIOR VIA EFFECTS ON INTERPHASE DEVELOPMENT

Control Variables

- **Material Selection**
  - fiber
  - surface treatment
  - sizing
  - resin combination
- **Processing Conditions**
  - time
  - temperature
  - dose
  - dose rate

→ **Interphase Processes** →

Behavior Characteristics

- strength
- fracture toughness
- residual thermal stress
- “curing”
- durability

DESIGN METHODOLOGY FOR THE INTERPHASE

CONTROL VARIABLES

↓

Physical and Chemical Processes of the Interphase:

Interphase Structure

↓

Relation to Interphase Material Properties

↓

Relation to Interphase Behavior

↓

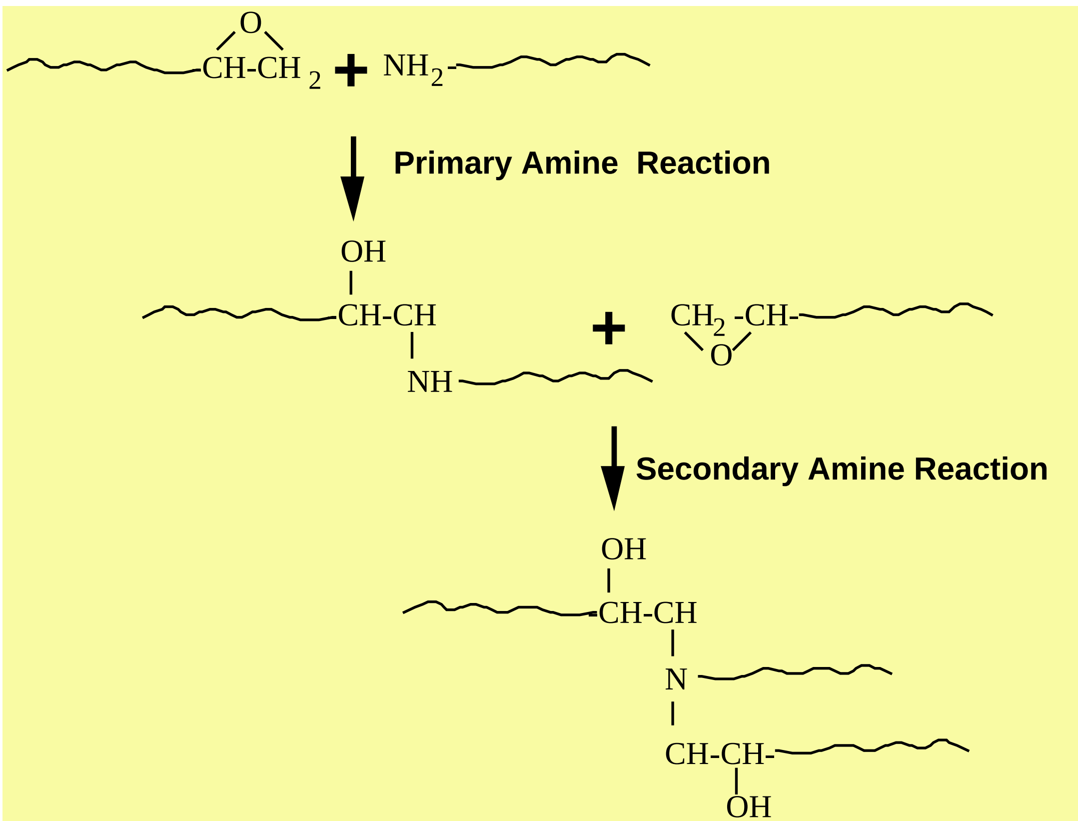
DESIRED COMPOSITE

BEHAVIOR CHARACTERISTICS

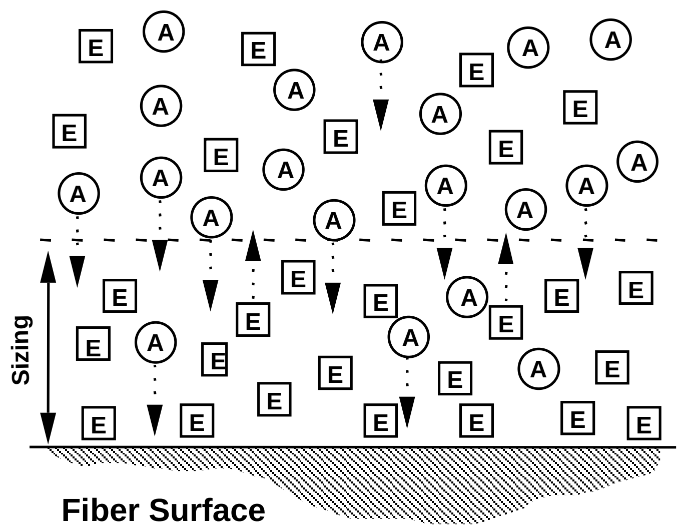
OUTLINE

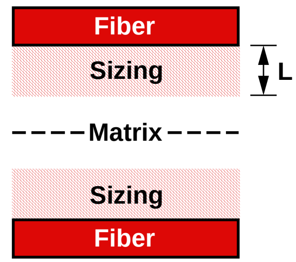
- Background
  - Interphase
- Epoxy-Amine-Carbon Systems
- Vinyl-Ester
  - Glass
  - Carbon
- E-Beam Systems
  - Free Radical
  - Cationic

EPOXY-AMINE CURE REACTIONS



MECHANISMS OF INTERPHASE FORMATION IN CARBON FIBER / EPOXY-AMINE SYSTEMS





Characteristic time for diffusion:
$t_d = L^2/D$

Characteristic time for reaction:
t_r = (time to vitrification)

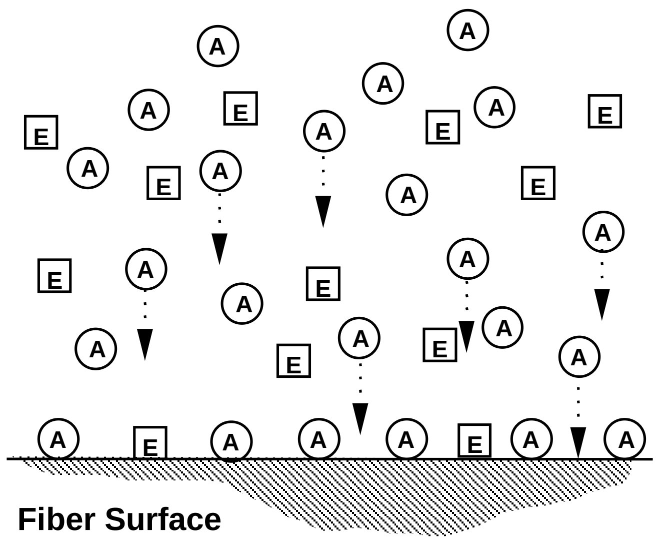
$t_d < t_r$	Fast arrangement of molecules following adsorption
$t_d - t_r$	Gradients frozen in place upon vitrification
$t_d > t_r$	Not enough time to form gradients before vitrification

Diffusion of amine curing agent into an epoxy rich sizing potentially resulting in structural gradients frozen in place as the system vitrifies

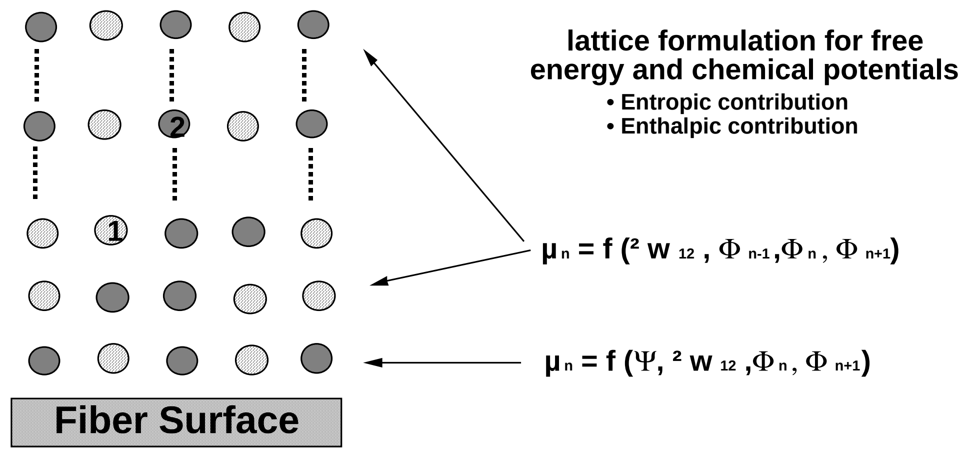
Palmese and McCullough, J. Adhesion, 44, pp. 29-49, 1994

University of Delaware Center for Composite Materials

MECHANISMS OF INTERPHASE FORMATION IN CARBON FIBER / EPOXY-AMINE SYSTEMS



Rearrangement of epoxy and amine monomers in the vicinity of fiber surface resulting from monomer-monomer and monomer-substrate interactions



