

REVIEW PAPER

Polymer-matrix Composites for High-temperature Applications

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ABSTRACT

Over the last decade, applications of fibre-reinforced composites using polymer matrices have seen tremendous growth. In spite of the complexity of their behaviour and the unconventional nature of fabrication and other aspects, the usage of such composites, even for primary load-bearing structures in military fighters and transport aircraft, and satellites and space vehicles has been beneficially realised. Most of such usage constituted structural applications (such as in airframe) where service temperatures are not expected to be beyond 120 °C. Attention is now focussed on expanding the usage of such composites to other areas where temperatures could be higher—in the range 200–400 °C. The intended applications are structural and non-structural parts on or around the aero-engines and airframe components for supersonic or hypersonic aircraft. The development of polymer matrices—such as bismaleimides, polyimides, cyanates, and liquid crystalline polymers and others—has brought such applications within the realm of practicability. The associated problems have been in terms of suitable processing technologies and in balancing the requirements of the performance with those of the processing. This paper describes briefly such developments and reviews the potential application scenario.

Keywords: Polymer-matrix composites, aerostructures, PMC, bismaleimides, polyimides, cyanates, BMI, LICP, liquid crystalline polymers, processing technology, high temperature, thermoplastic polyimides (TPI), aerospace structural components,, high-temperature fibre-reinforced composites

1. INTRODUCTION

The advent of fibre-reinforced composite materials has constituted a major breakthrough in the construction of lightweight structures. In particular, significant benefits have been realised in the aerospace sector to meet the severe performance requirements with stringent demands of reliability. Almost all aerospace structural components—airframes of fighter aircraft, helicopters, control surfaces and fins of civil aircraft, various panels in satellites, antennae, rocket motor casings, and some complete airframes of small aircraft are witnessing an increasing use of the advanced composites. An important technological development

that has contributed significantly to this growth of composites is the development of strong and stiff fibres such as glass, carbon, and aramid along with concurrent developments in the polymer chemistry, resulting in various polymeric materials to serve as matrix materials. In particular, the versatility of the technology of the carbon fibres having various properties has played a key role in this growth. With complementary developments in computer hardware and software technology, and in computational methods of analysis rendering help to analyse and understand the material behaviour and to provide predictive as well as design tools, the complexity

of the polymer-matrix composites has been overcome to facilitate the extensive applications.

The most commonly used composite class for load-bearing structural applications is the continuous fibre-reinforced polymer-matrix composites. The most popular material systems have been the epoxy-based resins reinforced with carbon, glass, or aramid fibres. Current military fighters such as European fighter aircraft (EFA), French rafale, Swedish JAS-39 or Indian light combat aircraft (LCA) have about one-third of the airframe structure built using carbon fibre polymer composites. These composite systems have service temperatures around 100-120 °C on continuous basis and around 135 °C for short duration.

For most structural applications in the current aircraft designs, this has been adequate and has led to successful applications. This success has spurred the engineers to consider polymer composites for a wide range of applications in other areas where higher temperatures are encountered. Such applications cover many parts on and around the aero-engine in current usage and will cover several airframe structural components in future high-speed transport aircraft. Further, aircraft structures in future, particularly leading edges, may be required to endure quite high temperatures (350 °C or above) as higher speeds and space re-entry features will become a part of the aeroplane designs. As the polymer matrix material is the most affected (rather than the reinforcing fibres such as glass or carbon) by high temperature, it is the matrix material that has been the focus of attention in the development of high-temperature polymer-matrix composites. Already, the research in polymeric matrices over the past couple of decades has come up with systems which can perform satisfactorily up to 300 °C. Further, the research and development efforts to produce polymer-matrices with higher service temperatures up to 500 °C have shown encouraging trends. With each new polymer system developed, the development of a process to make good quality composite components has been a challenge and this forms a key feature in the high-temperature polymer-matrix composites research.

This paper briefly describes the developments in high-temperature polymeric composites, reviews the current scenario, and indicates trends of future

research. Focus is placed on matrix-dominated issues. A significant portion of the paper is devoted to polyimide matrices, which form the bulk of the high-temperature composites at present.

2. PERFORMANCE REQUIREMENTS & TYPES OF MATERIALS

Based on the experience with composites for load-bearing applications in aerospace sector, which is mostly on the carbon-epoxy composites, typical mechanical property values and processing requirements for viable use of polymer-matrix composites in load-bearing applications are depicted in Table 1. The mechanical properties are to be achieved and retained under the worst environment of the component. This translates for most composites as the hot-wet properties, ie, properties at the continuous service temperature in fully moisture-saturated condition. While many of the properties (Table 1) are the fibre-based parameters, the matrix plays a significant role in translation of fibre properties into composite properties. Moreover, compression and shear behaviour is dominated by the matrix and the interface behaviour. Environmental resistance and impact-damage tolerance are also dominated by the matrix behaviour. The considerations of mechanical properties for high-temperature polymer-matrix composites systems are thus the same as presently used carbon-epoxy composites. The attention is focussed on their behaviour at high temperatures, and their suitability for practical applications. Thus, the emphasis is mainly on retention of properties at high temperatures, glass-transition temperature and its degradation by moisture, thermal stability, ageing, and oxidation. The important issue to be examined is one of achieving reasonable trade-offs amongst the service temperature, toughness, and ease of processing as a composite. The developments in high-temperature polymer composites are being considered in three groups:

- (a) The polymer-matrix systems with service temperatures ranging between 135–250 °C, mainly encompassing bismaleimides, cyanate esters, aromatic thermoplastics, thermoplastic polyimides, etc
- (b) The polymer-matrix systems with service temperatures ranging between 250–350 °C, mainly

Table 1. Typical requirements of PMC for application in aerostructures

Mechanical properties	Range of allowable values*
<i>Tension of UD lamina</i>	
Longitudinal modulus (GPa)	120–30
Transverse modulus (GPa)	8–10
Longitudinal strength (MPa)	1000–1200
Transverse strength (MPa)	35–65
<i>Compression of UD lamina</i>	
Longitudinal modulus (GPa)	110–125
Transverse modulus (GPa)	8–10
Longitudinal strength (MPa)	700–1000
Transverse strength (MPa)	65–150
<i>In-plane shear of UD lamina</i>	
Shear modulus (GPa)	4–5
Shear strength (MPa)	80–120
Interlaminar shear strength (ILSS) (MPa)	35–50
Interlaminar fracture toughness in mode I (G_{Ic}) (J/m^2)	> 150 (typ 400–1000)
Compression after impact strength (quasi-isotropic lay-up) at barely visible impact damage level (microstrain)	> 3300 (typ with improved resins 4000–5500)
Processing	
Suitability for making prepregs (hot-melt process/solution process)	Needs suitable viscosity and gelling behaviour with temperature
Curing and post-curing should be practicable with existing industrial equipment	Temperatures and pressures applied should be adequately low for practicability with current autoclaves. (170–320 °C; 7–15 bar). Curing times should be reasonably small from economic considerations but slow enough to be controllable
Reasonable outlife of prepregs so that large components can be laid up and cured	30–60 days

* Mechanical property values given are ranges of allowable values for composites using standard modulus carbon fibre ($E \sim 220\text{--}230$ GPa; UTS ~ 3 GPa) under the worst environment catered for in design

constituting polyimides with high glass transition temperatures

- (c) The developments towards higher service temperatures and other improvements.

