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Review

Engineering Matrix Materials for Composites: Their Variety, Scope and Applications

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Abstract: Matrices are essentially binders for the reinforcements of composite material. Appropriate selection of fine chemicals is vital for the creation of desired matrices for generating composite materials. In fact, matrix is a subclass of a composite material. Matrices are generally of four kinds such as (i) polymer (hard as well as flexible), (ii) metal, (iii) ceramic, and (iv) cement. Each type of these subclasses of the matrix is discussed with a brief of their pros and cons. Polymer matrices are generally organic based whereas metal or ceramic matrices are inorganic in nature. Hard plastic matrix as well as flexible rubbery matrix are also discussed in the light of their applications. Carbon as matrix material for hi-tech C/C (carbon/carbon) composite materials is also stated. Cement is a special kind of inorganic matrix material because of its very special solidification mechanism during the formation of concrete composite; and it carries bulk values in the engineering area. For higher temperatures, carbon, ceramic or metal matrix materials are useful. Ceramics possess various conductivities, but they have poor tensile strength despite their ability to afford high-temperature products. Generally lightweight metals such as titanium, aluminum, magnesium, and intermetallics such as Ni-aluminide and Ti-aluminide are used; and the operating temperature can be extended to 2000 °C. The advantages of metal matrices are higher strength and ductility than those of polymers. Carbon matrix based carbon/carbon (C/C) composites can be used even at the temperature of ~3000 °C, but are preferred only in critical engineering areas of applications. Different types of matrix material may also prove to be efficacious constituent item for innovative design of integrated structure in the ever challenging area of Blast and penetration resistant materials (BPRM).

***Keywords*:** Metal matrix composite (MMC), hard matrix, flexible matrix, carbon-carbon, ceramic matrix

1. Introduction

Engineers need to design materials to meet the requirements of specifications and deliver the products within a time schedule without disobeying the protocols of the contemporary environmental regulations.[1,2] In order to fulfil such need and honor the commitment, engineers evolved the concept of composite materials.

Chemicals are essential ingredients to develop matrix materials for composite system. Chemical and material engineering virtually are two sides of the same coin as they are involved in inventing, designing and maintaining a variety of material system meant for the construction of engineering structures. Engineers are also responsible for

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adhering to specifications for budget and timeline through innovative work, where interdisciplinary knowledge plays significant role. This article has touched upon essential points as well as latest material information to help engineering professionals to view across the characteristics of matrices and help fertilize fresh ideas for new innovation of matrix materials intended for the development of composite materials with competitive edge. Thanks to the scientific research, there are numerous matrix materials constantly being evolved, but all such matrix materials are not useful in meeting the engineers' choice for practical reason; only some family of matrix materials which can largely fulfill the basic requirements of engineers are highlighted here as engineering matrix materials. Illustratively, modern design of blast protective *Armour material systems* are based on the combination of different classes of composite material system involving items of ceramic, metal and polymer in an integrated structural framework. Like polymers, metals and ceramics require similar chemical process for use in the generation of composite materials. Organic-Inorganic-Combination together as matrix material (Polymer Cement) discussed at the end is an example of matrix material system that are very much useful for application in the field of innovative civil engineering.

Metals and alloys can only be useful if properly selected and processed.[3] Illustratively there are certain elements, such as *Mo*, *Mn*, Ta, *V*, etc., are judiciously added in several high temperature alloys and processed to improve their mechanical properties.[3] However, such elements can have a deleterious oxidation effect to reduce mechanical properties. For example, the presence of Mn in most of the Fe-base alloys, has no pronounced effect on the oxidation rate. On the other hand, *Mo* and *V*, if present in large quantities can act adversely with the formation of low-melting oxides (MoO_2 and V_2O_5) and can lead to catastrophic oxidation. The effect of certain tramp elements like boron has adverse effect on scale adherence and spallation resistance; however, boron, is also useful to strengthening the superalloys; so judicious addition and processing matter a lot to adjust the matrix properties.[4]

International Union of Pure and Applied Chemistry (IUPAC) defines Composite materials as a multicomponent material consisting of multiple, different (non-gaseous) phase domains in which at least one type of phase domain is a continuous phase; and nanocomposite is a composite in which at least one of the phase domains has at least one dimension of the order of nanometres.[3] In composite material, the discontinuous phase(s) are embedded in a continuous phase where the continuous phase is known as matrix. The matrix is homogeneous monolithic in nature and is the continuous phase in which the reinforcements are embedded and/or dispersed therein. The discontinuous phase is known as reinforcement. This article discusses the role and their influence on the mechanical, thermal and allied properties of different classes of matrix materials in a systematic manner besides their scope, service range and applications to suit the requirements.

1.1 *Role of matrices*

Generally matrix is a relatively ductile material which holds the reinforcements of different dimensions and shapes (fibre, particles, platelets, whiskers, etc) in such a manner that it functions together;[6] however, in case of ceramic matrix composite (CMC), brittleness of ceramic matrix is reduced in presence of reinforcements.[7] It envelops the reinforcements ensuring a continuous medium for binding the reinforcements together and consolidates them into a solid composite material; and it protects the reinforcements from abrasion, physical and environmental damage. Ideally matrices must act in harmony with the reinforcement to avoid failure as much as possible. Matrices maintain the reinforcements separated; and they reduce the chance of cracking by redistributing the load equally among all fibers and particles, even though only a small proportion of an applied load is sustained by the matrix phase as the elastic modulus of the matrix is less than that of reinforcements. The ability of engineering composite is to withstand against heat and mechanical load or to conduct heat or electricity; and that depends largely on the matrix properties since this is the continuous phase.[6,8]

Matrices have special role to play depending upon the type of applications. For example, the use of polymer network as matrix material to make polymer-bonded explosive (PBX) is a very special area of chemical engineering. Matrix-mediated crystallization of Explosive materials in crosslinked polymer network can provide reduced sensitivity to external mechanical stimuli such as impact or friction and the enhanced processability in macroscopic shaping.[9] If the polymer matrix is an elastomer (rubbery material), it tends to absorb shocks, making the PBX very insensitive to accidental detonation, and thus ideal for insensitive munitions. However, such polymers can produce PBX that should be tough enough so that it can ensure a precise engineering shape even under working stress. Special elastomers are used with more mechanically sensitive explosives like hydroxyl terminated polybutadiene (HTPB). The elasticity of the matrix lowers sensitivity of the bulk material to shock and friction; their T_g (glass transition temp.) is made to be below the lower boundary of the temperature working range (typically below -55 °C). Rubbers like HTPB (hydroxyl terminated polybutadiene), silicone rubbers and thermoplastic polyurethanes are used for these applications.[10]

Recently, polymer matrices are used as host material for various dopant guest molecules to prepare bio-inspired composite materials and evaluated their magnetic and optical properties.[11-13]

1.2 *Matrix and their influence on the properties*

Figure 1 represents typical qualitative comparative trends in the properties of the constituent materials (matrix and fibre reinforcement) vis-à-vis fibre reinforced composite material. The composite may show linear (a) or non-linear (b) stress-strain pattern depending of the hardness of the matrix.

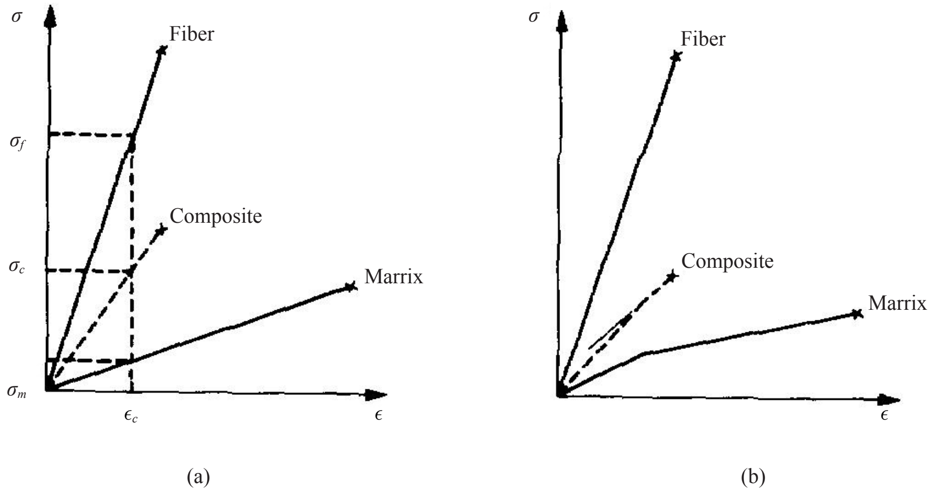


Figure 1. Qualitative comparative stress-strain pattern of composite material.

The matrix separates the fibers and, by dint of its relative softness and plasticity, prevents the propagation of brittle cracks from fiber to fiber, else could lead to catastrophic failure; in other words, the matrix phase serves as a barrier to crack propagation; in case a fibre is broken or fibre is discontinuous, then the matrix material helps to redistribute the load in the vicinity of the broken site. Matrix material enhances the properties; particularly the transverse strength of a lamina and for that matter impact resistance of the final structural product.[6,8]

Adequate bonding between the matrix and the reinforcement is achieved through proper coupling agents to maximize the stress transmittance from the weak matrix to the strong fibers. Coupling agents play important role for such bonding at the interface between matrix resin and reinforcement.

1.3 *Classification of matrices*

Materials are nothing but a judicious combination of chemicals. Matrices are subclass of materials;[14,15] and there are many ways to categorize materials; however, matrices are generally of four kinds ‘such as stated earlier (i) polymer, (ii) metal, (iii) ceramic and (iv) cement (Figure 2). In this chapter all these four kinds of matrices are summarized. Metal and ceramic matrices are inorganic in nature.

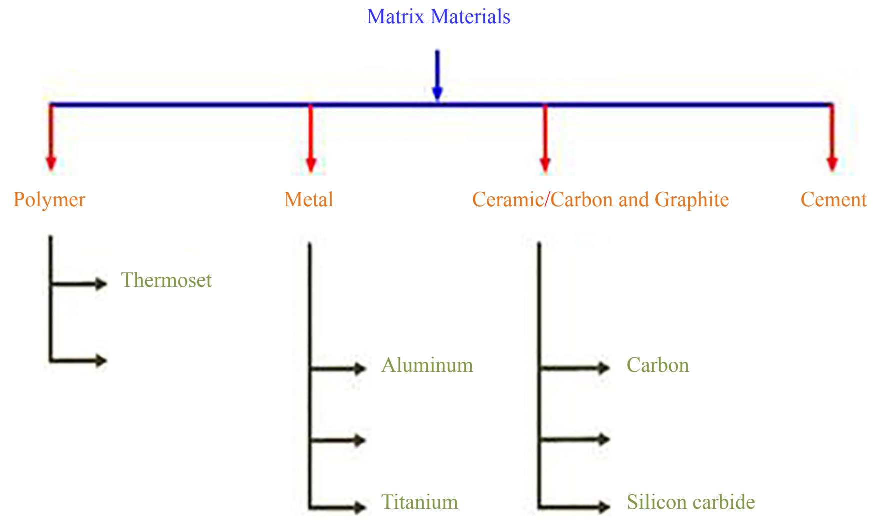


Figure 2. Major categories of matrix material; even though cement belongs to some kind of ceramics but cement acquires a special status because it is used in bulk quantities in all civil engineering construction.[14]

1.4 *Service temperature for matrices*

PEEK (Polyether ether ketone) has the ability to maintain stiffness at high temperatures and is suitable for continuous use at temperatures up to 170 °C. Nickel and steel are sought after materials for high temperature applications. Ultra-high-temperature ceramics (UHTCs) are a type of refractory ceramics that are stable at extreme temperatures, exceeding 2000 °C (Figure 3). The said useful temperature range is a critical parameter as matrix determines the practical use temperature for the composite material.[14]