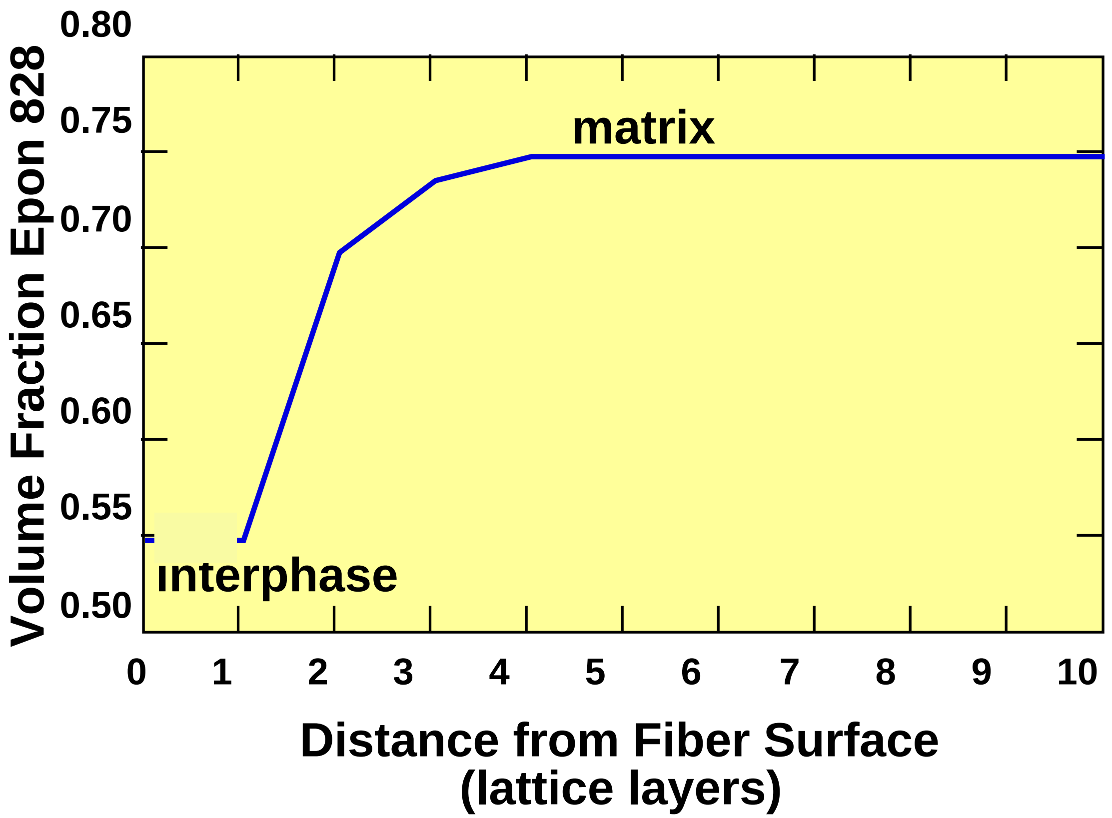
Interphase Composition

$\Phi_n = f(\Psi, {}^2w_{12}, \Phi_{bulk}, \Phi_{n-1}, \Phi_{n+1})$

$^2W_{12}$	epoxy-amine interchange energy
$\Psi = f(W_{11}, W_{22}, W_{12}, W_{10}, W_{20}, \Phi_{bulk})$	
W_{10}	epoxy-surface interaction energy
W_{20}	amine-surface interaction energy
W_{11}	epoxy-epoxy interaction energy
W_{20}	amine-amine interaction energy
Φ	volume fraction
1	epoxy
2	amine

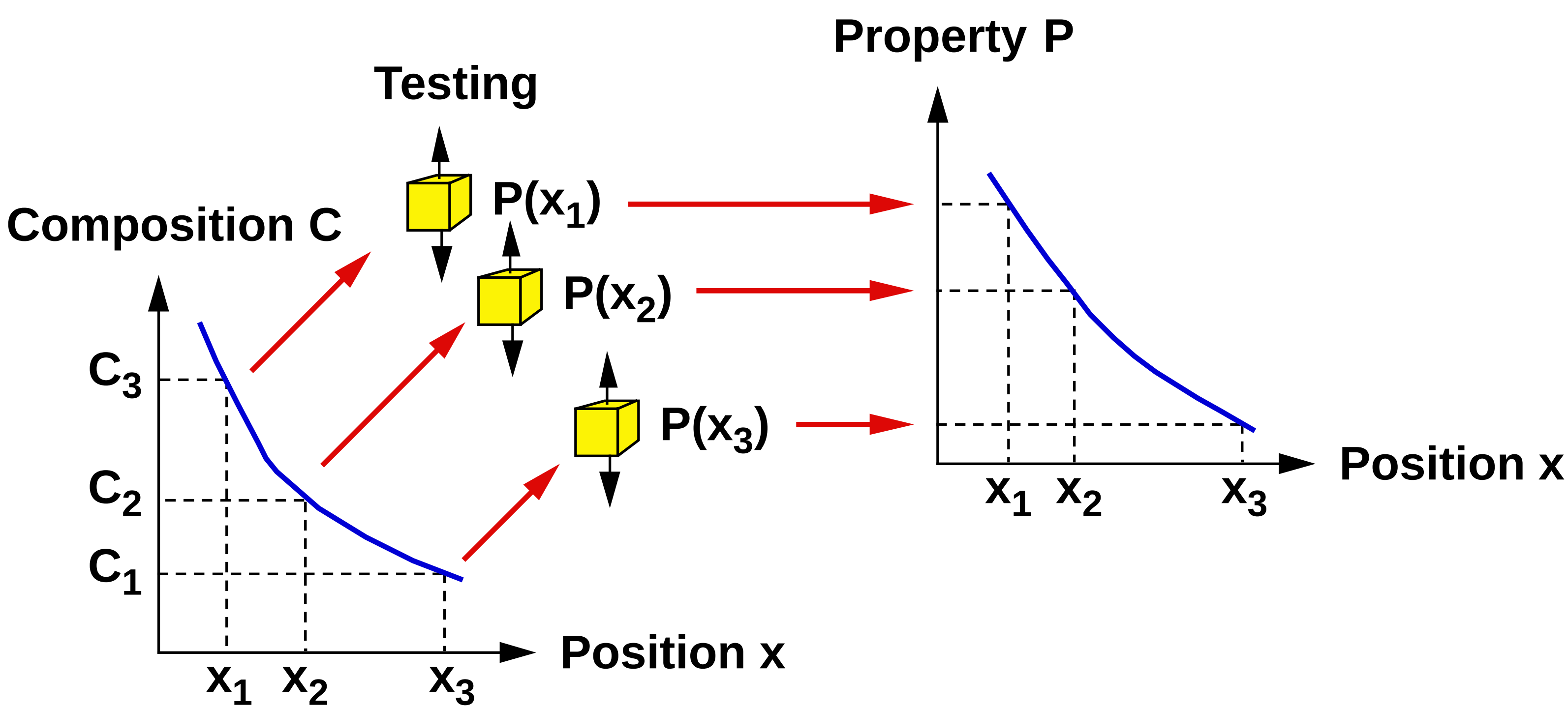
Palmese and McCullough, Composites: Part A, 30, pp. 3-10, 1999

PREDICTED INTERPHASE COMPOSITION PROFILE FOR EPON 828/PACM-20 WITH AS4 CARBON FIBER°



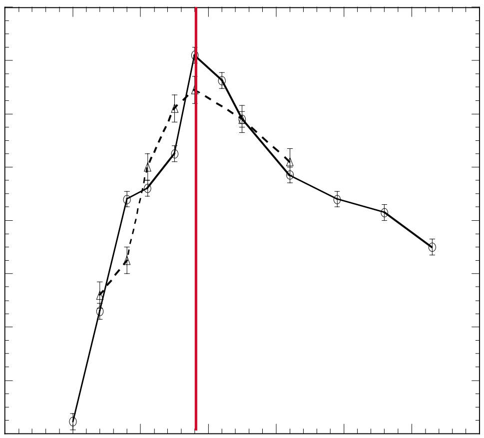
Palmese, 1992

MATCHING CHEMICAL STRUCTURE TO MEASURED MATERIAL PROPERTIES

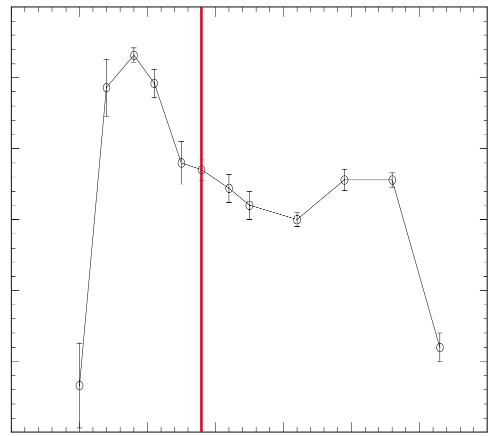


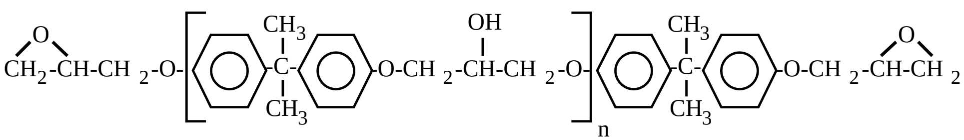
EFFECT OF STOICHIOMETRY ON Tg AND MODULUS FOR EPON 828/PACM-20

Glass Transition Temperature

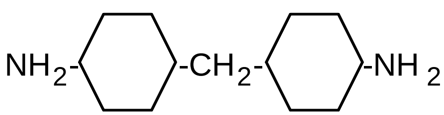


Flex Modulus (30°C)





Epon 828 DGEBA Epoxy (n = 0.2)

