Chapter 1

Polymers Matrix Composites: Materials, Processing, Characterization and Recent Advances
Scope of the chapter

This chapter gives a brief introduction of the subject and highlights the recent advances in polymer matrix composites. It also gives a brief description of the important thermosetting and thermoplastic matrix resins, different types and forms of reinforcements and the effect of interface quality on the performance of the composites. The methods adopted for the quality/performance evaluation of the composite and interphase, modification of interfaces and toughening of the matrix have been highlighted. A brief account of the recent advances in the composite arena, including nano-composites and syntactic foam composites, is also given. Finally, the techniques adopted for the formulation and characterization of high performance matrix resins and the advantages of using reactively blended matrix resins for advanced composite applications are also presented. The chapter concludes with the current developments in the field of high performance matrix resins including epoxies, bismaleimides and their co-reactive blends and indicates the prospects of R & D in this area.
1.1 Introduction

With the advancement in science and technology a drive for higher and higher performance materials is being felt in aerospace, military, defense and engineering applications. As a result, the conventional structural materials are being replaced by different types of composite materials, the properties of which can be tailored to meet any specific requirement by proper selection and modification of the matrix, reinforcement, interface and processing technique. A composite material can be defined as a macroscopic combination of two or more distinct materials having recognizable interface between them. The requirement for a composite material was felt because no single homogenous structural material can be found that has got all the desired attributes for a specific application. Composite technology is of an interdisciplinary nature, which extends over a wide range of subject fields like chemistry, physics, engineering, polymer science and engineering, material science etc.

The world is witnessing a spectacular growth in the application of composites in every conceivable use. In today’s world, market demand for cost effective material solutions for replacing metals, alloys and ceramics for a wide spectrum of applications is increasing every day.

Composites are classified by the type of matrix material (metal, ceramic, polymer and carbon\(^1\)) or by the geometry of the reinforcement (particulate, flake or fiber). The structure, properties and applications of various composites are investigated worldwide by several authors\(^2-7\). Composites possess a combination of properties like high specific strength and specific modulus, good design flexibility, high fatigue endurance limit and thermal cycling tolerance, corrosion and wear resistance, tailorable coefficient of thermal expansion etc. which make them superior to most of the conventional structural materials.

The term advanced composite has been coined to cover those reinforced plastics having more than 50\% by volume of fibers. These have been developed
primarily for aerospace industry in which the demand for strong and stiff lightweight structures overcomes the prohibitive costs of early composite materials.

The composite products, successfully tried out towards missile programmes fall under three major categories namely structural, electromagnetic and ablative areas. The primary structural domain includes airframe sections, foldable wing and frame, canister and rocket motor casing. Electromagnetic components are basically redomes for various frequencies. The ablative products consist of thermal protection liners for rocket motors, flex nozzles, re-entry heat shields, blast tubes etc.

The carbon-carbon (C-C) composites are the most sought after in satellite applications. Satellite in orbit dissipates tremendous amount of waste heat from absorbed solar radiation and internal heat sources. The C-C radiator panel conducts thermal energy more effectively than other materials currently in use for dissipating thermal energy on satellite. They are used in satellite structures like solar panels, antenna reflectors, yoke, optical support structures etc. They also have markedly higher specific thermal efficiency compared to aluminium and offer improved performance for lower volume and mass. Carbon composites are used extensively in ablative applications in re-entry vehicle nose cones, heat shield etc. and in launch vehicles for solid rocket motor case (C-epoxy), rocket nozzles and liners, pressure bolts, heat shields and exit cones. Carbon fiber-phenolic composites can withstand the high temperature and erosive gases of solid rocket motor operation and the high temperatures generated by aerodynamic heating in re-entry systems.

Extensive use of fiber reinforced polymer matrix composites has been identified as a viable means of reducing weight and thus increasing the fuel efficiency and payload in aerospace applications. In the development of reusable space transport systems, one of the major challenges is the development of materials and structures to meet the flight requirements, and withstand the loads and adverse conditions like high temperature and aggressive plasma environment. The clear and confident answer to these requirements is a composite. Composites, the wonder materials with light weight, high strength to weight ratio and stiffness properties, have
come a long way from their inception, in replacing conventional materials like metals, woods etc.

1.2 Polymer Composites

The rapid advancement in the field of macromolecular materials has helped to expedite the technological revolution in the field of aerospace, telecommunication, microelectronics, defense and transport. At present, more than 60% of the advanced composite market is within aerospace industry, identified primarily with aircraft/aerospace and in sports/leisure applications. The high specific strength, easy processability and corrosion resistance have given prime place for polymer composites as structural materials in aerospace. Weight reduction in aircrafts/spacecrafts and launch vehicles can obviously lead to benefits like improved performance and fuel economy, increased range and payload capability. Some of the superior properties and resulting applications of advanced polymer composites in contrast to conventional materials are given in Fig 1.1.

![Diagram showing thermal expansion, fatigue resistance, and corrosion resistance of CFRP, steel, and Al](image)

Parabolic antenna  | Machinery  | Biocompatibility
--- | --- | ---
Cryogenic application  | Sporting goods  | Chemical apparatus
Measuring instruments  | Music instruments  | Pipelines

Fig. 1.1 Advantageous properties of advanced composites (Carbon Fiber Reinforced Plastics) in contrast to conventional materials.
Polymer matrix composites (PMCs) constitute several vital components of satellite and launch vehicles ranging from motor cases and nozzle components to systems like honeycomb structures, equipment panels, cylindrical support structures, pressure bottles, solar array substrates and antenna reflectors\textsuperscript{11-12}. In Launch vehicles meant for small satellites, the structure is reported to be composed of PMCs to the extent of 80\%\textsuperscript{13}.

Composites have been used in space application from the start of 1950s. Building up on the first successful use of composite solid fuel rocket motor case in 1950s, composites have been continually developed for aircraft, launch vehicles, missiles and spacecraft structures. The key spacecraft environment includes transient, steady state, vibration, acoustic, pyro shock, pressure, handling and transport. In addition, the structural design may be affected by other environmental conditions such as salt and fog, humidity, ambient temperature and space environment. The space environment includes naturally occurring phenomena such as atomic oxygen, very low density atmosphere, ionizing radiation, plasma, charged particle plasma, neutral, atomic and molecular particles. The composites meant for aerospace applications must be capable of surviving in this hostile environment for sufficient length of time. Advanced composites have already started to play a major role in the game of weight saving, where every pound or fraction of a pound weight saved may spell the cliff between success and failure. Polymer matrix composite (PMC) materials in the form of braided, woven or stitched laminates are increasingly being used in critical aircraft structural parts that must be damage tolerant for reasons of safety, reliability, maintainability and supportability. This means that PMC structures must be durable and reliable under service conditions that can expose aircraft structure to many types of damage mechanisms.

Space launch vehicles of expendable type experience severe thermal environment during the ascent phase in the atmospheric regime of the flight. The reusable launch vehicle face a similar environment during the ascent phase but are subjected to a more severe and hostile environment during the re-entry phase. With
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the high speed advancements in science and technology, the urge for the development of miracle materials to survive in these hostile environment and loading conditions is badly felt. The effects of changing the reinforcements and matrix materials for producing composites with the properties essential for the system requirement have been studied extensively. An overview of the myriad material and configuration options available for polymer based composites was reported by many researchers.

1.3 Principles of Polymer Reinforcement

Composites are combinations of a reinforcement material such as particles, fiber or whisker and a matrix or binder material. This also implies that the materials are macroscopically identifiable, retaining their distinctive component properties. Composites reinforced with dispersed fillers, fibers and fabrics are widely used to manufacture structural components and load bearing elements in space technology and in aircraft, automotive and ship building industries. Therefore, the measurements, calculations and predictions of the strength of such materials are of great interest to engineers and researchers. The main feature of fiber and fabric reinforced composites is the strong anisotropy of properties like strength and elastic modulus. Greatest progress in exploitation of properties of continuous fiber reinforced composites has been made, owing to a relatively simple mechanism of failure.

The three important factors determining the performance of a composite material are the matrix, reinforcement and interphase.

1.4 Matrix Materials and Classifications

Matrix materials are generally classified in to four groups, ceramics, metals, carbon and polymers. Choice of the matrix depends upon performance requirement, service environment, available processing facilities, cost and several other factors. The matrix constitutes approximately 40% (by volume) of the composite and performs two major roles. The matrix component of these composites dictates many key
features like toughness, resistance to heat, corrosive environment and service temperature. The matrix material transfers loads to the reinforcement and protects it from adverse environmental effects. In addition, matrix controls the thermo-mechanical behavior of the composites. The resin matrix spreads the load applied to the composite between each of the individual fibers and also protects the fibers from damage caused by abrasion and impact.

1.5 Polymer Matrices

The matrix controls the processibility, upper use temperature, flammability characteristics and corrosion resistance of the composite. The composite mechanical performance depends to a large extent on the resin modulus, failure strain, and the fiber-matrix bond-strength.

Polymers are broadly classified into thermoplastics and thermosets. A number of polymer systems under each category have been utilized as matrices. The merits and demerits of each of these should be evaluated based on its chemical nature, ease of transformation into pre-preg, processing and fabrication and also on the resultant composite properties.

1.5.1 Thermoplastics

Thermoplastics permit easy repair of structures made out of them. Joints can be made by heating together and cooling, without need for cutting or welding. Owing to their excellent toughness and thermal performance even to cryo-temperatures, thermoplastics are being increasingly used in high performance applications. Unlike thermosets, thermoplastics do not require reactive cure cycles. They require only heat and pressure with subsequent cooling for composite fabrication. Some of the commercially available advanced thermoplastics are poly ether ether ketone (PEEK), poly phenylene sulfide (PPS), poly sulfide (PS), poly ether imide (PEI) and poly amide imide (PAI). Their glass transition temperatures normally range from 140 - 275°C and
processing temperature up to 350°C. High performance thermoplastics frequently contain rigid aromatic and/or heterocyclic repeating segments. These repeating segments have low mobility and thus provide high glass transition temperature, which in turn give good heat resistance and retention of material strength at elevated temperatures. Polymers containing high aromatic or heterocyclic structures require high energy for thermal degradation process and thus give a high char residue in the thermal breakdown process. These characteristics give polymers high decomposition temperatures and low flammability that meet major requirements needed for advanced structural applications. Typical high performance uncrosslinked polymers include polyimides, polybenzobisthiazoles, polybenzobisoxazole, aromatic polyamides, polybenzimidazoles, liquid crystalline polyesters, polyether sulphones, polyquinolines, polyamide imides, polyether ketones, polycarbonates etc.  

1.5.1.1 Polycarbonates

Polycarbonate has got exceptional total package of inherent properties such as impact strength, heat resistance, clarity, inherent flame retardance and good processability. Standard grade of polycarbonates are made from bisphenol A and phosgene. It can be blended with other polymers to enhance the specific properties such as chemical resistance. Co-polymers of polycarbonate have also been recently employed to achieve high thermal performance approaching that of high-end thermoplastics. Its superior impact strength and resistance to breakage and damage makes it suitable for appliances, automotive, computers, business equipments, electrical and electronic components, medical devices, transportation equipments, outdoor fixtures and household utensils. Its excellent electrical properties remain relatively constant over a wide temperature range.

1.5.1.2 Polyethersulphones

The polyether sulphone belongs to polysulphone group of thermoplastics. Its chemical structure consists of aromatic sulphone units linked through ether bridge.
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The former is mainly responsible for the high temperature stability and mechanical strength, while the later introduces sufficient chain mobility to permit melt processing at reasonable temperature. The properties of polyethersulphone (PES) that distinguish it from most other thermoplastics are its high temperature performance, good mechanical strength and low flammability. These properties are achieved without the penalty of difficult fabrication since PES can be melt processed in conventional moulding equipments. The thermal stability as measured by the half life of the tensile strength at a given temperature is very high for PES making it a candidate for class H electrical application. PES has got very high glass transition temperature (220°C) and hence its properties show small dependence on temperature. It is inherently flame retardant and does not require a flame retardant additive. Its dielectric constant and loss factor show minimum variation with temperature up to its glass transition temperature ($T_g$). Most of the moulding, extrusion and finishing operations associated with thermoplastic fabrication are applicable to PES. It has got very good creep resistance which is one of the important attributes of engineering thermoplastics. It is a very good electrical insulator. Little variation in dielectric constant or loss factor is shown in the range of $0$ to $-180$ °C. Its high temperature performance, dimensional stability and inherent fire / flame retardency make it suitable for electronic and electrical industry. They have excellent thermoformability and mechanical properties.

1.5.1.3 Polyesters

Polyesters (PE) are produced by the condensation polymerisation of difunctional acids or anhydrides with difunctional alcohols or epoxy resins. Different classes of polyester resins are general purpose resins, chlorendic resins, bisphenol A fumurate resins, vinyl ester resins etc. Within these classes of resins, specific polyester can be formulated by varying the starting materials. The physical properties of the resin do affect their durability and thermal performance. PE resins are generally used in the elevated temperature applications, especially in the electrical and
corrosion resistant areas. Monomer type also plays a vital role in the thermal stability of PE resins. PE resin is for application in corrosion resistant tanks, pipes, ducts and liners in chemical processes and in pulp and paper industry. Their improved UV resistance makes them a candidate material for outdoor applications.

1.5.1.4 Polyether ether ketone

Among the thermoplastics, polyether ether ketone (PEEK) is a selection candidate for many important high performance applications because of its special properties. It does not absorb significant amount of moisture. PEEK has got 25-40% crystallinity. It is relatively costly thermoplastic with good mechanical properties and toughness, and hence most apt to be employed in high performance composites. For example Carbon-PEEK is a competitor for carbon reinforced epoxy and Aluminium-Copper and Aluminium - Lithium alloys in aircraft industry. PEEK has got many essential qualities required for aerospace applications. The outstanding feature of PEEK is its excellent fracture resistance. PEEK and other aromatic hydrocarbon matrices have low hydrogen to carbon ratio and hence do not produce large amounts of combustible volatiles. Limiting Oxygen Index (LOI), which is a measure of inflammability, is as high as 35 for PEEK and its composites. Owing to its high $T_g$ and melting point ($T_m$), it is difficult to set fire to PEEK.