3. POLYMER MATRICES WITH SERVICE TEMPERATURE RANGE (135–250 °C)

3.1 Bismaleimides

One of the attempts to develop a polymer matrix for service temperature above 135 °C, which was the limit to which the popularly used epoxies could be stretched, was to develop several imide prepolymers end-capped with reactive maleimide groups resulting

in good thermal and thermo-oxidative stability. The outcome of these efforts was the bismaleimide resins, which have since then resulted into several standard commercial products.

3.1.1 Preparation of Bismaleimide Monomers

Bismaleimide monomers are prepared by the reaction of aromatic diamines with maleic anhydride in the presence of dehydrating agents [Fig. 1(a)]. These monomers are capable of curing through thermally-induced addition reaction which gives highly cross-linked void-free network of the polymer with high glass transition temperature (~ 300 °C), good thermal stability as well as better fire-resistance

and lower moisture absorption (~ 4 %) than the conventional epoxies¹⁻⁴. These homopolymers are, however, excessively brittle ($G_{ic} \sim 50 \text{ J/m}^2$) with very low elongation to fracture (~ 1.7 %), high modulus (~ 4.2 GPa) and low strength. A large number of structural modifications resulting in reduced cross-link density through chain extension have been developed over the years to improve the properties¹⁻⁶. Two of these have become quite established in the composite industry and the commercial products employing these have been in use for some time. These are:

- (a) Advancement of bismaleimide monomers with aromatic diamines to resin adducts by chain extension and ultimately to toughened thermoset resin
- (b) Coreacting bismaleimide monomers with diallyl bisphenols or dipropenyl phenoxides

Additional secondary toughening techniques using fine particles of thermoplastic polyimide have been found useful in meeting the damage tolerance requirements of the primary aircraft structures. A wide range of bismaleimide monomers and prepolymers are commercially available for use to formulate matrix resins satisfying rheological properties for RTM or tack and viscosity for prepreg formation or processing requirements for moulding compounds. Commercial products include several bismaleimide monomers, advanced resins, reactive tougheners with allyl or propenyl functionality and RTM resins³.

3.1.2 Properties of Bismaleimide Resins

Composites with bismaleimide resins indicate good translation of fibre properties. Toughened bismaleimides have shown good retention of compression strength after the impact with good performance under hot-wet conditions. The glass transition temperatures (dry) are in the range of 270–295 °C and wet-heat deflection temperatures are in the range 220–270 °C. The carbon/bismaleimide composites have been successfully used for primary structures of the aircraft rated for temperatures around 180 °C.

3.1.3 Research in India

In India, the bismaleimide resins have been studied extensively by at least three groups. The first group at the Vikram Sarabhai Space Centre, Thiruvananthapuram has developed a useful melt-processible formulation, BM-1000; with excellent thermal and mechanical performance for in-house applications⁷. Although the composite applications have not been many, the resin has found the use in self-lubricating components with graphite and molybdenum disulphide powder. The second group at the IIT Delhi (Varma and co-workers) has extensively investigated thermal stability and curing behaviour with various amines^{5,6}. The third group at the DMSRDE, Kanpur (Alam and co-workers), has synthesised and characterised several bismaleimide resins and the similar nadicimide resins⁸⁻¹⁰.

3.2 Cyanate Esters

The cyanate ester resins do not have as good thermal ratings as the bismaleimides, but these have superior dielectric loss properties and low-moisture absorption. These features have made these as strong contenders for special applications such as in radomes, antennae covers, stealth composites, etc.

3.2.1 Preparation of Cyanate Ester Composites

The cyanate ester monomers are prepared by reacting bisphenols or polyphenols with cyanogen chloride in the presence of an organic base. The prepolymer resins supplied by the commercial resin suppliers are amorphous oligomers prepared from the crystalline monomers by thermally advancing a cyclotrimerisation curing reaction [Fig 1(b)]. Generally, 15-50 per cent cyclotrimerisation is achieved in the closely-controlled reactor processing, which is normally required. The main reaction is the formation of *s*-triazine ring (cyanurate trimer) by the cycloaddition of three cyanate groups. The commercial producers of prepreg or composites can formulate resins using these amorphous prepolymer resins or monomers with the latent catalysts (metal carboxylates) that promote complete conversions to the thermoset polycyanurate with subsequent heating to 177-250 °C. The cyanates also serve to cure epoxy resins forming cost-effective hybrids retaining an anomalously high

