

Module-2: Basic Constituent materials in Composites

Learning Unit-1: M2.1

M2.1 Reinforcements and Matrices for Various Types of Composites

Composition of Fiber Reinforced Composites (FRP):

Common fiber reinforced composites are composed of fibers and a matrix. Fibers are the reinforcement and the main source of strength while the matrix '**glues**' all the fibers together in shape and transfers stresses between the reinforcing fibers. Sometimes, fillers or modifiers might be added to smooth manufacturing process, impart special properties, and/or reduce product cost.

M2.1.1 Fibers of FRP (Fiber Reinforced Composites):

The primary function of the fibers is to carry the loads along their longitudinal directions. Common fiber reinforcing agents include:

- Aluminum, Aluminum oxide, Aluminum silica
- Asbestos
- Beryllium, Beryllium carbide, Beryllium oxide
- Carbon (Graphite)
- Glass (E-glass, S-glass, D-glass)
- Molybdenum
- Polyamide (Aromatic polyamide, Aramid), e.g., Kevlar 29 and Kevlar 49
- Polyester
- Quartz (Fused silica)
- Steel
- Tantalum
- Titanium
- Tungsten, Tungsten monocarbide

M2.1.2 Matrix of Fiber Reinforced Composites:

The primary functions of the matrix are to transfer stresses between the reinforcing fibers (hold fibers together) and protect the fibers from mechanical and/or environmental damages. A basic requirement for a matrix material is that its strain at break must be larger than the fibers it is holding.

Most matrices are made of resins for their wide variation in properties and relatively low cost. Common resin materials include:

- Resin Matrix
 - Epoxy

- o Phenolic
- o Polyester
- o Polyurethane
- o Vinyl Ester

Among these resin materials, polyesters are the most widely used. Epoxies, which have higher adhesion and less shrinkage than polyesters, come in second for their higher costs.

Although less common, non-resin matrices (mostly metals) can still be found in applications requiring higher performance at elevated temperatures, especially in the defense industry.

- Metal Matrix
 - o Aluminum
 - o Copper
 - o Lead
 - o Magnesium
 - o Nickel
 - o Silver
 - o Titanium
- Non-Metal Matrix
 - o Ceramics

M2.1.3 FRP Composite Constituents:

1. Resins (POLYMERS)
2. Fibers
3. Fiber Reinforcement
4. Fillers
5. Additives
6. Sandwich Panels
7. Adhesives
8. Composite Designs

M2.1.3.1 Resins

Primary Function: “To transfer stress between reinforcing fibers and to protect them from mechanical and environmental damage”

Types:

- I. Thermoset Resin
 - a. Polyester
 - b. Vinyl Resin
 - c. Epoxy
 - d. Phenolic
 - e. Polyurethane

II. Thermoplastic

- a. Acetal
- b. Acrylonitrile Butadiene Styrene (ABS)
- c. Nylon
- d. Polyethylene (PE)
- e. Polypropylene (PP)
- f. Polyethylene Terephthalate (PET)

I. a. Polyesters:

- o Phthalic Anhydride (GP)
- o Dicyclopentadiene (DCPD) Types
- o Isophthalic Acid
- o Terephthalic Acid
- o Polyethylene Terephthalate (PET)

M2.1.3.2 Fibers:

Primary Function:

- “Carry load along the length of the fiber, provides strength and or stiffness in one direction”
- Can be oriented to provide properties in directions of **primary loads**

Fiber Types:

- I. Natural
- II. Man-Made
- III. Many Varieties Commercially Available

I. Natural Fibers:

- o Cellulose
- o Sisal

II. Man-Made Fibers:

- o Aramid
- o Boron
- o Carbon/Graphite
- o Glass
- o Nylon
- o Polyester

- o Polyethylene
- o Polypropylene

M2.1.3.3 Fiber Reinforcement:

- Glass
- Aramid
- Carbon
- **Glass Fiber Reinforcements**

- o E-glass
- o S-glass
- o C-glass
- o ECR-glass
- o AR-glass

- **Aramid (KEVLAR)**
Fiber Reinforcement:

- Superior resistance to damage (energy absorber)
- Good in tension applications (cables, tendons)
- Moderate stiffness
- More Expensive Than Glass

- **Carbon Fiber Reinforcement:**

- Good modulus at high temperatures
- Excellent stiffness
- More expensive than glass
- Brittle
- Low electric insulating properties

M2.1.3.3.1 Reinforcement Types:

1. Rovings (Continuous)
2. Chopped strand
3. Mat:
 - a. Chopped strand
 - b. Continuous strand
4. Woven roving
5. Stitched
6. Braided
7. Unidirectional
8. Veil

M2.1.3.3.2 Reinforcement Forms:

Woven Roving:

- o aka – Crimped
- o Plain
- o Satin
- o Twill
- o Basket

M2.1.3.4 Fillers/Additives/Modifies

Filler Types:

- Calcium Carbonate
- Clay
- Talc
- Aluminum Trihydrate
- Silica
- Micro Spheres
- Mica

M2.1.3.4.1 Types of Additives:

- Catalysts & Promoter
- Inhibitors
- Release Agent
- Pigments
- UV Absorber
- Fire Retardancy

M2.1.3.4.2 Fillers/Additives/Modifiers of Fiber Reinforced Composites:

The primary functions of the **additives** (modifiers, fillers) are to reduce cost, improve workability, and/or impart desired properties.

- Cost Reduction:
 - o Low cost to weight ratio, may fill up to 40% (65% in some cases) of the total weight
- **Workability** Improvement:
 - o Reduce shrinkage
 - o Help air release
 - o Decrease viscosity
 - o Control emission
 - o Reduce coefficient of friction on surfaces

- o Seal molds and/or guide resin flows Initiate and/or speed up or slow down curing process
- Property Enhancement:
 - o Improve electric conductivity
 - o Improve fire resistance
 - o Improve corrosion resistance
 - o Improve ultraviolet resistance
 - o Improve surface toughness
 - o Stabilize heat transfer
 - o Reduce tendency of static electric charge
 - o Add desired colors

M2.1.3.4.3 Common materials used as additives include:

- Filler Materials:
 - o Feldspar
 - o Glass microspheres
 - o Glass flakes
 - o Glass fibers, milled
 - o Mica
 - o Silica
 - o Talc
 - o Wollastonite
 - o Other microsphere products
- Modifier Materials:
 - o Organic peroxide, e.g., methylethylketone peroxide (MEKP)
 - o Benzoyl peroxide
 - o Tertiary butyl catechol (TBC)
 - o Dimethylaniline (DMA)
 - o Zinc stearate, waxes, silicones
 - o Fumed silica, clays

Learning Unit-2: M2.2

M2.2 Fibres/Reinforcement materials

M2.2.1 Introduction to Fibres

Organic and inorganic fibers are used to reinforce composite materials. Almost all organic fibers have low density, flexibility, and elasticity. Inorganic fibers are of high modulus, high thermal stability and possess greater rigidity than organic fibers and not withstanding the diverse advantages of organic fibers which render the composites in which they are used.

Mainly, the following different types of fibers namely, glass fibers, silicon carbide fibers, high silica and quartz fibers, alumina fibers, metal fibers and wires, graphite fibers, boron fibers,

aramid fibers and multi phase fibers are used. Among the glass fibers, it is again classified into E-glass, S-glass, A- glass, R-glass etc.

There is a greater market and higher degree of commercial movement of organic fibers.

The potential of fibers of graphite, silicon carbide and boron are also exercising the scientific mind due to their applications in advanced composites.

M2.2.2 Types of fibers

M2.2.2.1 Glass Fibers

Over 95% of the fibers used in reinforced plastics are glass fibers, as they are inexpensive, easy to manufacture and possess high strength and stiffness with respect to the plastics with which they are reinforced.

Their low density, resistance to chemicals, insulation capacity are other bonus characteristics, although the one major disadvantage in glass is that it is prone to break when subjected to high tensile stress for a long time..

However, it remains **break-resistant** at higher stress-levels in shorter time frames. This property mitigates the effective strength of glass especially when glass is expected to sustain such loads for many months or years continuously.

Period of loading, temperature, moisture and other factors also dictate the tolerance levels of glass fibers and the disadvantage is further compounded by the fact that the brittleness of glass does not make room for prior warning before the catastrophic failure.

But all this can be easily overlooked in view of the fact that the wide range of glass fiber variety lend themselves amicably to fabrication processes like matched die moulding, filament winding lay-up and so on. Glass fibers are available in the form of mats, tapes, cloth, continuous and chopped filaments, rovings and yarns.

Addition of chemicals to silica sand while making glass yields different types of glasses.

M2.2.2.2 Metal Fibers

As reinforcements, metal fibers have many advantages. They are easily produced using several fabrication processes and are more ductile, apart from being not too sensitive to surface damage and possess high strengths and temperature resistance.

However, their weight and the tendency to react with each other through alloying mechanisms are major disadvantages.

Steel wire is the most extensively used reinforcement in most large-scale metal filament applications. Wire is used for its capacity to enhance the tensile strength of concrete and

continuous metal fibers are the reinforcing constituents in metal and ceramic composite materials.

Ceramic fibers improve vastly in performance when a fine metal outline is incorporated with refractory ceramics by improving their thermal shock and impact resistance properties.

Metal wires, of the continuous version, also reinforce plastics like polyethylene and epoxy. Such combinations ensure high strength, light weight and good fatigue resistance.

Besides, continuous metal fibers are easily handled, unlike glass fibers. Better flexural properties are observed in some metal fibers reinforced plastic composites which also offer improved strength and weight, than glass fibers.

However, their poor tolerance of high temperatures and the resultant steep variation of thermal expansion coefficient with the resins are a discouragement that limits their application.

M2.2.2.3 Alumina Fibers

Alumina or aluminium oxide fibers, basically developed for use in metal matrices are considered a potential resin-matrix composite reinforcement. It offers good compressive strength rather than tensile strength. Its important property is its high melting point of about 2000°C and the composite can be successfully used at temperatures up to about 1000°C. Magnesium and aluminium matrices frequently use alumina fiber reinforced composites as they do not damage the fiber even in the liquid state.

M2.2.2.4 Boron Fibers

They are basically composites, in which boron is coated on a substance which forms the substrate, usually made of tungsten.

Boron-tungsten fibers are obtained by allowing hot tungsten filament through a mixture of gases. Boron is deposited on tungsten and the process is continued until the desired thickness is achieved. The tungsten however remains constant in its thickness.

Properties of boron fibers generally change with the diameter, because of the changing ratio of boron to tungsten and the surface defects that change according to size. However, they are known for their remarkable stiffness and strength. Their strengths often compare with those of glass fibers, but their tensile modulus is high, almost four to five times that of glass. Boron coated carbons are much cheaper to make than boron tungsten fiber. But its low modulus of elasticity often works against it.

M2.2.2.5 Silicon Carbide Fibers

Silicon carbide can be coated over a few metals and their room temperature tensile strengths and tensile moduli are like those of boron-tungsten. The advantages of silicon carbide-tungsten are several and they are more desirable than uncoated boron tungsten fibers. Elevated temperature

performance and the fact that they reported only a 35% loss of strength at 1350°C are their best qualities. Silicon carbide-tungsten and silicon carbide-carbon have both been seen to have very high stress-rupture strength at 1100°C and 1300°C. Uncoated boron-tungsten fibers tend to lose all their strength at temperatures over 680°C. Silicon carbide fibers do not react with molten aluminium, unlike uncoated boron and they also withstand high temperatures used in hot-press titanium matrices.

However, silicon carbide-tungsten fibers are dense compared to boron- tungsten fibers of the same diameter. They are prone to surface damage and need careful, delicate handling, especially during fabrication of the composite. Further, above 930°C, weakening reactions occur between tungsten and silicon carbide, making it difficult to maintain balance in high-temperature matrix formations.

Silicon carbide on 'carbon substrates have several advantages, viz. no, reaction at high temperature, being lighter than silicon carbide tungsten and possessing tensile strengths and modulus that is are often better than those of silicon carbide-tungsten and boron fibers.

M2.2.2.6 Aramid Fibers

Aramid fibers are made from aromatic polyamides which are long polymeric .chains and aromatic rings. They are structures in which six carbon atoms are bonded to each other and to combinations of hydrogen atoms. In aramid fibers, these rings occur and reoccur to form the fibers. They were initially used to reinforce automobile tires. Since then, they have also found other uses like bullet proof vests. As high strength applications, their use in power boats is not uncommon.

Aramid have high tensile strength, high modulus and low weight. Impact- resistant structures can be produced from aramid. The density of aramid fibers is less than that of glass and graphite fibers. They are fire resistant apart from being high-temperature resistant and also unaffected by organic solvents and fuels. But their resistance in acid and alkaline media is poor. They are supple and allow themselves to be woven into matrices by simple processes. Aramid fibers have a negative coefficient of thermal expansion in the fiber direction and the failure of aramid fibers is unique. When they fail, the fibers break into small fibrils, which are like fibers within the fibers. This unique failure mechanism is responsible for high strength.

