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HIGH PERFORMANCE COMPOSITES RESEARCH AT NASA-LANGLEY

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ABSTRACT

Barriers to the more extensive use of advanced composites in heavily loaded structure on commercial transports are discussed from a materials viewpoint. NASA-Langley matrix development activities designed to overcome these barriers are presented. These include the synthesis of processable, tough, durable matrices, the development of resin property/composite property relationships which help guide the synthesis program, and the exploitation of new processing technology to effectively combine reinforcement filament with polymer matrices. Examples of five classes of polymers being investigated as matrix resins at NASA-Langley will be presented, including amorphous and semi-crystalline thermoplastics, lightly crosslinked thermoplastics, semi-interpenetrating networks and toughened thermosets. Relationships between neat resin modulus, resin fracture energy, interlaminar fracture energy, composite compression strength, and post-impact compression strength will be shown. Powder and slurry processing techniques will be discussed.

BARRIERS TO COMPOSITE DEVELOPMENT

HIGH PERFORMANCE COMPOSITES for commercial transports can be categorized into two broad groups, lightly loaded (secondary) structure and heavily loaded (primary) structure. In 1976, the aircraft manufacturers had only modest experience building even secondary structure with continuous carbon fiber reinforced thermosets. Development and production costs of a composite structure were high and could not be estimated with any accuracy; user acceptance was virtually nil.

Today, over a decade later, these statements no longer reflect the state-of-the-art for secondary structure, mainly because of NASA- and DOD-sponsored R&D activities and company-supported IRAD efforts. Composite secondary components developed in NASA-sponsored programs and placed in regular airline service have accumulated over four million flight hours. Weight savings of these components over their aluminum counterparts averaged 24 percent; long duration performance and maintainability have been excellent. New transports built in Europe and the U.S. make extensive use of composites in portions of the structure, mostly in lightly loaded areas. This segment of the composites market has come a long way. Yet, a proliferation of barriers still exists today to the more extensive use of composites as heavily loaded primary structure (wings, fuselage) on commercial transports. Some of the barriers are listed in Figure 1.

From a materials viewpoint, the first three place severe restrictions on the types of resins and fibers acceptable as matrices and reinforcements, respectively, for advanced composites. Figure 2 outlines some of the desired properties of the constituents in relation to these three barriers. Improved damage tolerance requires impact and delamination resistance and good residual compression strength after sustained damage. These properties, in turn, require high fiber strains, good resin shear strength, high resin modulus and fracture toughness, and good fiber/resin interfacial adhesion.

Lower material costs imply that newly developed resins and prepregs should be less expensive than the current 350°F cure epoxy products. These generally run from $40 to $100 per pound for continuous fiber (tape) prepreg.

To overcome the third barrier, labor intensive manufacturing procedures, automated composite processing technology must be developed along with compatible matrix materials. To save labor costs, standard

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press and autoclave methods will be insufficient. Robotic tape laying, filament winding, pultrusion, resin transfer molding utilizing woven textile preforms, vacuum molding, trapped rubber and inflatable mandrel thermoforming, to name some of the techniques, each will find their place in this technology and require resins with specific processing properties.

A number of company IRAD, NASA and DOD programs are aimed at developing new matrix resin to meet these demanding requirements and help overcome the critical barriers. It is important to note that these program are categorized generally according to long term structural performance in three temperature ranges:

200°F wet - Subsonic Transports
350°F wet - Advanced Tactical Fighter
400-550°F wet - Supersonic Transports and
                Engines

Thermoplastic and thermoset matrices are being developed and evaluated in all three temperature ranges. It is the purpose of this paper to describe some of the polymer matrix research on-going at NASA-Langley.

NASA-LANGLEY MATRIX PROGRAM

The major focal areas of the program are to synthesize processable, tough, durable high performance matrices; develop relationships between molecular structure, neat resin properties and composite properties; and develop processing technology to effectively combine reinforcement filaments with polymer matrices. Examples from each of these areas will be summarized in this paper.

STRUCTURE-PROPERTY RELATIONSHIPS - Guidelines for the synthesis of improved matrices come mainly from past performance weaknesses, design criteria that consider the most dangerous threat to performance degradation, process limitations and relationships (often empirical) between neat resin properties and composite properties. Utilizing all of these sources, a list of desired resin and composite properties was assembled and is shown in Table 1. These properties and their interrelationships will be discussed in some detail.

Since high performance composites are used mainly in stiffness-critical designs, the tendency when developing new materials is to maximize longitudinal moduli (> 20 Msi; Table 1) while maintaining acceptable levels of strength, strain-to-failure, fracture toughness and impact resistance. Tensile properties are fiber dominated so the choice of fiber (level of modulus, strength, strain-to-failure) is dictated by the application. The properties in Table 1 are nominal values for a high tensile strength fiber.

Compressive properties in unidirectional laminates are both fiber and matrix dependent. While compressive moduli are controlled by the fiber, compressive strength is related to neat resin shear modulus, G (1a).* In turn, for homogeneous, isotropic materials, G, is related to resin tensile modulus, E, via Poisson's ratio, ν. Table 2 shows the relationship between E and composite unidirectional compressive strength for four hypothetical resins. From the table, it is easily seen that to achieve a room temperature 0° compressive strength above 200 Ksi, a highly desirable value, E should be near 500 Ksi (1b). The latter value represents a key goal in the design and synthesis of new materials. For values of E and ν of 500 Ksi and 0.35, respectively, a G near 200 Ksi is required.

Resin strengths should be relatively high to prevent or minimize intraply cracking in the composite under impact conditions and also to afford good transverse properties. Sufficient resin fracture toughness is required to prevent cracks or defects from propagating, especially to a crossply interface, and leading to delamination and severe diminution of mechanical properties. A resin fracture energy of 5-11 in.-lb./in.^{2} is suggested as sufficient and represents a second important goal in the design and synthesis of new matrices. This value will be further justified in a later discussion on post-impact compression properties.

A key property driver for high performance composites used in commercial transports is the retention of compressive strength and strain after impact. The test is usually performed on a 1/4-inch thick quasi-isotropic panel using as the impactor either a Gardner drop weight or a low velocity aluminum ball. Accepted compressive strengths in an undamaged quasi-isotropic panel range from 100 to 110 Ksi and strains from 1.5 to 2.0 percent. For a damaged panel, a residual strength of 50 Ksi with 0.6 percent strain is highly desired. What neat resin properties are needed to achieve such performance?

First, the neat resin modulus must be near 500 Ksi in order to yield a compressive strength near 200 Ksi for a unidirectional panel and near 100 Ksi or as high as possible for an undamaged quasi-isotropic panel.

Second, a modest amount of interlaminar fracture toughness is required to prevent impact-generated cracks from propagating and causing excessive delamination. In other words, while damage prevention is highly desired, damage containment is crucial. A plot of compressive strain after impact versus interlaminar fracture toughness, G_{Ic}, is shown in Figure 3 and indicates that post-impact compressive strain maximizes at approximately 4 in.-lb./in.^{2} of interlaminar fracture energy, then levels off (2). Higher G_{Ic} values do not help but may even hinder

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if they are achieved by compromising neat resin modulus. Apparently, delamination is the predominant mode of failure up to a given G_{Ic} level. Then, other failure modes not influenced by resistance to delamination dominate. To be conservative, an interlaminar fracture toughness range from 4 to 6 in.-lb./in.^{2} was chosen as desirable. Then, by using the relationship between interlaminar G_{Ic} and neat resin fracture energy, Figure 4, it can be seen that a desired value for resin fracture toughness ranges from 5-11 in.-lb./in.^{2} (3).

When two of the key synthetic properties, resin modulus and resin or composite fracture toughness are plotted together, Figure 5, it is tempting to conclude that as modulus increases toughness decreases, a traditional point-of-view (see shaded area) (4). But, as more recent data on high performance polymers such as PEEK, Torlon and K-III, have become available, it can be seen that high values of both properties can be achieved (5). This should be good news for both the synthetic chemist and the composites engineer, provided these neat resin properties are effectively translated to the composites.

It should be noted that both high resin modulus and modest fracture toughness are required for acceptable post-impact compressive properties. High modulus resin alone is unacceptable since impact will cause severe delamination and low compressive values. Apparently, a reasonable degree of transverse shear deformation in the composite is required to prevent/contain impact damage (6). This property is manifested through the ability of the matrix to yield and absorb energy while maintaining a reasonably high stiffness to support the fibers.