1.5.2 Thermosetting Resins

Thermosets are currently the predominant matrix resin for composites due to their availability, well established processing technologies, existence of large database and low material cost. The advancement in the area of high performance composite has led to a number of related R & D activities and availability of abundant literature on the topic. The widely used classes of thermosetting resins are polyesters, phenolics, polyimides and epoxies.
1.5.2.1 Phenolic Resins\textsuperscript{25}

Among the thermosetting high temperature resistant polymers, phenolics have a unique place in terms of their chemistry, applications, thermal and chemical resistance, and processability. Phenolic resins, both novolacs and resols are widely used commercially due to their excellent flame retardance and low cost\textsuperscript{28,27}. The low smoke and toxic evolution on burning make phenolics the material of choice for nonstructural applications like aircraft interiors. Phenolics have broad range of applications varying from construction to electronics and aerospace\textsuperscript{28,29}. Addition-cure phenolics offer viable alternatives to condensation type phenolics, avoiding need for high pressure cure\textsuperscript{30}. However, most of them require high cure temperature, posing processing difficulties. Phenolics excel over other matrix resins in terms of resistance to fire and the very low smoke and toxic evolution\textsuperscript{31}. Good heat and flame resistance, ablative characteristics and low cost are the major advantages of phenolics which find numerous applications apart from aircraft interiors, automotive components, rocket nozzles, appliance moulding etc.

Brittleness, poor shelf-life and need for high pressure curing are the major short comings of phenolic resins for structural applications. Brittleness is obviated by blending it with elastomers\textsuperscript{32}, risking the thermal properties. Blending the phenolic with polyesters\textsuperscript{33} and engineering thermoplastic like polyethersulphone\textsuperscript{34} is reported to yield tougher systems. Cyanate esters of novolac phenolic resin (Phenolic Triazins\textsuperscript{C}) have the combined advantages of high temperature resistance and flame retardancy of phenolic resins, epoxy-like processing and handling convenience coupled with excellent high temperature performance comparable to that of polyimides\textsuperscript{35}.

1.5.2.2 Polyimides\textsuperscript{36}

Among the numerous high-temperature resistant polymers, the polyimides(PI) have achieved by far the greatest commercial success, due to their ability to maintain acceptable mechanical properties at elevated temperatures together with the thermal stability for long term use at temperatures around 300°C\textsuperscript{37,38}. Polyimides are the most
popular heat resistant polymers due to their thermal stability, solvent resistance and retention of properties over a wide temperature range and hence have gained acceptance for use in aerospace composites, electrical electronic and industrial applications. It has wide-spread application as thermal control films, coatings, sealants and adhesives. New monomers based on different types of aromatic diamines, and aromatic di anhydrides have been synthesized with various specific properties such as processability and improved stability under thermal, chemical, electrical and radiation environments. They offer improved high temperature properties compared to the epoxy systems. Shao et al. reported the synthesis and properties of fluorinated polyimides from new unsymmetrical diamine. These polyimides showed outstanding solubility and good dielectric properties.

Thermoplastic polyimides are less expensive than their thermoset versions. However, their maximum use temperature is comparatively low. Condensation polyimides are formed by a two-step process involving formation of a polyamic acid followed by its imidisation. Thus, the processing times are much longer and require the application of high pressure for consolidation, due to evolution of water or alcohol as condensation by-products. Condensation polyimides are thermoplastics and remain melt fusible. Consequently, they are having good tractability. Structure 1.a gives the structure of a condensation polyimide. A number of polyimide systems have been developed that are well suited for use as matrix resins, adhesives and coatings for high performance applications in aerospace and electronic industries. However, major disadvantages of these thermoplastic systems include poor precursor shelf-life and processing difficulties, hydrolytic instability and need for removing volatiles. The growing demand for polyimides that are processable, solvent-resistant with good thermal stability provided a strong incentive for developing processable addition-type polyimide systems. These are low molecular weight, multifunctional monomers or pre-polymers that carry functional reactive terminations and imide functions in their backbone. The bismaleimides, itaconimides and nadimides are the versatile ones in this category. The structure of typical addition polyimides with nadimide terminals are
given in Structures.1.b. A large variety of addition polyimides, with good processibility and thermal stability has been successfully used as matrix resins in high performance and high temperature resistant composite applications.

![Structure 1](image)

In addition to the condensation and thermoplastic family of polyimides, the third type based on imide pre-polymers also has gained considerable importance recently because of their ease of processability. Among these, bismaleimides have been studied extensively mainly because they offer greatest benefits in terms of cost effectiveness and enhanced processability.

1.5.2.3 Bismaleimides

Among the addition type polyimides, bismaleimides (BMIs) still dominate the high temperature polymer scenario due to their thermal and oxidative stability, flame retardence, low propensity for moisture absorption, ease of synthesis and cost effectiveness. Bismaleimides are best defined as low molecular weight, at least difunctional monomers or pre polymers or mixtures thereof, that carry maleimide terminations. The general structure of bismaleimide is given in Structure.2.
The key to the improved BMI system is the properties of the co monomer employed for the BMI resin. The building blocks used in commercial BMI resins are 4, 4'-bismaleimido diphenyl methane, 2, 4- bismaleimido toluene, 1, 3-bismaleimido benzene etc. Because of the toxicity problems associated with methylene dianiline (MDA) (4, 4'-diaminodiphenylmethane), polyaromatic diamines and the BMIs based on them are of increasing interest. The structure of some of the bismaleimides based on specific polyaromatic diamines are given in Structure 3.

Cross linked BMI polymers are infusible, rigid, brittle and are insoluble in all solvents. They have relatively high densities (1.35 -1.40 g/cc) and exhibit Tₙs generally in the range of 250-300°C. The strain to failure is typically below 2%. The moisture absorption levels in BMI resins tend to be much the same as in Epoxy resins.
(4-5% by weight) but saturation occurs faster than in epoxy resins. New products such as Narmco X 5250\textsuperscript{46} aim for superior hot wet performance, compression-after-impact in composite, coupled with good processibility and longer shelf-life over currently used epoxy and BMI composites.

**Polymerisation of BMI resins:** BMI resins are reactive towards various reactive species. Such reactivities provide BMI resins with high versatility for various application through proper formulation with other thermosetting oligomers. A few curing reactions, such as thermal polymerization, addition reactions, Diels-Alder reactions etc have been developed to increase the application performance of BMI resins.

**Thermal polymerization:** The most important curing reaction of BMI resins has been their homo polymerisation at elevated temperatures (thermal polymerisation). The reaction produces no volatile byproducts and provides void-free thermosets. The BMI resins thermally set to rigid, solvent resistant, highly crosslinked thermosets. Grund Schober\textsuperscript{47} first reported their homo polymerization by simply heating the monomer to a temperature between 150-400\textdegree C.

**Michael Additions:** BMI resins contain reactive unsaturated olefinic groups that are further activated by two strong electron withdrawing carbonyl groups and are known to undergo Michael additions with hydrogen active moieties such as phenols, thiols and amines. The reactions have been used to prepare not only high molecular weight linear polymers but also high performance thermosets\textsuperscript{48}. The properties of BMI resins strongly depend on synthesis conditions. It can undergo a chain extension reaction with amino compound through Michael addition of the structure (Structure.4).
Ene reaction: One important class of high performance thermosets is derived from BMI resins and allyl phenol oligomers. Upon thermal curing, the mixture co-polymerize to produce polymers of high glass transition temperature. The applicability of BMI-allyl phenol resins as matrices for advanced composites have been studied extensively. CIBA-GEIGY introduced a unique cross linking chemistry into bismaleimide system by utilizing the so called "Ene" reaction with the maleimide double bond.

Diels-Alder polymerization: Diels-Alder polymerization requires reaction of a diene monomer and a monomeric dienophile, which is normally activated by electron withdrawing substituents. During the polymerization, a stiff, heat resistant ring structure is formed by every Diel-Alder reaction unit. Diels Alder reactions have been developed to increase the application performance of BMI resins. The type and extent of each reaction depend on the chemical and molecular characteristics of the bismaleimide.

Alder-ene reaction: Maleimides are known to react with allyl phenols through an Alder-ene reaction to give rise to cyclic network structures and are used as matrix resin with improved high temperature performance. A number of polymer systems based on the co reaction of BMIs and allyl phenols have been reported. Matrimide (Biisemaleimido diphenyl methane +diallyl bisphenol A) is a typical formulation. A few patent claims have been made on the blends of allyl phenol based novolac and
BMIs\(^\text{57}\). The Alder-ene type reaction in such systems proceeding via an intermediate Wagner-Jauregg reaction, leads to thermally stable, crosslinked, cyclic structures\(^\text{58}\).

High performance BMI resins are based on rigid aromatic structures and thus possess high melting points and a narrow processing window. Detailed studies were carried out on thermal behavior of different types of bismaleimide monomers in neat and blended forms using various thermo analytical techniques for composite application\(^\text{59}\).

The major disadvantage of all bismaleimide resins is their extreme brittleness. Much research is still being directed towards toughening of BMI resins. Tough compositions need blending with elastomers and/or chain extension using diamines. Several modified versions, particularly the PMR-type resins (with service temperatures up to 300°C for long duration) are currently in use in aerospace industry. The various members of the PMR family are designated by numbers, the PMR-15 being the best known. Ethynyl terminated imide and isoimide and norbornene terminated imide (PMR-15) oligomers are commercially available for high temperature applications\(^\text{60}\). Modifications of the PMR type addition polyimides with nadic\(^\text{61}\), paracyclophane\(^\text{62}\) and cyclobutene\(^\text{63}\) terminations also have been reported.

1.5.2.4 Cyanate Esters\(^\text{54}\)

Cyanate esters (CE) emerged as a compromise thermosetting matrix system in the late 80's, which encompasses several of the characteristics required for an ideal matrix. They possess the heat and fire resistance of phenolic resins, processing and handling convenience of epoxies and high temperature performance of polyimides. The cyanate compounds are stable at room temperature and undergo trimerisation to form s-triazine rings at elevated temperature in presence of catalysts and generate high crosslink density, which in combination with rigid aromatic rings, provide excellent high temperature properties, solvent resistance, electrical properties and mechanical strength. Moreover, highly desirable properties like built-in toughness, low dielectric constant and dissipation factor, radar transparency and low moisture
absorption make them the resin of choice in high performance structural composites for aerospace applications and in electronic industry. The low out-gassing, minimal dimensional changes during thermal cycling, low moisture absorption, low shrinkage, good long term stability, self adherend properties to honeycomb and foam cores and high service temperature are the key advantages of cyanate esters over state-of-the-art epoxy resins. Despite their high cost they find application in electronics, printed circuit boards, satellites and aerospace structural composites. They have been successfully employed in composite structures in INTELSAT. Cyanate esters can be reactively blended with other high performance matrices such as bismaleimides, and epoxies, wherein, the co-reaction or interpenetrating networks (IPNs) formation facilitates imparting a wide spectrum of properties to the blend, depending on composition and nature of the additive. One of the potentially and commercially important oligomers terminated with cyanate ester group is based on phenolic (novolac) resins. Novolac-cyanate provides an aerobic char yield of 58% at 800°C and an oxygen index of about 45. Novolac cyanate–graphite composite has got short beam shear strength of 74 MPa and flexural strength of 1300 MPa at 177°C. Novolac–cyanate based composite is reported to give good property retention after 12 weeks of air heat ageing at 240°C.

Basically cyanate ester resins have good rheological properties to meet the processing needs for laminate and composite preparation. One of the most serious concerns of current high-performance thermosetting resins, such as epoxy resin, BMIs, nadimides, and phenolics is their ability to pick up high percentage of moisture. Cyanate ester linkages are very resistant to hydrolysis at ambient service conditions and hence cyanate ester homopolymers absorb less water at saturation than epoxy, BMI and polyimide resins. Their high \( T_g \) (260-280°C), low shrinkage, excellent adhesion, excellent dielectric properties, low moisture uptake (<1%), and higher tensile strain (2-6%) make them a material of choice for many important applications. The most effective way to broaden the application scope of cyanate ester resins is the development of co-polymerisation systems. Copolymers of cyanate
ester with polyphenols, polyamines, cyanamides, organic anhydrides and epoxy resins yielded useful systems suitable for variety of applications.

1.5.2.5 Epoxy Resins

Since their introduction in 1940s, epoxy resins have found a myriad of applications due to their good thermal and chemical resistance, superior mechanical properties and excellent adhesion to variety of substrates. These materials are characterized by terminal epoxide groups. The alfa epoxy is the most common variety. Di-and multifunctional glycidyl compounds play a unique role among the thermosetting resins. Depending on the chemical structure of the synthesized epoxy component, the structure of the curing agent and curing conditions, uncured epoxy resins can be synthesized in a broad variety of physical forms ranging from low viscosity liquids to solids and from well defined di-, tri- and tetra functional glycidyl ethers to advancement products of oligomer type. It is possible to obtain toughness, good chemical and corrosion resistance, high adhesive strength, mechanical properties, good heat resistance and high electrical properties. The current state-of-the-art matrix resin in structural aerospace composites is epoxies. Their attractive features include ease of processing and handling convenience, good mechanical properties, excellent adhesion to a variety of reinforcements, toughness and low cost. In addition to applications in high performance aerospace composites, they are used in coatings, adhesives, floorings and electrical applications. Versatility in form, modification, properties, hardening methods, curing conditions and application is probably the most outstanding characteristic of epoxy resins. The thermoplastic bisphenol A type novolac resin was sequentially reacted with epichlorohydrin in alkali media to generate a bisphenol-A type novolac epoxy resin. Its molecular back bone consists of aromatic rings and as a result it can achieve excellent mechanical and thermal performance.