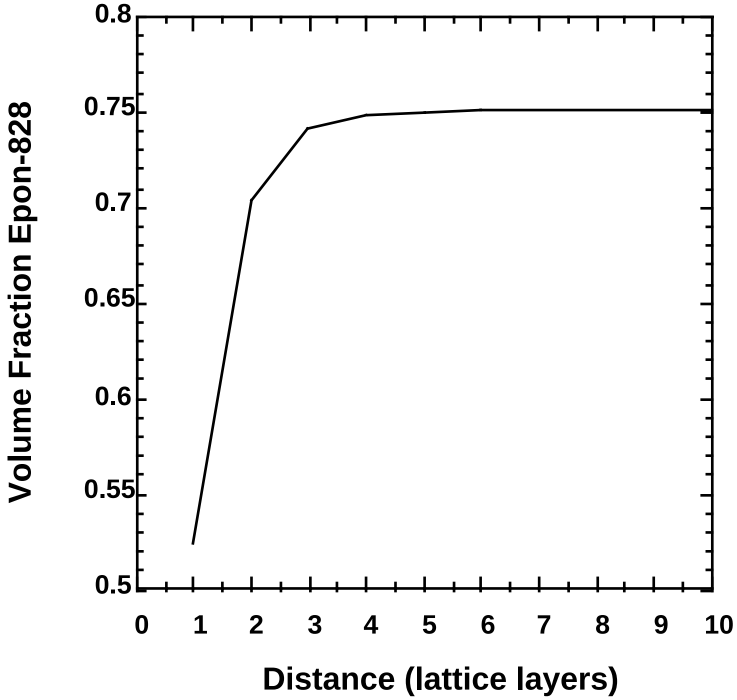


PACM-20 cycloaliphatic amine curing agent

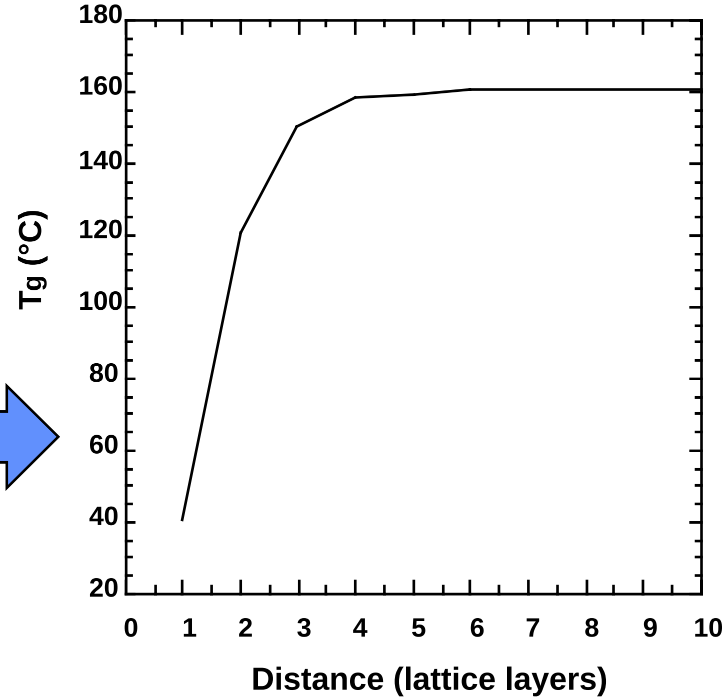
Palmese and McCullough, Journal of Applied Polymer Science, 46, pp. 1863-1873, 1992.

PREDICTED COMPOSITION AND Tg INTERPHASE PROFILES

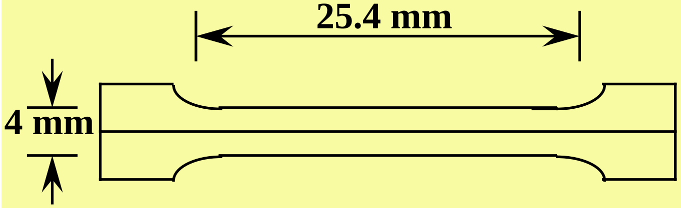
EPON-828/PACM-20/AS-FIBER INTERPHASE COMPOSITION PROFILE (no sizing)



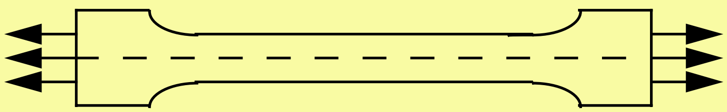
EPON-828/PACM-20/AS-FIBER INTERPHASE Tg PROFILE



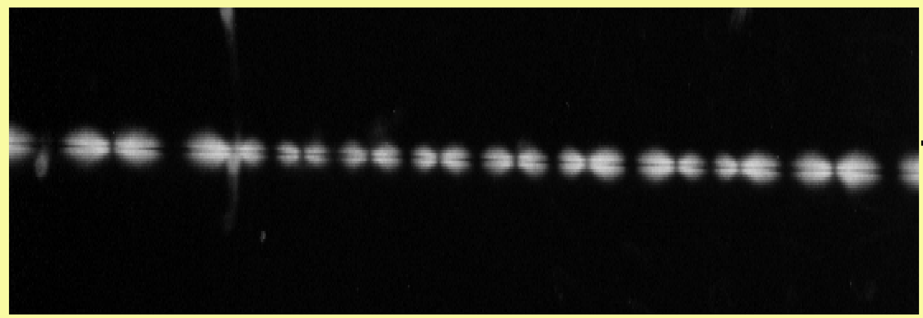
SINGLE FIBER FRAGMENTATION TEST



Tensile Specimen



Loaded Tensile Specimen



$$\tau = 1/2\, \sigma_f \,(d / l_c)$$

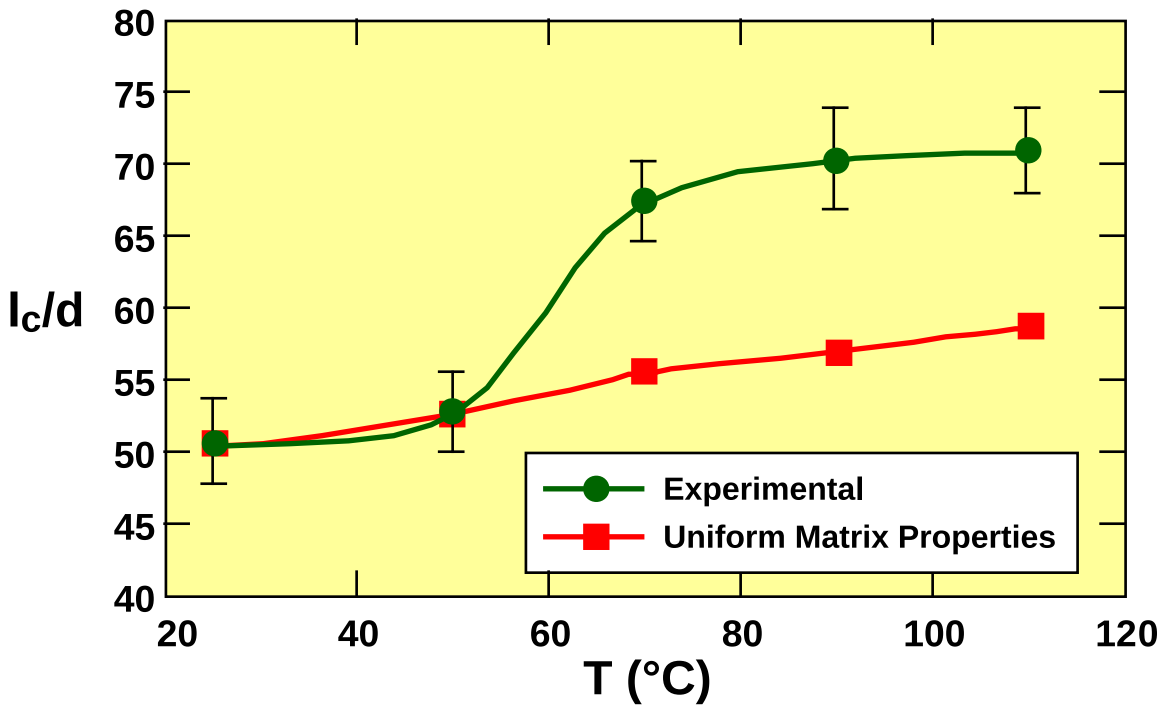
$$\frac{l_c}{d} = C\sqrt{E_f\left(\frac{1}{G_m} - \frac{2\nu}{E_f}\right)}$$

l_c / d = Critical Aspect Ratio

Shear Lag

SFF BEHAVIOR AS A FUNCTION OF TEMPERATURE INDICATING LOW Tg INTERPHASE ZONE EPON 828 / PACM-20 / AS4

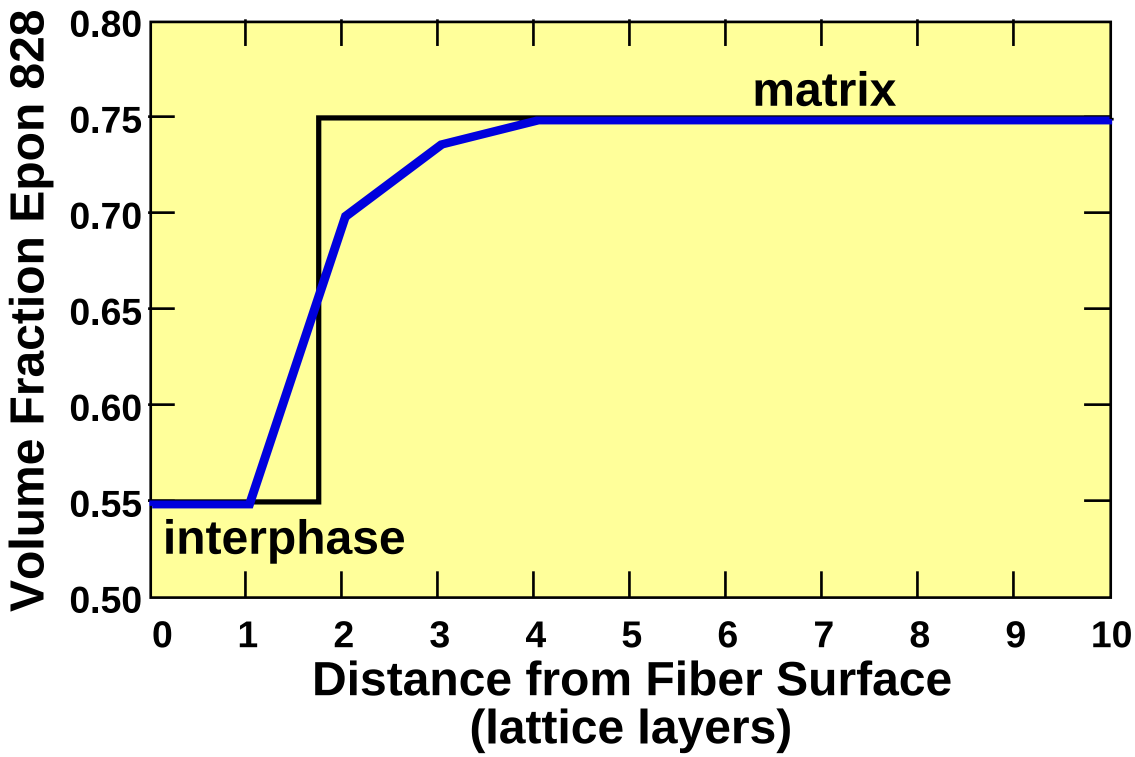
Uniform matrix property models give $\frac{l_c}{d} = C\sqrt{E_f / G_m}$

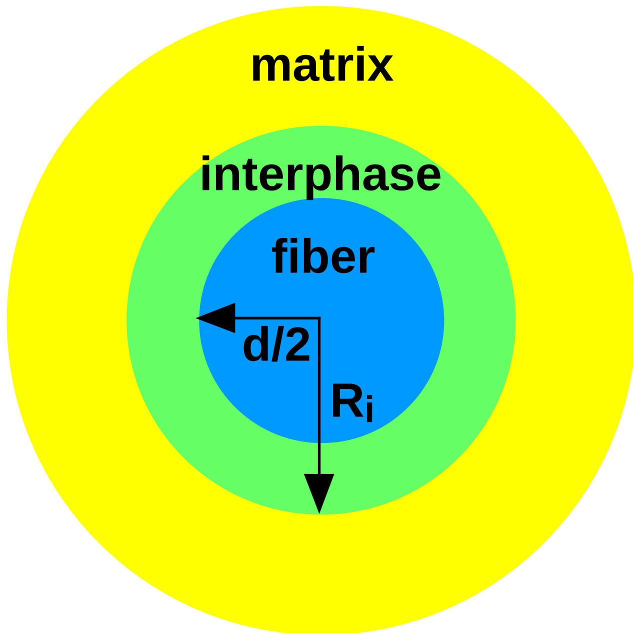


Skourlis and McCullough , Composites Science and Technology, 49, 363, 1993.