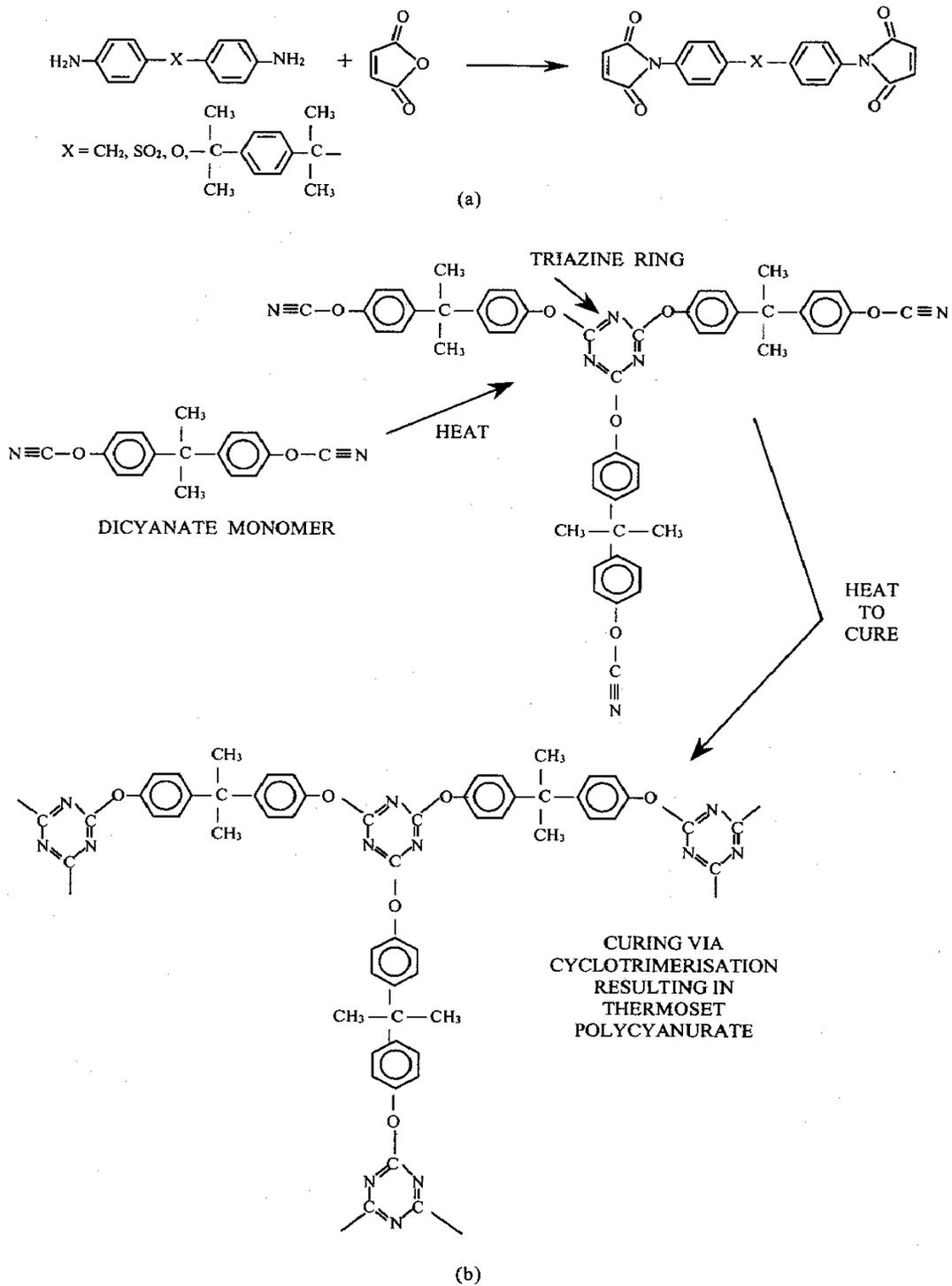


Figure 1. Chemistry of typical (a) bismaleimide resin and (b) cyanate ester resin

fraction of CE homopolymer properties. The cyanate esters have low toxicity profile and comparable storage stability when compared to epoxy resins³. The cyanate esters generally cure slowly and require catalysts to achieve practicable cure rates. Copper and cobalt acetylacetonates predissolved in alkyl phenols form stable liquid which is miscible with CE and can be used as catalysts³.

3.2.2 Properties of Cyanate Ester Homopolymer

The cyanate ester homopolymer glass transition temperature for the commercially supplied systems based on bisphenols range from 250-290 °C. These systems exhibit toughness comparable to toughened epoxies. For cyanate ester systems based on novolacs (eg, XU371 of Ciba) high glass transition temperature in the range 270-350 °C or above can be obtained. These can be quite brittle and exhibit low toughness. However, cyanate ester systems can be toughened by adding powdered amorphous soluble thermoplastics (PS, PES, PEI, PPO, co-polyesters, etc). These are added (dissolved) at the monomer or the prepolymer stage and are phase-separated on cure, forming a toughened structure. The addition of thermoplastics in quantities more than 15 per cent increases the G_{ic} significantly. Toughening can also be done through addition of reactive rubber particles or elastomeric thermoplastic. The moisture absorption is quite low (2-3%) in cyanate ester systems compared to epoxies and also BMIs. The cyanate esters can coreact with the epoxy resins and form various hybrids that can give a range of products with tailored properties, particularly suitable combinations of dielectric and thermal properties. The most significant characteristic of the cyanate ester resins is their dielectric performance. The dielectric constants of less than 3 and loss factor of less than 0.004 are common. Even when blended with epoxies, the cyanate ester blends give superior dielectric properties¹¹.

3.2.3 Applications of Cyanate Ester Composites

Principal applications of cyanate ester composites with aramid, glass or polyethylene fibres can be found in radomes¹¹, skin-covers for phase-array radars and other parts around radars, where their tailored dielectric properties are especially useful.

Composites with pitch-based carbon fibres have been used in space structures.

3.2.4 Research in India

Among the various investigations in India, the research and development efforts at the National Aerospace Laboratories (NAL), Bangalore have basically concentrated on the development of suitable cyanate ester formulation for making prepreps using hot-melt process¹². The thrust has been formulations based on bisphenol-A as well as dicyclopentadiene novolak. The latter, in particular, has shown good promise for prepregging resin system with good processibility and long outlife (~60 days) while retaining mechanical performance¹² up to 150 °C. The research workers at the VSSC have investigated various formulations with blending based on modifications of bisphenol-A dicyanate ester network¹³. Also, an oligomer preparation for composite processing based on deaconate ester has been developed with good mechanical properties and glass transition temperature of around 250 °C.

3.3 Thermoplastics

3.3.1 Thermoplastics as Matrix Materials

Need for better performance than epoxies at temperatures above 150 °C has led to the exploration of several thermoplastics as matrix materials. Amorphous thermoplastics, in general, have poor solvent resistance and exhibit a sudden drop in modulus at glass transition temperature. The other thermoplastic polymers have regions of molecular order, and thus exhibit a degree of crystallinity, which may be up to about 40 per cent. Such crystalline (actually only semi-crystalline) thermoplastics have excellent solvent resistance and show only a gradual decrease of modulus above glass transition temperature (even though the decrease in strength may be more drastic). The heat-deflection temperature for amorphous thermoplastics may be up to 20 °C below glass transition temperature. Also, even if HDT for crystalline systems may be comparable to glass transition temperature or even higher, strong creep effects near glass transition temperature will limit service temperatures to about 20 °C below glass transition temperature. The crystalline thermoplastics have,

however, relatively high processing temperatures in relation to the service temperatures, and this becomes a major handicap in their use. Table 2 lists some of the commercially available thermoplastics that can be used as matrix materials for making composites¹⁴.

3.3.2 Thermoplastics Processing

In addition to high processing temperatures, the processing with thermoplastics to make fibre-reinforced composites has raised several issues for the composite industry traditionally used to autoclave moulding and filament winding with thermoset resins. The thermoplastic prepregs can be made by solvent impregnation (with amorphous thermoplastics) or by melt-impregnation (with crystalline thermoplastics). However, the prepregs are generally too stiff and boardy with little drapability. This may result in several problems while making composite lay-up. New technologies such as powder-impregnated prepregs (where reinforcing fibres are coated with polymer powder or held together in small tubes) and commingled weaves (where the polymer is in the form of fibres woven together with reinforcing fibres) have been on the scene for some time. But, the composite industry has not yet

fully resolved the problems of inhomogeneous matrix distribution and resulting loss in performance.

3.3.3 Thermoplastics Performance

The most significant and desirable performance feature of thermoplastic composites is perhaps their high fracture toughness and resulting resistance to damage by impact. The carbon fibre composites with these resins exhibit G_{Ic} values of 1.0–2.5 kJ/m² compared to ~ 0.15 kJ/m² for early thermoset epoxies, and ~ 0.45 kJ/m² for later toughened systems. The shear mode G_{IIc} is also higher for thermoplastics than for thermosets but by a lesser margin. The composites with thermoplastic matrices have shown lower compressive strengths rather than with thermoset matrices. However, their better environmental resistance and interlaminar toughness allow the compression-after-impact strength under hot-wet conditions to be much better than the conventional thermoset epoxies and even superior to toughened thermoset systems.

3.3.4 Thermoplastics—Applications

Among the more popular thermoplastics developed and used, specifically for high-temperature fibre-reinforced composites, are the thermoplastic polyimides.

