Improving the Toughness of Electron Beam Curable Cationic Epoxy Resins

Chris J. Janke

Engineering Technology Division

Oak Ridge National Laboratory*

P. O. Box 2008, Oak Ridge, Tennessee 37831-8048

(865) 574-9247

jankecj@ornl.gov

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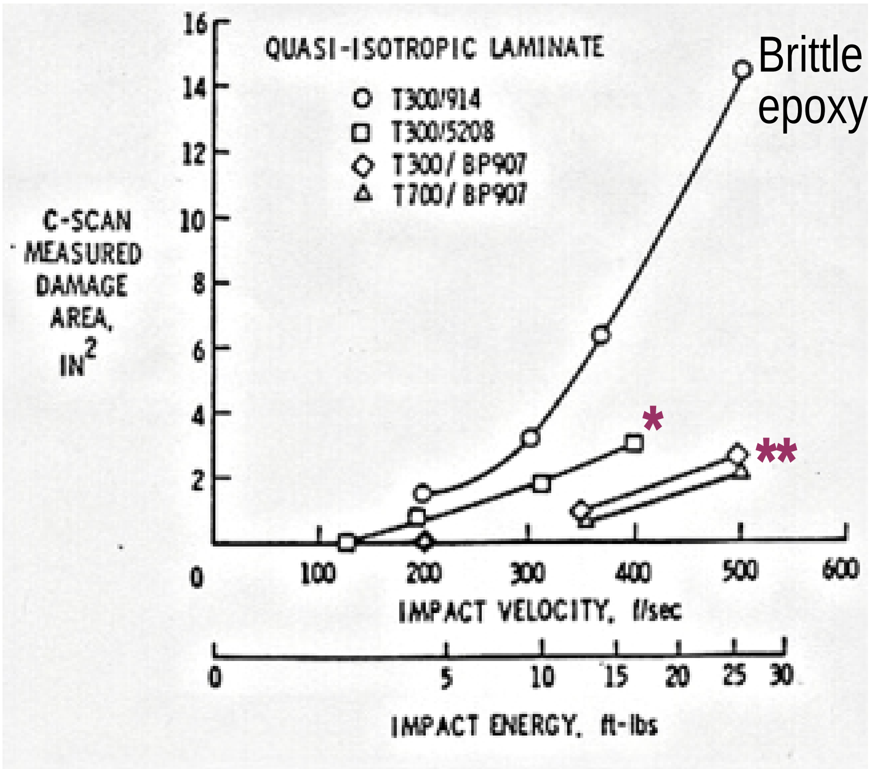
Outline

- Why are tough resins important?
- What is toughness and how is it measured?
- Relationships between fracture toughness and other composite properties
- Toughening strategies for conventional, thermally curable epoxies
- Previous toughening results on EB curable cationic epoxies from DOE DP CRADA (1994-1997)
- Latest toughening results on EB curable cationic epoxies from DOE LTR CRADA (1999-2002)

Effect of Resin Toughness and Impact Energy on Damage Size



*Untoughened epoxy (G_{Ic} = 100 J/m^2)

**Toughened epoxy (G_{Ic} = 324-397 J/m^2)

Johnston, et.al., course on "Chemistry and Properties of High Performance Composites," October 26-28, 1988, West Point, NY

- **Why are tough resins important?**
  - **Tough resins can significantly reduce the probability of catastrophic failure caused by impact damage**
  - **There is a significant decrease in the damage size for composites having toughened epoxies versus brittle epoxies**

Definitions

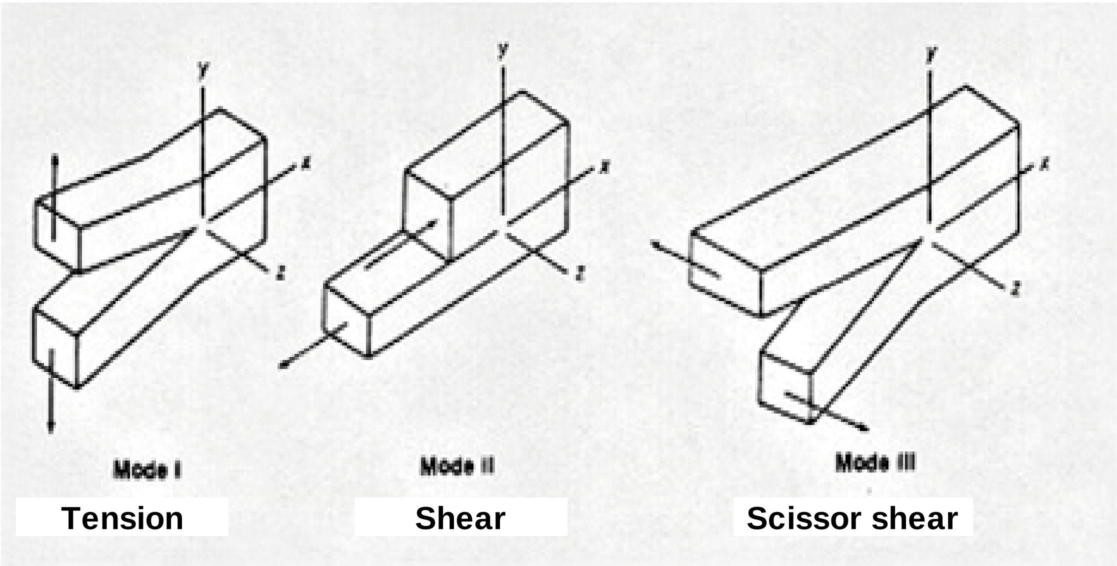
- **Fracture Toughness**
  - Measure of the damage tolerance of a material containing initial flaws or cracks
  - The resistance of a material to crack propagation
  - Fracture toughness, K_{Ic}, and fracture energy, G_{Ic} are measures of material toughness