Nature and amount of curing agent and its concentration are critical in deciding the properties of the cured network. Common curatives are aliphatic and
aromatic amines, dicyandiamide, acid anhydrides and Lewis acids such as BF₃, which are selected based on the applications of the final cured network. Fluorine-based epoxy systems exhibit low moisture uptake, improved toughness and heat resistance.

Epoxy resins are not generally recommended for applications in severe conditions due to poor hot/wet performance and high moisture sensitivity.

Epoxy resins dominate the structural composites in aerospace applications. Light weight motor cases use combinations of Kevlar and epoxy system. Satellite support structures, antenna, yoke and solar panel substrates are preferably made of epoxy-composites. The novolac epoxy resin being multi-functional, can produce a denser crosslinked network compared to the common epoxy resins. They are characterised by an outstanding combination of both mechanical and chemical properties in terms of high modulus, thermal stability, solvent resistance and therefore find widespread application as a sealing material for semiconductor devices. The acid anhydrides are characterized by long pot life, better heat aging in air at elevated temperatures and better electrical properties. Principal Lewis acid used in epoxy composite is boron tri fluoride. Phenolics have been used as curing agent for epoxy resins where the epoxy is usually the major component. In many cases, these systems make up the base resins for the semiconductor packaging due to their improved hydrophobicity relative to amine-cured epoxies, and their low cost. Ogata et al studied in detail the effect of crosslink densities on the physical properties of the epoxy networks. The primary resin in epoxy technology is the diglycidyl ether of bisphenol A (DGEBA) and its higher homologues. The glycidyl ethers of various novolac resins are the second most important class of epoxy resins. The glycidyl novolacs are characterized by better elevated temperature performance than bisphenol A (BPA) based systems. The diglycidyl ether of bisphenol F (DGEBA) has a lower viscosity than the BPA epoxies with minimal loss in Tg. The triglycidyl ether of triphenyl methane (TGMP), a relatively new comer to the epoxy family is said to have high Tg, thermal oxidative stability and excellent moisture resistance. Tetraglycidyl methylene dianiline (TGMDA) is the most widely used epoxy resin for the
fabrication of carbon fiber composites for aerospace industry. The structures of some of the higher functional epoxies are given in Structures.5.a, b & c.

Epoxies can be cured with various types of hardners to obtain a wide range of physical and mechanical properties²⁹. Most common curing agents are aliphatic amines, aromatic amines, acid anhydrides, Lewis acids and dicyan diamine (DICY). Aliphatic amines and their derivatives are recommended for ambient temperature curing. Diethylene tetramine (DETA) and triethylene tetramine (TETA) are common aliphatic amines. Cyclo aliphatic amines are curing agents at moderate temperature and have got good elevated temperature properties. Aromatic amines are high temperature curing agents. Their major advantages are long pot life, excellent chemical resistance, good electrical properties, and good elevated temperature performance. eg. methylene dianiline (MDA), m-phenylene diamine (MPDA). In epoxy amine curing, the reaction takes place in two steps. The efficiency of secondary reaction of amine with epoxy is generally 25% of that of primary reaction and hence takes more time for completion. Sulphone diamines are normally used in conjunction with a Lewis acid accelerator. They provide the best elevated temperature performance. 4, 4'-diamino diphenyl sulphone is a typical example. Combination of DDS with TGMDA resin is widely used in aerospace industry for carbon fiber composites. Acid anhydrides are characterized by long pot - life, better heat - ageing in air at elevated temperature and better electrical properties. Eg. n-hexa hydrophthalic anhydride (HHPA) and methyl tetra hydrophthalic anhydride (MTHPA) perform well at elevated temperatures. They have excellent electrical properties and give colourless laminates with superior weathering properties. But anhydrides of high functionality cause handling problem and have poor solubility. The chemistry of curing of epoxies with anhydrides is complex. It was found that Lewis acids and bases act as catalysts for this reaction.
Structure 5: Higher functional epoxy resins (a) Epoxy resin based on novolac (Poly functional) – EPN. (b) Tris (4-glycidyloxy phenyl) methane (TGETM) (c) N, N’-tetra glycidyl methylene dianiline (tetra epoxy) – TGMDA

At first, anhydride reacts with the catalyst to form a carbonyl anion, then the anionic process continues up to the completion of cure. The principal Lewis acid used in epoxy composition is boron trifluoride in the form of its mono ethyl amine complex (BF3-MEA). It has long pot life and high Tg and a storage life of over six months. Many critical products based on epoxies were designed and developed for launch vehicles viz. SLV, ASLV, PSLV, GSLV and INSAT programmes of ISRO. Multifunctional - tri-
and tetra functional - epoxies are used in most of the aerospace composites. A comparison of properties of conventional high performance thermoset matrix resins is given in Table 1.1 and in Fig. 1.2.

Table 1.1 Comparison of Common High Performance Thermosetting Polymer Matrices

<table>
<thead>
<tr>
<th>Property</th>
<th>Epoxy</th>
<th>Phenolic</th>
<th>Toughened BMI</th>
<th>Cyanate ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
<td>1.2-1.25</td>
<td>1.24-1.32</td>
<td>1.2-1.3</td>
<td>1.1 - 1.35</td>
</tr>
<tr>
<td>Cure Temperature (°C)</td>
<td>RT - 180</td>
<td>150-190</td>
<td>220-300</td>
<td>180-250</td>
</tr>
<tr>
<td>Mould Shrinkage (mm/mm)</td>
<td>0.0006</td>
<td>0.002</td>
<td>0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>Tensile modulus (GN/m²)</td>
<td>3.1-3.8</td>
<td>3-5</td>
<td>3.4-4.1</td>
<td>3.1-3.4</td>
</tr>
<tr>
<td>Use temperature (°C)</td>
<td>RT-180</td>
<td>200-250</td>
<td>~200</td>
<td>~200</td>
</tr>
<tr>
<td>TGA onset (°C)</td>
<td>260-340</td>
<td>300-360</td>
<td>360-400</td>
<td>400-420</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>3.8-4.5</td>
<td>4.3-5.4</td>
<td>3.4-3.7</td>
<td>2.7-3.2</td>
</tr>
</tbody>
</table>

1.5.3 Miscellaneous Thermally Stable Systems

High temperature heterocyclic polymers like acetylene terminated polyphenyl quinoxaline and polybenzimidazoles are of limited application due to difficulty in processing. Other thermally stable polymers reported include poly oxazole, polyphenylene oxide, polythiadiazole, propargyl ether resin etc. However, few have found commercial acceptance because of their high cost and poor processability.
The rigid aromatic backbones result in high $T_g$, high melt viscosities and low solubility and therefore, these are more intractable. Thus, the emphasis in recent years has been to introduce structural variations that allow improved processibility, solubility, etc. with no sacrifice of thermal properties.

1.6 Reinforcements

The reinforcement of the composite plays a major role in determining its strength, stiffness and dimensional stability. The different forms of reinforcements are particles, nano particulates, whiskers, continuous and short fibers and woven fabrics. Fibers are the most common type of reinforcement.

1.6.1 Particulates

Particles are used as fillers to improve strength, toughness, processability, dimensional stability, flame retardance and to lower the cost. Particles are available in
different forms like sphere (glass), cube and block (calcite) and flakes (talc, mica, wood flour) and the resulting composites are macroscopically isotropic. Whiskers are single crystals with aspect ratio >1. Typical lengths are in the range 2-50 nm. They have extraordinary strength (up to 1000 ksi).

Ceramic whiskers like SiC, Al₂O₃, B₄C and Si₃N₄ exhibiting high temperature capability up to 2000°C. However, the difficulty to collect, sort and distribute them, together with high costs have limited the application of whiskers. The knowledge of the filler properties such as its size (Surface area, size distribution), shape (crystallinity, anisotropy) and surface characteristics (roughness, particle aggregation & chemical structure) is essential for its effective utilization in the composite material.

The mechanical loss factor can be used to characterize the properties of the interface region formed in the matrix around each filler particle, as well as the effectiveness of various coupling agents. It is also known that the other factors such as filler particle shape, particle diameter, modulus ratio of filler to polymer, also have effect on polymer reinforcement.

Choice of the reinforcement for a particular application depends on a large number of parameters including strength, stiffness, environmental stability, long term characteristics and cost. At present carbon, glass and aramid fibers account for over 95% of industrial market. The stiffness, strength, and mechanical properties of the composite along the reinforcement direction are dominated by the properties of the reinforcements.

1.6.2 Low Density Fillers

Hollow micro spheres have recently evoked a lot of attention as low density fillers for the fabrication of syntactic foam composites. The syntactic foam composites have recently attracted lot of attention as low density composites for wide range of applications. Syntactic foams are composites consisting of hollow micro spheres dispersed in resinous matrix so as to have porosity at the microscopic level. Bibin et
Chapter 1

al's studied the effect of shell thickness and concentration of hollow glass microballoon on the physical, thermal and mechanical properties of modified epoxy and cyanate ester syntactic foam composites. This micro porous foam material has got additional advantages like lesser anisotropy and mechanical property enhancement including specific strength, shear strength, impact resistance and energy absorption. Their favourable thermal, dielectric and damping characteristics makes these foams multifunctional, and suitable for applications like bulkheads of ships, submarines, automotive and personal protection, heat shielding of missiles heads and aerospace structures. They find application in aerospace and automotive industries where reduction in energy conservation is one of the important factors. Syntactic foams as core material find application in the construction of sandwich structures.

Sankaran et at studied the effect of incorporation of small amounts of carbon nanotubes (CNTs) on microballoon filled epoxy- amine syntactic foam composites. The incorporation of small percentage of CNT was found to improve the storage shear modulus of the system by 50% while in the case of multiwalled carbon nano tube (MWCNT), the reported increase was 24%. The scanning electron micrograph (SEM) images indicated that the CNTs tend to occupy the interstitial spaces in the foam thereby decreasing the void- content. The property improvement in epoxy resin by nano-silica reinforcement was reported recently.

Continuous fiber composites routinely have strengths 2-3 times greater than discontinuous fiber composites. The fibers for resin matrix application should have the highest modulus, lowest density and highest tensile, compressive and interfacial bond strength between resin and fiber, while still failing in a non-catastrophic mode. The significantly higher strength of fibers in the longitudinal direction is provided by the orientation of molecules along the axis during drawing.

1.6.3 Inorganic Fibers

These have been developed with inorganic lattice structures. Inorganic fibers are extremely strong although inextensible and are intended for ultra high temperature
uses. The inorganic fibers commercially available mainly include glass, boron, silicon carbide, nitrides and alumina.

1.6.3.1 Glass Fibers\textsuperscript{96,97}

Glass fibers have been known and used for decades. Different types of glass fibers like E, S, C and quartz, depending on their chemical composition, are manufactured. The popularity of glass fibers results from their high tensile strength and durability, dimensional stability, low dielectric constant and relatively low cost, making them attractive in automotive, submarines and motor boat applications. Fibers are usually supplied with a finish or sizing with chrome complexes and silanes for better handleability and adhesion to the matrix. E glass fibers (Electrical grade) have relatively high energies to failure, providing their composites with good impact resistance compared to those of other fibers. The impact resistance of composites made from S-glass fibers is the highest of all fiber reinforced materials\textsuperscript{99}. The major limitation of glass fibers is their relatively low modulus.

1.6.3.2 Boron and Silicon Carbide Fibers\textsuperscript{100}

Boron (B) and silicon carbide (SiC) fibers find selective placement in the high value aerospace market where cost is often secondary to performance. Both are high modulus fibers, prepared by chemical vapour deposition process. The current principal use of B fibers is as reinforcement for B/epoxy composites for high performance applications, whose property retention at elevated temperatures is dictated by the epoxy matrix. Boron fibers being too expensive, are replaced by graphite fibers for commercial use. SiC fibers are also suitable for high temperature applications\textsuperscript{101} especially in ceramic matrix.

1.6.3.3 Alumina Fibers

Alumina fibers with very high modulus (2.7x10\textsuperscript{5} MPa) are specialty fibers introduced by Du Pont. These are used as reinforcements for metal and ceramic
matrices owing to their stability in molten metals, as well as radar transparent nature. Their strength and modulus are similar to Boron fiber but density is higher by around 10\%\textsuperscript{102}.

1.6.4 Organic Fibers\textsuperscript{103}

Organic fibers commonly used as reinforcements include aramids, ultra high molecular weight polyethylene and carbon. Most of the natural organic fibers- cotton, jute, sisal - and many synthetic organic fibers with the exception of aromatic polyamides (aramides), are of little interest for structural applications, because of their low modulus and modest mechanical properties.

1.6.4.1 Aramide Fibers\textsuperscript{104}

Du Pont has developed high strength and high temperature liquid crystalline fibers based on aromatic amide structures, by the name Kevlar in 1971. Kevlar is made by solution spinning in three different types, high toughness Kevlar-29, high modulus Kevlar 49 and ultrahigh modulus Kevlar-149\textsuperscript{108}. Kevlar - 49 has an axial modulus (124GPa) in between that of E-glass and high strength graphite and specific gravity of 1.44. Because of its higher stiffness, this is used more widely. Their compressive behavior is unique. The onset of compressive non linearity starts at lower stress / strain value and hence the compressive strength of composites reinforced with Kevlar-49 fibers is significantly lower than those using other reinforcements such as glass and graphite. The fiber has got excellent fatigue resistance and they are strongly anisotropic, with transverse extensional modulus and shear modulus about an order of magnitude lower than axial extensional modulus. Due to their good strength and modulus, light weight, toughness and excellent rigidity, they find key applications in ballistic protection, motorized combat vehicles, tire belts, high performance pressure vessels and rocket motor cases (hoop stress for filament wound Kevlar 49/epoxy is 450 ksi\textsuperscript{106}.
Aramid fiber is an insulator of both electricity and heat, resistant to organic solvents, fuels, and lubricants. As unprotected fibers, they are highly tenacious and do not behave in brittle manner as do both glass and carbon. Eventhough they have very high specific strength and specific modulus, they have inferior compressive properties.