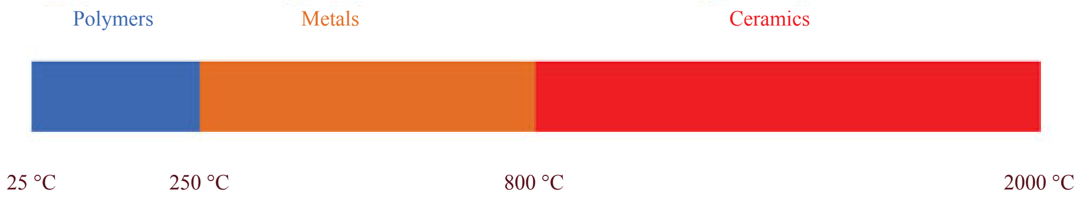


Figure 3. The useful temperature range of different matrices

2. Polymers

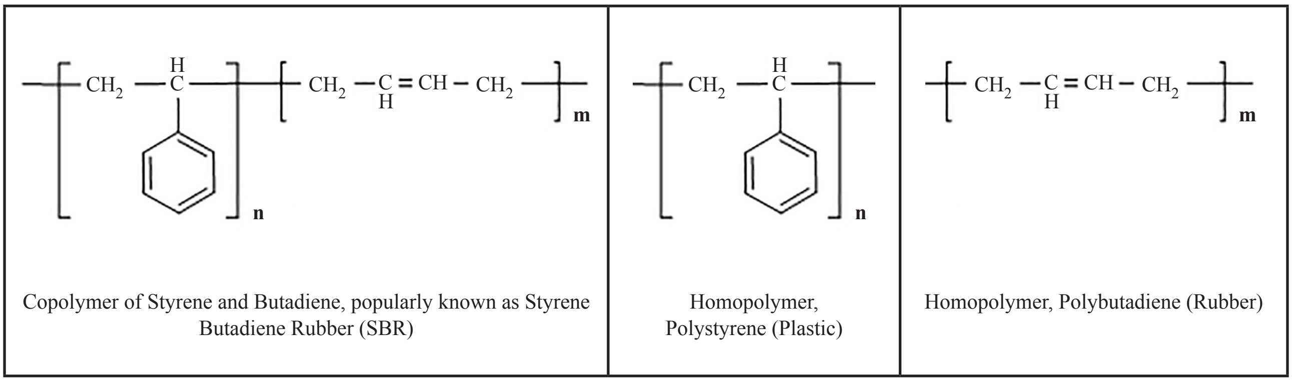
Polymers are often interchangeably referred as resins in the composite industries. Polymers are composed of long chain-like molecules derived from the combination of many ‘*mer*’s where *mer* is nothing but the simple chemical repeating units, and is often popularly known as ‘monomer’.[16-18] In a more simple way to consider that a polymer is nothing but a substance consisting of a large number of atoms bonded together in a long chain. Man-made polymers are generally called ‘synthetic polymers or synthetic resins’. Polymeric matrices are used in the engineering field because they are light weight and easy to fabricate. Polymers or resins are selected in accordance with the requirements for the design of a composite product.

Modern polymer synthesis techniques developed over the years permit considerable control over various structural possibilities in the form of its linearity in the chain, extent of branching, crosslinking in the network and its various isomeric forms. Polymer scientists are continuously searching for new materials that can be easily and economically synthesized by polymerizing monomer or by copolymerizing different kinds of monomers so as to be amenable to easy processability to fabricate engineering products with desired properties. The monomer chemicals are selected as per the requirement of properties to be generated in the polymer matrix.

Characteristics of the polymer or copolymer depend on the chemical composition of polymerizing monomer; homopolymers are derived from the polymerization of one type of monomer whereas copolymers are produced from the copolymerization involving more than one type of monomer (Figure 4).[16,17]

The physical characteristics of a polymer depend on various factors like molecular structure, its configuration, conformation, shape of the molecular chain and even molecular weight. It is important to note that even a polymer with the given chemical structure can differ in their physical structural characteristics either in the form of rubber, plastic or fibre. Such physical characteristic state for exhibition of their properties depends upon their molecular weight. Generally the order of molecular weight is $MW_{rubber} > MW_{Plastic} > MW_{fibre}$. For a given molecular structure, the polymer with the higher molecular weight exhibits rubbery characteristics. In fact, rubber is a class of polymer whose molecular weight is very high on the order of 10^6 D. The rubber like state is characterized by vibrational motion of units (tortional vibrations), as a result of which the polymer chain becomes flexible at ambient temperature; and the viscofluid state is characterized by mobility of the entire macromolecule as a whole.[16,17] The glassy state is characterized by vibrational motion of the atoms constituting the chain about an equilibrium position.

Polymer matrices are lighter than other category of matrices; so they are selected where the requirement of specific strength is high. It may be noted that the matrices of choice are polymers if the items to be used does not go beyond 250°. For example, artificial skin, used for severe burn victims, is a special form of composite materials that contains a polymer matrix.


Copolymer of Styrene and Butadiene, popularly known as Styrene Butadiene Rubber (SBR)

Homopolymer, Polystyrene (Plastic)

Homopolymer, Polybutadiene (Rubber)

Figure 4. Examples of copolymer (e.g., SBR, a rubber) and homopolymer (e.g., polystyrene, a plastic; polybutadiene, a rubber).

2.1 *Characteristics of polymers*

Polymer matrices are lighter than other category of matrix materials like metals and ceramics; so afford high specific strength. The mechanical characteristics of polymers, for the most part, are highly sensitive to strain rate or rate of deformation, and the chemical nature of the environment (Figure 5). Polymers are in many ways, mechanically dissimilar to metals; e.g., the modulus of highly elastic polymeric materials may be as low as 7 MPa, but may run as high as 4 GPa for some very stiff polymers; modulus of metals are much higher (48 and 410 GPa). Maximum TS of polymers are ~100 MPa but for some metal alloys 4100 MPa. Metals rarely elongate plastically beyond 100% but highly elastic polymers may elongate more than 1000%.[8,17]

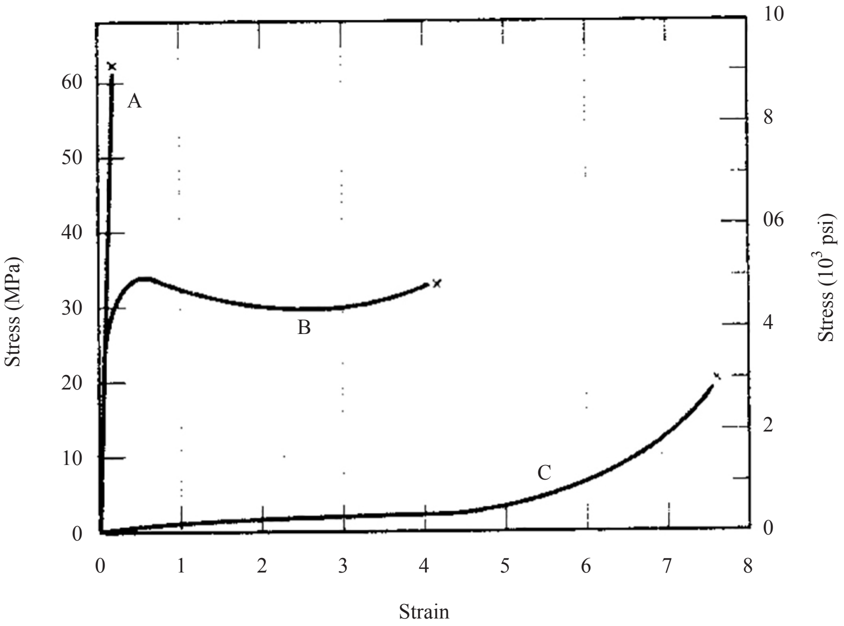


Figure 5. Typical stress-strain pattern for different types of polymer system (A) brittle polymer, (B) plastic polymer, and (C) rubber or highly elastic elastomeric polymers.[19]

2.2 *Types of polymer*

Polymers are broadly classified into two categories-(i) 'thermosetting' polymers; and (ii) 'thermoplastic'.[16,17]

2.2.1 *Thermosets*

They are formed from *in situ* non-reversible reactions to network structure infusible mass. The important classes of thermosetting resin are: (i) Unsaturated polyesters (ii) Epoxy resin (iii) Vinyl ester resin (iv) Dially phthalate (DAP) based polyester resin (v) Phenolic resin (vi) Cyanate ester resin[20] (vii) Polyimide resin.

Thermosets are prevalently used in industry as they are generally easier to process using compression moulding, autoclave, extrusion etc; and are more chemically resistant and generally less expensive than thermoplastics. However, they have toxic in their uncured state and are susceptible to cracking if over-cured.

2.2.2 *Thermoplastic matrices*

They are like metals, get soften on application of heat and eventually melt reversibly, thus can be processed repeatedly using different moulding techniques such as injection moulding, extrusion, blow moulding, rotational moulding etc. Major types of thermoplastics include (i) vinyl polymers like for example, polymethylmethacrylate (PMMA) (ii) condensation polymers like for example, polyether ether ketone (PEEK).[16-18]

2.2.2.1 *Major types of Thermosetting resin matrices*

2.2.2.2 *Polyester matrix resin*

Unsaturated polyester (UPE) matrix resins are also called "polyesters" in the industry. Polyester matrix resins are formed by the reaction of the glycol or polyol with a dibasic carboxylic acid. Polyester resins are the most widely used general purpose resin particularly suitable for glass fibre, and they can afford to provide a balance of properties in respect of mechanical, chemical, electrical, dimensional stability, ease of processing and lower cost. Polyesters withstand against many chemicals but not against alkaline substrate. They can be used to some moderate temperatures

(~80 °C) but not at high temperatures.[16,17]

2.2.2.3 *Epoxy matrix resin*

Epoxy resins are synthesised from the reaction of a dihydric phenol like bisphenol-A with excess epichlorohydrin in an alkaline medium.[21-23] Epoxy resins are used primarily for the fabrication of high performance composites with superior mechanical properties. Characteristically, they exhibit low cure shrinkage on curing thus has low internal stress, maintain better dimensional stability and adhesion properties to substrates. Epoxies are resistant to many corrosive liquids and environments. High performance epoxy matrices are generally achieved by multifunctional epoxies cured with multifunctional amines or organic acids or anhydrides. Epoxies are compatible with most composites manufacturing processes, particularly vacuum-bag molding, autoclave molding, pressure bag molding, compression molding, and hand lay-up. Epoxy resins are widely used in filament-wound composites and are suitable for moulding prepregs.[23-25]

The large family of epoxy resins represents some of the highest performance resins to ensure balanced properties in the composite product. Prepregs of epoxies have limited shelf life.[21,23-27] Cure time of epoxy systems is often relatively longer depending upon curing temperature. The matrix resin may be characterized according to the curing temperature in a DSC thermogram; and the logical approach for the selection of processing temperature and evaluation of curing exotherm of epoxy system based on the diglycidyl ether of bisphenol-A and different cyanoethylated aliphatic amines synthesized are reported.[23] The limitation of epoxies is that they do not show excellence in uv resistance.

2.2.2.4 *DAP based matrix resin-an improved version of unsaturated polyesters matrix resin*

Most polyester system contains liquid styrene as reactive vinyl monomer with its appreciable vapour pressure even at room temperature causing environmental problem. Moreover, its curing leads to very high shrinkage which causes lowering of properties for unsaturated polyester matrix resin. Thus, an improved version of polyester are evolved by using diallyl phthalate (DAP) (Figure 6) monomer in place of styrene in the unsaturated polyester resin formulations which can afford to give unexpectedly high level of mechanical properties in the composite.[28-30]

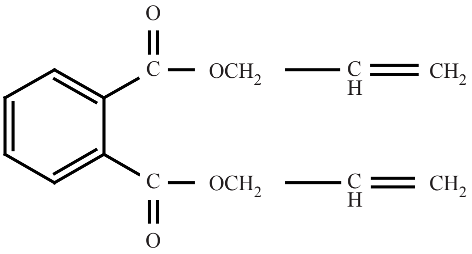


Figure 6. Diallyl phthalate (DAP) monomer or bis(prop-2-enyl) benzene-1,2-dicarboxylate

Most diallyl phthalate compounds are sold under military specification; and DAP is a commonly available product that is used in critical electrical and electronic applications requiring high reliability under long-term adverse environmental conditions.[28-30] Diallyl phthalate, popularly known by the name DAP can afford to provide excellent balance of physical and chemical properties of the material. Its vapour pressure is low unlike styrene thus contributing less environmental pollutions, thus is important to support green technology. Post cured shrinkage is the lowest of the commonly available monomers.