$$G_{Ic} = \frac{(1-\upsilon^2)K^2_{Ic}}{E}$$

Where υ is poisson's ratio and

E is Young's Modulus

Basic Fracture Modes of Loading Involving Different Crack Surface Displacements



Mode I - opening or tensile loading, the crack surfaces move directly apart
- weakest and most sensitive mode
- considered the single best measure for toughness

Mode II - sliding or in-plane shear, the crack surfaces slide over one another in a direction perpendicular to the leading edge of the crack

Mode III - tearing or antiplane shear (scissor shear), the crack surfaces move relative to one another and parallel to the leading edge of the crack

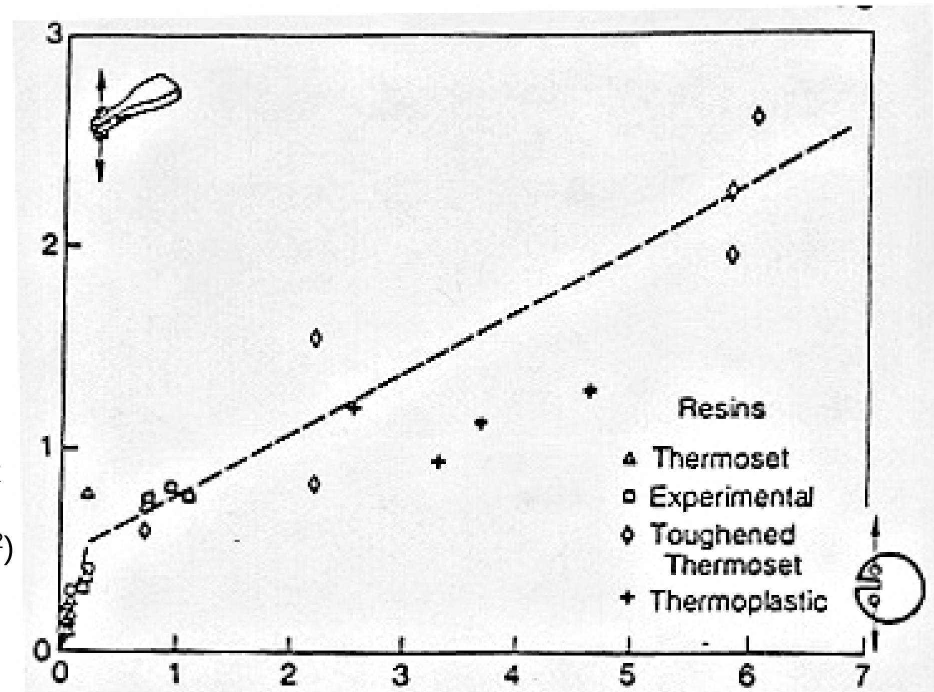
ASM Intl., "Vol. 1 Engineered Materials Handbook Composites," 1987

Battling Trade-Offs

- **CAI properties can be increased by toughening the resin matrix, BUT:**
  - **Improving CAI strength and toughness properties typically results in the reduction of 1 or more of the following:**
    - **T_g**
    - **Modulus**
    - **Hot/wet mechanical properties (esp. compression strength)**
    - **Processability**

What are the relationships between fracture toughness and other composite properties?