MODEL MODIFICATION

- Use of a three-concentric-cylinder model to simulate interfacial perturbations
- Fiber–interphase–matrix considered as constant property materials

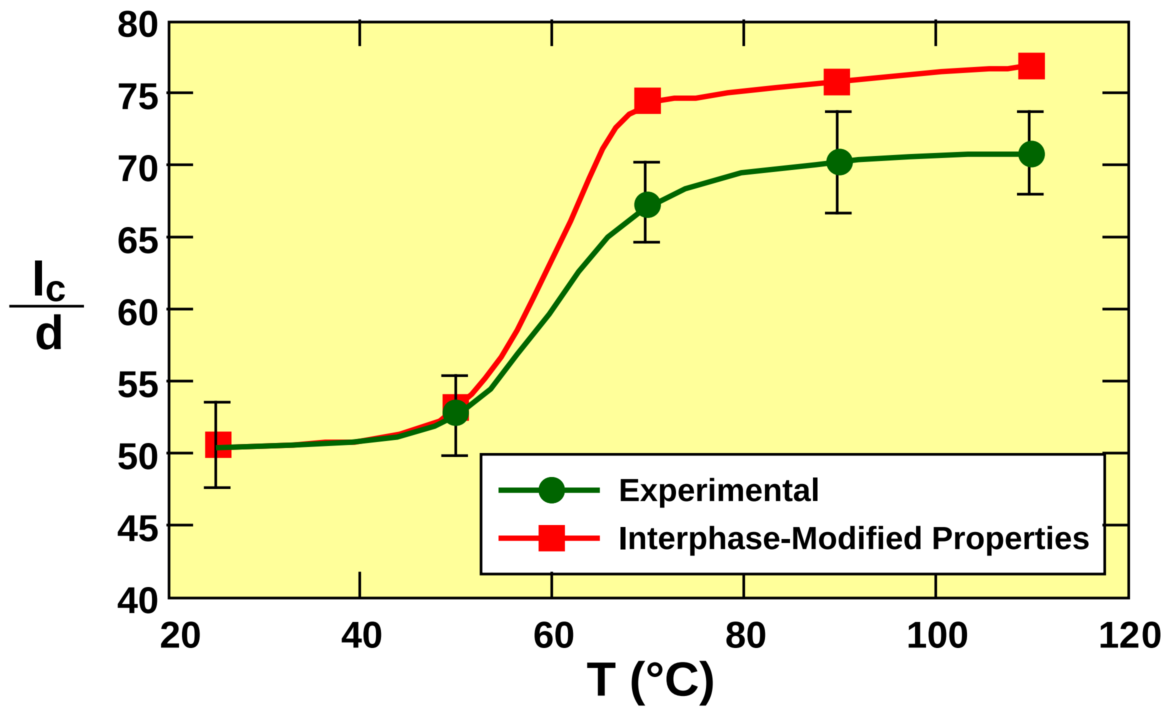




CRITICAL ASPECT RATIO PREDICTIONS USING PREDICTED INTERPHASE PROPERTIES

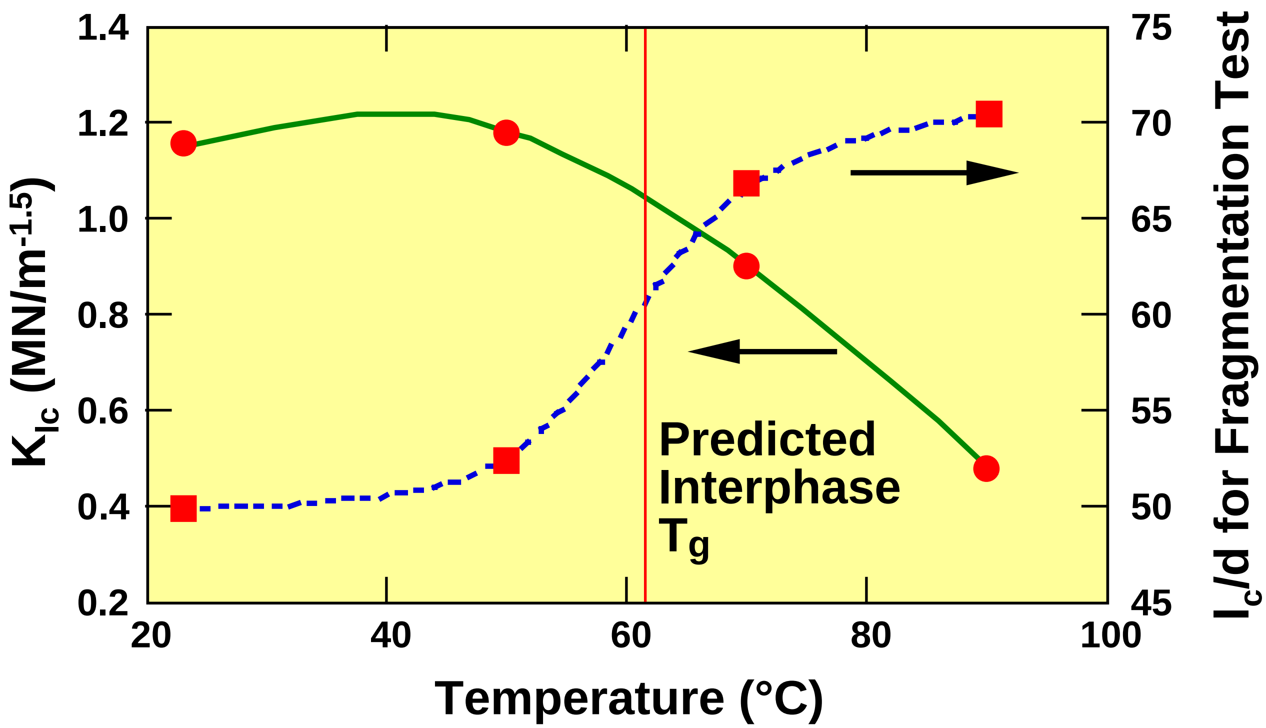
Modified Aspect Ratio

$$\frac{l_c}{d} = C\sqrt{E_f\left[\left(\frac{d/2}{R_i}\right)^2\left(\frac{1}{G_m}-\frac{1}{G_i}\right)+\frac{1}{G_i}-\frac{2\nu_f}{E_f}\right]}$$



Skourlis and McCullough , Composites Science and Technology, 49, 363, 1993.

INTERPHASE EFFECT ON MECHANICAL PROPERTIES
Epon 828 / PACM-20

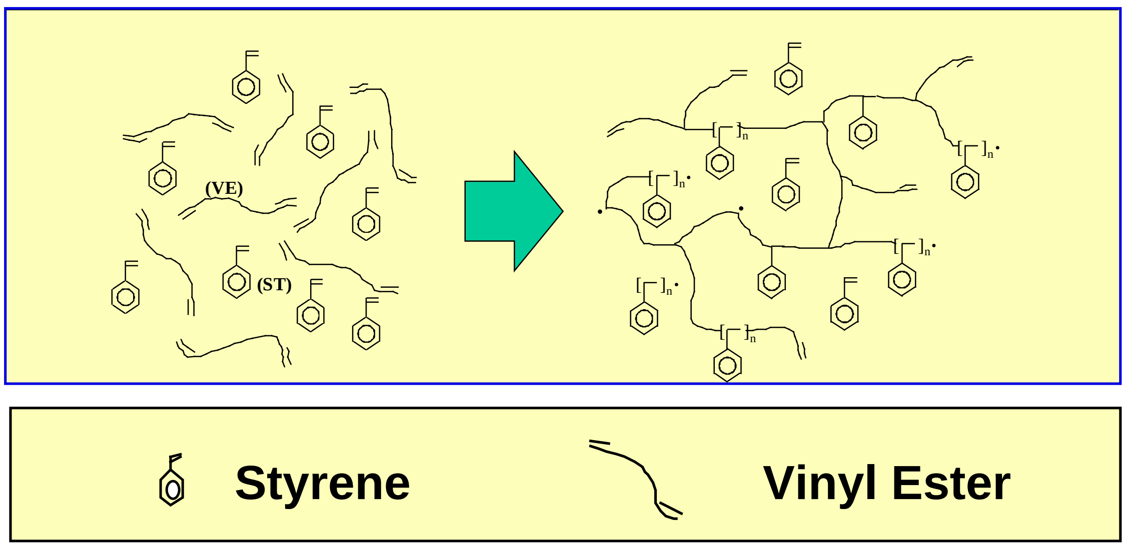


OUTLINE

- Background
  - Interphase
- Epoxy-Amine-Carbon Systems
- Vinyl-Ester
  - Glass
  - Carbon
- E-Beam Systems
  - Free Radical
  - Cationic

