

SYNTHESIS AND TOUGHNESS PROPERTIES OF RESINS AND COMPOSITES

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## TOUGHENED COMPOSITE MATERIALS PROGRAM

The multidisciplinary nature of the Langley Research Center toughened composite materials program is illustrated in figure 1, with each discipline shown in a different shaded section of the chart, from resin synthesis (upper left) clockwise to applications (lower left). Generally, materials technology, designed to develop new tougher matrices and to enhance our fundamental understanding of material behavior, is shown in the top half of the chart. Structures technology, aimed at the development and verification of new structural concepts for improved damage tolerance, is shown in the bottom half of the chart.

One of the basic objectives of the program is to establish key relationships between the various disciplines. Correlations between matrix chemistry, matrix-fiber micromechanics, fracture mechanics, and structural mechanics are sorely needed to expand both intra- and interdisciplinary capabilities and to establish trends. The main purpose of this paper is to propose relationships between matrix resin properties and selected composite properties. Such correlations will enable prediction of composite performance on the basis of resin evaluation and will be especially welcome to chemists and formulators for screening new polymer compositions without having to fabricate and test laminates.

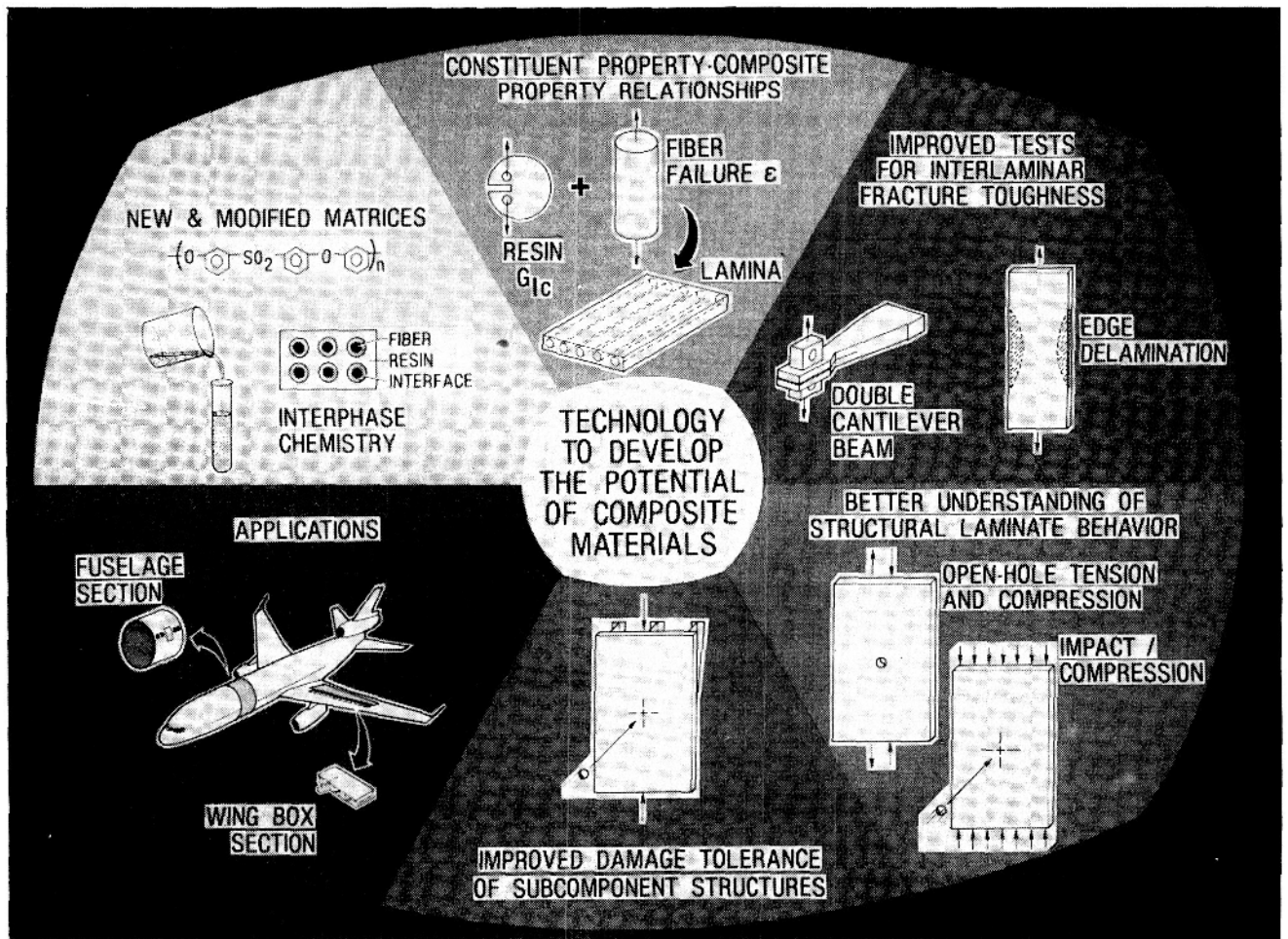


Figure 1

## OUTLINE

Three important composite properties are being investigated for their relationship to resin performance: stiffness, 0° compression strength, and interlaminar fracture toughness. Only two resin properties were used in these correlations: stiffness and fracture toughness. A list of desirable properties for neat resins used as matrices in composites for structural applications on commercial aircraft and some selected approaches to the synthesis of tough matrix resins will also be presented. An outline of the information to be discussed is shown in figure 2.

- ACEE resins and composites: 3502, 914, 2220-1, 2220-3
  - Tensile and shear moduli of resins
  - Composite modulus predictions from micromechanics
- Fracture toughness properties of resins and composites
- Relationship between neat resin properties and composite properties
  - Resin modulus/0° composite compression strength
  - Resin fracture toughness/composite interlaminar fracture toughness
  - Resin modulus/composite interlaminar fracture toughness
- Resin criteria and some synthetic approaches

Figure 2

## MATERIALS LIST

### THERMOSETS

#### First Generation Brittle Materials

|        |                        |
|--------|------------------------|
| 3502   | Hercules, Inc.         |
| 3501-6 | Hercules, Inc.         |
| 5208   | Narmco Materials, Inc. |
| V378A  | U.S. Polymeric         |
| 934    | Fiberite Corporation   |

#### First Generation Tough Materials

|       |                           |
|-------|---------------------------|
| 914   | Ciba-Geigy Corporation    |
| BP907 | American Cyanamid Company |
| F185  | Hexcel Corporation        |
| HX205 | Hexcel Corporation        |
| HX206 | Hexcel Corporation        |

#### Second Generation Tough Materials

|        |                           |
|--------|---------------------------|
| 2220-1 | Hercules, Inc.            |
| 2220-3 | Hercules, Inc.            |
| R6376  | Ciba-Geigy Corporation    |
| 5245   | Narmco Materials, Inc.    |
| 1806   | American Cyanamid Company |
| 985    | American Cyanamid Company |
| HST-7  | American Cyanamid Company |
| 1504   | Hexcel Corporation        |

### THERMOPLASTICS

|       |                                     |                              |
|-------|-------------------------------------|------------------------------|
| P1700 | Polysulfone (Udel)                  | Union Carbide Corporation    |
| PEEK  | Polyetheretherketone (Vitrex APC-1) | Imperial Chemical Industries |
| PEI   | Polyetherimide (Ultem)              | General Electric Company     |
| PC    | Polycarbonate (Lexan)               | General Electric Company     |
| PAI   | Polyamideimide (Torlon)             | Amoco Chemicals Corporation  |
| PPS   | Polyphenylenesulfide (Ryton)        | Phillips Chemical Company    |

## TENSILE MODULI OF NEAT RESINS

The University of Wyoming, under grant to NASA Langley, has a continuing program to fully characterize the mechanical and fracture properties of selected commercial and experimental resin matrix materials. In Phase I, four matrix resins used in composites being investigated by the ACEE contractors were chosen for study (refs. 1,2). Uncured neat resins were carefully deaired, poured into molds shaped to yield dogbone tensile and torsion specimens, and cured at temperatures similar to those used in composite fabrication. The cured specimens were tested both dry and moisture-saturated at three temperatures: room temperature (RT), 54°C (130°F), and 82°C (180°F). The specimens were instrumented, complete tensile and shear stress-strain curves to failure were obtained, and Poisson's ratio at each of the six exposure conditions was calculated. Coefficients of thermal and moisture expansion were determined from dilatometric measurements.