Table 2. Thermoplastic matrices for high-temperature PMC application

	Typical product	Structure*	T _g (°C)	HDT (°C)	MP (°C)	T _{proc} (°C)	T _{ser} (°C)
Polysulphone (PSU)	Udel P1700 (Amoco)	A	190	175	--	300-350	170
Polyethersulphone (PES)	Victrex 4100G (ICI)	A	220	203	--	300-320	200
Polyamideimide (PAI)	Torlon (Amoco)	A	290	278	--	350-400	270
Polyetherimide (PEI)	Ultem (GE)	A	217	200	--	335-420	197
Thermoplastic polyimide (TPI)	Avimid KIII (DuPont)	A	250	238	--	340-360	230
Thermoplastic polyimide (LaRC-TPI)	Aurum (Mitsui)	C	260	238	388	400-420	240
Polyketone	Victrex-HTX (ICI)	C	205	--	285	420-430	185
PEKEKK	Ultrapek (BASF)	C	175	--	375	400-420	155
Polyetherether-ketone (PEEK)	Victrex-PEEK (ICI)	C	143	160	343	380-400	

* A = Amorphous, C = Crystalline

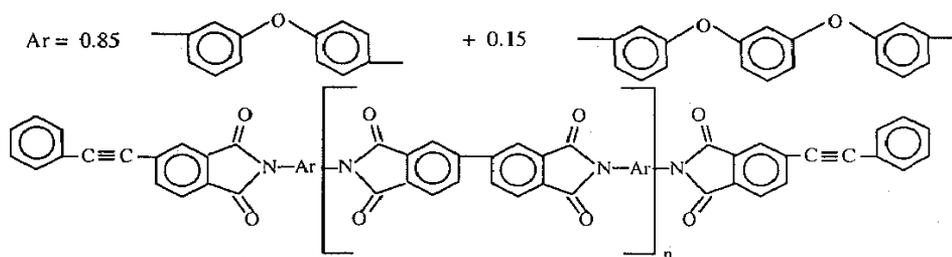


Figure 1(c). Chemistry of typical PETI-5 resin prepolymer

Originally developed by the NASA Langley Research Centre, USA, as LaRC-TPI¹⁵, these systems and other similar ones have been commercialised and are considered good candidates for aircraft components. One of the ways for combining the advantages of various (amorphous and crystalline) thermoplastic systems is to blend these. Such blends of polyetheretherketone (PEEK) with polyetherimide (PEI), etc have also been investigated^{16,17}.

3.3.5 Thermoplastics—Research at DMSRDE

In India, work on high-performance thermoplastics as matrix materials for composites is mainly on synthesis and characterisation of the PEEK and reinforcing with carbon fibres. The PEEK is now produced commercially in India; however, its use in fibre composites is only limited to a few laboratory trials. Other thermoplastics investigated, mainly at the DMSRDE include heterocyclic ring-based polyarylene ethers. Introduction of heterocyclic ring-based such as imides¹⁸, imidazole¹⁹⁻²⁰, oxazole²¹ and a few others in polyarylene ether backbone have been investigated to increase the glass transition temperature to around 200 °C.

3.4 Development of Matrix Resins & Adhesives

Some of the interesting developments of the recent years are the matrix resins and adhesives development using short imide molecules, which are oligomers terminated with phenylethynyl group²², [Fig 1(c)]. The oligomers provide low-melt viscosity for prepregging. The phenylethynyl reactive group has high-cure temperature and a good processing window can be obtained. A system based on this, namely, phenylethynyl-terminated imide, PETI-5, has been formulated by the group at the NASA

Langley Centre²³ and commercial prepregs using PETI-5 with intermediate modulus carbon fibres have also become available. The system has good processibility, no toxicity, good solvent resistance under stress, and high toughness resulting in good durability. It has been specifically qualified for aerospace components such as in high-speed civil transport aircraft with service temperatures²³ of 177 °C. Resin formulations based on PETI-5 for more efficient composite fabrication processes like resin transfer and resin-infusion moulding have also been developed.

4. POLYMER MATRICES FOR 250-350°C

The general principle for getting good high-temperature performance is to increase the aromatic heterocyclic repeat units and keep the aliphatic content to minimum. Among the various possible types of polymers based on this principle, the most successful has been the group of polyimides, which can provide matrix materials for service temperatures from 250-350 °C. The key to their success has been the development of several schemes to achieve a balance between their processibility as a composite and the resulting performance properties²⁴⁻²⁶. Both, condensation type and addition type polyimides have been investigated extensively and products based on these have been made commercially available, although mostly in the US.

4.1 Condensation Polyimides

The basic route to prepare polyimides is through the reaction of an aromatic dianhydride with an aromatic diamine in the presence of a polar solvent like DMA or NMP. However, monomeric solutions in this route are not suitable for prepregging or for

composite processing. To have suitable binder solutions (as the monomeric solution used for prepregging are called), the aromatic anhydride is first converted to either tetraacid or diester-diacid, which has an open ring structure. If such forms are commercially available, these can be directly used. Using these forms, it is possible to get high solid monomeric solutions with the modest viscosity suitable for prepregging or composite making. Two such reactions used in commercial products are shown in Fig. 2. Even though the processing and management of volatiles is difficult, composites using Skybond resins and prepregs based on NR150 resins (avimid-N) retain good mechanical properties at high temperatures (343-371°C). Also, as seen from Fig. 2, the polyimide produced with NR150 resin is essentially linear due to the inert nature of hexafluoroisopropylidene bridge and can be considered to be of thermoplastic nature.

It is to be noted that there is evolution of volatiles (water and solvent) during curing process. Proper management of these volatiles is the key to get good quality void-free composites. Impracticably low molecular weight (and melt-viscosity) of polymer would be required if all the volatiles are to be driven out before pressurisation. This is a basic problem in the use of condensation polyimides. A lot of ingenuity and skill is therefore required to make good quality low-void composites with these types of polyimides.

4.2 Addition Polyimides:PMR Resins

A common strategy adopted to get over the volatile problem presented by the condensation polyimides is to have a two-step process. In the first stage, an imide oligomer is produced *in situ* having sufficiently low molecular weight resulting in good melt-viscosity (and hence, good flow) and which therefore consolidates readily on applying pressure. In the second stage, on further application of heat, the imide oligomer polymerises to a much higher molecular weight polymer without further release of volatiles. The second stage of addition polymerisation is made possible using reactive-end groups capable of reacting with each other without evolution of volatiles. The resulting cross-

linking can adversely affect the toughness, making the cured resin brittle. Also, the addition polymerisation involves some aliphatic linkages and this may adversely affect the thermo-oxidative stability. Various schemes evolved over the years are basically various trade-offs between the processibility and the properties. Some of these are briefly described below:

The most well known among the polyimides are those obtained through polymerisation of monomer reactants (PMR). The PMR-15 polyimide (Fig. 3), developed in the mid-1970s at the NASA Lewis Research Centre^{24,27,28} has been widely used as high-temperature resin for composite applications in the temperature range 260-288 °C. The PMR-15 offers easy processing and good property retention at a reasonable cost. For these reasons, it is widely used in both military and commercial aircraft engine components. Further improvements have been particularly directed towards better thermo-oxidative stability (by reduction in aliphatic content) and better toughness (through reduction of cross-linking). Several such improved versions have been attempted and some of these have been commercialised²⁴ (Fig 4).