1.6.4.2 Poly Ethylene Fibers

Polyethylene fibers like Spectra 900 and Himont 1900, with excellent specific strength and modulus are manufactured respectively by extrusion and gel spinning. These low density fibers have very high molecular weights \((3\times10^6)\) and approximately 45% crystallinity. The fibers possess abrasion and solvent resistance, high impact toughness even at cryogenic temperatures and resistance to radiations. But their high temperature performance is inferior to Kevlar owing to low \(T_g\) and creep problems. The major applications are in radomes, ballistic penetration prevention and low dielectric applications.

1.6.5 Carbon Fibers

Carbon and graphite fiber technology have made enormous strides in recent years in combination with high performance synthetic resin matrices. Carbon fibers were developed as reinforcements with higher strengths and modulii than glass fibers. They are used for reinforcing composites for critical aerospace applications like re-entry vehicle structures, rocket motor cases, satellite structures, tanks and pressure vessels. Today, carbon fibers are among the highest strength and modulus materials and have become the dominant reinforcement for advanced composites because of their tailorable mechanical properties, strength retention at extreme high temperature (in non-oxidising environment) and reasonable cost. The mechanical properties of the carbon fiber are determined by the type of precursor and the temperature-time profile of the manufacturing process.
The carbon fiber-reinforced composites are most suitable for cryo temperature applications. The interlaminar shear strength of carbon fiber composites improves with lowering of temperature. They have good thermal and electrical conductivity and these properties do not disappear at the lowest temperature, because, the contribution by electrons is completely eliminated. These properties offer promising application in pulsed super conductive electromagnets. The specific stiffness of carbon fiber composite is 9.7 times that of glass composite. Carbon fibers can be prepared from mesophase pitch (P-100, P-120, P-75), polymers like polyacrylonitrile (PAN) and rayon (T300, T600, T1000) or carbonaceous gases like acetylene (VGCF). PAN and pitch based fibers comprise 80% of the carbon fiber market as they are more graphitisable and therefore can attain high thermal conductivity and low electrical resistivity. The black, thin (5-10micron dia) man made fiber embedded in polymer matrix has initiated a "revolution in materials" even they are reported to be a "Miracle material" having extremely low thermal expansion, better fatigue resistance and high corrosion resistance. The family of carbon fibers consisting of high tensile, high modulus and intermediate modulus cover a Youngs modulus value ranging from 200-700 G Nim2 and strength 2 – 4 G Nim2. The use of vapor grown carbon fibers in composites is reported to yield unprecedented high thermal conductivity and caused significant reduction in coefficient of thermal expansion of the polymer matrix.

1.6.5.1 Graphite Fibers

Carbon / graphite fiber is rapidly establishing itself as a top candidate for high performance applications. It is available in forms that offer high strength, high modulus, dimensional stability, electrical conductivity, inherent lubricity, excellent corrosion resistance, heat resistance and low density. Good adhesion between fiber surface and matrix resin is critical in maximizing properties and minimizing sensitivity to moisture. Many critical products made of epoxies were designed and developed for launch vehicles viz. ASLV, PSLV, GSLV and INSAT programmes. Since ASLV,
Kevlar-Epoxy has been replacing glass epoxy in many of their applications such as rocket motor cases, pressure bottles etc. due to 50% of their weight saving.

Graphite fiber sometimes referred to as carbon fiber, comprise one of the most important classes of reinforcement with enormous potential for future growth. Their primary advantages over glass fibers are higher modulus, lower density, better fatigue properties, improved creep rupture resistance and lower coefficient of thermal expansion. Creep at room temperature is generally considered to be negligible. On the negative side, because of their low strain to failure ratio, failure energies are relatively low and hence the impact resistance of graphite fiber composites is low. Graphite fibers of commercial importance are made from poly acrylonitrile (PAN) fiber, rayon fiber, and petroleum pitch. The high strength and moduli of graphite fiber regardless of precursor, result from their high degree of crystallinity and orientation. Because of their high degree of internal structure orientation, graphite fibers are strongly anisotropic. Transverse extensional modulus and shear modulus of most fibers are generally an order of magnitude lower than axial modulus.

1.6.5.2 Carbon Nanotubes

Since the discovery of carbon nanotubes, having extremely small physical size (diameter approximately 1nm) and many unique mechanical and electrical properties, they have been appreciated as ideal fibres for nano-composite structures. Carbon nanotubes (CNT) are long graphene sheets wrapped in different angles (chiral angles) with different circumferential lengths (chiral vector) depending on which they are able to offer wide range of mechanical, electrical and thermal properties. Based on the number of such sheets, these carbon allotropes may be classified as single walled nanotube (SWNT) or multi wall nanotube (MWNT). The versatility of these materials made them attractive candidates for reinforcing polymer matrices. It has been reported that nanotubes own remarkable mechanical properties with theoretical Young's modulus and tensile strength as high as 1 TPa and 200 GPa respectively. Lau et al has given a review of the recent researches and applications.
of carbon nano tubes. The surface co-valent encapsulation of MWCNT and formation of various grafted polymers using the same is reported by Liu et al\textsuperscript{123} The important mechanisms of load transfer are micromechanical interlocking, chemical bonding and Vander Waal bonding between the matrix and the nano tube.

The influence of nanotube / matrix interfacial interaction was evidenced by Gong et al\textsuperscript{124}. It was also reported that coating carbon fiber with Multiwalled carbon nanotubes prior to their dispersion into an epoxy matrix improves the interfacial load transfer possibly by the local stiffening of the matrix near the interface \textsuperscript{125}. Jianyu Huang\textsuperscript{126}, has demonstrated its stretchability to four times its original length at 2000\textdegree C.

1.6.6 Hybrid and Speciality Reinforcements\textsuperscript{127,128}

Hybrid reinforcements are commonly used for improving the properties, getting some specific properties and / or lowering the cost of conventional composites. The best properties of each of the reinforcements can be utilized. E.g. carbon fiber is used in conjunction with ductile fibers like glass or aramid (enhanced failure strain), PEEK (better drape and toughness), polyethylene fibers (toughness and damping ability), elastomer particles (toughness), alloy particles and whiskers (wear and fatigue resistance, increased transverse strength) and coating with niobium carbon nitride (super conducting fiber)\textsuperscript{129}. The potential advantage of combining two kinds of fibres in a single matrix has been described by many researchers\textsuperscript{120-31}. Investigations in the field of hybrid composites reveal that most of the studies were concentrated on systems which have been reinforced with carbon fibers.

Hybrids composites of glass fiber-epoxy laminates and aluminium foil (glare) are commonly used to obtain hybrid fiber-metal laminates (FMLS), which are candidates for the next generation structural materials for advanced aircrafts\textsuperscript{132}. The static mechanical performance and fatigue behavior of the hybrid composites is dominated by the behavior of the lower strain phase \textsuperscript{133}, often carbon fibers. The fiber arrangement is an important parameter in determining the strength of the composite.
Various types of fiber arrangements are possible in hybrid composites. Additional possibilities are the use of woven fabrics with one fiber in the warp and another in the weft and further variations using interspersed tows in woven configurations. Plies containing different fibers or mixture of fibers may be stacked with the fibers aligned in different directions to form different combination.

Owing to their unique properties, several fibers like carbon / fluoride, nitrides, polyether ether ketone (PEEK), poly benzoxazole (PBO), poly benzothiazine (PBT) are being developed for specific applications. Carbon/ fluoride fibers having good thermal conductivity and electrical resistivity (100 to 10 $\Omega \cdot \text{cm}$) are used as semiconductors. Boron and silicon nitrides are reported to possess high thermal shock resistance, low coefficient of thermal expansion and good retention of stiffness and strength at elevated temperatures. PEEK fibers, developed by melt spinning of aromatic PEEK are resistant to acid and alkali hydrolysis but susceptible to UV radiation. Liquid crystalline polyester fibers like Ekonol and Xylar are noted for high tensile strength and modulus.

1.6.7 Woven Fabrics

Woven fabric composites are characterized by better impact resistance, damage tolerance, dimensional stability over a large range of temperatures, subtle conformability and ease of manufacturing. But their in-plane properties are compromised by using the reinforcement in fabric form. The mechanical behavior of woven fabric (W.F) composites depends upon the type of weave, fabric geometry, fiber volume fraction, laminate configuration and the material system used. The fiber reinforcing efficiency depends on the percentage of curved fiber length and the severity of curvature. Two main forms of curvature are Twist and crimp. The fabric construction determines the reinforcing efficiency, conformability to complex surfaces (drape), resistance to distortion (stability) and extent of anisotropy. The fabric geometry should be so chosen that it should give the best possible properties for the application under consideration. The important fabric parameters are strand cross...
sectional geometry, strand fineness, number of counts and the weaving conditions like balanced or unbalanced.

1.7 Interphase

The interphase represents an interfacial region of finite volume between the fiber and the matrix wherein the material properties vary (either continuously or in a step-wise manner) between those of the fiber and the matrix material. The properties of the interphase are governed largely by the chemical / morphological nature and physical / thermodynamic compatibility between the two constituents. Hence, a thorough knowledge of the microstructure - property relationship at the interphase region is an essential key to the successful and proper use of composite materials. The importance of interphase in composite technology has caused ever increasing research interests in both experimental and micro-mechanical / numerical characterisation of the interphase. The optimization of the mechanical properties of composites is influenced by the behavior of interface / interphase. A great deal of research has, therefore, been focused on the analysis of interfacial phenomena in composite materials.

The interface is always involved in the failure of the composite, either as an initiation point or as a locus of failure. Its potential to have large influence on the composite performance arises from its large area compared to the composite area. The complexity of the interphase can best be illustrated with the use of a schematic model, which allows many different characteristics of this region to be enumerated as shown in Fig.1.3. There is now considerable evidence available which demonstrate the outstanding influence of interfaces on fracture toughness, in both transverse and interlaminar fractures, strength and stiffness of fiber composites in various failure modes and loading configurations. The sensitivity of the composite properties to fiber-matrix adhesion will be governed by, how matrix and fiber are connected and how the applied load is transferred and distributed in composite.
In the case of transverse tension, the matrix and fibers are connected through the fiber-matrix interface in series and all the three components fiber, matrix and interface/inter phase carry equal load. In such cases, the fiber-matrix adhesion should not be expected to have a dominant effect on composite properties\textsuperscript{140}. A comparison among the transverse flexural, tensile and short beam shear strength of composites made of epoxy matrix and three types of carbon fibers is shown in Fig.1.4a\textsuperscript{140}. There is a significant difference between transverse flexural and transverse tensile strengths. Not only is the transverse flexural strength more sensitive to fiber matrix adhesion, but it is also significantly higher than the transverse tensile strength. The mode-I and mode-II-inter laminar fracture toughness of composites are shown in Fig.1.4b\textsuperscript{140}. The fiber-matrix adhesion in the carbon fiber is varied by different surface treatments and is in the order AS-4C > AS-4 > AU-4.
A number of experimental techniques have been developed to characterize the interface/ inter-laminar properties of fiber reinforced composites. These techniques in general are classified into (1) testing of single fiber micro composites and (2) testing of laminates. The stress distributions in fibers and fiber matrix interface have also been measured extensively using novel techniques based on Laser Raman spectroscopy for various combinations of fibers and polymer matrices. The fiber / matrix interfacial degradation is generally reflected in short beam shear (SBS) tests. Surface roughness, surface functional groups and adhesion at the interface are some of the factors influencing the performance of the inter-phase.

1.7.1 Adhesion at the Interface

In order to get a complete picture of the properties of a composite, intensive study on the active involvement of interfaces is necessary. Adhesion between the matrix and fiber (physical, chemical and frictional) should be good for maximum stress.
transfer. Higher the resistance to shear, higher will be the stresses that can be applied to the specimen. Normal and shear stresses are effective at the interface, the latter arising from residual thermal stresses and difference in Poisson's ratio.

Work of adhesion is expressed as,

\[ W_A = \gamma (1 + \cos \theta) \]  

where, \( \gamma \) is the surface tension and \( \theta \) is the contact angle. Matrix also plays an important role in adhesion. Usually adhesion is stronger in polar polymers like epoxy, owing to their capability of hydrogen-bonding with the functional groups on reinforcement surface. Ductility also is important as it provides resistance to crack propagation.

1.7.2 Theories of Adhesion

The fiber matrix interface adhesion can be attributed to five main mechanisms. a) Adsorption and wetting b) Inter-diffusion c) Electrostatic attraction, d) Chemical bonding and e) Mechanical adhesion. Schematic representation of Fiber-matrix interface adhesion is shown in Fig. 1.5.

1.7.3 Fiber Surface and Interface Modifications

The interaction of fiber with a matrix material, depend strongly on the chemical / molecular features and atomic composition of the fiber surface layers as well as its topographical nature. A number of factors affect the microstructure of the inter phase, which in turn control the mechanical and physical properties of the composite. They are the topology and the chemical composition of the fiber surface, silane structure in the treating solution and its organo-functionality, acidity, drying conditions and homogeneity.
In recent years a surface technique, Time of Flight Secondary Ion Mass Spectroscopy (TOF SIMS) in combination with XPS has been extensively used by Wang et al.\textsuperscript{165} to observe the chemical reaction in the silane interface region during cure.

The inter phase material tends to have a lower glass transition temperature, higher modulus and tensile strength and lower fracture toughness than the bulk matrix. Since the details of the interface reaction is specific to each combination of fiber and matrix material, with totally different chemical and atomic compositions and morphological nature, no general conclusions can be drawn regarding the ductility and fracture toughness of the inter phase relative to the surrounding matrix. Suzuki et al.\textsuperscript{166} reported that the interlaminar fracture toughness of the glass fiber composite is influenced by the type and concentration of the silane solution. A schematic model for inter-diffusion and inter-penetration in a silane treated glass fiber polymer matrix composite is shown in Fig.1.6.