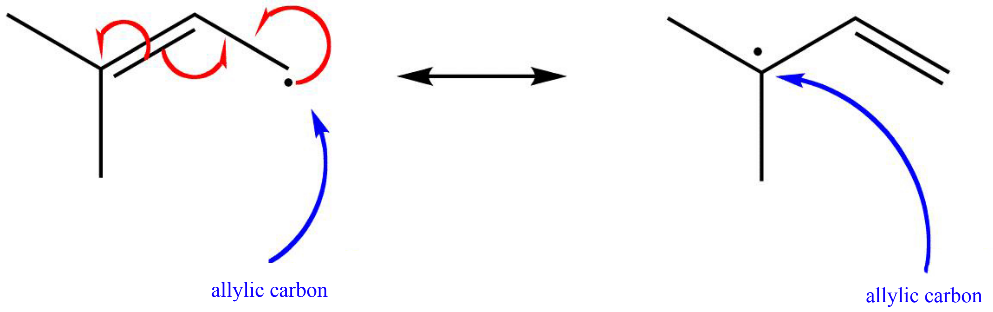


Figure 7. Allylic carbon is indirectly connected to double bond

In styrene reactive monomer contains vinyl carbon. In contrast to vinylic carbon, allylic carbon is indirectly connected to a double bond (Figure 7). A vinyl carbocation has a positive charge on the same carbon as the double bond. This is very unstable and ranks under a methyl carbocation in stability. Exothermic heat of curing of DAP is low compared to other monomers, causing less chance of cracking in the cured product[31], its ester linkages in the matrix make them more resistant against moisture.[31] Prepreg handleability during processing is excellent and it has good tack and drapability. Environmental hazards are minimal because of the absence of volatile monomers. Such advantages enabled DAP for certain special applications where epoxies are traditionally being used.

2.2.2.5 *Vinyl ester (VE) matrix resins*

VE is derived from the esterification of an epoxy resin and an unsaturated monocarboxylic acid like acrylic and/or methacrylic acids as shown in Figure 8 below.[32] It may be considered as a polyester resin strengthened with epoxy molecules in the backbone of the molecular chain; its cure is accomplished by vinyl polymerization in the presence or absence of other vinyl monomers like styrene etc. in UPE. Characteristically, VE resins stand between polyester and epoxy resins (Figure 9).

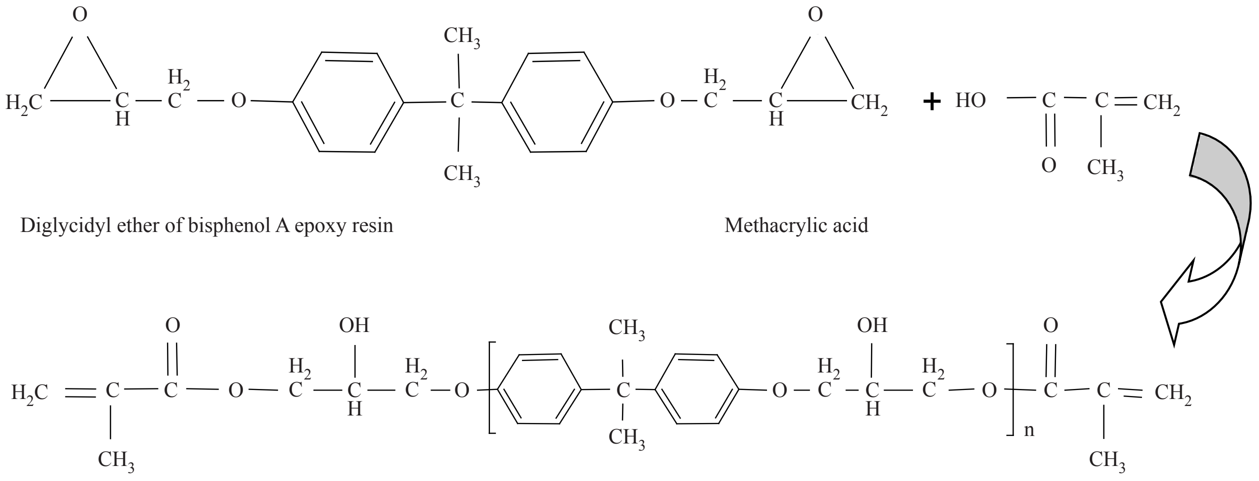


Figure 8. Steps of synthesis of a vinylester resin from diglycidylether of bisphenol-A (DGEBA) epoxide and a typical vinyl monomer like methacrylic acid.

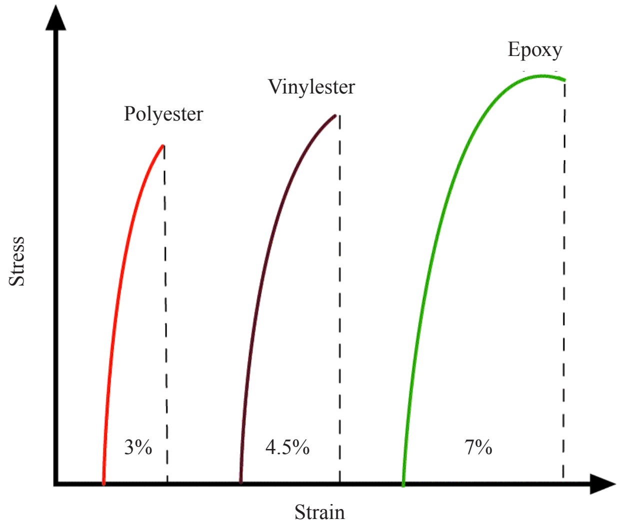


Figure 9. A comparative schematic view of stress-strain pattern of epoxy, vinyl ester and polyester resins where features of vinylester generally remains in between those of epoxy and polyester matrix resins.

2.2.2.6 *Interpenetrating Polymer Network (IPN)*

IPNs derived from the blend of two or more than two different kinds of thermoset resins; for example, unsaturated Polyester and Epoxy resins where crosslinking mechanism of one of them is different from that of the other; illustratively, epoxy is crosslinked by mechanism of condensation polymerization whereas unsaturated polyester resin undergoes crosslinking through the mechanism of free radical polymerization.[33] This interpenetration of network of the thermosetting resins' blend could improve the mechanical properties of the cured matrix than any of the individual thermosetting resin.

2.2.2.7 *Cyanate ester (CE) matrix resin*

Cyanate ester resins are relatively a new class of thermosetting matrix resin where its cyanate group (Figure 10) is the reactive group. The cyanate monomer is manufactured from the reaction of halogenated cyanide with phenolic compounds in the alkaline condition.[20]

$$\mathrm{ArOH + XCN = ArOCN + HX}$$

where "X" can be I, Br or Cl; and ArOH" can be single-phenols, aliphatic hydroxy compounds or polyphenols.

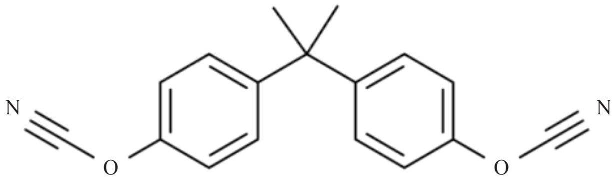


Figure 10. Two cyanate groups (-OCN) attached to an aromatic ring; the general chemical structure of bisphenol-A cyanate ester used in cyanate resin.

During curing the cyanate esters can undergo cyclotrimerization at high temperature (> 300 °C) through the cyanato functions; and essentially no volatile by-product is formed during curing reaction. More importantly, many cyanate esters do not shrink during cure.[20]

Cyanate esters constitute a high-temperature resin family traditionally associated with space applications because of their good thermal stability, low dielectric constant and extremely low moisture uptake compared with other resins of their class. Cyanate ester is known for its built-in toughness, micro-crack resistance and ease of processing. This class of resin has wide scope of applications starting from the area of microelectronics to aerospace composites.[20]

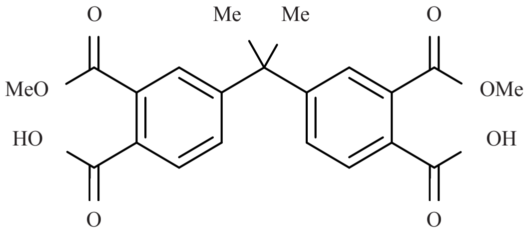
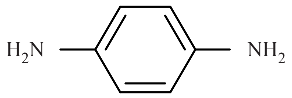
2.2.2.8 *Polyimide resins*

Polyimide Resins are a class of high temperature resin and are often known by the name PMR (*Polymerization of Monomer Reactants)* resin which is preferred to epoxy resin for fabrication of composite materials.[34]

In the PMR approach, the reinforcing fibers are impregnated with a solution containing a mixture of monomers dissolved in a low b.p. (boiling point) alkyl alcohol solvent. Such monomers remain dormant at room temperature, but become reactive *in situ* at elevated temperatures to form a thermo-oxidatively stable polyimide matrix. These addition-type polyimides (Table 1) are highly processable and can be processed by compression or by autoclave[22,34] moulding technique to realize high temperature polymer matrix composites.[22,34]

The first generation PMR material is designated as PMR-15 where 15 at the end signify molecular weight of PMR as 1,500. Condensation type aryl polyimides are generally synthesized by reacting aryl diamines with aromatic dianhydrides, aromatic tetracarboxylic acids or dialkyl esters of aromatic tetracarboxylic acids. PMR matrices employing BTDE are referred to as "first generation" materials. Further developments led to the second generation polyimide i.e., PMR II and other such resins.

Table 1. Typical chemicals used for the synthesis PMR resins.

Chemical Structure	Name of Chemicals	Acronym
	Dimethylester of 3,3',4,4'-(benzphenonetetracarboxylic acid)	BTDE
	4,4'-methylenedianiline	MDA

During composites fabrication, volatilization of the solvent and condensation by-products results in high void content in the composites to cause inferior mechanical properties and thermo-oxidative stability. To overcome the problem of volatilization, polyimides were developed through an addition reaction where low molecular weight amide-acid prepolymers are synthesised whose chain terminals were end-capped with norbornenyl groups. Such norbornenyl groups undergoes addition polymerization at elevated temperatures (275°-350 °C) without the evolution of volatiles making it possible to reduce void content in the composites. Thermoset polyimide matrix resins with high melt processability for high-temperature composites are prepared from the diethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) and the aromatic diamine mixtures consisting of *p*-phenylenediamine (*p*-PDA) and 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (6FBAB) with the monoethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) as the molecular-weight-controlling and reactive endcapping agent.[34,35]

2.2.2.8.1 *Polybismaleimides or Bismaleimides (BMI)*

Polybismaleimides (BMI) are high performance thermosetting addition-type polyimides; and they are known for their high-strength and high-temperature performance which lies between lower temperature resistant epoxy systems and very high temperature-resistant polyimides.[34-39]

A typical synthetic scheme for bismaleimide (BMI) indicating maleic anhydride reacts with phenylene diamine to form BMI as shown in the following (Figure 11).

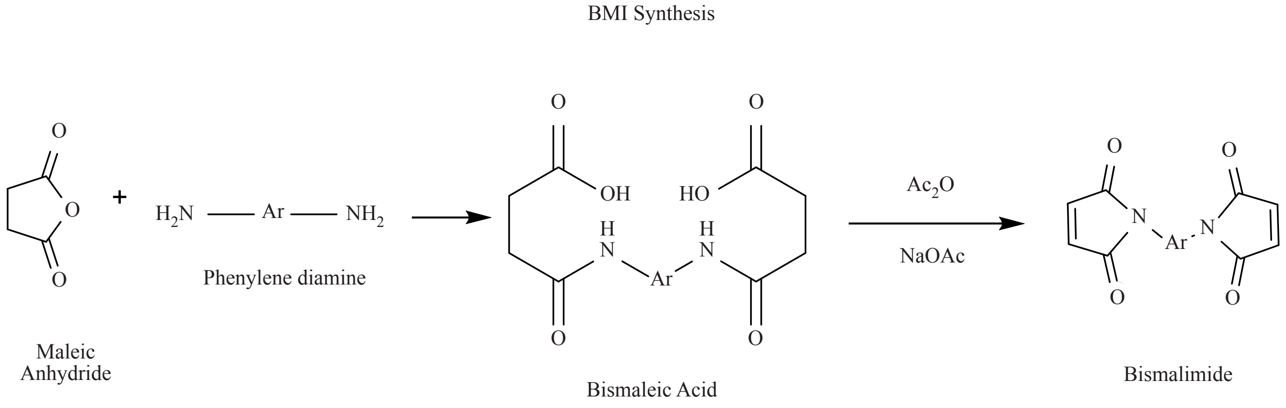


Figure 11. Reaction steps for the formation of bismaleimide resin

BMI is the acronym of bismaleimide family of compounds, which are among the most important resins employed in the aerospace/aircraft, nuclear and electrics/electronics industries because of their high thermal and thermo-oxidative stability, tractability, good retention of the mechanical properties even after long aging times at 250 °C, excellent radiation, fire, and chemical resistance, except having corrosion resistance, good water resistance and relatively low cost. BMI resins are primarily used in the manufacture of aircraft composite structures which can withstand at temperatures around 250 °C dry/230 °C wet during operation; such items are engine inlets, high-speed aircraft flight surfaces.[34-38] They are also of great interest because of their easy processability by resin transfer molding, without the generation of volatile by-products.[34-39] The areas of application for BMI resins are reinforced composites for printed circuit boards (with glass fabrics) and structural laminates.

