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**ABSTRACT**

Advanced composites are finding widespread use throughout the aerospace industry. However, conventional epoxy based systems are limited to continuous use temperatures around 130 deg C. There are many applications requiring continuous use temperatures substantially in excess of this, aero-engines and missiles are prime examples.

A considerable amount of effort has been directed towards the synthesis of high temperature resins. Systems are now available that have the capability of performing for thousands of hours at 200 deg C, for hundreds of hours at 300 deg C and for seconds at temperatures as high as 760 deg C.

In developing advanced composites for high temperature applications, attention must not only be paid to the matrix resin but to the fibre and fibre-resin interface as well. Also in the production of composite components adhesive bonding, with high temperature adhesives, is also desirable.

This paper will review the present state of high temperature composite technology with reference to matrix resins, fibres and adhesives. Applications and future needs and markets will also be discussed.

The major driving force for the use of composites is reduced weight brought about by high stiffness/weight and high strength/weight ratios. The figure below indicates the "driving force" in more recognisable terms. For a 747 one Kg of weight saved is worth about \$450 whilst a similar weight saved on the space shuttle is worth about \$30,000 (1).

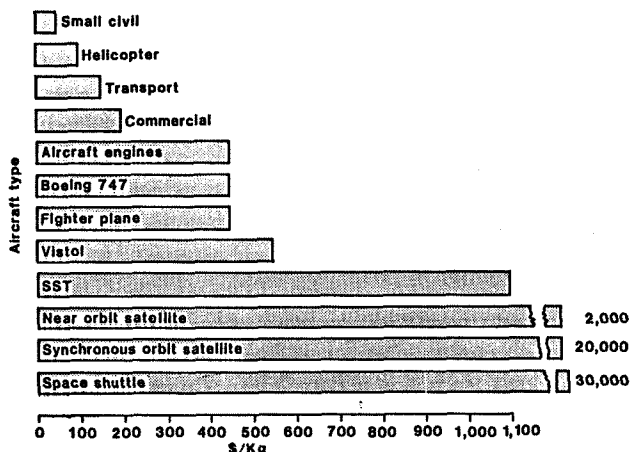


Figure 1. Value of weight saved in aircraft and spacecraft (after reference 1).

**1. INTRODUCTION**

In less than twenty years advanced composites have become established as efficient high performance structural materials and their use is expanding rapidly. A simple definition of a composite is a material consisting of any combination of fibres or particles in a common matrix.

The term "advanced composite" was coined to distinguish materials using the new high performance fibres such as boron, carbon and aramid from glass fibre reinforced plastic (fibreglass). The most important matrix materials at present are polymer based with epoxy resins predominating. Most composite components are made from woven fabrics or parallel arrays of unidirectional fibres (tapes).

Such fabrics and tapes are usually preimpregnated with an epoxy resin which is then partially cured or "B staged" to aid handling. These "prepregs" are then placed in a mould and cured under pressure at elevated temperature to their final shape. In many applications composite sheets are bonded to a honeycomb core to give a lightweight and stiff construction.

Up to now epoxy based composites have dominated the technology. However, their use is limited to temperatures of about 130 deg C.

There are many applications within the aerospace industry that require continuous use temperatures in excess of 130 deg C, missiles and aero engines are prime examples. However, the production of high quality composite components capable of surviving high temperatures is complex and fraught with difficulties.

This paper will review the more important developments in high temperature composites and outline some applications of these exotic materials.

**2. RAW MATERIALS**

**2.1 Resin systems**

**2.1.1 Development of thermally stable resins**

Thermal stability can be defined as the capacity of a material to retain useful properties for a required period of time under well defined experimental conditions such as temperature, time, atmosphere, stress, irradiation and chemical, mechanical or electrical action.

The key to achieving high temperature capability is the synthesis of polymers that contain mainly aromatic and heterocyclic units. However, such units whilst enhancing thermal stability, result in extremely difficult (or impossible) processing. Whilst many polymers have been synthesised that exhibit outstanding thermal stability only a few have been processed into useful articles.

Original US work led to the development of new thermally stable resins based on polyheterocyclic polymers. These included polyquinoxalines, polybenzimidazoles, polybenzothiazoles and polyimides. Generally, these materials fall into two broad classes. The condensation type are prepared by a polycondensation reaction with the evolution of water or other volatiles. Although high temperature materials can be prepared by this route, the volatiles generated in the reaction tend to produce voided composites. In the case of "addition" type polymers, volatile by-products are produced only at the first stage, at a time when the resin itself is fluid enough to facilitate their removal. As is usual in this type of work a trade off exists between high temperature capability and processability. The more well known resin systems will now be outlined:

### 2.1.2 Bismaleimide Resins

Over the last few years bismaleimide (BMI) resins have found increased favour as matrix resins for composites due to the ease of processing and good high temperature properties. Continuous use temperatures are around 200 deg C, some 70 deg C higher than "state of the art" epoxies.

#### Chemistry

The basic building block of BMI resins is 4,4'-bismaleimidodiphenyl methane. This material is prepared from the reaction of maleic anhydride and methylene dianiline:

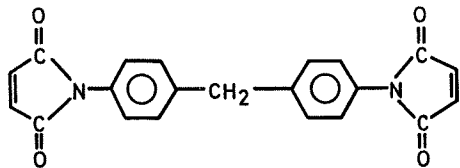


Figure 2. 4,4'-Bismaleimidodiphenylmethane

Polymerisation occurs through the maleimide double bond, without the evolution of volatiles, at temperatures in the range 150 to 250 deg C to produce a highly crosslinked and brittle product.

Monomeric bismaleimides are relatively easy to make with a wide variety of structural variations available for property modification. Such fine tuning has been necessary in order to produce materials with good processing characteristics and acceptable properties. By using a close to eutectic ternary mixture, Stenzenberger et al (2,3) have produced a commercial resin which melts in the range 70-125 deg C and has a melt viscosity of 150cP at a processing temperature of 120 deg C. This material coded Compimide 353 is believed to be the base resin used in a number of proprietary

formulations. Included in these is US Polymeric's prepreg formulation V378A which has been used in a number of applications (see Section 3.0).

Several other modifications have been used to develop commercial products. Rhone-Poulenc's Kerimid 601 makes use of a Michael addition reaction to increase the molecular weight of the precursor and to introduce a point of chain flexibility. The chain extension reaction also reduces the Tg and inherent brittleness whilst providing better processability, lower melting point and better reaction control. Kerimid 601 has found widespread use in printed circuit boards but only limited use in aerospace. The presence of the Michael addition product introduces a point of thermo-oxidative instability.

A variety of copolymer modifications to the basic BMI system have been examined. To improve toughness, tensile strength, elastic modulus and elongation at break the BMI can be modified by the addition of vinyl monomers, allyls, diamines, epoxies and elastomers. For example Narmco's 5245c BMI formulation is believed to be a reaction product of an epoxy and a BMI. Although tough, some reduction in high temperature capability is seen.

Recent reports have indicated that BMI systems can be successfully copolymerised with thermostable monomers such as vinylstyrylpyridine (4) or stilbazole (5).

#### Fabrication

Bismaleimide resins can be fabricated under similar conditions to those used in the processing of epoxies. Addition of catalysts allows curing at 180 deg C with a post cure at 210-220 deg C for 4-5 Hours. Minimal pressure is required and is normally about 60 psi.

BMI composites can be fabricated by a number of techniques including conventional autoclave and compression moulding, filament winding and resin transfer moulding.

#### Properties

In common with epoxies, BMI laminates absorb water which reduces mechanical properties particularly at high temperatures. The moisture acts as a plasticizer and reduces the glass transition temperature of the resin. In most cases, however the reduced Tg is still sufficiently high for service in many hot-wet environments.