Relationship Between Resin G_{Ic} and Composite Interlaminar G_{Ic}



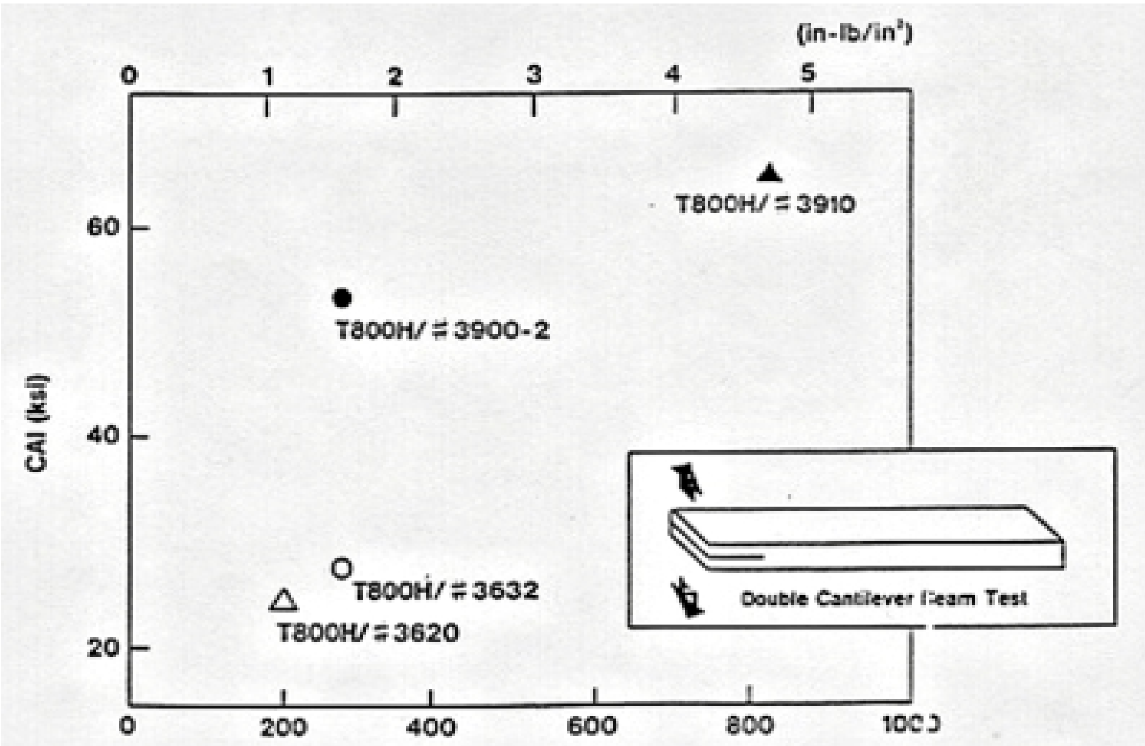
COMPOSITE INTERLAMINAR FRACTURE ENERGY (KJ/m^2)

RESIN FRACTURE ENERGY (KJ/m^2)

Hunston, Moulton, Johnston, and Bascom, ASTM STP-937, 1987

- **Composite G_{Ic} increases with resin G_{Ic}**
  - The relative effect being more significant for low values of toughness

Relation Between CAI and Mode I Fracture Toughness*

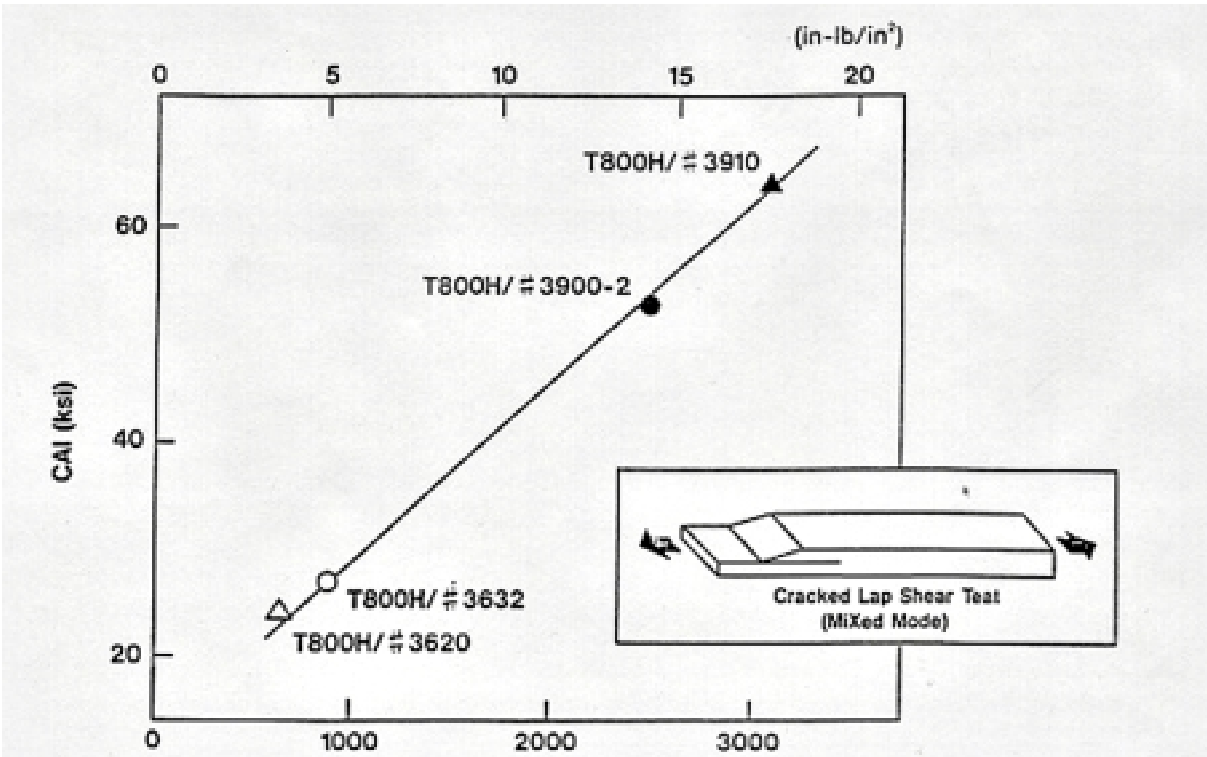


Laminate G_{Ic} (J/m²)