M2.2.2.7 Quartz and Silica Fibers

The glass-types typically contain about 50 to 78% silica. Silica glass is a purer glass fiber that can be made by treating fiberglass in an acid bath, which removes all impurities without affecting the silica. The final product contains 93 to 99% silica. Quartz is even more pure, and quartz fibers are made from natural quartz crystals that contain 99.9% silica, possessing nearly all the properties of pure solid quartz.

Ordinary fiberglass, high silica and quartz fibers share several characteristics and can be produced in a range of fiber diameters. Roving or yarns and other forms of fibers can be made

from high silica as well as quartz. All matrix materials that accept fiberglass are amenable to high silica and quartz too.

They differ from glass in many factors, however, especially in heat-related properties. Although quartz crystals are commonly available, pure crystals are hard to come by. On the other hand, high silica comes from the same material as glass fibers and is easily accessible. However, quartz makes up for its rarity with its capacity to withstand high temperatures, which silica is incapable of.

Barring this difference, silica and quartz are similar in other respects. They are highly elastic and can be stretched to 1 % of their length before break point. Both silica and quartz are not affected by acid attacks and are resistant to moisture.

Owing to their thermal properties, silica and quartz are the natural choice as fibers in several applications. They have good insulating properties and do not melt at temperatures up to 1600°C. In addition, they have low thermal expansion coefficients which make them withstand high temperatures.

M2.2.2.8 Graphite Fibers

While use of the term carbon for graphite is permissible, there is one basic difference between the two. Elemental analysis of poly-acrylo-nitrile (PAN) base carbon fibers show that they consist of 91 to 94% carbon. But graphite fibers are over 99% carbon. The difference arises from the fact that the fibers are made at different temperatures.

PAN-based carbon cloth or fiber is produced at about 1320°C, while graphite fibers and cloth are graphitized at 1950 to 3000°C.

The properties of graphite remain unchanged even at very high temperatures, but its willingness to react readily with most metals at the fabrication stage or during use at very high temperatures is often a stumbling block, as seen in aluminium matrices when carbides are produced at the interface. These carbides react with moisture with disastrous effects on the composite material. Graphite fibers are some of the stiffest fibers known. The stiffness of the fiber is as high as the graphite content. But a major drawback is that stiffness and strength are inversely proportional to each other.

Forbidding costs make the use of graphite fibers prohibitive. The best glass fibers are far less expensive than the cheapest, lowest quality of graphite, and in **PAN**-base fibers, other raw materials too are equally expensive. The carbonization and graphitization are time-consuming, apart from demanding excessive energy, materials and close controls throughout the process. Cheaper pitch base fibers are now being developed, with greater performance potential and there are possibilities of the increased use of graphite fibers.

M2.2.2.9 Multiphase Fibers

Spoolable filaments made by chemical vapour deposition processes are usually the multi phase variety and they usually comprise materials like boron, silicon and their carbides formed on surface of a very fine filament substrate like carbon or tungsten. They are usually good for high temperature applications, due to their reduced reaction with higher melting temperature of metals than graphite and other metallic fibers. Boron filaments are sought after for structural and intermediate-temperature composites.

A poly-phase fiber is a core-sheath fiber consisting of a poly-crystalline core.

M2.2.3 Mechanical Properties of fibers

Composite materials are not homogeneous. Their properties are dependent on many factors, the most important of which are the type of fibre, quantity of fibre (as volume fraction) and the configuration of the reinforcement. They are generally completely elastic up to failure and exhibit neither a yield point nor a region of plasticity. They tend to have low strain to failure (less than 3%). The resulting area under the stress/strain curve, which represents the work done to failure, is relatively small when compared to many metals.

The properties of composites are dependent on the properties of the fibre and the matrix, the proportion of each and the configuration of the fibres. If all the fibres are aligned in one direction then the composite relatively stiff and strong in that direction, but in the transverse direction it has low modulus and low strength. When a unidirectional composite is tested at a small angle from the fibre axis, there is a considerable reduction in strength. A similar but less significant effect occurs with the tensile modulus, as shown in Figure M2.2.1.

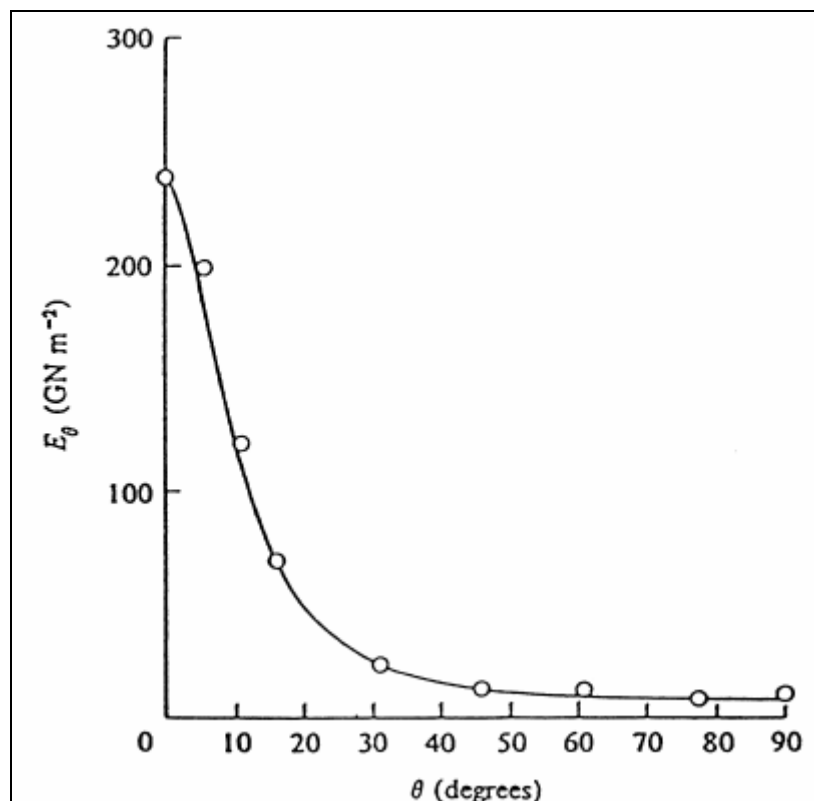


Figure M2.2.1: Theoretical variation in tensile modulus with the angle of load relative to the principal fibre direction (unidirectional carbon fibre reinforced plastic (UD CFRP), fibre volume fraction $V_f = 0.5$)

M2.2.3.1 Fibers

Strength and stiffness

M2.2.3.1.1 Glass fibre reinforced polymer (GFRP)

E glass fibres, which have a modulus of about 70GPa, produce composites with modest moduli. In the case of unidirectional fibres and the highest typical fibre volume fraction of 0.65, a composite has a modulus of about 45GPa and strength of around 1300MPa. At right angles to this, in the transverse direction, the modulus approaches that of the resin itself at about 4GPa and the strength would be 50–100MPa. The unidirectional composites used in the ROBUST Project, manufactured using the vacuum process with prepreg material in an epoxy matrix, had the following properties:

- **Longitudinal tensile modulus:** 36GPa
- **Longitudinal tensile strength:** 750MPa
- **Elongation at break:** 3.1%.

Bidirectional E glass laminates have a typical fibre volume fraction of about 0.4 and a tensile modulus at that volume fraction of about 14GPa. Random laminates (e.g. chopped strand mat) have a typical fibre volume fraction of about 0.2 and a tensile modulus at that volume fraction of about 9GPa. The use of S2 or R glass improves the composite modulus to about 60GPa for unidirectional and 20GPa for woven fabric (bidirectional) constructions. This is at some monetary disadvantage. They are both more expensive than E glass and they are only available in a fairly limited range of material types and resin compatibilities. Probably the most important virtue of S2 and R glass is their high strength, which is considerably higher than E glass.

M2.2.3.1.2 Carbon and graphite fibers

Carbon fibre reinforced plastic (CFRP)

The dominant carbon fibres in current use (typically Toray T700) have a tensile modulus of about 230GPa, a tensile strength of around 5000MPa and a strain-to-failure of 2%. Unidirectional composites produced from them in either an epoxy or vinyl-ester matrix have the following typical properties:

- **Longitudinal tensile modulus:** 155–165GPa
- **Longitudinal tensile strength:** 2500–3000MPa
- **Elongation at break:** 1.2–1.3%

Carbon fibres are available which will give a tensile modulus of about 250GPa in a unidirectional composite, comparing very favourably with steel at about 210GPa. However, as this composite is

unidirectional, it has extremely low modulus in the transverse direction. The principal attributes of carbon fibre composites are their very high specific stiffness (the ratio of modulus/density), excellent fatigue and environmental resistance.

Currently there are various pultruded CFRP plates available commercially for plate bonding applications. The pultruded plates used in the ROBUST Project, as well as the plates manufactured with prepreg materials, possessed a modulus of about 130GPa and a strength of 1500MPa. Pultruded plates now available from other sources typically exploit fibers with superior properties such as Toray T700, resulting in composites with the properties shown above. A financial penalty has to be paid for materials exhibiting properties significantly in excess of these; the strain-to-failure of composites made with them will also be reduced significantly.

Carbon and graphite have substantial capability as reinforcing fibers, with great flexibility in the properties that can be provided. Primary characteristics for reinforcing fibers in polymer matrix composites are high stiffness and strength. The fibers must maintain these characteristics in hostile environments such as elevated temperatures, exposure to common solvents and fluids, and environmental moisture. To be used as part of a primary structure material it should also be available as continuous fiber. These characteristics and requirements have substantial implications for the physical, chemical and mechanical properties of the fiber, which in turn implies processing and acceptance parameters.

Interest in carbon fibers for structural materials was initiated in the late 1950s when synthesized rayons in textile form were carbonized to produce carbon fibers for high temperature missile applications. One of the first distinctions to be made is the difference between carbon and graphite fibers, although the terms are frequently used interchangeably. Background information for these differences is contained in the following sections. The primary purpose of making this distinction here is to alert the reader that users may mean different things when referring to graphite versus carbon fibers.

Carbon and graphite fibers are both based on graphene (hexagonal) layer networks present in carbon. If the graphene layers or planes stack with three dimensional orders the material is defined as graphite. Usually extended time and temperature processing is required to form this order, making graphite fibers more expensive. Because the bonding between planes is weak, disorder frequently occurs such that only the two dimensional ordering within the layers is present. This material is defined as carbon. With this distinction made, it should be understood that while some differences are implied, there is not a single condition which strictly separates carbon from graphite fibers, and even graphite fibers retain some disorder in their structure.

M2.2.3.1.2.1 General material description

Three different precursor materials are commonly used at present to produce carbon fibers: rayon, **Polyacrylonitrile (PAN)**, and isotropic and liquid crystalline pitches. Carbon fibers are made predominately from carbonization of Polyacrylonitrile (PAN). The fibers consist of intermingled fibrils of turbostratic graphite with basal planes tending to align along the fiber axis. This forms an internal structure reminiscent of an onion skin. Pitch fibers may have a different internal structure, more like sheafs or spokes. The highly anisotropic morphology gives

rise to moduli in the range of 200-750 GPa parallel to the fiber long axis, and around 20 GPa in the normal direction. For comparison, single crystal (whisker) of graphite is about 1060 and 3 GPa, respectively, but these properties are not attainable in fiber form. Ultra high modulus fibers can be prepared from liquid-crystalline mesophase pitch; the higher degree of orientation in the precursor translates through to the final carbonized fiber leading to larger and more oriented graphite crystallites.

M2.2.3.1.2.2 Manufacture

The manufacturing process for carbon fiber described below is for the Polyacrylonitrile (PAN) variant, which is one of the most common. Some differences between Polyacrylonitrile (PAN) processing and the pitch and rayon precursors are then described afterwards. The manufacture of Polyacrylonitrile (PAN) based carbon fiber can be broken down into the white fiber and black fiber stages. Most manufacturers consider the details of these processes proprietary.

White fiber

Production of Polyacrylonitrile (PAN) precursor, or white fiber, is a technology in itself. Fairly conventional fiber processes are performed: polymerization, spinning, drawing, and washing. Additional drawing stages may be added in the process. Characteristics of the white fiber influence the processing and results for the black fiber processing.

Black fiber

The black fiber process consists of several steps: oxidation (or thermosetting), pyrolysis (or carbonizing), surface treatment, and sizing. In the oxidation process the Polyacrylonitrile (PAN) fiber is converted to a thermoset from a thermoplastic. For this oxidation process the fiber diameter is limited by waste gas diffusion. In the pyrolysis process, which is performed under an inert atmosphere, most of the non-carbon material is expelled, forming ribbons of carbon aligned with the fiber axis.

In the surface treatment step the fiber may be etched in either gas or liquid phase by oxidizing agents such as chlorine, bromine, nitric acid or chlorates. This improves the wettability for the resin and encourages formation of a strong, durable bond. Some additional improvement through removal of surface flaws may also be realized. This process can be electrolytic. The carbon fibers are often treated with solution of unmodified epoxy resin and/or other products as a size. The sizing prevents fiber abrasion, improves handling, and can provide an epoxy matrix compatible surface.