The synthetic chemist must also seriously consider the processability of a potential matrix. The impregnating resin must have a long shelf life and be easily quality controlled. It must be capable of penetrating carbon fiber tow bundles and wetting each filament. It should yield prepreg with the good tack and drape necessary for layup of curved articles. It should be capable of fast processing cycles. While 350°F cure toughened epoxies seem to dominate the subsonic transport market because they meet many of these processing standards, the ideal thermoset or thermoplastic matrix for elevated temperature applications has yet to be developed. In addition to those requirements just listed, some additional highly desired features of such a matrix are given below. They represent further key goals for the synthetic chemist to contemplate in his development of high performance matrix materials designed to overcome the critical barriers listed in Figure 1.

o Monomer or oligomer
o Simple stable formulation
o Liquid or low melting solid
o Polymerizes without evolution of

o volatiles
o Forms solvent resistant, tough, durable polymer

SYNTHESIS PROGRAMS - Five classes of polymers being investigated as matrix resins at NASA-Langley are listed below:

o Amorphous thermoplastics
o Semi-crystalline thermoplastics
o Lightly crosslinked thermoplastics - reactive groups terminal, pendent or within the chain
o Toughened thermosets
o Blends and semi-interpenetrating networks (thermosets)

The chemistry and properties of examples from each class will be briefly described.

AMORPHOUS THERMOPLASTICS - LARC-TPI, whose chemical structure is given in Figure 6, is a tough, high modulus (E = 540 Ksi) amorphous polyimide containing meta catenation in the diamine-derived portion of the molecule (7). It was developed at NASA-Langley as a high temperature adhesive for titanium, composite and polyimide film adherends (8). Its potential as a composite matrix appeared to be nil because of lack of melt flow during prepreg consolidation. Recent work at Langley has shown, however, that the addition of small quantities of low molecular weight bisamideacids to polyamic acid solutions enhance the melt flow properties of the corresponding polyimides (9). Preparation of the bisamideacid from PMDA and aniline is shown in Figure 7. Addition of 2.5 percent of this additive to LARC-TPI sufficiently improved melt flow properties to allow well-consolidated unidirectional graphite panels to be fabricated.

Short beam shear and flexural properties of these laminates are given in Table 3 along with the corresponding properties of poorer quality laminates made from LARC-TPI without additive (10). The enhancement in composite properties is striking. This technique of improving melt flow has been demonstrated with other low flow polyimides such as polyimide-sulfone (E = 719 Ksi), whose structure is shown in Figure 6; 6F-BDAF soluble polyimide; and a copolyimide derived from BDSDA, 4,4'-ODA, and m-PDA (9,10).

Another technique discovered at NASA-Langley for enhancing the melt flow of poly-imides was to add a low molecular weight, low melt viscosity, insoluble crystalline poly-imide powder to the polyamic acid solution (10). The resultant slurry was easily pre-pregged because the particle size of the pow-der was sufficiently small to allow penetra-tion of the tow bundles. The polyamic acid acts as a binder to aid the attachment of the polyimide powder to the individual filaments.

Studies at NASA-Langley have concentrated on the crystalline LARC-TPI 2000 imidized powder from Mitsui Toatsu. The complex viscosity of this powder versus cure time at three temperatures is given in Figure 8 (11).

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It can be seen that melt viscosities as low as 100-1000 poise can be achieved for up to one-half hour before chain propagation reactions cause an increase in molecular weight with a concomitant increase in melt viscosity. Melt flow numbers of various blends of LARC-TPI powder in LARC-TPI polyamic acid and LARC-TPI powder in $PISO_2$ polyamic acid are shown in Figure 9. These data were taken from parallel plate plastometer experiments at 325°C and 171 psi. The flow increases dramatically with increasing amounts of LARC-TPI powder.

Various ratios of crystalline to amorphous resin were studied as matrix materials. In all cases, well-consolidated unidirectional graphite composites could be fabricated. Outstanding short beam shear and flexural properties were obtained with both the LARC-TPI powder/LARC-TPI amorphous system, Figure 10, and the LARC-TPI powder/$PISO_2$ amorphous system, Figure 11, especially when these properties are compared with those from panels made with the virgin amorphous polymers.

The use of a powder slurry blend to increase melt flow and enhance prepreg consolidation should not be limited to crystalline-amorphous polyimide systems. Combinations of other polymer classes can be envisioned to produce high flow thermoplastic matrices. Also, the powder slurry blend technique when applied to polyimides can be used in combination with bisamide acid dopants to further enhance flow properties. Such studies are currently being investigated at NASA-Langley. Large skin-stringer panels containing up to 32 plies in some areas have been successfully fabricated in the autoclave with prepreg prepared from a slurry of LARC-TPI powder in amorphous $PISO_2$ solution containing 2.5 percent bisamide acid dopant (12).

CRYSTALLINE THERMOPLASTICS - The chemistry of a new class of semi-crystalline polyimides developed at Langley is shown in Figure 12 (13). The diamines are easily synthesized from halogenated diketones and aminophenol as shown on the bottom of Figure 12. The diketone is economically prepared via a Friedel Crafts reaction of bisacid chlorides and halobenzenes. Of the many polymers prepared by this scheme, one of the most attractive is shown along with some properties in Figure 13. The high Tg, modulus and toughness values are extremely attractive. Tensile properties of films soaked 100 hours in 30 percent sodium hydroxide or hydraulic fluid or held three days in boiling water remained virtually unchanged. Over 90 percent retention of room temperature film tensile properties was observed after 100 hours aging at 316°C in air. Most of these properties can be attributed to the semi-crystalline nature of this material. The material also has outstanding adhesion to titanium. Current investigations are aimed at controlling molecular weight in order to increase melt flow properties. Then, composite studies will be initiated.

BLENDS AND SEMI-INTERPENETRATING NETWORKS - These thermoset materials are made by addition polymerization of a precursor thermoset oligomer in the presence of a higher molecular weight linear polymer. One advantage to this approach is that the polymerization is conducted as part of the fabrication process and usually requires much milder conditions than those required to process thermoplastics. Another advantage is that the resulting network, if properly configured from compatible components, does not need to possess multiphase morphology to exhibit good fracture toughness and mechanical properties. A third advantage is that no volatiles are evolved during the polymerization. The technique has been used extensively to developed tough 350°F cure epoxy matrices such as Ciba 914 and Hercules 8551-7, which are multiphase systems. Studies at NASA-Langley have concentrated on polyimide semi-IPNs which are constructed from chemically similar building blocks and apparently do not exhibit separate phases.

One composition, still under investigation, was designed to toughen bismaleimides. The reaction scheme is shown in Figure 14. (14). A sulfone BMI powder was added to a $PISO_2$ polyamic acid solution to form a slurry which was prepregged onto carbon fiber and easily fabricated into well-consolidated graphite composite plates. Melt flow was exceptional. Short beam shear and flexural properties shown in Table 4 were outstanding. Further, short beam shear strengths at 400°F were almost identical to room temperature values. However, the composites did not exhibit improved interlaminar fracture toughness. Apparently, the molecular weight of the BMI was so low that it formed a crosslink density too high for the network to be "toughenable" (15). Higher molecular weight versions of this BMI have been synthesized and are under investigation.

The preparation of semi-2-IPNs from acetylene-terminated polyimidesulfone oligomer and high molecular weight polyimidesulfone is shown in Figure 15 (16). The crosslinked and linear components were combined in various ratios to optimize the formulation. Mechanical properties of woven graphite composites made from a 65:35 crosslink:linear system are also given in Figure 15. The values are quite respectable for fabric laminates. Similar studies were performed with linear high molecular weight LARC-TPI combined either with an acetylene-terminated LARC-TPI oligomer or with Thermid LR 600 acetylene-terminated oligomer (17).

LIGHTLY CROSSLINKED THERMOPLASTICS - Several approaches were studied to increase the processability, solvent resistance and moduli of polyarylene sulfones without severely compromising fracture toughness. They involved attachment of crosslinking groups either within the main chain, pendent

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to the chain or at the chain ends, in each case varying the chain length to control crosslink density and optimize the desired properties. The chemistry and properties from one approach utilizing ethynyl-terminated polysulfones are shown in Figure 16 (18). Various molecular weight hydroxyl-terminated polysulfones were synthesized and endcapped with p-ethynyl benzoyl chloride. Properties of neat resin moldings show that as the calculated number-average molecular weight decreased from 12,000 to 4000 g/mole, fracture toughness decreased proportionately - from 2100 to 790 J/m² (12 to 4.5 in.-lb./in.²), respectively. From guidelines given in the section on Structure-Property Relationships, the lowest value is still an acceptable fracture toughness number. Importantly, the cured polymer made from 4000 g/mole precursor was unaffected by hydraulic fluid although minor swelling was observed in chloroform. Flexural tests on unidirectional graphite composites indicated that the material retained a high degree of its room temperature strength to 350°F (Figure 17). The unmodified material could barely be tested at that temperature. Unfortunately, the cured neat resin moduli were marginal for advanced composite applications.

An extensive synthetic study was recently completed at Langley on new linear, amorphous, tough polyarylene ethers (19). Some of the basic polymer repeat units are shown in Figure 18. Tg values for most of the compositions varied from 114° to 170°C (237° to 338°F). Polymers containing the 9,9-fluorene moiety had higher Tg values, ranging from 223° to 243°C (433° to 470°F). Unfortunately, thin film tensile moduli were very low, varying from 307 to 390 Ksi. Flexure and short beam shear values for fabric composites made with several of these composites were low because of thermoplastic failure.