The interface adhesive behavior can be visualized into three. i) A sharp interface with a weak molecular force as in the case of a non-polar polymer with a polar polymer ii) A sharp interface with a strong molecular force, such as dispersion
force between a nonpolar polymer and a high energy material and iii) Diffuse interface with any molecular force; if there is sufficient molecular diffusion and entanglement, interfacial slippage will not occur.

![Diagram of Chemically bonded & Diffused Interface](image)

Fig. 1.6 Schematic model for interdiffusion and IPN in a silane treated glass fiber polymer matrix composite

The interfacial interaction depends on the physical and chemical structure and polarity of the components. The interfacial adhesion will be enhanced by chemically coupling the matrix to the reinforcement. Several processes such as chemical treatments, photochemical treatments, plasma treatments, surface grafting etc. have been developed to modify polymers and fiber surfaces. These cause physical and chemical changes on the surface layer without affecting the bulk properties. The plasma treatment, acetylation, benzoylation, acrylation, permanganate treatment, peroxide treatment etc. were found to effectively enhance the compatibility of fibers with polymers. Tethered chain is also reported to improve the mechanical properties of polymer blends.

The degree of adhesion between carbon fiber and matrix depends considerably on the quality and state of carbon fiber surface, which in turn depend on the internal structure of graphite (which is highly anisotropic on a nano scale). The techniques used for the
characterization of carbon fiber surface like inverse gas chromatography, at infinite and finite dilution\textsuperscript{166}, surface energy measurements\textsuperscript{167,168} and determination of active site concentration are discussed in the case of virgin, plasma treated and anodically oxidized PAN and pitch based carbon fibers. ESCA spectroscopy deconvolution\textsuperscript{169} is suggested to be a very interesting way to assess the Oxidation Degree of Spherical Carbon (ODSC) index. This index expresses the ratio of the surface concentration of more oxidized groups such as carboxylic acids and esters to less oxidized groups such as alcohols and ketones. The most effective surface treatment of carbon fiber-epoxy resin system are reported to be oxidative in nature\textsuperscript{170}. Schematic model for the chemical reaction between oxidized carbon fiber surface and epoxy matrix is given in Scheme 1. These treatments have been conjunctured to improve the fiber-matrix adhesion primarily through increased chemical bonding\textsuperscript{172} or by enhanced mechanical interlocking between the fiber and the matrix\textsuperscript{173}.

![Scheme 1 Schematic model for the chemical reaction between oxidized carbon fiber surface and epoxy matrix\textsuperscript{171}](image)

Reviews\textsuperscript{174} on the surface treatment of carbon fibers show that a range of active functional groups can be produced by different surface treatment methods, which can be classified into oxidative and non-oxidative treatments. The oxidative treatments are further divided in to dry oxidation in presence of gases, plasma etching and wet oxidation, the last of which is carried out chemically or electrolytically. Deposition of more active forms of carbon such as the highly effective whiskerization, plasma polymerization and grafting of polymers are among the non oxidative
treatments of carbon fiber surfaces. The surface treatment of carbon fibers results in substantial changes in the fiber surface area with associated variation in reactivity, removal of weak surface layer (the removal being more serious in plasma etching than in wet oxidation), increase in the polar surface energy and chemical modification by the formation of carboxyl, hydroxyl and carbonyl groups on the fiber surface.

To improve interfacial interaction and hence compatibility, the in situ reactive mixing of the two polymeric phases has been shown to be one of the most effective ways\textsuperscript{175}. The interaction between component phases may, however, be brought by addition of an agent that interacts with both the phases, and render them mutually compatible and by specific reaction between the two phases\textsuperscript{176-77}. The occurrence of reaction between the two polymeric components at the inter phase is expected to lead to a reduction in interfacial tension. The factors which directly influence the extent of reaction that happens include the intensity and time of mixing, functionality level, kinetics of reactive groups, and stability of the covalent bond to the processing conditions\textsuperscript{178}. In the future, micro engineering of the fiber-matrix inter phase will be used to optimize the properties and performance of composite materials.

1.7.4 Fiber Surface and Interface Characterization\textsuperscript{179}

Spectral and microscopic methods are mostly resorted to the fiber surfaces and interface characterization. The characterization gives evidence of chemical composition of the surface region as well as information on interactions between fiber and matrix. Electron spectroscopy for chemical analysis (ESCA)\textsuperscript{180}, Mass spectroscopy, X-ray diffraction, electron induced vibration spectroscopy and photo acoustic spectroscopy are shown to be successful in polymer surface and interfacial interaction characterization\textsuperscript{181,182}. Apart from Infrared spectroscopy\textsuperscript{183,184}, frequently used thermodynamic methods such as wettability studies, inverse gas chromatography measurement, zeta potential measurement, contact angle measurement and Neutron activation analysis are used for the characterization of reinforced polymers.
1.8 Fabrication of Composites

Different processing techniques are used for composite fabrication, depending on the desired properties, nature and properties of the matrix and shape of the product. Different manufacturing processes used for the fabrication of the composite leads to varying amounts of imperfections and air inclusions even though all manufacturing methods aim to avoid entrapment of air or formation of voids since these represent gross defects.

1.8.1 Thermoset Processing

The impregnation mechanisms and consolidation quality have got profound influence on the mechanical properties of composites. The main goal of consolidation is to produce a monolithic structure by inducing intimate contact and adhesion between individual plies and to minimize void content inside the composite. Consolidation is accompanied by applying pressure and heat at the system to squeeze the air and volatiles out of the composite.

The simplest method of consolidation is manual lay up (wet and pre-preg). High strength parts with irregular shapes can be manufactured by vacuum bagging. Application of vacuum assists in compressing the plies, simultaneously removing the volatiles. Autoclave molding gives better compression and elimination of volatiles as these are pneumatic pressure vessels with built-in heater and blower units. Therefore, this technique is used for molding complex and critical parts.

The impregnation techniques followed are generally classified into pre-impregnation techniques and post-impregnation techniques. The former includes melt impregnation and solvent aided impregnation and the latter constitutes film stacking, powder coating, co-weaving and hybridization.

Another important technique for fabrication of composites is filament winding. This method is suited for manufacture of pressure vessels, rocket motor cases, etc. Pultrusion method is employed for the production of rods, sheets, tubes, etc. In this,
continuous fibers are passed through a resin bath and then through the heated die so that the resin cures in the die itself.

Compression molding (matched die molding) is performed under heat and pressure. Depending on the form in which material is placed inside the mold, preform, sheet molding (SMC) and batch molding compound (BMC) methods are available to make complex shapes with good consolidation. Small parts with powder or short fiber reinforcements are manufactured by transfer molding. Reaction injection molding is also a fast growing process.

1.8.2 Thermoplastic Processing

The processing of thermoplastics is similar to that of thermosets with minor modifications depending on the matrix and fiber chosen. Instead of curing, thermoplastics are heated into molten stage and cooled during fabrication. Pultrusion, matched die molding, injection molding and extrusion are the common methods for processing of a thermoplastic resin.

1.8.3 Process Monitoring

Many process monitoring techniques are used to track the chemical reactions that take place during the processing of composite materials. Variety of techniques such as, differential scanning calorimetry\textsuperscript{187-190}, thermal scanning rheometry\textsuperscript{191}, dielectric spectroscopy\textsuperscript{192}, Raman spectroscopy\textsuperscript{193} and FTIR\textsuperscript{184-192} have been used to monitor cure reaction of epoxies. Epoxy –amine reaction was reported to follow autocatalytic mechanism\textsuperscript{197-199}.

The chemical reactivity and kinetics are controlling factors for the successful polymerization of composite resin matrix. Since chemical reactivity is related exponentially to the temperature, the heat-up rate and temperature difference within the laminate, the knowledge of its chemical kinetics is very important for obtaining acceptable composites. One of the mechanisms of understanding the chemical
kinetics of a resin system is the experimental determination of its time-temperature-transformation (TTT) diagram. These diagrams are made by subjecting the resin to predetermined conditions and measuring the response usually by rheometric methods. The results are usually plotted as viscosity vs. time for various temperatures.

1.9 Nano Composites

The goal of nano composite developments in composite industry is to create new materials that have unprecedented properties due to their small size. Nano-composite technology has been described as the next great frontier of material science. Polymer layered nano-composites represent a rational alternative to conventional filled polymers. The field of polymer nano-composites is stimulating both fundamental and applied research, because a minimal addition of <10% nano-scale materials often exhibit physical and chemical properties that are dramatically different from conventional micro composites. The polymer layered nano-composites can exhibit increased modulus, decreased thermal expansion coefficient, reduced gas permeability, increased solvent resistance and increased ionic conductivity compared to the polymer.

Hackman et al studied the basic concepts of nano composites, the physical and chemical requirements for attaining nanocomposites, the types of property improvements that have been generated by researchers in this field and nano composite fabrication techniques viz. conventional filling, intercalation and exfoliation. The incorporation of nano particles for the modification of fiber-reinforced composites also yielded high performance composites.

Wang et al reported the improvement in barrier properties of the nano composites over the pristine polymer. The nano particle addition was found to give extensive improvement in mechanical properties for the polymer having sub ambient T_g while modest improvement only was observed in the case of polymers of high T_g. Weiping Liu et al evaluated the performance of organo clay filled high performance
epoxy nano composites and reported an improvement in compressive strength and fracture toughness \((G_\text{ic} \text{ and } K_\text{ic})\) with filler concentration while the \(T_\text{e}\) and yield strength were found to be reduced.

Epoxy-nano clay composites are being studied extensively by various researchers which include the studies on filler concentration \(^{206}\), mixing methods-direct mixing method (DMM) vs. high pressure mixing method (HPMM) \(^{206}\) and types of smectite clays \(^{201}\). Subramonian et al\(^{205}\) have obtained improved properties for the exfoliated nano composites compared to the intercalated nanoclay- glass fiber composites.

1.10 Fiber Reinforced Composites

The fiber reinforced composites are classified into three, based on the type of fiber used viz. chopped, continuous or woven. The fibers are the load carrying members and the matrix which binds the fibers together, acts as a load transfer medium and protects the fiber from environmental damages due to elevated temperature, humidity and damage due to handling. The stiffness, strength and mechanical properties of the composites along the reinforcement direction are dominated by the properties of the reinforcement.

The continuous fiber composites are usually subdivided into straight fiber laminates that have only in-plane fiber orientations and braided or woven textile composites that have both in-plane and out-of-plane fiber orientations. Straight fiber laminates are used extensively in aircraft structures. However, the potential for delamination is a major problem because the interlaminar strength is matrix dominated. Textile composites that do not have distinct laminae are not susceptible to delamination, but their strength and stiffness are sacrificed due to fiber curvatures.

Predicting crack propagation in PMC structure is further complicated by the existence of a multiplicity of design options arising from the availability of numerous choices of fibers, fiber coatings, fiber orientation patterns, matrix materials, constituent material combinations, and hybridizations \(^{207}\). The performance of 3D woven
composites was found to far outstrip that of conventional 2D laminates or stitched laminates in many important regards. Thus, 3D braided fiber reinforced PMCs can be expected to exhibit similar, superior performance to 2D braided PMC materials. Further, tow size, strength and distributions in space of geometrical flaws are found to be key design and manufacturing parameters for controlling performance characteristics of 3D woven and braided PMCs.

The bidirectional fiber arrangement in a woven composite restricts matrix shrinkage. The small voids may not significantly affect the mechanical properties but show considerable effect on diffusion behavior. Moisture absorption is a matrix dominated property\textsuperscript{207}. Unlike the neat resin and uni-weave composites, the first stage diffusion of the woven fabric composite deviates from Fickian diffusion which predicts the moisture uptake to increase as a linear function of square root time during the early period\textsuperscript{208}.

Different mechanisms have been suggested to explain the matrix to reinforcement stress transmission. Klaus Friedrich et al\textsuperscript{209} have given a detailed picture of different deformation mechanisms in knitted fabric composites. Continuous fibers bear the maximum applied stress. Assuming a strong fiber-matrix interface, the tensile stress applied along the fiber direction will be distributed as

\[
\sigma_c = E_m V_m \varepsilon_c + E_f V_f \varepsilon_c
\]

where subscripts c, m and f refer to composite, matrix and fiber and E, V, \sigma and \varepsilon represent modulus, volume fraction, stress and strain respectively.

In the case of discontinuous fibers, stress transmission depends on the critical fiber length \(l_c\), which depends on the ultimate strength, \(\sigma^*_c\) of the fiber and its diameter.

\[
l_c = \frac{\sigma^*_c d}{2\tau}
\]
Where, \( \tau \) = shear strength between matrix and interface.
\( d \) = diameter

The critical fiber length, \( l_c \) is very important since in cases where the fiber length is shorter than this, the fiber will not be able to reinforce the matrix. For example the typical \( l_c \) for carbon/epoxy is 4mm. The properties of the composite are affected by several factors like the size, structure and distribution of reinforcement, matrix morphology and molecular restructuring during processing and residual stresses that can lead to dewetting\(^2\).

The properties of the woven fabric composites are determined by the fabric material, fiber orientation, stacking sequence, weaving pattern, void content, etc. The effect of fiber orientation on the work of fracture obtained by notched charpy impact test of commercial GFRP laminates are shown in Fig. 1.7\(^2\).
1.11 Characterization of Fiber Reinforced Composites

The composite materials are being extensively used in different areas where they are subjected to different loading and climatic environments. Hence a thorough understanding of their thermal, physical, mechanical, and dynamic mechanical properties under different climatic and loading environments is essential for assessing its suitability for the specific application. The knowledge of their on-axis and off-axis mechanical properties, fracture properties, and behavior under fatigue loading conditions are essential for their performance prediction. The properties of different types of composites and the factors influencing their properties were extensively studied by several authors \(^{212-216}\).

1.11.1 Thermophysical characterisation\(^{217}\)

The thermal properties of a material are characterized by its glass transition temperature, thermal and thermo oxidative resistance, flame resistance, ablative resistance, coefficient of thermal expansion, thermal decomposition temperature in nitrogen and air, and char yield. The highly polar groups will increase the intermolecular attraction. The stiff and bulky groups in the polymer backbone or sidechains inhibit the free rotation of the chain segments and increase \(T_g\) and heat resistance.