Dry and wet tensile moduli for the four resins at the three test temperatures are shown in figure 3. The largest drop in modulus from RT/dry to 180°F/wet was exhibited by 914, whereas 3502 retained the highest moduli under moisture saturation at all temperatures. Moduli at moisture saturation were almost identical for 914, 2220-1, and 2220-3.

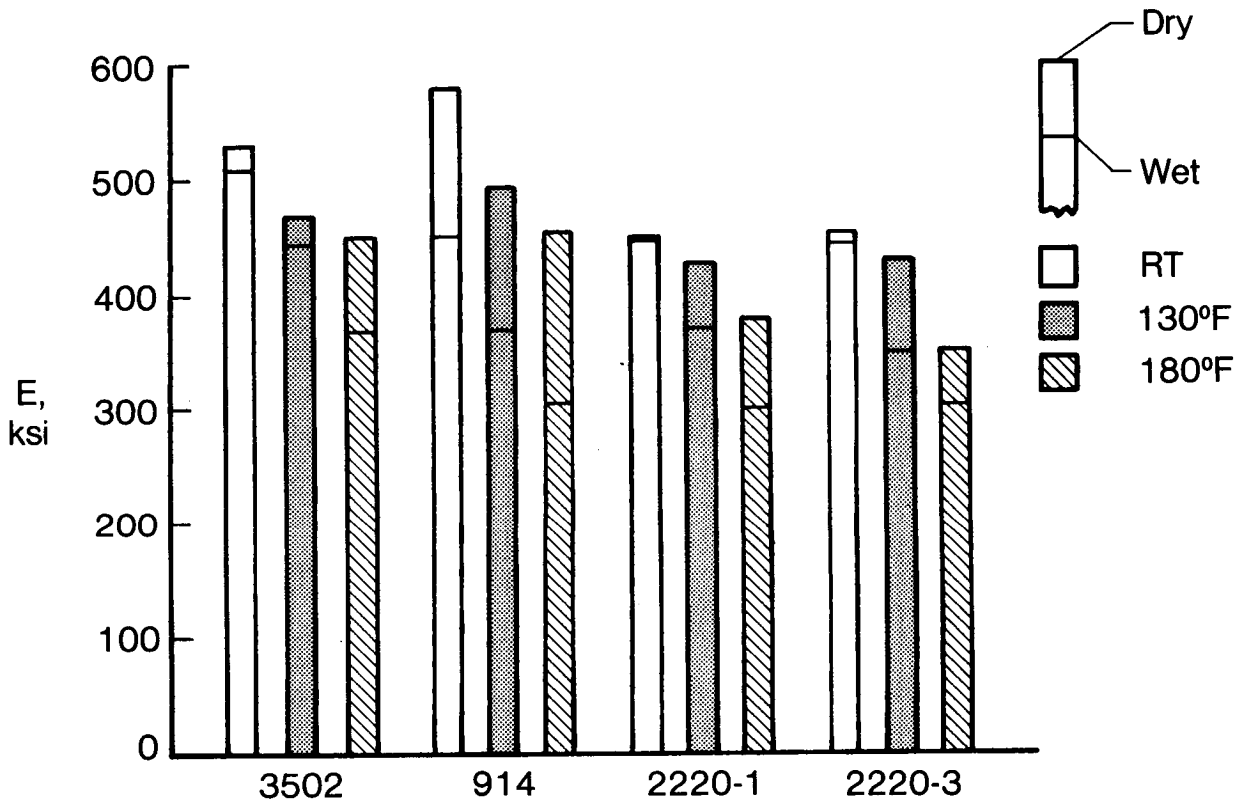


Figure 3

### SHEAR MODULI OF NEAT RESINS

Dry and wet shear moduli for the four matrix resins, 3502, 914, 2220-1, and 2220-3 (refs. 1,2), are shown in figure 4. Interestingly, 3502 had the largest drop in shear modulus from RT/dry to 180°F/wet. Shear moduli of 914, 2220-1, and 2220-3 were almost identical at all conditions except 130°F/dry.