Bismaleimide are generally sold as low molecular weight dry powder resins containing imide structures already in the monomer form. BMI resins can be polymerized by many different polyaddition reactions with themselves as well as with other co-monomers (Figure 12). The reactivity of the bismaleimide compounds is influenced by chemical nature of the bridge unit between the maleimide rings.

The reactivity of bismaleimides is determined by the ability of their double bond to add monomers bearing an active hydrogen atom, to act as a dienophyle in Alder reactions[34,36,39], and to enter reactions of radical and anionic homopolymerization and copolymerization with various monomers containing both unsaturated (vinyl, allyl) and saturated (propyl) bonds or with cyclic compounds (cyclobutane derivatives or heterocycles).

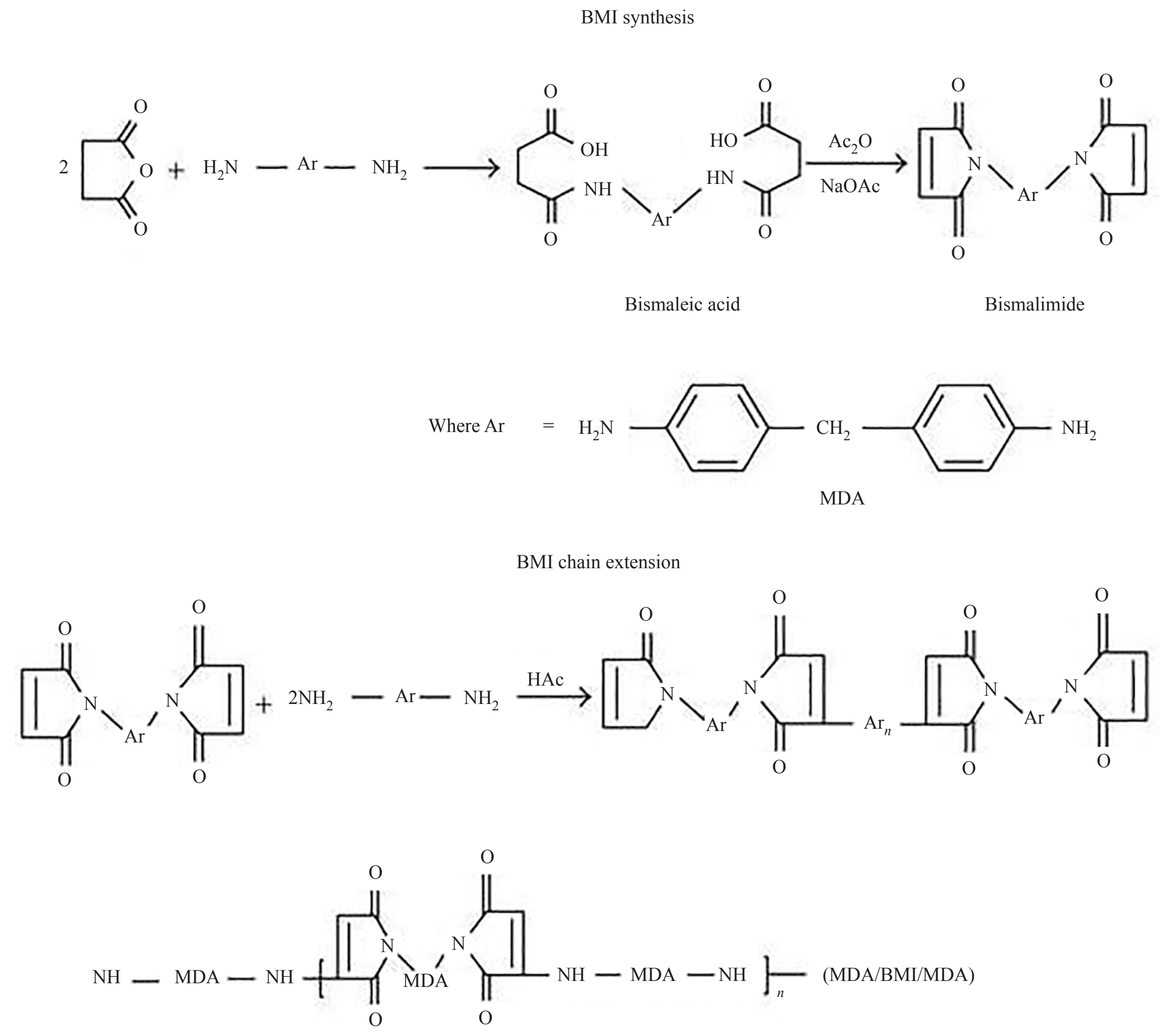


Figure 12. Formation of Bismaleimide (BMI) matrix resin; and further matrix modification by typical polyaddition reaction with itself as well as with other co-monomers like 4, 4’ methylene dianiline.

2.2.2.9 *Phenolic resin*

This family of resin are produced from the condensation reaction between phenol(s) and formaldehyde in acidic or in a basic condition depending upon the type of resin to be prepared. Broadly there are two types of phenolic resin such as Resol and novolac as generated from basic or acidic composition respectively.[17,18] An important use of phenolic resin is for the manufacture of Carbon-Carbon composite material.[40,41] Further details about C/C composite materials are given in Section 5.

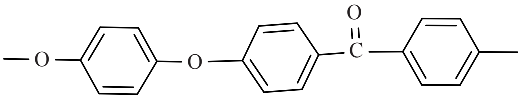
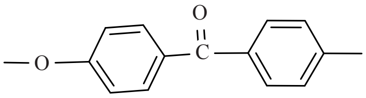
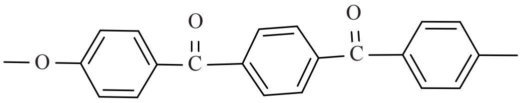
2.2.3 *Major types of thermoplastic resin*

Thermoplastic resins are generally recognized as ductile, tough polymer systems compared to thermosets but have only recently been utilized with graphite fibers for advanced composite applications. The mechanical behaviours of high performance thermoplastic resin (e.g., PEEK, polysulfone, PPS, polyphenylene sulfide, etc.) and their composites can manifest nonlinear curve with very high strain-to-failure. Such characteristic translates into higher transverse strain-to-failure with improved delamination resistance, improved impact strength and toughness.[17,19]

2.2.3.1 *Poly (aryl ether ketone)*

Polyaryether ketone (PAEK) is an important class of thermoplastic materialcame in the market in the early 1980s. The three most common of this family of resin are (i) polyether ketone (PEK), (ii) common poly(aryl ether ketone)s[42] as shown in Table 2.

Table 2. Different ketone containing repeat unit of the group of polyaryl ether ketone resins.

Polymer	Repeat Unit	K/E*	T_g	T_m
Poly(ether ether ketone)		0.5	142*	340*
Poly(ether ketone)		1.0	156*	370*
Poly(ether ketone ketone)		2.0	155	358

K/E* i.e., Ketone/ether ratio[42]

PEEK is a biocompatible, semicrystalline thermoplastic with excellent mechanical and chemical resistance properties.[42] PEEK is a high-temperature (up to 260 °C) engineering thermoplastic having m.p. of 335 °C and T_g of 143 °C, that is excellent for applications where thermal, chemical, and combustion properties are critical to performance. PEEK emits little smoke or toxic gas when exposed to flame. This material is tough, strong, and rigid and has superior creep resistance; and also resists radiation. With its resistance to hydrolysis, PEEK can withstand boiling water and superheated steam used with autoclave and sterilization equipment at temperatures higher than 250 °C. Carbon-reinforced PEEK provides excellent wear capabilities. PEEK HPV grade offers outstanding bearing performance. Typical applications are in the areas of marine, nuclear, oil-well, automotive and aerospace industries.[43,44]

2.2.3.2 *Other major types of thermoplastic matrices*

Major types of engineering thermoplastics include (i) Addition Polymers: Polyolefins, UHMWPE, PVC, PMMA etc (ii) Condensation polymers: PPS, PPO, Nylon, Polycarbonate etc.[16,17]

2.3 *Rubber as matrix material*

Elastomer is generally a special category of polymer that displays rubber-like elasticity. Rubber or elastomers are traditionally used in industrial components because of their special characteristics like flexibility toughness, high resilience, impact resistant, shock absorbing ability, relatively lighter, amenable to processing and mouldability.[17,45]

Reinforced rubber products are one of the largest classes of composite materials to provide certain important essential engineering properties for aviation and automobile pneumatic tyres of various kinds for vehicular transport items, marine components, hose pipes, conveyor and power transmission belts, skirts for air-cushion vehicle (ACV) or hovercraft.

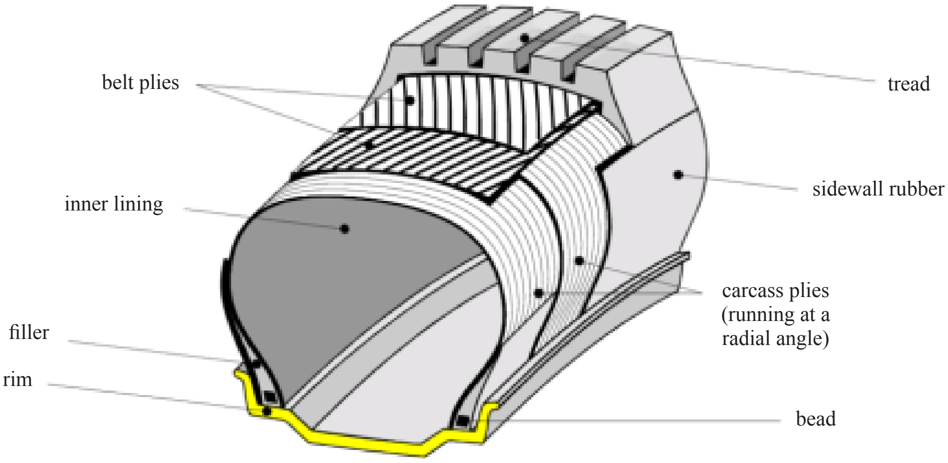


Figure 13. A general schematic view of a typical tyre derived from the combination of different components in the Tyre composite structure.

Tyre technology is quite an intricate technology; thanks to the development of appropriate matrix of reinforced rubber (FRR) composites. Both nanoparticulate as well as fibre reinforced rubber composites are used in the construction of Tyre (Figure 13).[45]

Rubber based engineering items are made of natural and various synthetic rubber matrices reinforced with different reinforcing materials. Raw rubber is not useful unless it is compounded and cured or crosslinked (Figure14) appropriately in presence of different rubber chemicals and additives. Such additives generally include carbon black (particulate reinforcing filler), zinc oxide (activator cum filler), Nonox-D (antioxidant), stearic acid (activator), process oil (processing aid), sulphur (curing agent) and mercaptobenzthiazole, MBT (accelerator).[45] Extent of crosslinking determines the degree of hardness of the rubber composite.[17,45,46]

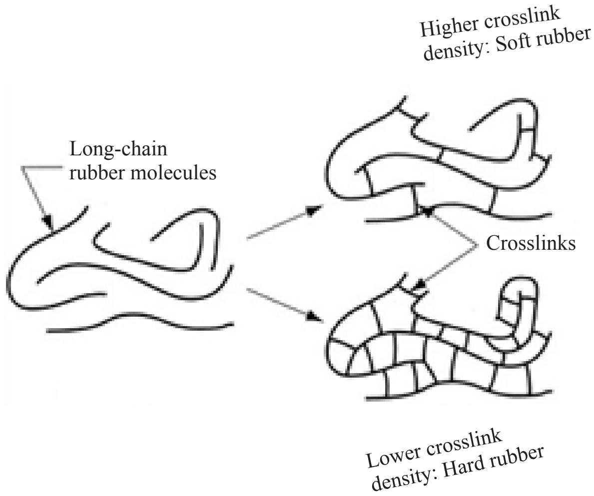


Figure 14. Crosslink formation during vulcanization of rubber or a thermosetting polymer

2.3.1 *Types of rubber*

There are two types of rubber such as (a) Natural rubber and (b) Synthetic rubber. The most commonly used rubber is Natural rubber which is chemically cis-polyisoprene. The important synthetic rubbers are Styrene butadiene rubber (SBR), polybutadiene, polyisoprene, butyl rubber, bromobutyl rubber, nitrile rubber, neoprene or chloroprene rubber, Hypalon rubber, Ethylene propylene diene rubber (EPDM), polysulfide etc. A common example of compatible blend is the blend of rubber (NBR) and plastic (PVC) can be generated by blending nitrile rubber (NBR)[46] and polyvinyl chloride (PVC). Some of the features of a few important rubbers are given below.