In PMR II, 6F dianhydride is used in place of BTDA, converted *in situ* to diethyl ester diacid derivative by pre-reacting with ethanol. The single-ring diamine, PPD, is used in place of 4,4'-methylene dianiline (MDA). Higher molecular weights (3000 and 5000 instead of 1500) are obtained. Further, the end-group chemistry can also be changed²⁸. In V-CAP resin, the end-group chemistry is changed by changing nadic anhydride to *p*-aminostyrene*. In another version, CYCAP, 2-amino-*p*-cyclophane (APC) is used as end-capping agent giving only two weak bonds per end-cap. Another concept that has been tried is to use low concentration of the end-capping agent, just sufficient to end-cap only one end of the chain. This would reduce the proportion of unstable groups, and thus result in improved thermo-oxidative stability. This has been used in AFR700B resin of TRW.

Yet another direction of development using PMR chemistry has been to avoid the use of MDA, which has been identified as a carcinogen. A recent development from these efforts is a low-cost, high

* The presence of only one weak bond per end-cap in V-CAP prepolymer compared to eight bonds with nadic end-caps.

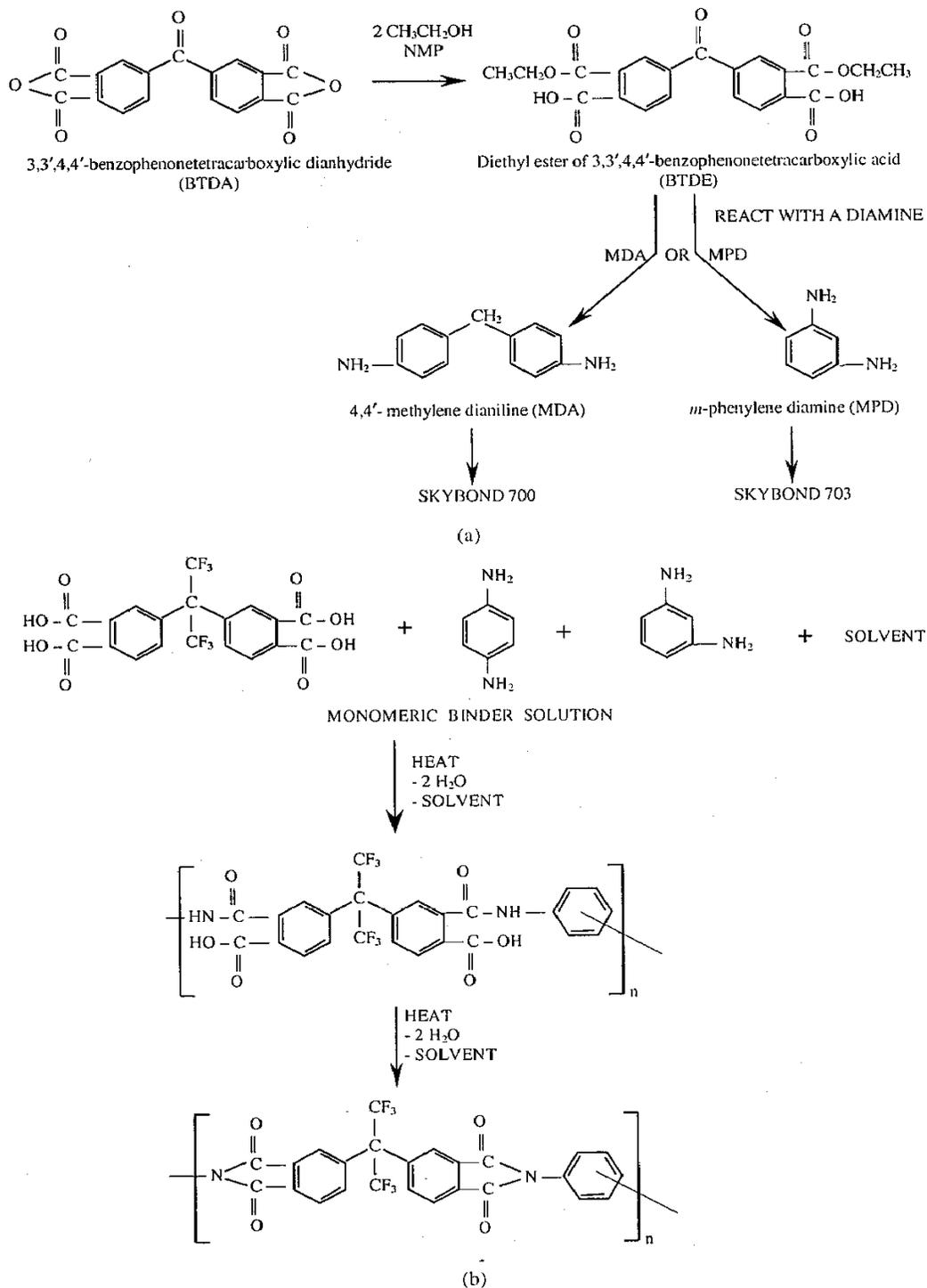


Figure 2. Examples of condensation polyimide matrix systems: (a) chemistry of skybond binder solutions of monsanto (b) chemistry of NR-150 binder solution of DuPont and its cure.

glass transition temperature, thermosetting polyimide (DMBZ-15), prepared from the BTDE and 2,2'-dimethylbenzidine (DMBZ) retaining nadic ester as the end-cap^{29,30}. The glass transition temperature of a DMBZ-15 polyimide composite with carbon fibre is about 50 °C higher than that of the corresponding PMR-15 composite. The DMBZ-15 polyimide-based composites exhibit good compressive strengths at room temperature and at elevated temperatures (233 °C and 288 °C), as well as good hot/wet

compressive strength. In addition, flexural strengths of PMR-15 and DMBZ-15 composites measured at room temperature, 288 °C, and 538 °C are comparable²⁹.