Attempts were made to improve the properties of these polyarylene ethers by lightly crosslinking through the use of ethynyl termination (20). As with the polysulfones, the chain length of the hydroxy-terminated polymer was varied prior to chain termination with p-ethynylbenzoyl chloride (Figure 19). Processability was markedly enhanced. Using a precursor polymer having a calculated number average molecular weight of 8500 g/mole, adhesive bonds could be made at 450°F/50 psi/0.5 hour. The adhesive bonds afforded excellent 200°F properties and exhibited better resistance to waterboil and hydraulic fluid exposure than did bonds made with the uncrosslinked polymer (Table 5). Composite studies are planned pending scale-up of the appropriate ethynyl-terminated polyarylene ether. Further modification of this polymer is discussed in the next section.

TOUGHENED THERMOSETS - A low molecular weight ethynyl-terminated polyarylene ether having a calculated number average molecular weight of ⁻4500 g/mole was combined with a very low molecular weight oligomeric acetylene-terminated polysulfone to form a compatible and unique blend that could be prepregged readily from ketone solvents. The chemistry of this precursor blend is given in Figure 20 (21). Crosslinking, branching and chain extension all occur during thermal cure.

Carbon fiber cloth laminates were easily fabricated from cloth prepreg at 450°F/80 psi/2 hours. Data on flexural and short beam shear specimens tested at 200°F wet and dry are shown in Table 6. The values are excellent, especially for cloth composites, and did not significantly drop after moisture saturation. This indicates that the resulting thermoset matrix is relatively impervious to moisture pickup. Fracture toughness and other mechanical properties have not been measured so it is unknown what properties were sacrificed to achieve these results. Higher molecular weight ethynyl-terminated polyarylene ethers could be used to increase toughness. Extensive composite evaluation is planned.

PMR-15 is a nadimide-terminated polyimide oligomer that thermally polymerizes to a high temperature brittle thermoset. Because of their high crosslink density, PMR-15 composites easily microcrack when thermally cycled. Several approaches are being investigated to toughen PMR-15 matrices in order to prevent or diminish matrix microcracking. One approach is to blend a specially formulated PMR-15 oligomer of higher molecular weight with high molecular weight thermally stable polyimides such as LARC-TPI, NR150B2 or Thermid LR 600 (22). Composites data for a PMR-15/LARC-TPI semi-IPN are given in Table 7. Interlaminar fracture toughness was significantly increased at some sacrifice in glass transition temperature and, therefore, operating temperature. However, this trade-off might be acceptable for many applications where microcracking needs to be eliminated or controlled.

PROCESSING TECHNOLOGY - A major problem in the processing of thermoplastics and high temperature thermosets is the difficulty of effectively combining the reinforcement with the polymer matrix. Thermoplastics have extremely high melt viscosities which make penetration into the tow bundle difficult.

Prepregging from organic solvents is not recommended because of toxicity and solvent handling problems. Further, most commercial tape prepregging machines are designed only for hot melt coating, especially for epoxies. Consequently, NASA-Langley has been investigating ways to powder coat carbon fiber. Fluidized bed, slurry, and electrodeposition techniques are being examined in cooperation with Clemson University and Georgia Institute of Technology. In addition, a proprietary powder slurry technique is being developed at BASF Structural Materials which is applicable to both thermosets and thermoplastics. Powder-coated prepreg should have good drape and perhaps even some tack, depending upon the

process. Powder-coated tow has the potential to be woven into cloth and preforms and to be filament wound and pultruded. It could help revolutionize composite processing technology by being cost-effective to produce and to fabricate.

FUTURE DIRECTIONS - Synthesis activities will continue to emphasize the development of an ideal processable high temperature thermoplastic, toughened high temperature thermosets, semi-crystalline polyimides, blends and semi-IPNS. In addition, processable inorganic matrices will be investigated for potential application above 600°F. Powder coating techniques for continuous reinforcements will continue to be exploited. Studies on fiber-matrix interfacial adhesion will be emphasized as thermoplastics which traditionally have poor fiber-resin interfaces become prime matrix materials.

Better relationships between composite compressive properties, fiber properties, neat resin properties and composite microstructure need to be established in order to improve both compression and post-impact compression behavior. This will require interdisciplinary cooperation between structures, mechanics and polymer technologists.

A recent NASA Research Announcement requested proposals in both composite structures and materials technology. It is the first action in a new NASA five year Advanced Composites Program that could involve expenditures in excess of 100 million dollars. The program was designed to help realize the full potential of composite materials in aircraft by developing optimally-designed composite structures which are more structurally efficient and more cost effective than current metallic or state-of-the-art composite structures. The program will emphasize three basic technologies: innovative structural design concepts, cost-effective fabrication techniques and advanced organic matrix materials. Materials technologies include synthesis, fatigue and fracture characterization, durability, interface research and advanced fiber placement techniques. The issues, approaches and payoff for the materials portion of the program are outlined in Figure 21.

TECHNOLOGY TRANSFER - The Polymeric Materials Branch at NASA-Langley has been extremely active transferring basic technology to industry. Technology transfer is viewed as essential to NASA's mission. Previous experience has shown that both parties benefit from the exchange and interaction. A list of companies which have received LARC-TPI polyimide technology developed at Langley is shown in Figure 22. This represents only a small portion of the total Langley polymer and composite activities involved in technology transfer.

REFERENCES

1a. B. W. Rosen, "Mechanics of Composite Strengthening," Fiber Composite Materials, American Society for Metals, 1965, pp. 37-73.

b. H. T. Hahn and J. G. Williams, "Compression Failure Mechanisms in Unidirectional Composites," NASA TM-85834, July 1984.

2. Unpublished results, N. J. Johnston, T. K. O'Brien and J. G. Williams, NASA Langley Research Center, 1986.

3. D. L. Hunston, R. J. Moulton, N. J. Johnston and W. D. Bascom, "Matrix Resin Effects in Composite Delamination: Mode - I Fracture Aspects," ASTM STP-937, 1987.

4. N. J. Johnston, "Synthesis and Toughness Properties of Resins and Composites," NASA CP-2321, 1984, pp. 75-95.

5. N. J. Johnston and P. M. Hergenrother, "High Performance Thermoplastics: A Review of Neat Resin and Composite Properties," Sci. Adv. Matl. Proc. Eng. Series, 32, 1400 (1987).

6. Unpublished results, J. H. Starnes, J. G. Williams and D. C. Jegley, NASA Langley Research Center, 1987.

7. V. L. Bell, B. L. Stump and H. Gager, "Polyimide Structure-Property Relationships. II. Polymers From Isomeric Diamines," J. Polym. Sci., Polym. Chem. Ed., 14, 2275 (1976).

8. D. J. Progar and T. L. St. Clair, "Preliminary Evaluation of a Novel Polyimide Adhesive for Bonding Titanium and Reinforced Composites," Intl. SAMPE Tech. Conf. Series, 7, 53 (1975). C. L. Hendricks and J. N. Hale, "High Temperature Adhesive Development and Evaluation," NASA CP-2387, 1984, p. 351.

9. J. R. Pratt, T. L. St. Clair, H. D. Burks and D. M. Stoakley, "Polyimide Processing Additives," Sci. Adv. Matl. Proc. Eng. Series, 32, 1036 (1987).

10. N. J. Johnston and T. L. St. Clair, "Thermoplastic Matrix Composites: LARC-TPI, Polyimidesulfone and Their Blends," Intl. SAMPE Tech. Conf. Series, 18, 53 (1986); SAMPE J., 23(1), 12 (1987).

11. H. D. Burks, T-H. Hou and T. L. St. Clair, "Characterization of Crystalline LARC-TPI Powder," SAMPE Quart. 18(1), 1 (1986). T-H. Hou and J. M. Bai, "Thermal Properties of Crystalline LARC-TPI Powder," Proceedings 1987 SPE ANTEC, Los Angeles, CA, April 1987.

12. Unpublished results, R. M. Baucom and N. J. Johnston, NASA Langley Research Center, 1987.

13. P. M. Hergenrother, N. T. Wakelyn and S. J. Havens, "Polyimides Containing Carbonyl and Ether Connecting Groups, J. Polym. Sci.: Part A: Polym. Chem., 25, 1093 (1987); P. M. Hergenrother and

S. J. Havens, "Adhesive Properties of LARC-CPI, A New Semi-Crystalline Polyimide," Sci. Adv. Matl. Proc. Eng. Series, 33, 000 (1988).