Shown below is a graph of interlaminar shear strength at various temperatures for a standard high performance epoxy and for a conventional BMI. The superior performance of the BMI at elevated temperatures is clearly seen:

#### Drawbacks

The major drawback of state of the art bismaleimides is their lack of toughness. Much effort is being directed to produce formulations that show outstanding toughness whilst retaining high temperature capability. Both Ciba-Geigy and Technochemie have produced toughened systems that

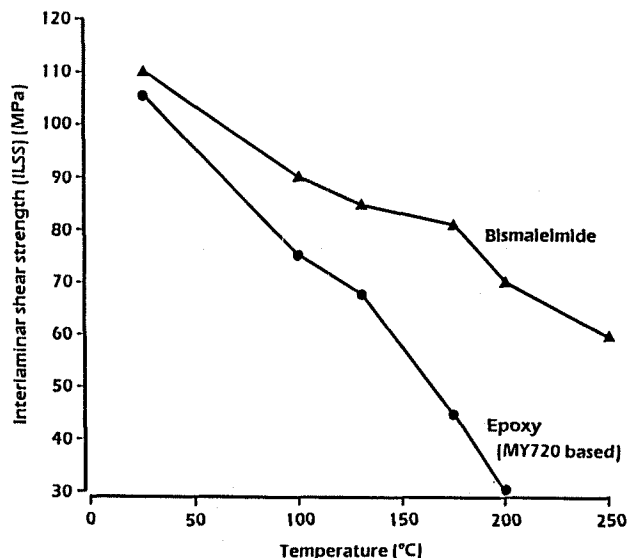


Figure 3. ILSS vs temperature for epoxy and BMI laminates.

rely on the copolymerisation of allyl compounds. Initial results seem to indicate that these materials are as good as the toughest epoxies yet exhibit considerably higher thermal stability. Whether or not very tough systems can be produced that will satisfy the rigorous demands of the new fighter aircraft is open to question.

Another potentially major drawback of BMI resins is their susceptibility to microcracking after thermal cycling. Such cycling, say between -50 and +250 deg C produces microcracks and loss of mechanical properties. This is likely to be due to a number of factors including mismatch of fibre and resin expansion coefficients, and the brittle nature of the resin.

### 2.1.3 Reverse Diels-Alder Systems

Reverse Diels-Alder (RDA) resins are so named because of the mechanism involved in the curing reaction (see Figure 4). This reaction was discovered by Lubowitz in 1970 (6). Patent rights to this invention were subsequently acquired by Ciba-Geigy. Further research resulted in the commercial launch of the moulding powder P13N. This material is a polyimide endcapped with the norbornene group. However, the material encountered processing problems and received little commercial interest. In 1972 Serafini et al (7) developed the "Polymerisation of Monomeric Reactants" approach (PMR) which has done a great deal to establish polyimides as viable engineering materials.

The PMR approach developed at NASA involves dissolving a dialkyl ester of an aromatic dicarboxylic acid, an aromatic diamine and the monoalkylester of 5-norbornene-2,3-dicarboxylic acid (NE) in a low boiling alkyl alcohol. The solution is used to impregnate the reinforcing fibres. At temperatures between 121 deg C (250F) and 232 deg C (450F) the monomers undergo in situ cyclodehydration to form a norbornene end-capped, low molecular weight imide prepolymer. Addition polymerisation of the norbornene end caps occurs

at high temperature without the evolution of volatile reaction by-products. Composites having void contents of less than 1% can be prepared. The most widely known RDA polyimide is PMR-15 but there are other variations.

#### 2.1.3.1 PMR-15 Polyimide

In the development of PMR-15, NASA carried out a series of experiments designed to optimise both the constituents and molecular weight. The best overall balance of processing characteristics, composite thermomechanical and physical properties and 316 deg C (600F) thermo-oxidative stability is provided by a monomer combination consisting of the dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE), methylene dianiline (MDA) and NE in a molar ratio of 2.087:3.087:2. This ratio corresponds to a formulated molecular weight of the imidised polymer of 1500 hence PMR-15. The final addition cure reaction is very complex and yet to be fully understood. However, it is generally accepted that a reverse Diels-Alder reaction of the norbornene end caps takes place. This produces maleimide end groups and cyclopentadiene. The maleic groups then proceed to copolymerise with the double bonds of the cyclopentadiene and unreacted norbornene groups to produce a crosslinked structure without the evolution of void producing volatile materials:

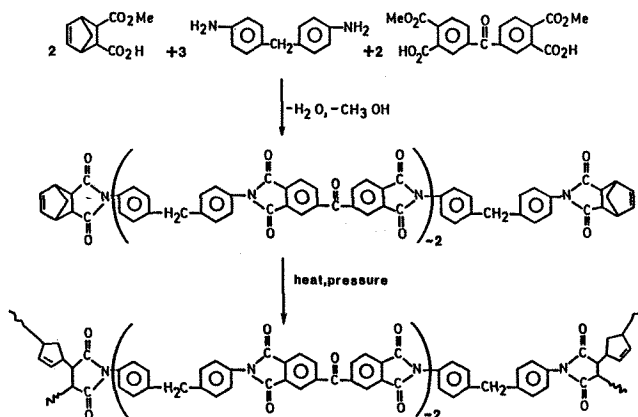


Figure 4. Synthesis of PMR-15 Polyimide

#### Fabrication

PMR-15 can be moulded either by compression or autoclave routes to yield high quality laminates. Both methods use a maximum cure temperature of about 330 deg C (650F) for 2-3 hours followed by a post cure at the same temperature for about 4 hours. Compression moulding uses pressures of about 500-1000 psi whereas autoclave moulding uses 200 psi pressure. There are many variations on this basic cure cycle used within the industry.

#### Properties of PMR-15 composites

In general the mechanical properties of PMR-15 composites are as good as state of the art epoxies. However, in comparison to such epoxies the thermal stability is much greater. Shown below is a graph of "resin endurance" indicating the superior nature of PMR-15 composites compared to epoxies and even bismaleimides:

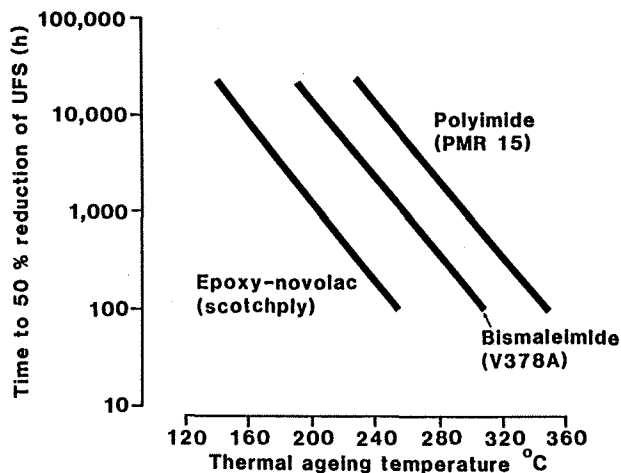


Figure 5. Thermal ageing of PMR-15, BMI and epoxy composites.

Many studies have been conducted to determine the effects of various hostile environments on the physical and mechanical properties of PMR-15 composites. Glass (8), Kevlar (9) and carbon (10,11,12,13) PMR-15 composites have been studied. Excellent retention of interlaminar shear properties of Celion/PMR-15 composites are shown on ageing at 316 deg C (600F) for 1600 hours.

#### Drawbacks

There are a number of drawbacks to the PMR-15 system. Some of these have been eliminated and others not:

Cure Temperature - The high temperature needed for curing PMR-15 places a strain on both energy costs and ancilliary materials. However, work at NASA (14,15) has shown that addition of mixed end caps of p-aminostyrene and endo-N-phenyl-5-norbornene-2,3-dicarboximide reduces the cure temperature from 316 deg C to 260 deg C. Compression moulded laminates exhibit similar properties, before and after ageing, to conventional PMR-15. Also work by Lauver (16) suggests that curing temperature can be reduced by the addition of nitrophenyl compounds.

Tack - PMR-15 prepreg relies for tack on the presence of residual methanol. Because of the high volatility of this solvent tack control is difficult and problems are encountered during processing. Tack can be enhanced and maintained by the use of a mixed solvent system (propanol/methanol), together with the use of certain higher esters of BTDA and NA (17).

Flow Control - In certain circumstances such as the fabrication of complicated parts, flow control of PMR-15 is necessary. Resin flow can be controlled by the addition of phenyl nadimide without upsetting the properties of the material (18).