Carbon fiber differences due to pitch/ Polyacrylonitrile (PAN)/rayon precursors

As a rule PAN precursor can provide higher strength carbon fibers, while pitch can provide higher moduli. Rayon based fibers tend to be less expensive but lower performance. Pitch fiber composites have been prepared with elastic moduli superior to steel and electrical conductivity higher than copper conductor. The shear strengths and impact resistance are degraded, however. Yield for PAN is approximately 50%, but for pitch can be as high as 90%.

M2.2.3.1.2.3 Typical properties of Carbon and Graphite fibers

Typically limitations on the end use for carbon fibers in composite structure depend more on the resin matrix than the fiber. Some exceptions to this are present, however, in which case the oxidative stability, thermal conductivity, coefficient of thermal expansion, or other properties of the fiber must be taken into account. Some key properties for carbon fiber, including cost, are listed in Table M2.2.1 typical values for glass, aramid, and boron are shown for comparison. While some carbon fiber properties are fairly universal, different products from different manufacturers can have substantially different properties. Three of the major manufacturers for the US are Amoco, Hercules and Toray. It should be noted that translation of fiber properties to composite properties is dependent on many factors in addition to rule of mixtures.

	Tensile Modulus, Msi	Tensile Strength, ksi	Density, g/cm ³	Fiber Diameter, micron	Cost, \$/#
Carbon (PAN)	30-50	350-1000	1.75-1.90	4-8	20-100
Carbon (Pitch)	25-110	200-450	1.90-2.15	8-11	40-200
Carbon (Rayon)	6	150	1.6	8-9	5-25
Glass	10-12.5	440-670	2.48-2.62	30	5-40
Aramid	20	410	1.44	--	25-75
Boron	58	730-1000	2.3-2.6	100-200	100-250

Table M2.2.1 Comparison of carbon and other fiber properties

M2.2.3.1.3 Aramid fibers

Aramid fibre reinforced plastic (AFRP)

Unidirectional aramid composites have high tensile strength (1200–1400MPa) and a very low density. This high specific tensile strength is an important attribute which makes them particularly suited to use as tension members. Some aramids exhibit relatively low compressive yield strength of about 230MPa. Thus composites using these fibres must be carefully designed, particularly for compression or bending. This makes them particularly suited to use in tension member applications, but often not suited to bending applications. It is usually the high modulus variants of aramids (e.g. Kevlar 49) which are most commonly used as composite reinforcement, conferring a tensile modulus for unidirectional composites of about 75GPa. This is very similar to aluminium; however, as this is a unidirectional composite the associated transverse modulus is only about 5GPa.

The tensile modulus of unidirectional and bidirectional aramid composites represents a reasonable compromise between the low modulus glass-fibre composites and the much higher carbon fibre composites. Similarly the tensile strength of aramid composites is a compromise between E glass and carbon fibre composites.

In the early 1970's, **Du Pont Company** introduced Kevlar™ aramid, an organic fiber with high specific tensile modulus and strength. This was the first organic fiber to be used as reinforcement in advanced composites. Today this fiber is used in various structural parts including reinforced

plastics, ballistics, tires, ropes, cables, asbestos replacement, coated fabrics, and protective apparel. Aramid fiber is manufactured by extruding a polymer solution through a spinneret. Major forms available from Du Pont are continuous filament yarns, rovings, chopped fiber, pulp, spun-laced sheet, wet-laid papers, thermoplastic impregnated tows, and thermoformable composite sheets.

Important generic properties of aramid fibers are: low density, high tensile strength, high tensile stiffness, low compressive properties (nonlinear), and exceptional toughness characteristics. The density of aramid is 0.052 lb/in^3 (1.44 gm/cm^3). This is about 40% lower than glass and about 20% lower than commonly used carbon. Aramids do not melt and they decompose at about 900°F (500°C). Tensile strength of yarn, measured in twisted configuration, can be varied from 500 - 600 ksi (3.4 - 4.1 GPa) by choosing different types of aramids. The nominal coefficient of thermal expansion is $3 \times 10^{-6} \text{ in/in/F}^\circ$ ($-5 \times 10^{-6} \text{ m/m/C}^\circ$) in the axial direction. Aramid fibers, being aromatic polyamide polymers, have high thermal stability and dielectric and chemical properties. Excellent ballistic performance and general damage tolerance is derived from fiber toughness. Aramid is used, in fabric or composite form, to achieve ballistic protection for humans, armored tanks, military aircraft, and so on.

Composite systems, reinforced with aramid, have excellent vibration-damping characteristics. They resist shattering upon impact. Temperature of use, in composite form with polymer matrix, range from -33 to 390°F (-36 - 200°C), the nominal tensile properties of composites reinforced with aramid are listed in Table M2.2.2 (a) - in thermoset and thermoplastic resin matrix. At 60% fiber volume fraction, composites of epoxy reinforced with aramid fibers have nominal tensile strength (room temperature) of 200 ksi (1.4 GPa) and nominal tensile modulus of 11 Msi (76 GPa). These composites are ductile under compression and flexure. Ultimate strength, under compression or flexure, is lower than glass or carbon composites. Composite systems, reinforced with aramid, are resistant to fatigue and stress rupture. In the system of epoxy reinforced with aramid, under tension/tension fatigue, unidirectional specimens ($V_f \sim 60\%$) survive 3,000,000 cycles at 50% of their ultimate stress. Recently, thermoplastic resin composites reinforced with aramid have been developed. These thermoplastic composite systems have exhibited equivalent mechanical properties compared to similar thermoset systems. In addition, thermoplastic systems provide potential advantages in economical processing, bonding, and repair. A unique thermoformable sheet product, in thermoplastic matrix reinforced with aramid fibers, is available. These composite systems are also used to achieve low coefficient of thermal expansion or high wear resistance. They are non-conductive and exhibit no galvanic reaction with metals. Aramid fibers are available in several forms with different fiber modulus (Table M2.2.2 (b)). KevlarTM29 has the lowest modulus and highest toughness (strain to failure $\sim 4\%$). These fibers are used mostly in ballistics and other soft composite systems such as cut- and slash- resistance protective apparel, ropes, coated fabric, asbestos replacement, pneumatic tires, etc. These are also used for composites where maximum impact and damage tolerance is critical and stiffness is less important. KevlarTM49 is predominantly used in reinforced plastics - both in thermoplastic and thermoset resin systems. It is also used in soft composites like core of fiber optic cable and mechanical rubber good systems (e.g., high pressure flexible hose, radiator hose, power transmission belts, conveyor belts, etc.). An ultra-high modulus Type 149 has been made available recently. It has 40% higher modulus than KevlarTM49. KevlarTM29 is available in fiber yarn sizes and two rovings sizes. KevlarTM49 is available in six yarn and two rovings sizes.

Kevlar™149 is available in three yarn sizes. Yarn sizes range from the very fine 55 denier (30 filaments) to 3000 denier (1300 filaments). Rovings are 4560 denier (3072 filaments) and 7100 denier (5000 filaments). Composite thermoplastic tows, several types of melt-impregnated thermoplastic reinforced with different Kevlar™ yarns and deniers, are also available.

Tensile Property	Units	Thermoset (epoxy)		Thermoplastic (J2)	
		unidirectional	fabric ¹	unidirectional	fabric ¹
Modulus	Msi (GPa)	11 (68.5)	6 (41)	10.5-11.5 (73-79)	5.1-5.8 (35-40)
Strength	ksi (GPa)	200 (1.4)	82 (0.56)	180-200 (1.2-1.4)	77-83 (0.53-0.57)

¹ Normalized from $V_f = 40\%$; fabric style S285

Table M2.2.2 (a) Nominal composite properties reinforced with aramid fiber ($V_f \sim 60\%$).

Aramid composites were first adopted in applications where weight savings were critical - for example, aircraft components, helicopters, space vehicles, and missiles. Armor applications resulted from the superior ballistic and structural performance. In marine recreational industries, light weight, **stiffness**, **vibration damping**, and **damage tolerance** are valued. Composites reinforced with aramids are used in the hulls of canoes, kayaks, and sail and power boats. These same composite attributes have led to use in sports equipment. Composite applications of aramid continue to grow as systems are developed to capitalize on other properties. The stability and frictional properties of aramids at high temperatures have led to brake, clutch, and gasket uses; low **coefficient of thermal expansion** is being used in printed wiring boards; and exceptional wear resistance is being engineered into injection-molded thermoplastic industrial parts. Melt-impregnated thermoplastic composites, reinforced with aramids, offer unique processing advantages - e.g., in-situ consolidation of filament-wound parts. These can be used for manufacturing thick parts where processing is otherwise very difficult.

Tensile Property	Units	Type of Kevlar™		
		29	49	149
Modulus	Msi (GPa)	12 (83)	18 (124)	25 (173)
Strength	ksi (GPa)	525 (3.6)	525-600 (3.6-4.1)	500 (3.4)

Table M2.2.2 (b) Nominal properties of aramid fiber

Aramid fiber is relatively flexible and tough. Thus it can be combined with resins and processed into composites by most of the methods established for glass. Yarns and rovings are used in filament winding, prepreg tape, and in pultrusion. Woven fabric prepreg is the major form used in thermoset composites. Aramid fiber is available in various weights, weave patterns, and constructions; from very thin (0.0002 in., 0.005mm) lightweight (275 gm/m²) to thick (0.026 in., 0.66 mm) heavy (2.8 gm/m²) woven roving. Thermoplastic-impregnated tows can be woven into various types of fabrics to form prepregs. These composites demonstrate good property retention

under hot and humid conditions. Chopped aramid fiber is available in lengths from 6 mm to 100 mm. The shorter lengths are used to reinforce thermoset, thermoplastic, and elastomeric resins in automotive brake and clutch linings, gaskets, and electrical parts. Needle-punched felts and spun yarns for asbestos replacement applications are made from longer fiber staple. A unique very short fiber (0.08 - 0.16 in., 2 - 4 mm) with many attached fibrils is available (aramid pulp). It can provide efficient reinforcement in asbestos replacement uses. Aramid short fibers can be processed into spun-laced and wet-laid papers. These are useful for surfacing veil, thin-printed wiring boards, and gasket material. Uniform dispersion of aramid short fiber in resin formulations is achieved through special mixing methods and equipment. Inherent fiber toughness necessitates special types of tools for cutting fabrics and machining aramid composites.

M2.2.3.1.4 Glass fibres

Glass in the forms used in commerce has been produced by many cultures since the early Etruscan civilization. Glass as a structural material was introduced early in the seventeenth century and became widely used during the twentieth century as the technology for flat pane was perfected. Glass fibrous usage for reinforcement was pioneered in replacement of metals and used for both commercial and military uses with the advent of formulation control and molten material which is die or bushing pulled into continuous filaments. These events lead to a wide range of aerospace and commercial high performance structural applications still in use today.

	%(wt)	E-Glass	S-2 Glass (Nominals)	H _R Glass (B)
Silicon Dioxide (SiO ₂)		52-56 (A)	65	63.5 - 65.0
Aluminum Oxide (Al ₂ O ₃)		12-16 (A)	25	24.0 - 25.5
Boron Oxide (B ₂ O ₃)		5-10 (A)		
Calcium Oxide (CaO)		16-25 (A)		<0.5
Magnesium Oxide (MgO)		0-5 (A)	10	9.5 - 10.5
Lithium Oxide (Li ₂ O)				
Potassium Oxide (K ₂ O)	O.C.	0.0-0.2		
Sodium Oxide (Na ₂ O)	O.C.	0-2		
Titanium Oxide (TiO ₂)	O.C.	0-1.5		
Cerium Oxide (CeO ₂)				
Zirconium Oxide (Zr ₂ O ₂)				
Beryllium Oxide (BeO)				
Iron Oxide (Fe ₂ O ₃)	O.C.	0.0-0.8		
Fluorine (F ₂)	O.C.	0.0-0.1		
Sulfate (SO ₂)				
Alkaline Oxides	PPG	0.5-1.5		
Calcium Fluoride (CAF)	PPG	0.0-0.8		
Finishes/Binders		0.5/3.0		

Table M2.2.3 Typical chemical compositions of glass fiber

M2.2.3.1.4.1 Advantages and disadvantages

For many years glass composites have had a distinct strength to weight advantage. Although the rapid evolution of carbon and aramid fibers has gained advantages, glass composite products have still prevailed in certain applications. Cost per weight or volume, certain armament applications, chemical or galvanic corrosion resistance, electrical properties, and availability of many product forms remain as examples of advantage. Coefficient of thermal expansion and modulus properties compared to carbon composites may be considered as typical disadvantages. When compared to aramid composites, glass has a disadvantage as to tensile properties but an advantage as to ultimate compression, shear properties, and moisture pick-up. Commercial uses for glass products are many-fold. These include filtration devices, thermal and electrical insulation, pressure and fluid vessels, and structural products for automotive and recreation vehicles. Many uses are applicable to military and aerospace products as well. A partial listing would include: asbestos replacement, circuitry, optical devices, radomes, helicopter rotor blades, and ballistic applications. Because of the many product forms, structural applications are limitless to fabricate. If there are limitations, compared to other fibers, they may include low thermal and electrical conductivity or perhaps melting temperatures when compared to carbon fibers.

Typical properties for glass fibers and composite materials reinforced with continuous glass fibers are shown in **Table M2.2.4 (a) to Table M2.2.4 (d)**.