14. Unpublished results, T. L. St. Clair, NASA Langley Research Center, 1987.

15. A. F. Yee and R. A. Pearson, "Toughening Mechanisms in Elastomer-Modified Epoxies. Part 1. Mechanical Studies," J. Matl. Sci., 21, 2462 (1986); NASA CR-3718, August 1983. R. A. Pearson and A. F. Yee, "Toughening Mechanisms in Elastomer-Modified Epoxies. Part 2. Microscopy Studies," Matls. Sci., 21, 2475 (1986); NASA CR-3852, December 1984.

16. A. O. Hanky and T. L. St. Clair, "Semi-2-Interpenetrating Networks of High Temperature Systems," SAMPE J., 21(4), 40 (1985).

17. A. O. Hanky, L. L. King and T. L. St. Clair, " Semi-Interpenetrating Polymer Networks of LARC-TPI," Intl. SAMPE Tech. Conf. Series, 18, 440 (1986).

18. P. M. Hergenrother, B. J. Jensen and S. J. Havens, "Thermoplastic Composite Matrices with Improved Solvent Resistance," SAMPE J. 20, 18 (1984).

19. P. M. Hergenrother, B. J. Jensen and S. J. Havens, "Polyarylene Ethers From Bis-1,3- and 1,4-(4-chlorobenzoyl)-benzene," Polym. Prepr., 26(2), 174 (1985); Polymer, 29(2), 000 (1988).

20. P. M. Hergenrother, B. J. Jensen and S. J. Havens, "New Poly(arylene ethers)," Intl. SAMPE Tech. Conf. Series, 18, 454 (1986).

21. Unpublished Results, R. M. Moulton and W. J. Hedges, NASA Contract NAS1-18260, 1987.

22. R. H. Pater and C. D. Morgan, "Interpenetrating Polymer Network Approach to Tougher and More Microcracking Resistant High Temperature Polymers. I. LARC-RP40," Proceedings 1988 SPE ANTEC, Atlanta, GA, April 18-21, 1988.

Table 1

Some Desired Properties of Resins and Composites

Resin	Property at RT	Composite
450 – ? Ksi	0° tensile & compressive moduli	20 Msi
170–220 Ksi	shear modulus	0.8–1.0 Msi (G_{12})
14–18 Ksi	0° tensile strength	280–300 Ksi
14–18 Ksi	0° compressive strength	200–240 Ksi
14–18 Ksi	shear strength	16 Ksi (τ_{12})
8–10 %	strain-to-failure	>1.5
5–11 in.-lb/in.^{2} (800–2000J/m^2)	G_{Ic}	4–6 in.-lb/in.^{2} (700–1050 J/m^2)
>50 %	retention of RT properties at elevated temp wet	>50 %
	compressive strength after 1500 in.-lb/in. impact on quasi-isotropic panel	50 Ksi (0.6 % strain)

Table 2

Relationship Between Neat Resin Modulus and 0° Composite Compression Strength

$$\sigma_c = KE_R$$

Hypothetical resin	E_{resin} (ksi)		σ composite (ksi)	
	RT/dry	180°F/wet	RT/dry	180°F/wet
1	600	450	232	182
2	500	370	203	160
3	400	300	167	138
4	300	200	138	94

Table 3

Short Beam Shear and Flexure Properties of AS-4/LARC-TPI Composites

Test temp., °C (°F)	SBS St., Ksi	Flex. St., Ksi	Flex. Mod., Msi
LARC-TPI *			
RT	9.2	137	12.8
93 (200)	8.8	121	12.6
149 (300)	8.4	111	11.1
177 (350)	7.8	99	12.1
LARC-TPI, 2.5 % Bisamideacid **			
RT	13.5	242	14.7
93 (200)	12.0	213	14.4
205 (400)	8.4	160	14.1

* 50 % fiber vol., Tg 253-258°C, C-scan bad
** 48 % fiber vol.; Tg 238°C; C-scan good

Table 4

Mechanical Properties of AS-4/2:1 Bismaleimide: Polyimidesulfone Semi-IPN Composites

	Short beam shear strength, Ksi	Flexural strength, Ksi	Flexural modulus, Msi
RT	14.9	326	16.7
350°F	12.8	298	16.3

Table 5

Ti/Ti Adhesive Properties of a Polyarylene Ether and an Ethynyl-Terminated Polyarylene Ether

TEST CONDITION	Ti/Ti ADHESIVE PROPERTIES , PSI (MPA)	
	POLYARYLENE ETHER(PAE)[2]	ETHYNYL TERM. PAE ($\bar{M}_N$ -8500)[3]
25°C	5300(36.5)	5700(39.3)
93°C	3900(26.9)	4500(31.0)
25°C AFTER 72 HR H_2O BOIL	2900(20.0)	3900(26.9)
93°C AFTER 72 HR H_2O BOIL	2400(16.5)	NOT TESTED
25°C AFTER 72 HR IN HYDRAULIC FLUID	1300(9.0)	5400(37.2)
93°C AFTER 72 HR IN HYDRAULIC FLUID	700(4.8)	4200(29.0)

[1] PASA-JELL 107 SURFACE TREATMENT
[2] RT - 204°C/50 PSI (0.34 MPA), HOLD 10 MIN
[3] RT - 177°C, CONTACT PRESSURE, 10 MIN; 50 PSI, HOLD 20 MIN; HEAT TO 232°C/50 PSI, HOLD 0.5 HR

Table 6

Mechanical Properties of Carbon Fiber Cloth Laminates Fabricated with an Ethynyl-Terminated
Polyarylene Ether/Acetylene-Terminated Polysulfone Matrix

TEST	TEST CONDITION	VALUE
FLEXURAL ST.	93°C, DRY	112 Ksi
	93°C, WET	105 Ksi
FLEXURAL MOD.	93°C, DRY	10.5 Msi
	93°C, WET	11.0 Msi
SHORT BEAM SHEAR ST.	93°C, DRY	9.2 Ksi
	93°C, WET	8.1 Ksi

*F3T584 CLOTH; AUTOCLAVE CURE, RT → 232°C, 80 PSI,
HELD 2 HR; THICKNESS, 0.115 INCH; FIBER VOLUME, 59%

Table 7

Properties of PMR-15 and PMR-15/LARC-TPI Semi-IPN Composites

	PMR-15	Semi-IPN PMR-15/LARC-TPI
Cure temp, °C	316	316
T_g, °C	352	259
G_{Ic}, J/m^2	85	476
Microcracks after 1000 thermal cycles, cracks/in.	58	0

- Poor damage tolerance and delamination resistance

- High material costs (fibers/toughened resins)

- Labor intensive manufacturing procedures

- Insufficient data base for accurate risk assessment

- Inadequate analytical tools to predict structural integrity

- Certification requirements

Figure 1. Barriers that limit composite applications to aircraft.

Impact {
1. Increased fiber strain
2. Good resin shear strength
}

Delamination {
3. Moderate interlaminar fracture toughness: G_{Ic}, G_{IIc}
4. Moderate resin fracture toughness
   (Empirical relationship between 3 and 4)
}

Compression {
5. Good fiber/resin interfacial adhesion
6. High composite 0° compressive strength
7. High post-impact compressive strength
   (Empirical relationship between 3 and 7)
8. High resin modulus
   (Empirical relationships between 6 and 8, 3 and 8)
9. Good time-dependent properties: fatigue, creep
}

Processing {
10. Low viscosity prepregging resin
11. Melt-processable resin
12. Solvent-resistant resin
}