5. PROCESSING OF POLYMER MATRICES

The polyimide binder solutions are generally formulated by prepreggers depending upon the requirements. Currently, preregs of PMR-15 with carbon or glass reinforcement are commercially

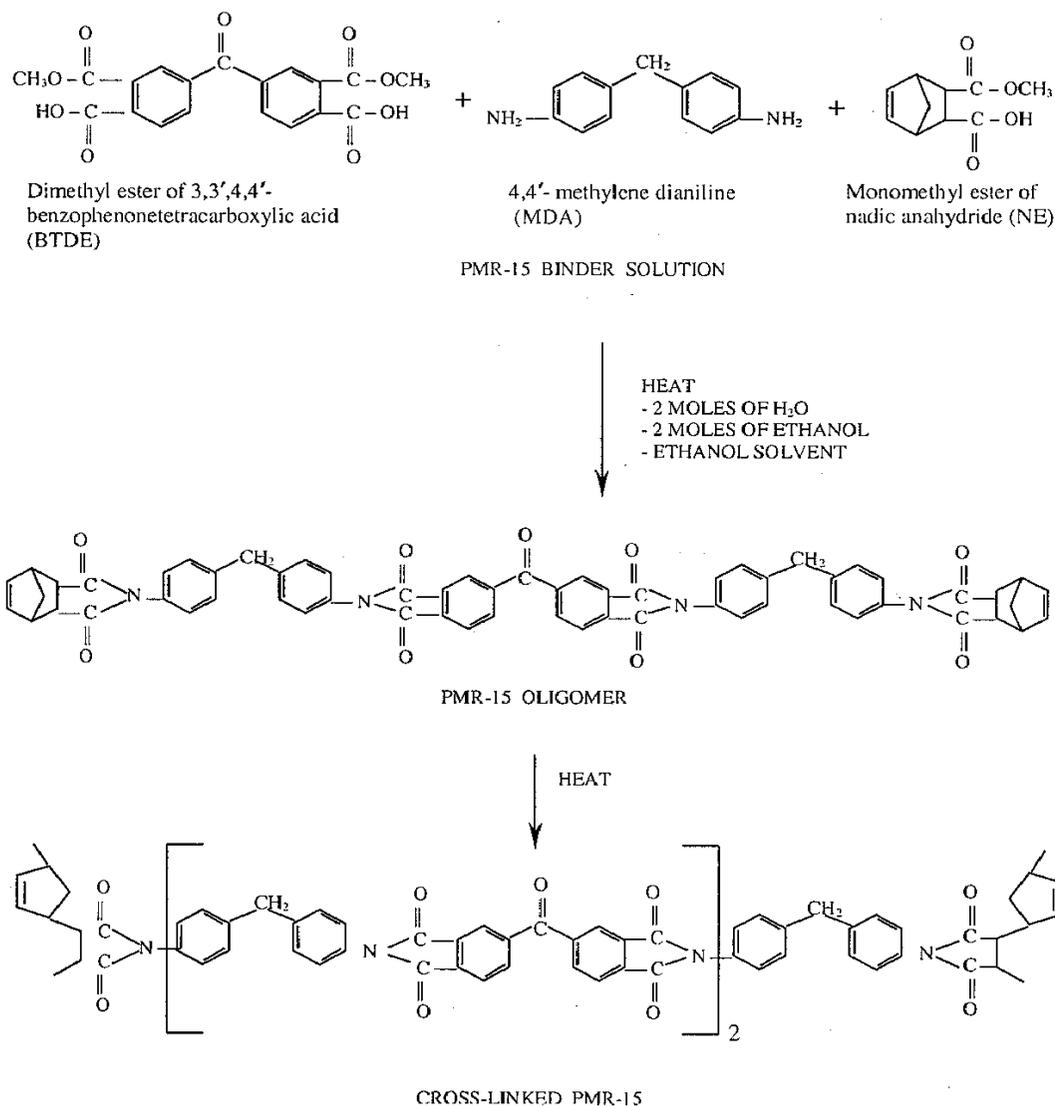


Figure 3. Chemistry of PMR-15 resin

made. As the use of most of the other resins is limited mostly to high-tech aerospace and defence sector for very specific applications, the information on processing is either proprietary or classified. However, certain general points can be made. The first regarding the volatile management has already been discussed. The other is regarding the cure temperature profiles, the schedule of pressure application, and the ease with which the post-cure

can be affected. The Skybond systems are the only ones that can be processed at 177 °C so that the conventional autoclaves used in the composites industry can be used. The free-standing post-cure can be carried out in stages up to 371°C in an oven²⁴. Thicker parts need longer post-cure. The resulting void content of composites is reported to be in 5-20 per cent range. For other systems, cure temperatures are in the range 300-350 °C. The

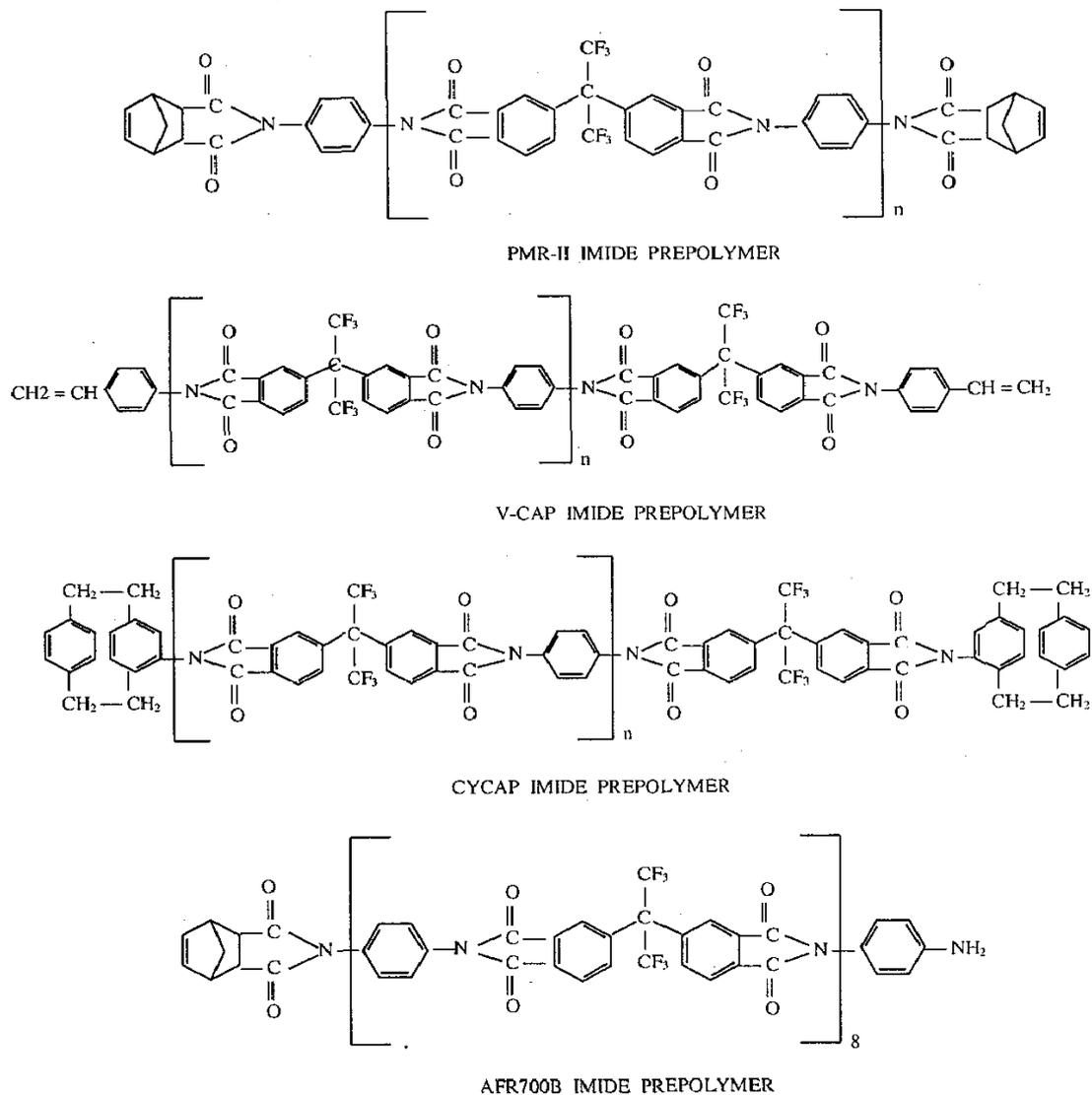


Figure 4. Improved versions of PMR type resins

pressure application and consolidation has to be after considerable amount of volatiles has been removed. At this stage, the resin flow may be reduced and significantly higher pressures (almost double) may therefore be required than with conventional epoxies. The autoclave processing of carbon/PMR preregs, including tack and drape retention under various conditions, has been studied and cure cycles have been reported by Vannucci³¹. A typical cure cycle for PMR-15 resin is given below²⁴:

Cure Cycle (autoclave)

- Apply vacuum, 7-21 kPa
- Heat up at 0.83-1.1 °C/min up to 227 °C
- Apply full vacuum at 163-177 °C
- Dwell at 227 °C, 1-4 h (depending upon the part thickness)
- Heat up at 1.1 °C/min to 238 °C
- Hold at 238 °C while applying pressure of 1.38 MPa for not more than 15 min
- Heat up to 316 °C at 2.2-3.3 °C/min
- Dwell at 316 °C for 3 h
- Cool to room temperature. Vent autoclave pressure below 204 °C.

Post-cure (free standing, in an oven)

- Heat up at 5.6 °C/min to 204 °C; then at 1.1 °C/min to 288 °C
- Dwell at 288 °C for 1 h
- Heat up at 1.1 °C/min to 316 °C

- Dwell at 316 °C for 10-16 h
- Cool to room temperature at 2.8 °C/min (maximum)

The other PI systems based on PMR chemistry also have similar cure and post-cure cycles except that the maximum cure and post-cure temperatures²⁴ are somewhat higher, around 370 °C.

6. MECHANICAL PROPERTIES & BEHAVIOUR

The mechanical properties of a typical carbon fibre composite using PMR-15 matrix are given in Table 3. It can be seen that the mechanical properties at the service temperatures of 288 °C are comparable to the conventional carbon-epoxy presently used in airframe structures. However, high-temperature application brings in additional factor of thermal and thermo-oxidative stability over a long period of operation. The matrix cracking and weight loss at higher temperatures, and also because of thermal cycling, can adversely affect matrix-dominated properties of the composite, such as compressive and shear strengths. Significant matrix-cracking has been observed in the PMR-15 laminates when cycled 5000 times from room temperature to the service temperature of 288 °C. The matrix cracking and weight loss increase steeply at higher temperatures. Thermo-oxidative stability of carbon/PMR-15 composites has been studied by various authors^{24,32}. The composites with improved resins (PMR-II, V-CAP, CYCAP, AFR700B) realise similar mechanical properties but have significantly smaller weight loss and matrix cracking, thus improving long-range performance or giving higher service

Table 3. Mechanical properties of PMR-15/carbon composites using standard modulus carbon fibre (E ~ 220-230 GPa; UTS ~ 3 GPa) and comparison with carbon/epoxy composites

	23 °C	288 °C	C/E _p @ 100 °C/wet
Compression strength (MPa)	827-965	758-896	750-800
Compression modulus (GPa)	97-117	83-110	110-120
Tensile strength (MPa)	1241-1448	1241-1448	1400-1600
Tensile modulus (GPa)	117-138	103-124	125-130
ILSS (MPa)	55-69	34-48	55-60
G _{fc} (J/m ²)	~ 500	--	100-150 (RT)

temperature²⁴. Almost all the PI systems may actually show higher ILSS after a long-term exposure to high temperatures (ageing) due to oxidative cross-linking and consequent marginal increase in glass transition temperature. However, the weight loss, shrinking, and matrix cracking will actually degrade the performance. Also, higher cross-linking may make the matrix more brittle. Thus, any assessment of long-term performance needs to be based on consideration of several factors and not just on reduction of strength or stiffness.

7. RESEARCH IN INDIA

The early polyimide research in India has been focussed on space applications. The research work at the Vikram Sarabhai Space Centre (VSSC), Thiruvananthapuram resulted in the technology of prepolymer resins that could be used for making shells by filament winding. One such formulation based on itaconic acid and an aromatic diamine has been commercialised as ABRON-R 750³³. The composites using silica and carbon fibre reinforcements can be made using DMF as the solvent. However, the service temperature of this is not as high as that of the PMR resin.

An improved version called ISRO-R-900 has been developed by the VSSC, which offers a higher glass transition temperature and is thermally stable up to 360 °C. Toughening using blending with flexible polypyromellitimide polymer³⁴, prepregging^{34,35} and other improvements of these resins have been studied by Nema, *et al.* Further, resins similar to the PMR-15 have been formulated and are currently slated for in-house use on prototype scale.

8. OTHER RESINS & THEIR COMPOSITES

8.1 Phenolics & PT Resins

Among some of the other systems used for high-temperature composites, phenolic resins are perhaps the most significant. Due to high shrinkage and extensive void formation (due to release of volatiles during cure), phenolics are not considered suitable candidates for high-quality composites of

load-bearing structures. However, their excellent flame resistance, low-smoke generation, low-toxicity emission have promoted their use in several high-temperature applications. The moulding material systems with glass transition temperature about 350 °C are available. The B-staged prepregs can be made using resole resins. The composites with carbon or glass fibres can be made with good retention of mechanical properties³⁶ up to 500 °C. Many components in aerospace systems which are not heavily loaded, but function at high temperatures have been made using composites of inexpensive phenolics. Examples of these are the nozzles, throat inserts, ablation covers, etc in aircraft engines, spacecraft, missiles, rockets, etc. The phenolic matrix plays an important role in ablation and erosion characteristics, which may dominate these components.

In India, superior performance has been achieved by making ash-free phenolic resins using appropriate catalysts and additives to the usual phenol formaldehyde. Phenolic resins curing by addition mechanisms through functional groups like maleimide propargylether and phenyl ethynyl have been synthesised. All these resins proved to be good matrices for silica cloth-reinforced composites for space applications. There is no volatile generation during cure and char yields are about 70 per cent at 700 °C. The carbon-phenolic and silica-phenolic composites have found applications in the various space³⁷, missile components³⁸ and have been proposed as part of multi-composite design for future reentry vehicles³⁹.

A further improvement over the phenolic resins can be achieved using the cyanate group chemistry. The reaction of cyanogen halide with phenolic resin leads to an intermediate polyfunctional cyanate containing resin which thermally crosslinks through trimerisation into phenolic triazine (PT) resin. These resins can be expected to have glass transition temperature above 300 °C, good retention of mechanical properties and char yields³⁶ of 70 per cent at 1000 °C. Such resins have been synthesised at the VSSC in India for their in-house use. Good thermal stability up to 470 °C has been achieved. Composites based on this development have found applications in nozzle systems and subsystems in rockets.