		E	S-2	H _R
Density				
	lb/in ³	0.094	0.089	0.090
	g/cm ³	2.59	2.46	2.49
Tensile Strength				
	ksi	500	665	665
	MPa	34,450	45,818	45,818
Modulus of Elasticity				
	Msi	10.5	12.6	12.6
	GPa	72.35	86.81	86.81
% Ult. Elongation		4.8	5.4	5.4
Dielectric Constant				
73°F (23°C) @ 1 MHZ		6.3-6.7	4.9-5.3	NA

Table M2.2.4 (a). Typical glass fiber electrical properties

	E	S-2	S _R
Coeff. Thermal Expan. 10 ⁶			
in/in/F°	2.8	1.3	
m/m/C°	5.1	2.6	
Softening Point °F (°C)	1530 (832)	1810 (988)	1778 (970.)
Annealing Point °F (°C)	1210 (654)	1510 (821)	1490 (810.)

Table M2.2.4 (b). Typical glass fiber thermal properties

Fluid	E	S-2	S _R
10% H ₂ SO ₄	42	6.8	NA
10% HCL	43	4.4	NA
10% HNO ₃	43	3.8	NA
H ₂ O (Distilled)	0.7	0.7	NA
10% Na OH	29	66	NA
10% KOH	23	66	NA

Conditions: 200°F (96°C) - one week immersion

Table M2.2.4(c) Typical corrosion resistance of glass fibers (Wt. Loss %)

E Glass, Woven 7781 Style	Standard Structural	Dual Purpose Structural/Adhesive
Tensile Strength, ksi (MPa)	63 (430)	48 (330)
Tensile Modulus, Msi (GPa)	3.8 (36)	2.8 (19)
Compressive Strength, ksi (MPa)	60. (410)	50. (340)
Compressive Modulus, Msi (GPa)	3.6 (25)	3.2 (22)
Flexural Strength ksi, (MPa)	80. (550)	65 (450)
Flexural Modulus Msi, (GPa)	3.7 (26)	3.3 (23)
Interlaminar Shear ksi, (MPa)	2.6 (18)	3.8 (26)
Sandwich Peel, lb/in width (N/m width)	N.A.	30. (3.4)
Metal-to-Metal Peel, lb/lin. in. (N/lin. m)	N.A.	55 (6.3)
Specific Gravity gm/cm ³ (lb/in ³)	1.8 (0.065)	1.6 (0.058)
Cured Resin Content % Wt.	33	48

Table M2.2.4 (d) Typical cured epoxy/glass mechanical properties

M2.2.3.1.5 Boron

Elemental boron fiber is formed as a deposition reaction on a hot tungsten wire which is continuously drawn through a reactor containing BCl_3 and H_3 . The tungsten wire substrate also reacts to form tungsten boride in the core. The crystalline structure of the deposited boron is considered amorphous due to its small size ($20\text{\AA}$). Boron is available as a cylindrical fiber in two nominal diameters, 4- and 5.6-mil (0.10 and 0.14 mm), which have a density of 2.57 and 2.49 g/cm^3 (0.0929 and 0.0900 lb/in^3), respectively. Chemical etching of the fiber surface produces a higher strength, but the process is not used commercially.

Boron fiber is unmatched for its combination of strength, stiffness, and density. The tensile modulus and strength of boron fiber are 60×10^6 psi and 0.52×10^6 psi (40 GPa and 3600 MPa). Thermal conductivity and thermal expansion are both low, with a coefficient of thermal expansion of $2.5\text{--}3.0 \times 10^{-6}/\text{F}^\circ$ ($4.5\text{--}5.4 \times 10^{-6}/\text{C}^\circ$). Typical end-use properties are shown in Table M2.2.5. Currently, the cost of boron fiber is approximately an order of magnitude higher than standard carbon fiber.

Available almost exclusively in filament or epoxy matrix prepreg form, boron fiber has been used for aerospace applications requiring high strength and/or stiffness, and for selective reinforcement in sporting goods. The most notable use of this fiber is the stabilizer sections of the F-14 and F-15 military aircraft, dorsal longerons of the B-1B bomber, and the repair of metallic airframe structures. High modulus (HM) or high strength (HS) carbon/epoxy composites can match either the tensile modulus or strength of boron composites at a more economical price, but boron/epoxy composites offer twice the composite strength.

		Value, ksi (MPa)
Moduli	Tensile, longitudinal	30 (207)
	Tensile, transverse	2.7 (19)
Strength	Tensile, longitudinal	192 (1323)
	Tensile, transverse	10.4 (72)
	Compressive, longitudinal	353 (2432)

Table M2.2.5 Typical end-use properties of a unidirectional boron/epoxy laminate ($V_f = 0.5$)

M2.2.3.1.6 Alumina

Continuous polycrystalline alumina fiber is ideally suited for the reinforcement of a variety of materials including plastics, metals, and ceramics. Alumina is prepared in the form of continuous yarn containing a nominal 200 filaments. It is supplied in bobbins containing continuous filament yarn, and alumina/ aluminum and alumina/magnesium plates. Alumina staple is also available for short fiber reinforcement.

Fibers that are more than 99% purity α alumina have excellent chemical resistance, and have higher modulus and temperature capabilities than ceramic fibers containing silica. The high

modulus of 55 Msi (380 GPa) is comparable to that of boron and carbon. The average filament tensile strength is 200 ksi (1.4 GPa) minimum. Since alumina is a good insulator, it can be used in applications where conducting fibers cannot. Nominal properties of alumina are listed in Table M2.2.6 (a). Cost projections for alumina are competitive with carbon.

Alumina, in continuous form, offers many advantages for composite fabrication including ease of handling, the ability to align fibers in desired directions, and **filament winding** capability. The fact that alumina is an electrical insulator combined with its high modulus and compressive strength makes it of interest for polymer matrix composite applications. For example, alumina/epoxy and aramid/epoxy hybrid composites reinforced with alumina and aramid fibers have been fabricated and are of potential interest for radar transparent structures, circuit boards, and antenna supports. Typical properties of unidirectional composites are listed in Table M2.2.6 (b).

Composition	> 99% α -Al ₂ O ₃	Filaments/yarn	200, nominal
Melting Point	3713°F (2045°C)	Tensile Modulus	55 Msi (385 GPa)
Filament Diameter	0.8x10 ⁻³ in. (20μm)	Tensile Strength	200 ksi (1.4 GPa) minimum
Length/Weight	(~4.7 m/gm)	Density	0.14 lb/in ³ (3.9 gm/cc)

Table M2.2.6 (a) Nominal properties of alumina

Moduli		
Tensile, axial		30-32 Msi (210-220 GPa)
Tensile, transverse		20-22 Msi (140-150 GPa)
Shear		7 Msi (50 GPa)
Strength		
Tensile, axial		80 ksi (600 MPa)
Tensile, transverse		26-30 ksi (130-210 MPa)
Shear		12-17 ksi (85-120 GPa)
Fatigue - Axial Endurance Limit		10 ⁷ cycles at 75% of static ultimate (tension-tension, R=0.1, and rotating-bending)
Average Thermal Expansion		
Axial		4.0 $\mu\text{in/in/}^\circ\text{F}$ (7.2 $\mu\text{m/m/}^\circ\text{C}$)
Transverse		11 $\mu\text{in/in/}^\circ\text{F}$ (20 $\mu\text{m/m/}^\circ\text{C}$)
Thermal Conductivity	68-750° (20-400°C)	22-29 Btu/hr-ft-°F (38-50 J/m-s-°C)
Specific Heat	68-750° (20-400°C)	0.19-0.12 Btu/lbm-°F (0.8-0.5 J/gm-°C)
Density		0.12 lbm/in ³ (3.3 gm/cm ³)

Table M2.2.6 (b) Nominal properties of alumina composite ($V_f \sim 50\text{-}55\%$)

M2.2.3.1.7 Silicon carbide

Materials and Processes - The Effects of Variability on Composite Properties

Various super-refractory fibers were first produced in the early 1950's based upon work by the **Arthur D. Little Co.** by various production methods. The primary of these based upon:

1. Evaporation for polycrystalline fiber process.
2. HITCO continuous process for polycrystalline fibers.
3. Vapor deposition of aluminum oxide single crystals.

The most recent advances in the **CVD type process** in use by **AVCO** consist of substrate wires drawn through glass reaction tubes at high temperature.

Silicon carbide fibers are produced with a nominal 0.0055 in. (140 μm) filament diameter and are characteristically found to have high strength, modulus and density. Fiber forms are oriented toward the strengthening of aluminum or titanium alloys for both longitudinal and transverse

properties. Additional forms are also produced as polycrystalline fiber whiskers of varying length and diameters

Several systems for describing the material morphology exist, the alpha and beta forms designated by Thibault and Lindquist being the most common.

Practically all silicon carbide monofilament fibers are currently produced for metal composite reinforcement. Alloys employing aluminum, titanium, and molybdenum have been produced.

General processing for epoxy, bisimide, and polyimide resin can be either via a solvated or solventless film impregnation process, with cure cycles equivalent to those provided for carbon or glass reinforced products. Organic matrix silicon carbide impregnated products may be press, autoclave, or vacuum bag oven cured. Lay-up on tooling proceeds as with carbon or glass composite products with all **bleeding**, **damming**, and **venting** as required for part fabrication. General temperature and pressure ranges for the cure of the selected matrix resins used in silicon carbide products will not adversely affect the **fiber morphology**.

Silicon carbide ceramic composites engineered to provide high service temperatures (in excess of 2640°F or 1450°C) are unique in several thermal properties. The overall thermal resistance is determined by the through conductivity, thermal expansion, thermal shock and creep resistance. Thermal conductivities of silicon carbide ceramics have a range in Btu-in/s-ft²-°F of 0.12 at room temperature to 0.09 at 1470°F (W/m·K of 60 at room temperature to 48 at 800°C). Expansion values range, in percentage of original dimension, from 0.05 at 390°F (200°C) to 1470°F (0.30% at 800°C). The creep resistance of the silicon carbide ceramic will vary as the percentage of intra-granular silicon phase increases. In general, the creep rate is very low when compared to aluminum oxide or zirconium oxide materials. Mechanical properties of silicon carbide materials are shown in Table M2.2.7 (a) and the corrosive weight loss is given in Table M2.2.7 (b). **Fracture toughness** as measured by double **torsion analysis** has reported literature values for K_{Ic} ranging from 0.55 ksi Jm (0.6 MPa m) for monocrystalline SiC/Si to 5.5 ksi Jm (6.0 MPa Jm) for hot pressed SiC ceramics.

Property	Reported Values (ksi) (MPa)		Reference Information
FLEXURAL STRENGTH	100-1000	700-7000	single crystal, 99+% purity (1)
	10-60	70-400	polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered (1)
	5-8	30-60	sintered SiC - graphite composites - epoxy, imide, polyimide matrix. (2)
COMPRESSIVE STRENGTH	500-1000	3000-7000	single crystal, 99+% purity (1)
	10-25	70-170	polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered.(2)
	14-60	97-400	Sintered SiC - graphite composites - epoxy, imide, polyimide matrix. (2)
TENSILE STRENGTH	~20	~140	single crystal, 99+% purity (1)
	5-20	30-140	polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered.(2)
	2.5-25	17-170	sintered SiC - graphite composites - epoxy, imide, polyimide matrix. (2)
MODULUS OF ELASTICITY	~9.5	~66	single crystal, 99+% purity (1)
	~7.0	~48	Polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered.(2)

Table M2.2.7 (a) Material properties of silicon carbide materials

TEST REAGENT	Si/SiC COMPOSITES 12% Si <i>mg/cm²·yr</i>	SiC - NO FREE Si <i>mg/cm²·yr</i>
98% Sulfuric Acid	55	1.8
50% Sodium Hydroxide	complete within days	2.5
53% Hydrofluoric Acid	7.9	< 0.2
70% Nitric Acid	0.5	< 0.2
25% Hydrochloric Acid	0.9	< 0.2

Table M2.2.7 (b) Corrosive weight loss at 212°F (100°C)

M2.2.3.1.8 Quartz

Quartz fiber is very pure (99.95%) fused silica glass fiber. Typical fiber properties are shown in Table M2.2.8 (a). Quartz is produced as continuous strands consisting of 120 or 240 individual filaments of 9 micron nominal diameter. These single strands are twisted and plied into heavier yarns. Quartz fibers are generally coated with an organic binder containing a silane coupling agent which is compatible with many resin systems. Strands for **rovings** are combined into multiple ends without applied twist. These strands are coated with a "direct size" which is compatible with many resins. **Woven fabrics** may be used as woven or may be "scoured" (washed) to remove the nonfunctional components of the binder and some, but not all, of the

silane coupling agent. Following scouring, the fabric may be finished with a variety of silane coupling agent finishes having specific resin compatibility.

Quartz fiber nomenclature is the same as that for E or S glass fibers except that the glass composition is designated by the letter Q as shown in Table M2.2.8 (b). Commonly used quartz fabrics are listed in Table M2.2.8 (c). Quartz rovings are continuous reinforcements formed by combining a number of 300 2/0 zero twist strands. End counts of 8, 12, and 20 are available having yields from 750 to 1875 yards per pound (660 to 264 g/km). Quartz fibers are also available in the form of chopped fiber in cut lengths from 1/8 inch to 2 inches (3 to 50 mm).