*Odagiri, et. al., SAMPE Preprints, 33, 272 (1988)

- **Laminate G_{Ic} typically tracks CAI**

Relation Between CAI and Mode II Fracture Toughness*

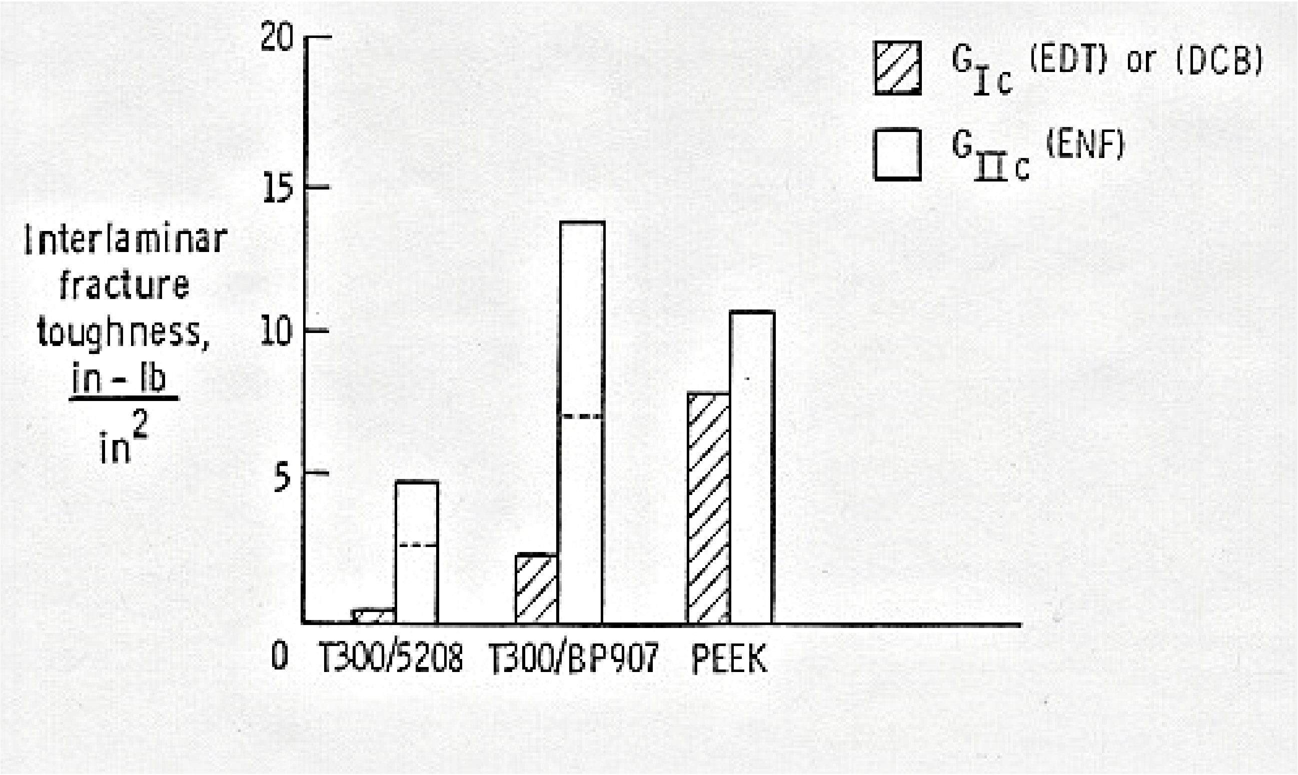


Laminate G_{IIc} (J/m^2)

*Odagiri, et. al., SAMPE Preprints, 33, 272 (1988)