1.11.1.1 Thermo Mechanical Analysis

Thermo mechanical analysis (TMA) is useful in determining the softening point, thermal expansion coefficient, and glass transition temperature of materials. TMA is used in expansion, flexure, and penetration modes to determine the glass transition temperature of the polymers and composites. Since the composite is a blend of the matrix and reinforcement having different thermal expansion coefficients, and the mismatch in their expansion coefficients can lead to the failure of the composite at the interface, the determination of expansion coefficient of composite and its constituents is of special concern. The coefficient of linear thermal expansion-\(\alpha\), undergoes a marked change in the \(T_g\) region and it is determined by the point of
intersection of the lines fit to the expansion data above and below the T_g range. Flexural TMA analysis is sensitive to the modulus of reinforcing fibers in the composite and this will give different results depending on the nature of the fiber\textsuperscript{218}. Uniaxially oriented fiber composites have different \( \alpha \) values in different directions which can be computed knowing the volume fractions, \( \alpha \) values and Poisons ratios of the individual components\textsuperscript{219}. In the transverse direction, \( \alpha \) can be more than that of the matrix material because of the fact that the rigid fiber prevents the expansion of the matrix in the longitudinal direction, so that the matrix is forced to expand in the transverse direction more in this case\textsuperscript{219}.

1.11.1.2 Thermo Gravimetric Analysis

Thermo gravimetric analysis (TGA) of the polymer matrix gives information on its thermal stability, char formation, and decomposition kinetics. The preferred method for determining the short-term thermal stability or thermo oxidative stability of high temperature polymers has been dynamic TGA. The weight loss in dynamic TGA is sensitive to experimental variables like heating rate, sample mass and atmosphere. Long-term stabilities have been most conveniently determined by iso-thermogravimetric analysis. Thermal stability is primarily determined by the bond energies between atoms in the chain. High thermal stability in polymers has been achieved by making full use of resonance stabilization. Cross linking generally results in improvement in thermal stability.

1.11.1.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) monitors the enthalpy changes in the polymeric matrix as a function of temperature. It gives useful informations on its cure and transition temperatures and enables to define processing window and fabrication conditions of the composite based on the cure behavior of the resin. Since the heat capacity of a polymer changes at \( T_g \), the differential scanning calorimeter is used to determine its \( T_g \). The temperature corresponding to the base line shift in heat flow vs
temperature curve gives the $T_g$ of the system which dictates the performance of the resin system under different climatic conditions.

1.11.1.4 Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analyser (DMTA) is a powerful tool for determining the glass transition temperature, understanding the cure behavior, and hence providing the processing conditions for the polymer matrix composite. The dynamic mechanical properties, especially damping, are sensitive to all kinds of transitions, relaxation process, structural heterogeneities, and morphology of the multy phase systems such as composites. Damping is often the most sensitive indicator of all kinds of molecular motions which are going on in the material. The DMA is the most common and preferred method of characterizing $T_g$ of organic matrix composites. The DMA technique provides curves of dynamic storage and loss modulus and loss tangent as a function of temperature and frequency. The tan $\delta$ reflects the amount of energy dissipated during each cycle of loading and goes through peak values during the $T_g$ region. The damping properties of the composite results from the inherent damping properties of the constituents especially that of the matrix material. It is associated with the movement of small groups and chains of molecules within the polymer structure. Laurence E Neilson has given a detailed picture of the effect of various parameters like temperature, test frequency, stress / strain amplitude, thermal history, molecular weight, crosslinking, crystallinity, crystalline morphology, copolymerization, plasticization, molecular orientation, strength of intermolecular forces and polymer blending and grafting on the dynamic mechanical properties of different polymer systems. In polymer matrix composites the damping characteristics of the polymer is altered by the incorporation of the reinforcement. The relationship between temperature and frequency for composites are well explained by Arrhenius relationship. The apparent activation energy $H$ for the relaxation process at $T_g$ region is calculated using the following equation.
\[
\log f = \log f_o - \frac{H}{2.303 RT} \tag{1.4}
\]

Where \( f \) is the measuring frequency, \( f_o \), the frequency when \( T \) approaches infinity \( T \) is the temperature corresponding to the \( \tan \delta \) peak. The activation energy of the composites is less than that of the neat resin. The composite damping property depend on the inherent damping properties of the constituents. The damping of composites can be expressed by the rule of mixtures equation\(^{223}\):

\[
\tan \delta_c = V_f \tan \delta_f + (1-V_f) \tan \delta_m. \tag{1.5}
\]

Where \( V_f \) is the volume fraction of fiber and \( \tan \delta_c, \tan \delta_m \) and \( \tan \delta_f \) are the damping values of the composite, matrix and the fiber respectively. In the case of rigid inclusions the first term can be neglected and the equation becomes\(^{224}\)

\[
\tan \delta_c = (1-V_f) \tan \delta_m. \tag{1.6}
\]

Several methods are reported to calculate the \( T_g \) from DMA data. The temperature, heating rate and frequency employed will also affect the results. ASTM \textit{D} - 4065 covers both forced and resonant vibration techniques for DMA analysis. The modulus in the glassy state is primarily determined by the strength of the intermolecular forces and the way the polymer chains are packed. The increase in modulii indicates good adhesion between the matrix and the fiber. The higher value of storage modulus below \( T_g \) indicate the reinforcing ability of the matrix in that temperature range.

Equations are available, which enable the calculation of mechanical properties from the dynamic mechanical properties and vise versa\(^{225}\).

1.11.2 Mechanical Characterisation\(^{226}\)
For structural applications, a material can be designed to maximize its mechanical properties that are normally defined by tensile, compression and flexural characteristics under various service environments. All of these three characteristics are defined by ultimate strength (yield and break strengths), modulus (stiffness) and extensibility. High cross-link density combined with rigid molecular structure embrittles a high performance thermoset and can cause early catastrophic failure of the material. Sankar Mal has reported the influence of different types of fibers - glass, carbon, graphite & aramid- on properties of epoxy unidirectional (UD) composites and also the influence of matrix type on the high and intermediate modulus graphite fiber composites. The effect of different types of reinforcements on the stress-strain properties of the composite was investigated by several authors.

The on-axis properties (longitudinal tensile, compressive and flexural properties) are dominated by fiber properties whereas the off-axis properties (transverse tensile and flexural, in-plane and inter-laminar shear) and inter-laminar fracture toughness are dominated by matrix and interfacial properties. The sensitivity of the composite properties to fiber-matrix adhesion is governed by how the matrix and fibers are connected and how the applied load is transferred and distributed in the composite. Laurence T Drzal has explained clearly the interphase and fiber-matrix adhesion effect on the composite mechanical properties. The mechanical properties of the PMCs under all loading environments are temperature dependent.

1.11.2.1 Tensile strength

The tensile properties of the composites depend among other things on the properties of the individual components, their volume fraction, interface characteristics and the quality, distribution and orientation of reinforcement. Laurence T Drzal has given a comparative evaluation of the on-axis and off-axis tensile, compressive and flexural properties of carbon-epoxy composites without and with different surface treatments. The fiber/matrix volume fraction and the testing mode determine whether the failure is fiber dominated or matrix dominated.
The fiber-matrix adhesion does not play a dominant role in the case of longitudinal tensile behavior. On the other hand, in the case of transverse tension, the matrix and fibers are connected through the fiber-matrix interface in series and since all the three components carry equal load, the fiber-matrix interface/interphase is expected to have a dominant effect.

Extensive studies were reported indicating the influence of stress direction and constituent volume % on the tensile strength of CFRP / GFRP UD composites.

1.11.2.2 Compressive Strength

Kink band formation is the most common compression mechanism in graphite-epoxy composites. With the help of Micro Raman Spectroscopy (MRS) which is capable of measuring fiber strain with 2 micrometer spatial resolution, Narayan et al. could monitor the strain in individual fibers in graphite-epoxy composites and correlate the inter phase behavior and strain concentration behavior to its kink band formation in compressive failure. Depending on the matrix properties, service environment and processing, the fiber, matrix or interphase can be the critical factor in initiating compressive failure.

1.11.2.3 Flexural Strength

Flexural properties are generally evaluated by determining the strength and modulus of the material in flexure mode either by three point bending or by four point bending method depending on the stiffness of the material. Not only is the transverse flexural strength more sensitive to changes in fiber-matrix adhesion, it is higher than the transverse tensile strength. It is reported to be due to the non uniformity in stress distribution in the flexure test.

1.11.2.4 Inter Laminar Shear Strength

The inter-laminar strength (ILSS) characteristics of the composite materials are generally determined by Short Beam Shear (SBS) test. In the case of short beam
shear test, increase in fiber matrix adhesion increases the ILSS, but levels off or shows slight decrease with highest level of adhesion. The interlaminar shear strength (ILSS) has been used for the assessment of bond strength between fiber and matrix resin in a laminated composites. The differences in the thermal expansion coefficients of the fiber and matrix and cure shrinkage in thermosetting matrices result in the development of residual stresses at the fiber/matrix interface\(^1\). The fiber/matrix interfacial degradation may be reflected in such short beam shear (SBS) tests\(^2\). Interfacial debonding is expected to introduce the intralaminar crack initiation for composite that contains weak fiber/matrix interface bonds\(^3\). The interlaminar shear properties are correlatable to many of the composite strength characteristics. Dai Gil et al\(^4\) correlated the short beam shear properties and impact energy absorption characteristics of fiber reinforced polymer composites. The ILSS is sensitive to poor material fabrication practices and damage induced by improper coupon machining and fiber alignment relative to loading direction.

1.11.2.5 Impact Resistance\(^2\)\(^4\)\(^5\)

The effective use of polymer matrix composites for high performance applications demands a thorough understanding of its damage resistance characteristics. Since the reinforcing fibers- glass, carbon or aramid - have elongation-to-break values of 3.5 % or less and such fibers constitute significant fraction of the structural composite, brittle failure will always be the primary mode of mechanical degradation. The laminated UD composites used for high performance structural applications are highly susceptible to impact damages because of their lower transverse tensile strength. Woven fabric composites are characterized by superior impact resistance and damage tolerance characteristics and higher fracture toughness.

The damage mechanisms due to an impact involve delamination, matrix cracking, and fiber breakage. The first two damage modes are purely matrix dependent. It is now widely accepted that the increase in failure strain or area under
the stress-strain curve of the matrix material could improve the residual strength of the composite after impact. The composites with tougher matrix have better impact resistance. This is also related to the interlaminar fracture toughness, $G_{IC}$ and $G_{IIIC}$ which are strain energy release rates to quantify resistance against delamination in tensile or shear modes respectively. The impact resistance show systematic increase with $G_{IC}$ and $G_{IIIC}$.

The techniques used for the evaluation of impact resistance can be classified in to three categories.  

1. Drop weight tests
2. Pendulum tests 
3. Ballistic tests

Several parameters may affect the impact behavior, including the type of impact test machine, characteristics of the impactor, velocity and mass of the impactor, and the specimen configuration. Many of the elastomers and thermoplastics used to toughen the epoxy resin have reactive functional groups. Impact tests enable the determination of important characteristics such as incipient damage, ductile to brittle transition point, maximum load and total energy absorbed in fracture. It is determined by the energy absorbed by the specimen at different stages of fracture, the relative contribution at different stages depending on the size and geometry of the specimen.

1.11.2.6 Fracture Toughness

Basic to the evaluation of durability and reliability of the composite is the analysis of fracture initiation and progression under static or fluctuating thermo-mechanical loading and fast rate of loading in variable environments. Fracture initiation is associated with defects such as voids, machining irregularities, stress concentrating design features, damage from impacts with tools or other objects resulting in discrete source damage (DSD), and non-uniform material properties. The toughness evaluation of unidirectional (UD) carbon fiber composites showed that the stiffness is largely determined by the type of fiber and the fiber content. Raghava et al has given a detailed account of the effect of different toughening mechanisms/matrix toughening on the impact strength and fracture toughness. He has given the equations for the energy absorption by fiber, matrix and interphase. A detailed picture
of the effect of curing agents, concentration of reactive functional groups, type and extent of elastomer\textsuperscript{281} / thermoplastic / hard particle modification\textsuperscript{282,283}, strain rate and test temperature\textsuperscript{284} on the fracture toughness of thermosets was also given with special reference to epoxies. Hunston\textsuperscript{285} examined the effect of toughening of twenty one matrix resins (thermoset, toughened-thermoset and thermoplastic) on the fracture energy of the composites and concluded that the increase in resin toughness enhanced the fracture toughness of their composites.

Important fracture properties are strength and strain-to-failure, fracture toughness, strain energy release rate, interlaminar fracture energy, fatigue crack growth resistance and compression-after-impact\textsuperscript{286}. The different energy absorbing mechanisms in the composites are fiber failure- $U_f$, resin crazing or cracking-$U_m$, fiber–resin debonding-$U_d$, fiber pull out from the matrix across a failure surface-$U_p$, fiber relaxation and stress distribution to the matrix-$U_r$, multiple fiber fracture- $U_{mf}$ and multiple matrix failure-$U_{mm}$. If all the failure mechanisms occur in one failure situation, the total energy absorbed ($U_t$) is given by\textsuperscript{287}

$$ U_t = U_f + U_m + U_d + U_p + U_r + U_{mf} + U_{mm} $$ (1.7)

If the interfacial strength is stronger than the matrix strength, the crack will prefer to go through the weaker resin rather than breaking the stronger fiber and the primary failure mode changes from the interfacial failure to matrix failure. When the fiber-matrix adhesion is strong, several energy absorbing phenomena, such as matrix deformation, matrix cracking, fiber pull out, interfacial failure and so on take place. The toughness of thermoplastic matrix composite is higher than that of the thermosets and the property more commonly characterized is the inter-laminar fracture toughness ($G_{ij}$) obtained using the double cantilever beam test (DCB). Several techniques are available for evaluating the interlaminar fracture toughness in different modes such as Mode-I\textsuperscript{256}, Mode- II\textsuperscript{254} and mixed modes\textsuperscript{259}. 