Quality Control - Presence of the higher esters of BTDE (tri and tetra) has a deleterious effect on the properties of PMR-15 at higher temperatures. This appears to be due to the

presence of voids arising from processing difficulties (19,20). However, by the careful control of processing parameters it is possible to fabricate high quality laminates from neat resin containing large quantities of the higher esters (up to 20%). Nevertheless, when standard cure cycles are being used it is necessary to use high quality prepreg free from contamination by the higher esters. To accomplish this, close control of prepreg purity must be maintained. High Performance Liquid Chromatography (HPLC) is the major analytical tool in this respect.

Toxicity - Methylene dianiline is a suspect carcinogen and the handling of PMR-15 must be carried out with care.

Microcracking - Thermal cycling of PMR-15 composites produces microcracking. In severe cases, such as 1000 cycles between -50 deg C and +250 deg C, drastic reductions in flexural properties have been observed (21). The problem has yet to be fully investigated by industry. Whether the phenomenon will restrict the use of the material to lightly loaded parts is still unclear. Microcracking is not fully understood and may be due to residual thermal stresses arising from the mismatch of fibre/resin expansion coefficients and the high temperature cure. On the other hand the problem may well be indicative of highly crosslinked structures and solutions may be difficult to find.

#### 2.1.3.2 Modifications to PMR-15

The PMR approach is extremely versatile and can be used to prepare a range of materials:

LaRC 160 - This modified PMR-15 was developed by workers at NASA Langley (22) and involves the substitution of methylene dianiline with an aromatic polyamine (Jeffamine AP22). LaRC 160 possesses superior tack and handling to PMR-15 but its high temperature ageing characteristics are inferior (23). AP22 is a complex mixture of amines and doubts exist about the security of supply.

PMR II - Second generation PMR polyimides have been developed. PMR-II consists of NE, p-phenylene diamine and the dimethyl ester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid) (HFDE). According to certain sources (24) this material exhibits improved thermo-oxidative stability over the first generation PMR resins. The limited availability and the cost of HFDE has restricted the acceptance of PMR-II as a matrix material.

Toughened PMR Polyimides - Certain applications require conventional PMR-15 to be much tougher and this can be achieved by use of flexible diamines. Early work at TRW resulted in the development of a novel monomer, 2,2-bis[4-(4-aminophenoxy)-phenyl] hexafluoropropane known as 4-BDAF. This material has been used to develop high performance thermoplastics (see Section 2.1.7.1) and also to toughen PMR-15 by replacement of MDA (26). The reduction in Tg can be offset by replacing BTDE with the dimethyl ester of pyromellitic dianhydride. The only drawback is the cost of 4-BDAF, an estimated \$1400/Kg.

#### 2.1.4 Resins derived from acetylene containing prepolymers

A particularly attractive route for the synthesis of high temperature resins is that employing acetylene containing prepolymers. Such resins cure through an addition reaction without the evolution of volatiles.

Acetylenic and substituted acetylenic groups have been placed on the ends of oligomers, pendent along polymer chains and within polymer backbones of parent materials such as sulphones, esters, imides and phenylquinoxalines. A variety of resin systems can be prepared whose properties are controlled primarily by the linear portion of the molecule, density and location of the acetylenic groups and cure conditions.

To illustrate the flexibility of this approach and drawbacks, three different systems will be considered:

##### Acetylene Terminated Polysulphones

A considerable amount of R&D, particularly by the USAFML, has been directed towards the synthesis and characterisation of polymers based on bis[(3-ethynylphenoxy)phenyl]sulphone (ATS) (see Figure 6). Several synthetic routes to this molecule have been investigated including a new low cost synthesis involving the Ullman reaction (27).

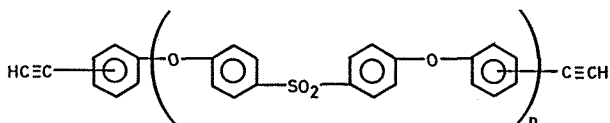


Figure 6. Acetylene Terminated Sulphone (ATS)

ATS can be cured by heating at 177C/1hr, 204C/1hr and 218C/16hrs to give a neat resin with reasonable mechanical properties. However, the material is very brittle (35 J/m<sup>2</sup>). Maximum Tg of ATS has been reported as 366 deg C.

Composites have been prepared with ATS and AS4 fibres but the laminates showed extensive microcracking due to the highly brittle nature of the resin. ATS/Celion fibre composites have shown good retention of properties at 177 deg C before and after high humidity exposure (28).

Other work on acetylene terminated polysulphones has involved the modification of Union Carbide's Udel. This material is a tough engineering thermoplastic that could show some promise as a matrix resin were it not for its poor solvent resistance. The introduction of crosslinks via acetylene terminated intermediates has been accomplished (29). Composite properties of ETS and Udel are similar but the former shows a much greater resistance to solvents. The use temperature of acetylene terminated polysulphones is around 150-180 deg C. There appears to be no commercial source of these materials as yet.

##### Acetylene terminated Phenylquinoxalines

Acetylene terminated phenylquinoxaline (ATPQ) can be prepared from a variety of routes (30). Unidirectional composites have been prepared from

ATPQ. ILSS values at room temperature (HT-S fibres) are 100 MPa. After 2000 hr at 232 deg C the value is about 50 MPa and after 500 hr at 260 deg C the value falls to about 40 MPa.

Phenylquinoxalines containing pendent phenylethynyl groups have also been prepared by several routes (31). These materials can be processed by compression moulding. Thermo-oxidative stability decreases as the content of the phenylethynyl group increases. Unidirectional composites have been made. With 5 mole% of the phenylethynyl group ILSS values of 82 MPa have been reported. After 1000 hr at 232 deg C, this value fell to 40 MPa. Curing conditions are 371 deg C/200 psi (32).

##### Acetylene terminated polyimides

Acetylene terminated polyimides can be prepared by the reaction of an aromatic tetracarboxylic acid dianhydride with an aromatic diamine. The oligomer is then reacted with an ethynyl substituted aromatic amine followed by chemical or thermal cyclodehydration to convert the amic acid to the acetylene terminated imide oligomer (ATI). Molecular weight can be controlled by stoichiometry adjustment.

Early work on ATI led to the development of "Thermid 600" by Gulf Oil. National Starch subsequently acquired all rights to the material. Shown below (Figure 7) is the synthesis of Thermid 600.

Composites made from this material show very respectable mechanical properties. Thermo-oxidative ageing is very good and long term service at 316 deg C (600F) is possible. ILSS values at RT are about 83 MPa. After 500 hr at 316 deg C and tested at 316 deg C the value is about 40 MPa (33).

Commercial acceptance of the material has been restricted, however, because of the very short process window. This is due to the reaction of the ethynyl groups which inhibit flow prior to the formation of a complete melt or soft state.

One solution to the problem lies in the use of corresponding isoimide. Synthesis is by the dicyclohexylcarbodiimide dehydration of the ethynyl terminated amic acid oligomer. The isoimide has better solubility and improved processability than the original ATI (34). At elevated temperatures the ethynyl groups react and the isoimide rearranges to imide. Process window is about 30 minutes but is still short for the fabrication of large and complex parts. The composite properties of the isoimide version are comparable to those exhibited by the polyimide.

So in conclusion, the use of acetylene terminated oligomers offers a useful and versatile route to the synthesis of high temperature resins. However, processing problems need to be ironed out before widespread commercial acceptance.

#### 2.1.5 Polystyrylpyridine resins

Polystyrylpyridine resins (PSP) were discovered in France in the mid 1970's by the Office National d'Etudes et de Recherche Aerospatiales and

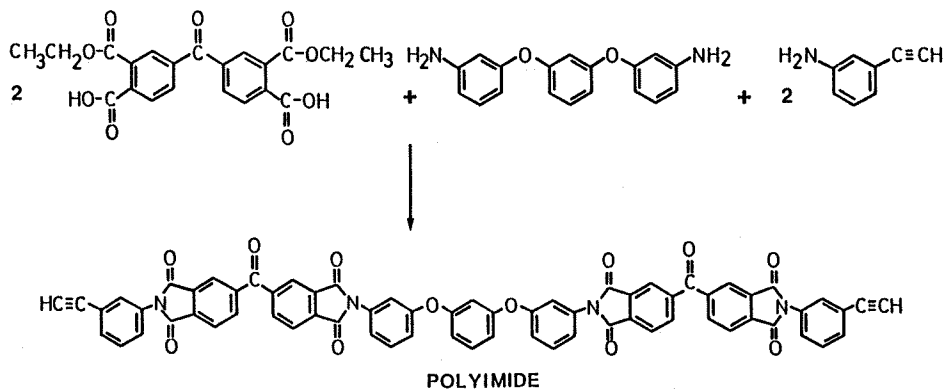


Figure 7. Synthesis of Acetylene Terminated Polyimide (Thermid 600).

subsequently developed by the Societe Nationale des Poudres et Explosifs.