Quartz fibers with a filament tensile strength of 850 ksi (5,900 MPa) have the highest strength-to-weight ratio, virtually exceeding all other high temperature materials. The quartz fibers can be used at temperatures much higher than "E" glass or "S" glass fiber with service temperatures up to 1920°F (1050°C) possible. Quartz fibers do not melt or vaporize until the temperature exceeds 3000°F (1650°C), providing potential in ablative applications. Additionally, these fibers retain virtually all of the characteristics and properties of solid quartz.

The quartz fibers are chemically stable. They are not affected by halogens or common acids in the liquid or gaseous state with the exception of hydrofluoric and hot phosphoric acids. Quartz fibers should not be used in environments where strong concentrations of alkalies are present. Quartz fibers, when combined with certain matrix systems, offer potential advantages in stealth application due to their high electrical resistivity properties. Quartz does not form paramagnetic centers, nor does it capture neutrons in high energy applications. These fibers offer a low dielectric constant and loss tangent providing excellent properties as electrical insulators. Typical properties for quartz fibers combined with three different polymer matrix systems are shown in Table M2.2.8 (d) to Table M2.2.8 (f). Quartz products are relatively expensive compared to "E" or "S-2" glass products.

Specific gravity	2.20
Density, lb/in ³	0.0795
g/cm ³	2.20
Tensile strength	
Monofilament, ksi	870
GPa	6.0
Roving, ASTM D2343 Impregnated	
Strand Test -	
Astroquartz II 9779, ksi	530.5
GPa	3.6
Modulus, Msi	10.0
GPa	72.0
Elongation, percent	
<u>Monofilament Tensile Strength x 100</u>	8.7
Modulus	
Thermal	
Coefficient of expansion	
10 ⁻⁶ in/in/°F	0.3
10 ⁻⁶ cm/cm/°C	0.54
Thermal conductivity	
Cal/sec/cm/°C	0.0033
Btu/hr/ft/°F	0.80
Btu/hr/sq ft/in/°F	9.5
Specific heat	
Joules/Kg/°C	7500
Btu/lb/°F	1.80
Electrical	
Dielectric constant, 10 GHz, 75°F (24°C)	3.78
Loss tangent, 10 GHz, 75°F (24°C)	0.0001

Table M2.2.8 (a) Properties of quartz fiber

Strand Number	Number of filaments	Strand Count		Filament Diameter	
		yds/lb	g/km	10 ⁻⁵ in.	μm
QCG 300 1/0	119 ^a	30,000	6.5	45	1.1
QCG 300 2/0	240 ^b	15,000	33	35	0.89
QCG 300 1/2	240 ^a	15,000	33	35	0.89
QCG 300 2/2	480 ^a	7,500	66	35	0.89
QCG 300 2/8	1920 ^a	1,875	264	35	0.89

^aUsed for fabric yarns.
^b Used for roving and fabric yarns.

Table M2.2.8 (b) Quartz continuous strands

Style	Count	Warp Fill	Fill Yarn	Weave	Weight Oz/Sq.Yd.
503	50x50	300 1/2	300 1/2	plain	3.5
507	27x25	300 1/2	300 1/2	plain	2.0
525	50x 50	300 1/0	300 1/0	plain	2.0
527	42x32	300 2/2	300 2/2	plain	5.6
531	68x65	300 1/2	300 1/2	8HS	5.1
557	57x31	300 2/2	300 1/0	crowfoot	5.0
570	38x24	300 2/8	300 2/8	5HS	19.3
572	17x16	300 2/8	300 2/8	plain	9.9
581	57x54	300 2/2	300 2/2	8HS	8.4
593	49x46	300 2/2	300 2/2	5HS	7.5

Table M2.2.8 (c) Construction of woven fabrics for aerospace applications

PROPERTY	Room Temperature		1/2 hr at 350°F (180°C)	
	U.S.	SI	U.S.	SI
Tensile Strength (ksi, MPa)	74.9 - 104	516 - 717	65.4 - 92.2	451 - 636
Tensile Modulus (Msi, GPa)	3.14 - 4.09	21.7 - 28.2	2.83 - 3.67	19.5 - 25.3
Flexural Strength (ksi, MPa)	95.5 - 98.9	658 - 682	53.9 - 75.9	372 - 523
Flexural Modulus (Msi, GPa)	3.27- 3.46	22.5 - 23.8	2.78 - 3.08	19.2 - 21.2
Compressive Strength (ksi, MPa)	66.4 - 72.4	458 - 499	42.6 - 49.9	294 - 344
Compressive Modulus (Msi, GPa)	3.43 - 3.75	23.6 - 25.9	3.10 - 3.40	21.4 - 23.4
Laminate Resin Content (wt%)	33.5 - 32.0			
Specific Gravity (g/cm ³)	1.73 - 1.77			

Table M2.2.8 (d). Typical properties for quartz/epoxy

PROPERTY	Room Temperature		180°F (82°C)	
	U.S.	SI	U.S.	SI
Flexural Strength (ksi,MPa)	129.0	889	111.7	770
Flexural Modulus (Msi,GPa)	4.0	27.6	3.9	26.9
Compressive Strength (ksi,MPa)	88.2	608	77.5	534
Compressive Strength, Wet (ksi,MPa)	76.6	528	70.8	488
Compressive Modulus (Msi,GPa)	4.2	29.0	3.8	26.2
Compressive Modulus, Wet (Msi,GPa)	3.7	25.5	4.0	27.6
Short Beam Strength (ksi,MPa)	13.2	91.0	11.8	81.4
Short Beam Strength, Wet (ksi,MPa)	9.2	63.4	9.3	64.1
Resin Content (wt%)	32.0			
Ply Thickness (in,mm)	0.009	0.23		

Table M2.2.8 (e). Typical properties for quartz/toughened epoxy

PROPERTY	Room Temperature		1/2 Hour at 350°F (177°C)	
	U.S.	SI	U.S.	SI
Tensile Strength (ksi,MPa)	79.1 - 105	545 - 724		
Tensile Modulus (Msi,GPa)	3.9	27		
Flexural Strength (ksi,MPa)	93.7 - 102	646 - 703	62.4 - 68.3	430 - 471
Flexural Modulus (Msi,GPa)	3.2	22	2.6 - 2.8	18 - 19
Compressive Strength (ksi,MPa)	67.0 - 67.4	462 - 465	38.6 - 45.2	266 - 312
Compressive Modulus (Msi,GPa)	3.5 - 3.7	24 - 26	2.8	19
Laminate Resin Content (wt%)	36.2 - 36.2			

Table M2.2.8 (f). Typical properties for quartz/polyimide

M2.2.3.1.9 Ultrahigh molecular weight polyethylene (UHMWPE)

Material Description

Ultrahigh molecular weight polyethylene fiber (UHMWPE) is the generic name for a high performance fiber which is more widely known today by the trade name Spectra, assigned by the major marketer of UHMWPE fiber, Allied Signal Inc. Non-oriented UHMWPE was first synthesized in the mid 1950s. A number of academic and commercial institutions in the United States and Europe worked to develop oriented UHMWPE fiber.

The generally accepted definition of what constitutes "ultrahigh molecular weight" is a molecular weight greater than 3,000,000. The properties of polyethylene depend strongly on the molecular weight and the degree of branching. UHMWPE fiber is a linear polymer and its molecular weight typically varies between 3,000,000 and 6,000,000. This fiber is highly oriented axially and the chains form a highly crystalline structure, between 95-99%, but the crystallinity is not in the form of folded chains as is typically found in thermoplastics. Instead, the chains are fully extended (Figure M2.2.2). The fiber is formed by a gel-spinning process where the polymer is dissolved in order to disentangle the polymer chains. From solution the fibers are then drawn and the molecules become axially aligned to an extremely high degree. The resulting fiber diameter is rather large at 27 microns (for Spectra 1000) compared to other high performance fibers (typical aramid fiber diameter is 12 microns; S-2 glass, 7; carbon fibers, 7).

The cost of UHMWPE relative to other high performance fibers is competitive, ranging from \$16/lb. for lower performance, high denier Spectra 900 products to as much as \$80/lb. for high performance, low denier forms of Spectra 1000.

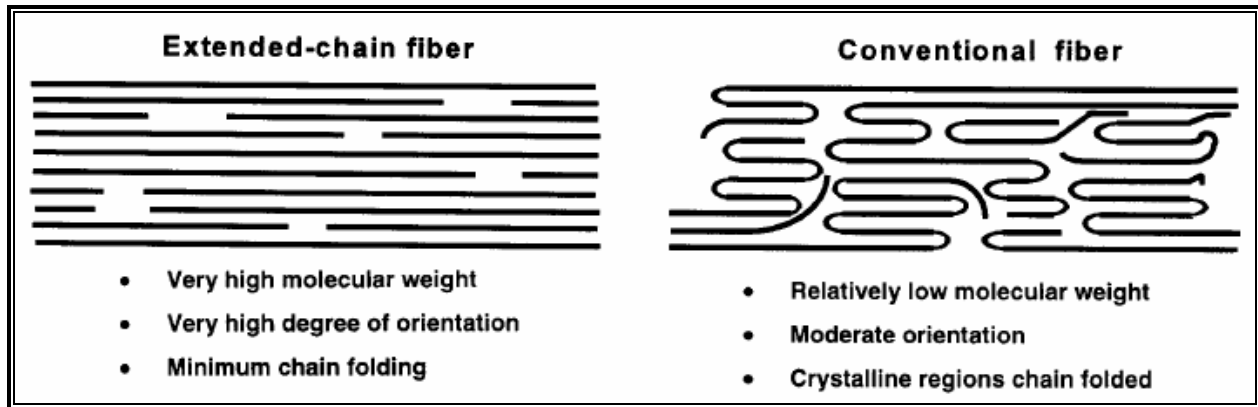


Figure M2.2.2 Schematic representation of a UHMWPE fiber compared to ordinary Polyethylene fiber

Advantages and Limitations

The main drawback to UHMWPE is poor temperature performance. The fiber melting point is 300°F (149°C) and the typical maximum service temperature is 230°F (110°C). Temperature is always a consideration when combining UHMWPE with a thermosetting matrix to form a composite by curing, post curing and/or molding. The upper processing limit of UHMWPE (250°F, 121°C) coincides with the recommended cure temperature of much commercially popular structural resin system. 350°F (177°C) cures are not possible. For all practical purposes UHMWPE can not be used in a high performance thermoplastic matrix due to the required high processing temperatures.

Creep is also a problem, even at room temperature (Figure M2.2.3). For this reason design for long-term constant-load-bearing applications should be carefully considered. Load bearing at elevated temperature will lead to serious creep problems.

When used in a composite UHMWPE bonds poorly to most matrix resins. This is due to its chemical inertness and poor wettability (low surface energy). To improve bonding, gas plasma treatments are often used to modify the fiber surface to make it more compatible with the various resins.

Although its temperature and creep limitations are severe, UHMWPE still has many applications.

Outstanding **impact strength**, even at **cold temperatures**, combined with a 33% weight reduction over aramid makes it an appealing choice in applications where temperature is not an issue. Ballistic protection is one of its major uses. The fiber is commercially successful in ballistic applications, particularly lightweight body armor and riot shield applications for military and law enforcement personnel. The U.S. Army is studying it as an alternative to aramid in the standard issue soldier helmet. Two other ballistic applications are ground vehicle mine blast shields and ultra-lightweight armor for aircraft. For example, the AC-130H Spectre Gunship, flown by the Air Force Special Operations Command, uses UHMWPE armor as its attack mode calls for low altitude (500 feet (150m)) flight. UHMWPE is also used in radomes, which take advantage of a low dielectric constant (2.2) and loss tangent (0.0002). Other applications include

cut-resistant fabrics, heavy lift cargo cables, snow and water skis and other sporting goods, and high-wear applications.

Mechanical properties of composites reinforced with UHMWPE fiber are generally quite good. Tensile strength and modulus, elongation, and toughness compare favorably with other fiber types, especially when normalized on a weight basis (although compression and shear properties do not compare as well).