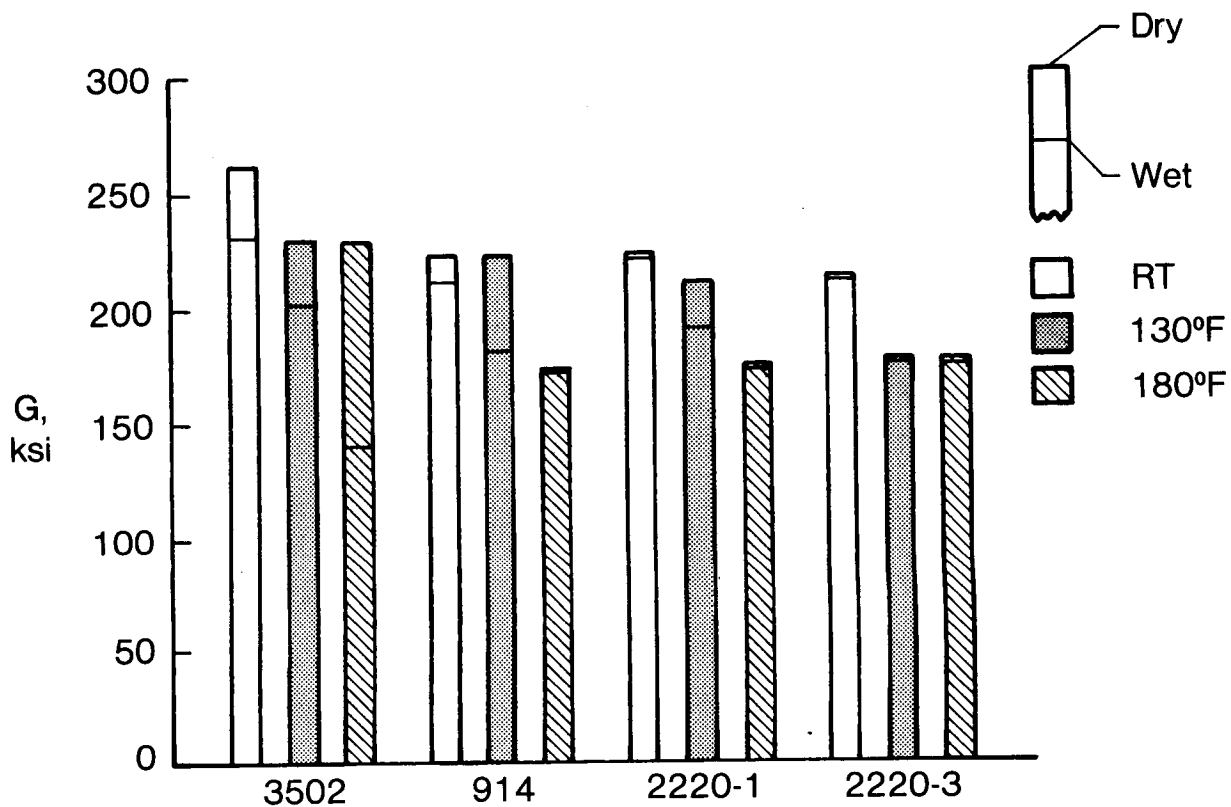


Figure 4

PREDICTIONS OF COMPOSITE PROPERTIES USING MICROMECHANICS

Using the neat resin data shown in figures 3 and 4 (refs. 1,2) and standard high tensile strength carbon fiber properties, predictions of composite longitudinal and transverse tensile moduli ( $E_{11}$ ,  $E_{22}$ ) and shear moduli ( $G_{12}$ ) were calculated using micromechanics relationships developed at the University of Wyoming (refs. 3-5). Predicted numbers for both dry and moisture-saturated conditions at two temperatures, RT and 212°F (100°C), are shown in figure 5. The  $E_{11}$ ,  $E_{22}$ , and  $G_{12}$  values for the four composite systems under any one set of conditions were very close. This would be expected for  $E_{11}$ , a fiber-dominated property. But most of the  $E_{22}$  and  $G_{12}$  values were also strikingly close, reflecting the similarities in resin moduli. Inexplicably low calculated values were observed for the 914 dry/100°C  $E_{22}$  and the 2220-3 dry and wet 100°C  $G_{12}$ .

Experimental lamina moduli under RT/dry conditions for composites made from the four resins were obtained as part of the edge delamination test program and are also listed in figure 5. These values correlated well with the predicted moduli in all cases except for the unusually high experimental RT/dry values for 3502  $E_{22}$  and 2220-3  $G_{12}$ . Notably, all experimental lamina moduli were higher than predicted.

|               | $E_{11}$ , msi |      | $E_{22}$ , msi |      | $G_{12}$ , msi <sup>★</sup> |      |
|---------------|----------------|------|----------------|------|-----------------------------|------|
|               | Calc.          | Exp. | Calc.          | Exp. | Calc.                       | Exp. |
| <u>3502</u>   |                |      |                |      |                             |      |
| Dry RT        | 20             | 21.4 | 1.40           | 1.64 | 0.69                        | 0.77 |
| Dry 100°C     | 20             | —    | 1.29           | —    | 0.69                        | —    |
| Wet RT        | 20             | —    | 1.43           | —    | 0.60                        | —    |
| Wet 100°C     | 20             | —    | 1.28           | —    | 0.54                        | —    |
| <u>914</u>    |                |      |                |      |                             |      |
| Dry RT        | 20             | 20.3 | 1.30           | 1.36 | 0.70                        | 0.80 |
| Dry 100°C     | 20             | —    | 0.88           | —    | 0.60                        | —    |
| Wet RT        | 20             | —    | 1.33           | —    | 0.62                        | —    |
| Wet 100°C     | 20             | —    | 1.18           | —    | 0.54                        | —    |
| <u>2220-1</u> |                |      |                |      |                             |      |
| Dry RT        | 20             | 20.2 | 1.36           | 1.49 | 0.65                        | 0.70 |
| Dry 100°C     | 20             | —    | 1.28           | —    | 0.58                        | —    |
| Wet RT        | 20             | —    | 1.39           | —    | 0.62                        | —    |
| Wet 100°C     | 20             | —    | 1.22           | —    | 0.60                        | —    |
| <u>2220-3</u> |                |      |                |      |                             |      |
| Dry RT        | 20             | 18.0 | 1.30           | 1.35 | 0.60                        | 0.95 |
| Dry 100°C     | 20             | —    | 1.20           | —    | 0.48                        | —    |
| Wet RT        | 20             | —    | 1.40           | —    | 0.60                        | —    |
| Wet 100°C     | 20             | —    | 1.18           | —    | 0.40                        | —    |

★ Secant modulus at 1% strain

Figure 5

RELATIONSHIP BETWEEN NEAT RESIN MODULUS AND 0° COMPOSITE COMPRESSION STRENGTH

The second important composite property to be related to resin properties is 0° compression strength. A parametric exercise involving four hypothetical resins is shown in figure 6. Values of RT/dry tensile moduli ( $E_R$ ) from 300 to 600 ksi were selected and then were decreased by about 25 percent to obtain 180°F/wet moduli. Shear moduli ( $G_R$ ) for both conditions were calculated from  $E_R$  using the standard equation shown and assuming a Poisson's ratio of 0.4. From either  $E_R$  or  $G_R$ , the 0° composite compression strengths at both conditions were calculated using an equation developed by Hahn and Williams (ref. 6) where  $K$  includes the volume fraction of the fiber, nonlinear material properties, and effects of local imperfections.

It is easily seen that if one desired a RT/dry 0° composite compression strength above 200 ksi, the RT/dry tensile modulus of the resin matrix should be above 500 ksi. Also, a 180°F/wet strength above 150 ksi would require a 180°F/wet resin tensile modulus above 350 ksi. It should be kept in mind that the 0° compressive strengths in undamaged composites should be as high as possible because of the severe strength reduction due to cross-ply construction and hole or impact damage. Thus, when developing tougher resin matrices, these strengths and their related resin moduli, especially under hot/wet conditions, should not be severely compromised.

$$G_R = \frac{E_R}{2(1+\nu)}$$

Assume  $\nu = 0.4$

$$\sigma_c = KG_R \quad \star$$

| Hypothetical resin | $E_{resin}$ (ksi) |           | $G_{resin}$ (ksi) |           | $\sigma_{composite}$ (ksi) |           |
|--------------------|-------------------|-----------|-------------------|-----------|----------------------------|-----------|
|                    | RT/dry            | 180°F/wet | RT/dry            | 180°F/wet | RT/dry                     | 180°F/wet |
| 1                  | 600               | 450       | 214               | 161       | 232                        | 182       |
| 2                  | 500               | 370       | 179               | 132       | 203                        | 160       |
| 3                  | 400               | 300       | 143               | 107       | 167                        | 138       |
| 4                  | 300               | 200       | 107               | 71        | 138                        | 94        |

★ From reference 6

Figure 6



PREDICTIVE CAPABILITY IMPROVED FOR UNIDIRECTIONAL COMPOSITE  
COMPRESSION STRENGTHS

The capability of the Hahn-Williams equation (ref. 6) to accurately predict 0° composite compression strengths from neat resin tensile moduli is shown in figure 7. Measured values of RT/dry and 180°F/wet tensile moduli for the four matrix resins, 3502, 914, 2220-1, and 2220-3 (refs. 1,2; cf. fig. 3), are given in the two columns on the left. For composites made with the four resins, predicted strengths at both conditions are listed along with measured values. The latter were obtained mostly from ACEE contractors and were usually measured on composites made with AS4 and T300 fibers. Where either experimental 0° compression data were unavailable or only one value could be found, strains from quasi-isotropic compression failures were used to calculate strengths. Overall, the agreement between prediction and experiment is very good and illustrates not only the efficacy of this predictive procedure but also the relatively high modulus values that candidate tough resins must have to afford good 0° compression strengths.