8.2 Other Systems

Apart from the resin systems discussed above, several other systems have been studied by various researchers as candidates for the high-temperature polymer matrix. Some of these such as acetylene-terminated^{40,41} and norbornene-terminated polyimides or other oligomers have also resulted in some commercial products³⁶. However, due to the complexities in processing these into high quality composites or the economics of their production, these have not become very popular. Nevertheless, the research interest in these continues and should the issues of processibility and cost be resolved, these systems can also be usefully employed for high-temperature composites.

9. FURTHER RESEARCH

Current approaches to new resins appear to be directed towards producing polymeric systems that can be processed in the way composites industry is used to (such as autoclave curing up to 180 °C). Two promising classes of materials under development are:

9.1 Polymerisable Liquid Crystalline Monomers

These monomers should result in thermoset resins with high-fracture toughness and $T_g \approx 170$ °C

with high retention (≈ 90 %) under hot-wet conditions. Comparing with thermoplastic PEEK, such resins will have almost similar fracture toughness (composite $G_{Ic} \approx 800$ J/m²) with the advantage of conventional processing. The system is being looked into for potential applications in civil transport aircraft. The approach for the development of these new resins being followed is to first synthesise controlled molecular weight backbones consisting of aromatic ethers, aromatic esters or rigid alicyclic systems with hydroxy end-groups and then to end-cap these backbones with reactive-end groups like cyanate ester group or glycidyl ethers. One such example is given in Fig. 5.

9.2 Phthalonitrile Resins

These are meant for high-temperature applications but can be cured in the conventional manner (at 180-200 °C) with a post-curing, albeit in inert atmosphere, at high temperatures up to 600 °C. When compared with the available PMR resins for high-temperature (250-350 °C) applications, the new resins will have better processibility, good-fracture resistance, better strength and modulus, very low-moisture absorption and indefinite shelf-life. Originally developed in 80's⁴², the phthalonitrile systems are under active investigations for the last few years⁴³ and products based on these are likely to come in the near future.

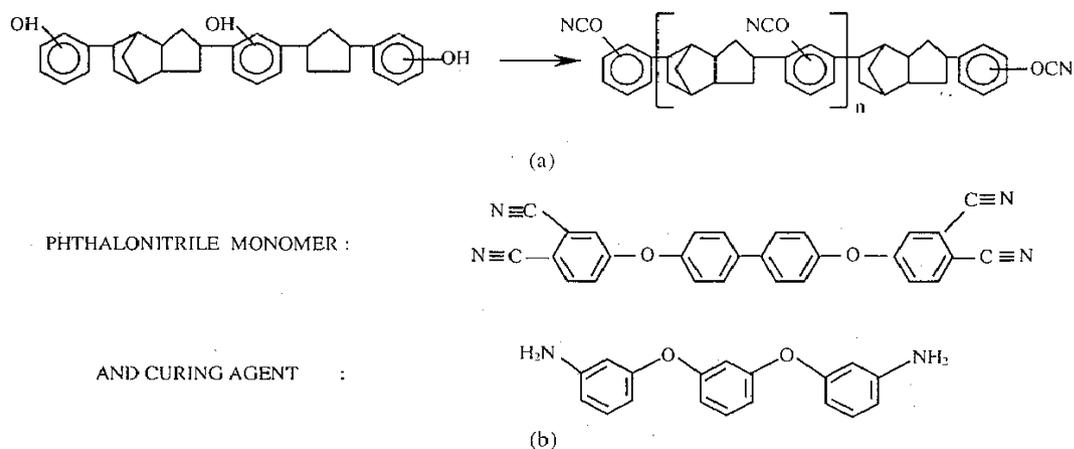


Figure 5. Examples of newer resins for high temperature polymer composites: (a) liquid crystalline polymers as matrix materials for composites: Example showing use of phenol-dicyclopentadiene novolac backbone and (b) phthalonitrile resin.

10. APPLICATIONS OF HIGH-TEMPERATURE POLYMER COMPOSITES

The high-temperature polymer composites have found applications mostly in the aerospace sector. The service temperatures specified for high-speed fighters and high-speed civil transport of the future are in the range 170-180°C. The toughened bismaleimides (BMIs), cyanate esters (CEs), and thermoplastic polyimide (TPI) composites are candidates for such applications. The toughened BMI carbon fibre composites have been used in the F-22 airframe structures. Also, BMI in conjunction with carbon or glass fibres find applications in the cowlings, nacelles, and thrust reversers of jet engines¹.

Main applications of the CE composites include radomes for fighter aircraft, missile nose cones, skins covering phase array radar, etc. The prototype components including wing skins have been made using TPI with carbon fibres. In the higher-temperature range, the PMR-15 polyimide composites have been used with most versatility. Applications of the PMR-15 include engine ducts for GE F404 engines, firewall in GE F90 engine, various splitters and fairings in the F110 engine. The compression-moulded carbon composites with polyimides (such as PMR-15, PMR-II, Avimid-N, etc) have been used for vane bushings, washers, etc of aircraft jet engines. Other applications include missile fins, nozzle flaps, fairings, cowls, and inlet guide vanes in jet engines, gear cases for helicopters.

The PMR polyimide resins of the VSSC are also candidate materials for bypass duct, nozzle flaps, fan-inlet casings, and nose cone in the jet engine under development for the Indian LCA. An interesting application in the non-aerospace sector is in the jaws used for grabbing hot-moulded glass bottles for transporting these during fabrication²⁴. The polyimides have also been used for heat shields. Phenolics, which are cheaper, have found applications where structural load-bearing capacity or durability is not required such as in rocket nozzles, ablative heat-shields, missile fins, etc. New applications in reusable launch vehicles require lightweight materials that can perform for short times (tens of hours) at temperatures between 425 °C and 538 °C. Achieving

this increase in the upper use temperature without sacrificing polymer and composite processibility is a major technical challenge.

11. CONCLUSION

A brief outline of the developments in the polymer matrices for fibre-reinforced composites for high-temperature applications has been given. The main emphasis in the present scenario is on applications in aerospace components of two categories: One, which basically comprises structural components with lower end service temperatures around 180°C and the other in aero-engine sector where temperatures ranges from 250-350 °C. Whereas BMI, CE, and TPI composites dominate the lower temperature range, polyimides of PMR type dominate the higher temperature range. An important issue in the development, apart from the performance requirements, is the ease of processing. Most of the processes used currently remain proprietary or confidential and little comparative information is available in the open literature. Familiarity of the composite fabricator with the resin chemistry appears to be an essential feature for getting good quality components. Where performance of current composites is satisfactory for the end-use application, further research is aimed at reducing the cost and making processing easier—rather, bringing it in tune with the current autoclave moulding of epoxy composites with which the industry is familiar. The research efforts for better performance are directed towards achieving higher service temperature and improved fracture toughness without making the processing too complicated for realistic composite components. The liquid crystalline polymers and phthalonitrile resins appear to be the promising routes in this direction.

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