VINYL ESTER - BACKGROUND

- **Two component resin system typically comprised of a methacrylated DGEBA epoxy and styrene reactive diluent**
- **Cure is achieved via a free radical bulk copolymerization reaction.**



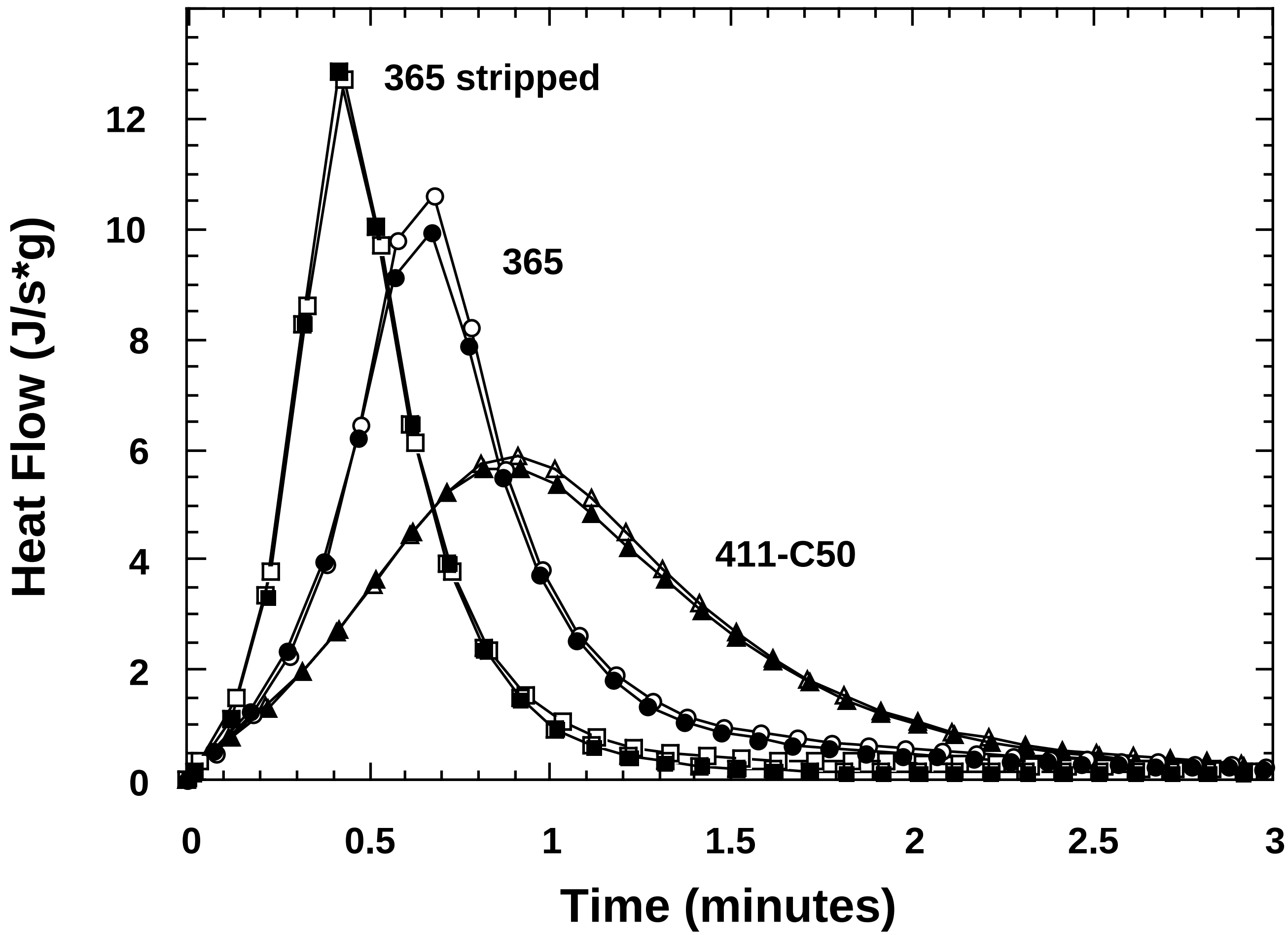
I	→	2R•	Initiator decay
R• + VE	→	VE•	Radicals attack monomer
R• + ST	→	ST•	
VE• + VE	→	(VE-VE)•	VE homopolymerization
VE• + ST ST• + VE	→	(VE-ST)•	VE-ST copolymerization
ST• + ST	→	(ST-ST)•	ST homopolymerization

bulk copolymerization

DSC THERMOGRAMS FOR S-2 GLASS FILLED AND UNFILLED VINYL ESTER AT 110° C

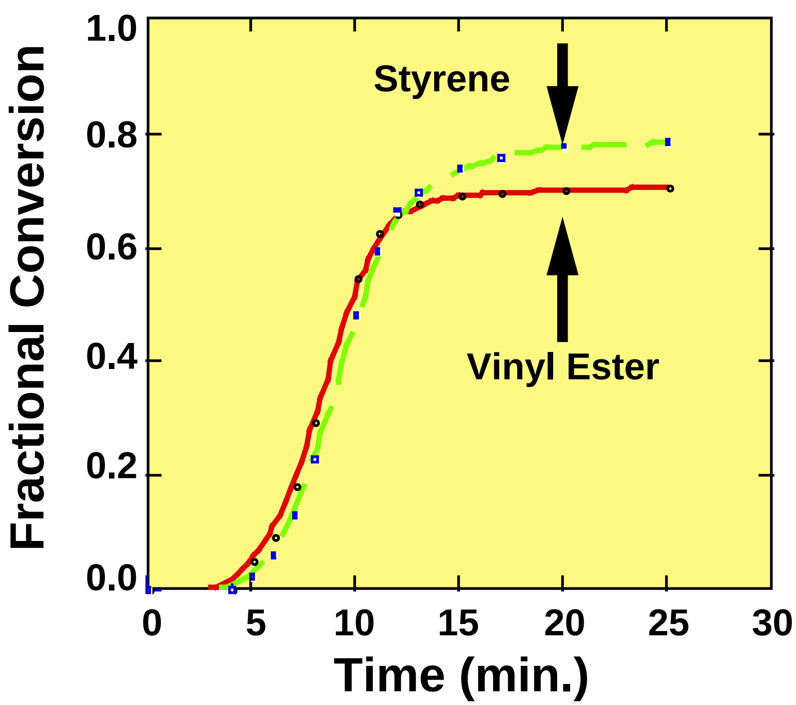
Dow Derakane 411-C50 / Owens Corning S-2 Glass 365, stripped 365

Palmese et al., Composites: Part A, 30, pp. 11-18, 1999.