#### Chemistry

PSP represent an unusual family of high temperature resins based on heterocyclic aromatic polymers obtained by condensation of aromatic aldehydes with di or tri methyl pyridines. Structure is as follows:

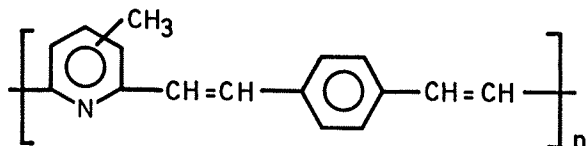


Figure 8. Polystyrylpyridine resin

PSP resins can be cured between 200-250 deg C by a mechanism which has not been completely elucidated.

A modified resin based on a vinyl terminated polystyrylpyridine (VPSP) prepared by capping PSP oligomers with 2-methyl-5-vinylpyridine has been developed (35). The modified resin is ideally suited to copolymerisation with bismaleimides. The copolymer is used in honeycomb constructions in fire blocking applications.

#### Fabrication

PSP resins can be fabricated by an autoclave route using a maximum temperature of 200 deg C for 9 hours under a pressure of 0.7 MPa. Post cure can be varied depending on the desired final use temperature and is usually between 4-16 hours at 250 deg C.

#### Properties

Typical RT ILSS values are 90-100 MPa for unidirectional PSP resins (PSP 6022/Toray T300) and is only slightly affected by post cure. After post cure (16 hours at 250 deg C) ILSS values are 55 MPa at 300 deg C, 49 MPa at 325 deg C and 44 MPa at 400 deg C. PSP resins exhibit comparable properties to state of the art polyimides. Thermal ageing of PSP resins is also impressive. RT ILSS value of 85 MPa is only

reduced to 60 MPa after 1500 hours at 250 deg C. A value of 40 MPa is obtained after such ageing and testing at 250 deg C.

In addition to the high temperature properties, PSP resins also possess good low smoke emission properties and moisture resistance. The resins are relatively easy to make from low cost starting materials.

#### Drawbacks

On first impression PSP resin seems to be an attractive high temperature resin system. However, in spite of the excellent properties the PSP resin has failed to attract widespread commercial attention. This is probably a result of long cure schedules and the evolution of volatiles during cure. In addition the starting materials, being pyridine based, possess an obnoxious odour, although it is believed that SNPE are trying to overcome this problem.

#### 2.1.6 Polybenzimidazoles

Polybenzimidazole (PBI) composites can be fabricated into structures which will withstand short time exposures to 650-760 deg C (1200-1400F). In this respect such composites are superior to bismaleimides and even polyimides. See Figure 8 below.

#### Chemistry

PBI has been around since 1966 when Marvel (37) synthesised poly-2,2'-(m-phenylene)-5,5'-benzimidazole from 3,3'-diamino-benzidine and diphenylisophthalate.

In the polymerisation the tetraamine is consumed to form an aldol type intermediate which evolves water to form a Schiff's base which subsequently evolves phenol to form the final polymer structure.

The evolution of water and phenol during polymerisation causes difficulties in prepreg manufacture and laminate fabrication. As a result components fabricated during the 1970's using conventional methods had void contents in excess of 10%.

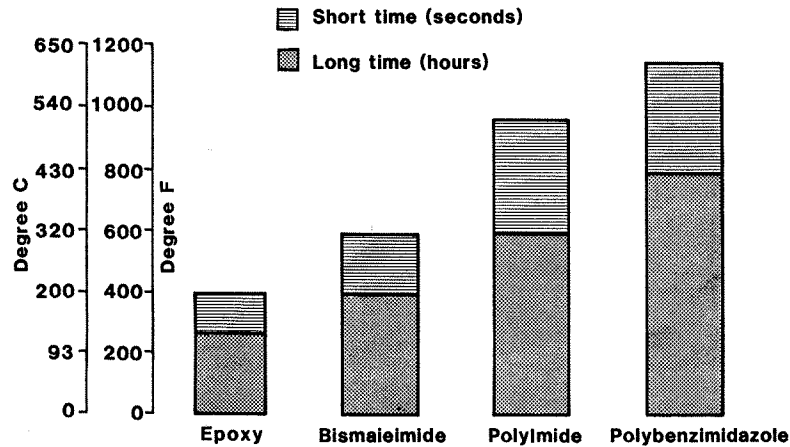


Figure 9. Use Temperatures for Matrix Resin Composites.

### Fabrication

Workers at McDonnell Douglas have developed a method of producing PBI laminates with low void contents (38). Here a low molecular weight PBI is impregnated by hot melt on carbon fibre tows laced with PBI fibre. The prepreg is laid up and compressed at high temperature and pressure. A small particle ceramic powder is used to transfer load from the press to the part. For maximum temperature resistance of the cured laminate the final conditions are a somewhat severe 450 deg C and 2500 psi. In the fabrication process a complicated schedule must be used to keep the volatiles in an appropriate physical state for removal from the composite.

### Properties

The high temperature properties of PBI composites are quite remarkable for an organic material. At 400 deg C (750F) tensile shear strength is about 62 MPa which drops to about 21 MPa at 510 deg C (950F). Although at this latter temperature properties are low, load is still carried by the fibre through the matrix. Other high temperature matrices such as polyimides were also tested in shear. At 510 deg C these matrices had softened and vaporised giving no residual shear strength.

### Drawbacks

PBI composites are extremely attractive for applications requiring very high temperatures for short times (eg, missiles). However, a significant amount of work still remains to be done to develop a low cost manufacturing process and design data base for this type of composite. In addition, the benzidine based starting materials are highly toxic!

#### 2.1.7 Thermoplastic Systems

There are a variety of thermoplastic or linear resins that exhibit useful high temperature properties. This section will review the more well known systems.

#### 2.1.7.1 Condensation Polyimides

Condensation type polyimides can be prepared by reacting aromatic diamines with aromatic dianhydrides. Polyimide prepreg is prepared by dissolving the appropriate reactants in a high boiling aprotic solvent (eg NMP). The major drawback of this approach is that the high boiling point of the solvents coupled with their tendency to form complexes with the polymer make removal during processing difficult. Complex formation can also interfere with imidisation which can result in reduced performance. Composites with low void contents are difficult to achieve. Despite these obvious drawbacks some systems have received considerable attention:

#### Skybond and Pyralin Resins

These systems manufactured by Monsanto and Du Pont respectively were developed in the early 1960's. Both systems are based on the anhydride, BTDA, with the Skybond series employing methylene dianiline as the aromatic amine. Several components have been made with these systems but interest is now declining. Both systems exhibit good long term ageing at 316 deg C but processing is the main problem.

#### Avimid K

Avimid K is a thermoplastic polyimide of undisclosed structure. Although this material exhibits both high temperature performance (Tg 277 deg C, use temperature about 230 deg C) and exceptional toughness, major problems have been encountered in the production of void free composites. Du Pont have spent considerable time and effort in developing a suitable fabrication method. The company has made some progress but further work appears to be necessary.