13. Thermooxidative stability

Figure 2. Desired constituent property needs for high performance composites.
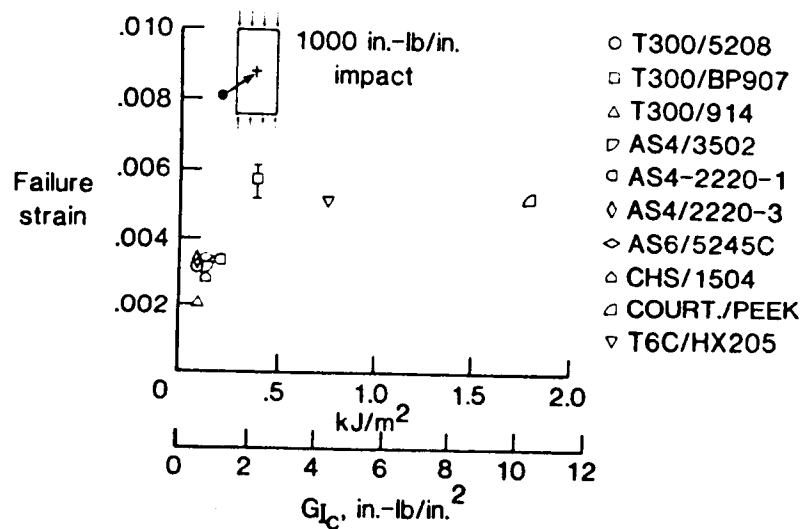
Figure 3. Compression after impact failure strain versus composite interlaminar fracture toughness (G_{Ic}).
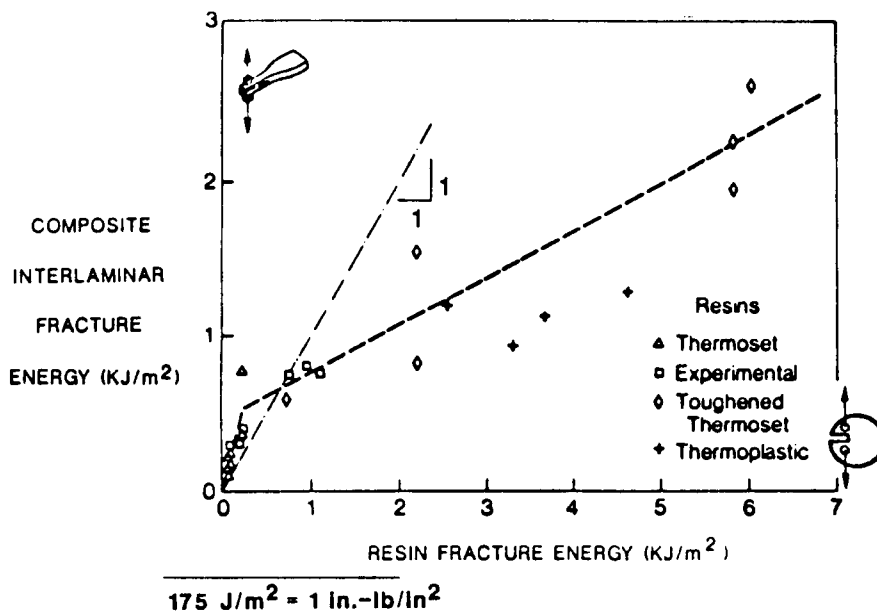
Figure 4. Resin fracture toughness versus composite interlaminar fracture toughness (G_{Ic}).
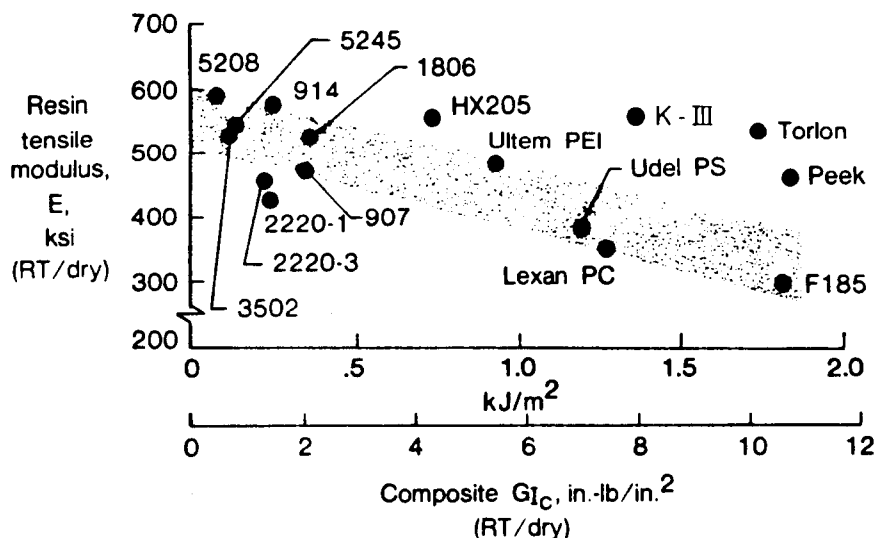
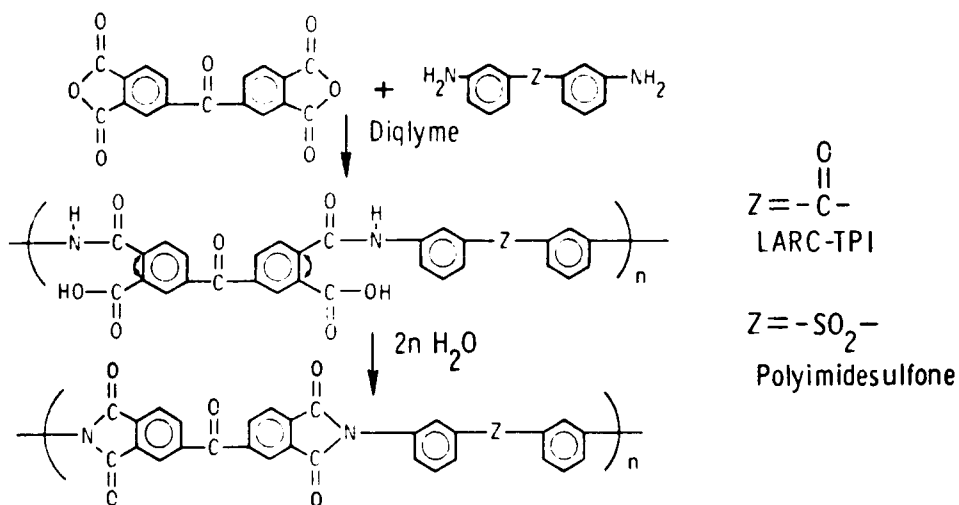Figure 5. Resin modulus versus composite interlaminar fracture toughness (G_{Ic}).

Figure 6. Chemistry of LARC-TPI and polyimidesulfone.
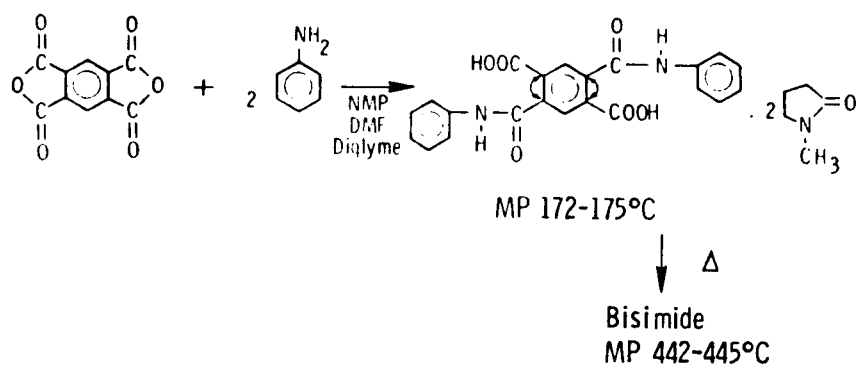
12

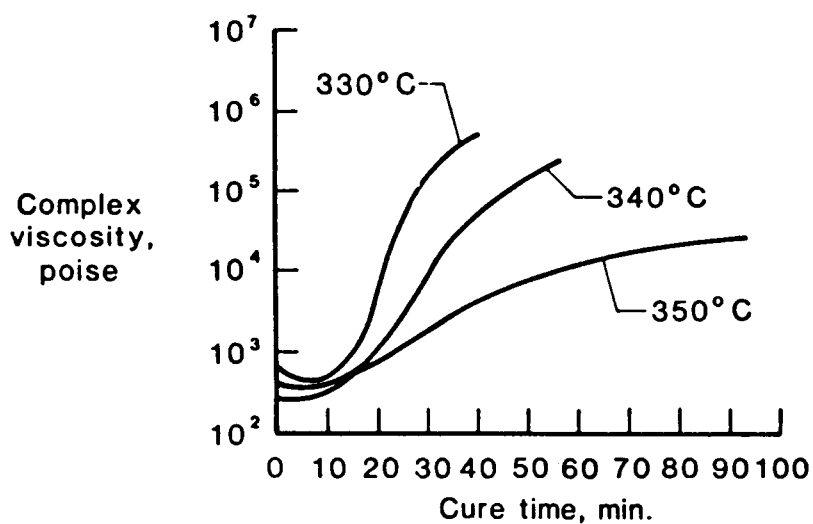Figure 7. Bisamideacid from PMDA and aniline.

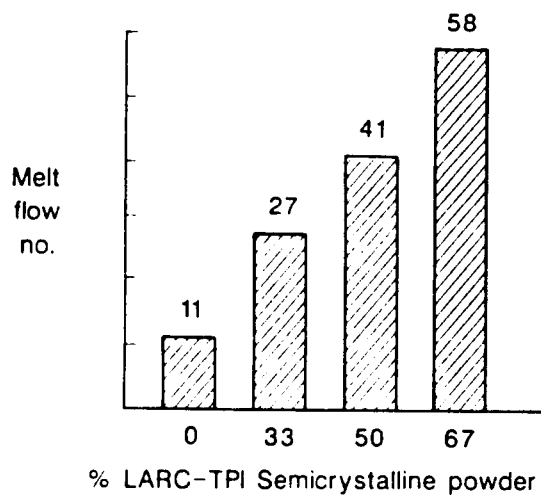Figure 8. Complex melt viscosity versus cure time for LARC-TPI powder.