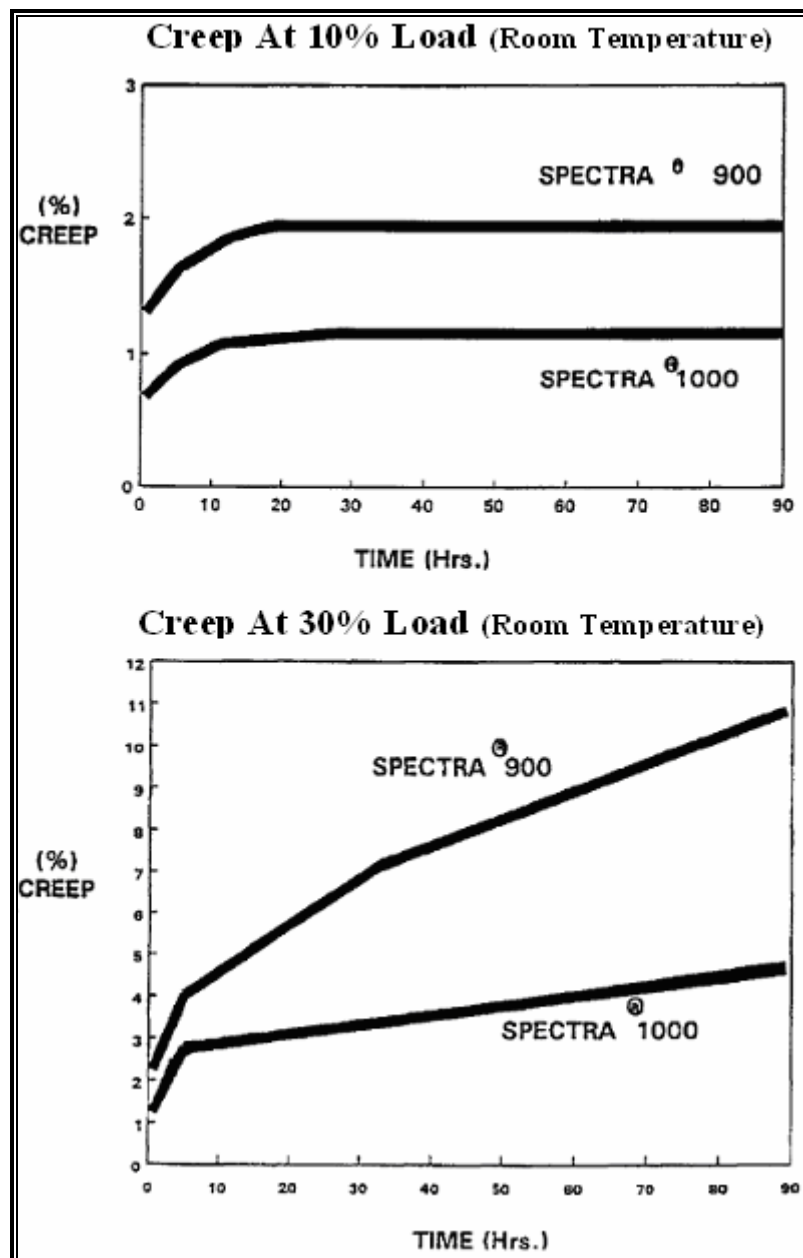


Figure M2.2.3 Room temperature creep properties of Spectra fiber at 10% and 30% loading

UHMWPE is a hydrophobic material and is extremely resistant to moisture effects. In fact, with the exception of its poor high temperature performance, UHMWPE stands up well to the environment, including prolonged exposure to sunlight. It has superior solvent resistance (**chemical inertness**) even to strong acids and bases. Its stability is outstanding in common solvents such as water, gasoline, hydraulic oil and cleaning solvents. The fiber also exhibits good abrasion resistance and self-lubricating properties.

One feature unique to UHMWPE among high performance fibers is that it floats on water. Of the four common high performance fibers, UHMWPE is by far the lightest with a density of 0.97 g/cm³ (0.035 lb/in³) (the density of aramid is 1.4 g/cm³ (0.051 lb/in³); carbon is 1.8 g/cm³ (0.065 lb/in³); S-2 glass is 2.5 g/cm³ (0.091 lb/in³)). UHMWPE is most often compared to aramid fibers. The strength and modulus of this fiber are about the same as aramid, but due to a lower density its specific strength and modulus are higher, reaching nearly as high as today's high modulus carbon fibers on a weight basis. Machining UHMWPE is difficult without special equipment. Generally, the machining requirements of UHMWPE are the same as those of aramid, except that, due to its low melting temperature, UHMWPE can also be cut with a hot knife. Table M2.2.9 lists some key properties of two grades of Spectra fiber.

Property	Spectra [®] 900	Spectra [®] 1000
Filament Diameter, microns(mils)	38(1.5)	27(1.1)
Density, g/cm ³ (lb/in ³)	0.97(0.035)	0.97(0.035)
Tensile Strength, ksi(MPa)	375(2.58)	435(3.00)
Tensile Modulus, Msi(MPa)	17.4(120)	24.8(171)
Spec. Tensile Strength, M-in(M-m)	10.7(0.272)	12.4(0.315)
Spec. Tensile Modulus, M-in(M-m)	486(12.3)	714(18.1)
Elongation, %	3.5	2.7
Dielectric Constant	2.2	2.2
Loss Tangent	0.0002	0.0002

Table M2.2.9 Properties of Spectra 900 and Spectra 1000 Fibers

M2.2.3.2 Resins

M2.2.3.2.1 Overview

Resin is a generic term used to designate the polymer, polymer precursor material, and/or mixture or formulation thereof with various additives or chemically reactive components. The resin, its chemical composition and physical properties, fundamentally affect the processing, fabrication and ultimate properties of composite materials. Variations in the composition, physical state, or morphology of a resin and the presence of impurities or contaminants in a resin may affect handleability and processability, lamina/ laminate properties, and composite material performance and long-term durability. This section describes resin materials used in polymer matrix composites and adhesives, and considers possible sources and consequences of variations

in resin chemistry and composition, as well as the effects of impurities and contaminants, on resin processing characteristics and on resin and composite properties.

M2.2.3.2.2 Epoxy

The term epoxy is a general description of a family of polymers which are based on molecules that contain epoxide groups. An epoxide group is an oxirane structure, a three-member ring with one oxygen and two carbon atoms. Epoxies are polymerizable thermosetting resins containing one or more epoxide groups curable by reaction with amines, acids, amides, alcohols, phenols, acid anhydrides, or mercaptans. The polymers are available in a variety of viscosities from liquid to solid.

Epoxies are used widely in resins for preregs and structural adhesives. The advantages of epoxies are high strength and modulus, low levels of volatiles, excellent adhesion, low shrinkage, good chemical resistance, and ease of processing. Their major disadvantages are brittleness and the reduction of properties in the presence of moisture. The processing or curing of epoxies is slower than polyester resins. The cost of the resin is also higher than the polyesters. Processing techniques include **autoclave molding**, **filament winding**, **press molding**, **vacuum bag molding**, **resin transfer molding**, and **pultrusion**. **Curing temperatures** vary from room temperature to approximately 350°F (180°C). The most common cure temperatures range between 250° and 350°F (120° and 180°C). The use temperatures of the cured structure will also vary with the cure temperature. Higher temperature cures generally yield greater temperature resistance. Cure pressures are generally considered as low **pressure molding** from vacuum to approximately 100 psi (700 kPa).

M2.2.3.2.3 Polyester (thermosetting)

The term thermosetting polyester resin is a general term used for orthophthalic polyester resin or isophthalic polyester resin. Polyester resins are relatively inexpensive and fast processing resins used generally for low-cost applications. In combination with certain fillers, they can exhibit resistance to breakdown under electrical arc and tracking conditions. Isophthalic polyester resins exhibit higher thermal stability, dimensional stability, and creep resistance. In general, for a fiber-reinforced resin system, the advantage of polyester is its low cost and its ability to be processed quickly.

Fiber-reinforced polyesters (FRP) can be processed by many methods. Common processing methods include matched metal molding, wet lay-up, press (vacuum bag) molding, injection molding, filament winding, pultrusion, and autoclaving. Polyesters can be formulated to cure more rapidly than do phenolics during the thermoset molding process. While phenolic processing, for example, is dependent on a time/temperature relationship, polyester processing is primarily dependent on temperature. Depending on the formulation, polyesters can be processed from room temperature to 350°F (180°C). If the proper temperature is applied, a quick cure will occur. Without sufficient heat, the resin/catalyst system will remain plasticized. Compared to epoxies, polyesters process more easily and are much tougher, whereas phenolics are more difficult to process and brittle, but have higher service temperatures.

M2.2.3.2.4 Phenolic

Phenol-formaldehyde resins and their direct precursors were first produced commercially in the early 1900's for use in the commercial market. Urea formaldehyde and melamine-formaldehyde appeared in the 1920 - 1930's as a less expensive alternative for lower temperature use. Phenolics, in general, cure by a condensation route with the off-gassing of water. The resulting matrix is characterized by both chemical and thermal resistance as well as hardness, and low smoke and toxic degradation products.

The phenolic polymers, often called either phenolic resole or novolacs resins are condensation polymers based upon either a reaction of excess formaldehyde with a base catalyst and phenol (resole), or a reaction of excess phenol with an acidic catalyst and formaldehyde (novolac). The basic difference between resoles and novolacs consist of no methylol groups in the novolacs and the resulting need for an extension agent of paraformaldehyde, hexamethylenetetraamine, or additional formaldehyde as a curative. These resins have higher molecular weights and viscosities than either parent material. Consequently, they are optimal for processing parts of unusual conformations and complex curvature. The resins allow either press or autoclave cure and allow relatively high temperature free-standing postcures.

M2.2.3.2.4.1 Resoles

The reaction of phenol and excess formaldehyde in the presence of base is characterized by low molecular-weight prepolymer that are soluble in base and contain a large degree of methylol groups ($-\text{CH}_2\text{OH}$). These prepolymer are processed to a workable viscosity (resites) and then cured to an intractable solid of high crosslink density. Water is lost as a volatile (as much as 10-12% of the resin by weight).

M2.2.3.2.4.2 Novolacs

The second type of phenolic consists of excess phenol reacted in the presence of an acid catalyst with formaldehyde. These prepolymer resins are complex mixtures of low molecular weight materials slightly soluble in acids and exhibiting random methylene ($-\text{CH}_2$) at the ortho-, para-, and ortho-parapositions on the aromatic ring. Unless a large excess of phenol is present, the material will form an infusible resin. The excess phenol used to moderate the processing viscosity can be varied as the application requires. Both water and formaldehyde are volatile products.

M2.2.3.2.5 Bismaleimide

Bismaleimides are a class of thermosetting resins only recently available commercially in prepreg tapes, fabrics, rovings, and **sheet molding compound (SMC)**. Bismaleimide resins, as the term implies, are the maleimide formed from the reaction of a diamine and maleic anhydride. Typically the diamine is aromatic, with **methylenedianiline (MDA)**, the most common by far.

Bismaleimides form useful polymers by homopolymerization or by polymerization with diamines, epoxies, or unsaturated compounds, singular or in mixtures. A wide range of materials

like allyl-, vinyl-, acrylate-, epoxy-, and polyester-, and phenolic-type reactive diluents and resins can be used to tailor the properties of the bismaleimide system. However, attention to the specific components is required for useful polymers.

The physical form of the bismaleimide resin depends on the requirement of the final application. The form can vary from a solid to a pourable liquid at room temperature. For aerospace prepreps, sticky resins are required resulting in proprietary specific formulations.

The advantages of **bismaleimide (BMI) resins** are best discussed in the relation to epoxy resins. Emerging data suggests that BMI's are versatile resins with many applications in the electronic and aerospace industries. Their primary advantage over epoxy resins is their high glass transition temperature, in the 500-600°F range (260-320°C). Glass transition temperatures for high temperature epoxies are generally less than 500°F (260°C). The second advantage of BMI resins is high elongation with the corresponding high service temperature capabilities. While the high temperature epoxies have approximately one percent elongation when cured with **diaminodiphenylsulfone (DDS)**, BMI's can have two-three percent elongation. Thus, bismaleimide resins deliver higher temperature capability and higher toughness providing excellent performance at ambient and elevated temperatures.

The processing of bismaleimide resins are essentially like that of epoxy resins. BMI's are suitable for standard autoclave processing, injection molding, resin transfer molding, and SMC, among others. The processing time of BMI's is similar to epoxies, except that for the additional higher service temperature, a free-standing post-cure is required. The only limitation is that room temperature curing BMI's have not yet been developed.

The cost of current BMI's is generally higher than the high temperature epoxies. The main disadvantage of bismaleimide resins is their recent commercial introduction. This results in few literature sources or authoritative reviews. Additionally, the suppliers are as limited as the types of BMI's. This latter disadvantage is partially offset by the wide variety of suitable comonomers.

M2.2.3.2.6 Polyimides

The polyimide resin family comprises a diverse number of polymers all of which contain an aromatic heterocyclic ring structure.

Other polyimides are synthesized from a variety of cyclic anhydrides or their diacid derivatives through reaction with a diamine. This reaction forms a polyamic acid which then undergoes condensation by the removal of water and/or alcohol.

Polyimide matrix composites excel in high temperature environments where their thermal resistance, oxidative stability, low coefficient of thermal expansion and solvent resistance benefit the design. Their primary uses are circuit boards and hot engine and aerospace structures.

A polyimide may be either a thermoset resin or a thermoplastic. Thermosetting polyimides characteristically have crosslinkable end-caps and/or a rigid polymer backbone. A few

thermoplastic polyimides can become thermoset polymers if a sufficiently high Postcure temperature is employed during part processing. Alternately, partially cured thermoset polyimides containing residual plasticizing solvents can exhibit thermoplastic behavior. Thus, it is difficult to state with certainty that a particular polyimide is indeed a thermoset or thermoplastic. Polyimides, therefore, represent a transition between these two polymer classifications.