2.3.1.1 *Natural rubber (NR)*

It is very useful matrix material because of its high resilience and a low hysteresis characteristic thus generates less heat build up during dynamic condition. However, natural rubber alone cannot meet the market demand for obvious reason; and thus, synthetic rubbers are being produced to cater the market demand. Each of the synthetic rubbers has their own special characteristic properties.

2.3.1.2 *Styrene butadiene rubber (SBR)*

Styrene butadiene rubber (SBR) is a synthetic rubber obtained from the copolymerization of styrene and butadiene (Figure 15). Its properties are similar to those of NR. SBR has better heat resistance, abrasion resistance, hardened on aging whereas NR gets softened on aging. SBR is better resistant to oxygenated solvent, mild acid, relatively lower ozone, oxygen, uv light resistant in absence of stabilizer.[45]

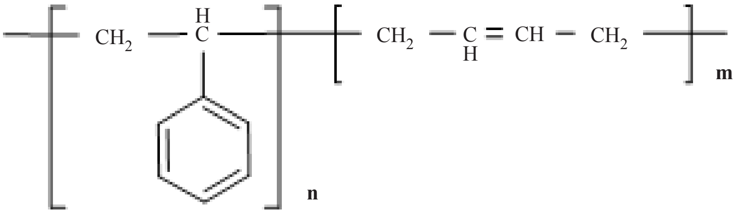


Figure 15. Chemical structure of SBR synthetic rubber

2.3.1.3 *EP and EPDM (Ethylene Propylene diene modified) rubber*

This synthetic elastomer is known in the market as EP or EPDM as they are synthesized from the copolymerization of ethylene and propylene (EP) in absence or presence of diene monomer like ethylidene norbornene. EP is cured by peroxides whereas EPDM can be cured using sulphur.[45] Its dynamic and mechanical properties are in between NR and SBR. It is resistant to steam, oxygenated solvents, brake fluid, weather resistant. However, it is relatively less resistant to petroleum, hydrocarbon, and oils.

2.3.1.4 *Nitrile butadiene rubber (NBR)*

Nitrile butadiene rubber (NBR) is the copolymer of acrylonitrile (ACN) and butadiene. It is variously known by the name as Nitrile rubber or Buna-N or NBR.[45,46] This rubber is resistant to oil, fuel, and similar chemicals; so is generally found suitable for use in the manufacture of sealant, hose pipes for use in the oil field, automotive and aeronautical industry. The stability of NBRs in the temperature range from -40° to 108 °C makes them an ideal material for aeronautical applications. NBR based products are also used in the nuclear industry to make protective gloves. NBR based gloves are more resistant to puncture than those of natural rubber.

2.3.1.5 *HNBR*

It is a modified version of NBR is known by the name hydrogenated nitrile butadiene rubber (HNBR) is better resistant to ozone high temp steam and is less vulnerable to chemical degradation.[47]

2.3.1.6 *Polychloroprene or Neoprene*

Polychloroprene or Neoprene is a synthetic polymer produced by polymerization of chloroprene (Figure 16); and they exhibit good chemical stability and retain flexibility over a wide temperature range.[45,48] Neoprene is sold either as solid rubber or in latex form and is used in a wide variety of applications where its products face oil and chemical resistance. Neoprene based products have good electrical insulation characteristics.

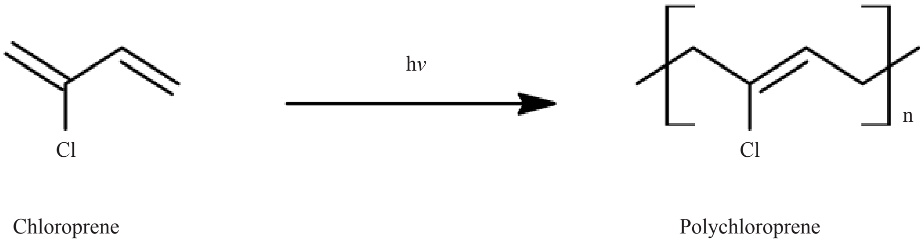


Figure 16. Chemical structure of polychloroprene or neoprene synthetic rubber

Polychloroprene is more resistant to degradation than natural or other synthetic rubber which makes it well suited for demanding applications such as hoses, gaskets, and corrosion resistant coating.[45] Generally, neoprene rubber is a very pliable material with insulating properties similar to rubber or other solid plastics.

2.3.1.7 *Butyl rubber*

Butyl rubber is a synthetic copolymer of isoprene and isobutylene (Figure 17); and thus its acronym became IIR. Generally IIR is produced by copolymerization of 98% of isobutylene with a smaller amount of about 2% of isoprene such that isobutylene part can provide for a highly saturated backbone whereas isoprene component can ensure proper crosslinking.[45,49]

Butyl rubber has very low permeability to air, gases and moisture[45,49]; excellent air-barrier performance and used for design automobile tire liner and inner tubes, football bladder and in many applications requiring an airtight rubber. An important area of its application is in the manufacture of inner tubes. Some of the characteristics of butyl rubber are low glass transition temperature, low modulus elastomer, low compression set, resistance to aging and to weathering from atmospheric exposure, wide vulcanization versatility.[49]

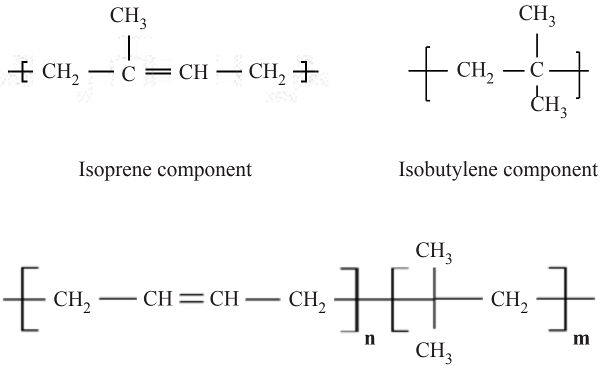


Figure 17. Chemical structure of Butyl synthetic rubber

2.3.1.8 *Polybutadiene*

Polybutadiene, a synthetic rubber and is also known as butadiene rubber or Buna rubber; synthesised from the polymerization of 1,3 butadiene. Characteristically PB is relatively resistant to wear and is used especially in the construction of tire. Its other major use is in the manufacture of toughened plastics where it acts as an additive to improve the toughness (impact resistance) of plastics like ABS (acrylonitrile butadiene), polystyrene.[45]

2.3.1.9 *Toughened matrix resin*

Incorporation of rubber particles can improve the toughness in the matrix and can enhance the matrix dominated properties including the transverse tensile strength and interlaminar shear strength, Brittle matrix can be toughened by incorporating rubber particles like hydroxy terminated polybutadiene (HTPB), carboxy terminated polybutadiene (CTPB).[50,51]

Matrix acts as a binder for composite propellant in which solid granular ingredients are held together by the matrix resin. Ammonium perchlorate (AP)-based composite propellants are workhorse in the field of solid rocket propulsion for many decades. This type of propellant typically contains a multi-modal distribution of AP (NH_4ClO_4) grains (~20 to 200 mm) embedded in the hydroxyl-terminated polybutadiene (HTPB) matrix. HTPB matrix is popular because it can accommodate higher solid fractions (total 88-90% of AP and Al) and provides relatively good physical properties.[50,52]

2.3.1.10 *Acrylic rubber*

It is a specialty polar rubber, known by names ACM and HyTemp and is a copolymer or terpolymer of ethyl acrylate and other acrylates (acrylic acid ethyl or butyl ester) (Figure 18), with a small amount of a vulcanisation-supporting monomer; and is produced by free radical emulsion or by suspension polymerisation.[52,53]

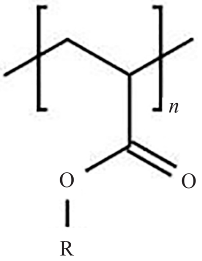


Figure 18. Chemical structure of Acrylic rubber

ACM has outstanding resistance to hot oil and oxidation with the ability to withstand temperatures of 170-180 °C. It has polar and saturated structure, so ozone resistant and has low permeability to gases but has low resistance to moisture, acids and bases; its use is prohibited below -10 °C. It is commonly used in automotive transmissions, beltings, hoses, special adhesive, shaft seals, O-rings, gaskets, and in vibration damping mounts.[52,53]

2.3.1.11 *Fluoroelastomers*

Fluoroelastomers are made by copolymerizing various combinations of fine chemicals like vinylidene fluoride ($CH_2 = CF_2$), hexafluoropropylene ($CF_2 = CFCF_3$), chlorotrifluoroethylene ($CF_2 = CFCl$), and tetrafluoroethylene ($C_2 = F_4$).[45] Such elastomers have outstanding resistance to oxidation, heat, fuels and oils. Exhibiting service temperatures up to about 250 °C, fluorocarbon elastomers; for example, Viton rubber of DuPont's is a copolymer of vinylidene fluoride and hexafluoropropylene) is a material of choice for use in aerospace and industrial equipment subjected to severe conditions. However, they have a high density, are swollen by ethers and ketones, are affected by steam, and become glassy at temperatures not far below room temperature; and their low chemical reactivity makes the interlinking of the polymer chains (essential for the production of useful rubbery matrix) a long and complex process. Major applications are as temperature-resistant Seals, O-rings, and gaskets.

2.3.1.12 *Hypalon*

It is a synthetic elastomer, more precisely a chlorosulphonated polyethylene and is known for its resistance to chemicals, temperature extremes, and uv light for use in high performance and critical areas of a wide range of industrial and automotive products. It offers extreme resistance to UV light and water.[54]

3. Metal matrix materials

Metal matrix composites (MMCs) are a class of materials like metals, alloys or intermetallic compounds in which incorporated with various reinforcing phases, such as particulates, continuous fibres or whiskers.[55] A metallic matrix, can be significantly strengthened even by very low weight fractions (~1 wt%) of well-dispersed nanoparticles.[56]

Matrices in MMC are ductile metals; superalloys, and alloys of lighter metals like Al, Mg, Ti and Cu; and are commonly used matrix materials[19,57,58]; the matrix is usually a low density metal alloys. One of the most important parameters of a metal for the development of MMCs is the density; and is so important that many times MMC is taken as equivalent to *Light metal matrix composites*. In structural applications, the matrix is normally a lighter metal such as Al, Mg, or Ti, and provides a compliant support for the reinforcement; and in high-temperature applications, Co and Co/Ni alloy matrices are common.[59]

MMCs have great potential to replace monolithic metals in many engineering applications because of their enhanced properties, for example higher strength and stiffness, better wear resistance or higher operating temperature.[56,57] However, the application of MMCs has been limited primarily due to their high cost and relative low fracture toughness and reliability despite of their attractive mechanical properties.[57-60]

Substantial progress in the development of light MMCs has been so achieved in last several years that the newly innovated competitive products could be introduced into the most important application areas especially in the automotive industry. In fact, MMCs are now innovated in commercial scale for use in fiber reinforced pistons and aluminum crank cases with strengthened cylinder surfaces as well as particle-strengthened brake disks.[59]

3.1 *Mechanical features*

For most metallic materials, elastic deformation persists only to strains of about 0.005. As the material is deformed beyond this point, the stress is no longer proportional to strain (Hook's law ceases to be valid); but permanent, nonrecoverable, or plastic deformation occurs (Figure 19).

The transition from elastic to plastic is a gradual one for most metals. From atomic perspective, plastic deformation corresponds to the breaking of bonds with original atom neighbours and then reforming bonds with new neighbours as large number of atoms or molecules move relative to one another; upon removal of the stress they do not return to their original positions. The mechanism of the deformation is different for crystalline and amorphous materials. For crystalline solids, deformation is accomplished by means of a process called slip, which involves the motion of dislocations. Plastic deformation in non-crystalline solids occurs by a viscous flow mechanism.

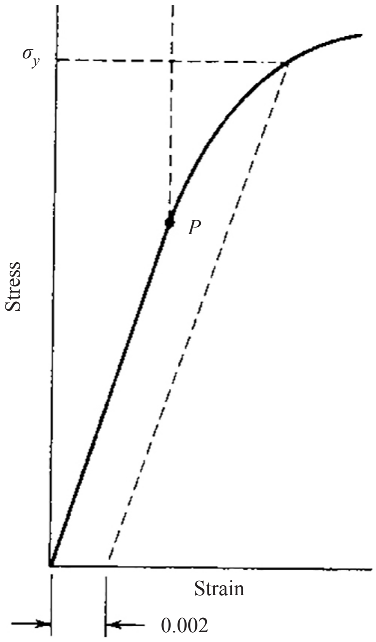


Figure 19. Schematic profile of the tensile stress-strain behaviour into the plastic region for a typical metal.[19]

3.2 *Importance of metal matrix composites*

MMCs have great potential to replace monolithic metals in many engineering applications because of their enhanced properties. For example, higher strength and stiffness, better wear resistance or higher operating temperature. However, the application of MMCs has been limited primarily due to their high cost, complexity involved in the synthesis process and relative low fracture toughness and reliability despite of their attractive mechanical properties.