#### Avimid N

Avimid N (previously known as NR 150) is, in terms of temperature capability, the big sister of

Avimid K. The material is based on the oxidatively stable 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane:

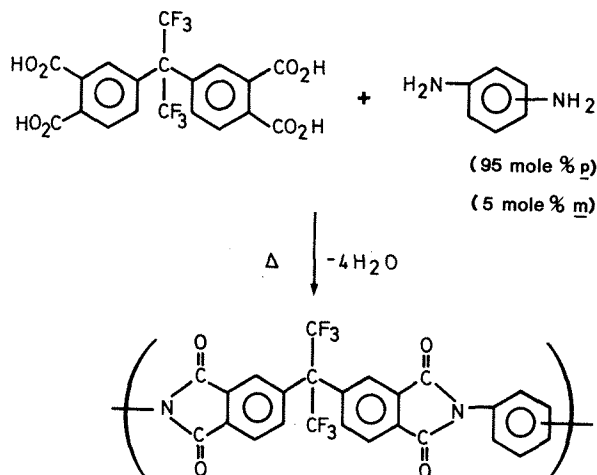


Figure 10. Synthesis of "Avimid N"

Avimid N laminates prepared by compression moulding using a final mould pressure of 2500 psi exhibit outstanding elevated temperature property retention characteristics. For example ILSS of a carbon composite at 316 deg C (600F) is about 44 MPa and after 500 hours at 316 deg C the value is reduced to 29 MPa (39). Unreinforced Avimid N exhibits excellent retention of properties even after 100 hr exposure in nitrogen or air at 371 deg C (700F). Tg of the material is about 360 deg C. However, severe processing problems have been encountered in the fabrication of composites due to a combination of factors such as condensation volatile evolution, low flow and tenaciously held solvent.

In the early 1980's Du Pont withdrew Avimid N from the market because of limited interest. The company claims that it will be re-introduced in the near future, possibly highly modified to ease processing problems.

#### TRW Partially Fluorinated Polyimide

The use of the novel monomer, 4-BDAF, to toughen PMR-15 has been discussed in Section 2.1.3. This diamine was originally developed by TRW to prepare a family of high performance thermoplastics. One of the more promising is based on pyromellitic dianhydride and 4-BDAF (designated PFPI for partially fluorinated polyimide).

Samples of PFPI have been provided to General Electric for evaluation. Carbon composites were prepared using compression moulding. These were then machined into compressor stator vane bushings. A one hundred hour exposure at 357 deg C under a four atmosphere flow of compressed air produced a weight loss of only 8%.

Preparation of large components from the PFPI system has not been reported. Processing problems could be a major drawback. PFPI technology has now been licensed to the Ethyl Corporation, from the original licensee Morton Thiokol.

#### LaRC TPI

LaRC TPI is a thermoplastic polyimide developed by NASA Langley Research Centre primarily as a high temperature adhesive (see Section 2.3). It is based on BTDA and 3,3'-diaminobenzophenone:

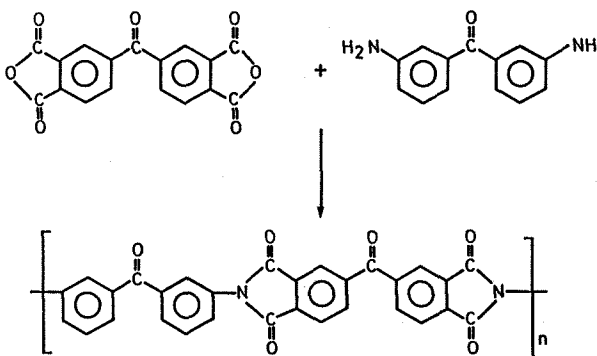


Figure 11. Synthesis of "LaRC TPI"

The general properties of this material make it suitable as a composite matrix. However, only limited work has been carried out in the area. Problems could be encountered in processing due to the difficulty in removing residual solvent.

#### Matrimid 5218

Matrimid 5218 is a thermoplastic polyimide produced by Ciba-Geigy. The polymer is based on a proprietary diamine, 5(6)-amino-1-(4-aminophenyl)-1,3-trimethylindane and BTDA. The material is fully imidized during manufacture. It is soluble in a number of solvents.

Prepregging of Matrimid 5218 can be carried out from butyrolactone. Composites can be prepared by press moulding at 316 deg C (600F) at 100 psi. Panels prepared show a high level of fracture toughness. Use temperature is around 230 deg C with a Tg of 280 deg C. Very little other data is available. Because of the solubility of the material its use as a composite matrix may be limited to certain applications.

#### 2.1.7.2 Other Thermoplastic Systems

There are a number of other thermoplastic polymers that are worth a mention:

##### Polvetheretherketone (PEEK)

PEEK was developed by ICI and shows great promise as a thermoplastic matrix for composites. The material exhibits outstanding toughness and solvent resistance. Tg is about 140 deg C which limits the use temperature to about 100 deg C. Although, because of its highly crystalline nature, use temperatures considerably higher than 100 deg C may be possible.

##### Polyphenylenesulphide (Ryton)

Ryton is a crystalline, aromatic thermoplastic polymer made by reacting dichlorobenzene with sodium sulphide. Tg of the material is 88 deg C



and Tm 277 deg C. Again because of the high crystallinity possible use temperatures may be in excess of the Tg.

#### Polysulphones

ICI's Victrex polyethersulphone has been evaluated by a number of people for use as a composite matrix (41). Although high quality prepreg and laminates can be prepared from polyethersulphone doubts exist about solvent resistance and moisture sensitivity.

#### Polyphenylquinoxalines

These polymers are generally prepared from an aromatic bis(o-diamine) with a bis(phenyl-1,2-diketone). Polyphenylquinoxalines are amorphous due to configurational disorder, readily soluble in solvents such as chloroform or m-cresol and show a low moisture uptake. PPQ film does not become brittle after ageing in air at 316 deg C (600F) for 630 hours and a weight loss of only 1.24% after 1100 hours at 316 deg C has been recorded (42).

Work at Lockheed has shown that PPQ can be readily fabricated to yield void free composites of good mechanical properties. Use temperatures have been quoted of around 260 deg C (500F). Postforming of panels, stiffeners and complex contours was demonstrated as was the reworking of poor-quality panel stock. No commercial source of PPQ prepreg is known.

#### Polyetherimide (Ultem)

General Electric's polyetherimide, Ultem, is a very attractive polymer and shows potential as a composite matrix. The material is extremely tough and exhibits good mechanical properties. However, it is very sensitive to solvent, especially while under stress. Little work on composite properties has been published.

#### Polyamideimide (Torlon)

Another material that has been considered as a composite matrix is Amoco's Torlon. This is a polyamideimide based on methylene dianiline and an aromatic anhydride. Although a thermoplastic, Torlon requires extensive processing involving high temperatures/pressures and long cure times. The Tg of the material is about 280 deg C. Little interest has been shown by the aerospace industry but it is believed that Amoco are developing processable versions using flexibilising groups based on hexamethylene diamine.

#### Xydar

Xydar is produced by Dartco and is based on polyhydroxybenzoic acid. The material is classed as a liquid crystalline polymer and was primarily developed for oven-proof Tupperware! The Tg of the material is extremely high and difficult to measure due to polymer decomposition. Prepreg production could be hindered due to problems associated with poor wetting of the fibres and a poor resin-fibre interface.

## 2.2 FIBRES

Composites intended for high temperature applications can employ a variety of fibres such as glass, carbon, boron and Kevlar. Glass is sometimes used for applications requiring radar transparency, eg radomes. Kevlar is little used due to its poor high temperature performance and boron not at all due to expense and limited properties. Carbon is the dominant type of fibre.

The long term durability of carbon fibre composites at elevated temperatures is dependent on two factors. Firstly, the thermal and thermo-oxidative stability of the individual components and secondly the influence of the interface region between fibres and matrix on resin stability.

Work by Scola (43) has shown that fibre type has a profound effect on PMR-15 composite properties. Laminates prepared from a variety of fibres show different properties at room temperature and after isothermal ageing. ILSS of 350 deg C aged laminates show Celion 6000 unsized fibres to perform well whilst fibres such as Fortafil performed badly even though its oxidative stability is high. The poor mechanical/thermal properties of laminates derived from fibres of good thermal stability could be due to poor resin-fibre bonding and the presence of contaminants on the fibre surface such as sodium or potassium. The presence of these materials, as determined by secondary ion mass spectrometry (SIMS), may cause resin degradation.

Scola also observed that stability of some composites was greater than that of the individual components (ie, fibre and resin). This was attributed to an overall "protective blanket" around the matrix provided by fibre decomposition.

Work by Petker and Stern (45) also reinforces the importance of fibre type on composite properties. In this work PMR-15 composites were fabricated from a variety of fibres. After post curing at 316 deg C (600F) the laminates were then aged at temperatures up to 371 deg C (700F). This final heat treatment raises the rigidity of the composite but reduces the RT ILSS values, the extent of which is dependent on the type of fibre used. The occurrence and degree of microcracking in oriented composites was also observed to differ for different fibres. For Fortafil 5A, Celion 6000 and HT-S the relative frequency of occurrence of microcracks was in the ratio 1:5:22. The work concluded that the observations were due to thermal decomposition at the fibre/resin interface. The superior performance of the F5A fibres in regard to microcracking was ascribed to a treatment applied to the fibre after surface treatment, which is designed to remove unstable material from the surface.