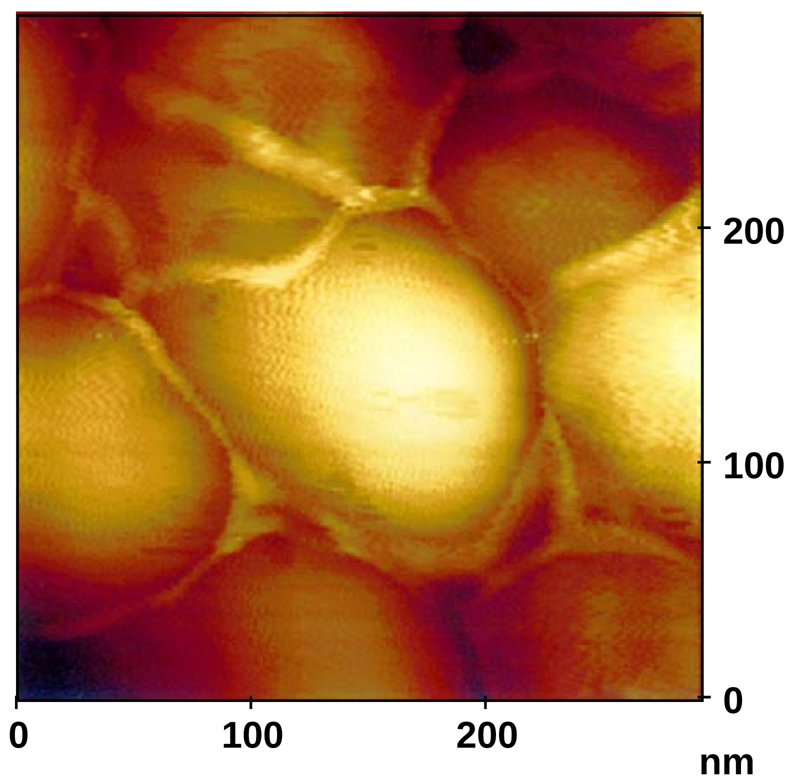


COMPOSITION AND PROCESSING EFFECTS ON THE CURE AND PROPERTIES OF VINYL-ESTER RESIN SYSTEMS

Cure Behavior of Vinyl-Ester Resin Components Monitored Using FTIR

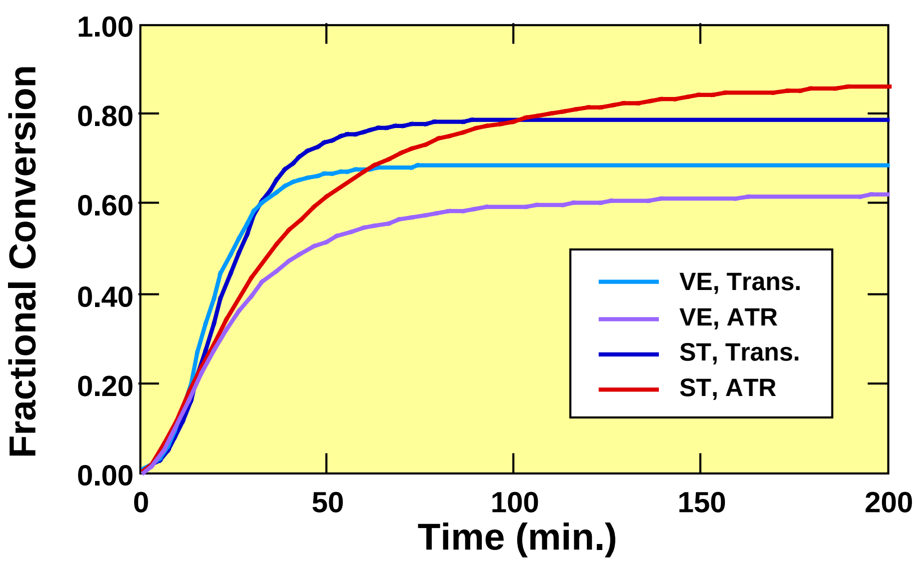


AFM Micrograph of Vinyl-Ester Microgels

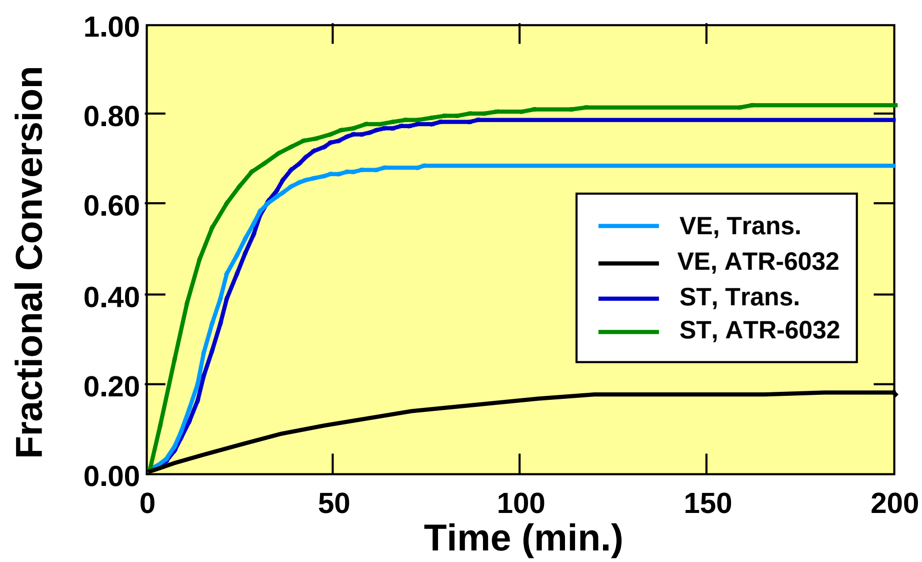


Ziaee and Palmese, J. Polymer Science: Part B, 37, pp. 725-744, 1999.

EFFECT OF SURFACE TREATMENT ON VINYL-ESTER COPOLYMERIZATION BEHAVIOR AS MEASURED BY ATR - FTIR



Germanium Surface



Silane Treated Surface

Disruption of Bulk Reactions

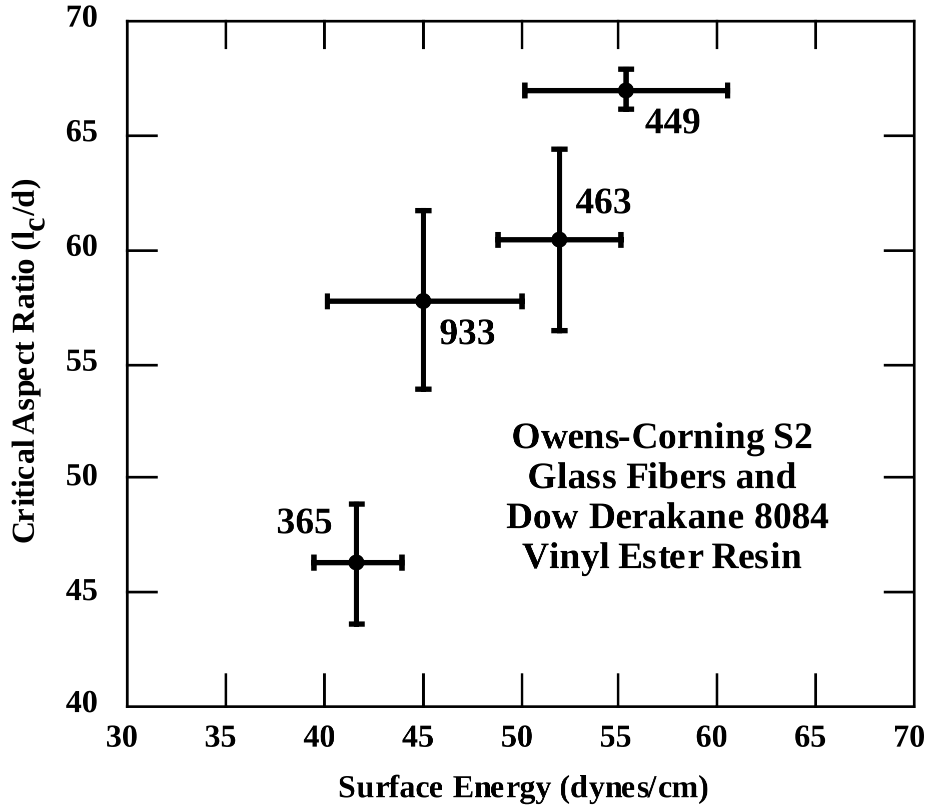
80°C

1.5% USP 245 initiator

Dow 441-400 resin

Brill and Palmese

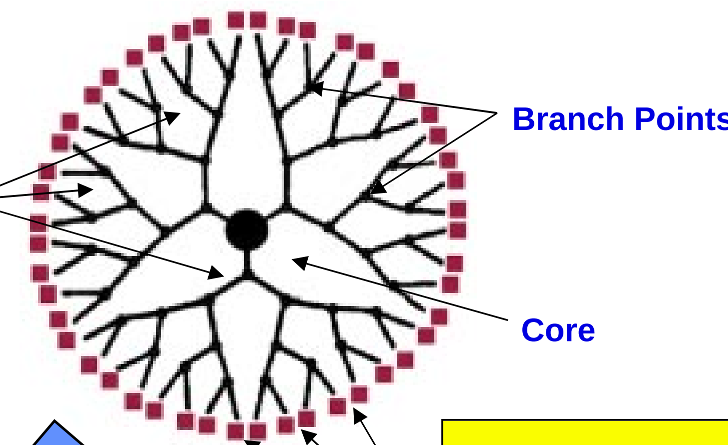
CRITICAL ASPECT RATIO VERSUS SURFACE ENERGY



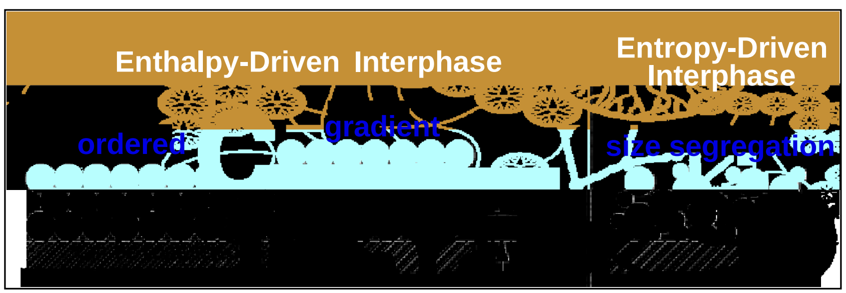
Palmese et al., Composites: PartA, 30, pp. 3-10, 1999.