- There is a close connection between laminate G_{IIc} and CAI

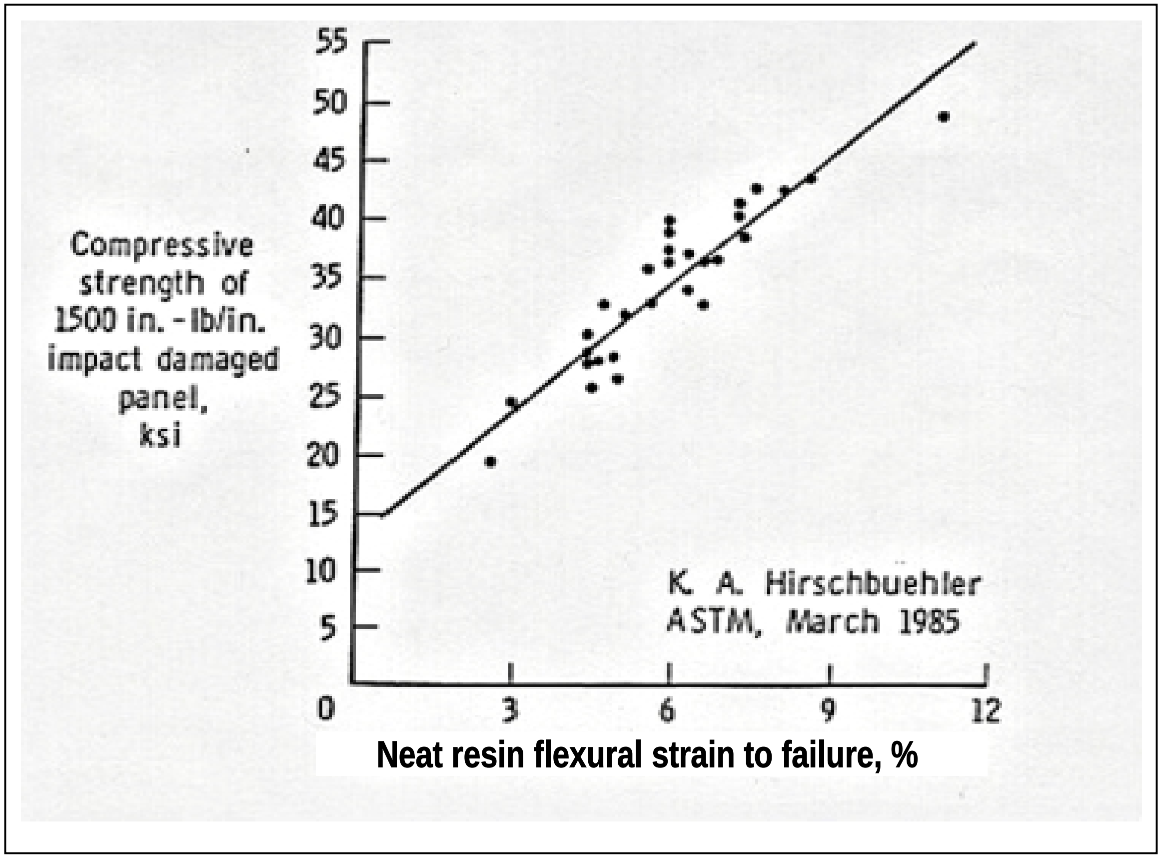
Relationship Between Composite Mode I & II as Resin Toughness Increases



Johnston, et.al., course on "Chemistry and Properties of High Performance Composites," October 26-28, 1988, West Point, NY

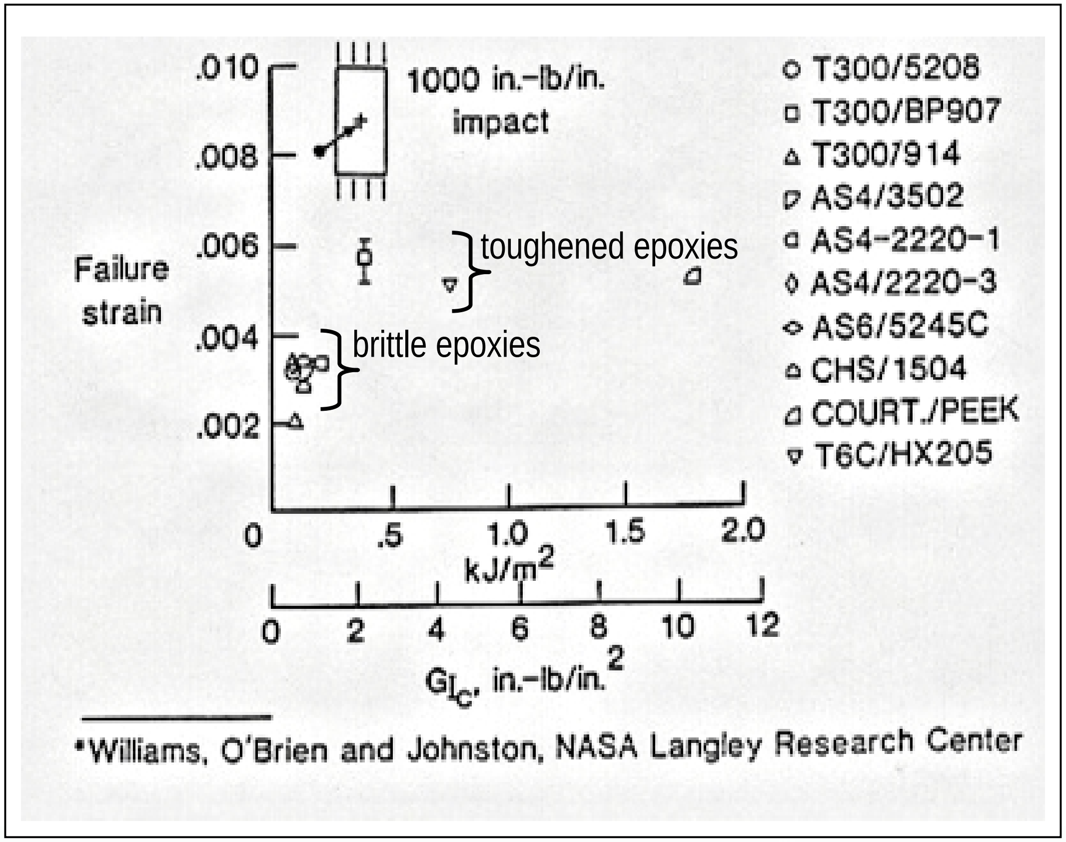
- G_{Ic} and G_{IIc} values merge closer as resin toughness increases