| Resin             | E <sub>resin</sub> (ksi) |           | σ <sub>composite</sub> (ksi) |   |                        |  |
|-------------------|--------------------------|-----------|------------------------------|---|------------------------|--|
|                   | RT dry                   | 180°F/Wet | RT/dry                       |   | 180°F/wet              |  |
|                   | Measured                 |           | Predicted <sup>a</sup>       | Measured                                    | Predicted <sup>a</sup> | Measured                                       |
| 3502 (Hercules)   | 530                      | 370       | 210                          | 178 <sup>b</sup> , 236,<br>270 <sup>b</sup> | 160                    | 151 <sup>b</sup>                               |
| 914 (Ciba Geigy)  | 580                      | 310       | 225                          | 160 <sup>b</sup> , 203                      | 139                    | 158 <sup>c</sup>                               |
| 2220-1 (Hercules) | 430                      | 300       | 181                          | 174 <sup>b</sup> , 181,<br>220 <sup>b</sup> | 138                    | 140 <sup>b</sup> , 148 <sup>c</sup>            |
| 2220-3 (Hercules) | 460                      | 310       | 189                          | 183-240,<br>240 <sup>b</sup>                | 139                    | 118-148 <sup>d</sup> ,<br>161-168 <sup>c</sup> |

<sup>a</sup> From reference 6

<sup>b</sup> Calculated from  $\epsilon_{quasi} \times E_0$

<sup>c</sup> 200°F/dry

<sup>d</sup> 200°F/wet

Figure 7

## RESIN MODULUS VERSUS COMPOSITE 0° COMPRESSIVE STRENGTH

In figure 8, resin experimental E and G values for RT/dry and 180°F/wet conditions are plotted against respective experimental RT/dry and 180°F/wet 0° composite compressive strengths. The four materials discussed previously (3502, 914, 2220-1, and 2220-3) are included as well as an additional six (PEEK, 985, 1805, 5245, 5208, and P1700). The data for the latter materials were obtained from the open literature and product data sheets. Roughly, a linear relationship with a slope of 2.5 seems to exist between resin E and compression strengths in the E range from 300 to 600 ksi. Based on data available from product literature, PEEK appears to be an exception, possibly because its neat resin modulus does not coincide with the resin modulus in the composite. The relationship between resin G and composite compression strength is also linear for the range shown with a slope of about 1.

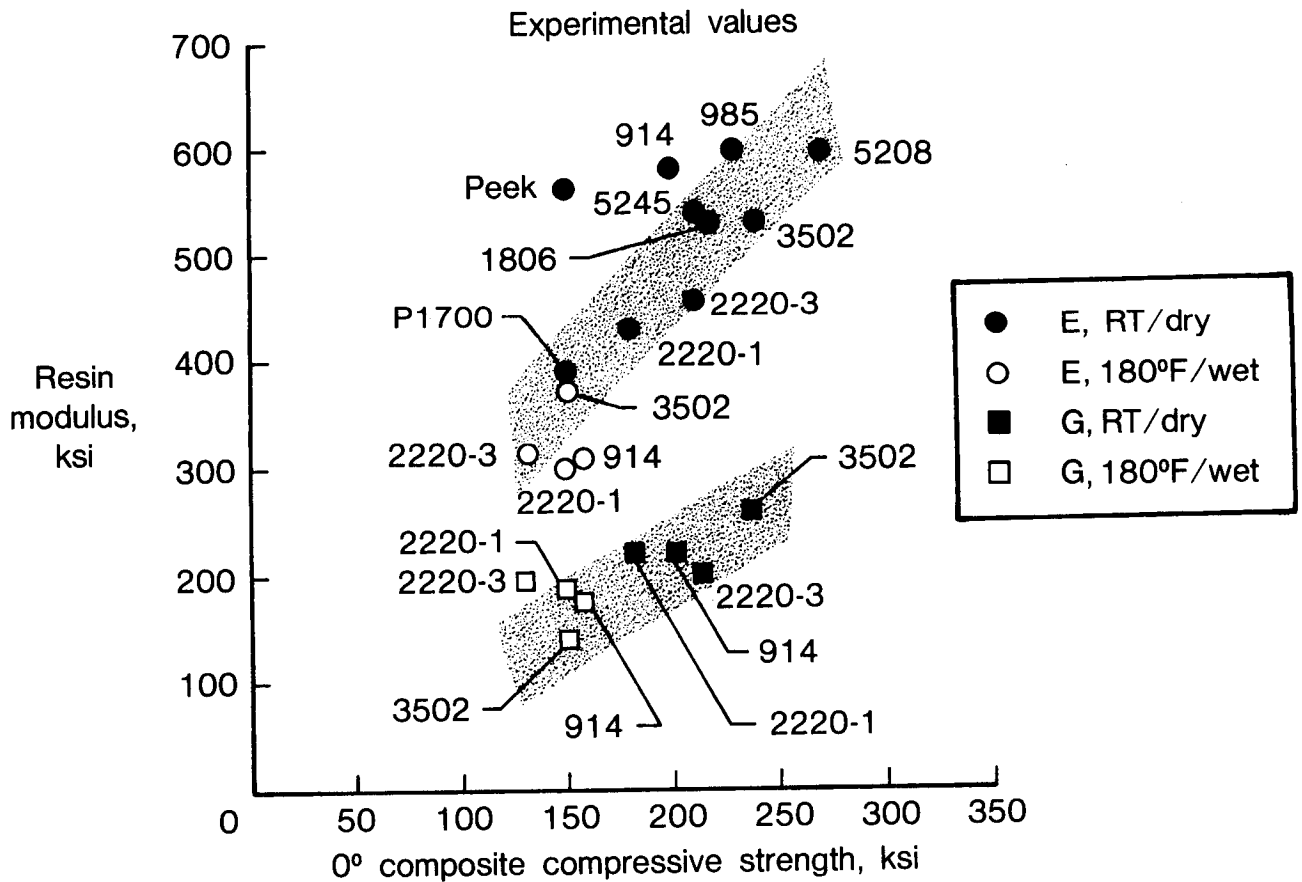


Figure 8

## INTERLAMINAR FRACTURE TOUGHNESS OF COMMERCIAL GRAPHITE COMPOSITES

The third composite property that can be related to resin performance is interlaminar fracture toughness. A long list of  $G_{Ic}$  values (measured using double cantilever beam and edge delamination tests) from in-house research, open literature, and product brochures was compiled and the data summarized on the bar charts in figure 9. Although the data are not exhaustive, they are sufficient to illustrate the following general trends.

1. Second generation 350°F cure (toughened) thermosets have, on the average, about double the  $G_{Ic}$  fracture toughness values exhibited by the first generation 350°F thermosets. Since the latter were so low, it is doubtful if this increase is significant, although the desired  $G_{Ic}$  value for optimum retention of properties in damaged panels has yet to be defined.

2. Thermoplastic materials yield significantly higher interlaminar  $G_{Ic}$  values than thermosets, even those from second generation materials. The price to be paid for this gain is an increase in fabricating temperatures and, in some cases, solvent and creep sensitivity.

3. The large gap between  $G_{Ic}$  values of 350°F thermosets and thermoplastics needs to be closed by further innovative research without compromising resin modulus and composite compression properties. This "third generation" of thermosets would fill a current need until an adequate data base and improved fabrication technology could be generated for thermoplastics.