TAILORING THE INTERPHASE USING DENDRITIC POLYMERS

Interior Repeat Units
- polyester
- polypropylenimine
- prolyamidimine …



Terminal Groups
- amine
- hydroxyl
- epoxy
- aliphatic …

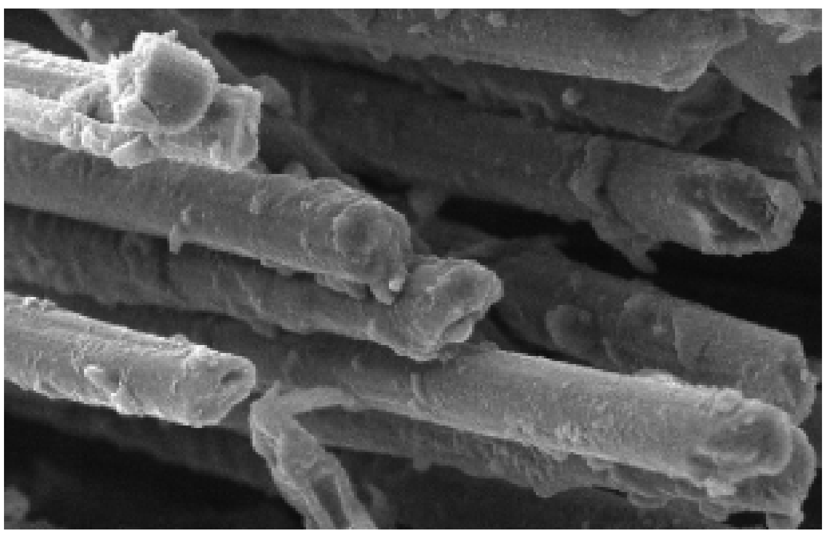


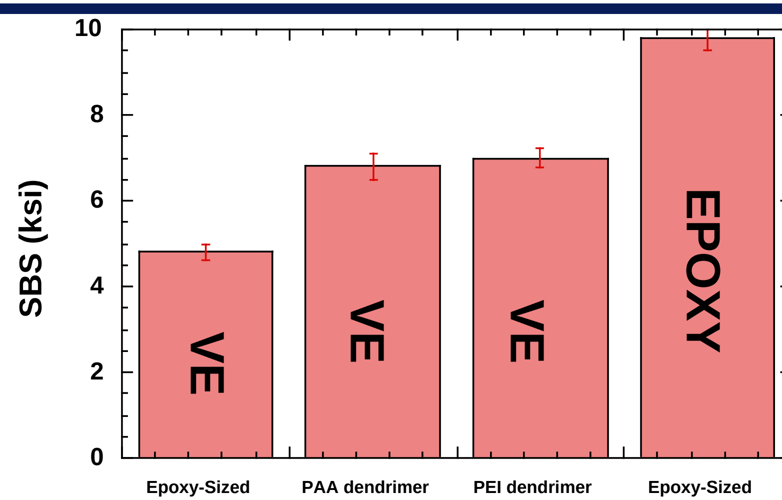
IMPROVEMENT OF VE-CARBON COMPOSITE PROPERTIES USING DENDRITIC POLYMERS

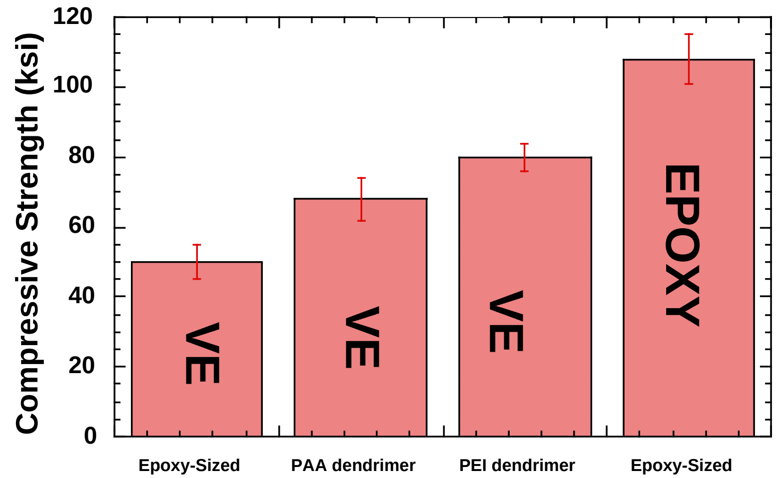
VE: Dow Derakane 411-C50

Epoxy: Epon 862-Lindide 6k

Akzo 50k stitched unidirectional





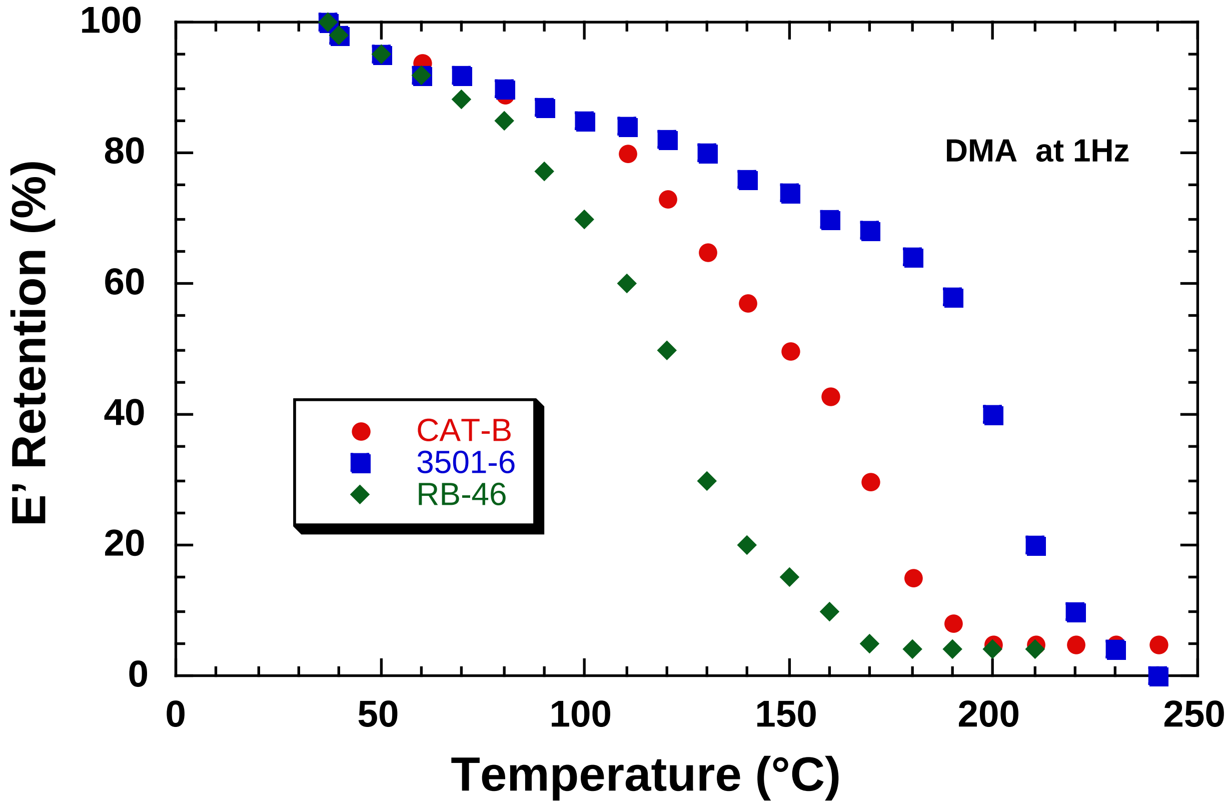


OUTLINE

- Background
  - Interphase
- Epoxy-Amine-Carbon Systems
- Vinyl-Ester
  - Glass
  - Carbon
- E-Beam Systems
  - Free Radical
  - Cationic

University of Delaware Center for Composite Materials

COMPARISON OF STORAGE MODULUS RETENTION FOR STANDARD EB AND THERMAL CURE SYSTEMS

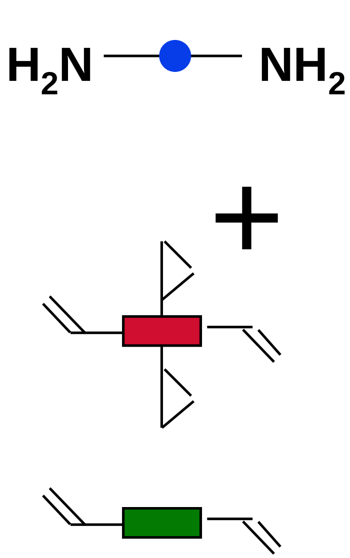


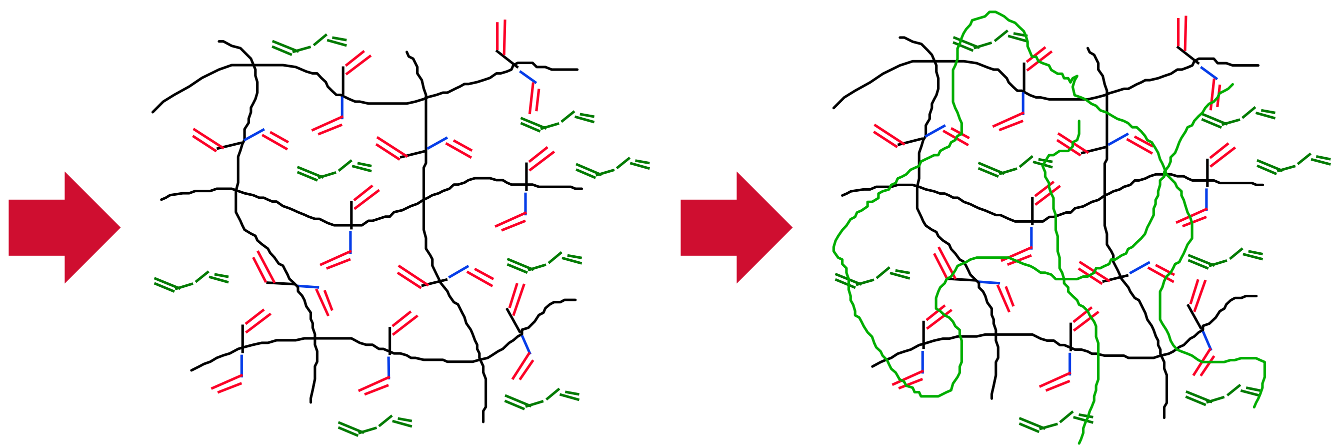
CAT-B (cationically cure epoxy for EB)

RB-46 (Aerospatiale free radical system for EB)

3501-6 (standard thermal cure epoxy-amine system)