The low interlaminar fracture toughness of thermosetting matrix composites has been one of the main limitations to their use in service, due to the ease with which delamination can initiate and propagate. The matrix properties play a vital role in controlling the interlaminar fracture resistance of composites. The role of matrix properties on the toughness of thermoplastic and thermosetting composites has been reported by several authors. Latest publications on the toughening studies on the DDS-cured epoxy (DGEBA) claims more than 50% increase in fracture energy for the DDS-cured epoxy (DGEBA) system using PEEK with pendent ditert-butyl group. In toughened matrices the type of reinforcement, resin-reinforcement interaction, ply stacking sequence, fatigue properties, interleaving etc. play significant role in determining the toughness of the laminate composite.

Hedrick et al. used phenolic hydroxyl and amine terminated polysulphone oligomers to toughen epoxy resin. High molecular weight PSF increased fracture toughness (FT) by 100% without any loss in high temperature properties. Epoxy modification using several thermoplastics - poly sulphone, polyetherimide, polycarbonate, polyester, poly ether ether ketone, polymethyl methacrylate and poly ethylene oxide was tried earlier by several others.

The important mechanisms responsible for enhancement of F.T of thermoplastic modified epoxies are crack pinning or bowing, crack deflection and bifurcation, shear banding, and micro cracking. The generally observed toughening mechanisms in rubber toughened polymers are shown in Fig.1. It was reported in literature that the flexibility of short glass fiber reinforced epoxy resin was improved with HTPB modification. Barcia et al reported that the reinforcement of epoxy resin using carbon fiber grafted with HTPB, when used to reinforce epoxy resin, improved the toughness and impact resistance of the composite.

The interphase also plays a significant role and a strong interphase is required in order to achieve the potential toughness of the polymer matrix. The effect of temperature and test rate on the fracture toughness has been examined.
The rubber toughening was found to increase the mode-1 delamination energy more than that of mode II. It was found that generally the improvement in $G_{1c}$ was considerably less than $G_{IIc}$ and hence $G_{1c}$ is not as good an indicator of impact resistance as $G_{IIc}$.

![Diagram of toughening mechanisms in rubber toughened polymers]

**Fig. 1.8 Toughening mechanisms in rubber toughened polymers.**
1) Shear band formation near rubber particles
2) Rubber particle fracture after cavitation
3) Stretching
4) Debonding
5) Crack deflection by hard particle & shearing of rubber particles
6) Trans particle fracture
7) Debonding of hard particles
8) Voided / cavitated rubber particles
9) Crazing
10) Plastic zone at the crack tip
11) Diffused shear yielding
12) Shear band/craze interaction

The most interesting approach taken towards the toughening of BMI resin is by the incorporation of a high modulus, high $T_g$ thermoplastic to form a semi interpenetrating network after cross linking of the BMI resin. Friedrich concluded in his studies that the reinforcement geometry and matrix ductility are important fracture toughness considerations. Although various attempts have been made to increase the toughness by adding a ductile third phase material either dispersed in the matrix or selectively located at the interphase, there is still no good format for predicting, a priori, the toughness of the composite system.

### 1.11.2.7 Fatigue Resistance

Fatigue is defined as the degradation of the integrity of the material as a result of external conditions that vary with time. These external conditions can be fluctuating...
mechanical stress/strain, thermally induced cyclic stress or cyclic moisture exposure. Fatigue resistance is measured to understand its behavior under cyclic loading environments encountered under certain service conditions. Extensive studies were carried out on the fatigue resistance of different structural materials.

The fatigue life is determined by number of experimental, environmental and molecular variables. The temperature, pressure and humidity are among the environmental variables. The test frequency, type of loading -tensile, compressive, flexure, shear and their combinations -come under the experimental variables while the surface characteristics of the reinforcement, matrix type and its properties and inter phase quality come under the molecular characteristics. Fatigue damage in composite materials is very complex due to several damage mechanisms occurring at many locations, throughout a laminate. Matrix crack, fiber fracture, longitudinal cracking, crack coupling and delamination growth are the five major damage mechanisms. The S-N curves quantify the relationship between fatigue life and applied stress amplitude.

Thermo mechanical fatigue (TMF) tests simulate the combined effect of thermal cycling and mechanical fatigue on advanced materials to ensure that they can withstand the arduous operating conditions (temperatures of the order of 2000°C, under hypersonic heating rates and dynamic loading conditions) expected to be encountered by the various structural components of the space vehicle during the different phases of ascend, in-orbit manuaring, re-entry and landing phases. The stiffness reduction during the fatigue of the woven material appeared to have regions of damage (Fig. 1.9) as described by Reifsnider. From experimental observations, the authors hypothesize that the damage progressed in the following way. The rapid modulus decay at the beginning of the fatigue process was caused by the initiation and accumulation of debonds in the weft and matrix cracks. This behavior is similar to that commonly observed in orthotropic laminates. However, the woven system behavior differs in that these debonds occur at
each region surrounding a fiber undulation. Matrix cracking and weft debonding were observed to stop progressing.

Various authors have studied the effect of test frequency on the fatigue of polymer composites. The fatigue properties of composites have been reviewed by Moore and Dickinso et al. examined the behavior of PEEK composite in comparison with epoxy matrix composites. The studies confirmed superior fatigue properties for PEEK in comparison with epoxies. Considerable reduction in fatigue resistance is reported for [+/- 45] lay up.

![Fig. 1.9 Damage progression during fatigue life](image)

1.11.3 Chemical resistance

Depending on the requirement for specific application the composite should have excellent chemical resistance including resistance to solvent, adjacent materials, solubility, solvent crazing, and swellability.
1.11.4 Dielectric Properties

In addition to mechanical, thermal and chemical properties, the polymer should resist electric failure under service conditions. The electric storage ability for a material can be quantitatively expressed by the dielectric constant that may be viewed as the average energy stored per unit volume per unit electric field strength. The polymer breakdown under electric potentials can be from three possible mechanisms: electrical, thermal and electro-mechanical breakdowns\(^2\). High performance thermosets used for fabricating electronic components should possess good thermal conductivity, so as to dissipate heat, high electric strength, high surface break down strength, low dielectric constant, low dielectric dissipation factor, and low water absorption in addition to the necessary thermal and mechanical properties.

1.11.5 Physical properties

Composite physical properties of particular interest to designers and fabricators include density, fiber volume fraction and void volume. The fiber volume fraction can influence the strength characteristics of the composite. The increase in fiber volume fraction was found to increase the area under the load displacement curve and caused the change in failure mode from propagation-dominated delamination to initiation-dominated delamination\(^3\). Many applications require knowledge of hygrothermal properties of the composite including thermal conductivity, thermal expansion and moisture expansion. The water absorption and moisture expansion of composite materials influence the composite performance to a considerable extent.

1.11.6 Scanning Electron Microscopy

The defects in the laminates like delamination, disbands, porosity or bond lines, fiber mis-orientation, missing plies, variation in fiber volume fraction, and resin-rich and resin-starved areas and foreign inclusions determine its performance. SEM
photographs enable the detailed surface and inter-phase characterization of composites.

1.11.7 Moisture resistance

Water acts aggressively on polymer - reinforcement bonds and leads to the movement of the locus of failure from being cohesive in adhesive to purely interfacial. The amount of moisture absorbed by the organic matrix depends on the polymer type, exposure time, component geometry, temperature, relative humidity and exposure conditions.

A number of effects results from the ingress of moisture to an adhesive joint and these include plasticization of the system and disruption of the interfacial region between the substrate and the organic phase. The moisture uptake characteristics of the resin are extremely important. The absorption of water lowers $T_g$ and produces changes in matrix and interphase related properties. There are two moisture properties: moisture diffusivity and equilibrium moisture content. These are determined by gravimetric methods (ASTM D 5229 / D 5229M). The rate of moisture absorption is controlled by moisture diffusivity. It usually follows an Arrhenius type exponential relation with absolute temperature. It is a function only of temperature and weakly related to relative humidity. But equilibrium moisture content is weakly related to temperature and is a function of relative humidity of the environment.

The hygrothermal effects not only induce moisture expansion or contraction, but also change properties such as strength, modulus, impact and fatigue resistance. The absorption rate of the composite can be reduced drastically when diffusivity of the outer plies is reduced. In all composites, both the neat resin and composite exhibit similar two stage diffusion behavior, suggesting moisture diffusion in the composite is matrix dominated. The initial fast process may be related to the cure induced voids and the later slow process is due to the intrinsic diffusion in the matrix.
1.12 Advances in Epoxies, Bismaleimides and their co-cured Systems

A high performance thermoset is designed for use in highly demanding environments. The ideal high temperature polymeric system for use as a laminating resin for structural composites should have the following characteristics: easy tape and pre-preg preparation, good shelf life, acceptable tack and drape, acceptable quality control procedures, no evolution of volatiles during processing, retention of mechanical properties over the specific temperature-time ranges and environmental conditions and acceptable repair. Its performance criteria include processibility, fabrication procedure and physical properties. Various high performance oligomeric segments, such as imide, quinoline, quinoxaline, amide, amide-imide, ester, sulphone, ether-sulphone and ether-ketone have been synthesized from a number of different monomers to meet the performance requirements. As a result of the molecular weight reduction, the properties of a high performance thermoset become significantly dependent on the type of reactive functional groups. The high content of aromatic and heterocyclic segments in a thermosetting resin reduces the solubility and increases the melting point and melt viscosity. Hence, poor processibility is a common concern for high performance thermosetting resins. High melting temperature causes increase in rate of polymerization at high temperature. A wide processing window is desired to provide more room for fabrication design and performance control. A good account of the various thermoset systems have been given in section 1.5.2 of this chapter.

BMI constitute one class of high performance polymer. The research in the area of improved BMI resin systems is still ongoing. Among the addition polyimides, bismaleimides are the most important system currently used for advanced material applications due to its high performance to cost ratio. Various arylendiamines have been used for the preparation of BMIs to provide high stiffness and heat and thermal resistance after crosslinking. The properties of the BMI resin vary with synthetic
conditions. The introduction of rigid rings in the structure increases its melting point and narrows down its processing window which is of concern and unless solution processing is employed. Lin et al. have given a detailed picture of the different characteristics of several BMI resins.

The thermally cured bis (4-maleimidophenyl) methane has excellent mechanical properties and heat resistance. It has got high property retention at elevated temperatures, good electrical properties—dielectric strength, volume resistivity, dielectric constant and dissipation factor—and is useful as insulation material in radiation environments. However, low elongation to failure and poor toughness are concerns for structural applications. They suffer from high brittleness due to their high crosslinking densities. Toughness improvement of the cured BMI resin can provide the required fatigue resistance and prevent the fracture propagation. Several approaches have been developed to toughen or increase the impact resistance of the cured BMI resins. Many chemical concepts to modified BMI systems have been published. But only few combine all the desired properties required for use in advanced fiber composites.

1.12.1 Toughening of Bismaleimides

1.12.1.1 Changing the basic structure

The first approach towards the improvement of toughness and other physical properties is to change the basic structure of the backbone between two maleimide end groups. Generally, the aromatic linkages have higher rigidity than the aliphatic ones. This rigidity normally contributes to high melting point, glass transition temperature, thermo oxidative resistance, decomposition temperature and modulus of these polymeric materials. However, the processability and fracture resistance of aromatic BMI resins are drastically reduced by the increased molecular rigidity. The introduction of ether linkages to a BMI molecule increases the strength and flexibility of the cured resin. The undesired effect is the reduction in heat resistance related to the decreased glass transition temperature. The modification of BMI resins with
aromatic amines has been the most attractive and important approach for practical use. M/s Technochemie has synthesized poly-phenyl-group functionalised poly-arylene ether ketone high polymers and could demonstrate that these are excellent tougheners for BMIs.

1.12.1.2 Thermoplastic modification

The most interesting approach taken towards the toughening of BMI resin is the incorporation of a high modulus, high $T_g$ thermoplastic to form a semi interpenetrating net work after cross linking of the BMI resin. The introduction of engineering thermoplastic segments between two maleimide groups is an attractive way to achieve high heat resistance and improved toughness. Poly (arylene ether sulphones) and Poly (arylene ether ketones) are important industrial high temperature thermoplastics which possess excellent tensile properties and fractural toughness. Polybenzimidazole (PBI) is a high temperature thermoplastic polymer with $T_g$ of 435 °C has an excellent chemical resistance and does not melt or burn in air. The addition of PBI causes very little difference in the thermal and mechanical properties. But it helps in enhancing the toughness of the system. Polysulphone is reported to provide excellent improvement in toughness, but reduces heat resistance.

1.12.1.3 Chain Extensions

Two approaches have been generally adopted to change the performance of the BMI thermoset- the extension of an oligomer structure between two maleimido groups and the reaction of a basic BMI resin with modifiers.

Extension by bridging segment: The chain extension between two crosslinking sites is one of the ways for achieving improved toughness. The increase in molecular weight between two maleimide groups decreases the crosslink density. This technique generally provides improvement in toughness and strength but reduces the $T_g$, modulus and processability.
Extension by Michael addition: The modification of BMI resins with aromatic amines has been the most attractive and important approach for practical use. The performance of the cured BMI resin depends on the structure of the BMI resin and the extender, the ratio of the BMI to the diamine modifier and the curing conditions. Many diamines have been used to modify the properties of various BMI resins. The diamine terminated amide resins were used to modify bis-(4-maleimido diphenyl) methane to lower the crosslinking density and to increase the toughness\textsuperscript{299}. The same resin was chain extended with aliphatic amines\textsuperscript{300}. In general, the onset of curing occurs at a reduced temperature when the aliphatic amine is used as the chain extender. The heat of curing also decreases significantly by chain extension.