However, the synthesis of discontinuous reinforcement incorporated MMCs was successfully attempted using a range of processing techniques.[57,58] Incorporation of nano-scale reinforcements primarily selected from oxide, carbide, boride, and nitride families led to offer promising results in improving a wide range of properties pertaining to metallic matrices. With the advent of carbon nanotubes (CNT), graphene, buckyballs, and carbon nanoplatelets were also critically investigated in the both the areas, MMC as well as in polymer composites. Some of the properties which can be enhanced by using nano-scale reinforcements in the development of MMCs are tensile and compressive behavior, ductility or elongation to failure, a must for 'bend than break' design philosophy; high-temperature mechanical properties; creep; dynamic mechanical properties; wear resistance, including scratch resistance; coefficient of thermal expansion; damping; machining; ignition resistance; dry/wet corrosion resistance.

MMCs are lightweight structural materials used in a specific number of aircraft, helicopters and spacecraft. MMC material comprises hard reinforcing particles embedded within a metal matrix phase.

3.3 *Microstructure*

Development of high performance MMCs requires careful microstructure design which can improve material's fracture toughness while maintaining high strength. The microstructure influences the fracture toughness of MMCs[57,58,60], their effects on the interplay between plastic deformation and crack formation, as well as their effects on the competing failure mechanisms are known.

Hybrid MMCs are advanced materials used for light weight high strength purpose in automobile and aerospace sector.

The attractive feature of the MMCs is their higher temperature use; aluminum matrix composite can be used in the temperature range above 300 °C while the titanium matrix composites can be used above 800 °C.[19,57,58] Metal matrices for composite materials have an intermediate working temperature range between 200-800 °C. Metal matrices provide high mechanical properties like strength, stiffness, ductility and electrical conductivity. Alloys are metallic substance made by fusing two or more metals, or a metal and sometimes a nonmetal, to obtain desirable qualities such as hardness, lightness, and strength and for designing an extended temperature range for a given application. Brass, bronze, and steel are some of the examples of alloys.

3.4 *General information about metals*

Among the metals only a few of them have acquired practical value so far their utility as engineering matrix material is concerned. It may be noted that most of the engineering materials are alloys and only a few are used as pure metals.

2.4.1 *Types of metals*

Metals may be categorized into ferrous materials and non-ferrous materials.[55] The largest use in the industry perhaps is of ferrous metals and alloys.

Non-ferrous materials include all other metals; amongst them the important practical materials are copper (Cu), nickel (Ni), aluminium (Al), titanium (Ti), zinc (Zn), tin (Sn) and lead (Pb) and their alloys. Properties and uses of the some of the important metals are summarised in the Table 3.

There is another category of metals known as special metals which include chromium (Cr), manganese (Mn), tungsten (W), antimony (Sb), bismuth (Bi), boron (B), etc.; and are mostly used as alloying elements for matrix development. However, other metals like zirconium (Zr), (Ta), silver (Ag), gold (Au), etc., and their alloys are used for very specific applications as they are too expensive.[55-58]

2.4.1.1 *Non-ferrous materials*

2.4.1.1.1 *Aluminium and aluminium alloys*

Table 3. Some important metals with their physical properties, features and use

Metals	Density, g/cm^3	Poisson's Ratio	Melting point, °C	Use upto Temperature
Aluminium (Al)	2.70	0.350	660	Major characteristic features of aluminium is that it is much lighter than iron.
Titanium (Ti)	4.506	0.320	1670	Nickel alloys are oxidation and corrosion-resistant materials well-suited for extreme environments.
Zinc (Zn)	7.134	0.245	419.5	Zinc is not used in heavy-load applications, but often used for die-casting mechanical parts from zinc.
Copper (Cu)	8.96	0.340	1085	Most copper is used in electrical equipment. This is because it conducts both heat and electricity very well, and can be drawn into wires. It also has uses in construction (for example, roofing and plumbing), and industrial machinery (such as heat exchangers).
Nickel (Ni)	8.908	0.31	1455	Ni alloys are oxidation and corrosion-resistant materials well suited for extreme environments.
Tin (Sn)	7.3	0.325	231.9	Tin has long been used in alloys with lead as solder, in amounts of 5 to 70% w/w. Tin with lead forms a eutectic mixture at the weight proportion of 61.9% tin and 38.1% lead (the atomic proportion: 73.9% tin and 26.1% lead), with melting temperature of 183 °C. Such solders are primarily used for joining pipes or electric circuit.
Lead (Pb)	11.34	0.44	327	Lead and its alloys as engineering material have limited but important uses. It is soft and easily worked into sheets and formable; and corrosion-resistant metal has been used for pipes.

Aluminium is soft and has relatively low melting point (660 °C), low strength; its density is 2.70 g/cm^3 and poisson's ratio is 0.35. Among the non-ferrous metals, aluminium occupies the highest position so far tonnage of production is concerned. The major characteristic features of aluminium is that it is much lighter than iron, about 1/3 of the density of that of iron, good resistance to corrosion, good electrical conductivity, relatively less costly and is used as matrix material for production of MMC.[61] Aluminium and its alloys are extensively used in aerospace industry because of its ability to develop considerable strength by suitable alloying and in some cases by subsequent heat treatment for annealing.[19,57-61]

2.4.1.1.2 *Copper and Copper Alloys*

Copper is the second most important non-ferrous metal after aluminium; its density is 8.96 g/cm^3 and poisson's ratio is 0.34. Copper and its alloys are highly ductile and can be easily cast and processed to produce various engineering components; the largest use of copper alloys in process industries is in tubing and piping particularly where resistance to certain specific corrosive media is required, the preferred method of using copper and its alloys is to use as lining over steel base for fabrication of pressure vessels, tanks, etc.[19,55]

2.4.1.1.3 *Nickel and nickel alloys*

Nickel is costlier than aluminium and copper; its density is 8.908 kg/m^3 and poisson's ratio is 0.31. Selection of nickel and its alloys is specially made where resistance to highly corrosive environment is required specifically as in strong caustic or hydrofluoric acid service environment.[55]

2.4.1.1.4 *Lead and lead alloys*

Lead and its alloys as engineering material have limited but important uses; its density is 11.34 kg/m^3 and poisson's ratio is 0.44. Lead has relatively low melting point (327 °C), but by alloying, its normal strength and creep can be increased; and are often utilized as lining material; its alloys are used for soldering (Pb-Sn, Pb-Sn-Sb) and bearings (Pb-Sn-Sb, Cu-Pb, Cu-Sn-Pb).[19,55] Lead based matrices are used in the service condition of corrosive environment, specifically when it has to face an environment involving dilute sulphuric acid.

2.4.1.1.5 *Titanium and titanium alloys*

Titanium is approximately 50% lighter metal than iron; thus has the advantage to provide higher specific strength; its density is Ti 4.506 g/cm^3 and poisson's ratio is 0.32. Ti6 Al-4V is a widely used alloy where strength and toughness properties are important requirement.[19,62]

In process industry unalloyed titanium (i.e., commercially or chemically pure titanium) is commonly used. Titanium has excellent corrosion resistant properties against a large variety of environment; however, they are selected where high strength is not required. It is a costly metal, thus use is limited to exchanger tubes involving sea water as coolant and some specific corrosive chemicals.[62,63] Titanium is available in four ASTM grades (1, 2, 3 and 4) where strength of the material increases gradually from 240 to 640 MPa. The variations in mechanical properties are dependent on interstitial solid solution (oxygen, hydrogen, nitrogen) and impurity (iron) levels.

2.4.1.1.6 *Other non-ferrous netals*

The other non-ferrous metals have either limited use under special conditions (magnesium, tantalum, zirconium, cobalt, etc.) or no utility in process industries (silver, zinc, tin, etc.).[63,64] Others like silicon, antimony, barium, etc., are used in small quantities as minor or micro-alloying elements; for example, magnesium is used for handling hydrofluoric acid, zirconium for its resistance to carbamate solution, tantalum for its resistance to many highly corrosive solutions.

4. Ceramic matrices for ceramic matrix composites

Ceramic matrix composite (CMC) is a novel emerging technology for improving the hardness and durability of ceramics at extremely high-temperature applications, like engine hot area elements.[58-60] By combining different ceramic matrix materials with special and suitable reinforcement fibers, new properties can be tailored to obtain products for hi-tech applications to meet the urgent demand of multi-functional composites[7] involving oxidation resistance, high strength and strong microwave attenuation in application of future high speed stealth vehicle, ceramics and their derivative architectures have considered to be a promising candidate in the field of high-temperature microwave absorption (HTMA) owning to tunable dielectric properties as well as intrinsic excellent thermo-physical properties.[7,65,66] Ceramics are inorganic and nonmetallic materials. Their main constituents are generally silica (SiO_2), alumina (Al_2O_3), and other inorganic non-metallic substances. Ceramic material comprises all kinds of constituents in the sense that they are a combination of a metal (e.g., aluminum) or intermediate-metal (e.g., silicon) with a non-metal (i.e., oxygen, nitrogen, or carbon). Ceramics are also used as matrix materials to develop Ceramic matrix composite materials (CMCs) to obtain desired engineering properties. Although ceramics are generally insulators, they can also be formed to serve as electrically conductive materials; however some ceramics, like superconductors, also display magnetic properties.[66,67]

Ceramics matrices are generally brittle. In order to overcome their brittleness, reinforcements are incorporated into them to effect extrinsic toughening mechanism in the system of ceramic-matrix composite materials (CMCs). Unlike PMCs and MMCs, CMCs are known as inverse composites as the failure strain of the matrix is lower than that of fibers that results in the failure of the matrix first.[68] The compressive strength of CMCs is less than that of traditional ceramics; however, this is due to the porosity of the matrix material. On the positive side, they have high corrosion resistance even at elevated temperatures and can handle dynamic loadings nicely. CMCs have high toughness and exhibit a high failure stress if the fiber matrix bonding is not too weak or too strong but optimum achieved through the use of fiber coating referred to as the interface. CMCs are classified as per the type of reinforcements used in the matrix such as particulate, whisker, short fibre-reinforced and Continuous fibre-reinforced ceramic-matrix composites (CFCCs).[7] However, Ceramics and Ceramic matrix composite materials (CMCs) terms are often used interchangeably because the ceramics are generally need modification by incorporating another ceramic of its own or different to develop CMC.[7,68] Generally CMC comprises ceramic fibers embedded in a ceramic matrix.

4.1 *Preparation of ceramic matrices*

Ceramics are generally made by taking mixtures of earthen elements, clay, powders, and water and shaping them into desired forms; once it is shaped, it is fired in a high temperature oven kiln. Depending on their processing procedural method of formation; ceramics can provide a wide range of products with controlled density from lightweight to dense products.[66]

4.2 *Manufacturing processes*

There are several processes to generate ceramic matrix to create CMC. Some of these techniques are stated below.

4.2.1 *Matrix deposition from a gas phase*

CVD (chemical vapour deposition) is an established technique for this purpose. In the presence of a fiber preform, CVD takes place in between the fibers and their individual filaments and therefore is said as chemical vapour infiltration (CVI).[69] Illustratively, for the manufacture of C/C composites, a C-fiber preform is exposed to a mixture of hydrocarbon gas methane, propane etc. at a pressure ≤ ca. 100 kPa at above 1000 °C where gas gets decomposed and carbon deposited on and between the fibers. Another example is the deposition of SiC where a mixture of methyltrichlorosilane (CH_3SiCl_3, MTS) and hydrogen where this gas mixture deposits fine and crystalline SiC on the hot surface preform.[69]

4.2.2 *Matrix formation via pyrolysis of C- and Si-containing polymers*

Liquid polymer infiltration (LPI), or polymer infiltration and pyrolysis (PIP) process are used to generate matrix via pyrolysis of C- and Si-containing polymer.[69-71] Hydrocarbon polymer can be pyrolysed to get carbon; upon degassing and heat treatment leads to formation of graphite-like structure. Some special type of polymers known as 'preceramic polymers, for example polycarbosilanes yield amorphous silicon carbide. A large variety of such silicon carbide, silicon oxycarbide, silicon carbonitride, and silicon oxynitride precursors are available; and more such preceramic polymers are being developed. Fiber preform is infiltrated with the desired polymer followed by curing and pyrolysis yield a highly porous matrix which is generally undesirable; however, further cycles of polymer infiltration and subsequent pyrolysis leads towards desired quality. Five to eight such cycles are used to achieve the desired CMC.[69-71]

4.2.3 *Matrix formation via sintering*

This process is used to manufacture oxide fiber/oxide matrix CMC materials. It may be noted that the normal sintering temperature is quite high ~1600 °C; and fibers cannot withstand such high temperature; thus, special precursor liquids are used to infiltrate the preform of oxide fibers. And such precursors allow sintering for ceramic-forming processes at ~1000-1200 °C. For example, mixtures of alumina powder with the liquids tetra-ethyl-orthosilicate (as Si donor) and aluminium-butylate (as Al donor) yield a mullite matrix. Sol-gel process chemistry can also be a technique used for this purpose. CMCs with a high porosity of ~20%[72-74] are generally obtained by this process.