Polyimide properties, such as toughness and thermal resistance, are influenced by the degree of crosslinking and chain extension. Molecular weight and crosslink density are determined by the specific end cap group and by the stoichiometry of the anhydride: amine mixture which produces the polyamic acid by stepwise chain growth, after which the polyamic acid is recycled by continued thermal cure to form the final polymer structure. The choice of solvent employed in the resin formulation has a significant impact on crosslinking and chain extension. Solvents such as N-methyl 2-pyrrolidone (NMP), promote chain extension by increasing resin flow, chain mobility and molecular weight prior to formation of a substantial crosslink network. From a practical standpoint, these solvents are beneficial to polymerization, but they are detrimental to part manufacture because of their tendency to cause ply delaminations.

Most polyimide resin monomers are powders. Some bismaleimides are an exception. As a result, solvents are also added to the resin to enable impregnation of unidirectional fiber and woven fabrics. Commonly, a 50:50 by weight mixture is used for fabrics and a 90:10 by weight high solids mixture is used to produce a film for unidirectional fiber and low areal weight fabric prepregs. Solvents are further used to control prepreg handling qualities, such as tack and drape. Most of the solvents are removed in a drying process during impregnation, but total prepreg volatiles contents typically range between 2 and 8% by weight. This includes all volatiles, including those produced by the condensation cure reactions.

Polyimides require high cure temperatures, usually in excess of 550°F (~90°C). Consequently, normal epoxy composite consumable materials are not usable, and steel tooling becomes a necessity. Polyimide bagging and release films, such as Kapton and Upilex, replace the lower cost nylon bagging and polytetrafluoroethylene (PTFE) release films common to epoxy composite processing. Fiberglass fabrics must be used for bleeder and breather materials instead of polyester mat materials.

M2.2.3.2.7 Thermoplastic materials

M2.2.3.2.7.1 Semi-crystalline

Semi-crystalline thermoplastics are so named because a percentage of their volume consists of a crystalline morphology. The remaining volume has a random molecular orientation termed amorphous, the name given to thermoplastics containing no crystalline structure. The total percentage of volume which can become crystalline depends on the polymer. Low density polyethylene, for example, can be as high as 70% crystalline. Semi-crystalline thermoplastics are characterized by the ability of their molecules to form three-dimensionally ordered arrays. This is in contrast to amorphous polymers that contain molecules which are unable to pack in an ordered crystalline structure. A partial list of semi-crystalline thermoplastics includes polyethylene,

polypropylene, polyamides, polyphenylene sulfide, polyetheretherketone (polyetherketoneketone) and polyaryletherketone.

Semi-crystalline thermoplastics can be converted into several physical forms, including films, powders and filaments. Combined with reinforcing fibers, they are available in injection molding compounds, compression-moldable random sheets, unidirectional tapes, towpregs, and woven prepregs. Fibers impregnated include carbon, nickel-coated carbon, aramid, glass, quartz, and others.

Semi-crystalline thermoplastics reinforced with short fibers have been used for over two decades in the injection molding industry. The inherent speed of processing, ability to produce complicated, detailed parts, excellent thermal stability, and corrosion resistance has enabled them to become established in the automotive, electronic, and chemical processing industries.

The combination of long and continuous fibers with higher performance semi-crystalline thermoplastics is a recent development, but these composites have already shown several advantages over existing materials. The chemical stability of the materials provides for unlimited shelf life. Pot life problems and the need for cold storage are eliminated. The semi-crystalline materials usually possess better corrosion and solvent resistance than amorphous polymers, exceeding that of thermosets in some cases. This corrosion resistance is exploited in chemical processing industry equipment. Another benefit of the crystal structure is retention of properties above the glass **transition temperature** (T_g) of the material. These materials may be used in applications above their T_g depending on loading requirements. One example is down-hole oil field sucker rod guides.

Some semi-crystalline thermoplastics possess properties of inherent flame resistance, superior toughness, and good mechanical properties at elevated temperatures and after impact, and low moisture absorption which have led to their use in the aerospace industry in secondary and primary structures. Inherent flame resistance has made these materials good candidates for aircraft interiors and for ship and submarine applications. The superior toughness makes them viable candidates for aircraft leading edges and doors where impact damage resistance is required. Low moisture absorption and low outgassing has stimulated interest in space structures where moisture swelling is a problem. Also nickel-coated carbon/thermoplastic systems are finding uses in EMI shielding applications.

The primary disadvantages of semi-crystalline thermoplastic composites are lack of a design data base, 0° compression properties that are lower than those of 350°F (180°C) epoxy systems, and creep resistance. The creep resistance of semi-crystalline thermoplastics is superior to that of amorphous thermoplastics. Creep resistance in the fiber direction of a laminate is not expected to be a problem.

Processing speed is the primary advantage of thermoplastic materials. Chemical curing of the material does not take place during processing. Therefore, reduced cycle times compared to thermoset composites are experienced. However, thermoplastic prepregs are typically boardy and do not exhibit the tack and drape of thermosets. Forms are available that consist of thermoplastic

and reinforcing fibers interlaced together, known as commingled which are drapeable. The present costs of high performance engineering thermoplastic materials are slightly higher than equivalent performance epoxies, and tooling costs may be higher. However, final part cost may be reduced, due to the decreased processing time. The ability to postform or reprocess molded parts also offers cost saving advantages.

A wide variety of methods and techniques are available for processing semi-crystalline thermoplastics, including stamp molding, thermoforming, autoclave molding, diaphragm forming, roll forming, filament winding, and pultrusion. Semi-crystalline thermoplastics differ from amorphous ones in that the morphology can change based on the time/temperature history of the material during molding. Therefore, the degree of crystallinity can be controlled by controlling the cooling rate. The material must be processed above its melt temperature, which requires temperatures ranging from 500 to 700°F (260 - 370°C) for the higher performance materials. Thermal expansion differences between the tool and the thermoplastic material should be addressed, due to the high processing temperature. The actual pressure required varies with the process, but can be as high as 5000 psi (34 MPa) for stamp molding and as low as 100 psi (0.7 MPa) for thermoforming. Once formed, semi-crystalline thermoplastics can be joined by a variety of methods, including ultrasonic welding, infrared heating, vibration, hot air and gas, resistance heating, and conventional adhesives.

M2.2.3.2.7.2 Amorphous

The majority of thermoplastic polymers is composed of a random molecular orientation and is termed amorphous. The molecules are unable to align themselves in an ordered manner, since they are non-uniform or composed of units which have large side groups. In contrast, semi-crystalline thermoplastics have molecules that form ordered three-dimensional arrays. Some amorphous thermoplastics include polysulfone, polyamide-imide, polyphenylsulfone, polyphenylene sulfide sulfone, polyether sulfone, polystyrene, polyetherimide, and polyarylate.

Amorphous thermoplastics are available in several physical forms, including films, filaments, and powders. Combined with reinforcing fibers, they are also available in injection molding compounds, compressive moldable random sheets, unidirectional tapes, woven preregs, etc. The fibers used are primarily carbon, aramid, and glass.

Amorphous thermoplastics are used in many applications; the specific use depends on the polymer of interest. Their applications are well established in the medical, communication, transportation, chemical processing, electronic, and aerospace industries. The majority of applications use the unfilled and short fiber form. Some uses for the unfilled polymers include cookware, power tools, business machines, corrosion resistant piping, medical instruments, and aircraft canopies. Uses for short-fiber-reinforced forms include printed circuit boards, transmission parts, under-the-hood automotive applications, electrical connections, and jet engine components.

The use of amorphous thermoplastics as matrix materials for continuous fiber reinforced composites is a recent development. The properties of composites have led to their consideration

for primary and secondary aircraft structures, including interior components, flooring, fairings, wing skins, and fuselage sections.

The specific advantages of amorphous thermoplastics depend upon the polymer. Typically, the resins are noted for their processing ease and speed, high temperature capability, good mechanical properties, excellent toughness and impact strength, and chemical stability. The stability results in unlimited shelf life, eliminating the cold storage requirements of thermoset prepregs. Several amorphous thermoplastics also have good electrical properties, low flammability and smoke emission, long term thermal stability, and hydrolytic stability.

Amorphous thermoplastics generally have higher temperature capabilities than semi-crystalline thermoplastics. Polymers with glass transition temperatures as high as 500°F (260°C) are available.

Also, processing is simplified, because the formation of a crystalline structure is avoided, resulting in less shrinkage due to their lower melt viscosities. Amorphous polymers generally have lower solvent and creep resistances and less property retention above the glass transition temperature than semi-crystalline thermoplastics.

The primary advantages of amorphous thermoplastics in continuous fiber reinforced composites are potential low cost process at high production rates, high temperature capability, and good mechanical properties before and after impact, and chemical stability. High temperature capability and retention of mechanical properties after impact have made amorphous thermoplastics attractive to the aerospace industry. A service temperature of 350°F and toughness two to three times that of conventional thermoset polymers is typical. The most significant advantage of thermoplastics is the speed of processing, resulting in lower costs. Typically, cycle times in production are less than for thermosets since no chemical reaction occurs during the forming process.

Amorphous thermoplastics share many of the disadvantages of semi-crystalline thermoplastics, such as a lack of an extensive database and reduced 0° compression properties compared to 350°F (180°C) cure thermosets. Solvent resistance, which is good for semi-crystalline thermoplastics, is a concern for most amorphous ones. They can be attacked to varying degrees, depending on the polymers and solvents of interest. The creep resistance of the polymer is a concern, but should be good for composite forms loaded in the fiber direction. The materials do not have tack and drape as thermosets do; however, some amorphous thermoplastics are available in commingled forms, which are drapable.

The costs of amorphous thermoplastics prepreg used for advanced composites are higher than equivalent performance epoxies. Finished part costs may be lower due to the processing advantages discussed above. Reprocessability of material results in reduced scrap rates, translating into additional cost savings. For example, the same sheet laminate can be thermoformed several times until the desired configuration is achieved. In addition, certain forms can be recycled.

The processes used with continuous reinforced composites include stamp molding, thermoforming, autoclave molding, diaphragm forming, roll forming, filament winding, and pultrusion. The high melting temperatures require process temperatures ranging from 500°F to 700°F (260 to 370°C). Thermal expansion differences between the tool and the thermoplastic material should be addressed due to the high processing temperatures. Forming pressures range from 100 psi i.e., 0.7 MPa (for thermoforming) to 5000 psi i.e., 35 MPa (for stamp molding). Several amorphous thermoplastics that are hygroscopic must be dried before processing. Hot molds are also recommended to increase material flow. The materials can be joined by several methods, including common adhesives, or fusion bonding such as; ultrasonic welding, infrared heating, hot air and gas, and resistance heating. Surface preparation techniques for using adhesives can be different from those for thermosets. Solvent bonding techniques can be used for joining amorphous thermoplastics but not most semi-crystalline thermoplastics.

One important class of amorphous thermoplastic matrices is the condensation cure polyimides. Examples include polyamideimides, such as Torlon, and polyimides having more flexible backbones, such as Avimid RK3B, NR 150B2 and the LaRC polymers developed by NASA. The polyimides represent a transition between thermoset and thermoplastic polymers. Thus, these thermoplastics also have many characteristics typical of epoxy and phenolic thermoset polymers (e.g., excellent solvent resistance and high maximum operating temperature limits).

Due to negligible crosslink density, these polymers impart some toughness to composite laminates and permit limited flow during processing, although this flow is more like the high creep rates exhibited by superplastic metals. Unlike other thermoplastics, these polymers do not produce liquid flows, even under high consolidation pressures. Typical processing conditions for the condensation cure thermoplastics are 550°F (290°C) and greater temperatures with consolidation pressures starting at 200 psi (1.4 MPa).

Many of these thermoplastic polymers have been developed with the intent to rapidly stamp or compression mold structural composites parts at low cost. However, this potential has yet to be realized because of low production volumes, high capital equipment and tooling costs as well as excessive fiber distortion in the formed part. The most successful structural applications of these polymers have utilized autoclave processing to reduce tooling costs and fiber distortion. Other polymers in this class have been developed for use in circuit boards because of their low dielectric constant, low moisture absorption and low coefficient of thermal expansion. In these applications, compression molding had been found to be advantageous and cost effective.

Compared to other thermoplastic polymers, the condensation cure thermoplastics have not found a wide variety of applications. Their processability is very similar to the thermosetting polyimides, and this has been a limiting factor. Volatiles are produced by the condensation reaction, and they cause laminate porosity unless consolidation pressures are high enough to suppress void nucleation and growth. Costly high temperature tooling and consumable materials (e.g., vacuum bags and release films) are also required for part processing. While the toughness and processability of many of these condensation cured thermoplastic polyimides are slightly better than those of competing thermosetting polyimides, their maximum operation temperature limit is somewhat lower. For the present, these thermoplastic polymers are limited to special niche markets which take advantage of their unique performance capabilities.

M2.2.3.2.8 Specialty and emerging resin systems

M2.2.3.2.8.1 Silicone

The silicones are a synthetic resin, composed primarily of organ silicon. The term silicone resin is a general term used for high temperature poly methyl siloxane. Silicone resins are available from a low viscosity liquid to a solid friable resin.