In commercially available PMR-15, epoxy sized Celion fibres are used because of their superior performance on isothermal ageing (see Figure 12 below).

The "size" applied to a carbon fibre serves to prevent fibre damage during handling. Enhanced fibre-resin bonding may also result.

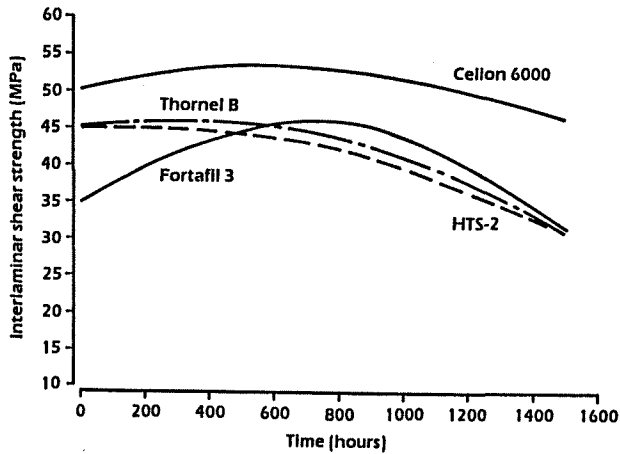


Figure 12. Thermal ageing of PMR-15 laminates (after reference 24).

At present most commercial fibres used in composites for high temperature applications are sized with a conventional epoxy resin at levels up to 1.0-1.5% by weight.

There has been only a limited amount of work published on the effect of size on composite properties. Luippold (45) has investigated the effect of different fibres and sizes on the composite properties of PMR-15 and LaRC 160. He concludes that after 1600hrs at 316 deg C (600F) epoxy sizing on both tape and woven carbon reinforced PMR-15 and LaRC 160 was at least as good as polyimide-sized products (PI03-Celanese, Thermid AL600-National Starch). However, sizing differences (as measured by a range of mechanical properties) could have been masked by matrix resin degradation after extended times at 316 deg C. A difference was noted in the two polyimide sized materials. After 1600 hr at 316 deg C, Thermid 600 sizing gave panels of better 316 deg C properties than PI03 sized material.

In designing composites intended for high temperature applications the fibre type and size must be considered. In many people's views a "system" is needed with the resin matched with the size and with the fibre.

### 2.3 ADHESIVES

As with metal components, the bonding of individual composite parts is sometimes necessary. However, traditional metal fastening techniques such as bolting or riveting are not suitable for composites. Holes drilled in composite parts cut through load carrying fibres. Consequently, adhesive bonding of composites is an extremely attractive alternative; no holes are required and the lightweight aspect is maximised. In addition stress levels are reduced and more evenly distributed. Historically, the development of composite adhesives has lagged behind that of the composite despite the fact that to produce a component, bonding of individual parts is often necessary. Several types of adhesive will be discussed:

#### \* Epoxy Adhesives

Epoxy adhesives based on multifunctional resins are available which exhibit good strength retention at temperatures up to about 200 deg C. Epoxies are comparatively low in cost and are by far the simplest and most economical adhesives to process. Full cures may be accomplished at moderate temperatures (150-200 deg C) without the evolution of volatiles, thus permitting dense, non-porous glue lines to be obtained with low pressure bonding. However, where long term ageing is required epoxies are limited to applications requiring continuous service temperatures no higher than 150 deg C.

#### Epoxy-Phenolic Adhesives

Epoxy-phenolic adhesives are capable of withstanding high temperatures for short times and as such are suitable for use on missiles. These adhesives are of low cost and are easily processed requiring low pressures (0.28 MPa/40 psi) and low temperatures (150 deg C/300F). Heat ageing of epoxy phenolics is also good provided the atmosphere is nitrogen. With steel substrates in air lap shear strength drops to zero after only 100 hours heat ageing.

#### Bismaleimide Adhesives

Bismaleimide adhesives are suitable for use up to about 200 deg C and as such fill a niche between epoxy based adhesives and the polyimides. However, the same drawbacks apply to these adhesives as to the matrix grades (see Section 2.1.2). Unmodified bismaleimide adhesives are extremely brittle and modification is necessary usually with a reactive diluent such as diallyl phthalate or with a toughening agent such as a reactive elastomer (eg, carboxy terminated butadiene-nitrile rubbers). Much work is being directed towards the synthesis of toughened systems. One of the major applications is in the production of BMI/honeycomb constructions.

#### Condensation Reaction Polyimides

Condensation type polyimides (otherwise known as linear or thermoplastic polyimides) have been commercially available for some time. In 1972 Du Pont began marketing NR150 type adhesives (see Section 2.1.7). This material shows excellent high temperature adhesive properties but was difficult to process because of the presence of condensation volatiles and a high boiling solvent. The material was widely evaluated as an adhesive until its removal from the market in 1980. Other linear aromatic adhesives have been available from a number of companies over the last few years. Most of these adhesives are capable of bonding small areas for applications at 316 deg C. Large area bonding is possible provided the joint is well vented to allow for the escape of volatiles.

Because of the problems associated with the bonding of linear polyimides research has focussed on the development of other linear polyimide film adhesives. One of the leading materials developed at NASA Langley Research Centre is termed LaRC-TPI (46) (for chemistry see Section 2.1.7). LaRC-TPI is currently being investigated

as an adhesive for laminating large areas of polyimide film for both aerospace and industrial applications in the production of flexible electrical circuitry. In addition the adhesive is also a leading candidate for the bonding of composite structures. The ability to form large area, void free bond lines is, according to NASA, "unique for fully aromatic linear polyimide adhesives". The retention of properties after long term exposure is extremely good. Lap shear strength on titanium adherends after 3000 hr at 232 deg C and tested at 232 deg C is about 21 MPa.

Other work at NASA also looks of interest. A polyimidesulphone adhesive has also been developed based on BTDA and 3,3'-diaminosulphone (47). This material combines the thermoplastic properties of polysulphones with the solvent resistance of polyimides. Processing can be carried out in the range of 260-325 deg C to yield strong, high temperature adhesive bonds. On titanium, room temperature lap shear strength values are about 31 MPa and only drop to 18 MPa at 232 deg C.

Addition Reaction Polyimides

Addition reaction polyimides remain thermoplastic after imidisation and solvent removal has occurred. When pressure is applied a dense non-porous glue line is obtained. Upon further heating curing takes place via an addition reaction to give a high strength bond.

Most addition type polyimide type adhesives are based on PMR type chemistry (see Section 2.1.3). Much work has been carried out in the synthesis of addition polyimide adhesives containing various end groups (48). One of the favoured systems developed by St. Clair and Progar (49), known as LaRC 13, is based on BTDA, NA and 3,3'-methylene dianiline. LaRC 13 can be autoclave processed with its high degree of flow arising from the meta linkage. The adhesive can be used at temperatures in excess of its glass transition temperature of 270 deg C. A major usage of the

adhesive has been in the bonding of honeycomb sandwich structures. Lap shear strength values on titanium are 21 MPa at room temperature and 10 MPa at 316 deg C. On carbon/PMR-15 composite the values are 16 MPa at room temperature and 13 MPa at 316 deg C.

Further work on LaRC 13 has been directed to increasing the toughness by incorporation of elastomers (50). However, widespread commercial use of the LaRC type adhesives has been hindered because of the expense of synthesising the meta diamines.

Acetylene terminated Thermid materials have also been evaluated as adhesives (see Section 2.1.4). These materials perform well but processing difficulties have limited their acceptance.

3. APPLICATIONS

Applications for high temperature composites vary from supersonic transport aircraft to missiles. Time and temperature requirements differ. See Figure 13 below.