CAI Strength Versus Neat Resin Flexural Strain



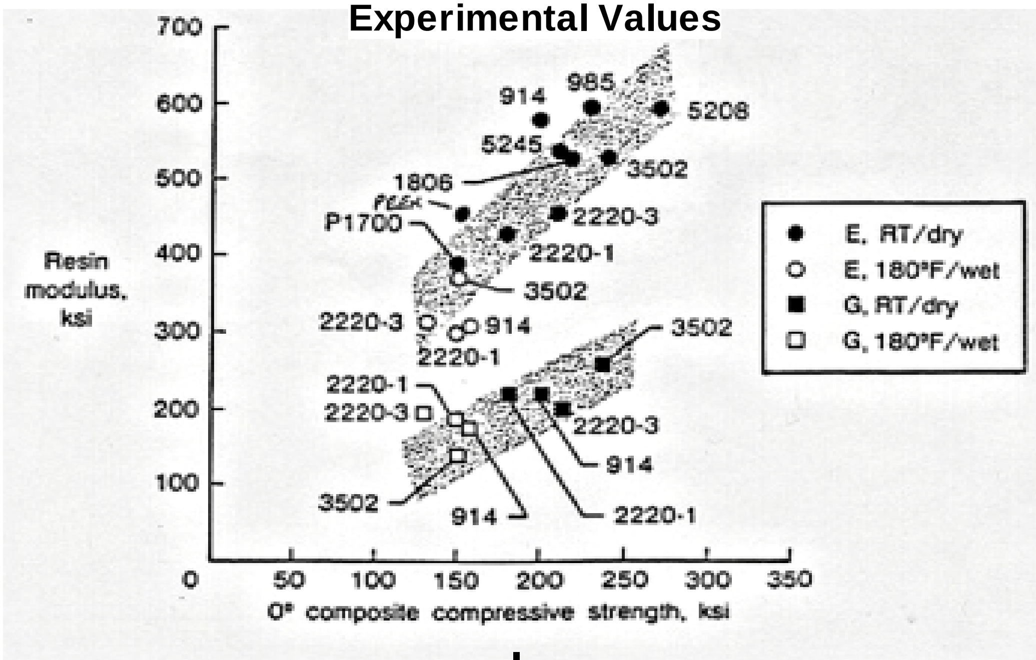
- **CAI improves as resin strain to failure increases**

CAI Failure Strain Versus Fracture Toughness*



- **Tougher resins exhibit higher CAI failure strain and composite G_{Ic}**

Resin Modulus Versus 0° Composite Compressive Strength

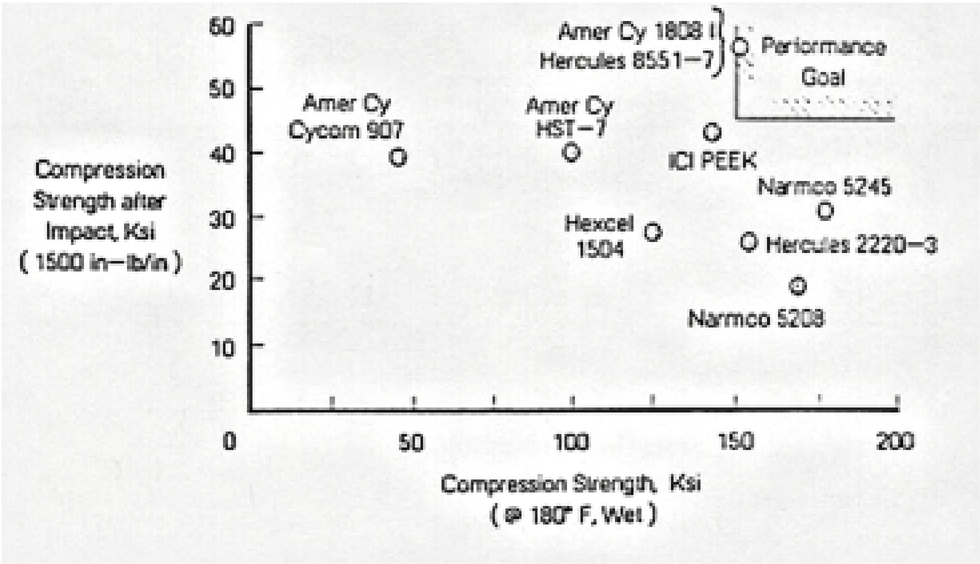


Untoughened epoxies	G_{Ic} (J/m²)	Toughened epoxies	G_{Ic} (J/m²)
5208	100	2220-1	256
3502	120-150	2222-3	220-250

Johnston, et.al., course on “Chemistry and Properties of High Performance Composites,” October 26-28, 1988, West Point, NY

- **High resin modulus is required for achieving high composite compression strength**

CAI Strength Versus Compression Strength



Untoughened epoxies	G_{Ic} (J/m^2)	Toughened epoxies	G_{Ic} (J/m^2)
5208	**100**	**8551-7**	**500**
1504	**95-123**		

*Johnston, et. al., course on "Chemistry and Properties of High Performance Composites," October 26-28, 1988, West Point, NY

- **Maximizing either CAI or compression strength alone typically results in the reduction of the other**
- **Goal is to maximize both properties by developing high modulus, highly toughened resins**