SCHEMATIC OF NETWORK FORMATION FOR FREE RADICAL CURED IPN SYSTEMS





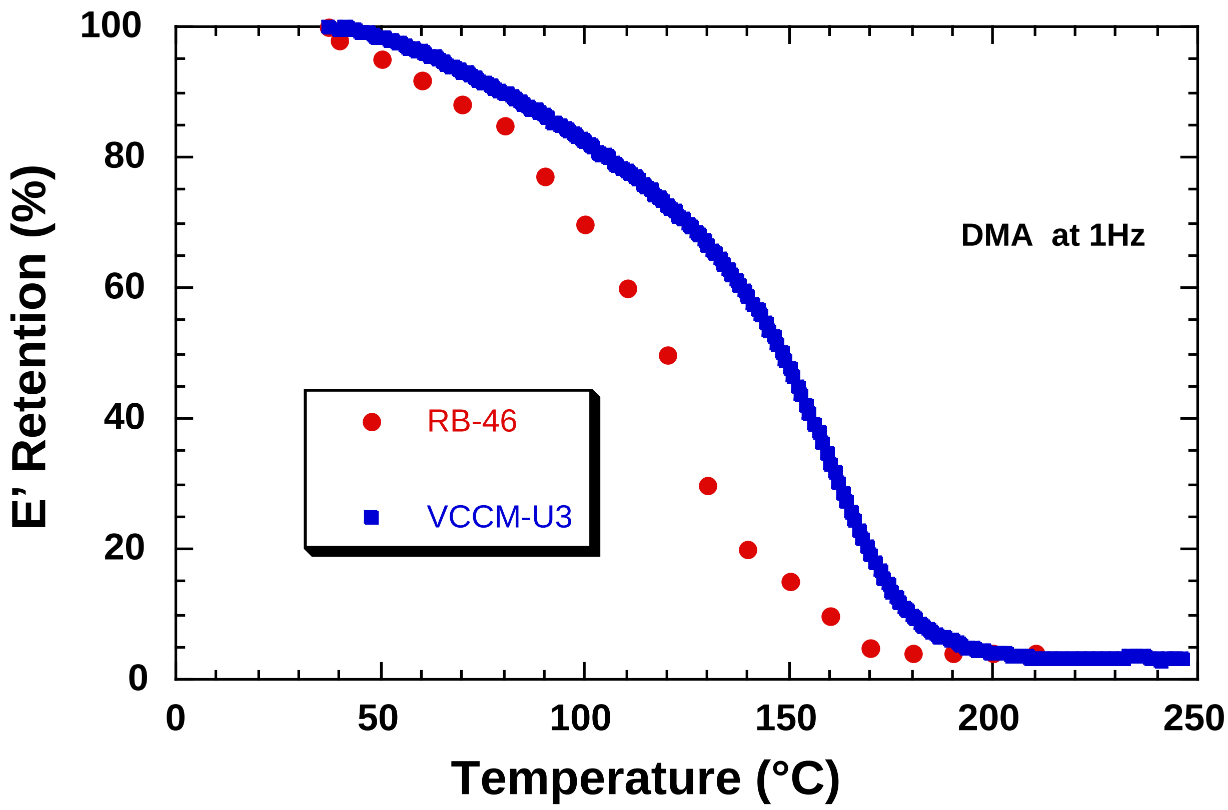
Heat to C-Stage

Radiation Crosslinking

Reactants

Goodman and Palmese U.S. Patent 5891292

IMPROVED PERFORMANCE OF IPN BASED FREE RADICAL SYSTEMS

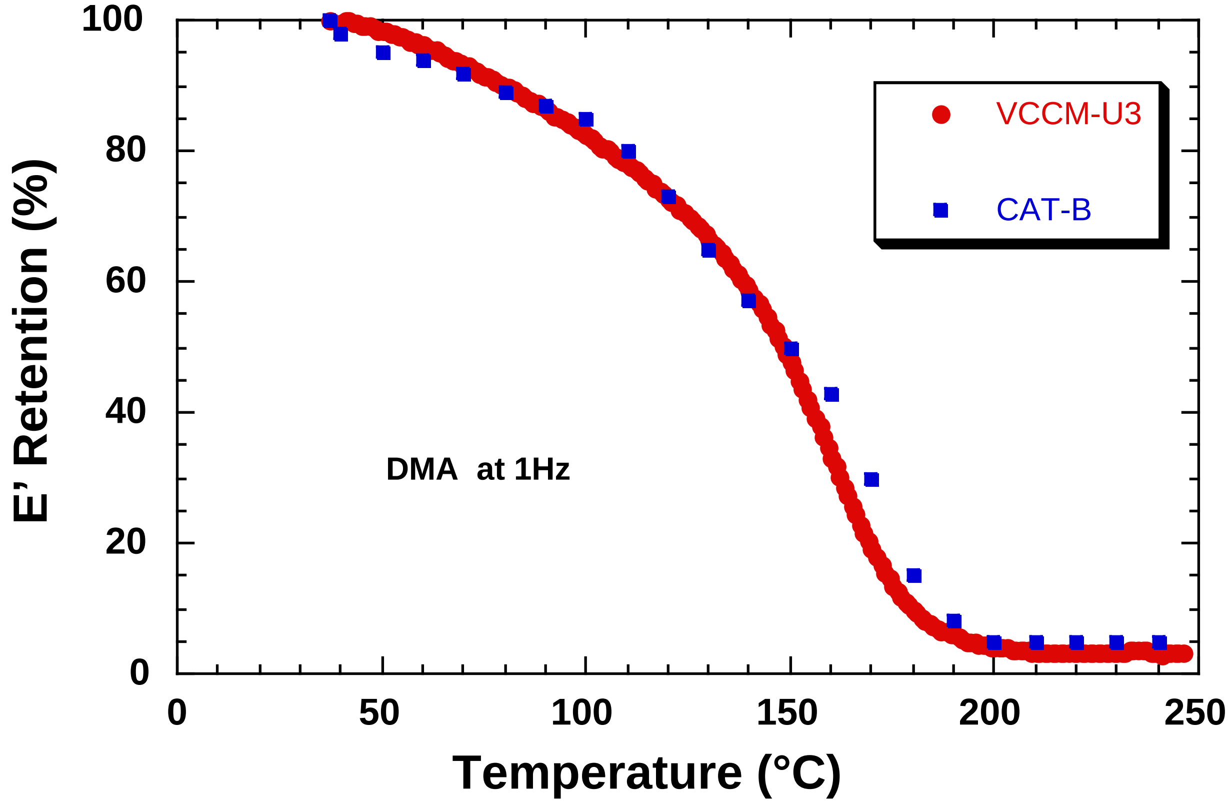


RB-46 (Aerospatiale free radical system for EB)

VCCM-U3 (free radical - epoxy IPN for EB)

University of Delaware Center for Composite Materials

COMPARISON OF STORAGE MODULUS RETENTION FOR EB-CURED CATIONIC AND FREE RADICAL IPN SYSTEMS



CAT-B (cationically cure epoxy for EB)

VCCM-U3 (free radical - epoxy IPN for EB)

RESIN PROPERTIES OF IPN BASED VARTM RESINS BEING DEVELOPED

	Viscosity (cps) R.T.	Viscosity (cps) 50°C	Tg (°C) E" (DMA)	E' (30°C) (Gpa) (DMA)	Flexural Strength (Ksi)	Flexural Modulus (Msi)	G1c (J/m2)	K1c (Mpa *m^.5)
VCCM-1	**200**	**95**	**125**	**2.5**	**16±1**	**0.57±0.03**	**380**	**1.4**
VCCM-4	**550**	**275**	**122**	**3**	**17±2**	**0.55±.04**	**710**	**1.8**
VCCM-2	**340**	**175**	**164**	**2**	**6±1**	**0.51±0.02**	**44**	**0.5**
VCCM-6	**900**	**260**	**148**	**2.2**	**7±2**	**0.48±.03**	**70**	**0.6**
VCCM-U3	**700**	**275**	**165**	**2.5**	**16±1**	**0.58±0.09**	**280**	**0.8**

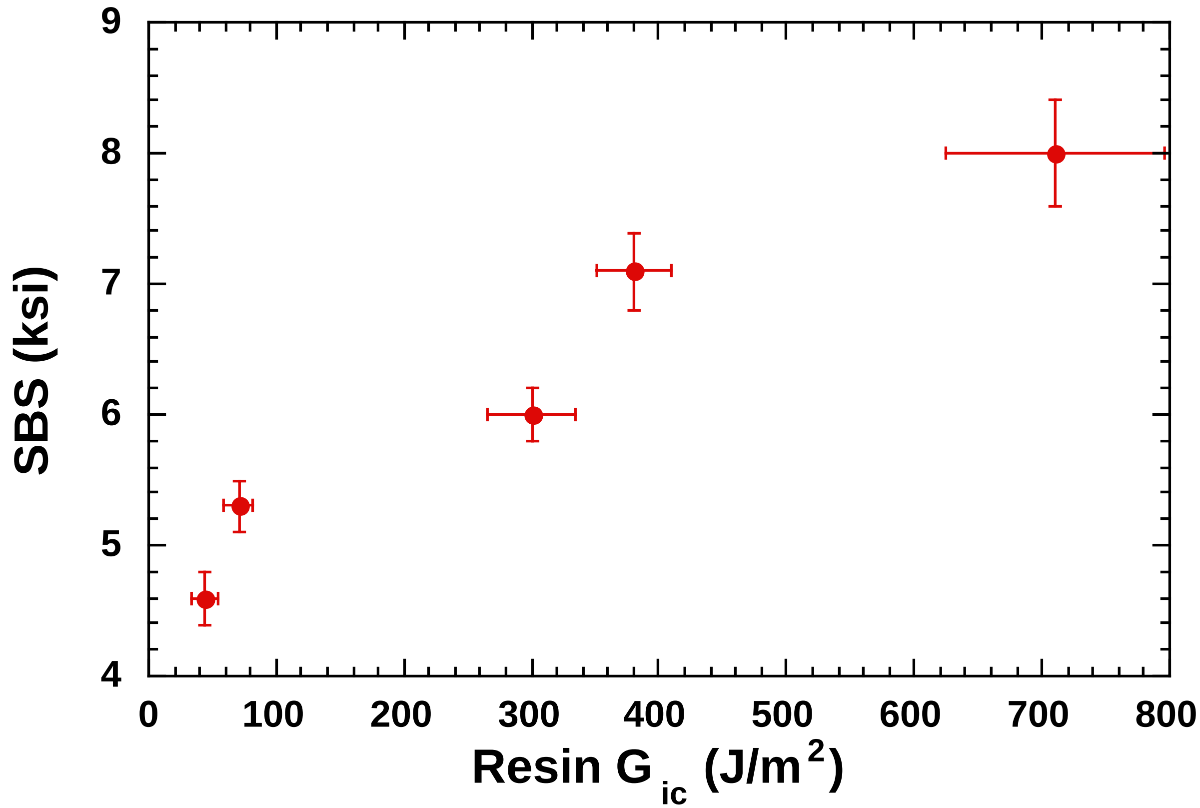
COMPOSITE PROPERTIES OF CARBON - IPN RESIN SYSTEMS PROCESSED BY VARTM

12k 5HS Grafil TR 30S

	Vf (%)	Void Content (%)	Tensile Strength (ksi)	Tensile Modulus (msi)	Compressive Strength (ksi)	Compressive Modulus (Msi)	Iosipescu Shear Strength (ksi)	Iosipecu Shear Modulus (msi)	SBS Strength (ksi)	Flexural Strength (ksi)	Flexural Modulus (msi)
VCCM-1	55	< 1	95±6	10.2±0.8	59±7	8.2±0.3	12.9±0.7	0.65±0.03	7.1±0.4	92±4	6.5±1.8
VCCM-4	55	< 1	99±3	10.0±0.6	71±5	8.7±0.3	11.6±0.4	0.64±0.04	7.9±0.3	100±4	7.7±0.6
862/lindride 6k	55	< 1	113±10	9.7±1.2	73±4	8.2±0.3	12.7±0.4	0.59±0.11	8.0±0.4	105±5	8.0±1.0
VCCM-2	55	< 1							4.6±0.2		
									VCCM-6	55	< 1

RELATION OF EB-RESIN FRACTURE TOUGHNESS AND COMPOSITE PROPERTIES

Epoxy - Acrylate IPN Systems



NOT ONLY IS INTERFACIAL BEHAVIOR IMPORTANT IN DETERMINING COMPOSITE SHEAR AND COMPRESSIVE PROPERTIES BUT ALSO THE CHARACTERISTICS OF THE RESIN, PARTICULARLY FRACTURE TOUGHNESS