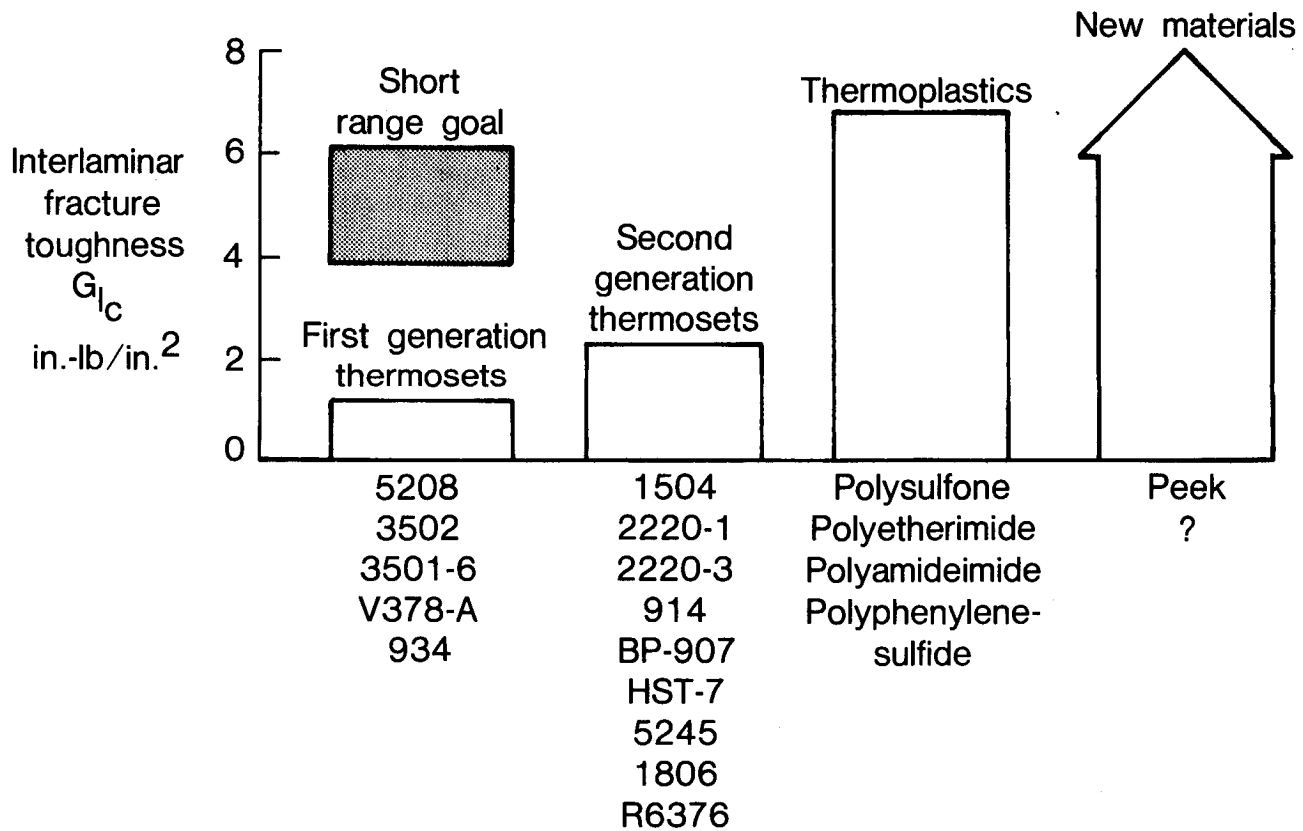


Figure 9

EMPIRICAL RELATIONSHIP BETWEEN RESIN  $G_{Ic}$  AND COMPOSITE  
INTERLAMINAR  $G_{Ic}$

Figure 10 illustrates an initial attempt to establish a relationship, albeit empirical, between composite interlaminar fracture toughness and neat resin fracture toughness. The correlation can be divided into two ranges. At low  $G_{Ic}$  values, the points for brittle materials such as 5208, 3502, and 3501-6 fall roughly above a line of slope 1, indicating the resin behavior is generally transferred fully to the composite. Because of the relatively low  $G_{Ic}$  values of second generation materials, we may speculate that the points for these materials will also fall close to this line. For the tougher materials, such as rubber-toughened epoxies (F155, HX206, F185) and the thermoplastics (P1700, PAI, PEI, PC), this relationship does not hold. The neat resin fracture behavior is not fully transferred into the composite; the relationship is roughly 3:1 to 4:1, as shown by the dotted line. One simple explanation for this is that the fibers restrict the size of the crack tip deformation zone in the composite compared to the size of the large plastic zone normally obtained with tough materials in the bulk, thereby limiting interlaminar  $G_{Ic}$ . The fact that three of the four thermoplastics fall below the dotted line can be attributed to resin-fiber interfacial failures which tend to decrease interlaminar  $G_{Ic}$  values. More data will be required, especially at the higher  $G_{Ic}$  levels, before the two relationships depicted in figure 10 can be more firmly established. Also, micromechanics analysis will be needed to understand and predict this behavior.