Figure 9. Melt flow numbers for blends of LARC-TPI semi-crystalline powder in LARC-TPI amorphous polymer.
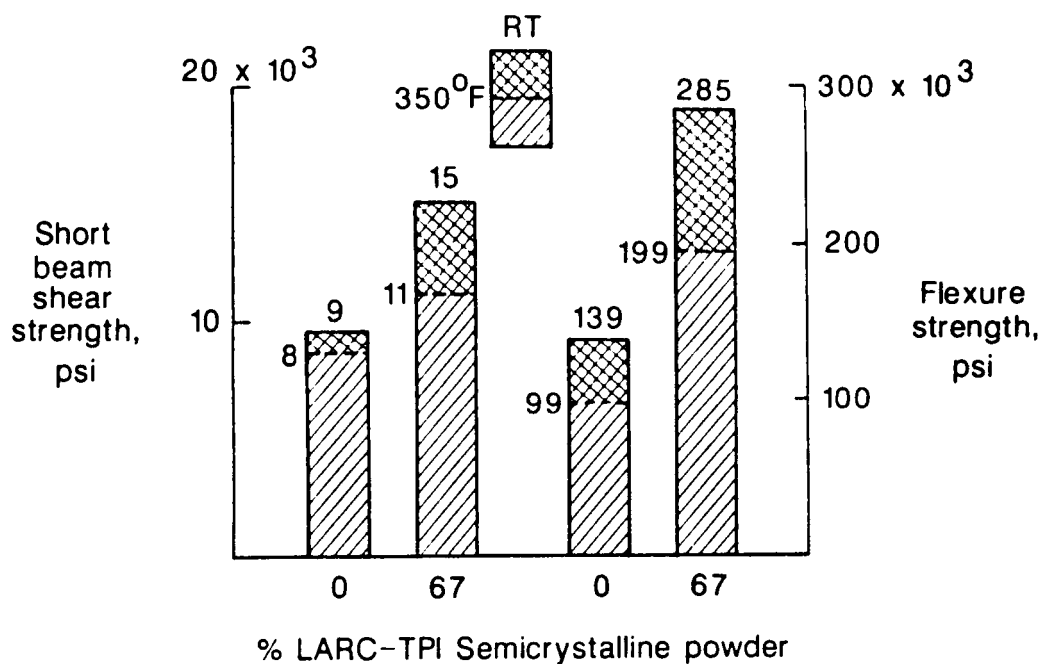
13

Figure 10. Mechanical properties of AS-4 composites made with LARC-TPI amorphous polymer and 67:33 blend of LARC-TPI semi-crystalline powder: LARC-TPI amorphous polymer.
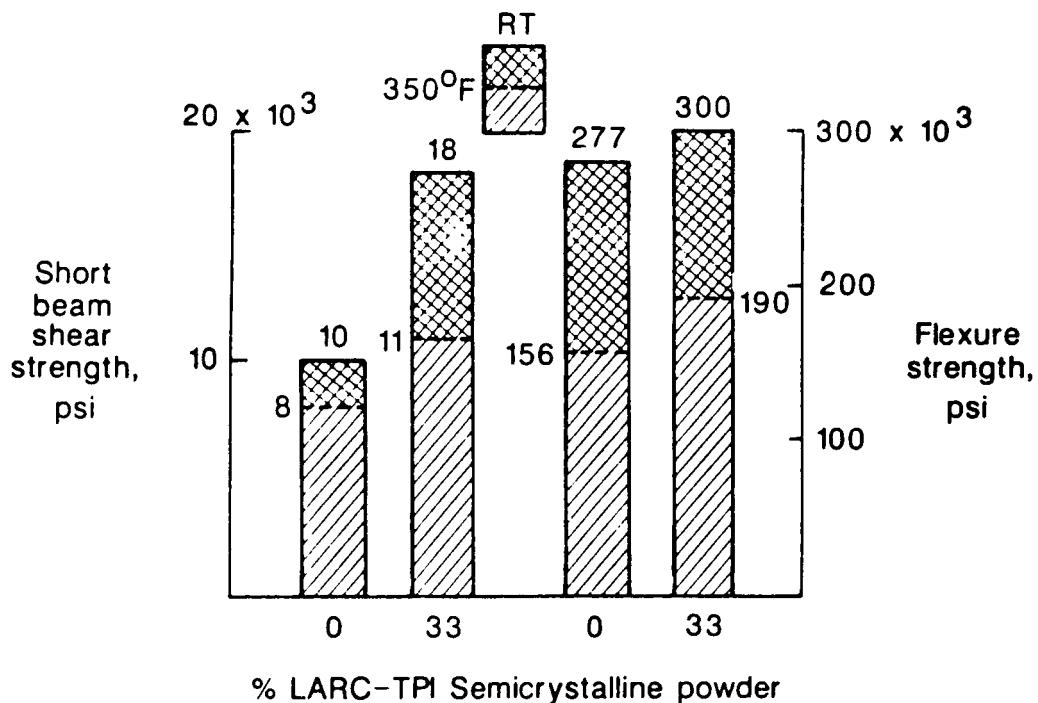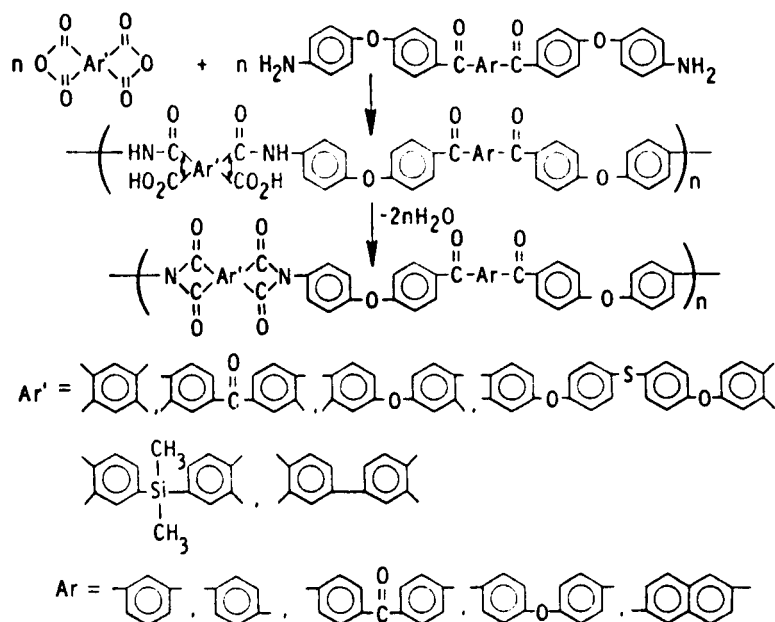

Figure 11. Mechanical properties of AS-4 composites made with polyimidesulfone amorphous polymer and 33:67 blend of LARC-TPI semi-crystalline powder: polyimidesulfone amorphous polymer.

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SYNTHESIS OF POLYIMIDES
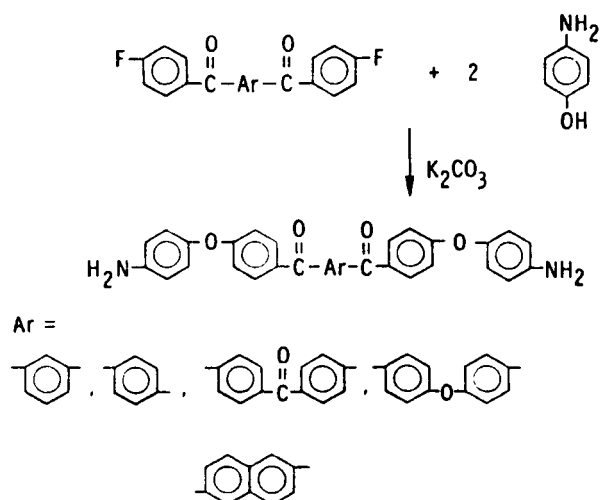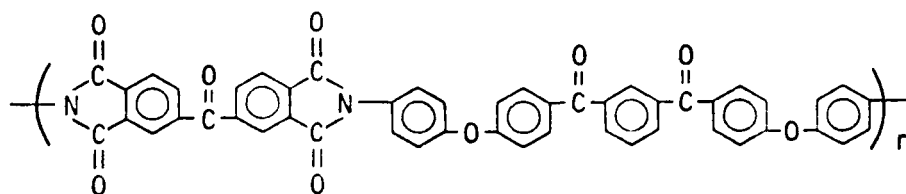
SYNTHESIS OF DIAMINES

Figure 12. Synthesis of new crystalline polyimides and new diamine monomers.