Fracture Toughness Trends

- **Modest interlaminar fracture toughness is required to prevent delamination of the composite**

- **Composite G_{Ic} increases with resin K_{Ic} and resin G_{Ic}**
  Relative effect is more important for low values of toughness

- **CAI strength is related to:**
  - **Composite G_{Ic}**
  - **Composite G_{IIc}**
  - **Resin strain to failure**

Fracture Toughness Trends Continued

- **High resin modulus is required for achieving high composite compression strength**
- **Fatigue lowers interlaminar fracture toughness**
- **Poor fiber/resin interfacial adhesion lowers interlaminar fracture toughness**

Attributes of High Performance Epoxy Resins for Military Aircraft Applications

- High toughness → High CAI
- High modulus → High compression strength
- High T_g → High service temperature

- Easily processable

Typical Methods Used for Toughening Thermally Curable Epoxy Resins

- Addition of a 2nd phase
  - Reactive rubbers (CTBN-ATBN types)
    - Acrylonitrile group inhibits cure of EB curable cationic epoxies
  - Core shell rubbers
  - Thermoplastics
- Addition of Thermoplastics (single phase)
- Increase length between crosslinks
- Interleafing
- Combinations of above

Core-Shell Rubbers

- **Description**

  Preformed particles containing an acrylic based outer-shell and a rubber core

  Outer shell may contain a reactive functional group to increase compatibility to the epoxy resin

- **Important factors affecting fracture toughness**

  Shell chemistry greatly influences resin/CSR interfacial adhesion

- **Fracture toughness mechanisms**

  Localized matrix shear-yielding

  Particle cavitation

  Rubber particle-bridging across and behind the crack tip

Advantages of CSRS Over Reactive XTBN Rubbers

- CSR particles having specific sizes are relatively easy to make
- CSRs enhance toughness with less tradeoff in thermomechanical properties
- Offers superior UV-light and thermal-oxidative aging properties

Disadvantages of CSRs

- Relatively high initial viscosity
- Particle agglomeration

Chain Extended Polymers (Increased Length Between Cross-links)

- **History (1980s)**

  Dow and Shell Chemical developed single phase, lightly crosslinked, toughened epoxy resins:

  – **Crosslinkable epoxy thermoplastics (CET resins) and**

  – **Lightly crosslinked thermosets (LXT resins)**

- **Description**

  CETs and LXTs are tough, thermoplastic-like molecular structures made in-situ using "stiff backbone" components and "flexible backbone" components

Chain Extended Polymers (Increased Length Between Cross-links)

- **<u>Advantages of CETs and LXTs</u>**

  High T_gs

  High modulus

  Excellent inherent toughness

- **<u>Disadvantages</u>**

  High temperatures (150-200°C) are required for proper chain extension reactions to occur

  EB curing favors reactions which result in poor chain extension

  Prepolymers are too viscous for EB processing

One of the Preferred Methods for Toughening High Performance, Thermal Cure Epoxies

- **Modification of epoxy resins with engineering thermoplastics (TP)**

  – **Note: Rubber-toughened epoxies (ie., XTBNs) are not used in high-performance structural composites**

    - **XTBNs improve CAI strength and strain but fail to meet hot/wet compression strength requirements due to the rubber's low T_g and low modulus**

Several Cured Morphologies Are Possible for Epoxy/TP Blends, but Not All Morphologies Are Effective

- **Non-preferred morphologies**
  - **Homogeneous, single phase**
  - **TP or epoxy particulate, second phase**
- **Preferred morphology**
  - **Co-continuous, two-phase Spinodal**

Co-continuous (Two-Phase Spinodal) Morphology Yields Optimum Fracture Toughness

- **Consists of epoxy continuous and TP continuous phases**
- **Submicron phase sizes**
- **Requires TP loadings exceeding 15-20%**
  - **TP loadings of 30-40% are the norm for high-performance, epoxy formulations**
- **Morphology, phase sizes, and ultimate toughness is controlled by TP backbone, reactive end group, molec. wt. and epoxy type**
- **Nature of the toughening mechanism is not apparent other than a roughened fracture surface**
- **Kinetics and thermodynamics of the phase separation process during cure is extremely complex**

Relevance of Co-continuous Morphology to EB Curing

Co-continuous, spinodal morphology is <u>not</u> considered a viable method for toughening EB curable resins because:

- **High TP loadings make resin viscosities too high for processing and consolidation**
- **Spinodal formation during cure may not be possible with EB due to incompatible phase separation kinetics**

Toughening Composites by Interleafing

- Interleafing incorporates high strain, resin rich zones between prepreg plies and a separate resin which surrounds the fiber
- The interleaf concept consist of an inhomogeneous resin matrix
  - Resin A between plies is significantly different from Resin B surrounding the fiber bundles
- Interleafing can produce extremely high, damage tolerant composites, but
  - Resin B must have high toughness
  - Resin A must have a rheological profile that is conducive to EB processing

Previous Toughening Results on EB Curable Cationic Epoxies From DOE DP CRADA (1994-1997)