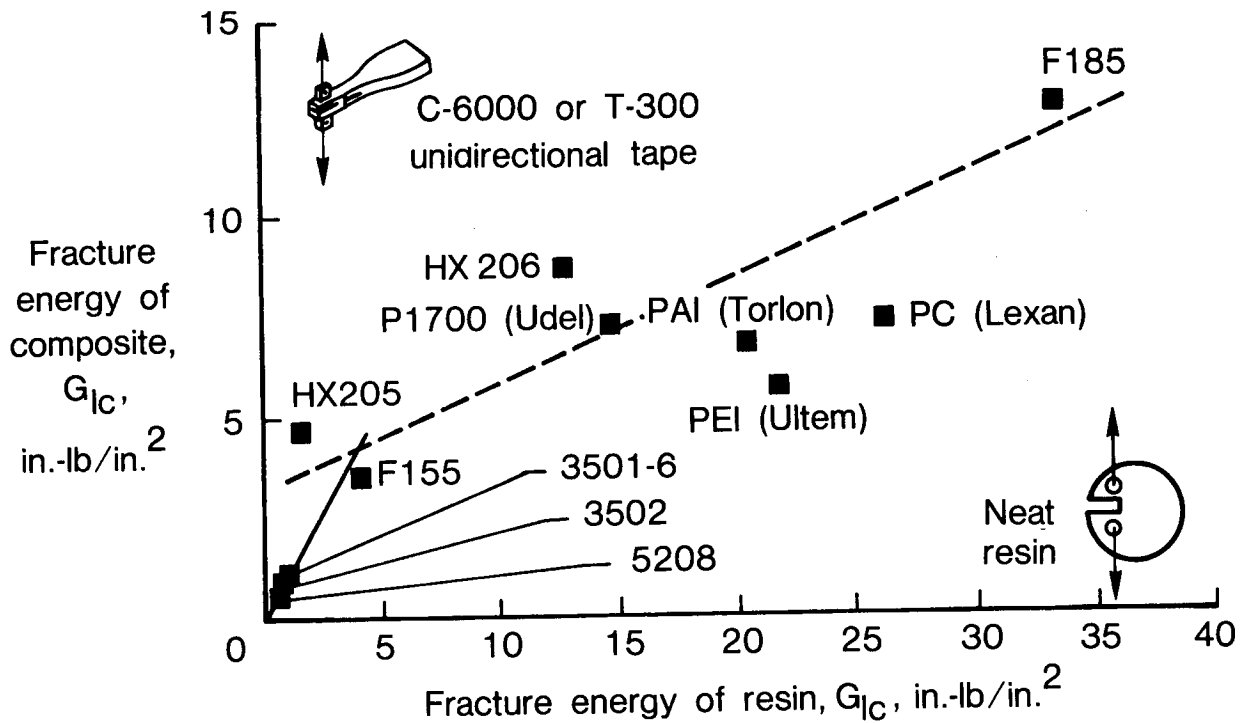


Figure 10

## RESIN MODULUS VERSUS COMPOSITE INTERLAMINAR FRACTURE TOUGHNESS

Resin tensile and shear moduli, RT/dry and 180°F/wet, were also correlated with composite interlaminar fracture toughness. Figure 11 shows the relationship for tensile modulus only, using data from the University of Wyoming studies (refs. 1,2) and commercial product literature. As expected, the trend is toward lower resin moduli as  $G_{Ic}$  values increase. However, several notable exceptions exist, namely, the values for Torlon (polyamideimide or PAI) and PEEK (polyetheretherketone). The challenge for the chemist is to develop materials such as these that do not severely compromise resin modulus (and, therefore, composite compression strength) in order to increase  $G_{Ic}$ .

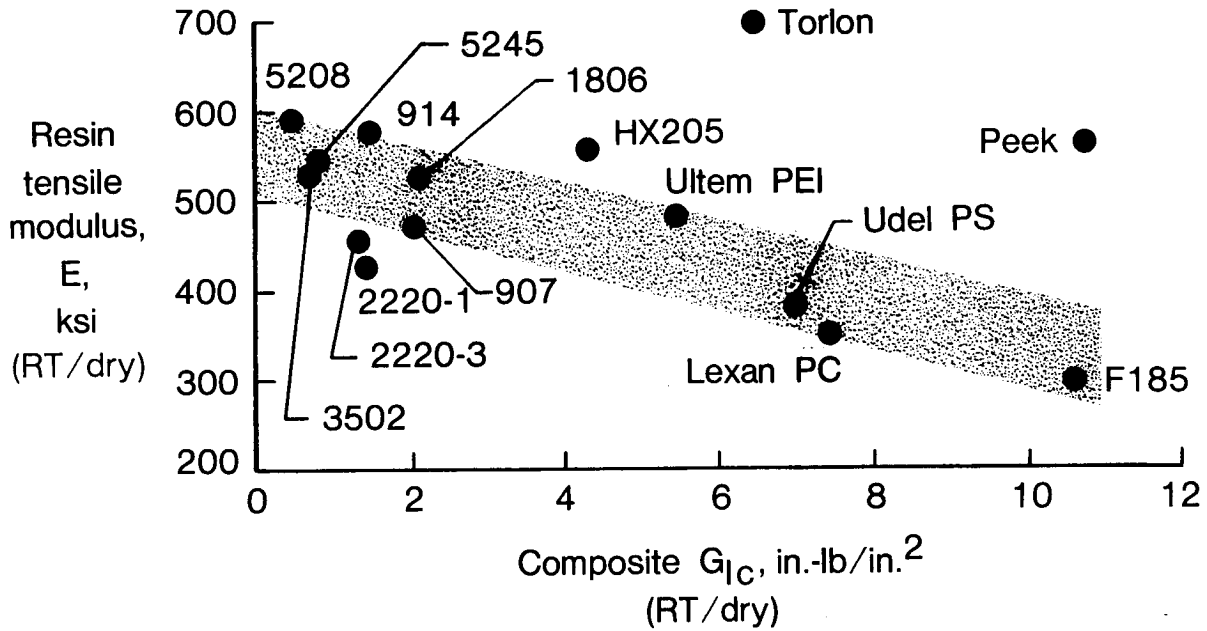


Figure 11

DESIRABLE PROPERTIES OF NEAT RESINS FOR USE AS COMPOSITE MATRICES  
ON COMMERCIAL AIRCRAFT

A list of desirable properties that a "third generation" of resins might possess in order to qualify as matrices for graphite composites to be used in structural applications on future commercial transports is proposed in figure 12. Until such time as an adequate data base and required fabrication technology can be built for thermoplastics, it is suggested that a maximum 350°F/200 psi processability be required. Resin  $G_{Ic}$  values of 11 to 17 in-lb/in<sup>2</sup> (1900 to 3000 J/m<sup>2</sup>) should be sufficiently high to afford (after a 3- to 4-fold decrease) composite interlaminar  $G_{Ic}$  values of 4 to 6 in-lb/in<sup>2</sup> (700 to 1050 J/m<sup>2</sup>). Resin tensile moduli should be well above 400 ksi, RT/dry, and above 350 ksi, 180°F/wet, to achieve acceptable composite compression strengths. For the same reason, resin shear moduli should be above 200 ksi, RT/dry, and 150 ksi, 180°F/wet.

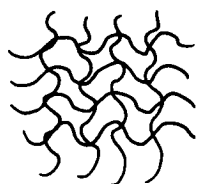
- Thermal performance range: -65° to +200°F
- Solvents: Resistance to dissolution and swelling in organic solvents in stressed state
- Moisture: Tg values sufficiently high to allow satisfactory hot/wet strengths at 200°F
- Autoclave processability: Max 350°F/200 psi
- Fracture toughness: 11 - 17 in.-lb/in.<sup>2</sup> (1900-3000 J/m<sup>2</sup>)
- Impact resistance: No requirement established for neat resin
- Stiffness: Young's modulus >400,000 psi  
Shear modulus >200,000 psi

Figure 12

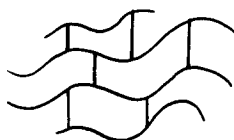
## SYNTHETIC APPROACHES

Four general approaches to the synthesis of tough resins are shown in figure 13. Examples will be presented for three of these approaches: toughened thermosets (specifically, elastomer-toughened epoxies), lightly crosslinked thermoplastics (specifically, ethynyl-terminated polysulfones), and linear thermoplastics (specifically, flexible polyimides). Some basic research into toughening mechanisms for thermosets will be presented first.

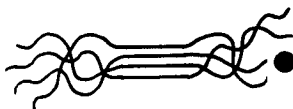
Methods for toughening thermoset matrices include adding thermoplastics, interleaving "soft" and "hard" layers, increasing the length between crosslinks, creating interpenetrating networks, using novel curing agents, and adding a second phase. Second phases may consist of a reactive rubber, an unreactive rubber, chopped fiber, fibrils, a thermoplastic, or a crystalline segment. The approach described herein is that of adding to an epoxy a reactive rubber which precipitates as a second phase when cured.