3.1 Military Aircraft

One of the earliest applications for high temperature composite structures was in the development of polyimide radomes for US Navy Aircraft the EA-6B and A-6E (51). Fabrication was carried out by Grumman using Monsanto's Skybond resin. The EA-6B radome measures 4.5 x 0.5 x 0.6m and more than 200 of these structures have been produced to date. Following on from this technology Grumman fabricated the weapon bay radome for the EF-111a aircraft. This is a 4.9 x 0.6 x 0.6m sandwich structure based on glass/polyimide facesheets bonded to polyimide honeycomb with polyimide film adhesive. The radome is presently in production and represents the biggest polyimide component yet made.

Some of the production difficulties associated

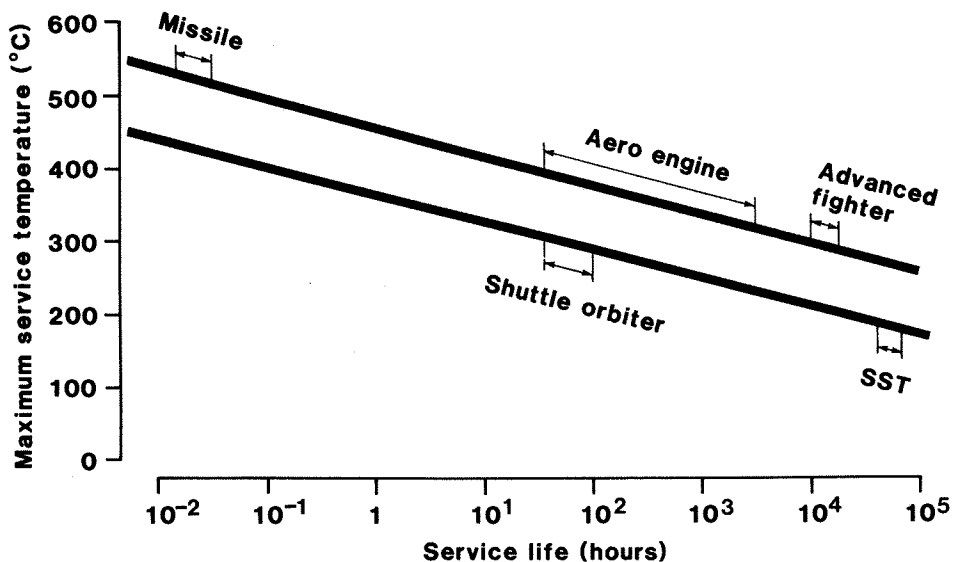


Figure 13. Time/Temperature requirements for various applications.

with condensation polyimides, such as Skybond were removed with the emergence of the bismaleimide class of resins. One of the first major applications for BMI composites was in the production of the wing skins and ribs for the F16-XL cranked arrow fighter plane. The material used was V378A from US Polymeric. The first prototype flew in July 1982 and no major problems were encountered (52).

The same BMI formulation has also been used in the fabrication of a number of parts for the AV8B. The ventral fin, inboard trailing edge, strakes and gun pods have been produced successfully.

A similar bismaleimide, Compimide 800 from Technochemie, has been used in the fabrication of the airbrakes for Dornier's alpha jet. Another interesting application is the radome for the B1 Bomber. This is made from Hexcel's F178 BMI together with glass or quartz reinforcement.

The incorporation of composites in fighter aircraft over the last few years has risen dramatically:

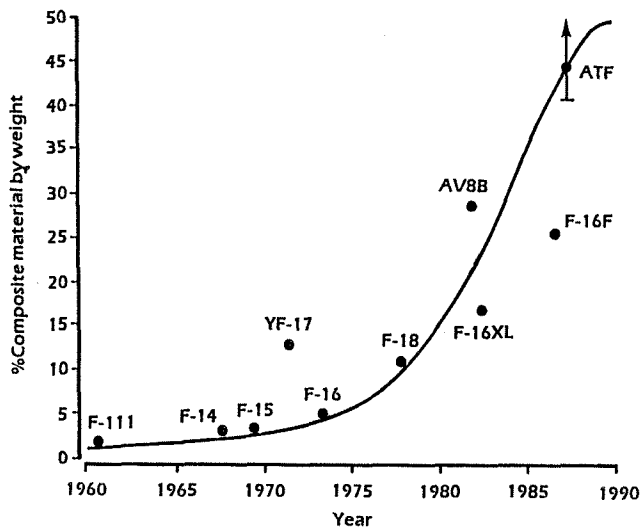


Figure 14. Composite usage in military aircraft.

At present the AV8B is 26% by weight advanced composite (mainly epoxy). The advanced tactical fighter (ATF) and the European Fighter Aircraft (EFA) are likely to be 40% by weight composite. Perhaps the shape of things to come is exemplified by the "Bismaleimide Composite Fuselage Structures Programme". The objective of this is to design and develop a fuselage structure which can satisfy the load and environmental requirements of a fighter/attack V/STOL aircraft. Potential advantages claimed are a 28% weight saving, damage tolerance, structural integrity/reliability, reduced maintenance and 10% lower production costs. The programme is being carried out by Grumman using Hercules 4001 BMI resin.

### 3.2 Aero Engines

The application of organic matrix composites to gas turbine engines has been the subject of numerous Government and company funded programmes since the 1960's.

One of the first applications of high temperature composite in engines was for the Rolls-Royce RB 162 engine. The compressor rotor blades, stator vanes and shrouds, the inlet guide vanes, the bearing housing and compressor casings were manufactured in glass reinforced Keramid 601 bismaleimide. The engine is still in service today (53).

Despite this early work very little of the potential of advanced composites has been exploited even though a significant number of components have been designed, fabricated and tested. This slow rate of incorporation can be attributed to factors including the critical nature of the component, lack (until recently) of high temperature matrices, small component size, (compression moulding needed - high tooling cost), small production volumes and the problem of interfacing with metal components. Nevertheless, activity at present is intense with much effort being directed to the development of high temperature components.

In the low bypass ratio augmented turbofan engines, that are best suited to fighter aircraft, very few of the components operate at temperatures low enough for epoxy matrix composites. However, the number of components suited for polyimide composites is quite significant. Pratt and Whitney, for example, have considered several components including compressor shrouds, intermediate case fairing, airframe interface ring, augmentor duct, external nozzle flap and nozzle case.

Other organisations are actively involved in the production of components for military engines. In the main, PMR-15 has been selected as the matrix resin.

Ultra high speed fan blades were the first structural components selected for fabrication in PMR-15. Pratt and Whitney designed the blade which was fabricated on TRW equipment. Blade span is 11" and chord 8". At its thickest section the composite structure consists of 77 plies of material arranged in varying fibre orientation. Ultrasonic and radiographic scans of the compression moulded blades indicated that they were defect free (54).

Under contract from NASA Lewis, General Electric developed an inner cowl for a "Quiet Clean Short-Haul Experimental Engine"(QCSEE). The cowl, which was autoclave fabricated, has a maximum diameter of about 36" and is primarily of honeycomb construction. The cowl was installed in the QCSEE engine and did not exhibit any degradation after more than 300 hours of ground engine testing.

General Electric are also involved in the development of a T300 carbon fabric/PMR-15 composite to replace the titanium duct presently used on the F404 engine for the US Navy F18 fighter. The titanium duct is a sophisticated part made by forming and machining titanium plates, followed by chem-milling to reduce weight. Preliminary studies indicated that significant cost and weight savings could be achieved by using the composite version. The F404 duct is a monolithic structure which needs to withstand

fairly high loads. The fabrication process is complex and consists of many operations after the initial autoclave fabrication of the shell. The duct has been installed on an F404 engine and successfully withstood 300 accelerated mission test cycles (50). The duct was tentatively scheduled for production in late 1985. It is not known whether the target was achieved.

For transport aircraft where high bypass ratio engines are used, inlet temperatures are low enough to allow epoxy matrix composites to be used for the fan outer ducts. The inner ducts and cowlings operate at higher temperature and are prime candidates for polyimide matrix materials.

Several organisations have identified components suitable for fabrication in polyimide composite. Boeing, for example, in collaboration with other companies are involved with the development of a 747 nacelle cowl structure and a 757 thrust reverser 'C' duct (56). Major concerns at present include long term thermal exposure durability requirements, lack of high temperature design data and tooling techniques. In addition, recent problems have arisen concerning microcracking and prepreg variability.

A further application at present being considered by Boeing is the 747 Engine Start and Thermal Anti-Icing Duct System. The current system, made from titanium weighs about 800lb. Boeing is at present finalising feasibility studies.