GLASS TRANSITION TEMPERATURE (T_G): 222°C
CRYSTALLINE MELT TEMPERATURE (T_M): 350°C
CRYSTALLINITY INDUCEMENT: THERMAL
SOLVENT RESISTANCE: EXCELLENT
FRACTURE TOUGHNESS (G_{Ic}) AT 25°C: 38 IN.-LB/IN.^{2} (6600 J/M^2)
Ti/Ti TENSILE SHEAR STRENGTH AT 25°C: 6250 PSI   AT 232°C: 590 PSI
                     AT 177°C: 4510 PSI   AT 232°C AFTER
                                      5 HR AT 300°C: 2800 PSI

THIN FILM PROPERTIES

TEST TEMP., °C	TENSILE ST., Ksi	TENSILE MOD., Ksi	ELONGATION (BREAK), %
25	22.0	630	8.3
177	14.2	540	21.1
232	5.2	245	76.1

POTENTIAL USES: ADHESIVES, COMPOSITE MATRICES, FILMS AND MOLDINGS

Figure 13. Properties of a new crystalline polyimide, LARC-CPI.

15

POLYIMIDESULFONE
AMIDE ACID

+

BISMALEIMIDE DDS

COMPATIBLE
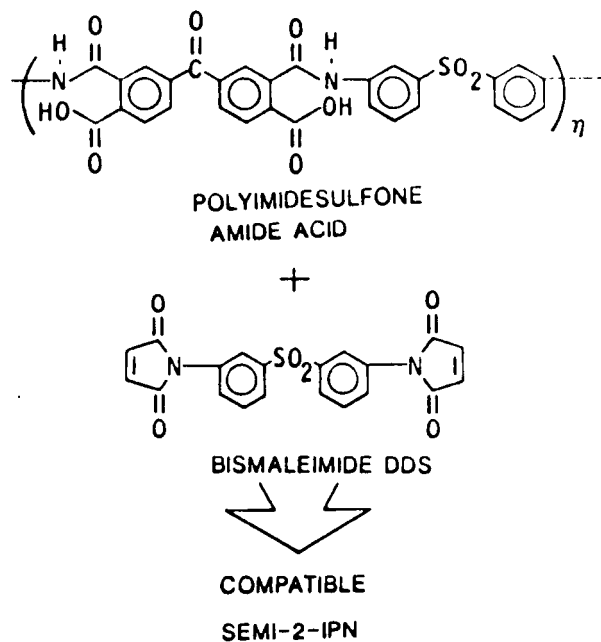
SEMI-2-IPN

Figure 14. Chemistry of a bismaleimide: polyimidesulfone semi-IPN.

Crosslinking polyimidesulphone

+

Linear polyimidesulphone

+

Semi-interpenetrating
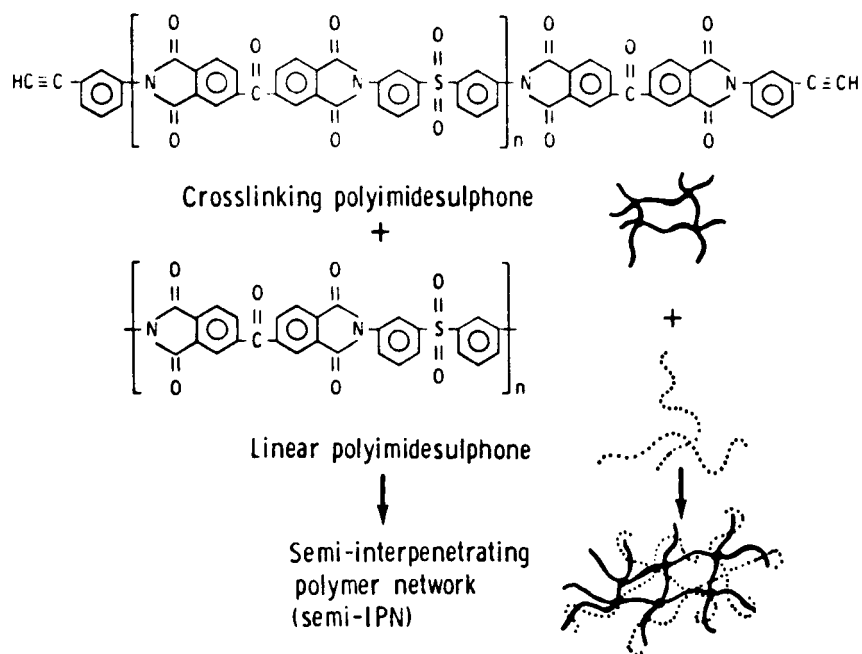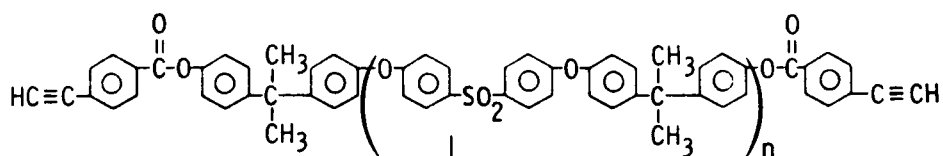polymer network
(semi-IPN)

Figure 15. Preparation of a semi-2-IPN from an acetylene-terminated polyimidesulfone and a linear
polyimidesulfone.

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CHAIN EXTENSION, BRANCHING, CROSSLINKING

n=~7 TO~59 ($\overline{M}_n$ ~3,000 TO ~26,000 g/mole)

THIN FILM PROPERTIES (ETS WITH $\overline{M}_N$ ~12,000 G/MOLE)

TEST TEMPERATURE	26°C	93°C
TENSILE STRENGTH, KSI	12.1	9.6
TENSILE MODULUS, KSI	355	336
ELONGATION, %	4.6	8.2

MOLDED RESIN PROPERTIES

$\overline{M}_N$, G/MOLE	4000	8000	12,000
T_G, °C (250°C CURE)	202	200	196
SWELLING IN CHLOROFORM, %	<10	~20	~55
G_{Ic}, J/M²	790	1300	2100

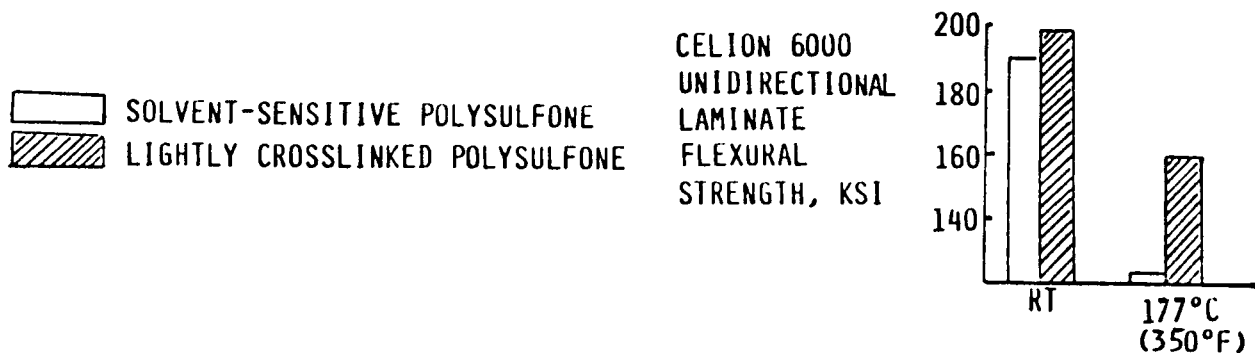Figure 16. Properties of cured ethynyl-terminated polysulfones.

Figure 17. Flexural strength of composites made with a linear polysulfone and an ethynyl-terminated polysulfone.
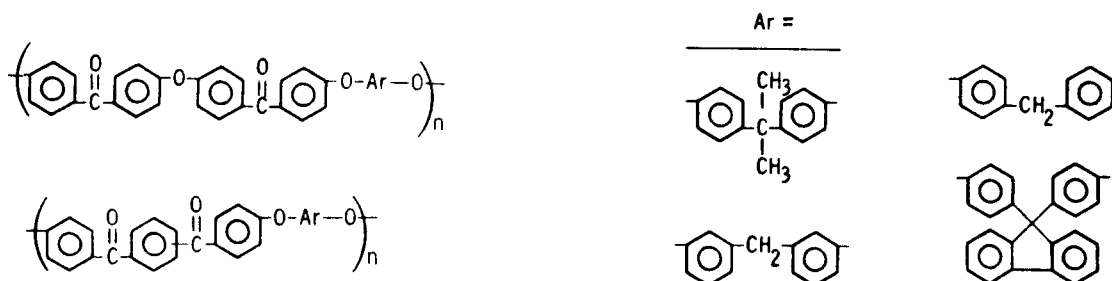
Figure 18. Chemistry of new polyarylene ethers.