4.2.4 *Matrix formed via electrophoresis*

Electrophoretic process is emerging as a technique for the formation of matrix in which the electrically charged particles dispersed in the desired liquid are transported through an electric field into the perform bearing opposite electrical polarity.[75-78]

4.2.5 *Matrix formation via chemical reaction*

With this method, one material located between the fibers reacts with a reinforcement material to form the ceramic matrix to generate CMC. Some conventional ceramics are manufactured by chemical reactions. For example, reaction bonded silicon nitride (RBSN) is produced through the reaction of silicon powder with nitrogen, and porous carbon reacts with silicon to form RBSN, a silicon carbide which contains inclusions of a silicon phase. Here reaction of silicon with a porous preform of C/C gives CMC for the production of brake discs[40,79,80]; the process temperature is above 1414 °C, that is above the melting point of silicon, and in the process conditions adjusted such that the carbon fibers of the C/C-preform retain their mechanical characteristics. This process is called *liquid silicon infiltration* (LSI).[40,79,80] It started with C/C, and so sometimes the material is abbreviated as *C/C-SiC*. In such process can produce a very low porosity of ~3%.

4.3 *Characteristics of ceramic matrices*

Ceramics exhibit excellent strength and hardness properties and provide high elastic modulus yet low density; however, the disadvantages of ceramic materials are their relatively lower tensile strength and brittleness which causes susceptible to failure. Ceramic materials are somewhat limited in applicability by their mechanical properties, however, in many respects are inferior to those of metals. The principal drawback is a disposition to catastrophic fracture with very little energy absorption. Both crystalline and noncrystalline ceramics almost always fracture without any plastic deformation in response to a tensile load.[19,61,65,68]

4.4 *Toughened ceramics*

The brittleness of ceramics can be reduced by using reinforcing material. For example, the Al_2O_3/Al is a ceramic composite where a ductile material like aluminium serves as the reinforcing phase.[68] The carbon, silicon carbide and silicon nitride are ceramics and used as matrix materials.

By taking advantage of the inherent high strength and Young's modulus of the ceramic matrix, it has been possible by incorporating reinforcements in the matrix to enhance the fracture toughness of CMC.

Sialon ceramic materials are produced through pressureless sintering, which involves densifying ceramic powders in a nitrogen atmosphere at temperatures > 1700 °C; and such advanced ceramics are often very sensitive to sintering parameters that can result in microcrack and flawed end-products if sintering processing conditions are not stringently controlled.

The measure of a ceramic material's ability to resist fracture is specified in terms of fracture toughness.[19,65] The plane strain fracture toughness K_{Ic}, is defined according to the expression

$$K_{Ic} = Y\sigma\sqrt{\pi a} \quad (1)$$

where Y is a dimensionless parameter or function that depends on both specimen and crack geometries, σ is the applied stress, and a is the length of a surface crack or half of the length of an internal crack.[19] Crack propagation will not occur as long as the right-hand side of the Eq. 1 is less than the plane strain fracture toughness of the material. Plane strain fracture toughness values for ceramic materials are smaller than for metals: typically they are less than 10 MPa √m.[17] However, under some circumstances, fracture of ceramic materials will occur by the slow propagation of cracks, when stresses are static in nature, and the right-hand of Eq. 1 is less than K_{Ic}. This phenomenon is called *static fatigue,* or *delayed fracture.* Fracture toughness values for ceramic materials are low and typically lie between 1 and 5 MPa √m. By way of contrast, K_{Ic} values for most metals are much higher (15 to greater than 150 MPa √m).

4.5 *Features of fracture*

The brittle fracture process consists of the formation and propagation of cracks through the cross section of material in a direction perpendicular to the applied load.[60] Crack growth in crystalline ceramics may be either transgranular (i.e., through grains) or intergranular (i.e., along grain boundaries); for transgranular fracture cracks propagate along specific crystallographic (or cleavage) planes, planes of high atomic density.[60,65]

Fracture toughness of ceramics have been improved significantly by the development of a new generation of ceramic-matrix composites (CMCs)-particulates, fibres, or whiskers of one ceramic material that have been embedded into a matrix of another ceramic. CMCs have extended fracture toughness between 6 MPa-20MPa √m.[19,60,65] Crack initiation normally occurs with the matrix phase, whereas crack propagation is impeded by the reinforcement phase.

4.6 *Thermal features*

The bonding in ceramics may be either ionic or covalent; and generally, they are hard, strong with high compressive strength particularly, oxidation resistant, corrosion resistant, and can withstand even at very high temperatures range even more than 2000 °C. The thermal conductivity of ceramic materials plays an important role in desired applications as it can be enhanced by some suitable methods to facilitate the heat conduction, convection and heat radiation, so as to further expand its scope of applications in desired fields. Ceramic materials with high thermal conductivity are mainly composed of nitrides, carbides, oxides, and borides, such as polycrystalline diamond ceramics, aluminum nitride, silicon nitride, silicon carbide, beryllium oxide.[19,68,73-77]

4.7 *Different types of ceramics*

In general, nomenclature of a CMC is made in accordance with the type of reinforcement and type of matrix selected (i.e., *type of fiber/type of matrix*). Illustratively, *C/C* stands for carbon-fiber reinforced carbon (C/C) ceramic composite, or for that matter carbon fiber reinforced silicon carbide (*C/SiC*) ceramic composite.

Ceramic fiber reinforcement increases the initial resistance to crack propagation and ensures the CMC to avoid catastrophic failure as generally observed characteristically in the case of monolithic ceramics.[19] More importantly, such behaviour is distinct from those of ceramic fibers in MMC and in PMC (polymer matrix composites) in which case the fibers typically fracture first before the matrix starts to fail as a result of higher failure strain capabilities of these matrices. A special form of bending test is Single-edge-notch-bend (SENB) tests is practiced to estimate fracture mechanics properties in pipes (Figure 20).

Interestingly, incorporation of a ceramic reinforcement material to a ceramic matrix can generate a ceramic composite material system.[68] For example, Special silicon carbide (SiC), alumina (Al_2O_3), mullite (Al_2O_3-SiO_2), and Carbon fibers are most commonly used ceramic material for CMCs where the matrix materials are usually the same i.e., SiC, Al_2O_3, Al_2O_3-SiO_2,Carbon. A separate class of ceramics known by the name Ultra high temperature ceramics (UHTC); and this ceramic particle or fibre reinforces the ceramic matrix to produce ultra high temperature ceramic composite (UHTCC).[61,68,77,79,80]

Silicon carbide has dual role depending upon how it is applied as matrix or as reinforcing fibre; for example, Carbon fiber reinforced silicon carbide *matrix* composites (C/Si), and Silicon carbide *fiber* reinforced silicon carbide *matrix* composites (SiC/SiC); and interestingly, silicon carbide is a hard material with a low erosion and it forms a silica glass layer during oxidation which prevents further oxidation of inner material.[73]

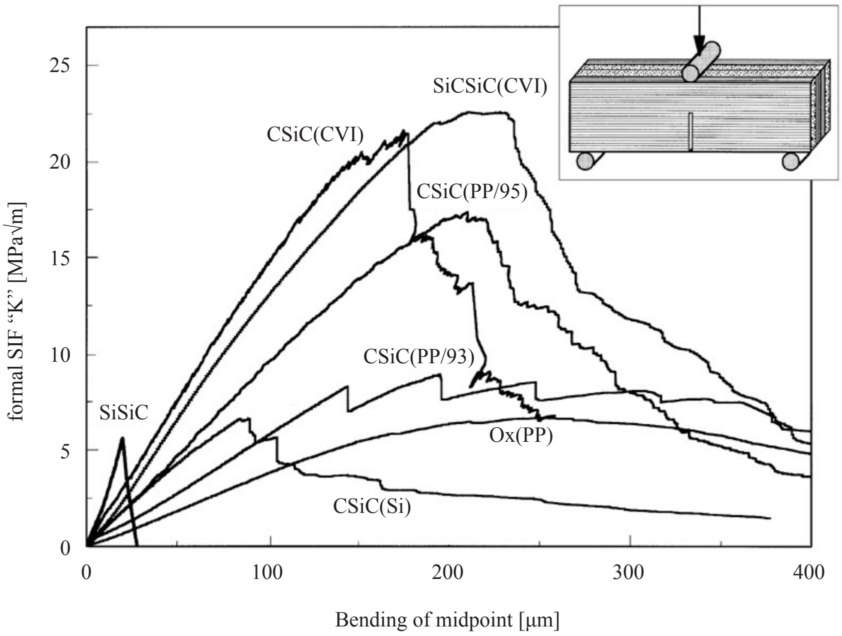
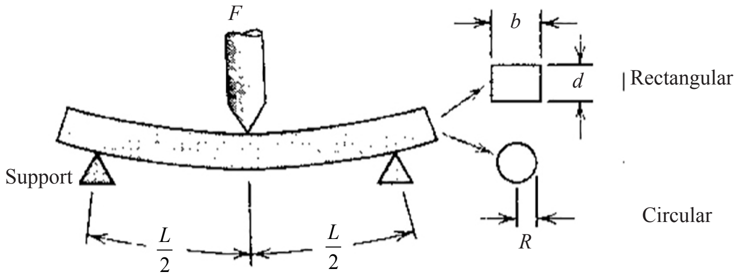


Figure 20. Single-edge-notch-bend (SENB) tests for different CMCs (Courtesy: Kurtz, M. (1992), Ceramic Matrix Composites. Bericht der DKG).

4.8 *Flexural load in ceramics*

Ceramics are rather brittle; so it is difficult to grip such materials without being fractured. In fact, ceramics fail after only about 0.1% strain[79,80], thus essentially their tensile specimens are perfectly aligned to avoid the bending stresses. Thus, a more suitable transverse bending test is generally used, in which a circular or rectangular cross sectional specimen is bent until fracture in a 3-(Figure 21) or 4-point loading method.[80]



$$\sigma = \text{stress} = \frac{Mc}{I}$$

Figure 21. The 3-pointloading testing scheme.

It represents a typical three-point bending for ceramic materials where M = maximum bending moment; c = distance from center of specimen to outer fibers; I = moment of inertia; F = applied load; Stress $\sigma = 3FL/2bd^2$ (rectangular), $\sigma = FL/\pi R^3$ (circular).[19,80]

At the point of loading the top surface of the specimen experiences compression while the bottom surface remains in tension.[80] Since the tensile strengths of ceramics are about one-tenth of their compressive strengths, so the fracture has to occur on the tensile specimen face; thus the flexure testis a reasonable substitute for the tensile test.

4.9 *Applications*

Ceramic materials are inherently resilient to oxidation and deterioration at elevated temperatures; specifically for components in automobile and aircraft gas turbine engines. Development of CMC-based heat shield systems promises the advantages; for instance, reduced weight; higher load-carrying capacity; better steering during the re-entry phase with CMC flap systems; reusability for several re-entries.

However, for such applications, the high temperatures preclude the use of oxide fiber CMCs, because of the creeping problem at higher temperature; and amorphous silicon carbide fibers lose their strength due to the re-crystallization at temperatures above 1250 °C. So carbon fibers in the silicon carbide matrix (C/SiC) are used for these applications.[69,75,82-84] Ceramics are also used in the development of armour against high speed projectiles.