- TOUGHENED THERMOSETS  
EPOXIES, BISMALEIMIDES + THERMOPLASTIC ADDITIVES



- LIGHTLY CROSSLINKED THERMOPLASTICS  
POLYSULFONES, POLYIMIDES + CROSSLINKERS



- CRYSTALLINE THERMOPLASTICS  
POLYESTERS, POLYARYLEETHERS (PEEK, ETC.,)



- LINEAR THERMOPLASTICS  
POLYIMIDESULFONE, TPI

Figure 13

## FRACTURE TOUGHNESS IN EPOXIES CONTAINING SYSTEMATIC CHANGES IN CROSSLINK DENSITY

It is well known that brittle epoxies can be toughened by addition of a second phase, although the nature of the toughening mechanism has remained unclear. Contractual research by the General Electric Research and Development Laboratory (refs. 7,8) has elucidated this mechanism. The fracture toughness and volumetric tensile behavior of three DGEBA-DDS epoxies of varying epoxy equivalent weight were studied with and without CTBN reactive elastomer additives. Some of the data are presented in figure 14. Very little toughness enhancement occurred in the unmodified resins in spite of the reduction in crosslink density. However, for the elastomer-modified epoxies, which displayed much voiding and shearing along the fracture surface, a pronounced toughening effect of almost two orders of magnitude was observed. These results indicate that the main source of the toughness is the intrinsic ductility (as measured by crosslink density) of the host resin, in combination with enhanced shear band formation promoted by the presence of a second phase elastomer. Such information should prompt innovators to search for (1) appropriate second phases which do not compromise hot/wet properties and (2) host polymers which possess the intrinsic ductility required to unleash the toughening mechanism without severely compromising modulus.

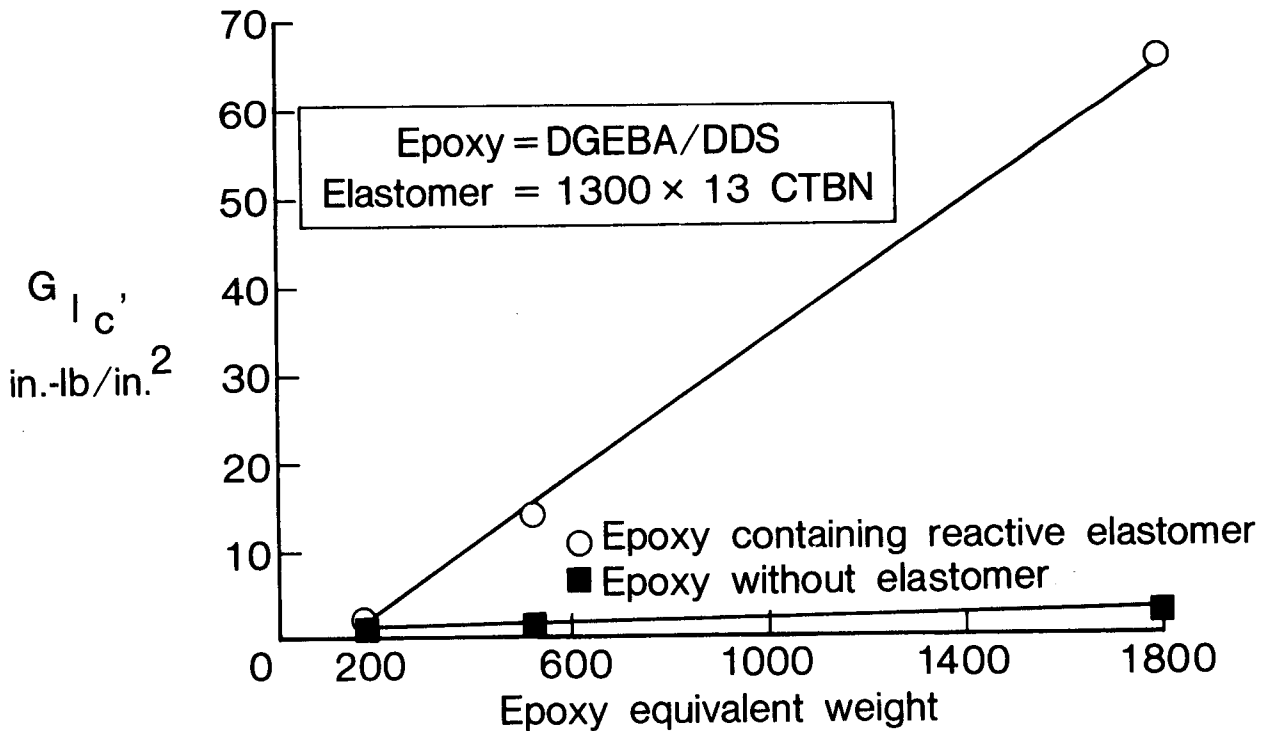


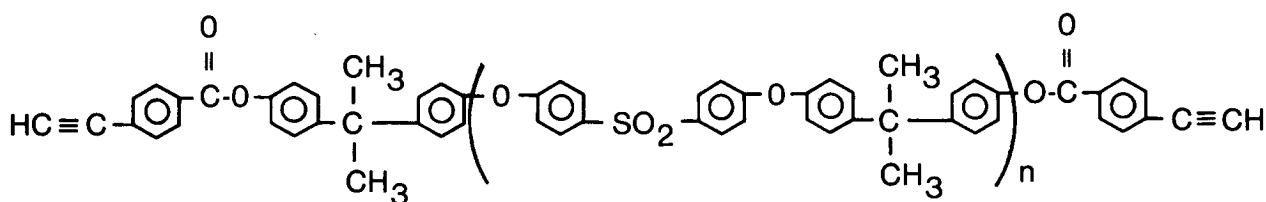
Figure 14



CROSSLINKED THERMOPLASTICS: CHEMISTRY OF CURED ETHYNYL-TERMINATED  
POLYSULFONES

Hergenrother and coworkers (ref. 9-11) have recently synthesized and characterized thermoplastic precursor polymers which contain thermally crosslinkable ethynyl groups either pendant or terminal to the main chain. The main chain repeat units included sulfone, ester, phenoxy, and phenylquinoxaline. Main chain lengths were systematically varied to determine the effect on various cured resin properties.

Figure 15 outlines the chemistry of the ethynyl-terminated polysulfone system. The repeat unit,  $n$ , was varied from approximately 7 to 59, thereby affording number average molecular weights ranging from approximately 3000 to 26000 g/mole. On thermal treatment at temperatures up to 250°C (488°F), the terminal ethynyl groups react to yield a mixture of products involving chain extension, branching, and crosslinking.



Thermoplastic precursor



Cured resin

Chain extension, branching, crosslinking  
 $n = \sim 7$  to  $\sim 59$  ( $\bar{M}_n \sim 3,000$  to  $\sim 26,000$  g/mole)

Figure 15

PROPERTIES OF CURED ETHYNYL-TERMINATED POLYSULFONES

Figure 16 presents some key properties of the cured ethynyl-terminated polysulfones (refs. 9-11). Molded specimens made from three molecular weight species, 4000, 8000, and 12000 g/mole, displayed increased resistance to swelling in chloroform as the molecular weight between crosslinks decreased. The property tradeoff to achieve this was fracture toughness ( $G_{Ic}$ ), which decreased perceptively from 12 to 4.5 in-lb/in<sup>2</sup> (2100 to 790 J/m<sup>2</sup>) as molecular weight decreased.

The properties of cured thin film having a molecular weight between crosslinks of 12000 g/mole are also shown in figure 16. The percentage elongation indicates strains to failure that are desirable in toughened materials, but the tensile modulus does not appear to be sufficiently high to produce good composite compressive strengths. The overall desirable balance of properties (modulus, solvent resistance, and fracture toughness) required in a matrix material has not yet been achieved with this class of polymers, but further property enhancements seem possible.