1.12.1.4 Co polymerisation

The simplest way for polymer modification is the use of two or more monomers in a thermosetting compound. High performance BMI resins are based on rigid aromatic structures and thus possess high melting point and a narrow processing window. An approach using eutectic mixture has been applied to improve the processibility and performance of the final thermoset. BMI resins are reacted with other high performance thermosetting compounds such as cyanate ester and bisbenzocyclobutene (BCB) resins. Mixtures of precursors of BMI resins with cyanate esters known as BT resins are important commercial products for high performance thermosets. BCB- BMI mixtures can be cured to high heat resistant thermosets through a rearrangement and Diels- Alder reaction at elevated temperatures. A Diels- Alder co-monomer for BMI is bis-(o-propenyl phenoxy) benzophenone available from M/s Technochrome under the trade name Compimide TM123. The BMI/ Compimide TM123 copolymer resin is attractive because of its extremely high temperature stability. It shows better thermal oxidative stability than all other commercially available BMI systems.
Of the several approaches reported for BMI matrix toughening, co-reaction with allyl phenol is now gaining wide spread acceptance. Alkenylphenyl compounds are used as co-reactants and tougheners for BMI resins. The most effective method developed so far for the toughness improvement of BMI resin is the incorporation of alkenylphenyl compounds such as allylphenyl and propenylphenyl derivatives as co-reactants and tougheners. The final crosslinked products provide improved toughness and heat and thermal resistance due to the formation of cyclic structures and high crosslinking density through Diels-Elder reaction, addition polymerisation and ene reaction. A technology using alkenyl phenols or alkenyl phenol ethers to react with BMIs to form processable pre-polymers was developed by Zaire et al. to improve the toughness and humidity resistance of BMI resins.

Zhongming Li et al. reported the synthesis of modified bismaleimido diphenyl methane (BDM), with high heat and hot / wet resistance and high mechanical properties by modifying the Bismaleimide resin using diallyl bisphenol A and diallyl p-phenylene diamine. A copolymer of bismaleimide and a new allyl compound containing diglycidyl ether of bisphenol A backbone, with improved tack and drape properties was prepared by Aijuan Gu et al. Takao Iijima et al. modified a three component bismaleimide resin system composed of 4, 4'-bismaleimido diphenyl methane (BDM), o, o'-diallyl bisphenol A (DABA) and o, o'-diethallyl bisphenol A (DBA), by blending it with poly(ether ketone ketone) like poly(phthaloyl diphenyl ether) (PPDE), poly(phthaloyl diphenyl ether-co - isophthaloyl diphenyl ether) (PPIDE) and poly(phthaloyl diphenyl ether-co - terephthaloyl diphenyl ether) (PPTDE), so that the new system gave an improvement in $K_c$ with no deterioration in flexural strength and modulus. Co-reactive curing agents act as a monomer in the polymerization process.

Yehai Yan et al. developed and characterized a resin system based on novolac and bismaleimide by curing the allylated novolac resin using BMI and using allyl phenyl ether as the diluent and the woven fabric composites based on this system showed very good flexural properties and high retention rates at 200 and
300°C. Kancheng Mai et al.\textsuperscript{308} attempted the stability studies on bismaleimide-o, o'-diallyl bisphenol A (BMI-DABA) blends modified using thermoplastic bisphenol A polysulphone (PSF), Polyether ketone (PEK-C) and polyether sulphone (PES-C) and found that the stability of the thermoplastic can be improved by the formation of semi-interpenetrating polymer networks (SIPN). An alkenylphenol compound is reactive in both maleimide and epoxy resins and a thermoset compound of these three resins have been developed providing high performance characteristics\textsuperscript{309}. The Michael addition adduct of BMI resins using excess diamines should produce amino end groups useful for reacting with other species, such as epoxy resins, unsaturated olefins and esters\textsuperscript{310}. The combination of rigid rod benzimidazole structure, Michael addition of BMI resin, and BMI-allylphenyl reactions has resulted in the preparation of molecular composites with simultaneous improvement of tensile strength, modulus and elongation. No phase separation was observed in these matrix systems\textsuperscript{311}.

Modified epoxies are used in many high performance applications. Dual photo and thermally initiated cationic polymerisation of epoxy monomers has been reported by Crivello et al.\textsuperscript{312}. These dual cure systems have potential application in adhesives, potting resins and composites. The flame retardance of epoxy resin can be improved by incorporating bromine in to the structure, but bromine increases the toxic smoke emission\textsuperscript{313}. Fluorine containing bismaleimides find application in multilayer printed circuit boards. The chemical nature of two fluorine containing bismaleimides investigated in Hitachi Research institute, Japan\textsuperscript{314} are given in Structure 6. Tyberg et al.\textsuperscript{318} carried out cure reaction of phenolic resin using epoxies to achieve an improved void-free system, as strong as epoxy net work, which retain the fire retardance of phenolics\textsuperscript{316}. Gonzalez et al.\textsuperscript{317} reported the synthesis and properties of an epoxy thermoset with reduced shrinkage and thermal degradability with increase in ratio of the co-monomers-diglycidyl ether of bisphenol A and 6, 6 dimethyl-(4, 8 dioxaaspiro [2.5] octane- 5,7 dione).
Blending of trifunctional solid epoxy with difunctional liquid epoxy was found to reduce its viscosity to a level suitable for the pre-pregging operation\textsuperscript{318}. The dry $T_g$ was found to be lowered from 310 to 302$^\circ$C by the addition of 25 weight % of the difunctional epoxy when cured using DDS. Blending with epoxy monomer can also be used to impart good processing quality to more interactable thermosetting resins such as polyimides or to reduce the intrinsic brittleness of bismaleimides\textsuperscript{319,320}. The lower crosslink density of the epoxy component will result in the lowering of the thermal performance of the polyimide.

The best known way to alter the properties of an epoxy resin, both in terms of its cure kinetics and the properties in the cured state, is by changing the nature of the chemical agent used for its polymerization. Patridge\textsuperscript{321} has studied the effect of DDS and dicy hardner on the chemoviscosity and $T_g$ of TGDDM epoxy. A mixture of these two hardners can also be used so that dicy acts as an accelerator for the DDS cure.

An alternate approach to epoxy cure, which aids the introduction of flexible crosslinks, is to use an isocyanate compound. This type of cure gives rise to both chain extension and crosslinking via stiff heterocyclic structures, the oxazolidone and isocyanurate ring respectively. Nevertheless the epoxy resin cured in this way combine toughness and high $T_g$ values.

A rapid development in the formulated high performance epoxies and bismaleimides based on the principle of dissolving a high temperature thermoplastic
or rubber additive in the monomer often with the aid of a common solvent. Good adhesion between the two phases can be obtained by sufficient grafting between the additive and the monomer. The polymeric modifiers such as functionalized thermoplastics\textsuperscript{322} yield sufficient toughness without much deterioration in high temperature performance.

Novel thermosetting resin with very high $T_g$ based on bismaleimide and allylated Novolac (BMAN) has been reported by Yuan Yao et al\textsuperscript{323}. BMAN -15 resin with high allylation degree and low BMI proportion was found to give high performance composite matrix with high strength and modulus retention at 350°C. The thermosetting resin based on BMI and allyl compounds such as bisphenol A diallyl ether\textsuperscript{324} allylated novolac \textsuperscript{325,326} and allylated xylok showed $T_g$s up to 350°C. Diallyl bisphenol A novolac was cured with BMI to get high temperature resistant matrix which retained its lap shear strength up to 200°C\textsuperscript{327}. Bindu et al\textsuperscript{328} reported a co-cured matrix composed of novolacs derived from maleimido phenol and phenol-allyl phenol. A dual cure maleimido phenol- epoxy system exhibited excellent thermo-adhesion profile in contrast to novolac cured epoxy resin\textsuperscript{329}.

**Scope and Objective**

The increasing need of materials for high performance, high temperature resistant aerospace structural composite applications pose great demand for the development of speciality thermoset matrix resin systems which can outdo the most commonly used epoxy resin in terms of thermal capabilities, toughness and moisture resistance, and bismaleimide in terms of toughness and mechanical properties. Epoxy-based laminates largely find applications as aerospace structural components. The most important property that has made epoxy composite laminate as a competent aerospace material is its ease of processing, superior heat ageing, lower laminating pressures, freedom from condensation volatiles, less complicated cure cycles and superior flexural strength. Epoxy composites find numerous other applications in marine, construction, tooling, electrical and sports goods. The use of epoxy
composites is increasing rapidly in commercial and military aircrafts, light compact aircrafts, helicopters, launch vehicles, satellites and spacecrafts. The BMI emerged as an alternative matrix system with enhanced thermal capability and replaced the epoxies to some extent in areas where their thermo-mechanical profile is of advantage. The inherent brittleness of the system, poor impact resistance and high cure cycles were major concern for their wide spread applications. Blending of BMI with allylated derivatives could solve these issues to a great extent resulting in the emergence of commercial products based on BMI and diallyl bisphenol adduct. In many cases a compromise matrix system, with tailored properties can be derived by way of blending one or more polymer system to form polymer blends, alloys or IPNs depending on the physical and chemical interactions among the components and the resultant morphological features. A control of the parameters can impart desirable properties to the resultant blends.

This thesis concerns the research efforts to derive a blend of epoxy resin and bismaleimide. There are limited literature on the blends of epoxies and BMI. Epoxy – phenol systems have been reported as low T_g, tough, hydrophobic matrices. Allyl phenol- BMI systems have a success story as high temperature resistant tough matrices. It was of interest to derive a combination of epoxy- phenol and allyl phenol-BMI through a multi reaction ternary system constituted by epoxy- allyl phenol- BMI. The literature survey on matrix resin and composites and presented in chapter 1 reveals that epoxy-allylphenol- BMI systems have been little addressed in open literature.

The effect of modification of epoxy- phenol system by co-reacting it with bismaleimide and the evaluation of the influence of BMI concentration on the thermo-physical, mechanical and rheological properties of the ternary blend and their fabric reinforced composites form the major objective of the thesis. Another objective of the study is to examine the performance and properties of the ternary reactive polymer blend of epoxy- diallyl bisphenol-BMI system with the structural variations of the epoxy and bismaleimide components. The thesis concerns the properties of the composites
with different reinforcements, fillers, fiber orientation etc. Typical applications of the
ternary matrices have also been explored. The gist of the research work carried out in
this perspective and presented in the thesis is as follows.

The first chapter gives a summary of the literature survey carried out on
polymer matrix composites with special emphasis on matrix resins, reinforcements,
interphase, composite fabrication and characterization. It also throws light on the
recent trends in matrices, reinforcements and composites with special emphasis on
the epoxy-phenol-BMI constituted polymer matrix composites.

The second chapter gives a brief description of the sources and properties of
the materials used for the study, techniques used for their characterisation,
optimisation of the processing condition of the matrix resin and composites, and the
methods used for their performance evaluation.

Prelude to the evaluation of the properties of the ternary system, the
properties of the precursor epoxy-diallyl bisphenol was studied. The third chapter
gives an account of the cure kinetics of the novolac epoxy-diallyl bisphenol system.
Studies using dynamic DSC experiments revealed the influence of catalyst
concentration on the epoxy-phenol cure reaction, which enabled the selection of
optimum catalyst concentration and cure conditions.

Studies on the mechanical characterization of novolac epoxy-diallyl bisphenol
system are dealt with in chapter four. The effect of varying the molar ratio of epoxy
resin and diallyl bisphenol on their cure behavior, mechanical and thermo-mechanical
properties was investigated. The influence of the extent of allyl group curing on the
properties of the epoxy-phenol matrix system and its glass composite was also
evaluated.

Though the epoxy-diallyl bisphenol system provided a matrix with good
mechanical properties, it was inferior in respect of its high temperature performance.
To address this, the matrix was co-reacted with BMI and the resultant resin was
characterized for its cure behavior, thermal stability and composite properties. Thus,
the fifth chapter focuses on the studies on the modification of stoichiometric blend
(1:1) of the epoxy-diallyl bisphenol matrix system by co-reaction with BMI to form an epoxy-phenolic-bismaleimide (EPB) ternary blend. The effect of BMI concentration on the rheological, mechanical and thermo-physical properties of the ternary blend was examined. The system was evaluated at composite level using glass fabric as reinforcement composites. The matrix composition with optimum concentration of BMI was chosen for further studies.

The sixth chapter mainly concentrates on the evaluation of the effect of different types of reinforcements on the performance of the epoxy-diallyl bisphenol-bismaleimide (EPB) composite. Comparative evaluation of the performance of the fabric reinforced EPB composites with different reinforcements such as glass and carbon fabrics of different fiber orientations and stacking sequences was carried out by determining their tensile, compressive, flexural and interfacial / inter-laminar properties and fracture toughness. Their moisture absorption characteristics, coefficient of linear expansion, constituent content and surface morphology were also compared. To illustrate the utility of the new matrix system in diverse compositions, other than laminates, the resin was evaluated as a matrix for the processing of syntactic foam composites. Syntactic foam composites with varying concentrations of hollow glass microballoon were characterized for their physical, thermal and mechanical properties and the performance variation of the foam composite with microballoon type and concentration was examined. The use of blended microballoon fillers on the properties of the syntactic foam composite was also studied. The utility of the matrix as high temperature adhesive was also explored.

The influence of the structural variations of both the epoxy resin and bismaleimide on the thermal, physical and mechanical properties of the ternary blend was examined and presented in the seventh chapter. EPB compositions were prepared using bismaleimide, diallyl bisphenol-A and three different epoxy resin systems viz. Novolac epoxy, LY-556 and Triepoxy, having different physical and molecular characteristics. The effect of structural variations of BMI resin on the performance of the EPB system was studied using EPB compositions containing three
different types of bismaleimides in combination with the novolac epoxy and diallyl bisphenol A. The variation in high temperature performance of these EPB systems with nature of the bismaleimide was studied by determining their strength retention at different climatic temperatures.

The overall conclusions from the above studies are summarized in chapter eight and the prospects for future work is also indicated.

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