17

0.93n

DMAc/ØCH$_3$ | K$_2$CO$_3$, ~155°C

PAE

EBC

Ethynyl Terminated Polyarylene Ether

Δ

Crosslinking, branching, chain extension

EBC =
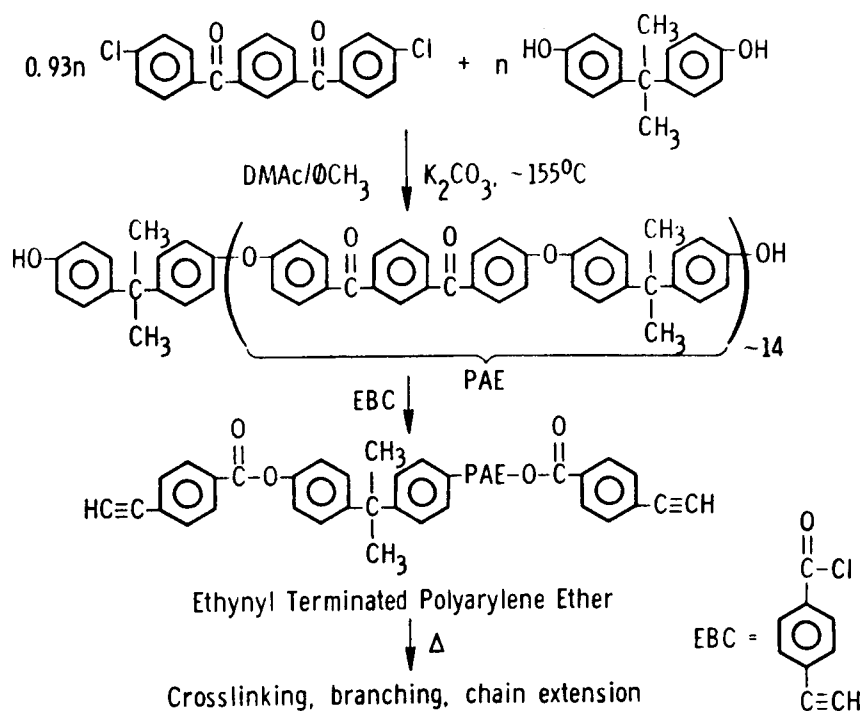
Figure 19. Synthesis of ethynyl-terminated polyarylene ethers.

PAE =

ETPAE ($\bar{M}_n$ ~ 4500 g/mole) (2 parts)

+

95% 1,3 / 5% 1,4   79% where n = 1, 21% where n = 2 and 3
ATS (1 part)

2:1 ETPAE/ATS blend
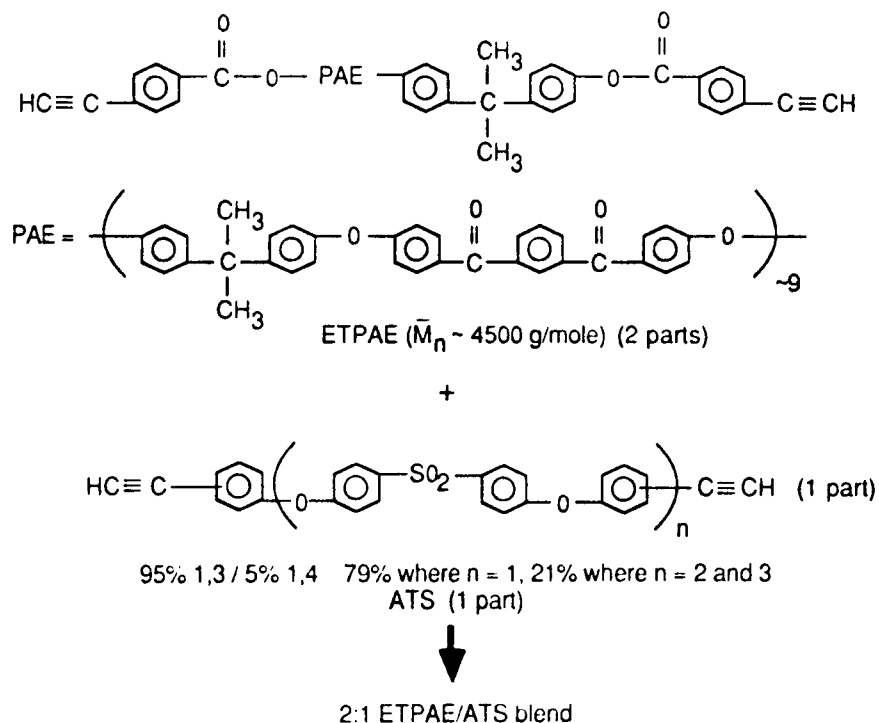
Figure 20. Synthesis of an ethynyl-terminated polyarylene ether/acetylene-terminated sulfone blend.

Issues

• Damage tolerant materials

• Cost effective processing

• Analysis/prediction

Approach

• Advanced resins

• Advanced material forms

• Innovative prepregging - powder

• Automated material placement

• Damage development models

Schedule

	88	89	90	91	92
Material development	████				
Processing		████████████			
Fatigue/fracture prediction models		████████			
Subcomponent fab & test				████	

Payoff

• Improved toughness and durability

• Significantly reduced fabrication costs

• Fundamental understanding of microstructural property relationships

• Improved life prediction methodology for advanced material concepts
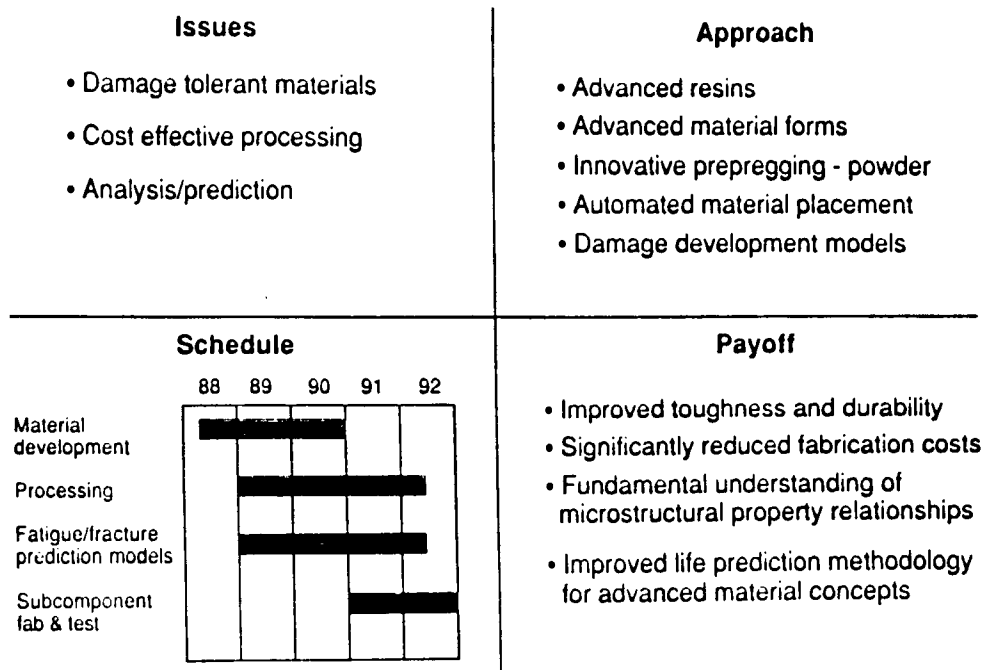
Figure 21. NASA-Langley Advanced Composites Program in Materials.

● **SYNTHESIS TECHNOLOGY: POLYMER CHEMISTRY**
  ● HEXCEL CORP.
  ● HIGH TECH SERVICES
  ● ROGERS CORP.
  ● CELANESE CORP.
  ● M&T LABS

● **PREPREG TECHNOLOGY: CARBON FIBER UNITAPE PREPREGGING**
  ● HEXCEL CORP.: SLURRY
  ● DEXTER - HYSOL : SLURRY
  ● COMPOSITE PRODUCTS, INC.: SLURRY

● **POWDER TECHNOLOGY: CRYSTALLINE POLYIMIDES FOR SLURRY AND POWDER PROCESSES**
  ● HEXCEL CORP
  ● ROGERS CORP.
  ● HIGH TECH SERVICES

● **COMPOSITES TECHNOLOGY: FABRICATION PROCEDURES AND PREPREG SHIPMENTS**
  ● LOCKHEED CALIFORNIA CO.
  ● BOEING AEROSPACE CO.
  ● BRUNSWICK CORP.
  ● NORTHRUP CORP.
  ● AEROJET GENERAL

Figure 22. NASA-industry technology transfer involving Langley polyimides.

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16. Abstract

Barriers to the more extensive use of advanced composites in heavily loaded structure on commercial transports are discussed from a materials viewpoint. NASA-Langley matrix development activities designed to overcome these barriers are presented. These include the synthesis of processable, tough, durable matrices, the development of resin property/composite property relationships which help guide the synthesis program, and the exploitation of new processing technology to effectively combine reinforcement filament with polymer matrices. Examples of five classes of polymers being investigated as matrix resins at NASA-Langley will be presented, including amorphous and semi-crystalline thermoplastics, lightly crosslinked thermoplastics, semi-interpenetrating networks and toughened thermosets. Relationships between neat resin modulus, resin fracture energy, interlaminar fracture energy, composite compression strength, and post-impact compression strength will be shown. Powder and slurry processing techniques will be discussed.

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