Interestingly, C/SiC bolts and nuts and the bearing system of the flaps are qualified for application. The latter were ground-tested at the DLR in Stuttgart, Germany, under expected conditions of the re-entry phase:

The Intermediate experimental vehicle (IXV),[75,79] is Europe's first lifting body re-entry vehicle. The thermal protection system for the underside of the vehicle, comprising the nose, leading edges and lower surface of the wing, were designed using a ceramic matrix composite (CMC), carbon/silicon-carbide (C/SiC) as the vehicle's heat shield during its atmospheric re-entry.[73,75,79,83-85]

The European Commission funded a research project, C3HARME for the design, development, production, testing and evaluation of a new class of Ultra high temperature ceramic matrix composites (UHTCMC) reinforced with SiC fibers and carbon fibre suitable for applications in severe aerospace environments such as propulsion and Thermal protection systems (TPSs).[83-85]

At present, the absorbing performance of high-temperature stealth ceramic matrix composites (CMCs) is mainly focused in X-band[86,87], the effective absorption band is narrow; and the high-temperature resistance of IR (infrared) low emissivity coating is poor. So, the main research direction is now to further improve the stealth performance of ceramic matrix composites by using continuous fiber, low dimensional materials such as nanoparticles, nanotubes, nanowires composition, precursor doping, multiphase heterogeneous interface.

In addition, combined with the design ideas of metamaterials, the absorbing structural units of composite materials are miniaturized in size, and the design methods of single structural unit deep absorption and multiple broadband absorption provides a new way to improve the wideband stealth performance of composite.[65,66] Using metamaterials engineers' focus is to achieve impedance matching design, through structural design and thermal protection layer to form an integrated structure of infrared stealth and thermal protection performance of ceramic composite.[65-67,87] Ceramic matrix composites (CMCs) are composed of fiber, interface layer and matrix. Overall microwave absorbing performance strongly depends on the ceramic fiber, interface layer, matrix densification process and metamaterial structure design.[65,66]

5. Carbon matrix material

As can be seen in Section 5 that both the fibers and the matrix can consist of any ceramic material; thus likewise in corollary carbon fibres in carbon matrix can also be considered as a ceramic material of special kind. However, many of the material scientists consider Carbon-carbon (CC) materials are a generic class of composites.[88] Phenolic resins are generally used as carbon precursors for the generation of carbon/carbon (C/C) composites owing to their high carbon yield and aromatic nature[89] where fibre and the matrix carbons can have different structures and textures. Characteristically C/C composites are special and rank first among ceramic composite materials with a spectrum of properties for hi-tech applications. Carbon fibre reinforced carbon (CFRC), carbon-carbon (C/C), or reinforced carbon-carbon (RCC)[41,90,91] is a special type of composite material consisting of carbon fibre reinforcement in a matrix of graphite are developed for use in the re-entry vehicles of intercontinental ballistic missiles, and is most widely known as the material for the nose cone and wing leading edges of the Space shuttle orbiter.

The microstructure and morphology or the microtexture of carbon-carbon composites differ as per the nature of raw materials used and the processing conditions applied. Further complication arises from the 'subtle' treatments like surface modification of reinforcing fibres and inclusion of additives for protection against oxidation. The variations in microtexture influence the properties considerably.[41,92]

C/C composites are employed in rocket motors, as friction materials in aircraft and high performance automobiles, for hot pressing moulds, in components for advanced turbine engines, and ablative shields for re-entry vehicles. However, C/C composites are very expensive because of their relatively complex processing techniques. They are prepared from the 2D or 3D carbon fibre structure impregnated with resins like phenolic resin[89], then moulded and pyrolysed in an inert atmosphere. It is then heat treated at high temperature for densification for strengthening.[89,91] The state-of-the-art research activities regarding different 1D nanoreinforcements applied in C/C composites are systematically summarized[94] where it reported great improvement in mechanical and functional properties.

When the polymer matrix is exposed to high temperatures, it undergoes pyrolysis or carbonization processes with the generation of volatile; and C/C composite materials are formed.[85,91] As a result of matrix decomposition, permeability and porosity are continually being developed within the composite. This pressure gradient across the thickness enables the decomposition gases to flow through a network of developed pores. Simultaneously, a temperature gradient is also developed within the degrading matrix. Obviously, this temperature gradient is kept to a minimum to obtain uniform composite parts after carbonization. The pressure build-up and temperature gradients, as well as the developed pore structure, are considered important in the processing steps. And the initial carbonization process is considered as the rate-determining step in the manufacture of C/C composites, affecting the final performance of C/C composites.[93] Their properties depend on the type and volume fraction of resin matrix precursor used and heat treatment temperature. Composites made with thermosetting resins as matrix precursors possess low densities (1.55-1.75 g/cm^3) and well-distributed microporosity whereas those made using pitch as the matrix precursor, exhibit densities of 1.8-2.0 g/cm^3 with some mesopores, and those made using CVD technique, possess intermediate densities and matrices with close porosities. The former (resin-based) composites exhibit high flexural strength, low toughness and low thermal conductivity, whereas the latter (pitch- and CVD-based) can be made with very high thermal conductivity (400-700 W/MK) in the fibre direction.[92]

Carbon reinforced carbon matrix (C/C) can be used up to 3000 °C because Carbon is the element with the highest melting point; however, C/C is ablative materials that dissipate energy through self sacrificing. C/C is well-suited to structural applications at high temperatures, or where thermal shock resistance and/or a low coefficient of thermal expansion are needed. Although it is less brittle than many other ceramics, it lacks impact resistance. However, for extended service life, they need to be protected against oxidation either through matrix modification with Si, Zr, Hf etc. or by protection coatings of SiC, silica, zircon etc.[92]

6. Cement as matrix material

Cement is a kind of binder which is used for construction that sets, hardens, and adheres to other materials like reinforcement to bind them together. As such cement is seldom used on its own but rather to bind sand and gravel (aggregate) together.[95]

Concrete is a common large-particle composite in which both matrix and dispersed phases are ceramic materials. Since the terms "concrete" and "cement" are sometimes incorrectly interchanged, perhaps it is appropriate to make a distinction between them. Broadly speaking, concrete implies a composite material comprising aggregate of particles that are bound together in a solid matrix binding medium as cement. The terms cement and concrete often are used interchangeably; however, in fact, cement is actually an ingredient of concrete. Basically concrete is a mixture of aggregates and paste. Generally such aggregates are sand and gravel or crushed stone; and the paste is a combined mixture of water and Portland cement where water takes part in the hydration process by which the cement and water harden and bind the aggregates into a rocklike mass. Of particular importance for the strength of the concrete is a thin layer of calcium hydroxide (portlandite) directly adjacent to aggregate particles.[95] This layer shows a strong growth texture with *c*-axes aligned perpendicular to the aggregate surface; and the strength of the texture increases with ageing

(Figure 22) which appears to be preferable.

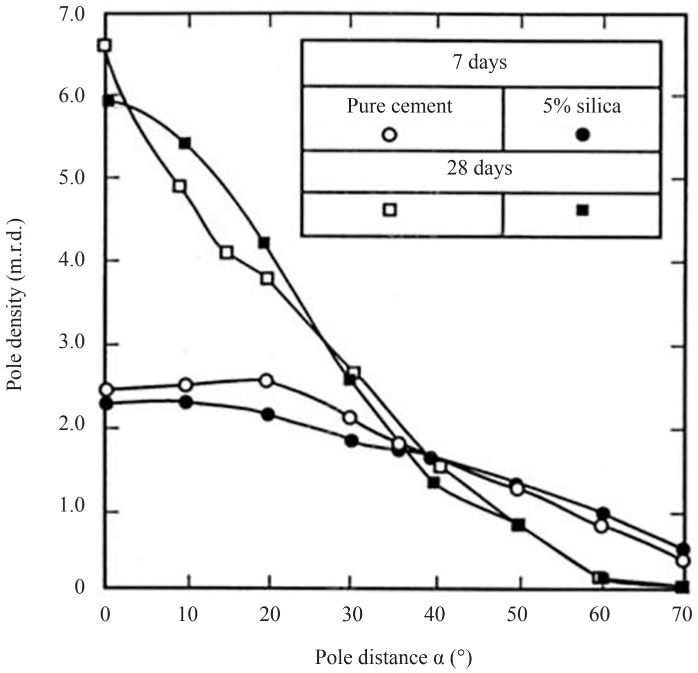


Figure 22. Texture of calcium hydroxide on cement paste-aggregate interface. Plot of pole density against angle to surface interface showing the effect of adding 5% silica fume to the paste (none) and of ageing (increase in texture strength).[96]

Generally, cement constitutes around 10 to 15 % of the concrete mix by volume.

Organic polymers are sometimes used as cements in concrete. Polymer cements[97-99] are made from organic chemicals that polymerize and ensure water proofing with useful tensile strength.

Two most common concretes are those made with Portland cement and asphaltic cements, where one of the matrix binders is inorganic but the other is organic in nature, and the reinforcements are in the form of aggregates of gravel, and sand. Asphaltic concrete is widely used primarily as a paving material; on the other hand, Portland cement concrete is employed mostly as a structural building material; of late also used to construct metal road. Asphalt cement requires petroleum based binder.[100]

6.1 *Types of cements*

Cement materials are classified into two distinct categories (i) hydraulic cements and (ii) nonhydraulic cements in accordance with their setting and hardening mechanisms.[97-101] Hydraulic cements setting and hardening involve hydration reactions and therefore require water, while non-hydraulic cements only react with a gas and can directly set under air.

6.1.1 *Hydraulic cement*

Cements are generally hydraulic cement and they harden by hydration of the clinker minerals (limestone and alumina silicate clay based materials during cement kiln stage) on water addition.[99-103] Hydraulic cements or Portland cement are made of a mixture of four major mineral phases of the clinker such as allite silica based ($3CaO \cdot SiO_2$); belite silica based ($2CaO \cdot SiO_2$), celite or alumina based tricalcium aluminate ($3CaO \cdot Al_2O_3$) and alumina and iron oxide based brown millerite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). The silicates are responsible for the cement’s mechanical properties.

6.1.2 *Nonhydraulic cement*

Another kind of cement, even though less known, is *non-hydraulic cement* such as slaked lime that is calcium oxide mixed with water which gets hardened by carbonation in presence of the atmospheric carbon dioxide.

6.1.3 *Organic inorganic blend of matrices-polymer cement matrix materials*

Polymer concretes are some kind of particulate polymer composite; they are a type of concrete in which polymer latex emulsions act as binder to replace the lime-type cements in varying extent; thus a type of 'composite matrix'.[93-96] However, if polymer is used in addition to Portland cement in the composition is known as Polymer Cement Concrete (PCC) or Polymer Modified Concrete (PMC).[103-105] Polymers in concrete are actually overseen by American Concrete Institute since 1971.

Polymer concrete may be used for new construction or repairing of old concrete.[98,102,105-107] The adhesive properties of polymer concrete allow repair of both polymer and conventional cement-based concretes.

Generally speaking such materials has certain important characteristics; for example, such materials have significantly greater tensile strength than unreinforced Portland concrete because plastic is 'stickier' than cement and has reasonable tensile strength; low permeability to water and aggressive solutions; good chemical and corrosion resistance. Such polymer concretes exhibit similar or greater compressive strength to Portland concrete. It undergoes much faster curing yet proves good adhesion to most surfaces, including to reinforcements. Because of the presence of polymer, they have good long-term durability against exposure to fluctuation temperature for their ability to withstand under freeze and thaw cycles. Obviously their density is lower and it can be controlled by adjusting the resin content of the mix and are thus lighter in weight than traditional concrete.[95-98,103-107] Combinations of concrete walls, steels, polymers, and suitable laminates can lessen shock and fragment propagation effectively through various mechanisms of shock or impact energy attenuation.[108-110]

7. Summary

This chapter has provided a glimpse of different classes of matrix materials used for the fabrication of composite materials. Such matrix materials should be selected in accordance with the need for the design of engineering composite materials for host of purposes. Polymer matrices are used for the design of lighter composite materials with high specific strength. MMCs are tough and are used when the material has to face higher temperature. Ceramic matrices are used for composites in hi-tech areas where desired conductivity, rigidity and high heat resistance properties are to be maintained. Carbon matrices are used for Carbon/Carbon composite materials which are generally used in the critical areas of applications. Different ID nanoreinforcements applied in C/C composites can improve in mechanical and functional properties. Cement in combination with polymer latexes is also a kind of special matrix materials innovated for engineering construction of reinforced concrete structure to ensure better tensile properties and durability.

Hyper velocity impact requires special design of armour construction; and modern armour items and blast protective systems are accomplished with a plethora of materials and material combinations where matrix materials can play significant role. To mitigate dynamic response of structures under impulsive loading, different materials such as fiber-reinforced polymer composites, porous materials, more recently metal foams and sandwich structures are used. In fact, different types of matrix materials can prove to be efficacious constituent item for innovative design of integrated structure using combination of composite materials to ensure attenuation, for example through rarefaction of waves, impedance mismatch, irreversible compression and plastic deformation and the like for application in the ever challenging area of BPRM (Blast and penetration resistant materials).

Conflict of interest

The authors declare no competing financial interest.

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