Molded resin

|  | <u>Molecular weight, <math>\bar{M}_n</math> (g/mole)</u> |               |               |
|--|--|---------------|---------------|
|  | <u>4000</u>  | <u>8000</u>   | <u>12,000</u> |
| $T_g$ , °C (250°C cure)                                | 202  | 200           | 196           |
| Swelling in chloroform, %                              | < 10   | ~ 20          | ~ 55          |
| $G_{Ic}$ , in.-lb/in. <sup>2</sup> (J/m <sup>2</sup> ) | 4.5<br>(790)   | 7.4<br>(1300) | 12<br>(2100)  |

Thin film ( $\bar{M}_n \sim 12,000$  g/mole)

|                        | <u>Test temperature</u> |             |
|------------------------|-------------------------|-------------|
|                        | <u>26°C</u>             | <u>93°C</u> |
| Tensile strength (ksi) | 12.1                    | 9.6         |
| Tensile modulus (ksi)  | 355.0                   | 336.0       |
| Elongation, %          | 4.6                     | 8.2         |

Figure 16

## HOT MELT PROCESSABLE POLYIMIDE

Figure 17 presents the chemistry and characterization data for a new breed of hot melt processable linear polyimides (refs. 12,13). Their main chemical structural feature is the large number of flexibilizing atoms located between the aromatic rings. These atoms serve to reduce the rigidity of the polymer backbone and, combined with the phenyl groups, tend to dilute the effect of the intractable imide moieties. The overall result is a large decrease in melt viscosity vis-a-vis ABS rubber and Torlon polyamideimide. The excellent fracture toughness combined with the high flexural modulus value and solvent resistance make these materials attractive candidates for scale-up and further evaluation as composite matrices for a variety of structural applications.

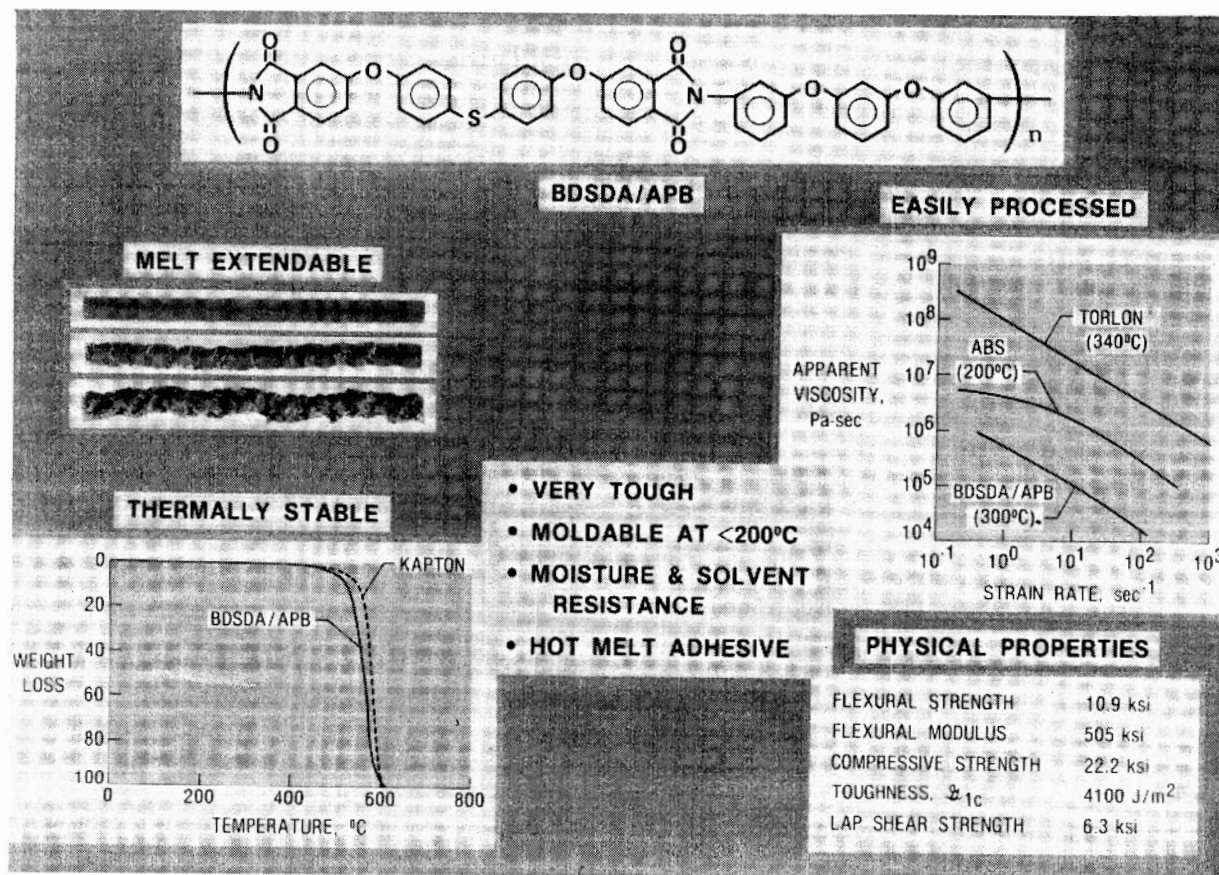


Figure 17

## CONCLUDING REMARKS

Measurements of the stiffness properties of 3502, 914, 2220-1, and 2220-3 neat resins at RT, 130°F, and 180°F under dry and moisture-saturated conditions showed that 3502 had the best retention of tensile moduli at all temperatures after moisture exposure but the poorest retention of shear modulus under 180°F/wet conditions. The largest drop in tensile modulus from RT/dry to 180°F/wet was observed for 914. The moisture-saturated tensile and shear moduli for 914, 2220-1, and 2220-3 were almost identical.

Using micromechanical relationships, stiffness properties of carbon fiber reinforced composites made from these four resins were predicted for RT and 212°F exposures under both dry and wet conditions. The RT/dry values correlated well with experimental RT/dry data. Interestingly, the predicted  $E_{11}$ ,  $E_{22}$ , and  $G_{12}$  values for the four composites under any one set of conditions were very close.

The ability to accurately predict 0° composite compression strengths from resin tensile moduli was demonstrated using an equation recently developed by Hahn and Williams (ref. 6). The relationship shows that candidate tough resins must have relatively high resin moduli to afford good 0° composite compression strengths. Experimental data from nine resins demonstrated a linear relationship in the range from 300 to 600 psi for tensile modulus versus 0° composite compression strength (approximately 2.5:1) and for shear modulus versus 0° composite compression strength (approximately 1:1).

Composites from second generation 350°F toughened thermosets have, on the average, about double the interlaminar  $G_{Ic}$  exhibited by those from first generation thermosets while thermoplastics have significantly higher values. An empirical relationship was established between resin  $G_{Ic}$  and composite interlaminar  $G_{Ic}$  in which the ratio for brittle resins is about 1:1 while the ratio for toughened resins is roughly 3:1. The latter indicates that the neat resin fracture toughness is not fully transferred into the composite.

Correlations of resin tensile and shear moduli with composite interlaminar  $G_{Ic}$  show that, with few exceptions, the trend is toward lower resin moduli as  $G_{Ic}$  values increase. This indicates that high  $G_{Ic}$  is difficult to attain without a compromise in resin modulus and related composite compression strength.

A list of desirable properties for a "third generation" of toughened 350°F cure thermosets is proposed.

For two-phase toughened thermosets, the main source of toughness was shown to be the intrinsic ductility of the host resin.

Synthetic studies show that while lightly crosslinked polysulfones do not yet exhibit the desirable balance of properties required in a matrix material, linear "flexibilized" polyimides remain attractive candidates for further evaluation.

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