### 3.3 Space Shuttle

The use of advanced composites has reduced the empty weight of the Space Shuttle by an estimated 1500 Kg over the initial all metal designs. The Shuttle employs boron/epoxy for much of its aft thrust structure. Graphite/epoxy skins over "Nomex" honeycomb are used on its orbital manoeuvring systems and on the cargo doors.

Several components of the shuttle are being considered for fabrication in polyimide/carbon composite. These include the body flap, elevon and vertical tail.

An early programme at NASA was initiated to develop the technology to build the aft body flap from advanced composites. This structure is about 2m wide by about 7m long. Both a matrix and a high temperature adhesive were needed. Use temperature is around 316 deg C (600F) for a minimum of 125 hours. A 27% weight saving over an equivalent titanium structure was a major target.

Four matrices were evaluated for the programme; Du Pont's Avimid N, Thermid 600 from National Starch and the NASA developed systems PMR-15 and LaRC 160. Processing problems were encountered with all these materials. Eventually Boeing produced a half size component from the leading contender, PMR-15. Ground testing under simulated flight conditions was successful.

High temperature adhesives are also needed for use in the Shuttle. Workers at Rockwell (57) have studied adhesives for bonding both titanium and polyimide/carbon components. The conclusion was that modified LaRC 13 and LaRC 160 systems

satisfied the Shuttle Target requirements in terms of processability, ability to form large area, void-free bonds and in bond strengths to substrates of titanium, carbon/polyimide composites and steel.

One of the major drawbacks of most organic structures is their susceptibility to degradation by atomic oxygen encountered in the residual atmosphere of low earth orbits. Research is ongoing to develop silicon, fluoropolymer and metal coatings. The proposed US space station may well be built from carbon/epoxy struts thinly coated with metal.

### 3.4 Missiles

Missiles, operating supersonically, easily exceed the temperature limits for most resin matrix composites. However, a number of the currently postulated tactical missiles have short time, high temperature requirements in the range 200-300 deg C (400-900F) range (See Figure 15 below).

Such requirements can be met with polyimide and polybenzimidazole matrix composites.

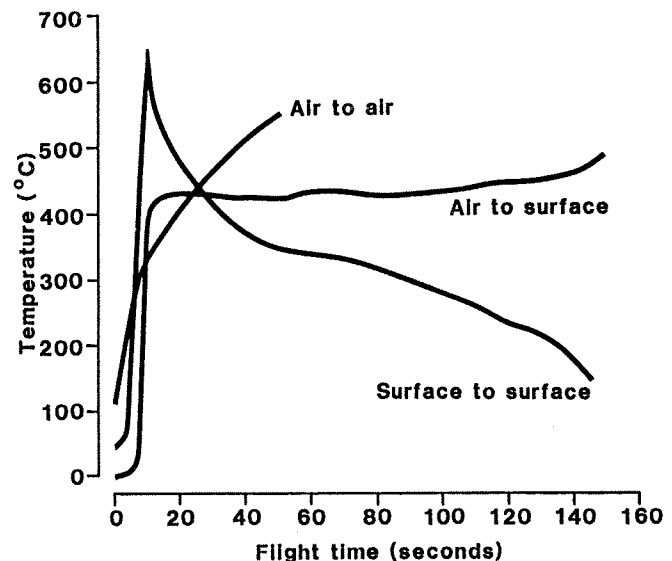


Figure 15. Typical Thermal profiles for Tactical Missiles (after reference 58).

Initial design studies carried out by Vought (58) on typical missile components such as fins, inlet fairings and nose cone have indicated weight savings of 50-67% compared with steel.

Inlet fairings have been successfully fabricated from PMR-15/carbon composites with close dimensional tolerance and smooth aerodynamic surfaces. Wind tunnel testing has shown that test panels exceeded their 370 deg C (700F) design temperature and survived the 100 seconds of exposure with very little deterioration of the material. A 67% weight saving was achieved.

For higher temperatures at shorter times, polybenzimidazoles have been considered. Workers at McDonnell Douglas (59) have successfully produced a PBI missile fin using a low cost augmented press cure process. "Only by a thorough

understanding of the chemistry, rheology, kinetics etc of the PBI resin was this possible", states the paper.

The missile fin has been tested in a wind tunnel. Conditions were 100 second tests at Mach 4 and 59,000ft. Leading edge temperatures reached 398 deg C (750F). In a second test the fin withstood 350 seconds continuous exposure to Mach 4.4 at 70,000ft. The fin was in good condition after these tests with only the degradation on the resin-rich leading edge.

Missile radomes are also prime candidates for high temperature composites. Bismaleimide resin systems have been used to fabricate radomes by a resin transfer moulding technique (60). Matched metal tooling was used with woven fabric shapes as reinforcement. Electrical and mechanical testing of the radomes showed them to be of high quality.

#### 4. FUTURE FOR HIGH TEMPERATURE COMPOSITES

Recent predictions of aerospace technology in the year 2000 (61) indicate that the development of the following craft is a possibility:

- High speed, high capacity rotorcraft with 40% increase in fuel efficiency
- Transport aircraft operating up to Mach 1 with large payloads/range
- High altitude reconnaissance aircraft (300 Knots, 80,000ft, one week duration)
- Advanced fighters with cruise capability at Mach 3.5 above 70,000ft
- Supersonic transport aircraft capable of carrying 300 passengers at Mach 2.7 over 4500 miles
- Manned fighters or interceptors flying at Mach 6-8 and unmanned interceptor missiles flying at Mach 8-12
- Transatmospheric vehicles such as space shuttle, "Orient Express" and HOTOL.

For all these craft there is a need for advances in technology such as propulsion systems, aerodynamics, structures, computing and materials. Many of the futuristic craft will need to be light weight and capable of surviving high temperatures.

As well as advanced polymer composites extensive use will be made of other composites such as ceramic and metal matrices and carbon/carbon.

For high temperature polymer composites to be used to any great extent in the futuristic craft outlined above several problems will have to be overcome:

\* High temperature processable resins will have to be developed that exhibit good mechanical properties up to 400 deg C, that are resistant to solvents/chemicals/fuel, to impact and to thermal cycling. Novel curing reactions may have to be

devised, perhaps using strained ring systems such as benzocyclobutene recently developed by Arnold (62). New approaches also will be needed. The use of reactive oligomers coupled with novel end caps and chain extending monomers recently pioneered by Shepperd and Lubowitz (63) looks of great interest. In addition more use will need to be made of computer molecular modelling to aid the synthesis of optimised resin systems.

\* Fibres and fibre sizes will need to be developed in conjunction with the resin to produce high quality composites capable of surviving hostile environments. Emphasis will be placed on a thorough understanding of surface science.

\* Adhesives will need to be developed that can bond large areas, that are durable and show resistance to high temperatures. Effort will need to be directed towards an understanding of composite bonding.

\* Better control of processing is needed, the ultimate goal being rapid low cost fabrication. Here thermoplastic sheet stock that can be thermoformed may offer a route forward. For "conventional" thermosetting systems better control of the curing cycle is needed. The use of real-time computer control employing remote sensing probes to assess the physical/chemical state of the reaction will be needed.

#### 5. CONCLUSIONS

1. There is a need to develop advanced polymer composites capable of continuous use above 150 deg C for applications in jet engines, aircraft, missiles and spacecraft.

2. Much work has been carried out in the synthesis of resin systems to operate in the temperature range 150-350 deg C. In the range 150-200 deg C the bismaleimide resins appear favourite but problems associated with toughness and microcracking need to be overcome. For 200-300 deg C use, PMR-15 is the leading candidate. Many components have been made and flight tested. Problems associated with prepreg quality and microcracking need to be solved.

3. Although fibres are available of high thermo-oxidative stability more attention needs to be paid to the fibre-resin interface and the development of compatible fibre sizes.

4. To maximise the lightweight aspect of composite materials, high temperature adhesives need to be developed that are both tough and durable.

5. The processing of high temperature resins (for use above 200 deg C) remains a problem. Cheap and fast methods need to be introduced.

6. The future for high temperature polymer composites looks bright providing certain problems can be overcome.

## 6. ACKNOWLEDGEMENTS

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