Many Toughened and Untoughened EB Curable Cationic Epoxy Resin Systems Were Developed During DOE DP CRADA (1994-1997)

Epoxies

- Bisphenol A liquid epoxy resins
- Bisphenol F epoxy liquids
- Epoxy novolac resins
- Multifunctional epoxy resins
- Cycloaliphatic epoxy liquids
- Hydrocarbon epoxies
- Toughened epoxies
- Flexible epoxies
- Fusion solid epoxies
- Multi-epoxy resins (blends)
- Diluted liquid epoxy resins
- Multifunctional epoxy diluents

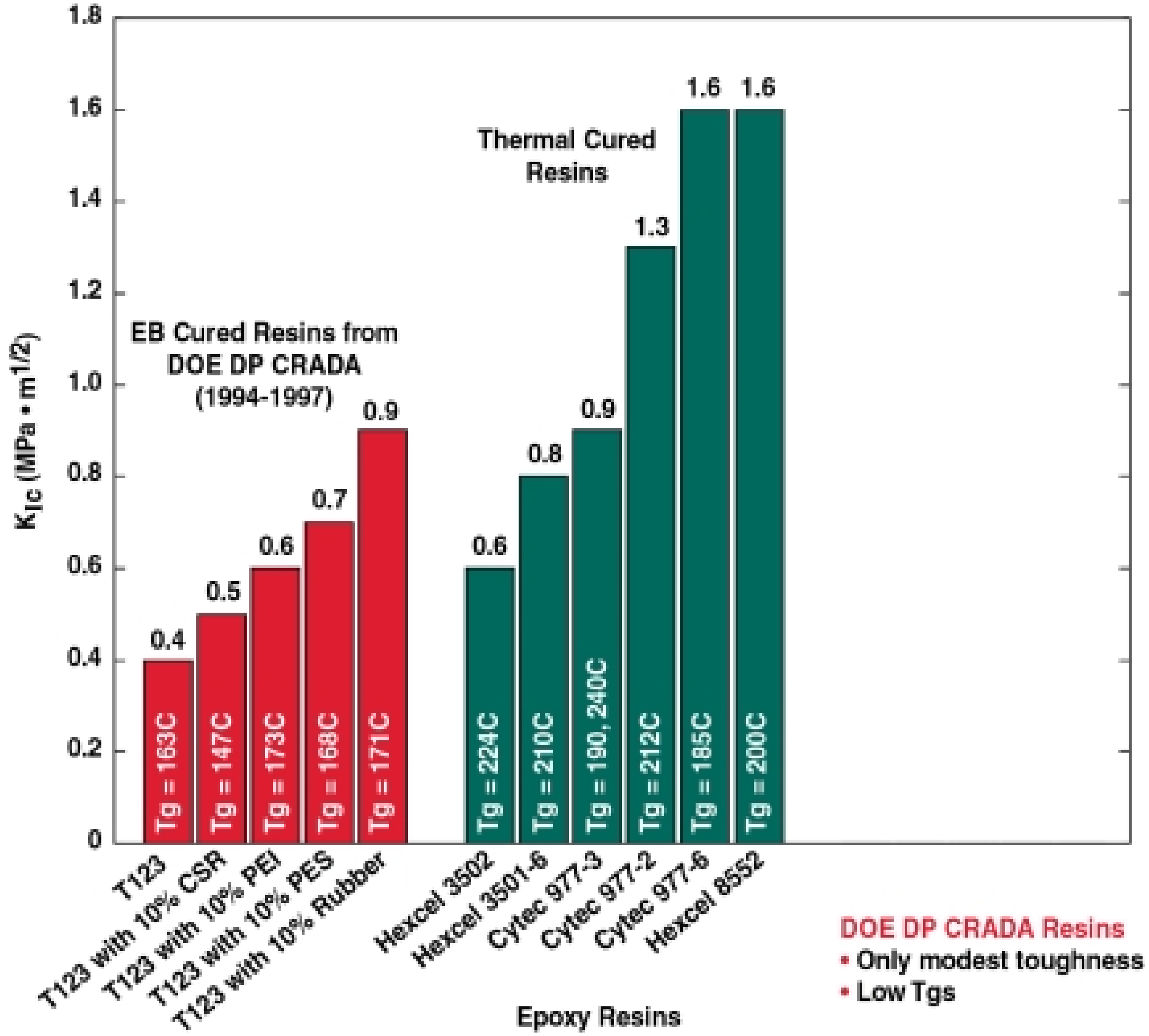
Cationic initiators (w/ various anions)

- Diaryliodonium salts
- Triarylsulfonium salts
- Iron complexes
- Diaryldisulfones
- Triazine compounds

Tougheners

- Engineering thermoplastics
- Hydroxy-containing thermoplastics
- Reactive flexibilizers
- Elastomers
- Rubbers
- Undissolved thermoset particles
- Undissolved thermoplastic particles
- Polyarylates

K_{Ic} Fracture Toughness Properties on EB Cured and Thermal Cured Epoxy Resins



Latest Toughening Results on EB Curable Cationic Epoxies From DOE LTR CRADA (1999-2002)

K_{Ic} Fracture Toughness Properties on EB Cured and Thermal Cured Epoxy Resins