The silicone resin is used where high temperature stability, weatherability, good electrical properties and moisture resistance are required. These excellent properties have allowed the silicone resin to be used in laminates, varnishes, mineral filled molding compounds, and long glass fiber molding compounds. The silicone resin has been used as an impregnant for mica paper, flexible glass tape, glass cloth, and mica products. The **molding compounds** may be processed by conventional methods: injection, compression, and transfer molding. The cure temperature varies from 250°F to 450°F (120°C to 230°C). The cure time varies from 30 minutes to 24 hours, depending upon cure temperature, wall thickness of molded part, and the desired cured properties. In some applications, additional post cure will be required.

Learning unit-3: M2.3

M2.3 Matrix Materials

M2.3.1 Introduction of Matrix Materials:

Although it is undoubtedly true that the high strength of composites is largely due to the fibre reinforcement, the importance of matrix material cannot be underestimated as it provides support for the fibres and assists the fibres in carrying the loads. It also provides stability to the composite material. Resin matrix system acts as a binding agent in a structural component in which the fibres are embedded. When too much resin is used, the part is classified as resin rich. On the other hand if there is too little resin, the part is called resin starved. A resin rich part is more susceptible to cracking due to lack of fibre support, whereas a resin starved part is weaker because of void areas and the fact that fibres are not held together and they are not well supported.

M2.3.1.1 Desired Properties of a Matrix

The needs or desired properties of the matrix which are important for a composite structure are as follows:

- Reduced moisture absorption.
- Low shrinkage.
- Low coefficient of thermal expansion.
- Good flow characteristics so that it penetrates the fibre bundles completely and eliminates voids during the compacting/curing process.

- Reasonable strength, modulus and elongation (elongation should be greater than fibre).
- Must be elastic to transfer load to fibres.
- Strength at elevated temperature (depending on application).
- Low temperature capability (depending on application).
- Excellent chemical resistance (depending on application).
- Should be easily processable into the final composite shape.
- **Dimensional stability** (maintains its shape).

As stated above, the matrix causes the stress to be distributed more evenly between all fibres by causing the fibres to suffer the same strain. The stress is transmitted by shear process, which requires good bonding between fibre and matrix and also high shear strength and modulus for the matrix itself. One of the important properties of cured matrix system is its glass transition temperature (T_g) at which the matrix begins to soften and exhibits a decrease in mechanical properties. The glass transition temperature is not only an important parameter for dimensional stability of a composite part under influence of heat, but it also has effect on most of the physical properties of the matrix system at ambient temperature.

As the load is primarily carried by the fibres, the overall elongation of a composite material is governed by the elongation to failure of the fibres that is usually 1-1.5%. A significant property of the matrix is that it should not crack. The function of the matrix in a composite material will vary depending on how the composite is stressed. For example, in case of compressive loading, the matrix prevents the fibres from **buckling** and is, therefore, a very critical part of the composite since without it; the reinforcement could carry no load. On the contrary, a bundle of fibres could sustain high tensile loads in the direction of the filaments without a matrix. Some of the physical properties of the matrix which influence the behaviour of composites are:

- **Shrinkage** during cure,
- Modulus of elasticity,
- Ultimate elongation,
- Strength (tensile, compressive and shear), and
- **Fracture toughness**.

M2.3.2 General types of Matrix Materials

In general, following general following types of matrix materials are available:

- Thermosetting material;
- Thermoplastic material;
- Carbon;
- Metals;
- Ceramics;
- Glass Matrix.

A thermosetting material is the one which when cured by heat or chemical reaction is changed into an infusible and insoluble material. Thermosetting resins undergo irreversible chemical

cross-linking reaction upon application of heat. On the other hand, thermoplastics do not undergo a chemical reaction on application of heat. They simply melt on application of heat and pressure to form a component. Thermoplastics can be softened and they undergo large and rapid change in viscosity with variation in temperature. Thermoplastics can be repeatedly softened by heating and hardened by cooling.

Some of the significant differences between thermosets and thermoplastics are given below:

Thermosets	Thermoplastics
• Resin cost is low.	• Resin cost is slightly higher.
• Thermosets exhibit moderate shrinkage.	• Shrinkage of thermoplastics is low
• Interlaminar fracture toughness is low.	Interlaminar fracture toughness is high.
• Thermosets exhibit good resistance to fluids and solvents.	• Thermoplastics exhibit poor resistance to fluids and solvents.
• Composite mechanical properties are good.	• Composite mechanical properties are good.
• Prepregability characteristics are excellent.	• Prepregability characteristics are poor.
• Prepreg shelf life and out time are poor.	• Prepreg shelf life and out time are excellent.

Table M3.2.1. Some significant differences between thermosets and thermoplastics

Thermosets	Thermoplastics
• Phenolics & Cyanate ester	• Polypropylene
• Polyesters & Vinyl esters	• Nylon (Polyamide)
• Polyimides	• Poly-ether-imide (PEI)
• Epoxies	• Poly-ether-sulphone (PES)
• Bismaleimide (BMI)	• Poly-ether-ether-ketone (PEEK)

Table M3.2.2 Different types of thermosets and thermoplastic resins

M2.3.2.1 Thermosetting Materials

The major group of materials used today in the aircraft industry contains thermosetting matrix resins.

Thermoset Resin

Polyesters, epoxy and other resins in liquid form contain monomers (consisting of simple molecules), which convert into polymers (complex cross-linked molecules) when the resin is cured. The resulting solid is called **thermosets**, which is tough, hard, insoluble and infusible. The property of infusibility distinguishes thermosets from the thermoplastics. Cure and **polymerization** refer to the chemical reactions that solidify the resin. Curing is accomplished by

heat, pressure and by addition of curing agents at room temperature.

Thermosetting materials can be further divided into two groups depending on how they react to form their network structure. For example, epoxies and polyesters react to form a network structure without formation of a volatile by-product. Phenolics react to form a volatile by-product i.e., water. The fact that some thermosets form volatile by-products means that high pressure laminating techniques must be used to prevent the formation of voids or other defects. Epoxies and polyesters can be cured at atmospheric pressures and also at ambient temperatures.

Polyester matrices have been in use for the longest period in the widest range of structures. Polyesters cure with the addition of a catalyst (usually a peroxide) resulting in an exothermic reaction, which can be initiated at room temperature. The most widely used matrices for advanced composites have been the epoxy resins. These resins cost more than polyesters and do not have the high temperature capability of the Bismaleimides or Polyimides. However, they are widely used due to the following advantages:

- Adhesion to fibres and to resin;
- No by-products formed during cure;
- Low shrinkage during cure;
- High or low strength and flexibility;
- Resistance to solvents and chemicals;
- Resistance to creep and fatigue;
- Wide range of curative options;
- Adjustable curing rate;
- Good electrical properties.

Epoxies do have few inherent disadvantages also, viz.

- Resins and curatives are somewhat toxic in uncured form;
- Moisture absorption resulting into change in dimensions and physical properties;
- Limited to about 200°C (392°F) upper temperature use;
- Difficult to combine toughness and high temperature resistance;
- High thermal coefficient of expansion;
- High degree of smoke liberation in a fire;
- May be sensitive to ultraviolet light degradation;
- Slow curing.

There are two resin systems in common use for higher temperatures, bismaleimides and polyimides. New designs of aircraft demand a 177°C (350°F) operating temperature requirement not met with by other common structural resin systems. Bismaleimides, with higher modulus values and established higher thermal ratings, earned a strong position for use in military aircraft primary structures with recent selection for the F-22 fighter. Bismaleimides offer mechanical properties higher than those of epoxies at elevated temperature resulting in either lower weight or increased safety margins; epoxy-like processing using standard autoclave cure processes; and cost comparable to epoxy parts.

Polyimides are the highest temperature polymers in advanced composite use with a long-term upper temperature limit (T_g) of 232°C (450°F) or 316°C (600°F).

The Cyanate ester resins have shown superior dielectric properties and much lower moisture absorption than any other structural resin for use in composites. The dielectric properties have enabled their use as adhesives in multilayer microwave printed circuit boards and the low moisture absorbance have caused them to be the resin of universal choice for structurally stable spacecraft components. The phenolic triazine resins also have superior elevated temperature properties along with excellent properties at cryogenic temperature. Both Bismaleimide and Cyanate ester resins have been evolved as easy-to-process thermosetting resins qualified for 177°C (350°F) hot-wet service.

Vinyl ester resins are the most recent addition to the family of thermosetting polymers. There are two basic types of vinyl esters having commercial significance, viz., the general-purpose lower molecular weight vinyl esters and the higher heat resistant vinyl esters. General-purpose vinyl esters have excellent mechanical properties and outstanding chemical resistance to acids, bases and many solvents. Heat resistant vinyl esters increase the heat resistance of composites by 17-27°C (30-50°F) over the general-purpose type. This often translates into higher useful operating temperatures for vinyl esters based reinforced plastics even in corrosive environment. Resins of this type are more reactive and more caution is required in fabrication of composite laminates.

M2.3.3.1.1 Typical Properties of Thermosetting Materials

Salient properties of some of the above-referred thermosetting materials are given in the following paras.

M2.3.3.1.2 Phenolics

- Low cost,
- Capability to be B-Staged,
- Excellent high temperature resistance up to 205-260°C (400-500°F),
- Good mechanical strength,
- Dimensional and thermal stability,
- Good laminate properties,
- Hot molding (cold molding very rarely),
- Good fire resistance and very low smoke emission,
- Curing temperature is 175°C (350°F),
- High chemical resistance, and
- Good dielectric properties.

Some of the disadvantages are: by-products are produced during curing, there is high shrinkage on cure, and phenolic laminates are porous.

M2.3.3.1.3 Polyesters

- Low cost,
- Good handling characteristics,
- Low viscosity and versatility,
- Good mechanical strength,
- Good electrical properties,
- Good heat resistance,
- Cold and hot molding,
- Flame resistant with fire proof additive ,and
- Curing temperature is 120°C (250°F).

Some of the disadvantages are: interlaminar shear is less than that of epoxies, lower strength than that of epoxies, fair weatherability, high curing shrinkage, and poor chemical resistance.

M2.3.3.1.4 Vinyl Ester

- Vinyl ester combines inherent toughness with outstanding heat and chemical resistance,
- Corrosion-resistance, and
- Possesses low ester content and low instauration resulting in greater resistance to hydrolysis and less shrinkage during cure.

Some of the disadvantages are: vinyl esters are not as good as epoxy resins with regard to bondability to other surfaces and high cost.

M2.3.3.1.5 Polyimides

- Excellent strength retention for long term in 260-315°C (500-600°F) range and short term in 370°C (700°F) range,
- Excellent electrical properties,
- Excellent mechanical strength,
- Good fire resistance and low smoke emission,
- Hot molding under pressure, and
- Curing temperature is 175°C (350°F) and 315°C (600°F).

Some of the disadvantages are: laminates are porous, volatile by-products are given off during cure, and long post cure is required.

M2.3.3.1.6 Epoxies

- Make an excellent matrix material because of their versatility,
- Good handling characteristics,
- Low shrinkage,
- Excellent adhesive properties,
- Flame resistant,
- Good chemical resistance,

- Good mechanical properties including toughness,
- Offer considerable variety for formulating Prepreg resins,
- Hot molding (cold molding rarely),
- High smoke emission,
- Curing temperature is 120-175°C (250-350°F), and
- No by-products formed during cure.

Some of the disadvantages are: require 4.4°C (40°F) storage and shipment, service temperature is only 93-107°C (200-225°F) and laminate displays light brittleness.

M2.3.3.1.7 Bismaleimide

- Superior to epoxy in maximum hot-wet use temperature.
- In comparison to conventional epoxies, bismaleimides have higher temperature resistance.
- Damage tolerance is generally comparable to that of commercial aerospace epoxy resins.

One factor that limits wider use of Bismaleimide is that they require higher curing temperatures than used for epoxies.

M2.3.3.2 Thermoplastic Resin

As stated earlier, thermoplastics can be repeatedly softened by heating, and hardened by cooling. Thermoplastics possess several advantages over the thermosets, one of the most important being that they do not need storing under refrigeration. They also possess improved damage tolerance, environmental resistance, fire resistance, recyclability and potential for fast processing. Primary reason for the use of thermoplastics is their cost effective processing. Increased use for thermoplastics is also due to three different reasons, viz.

- First - Processing can be faster than that of thermoset composites since no curing reaction is required. Thermoplastic composites require only heating, shaping and cooling.
- Second - The properties are attractive, in particular, high delamination resistance and damage tolerance, low moisture absorption and the excellent chemical resistance of semi-crystalline polymers.
- Third- In the light of environmental concerns, thermoplastic composites offer other advantages also. They have low toxicity since they do not contain reactive chemicals (therefore storage life is infinite).

Because it is possible to remelt and dissolve thermoplastics, their composites are also easily recycled or combined with other recycled materials in the market for molding compounds. Since the release of gases during processing and inherent brittleness is serious disadvantage of some thermoset resins, thermoplastic composites are of great interest. Thermoplastics usually require high temperature and pressure during processing and generally lack good solvent resistance. Process conditions for high performance thermoplastics are temperature in the range of 300 to 400°C (570 to 750°F) and pressure between atmospheric pressure for thermofolding process to 20 times the atmospheric pressure for high performance press forming. Due to their high strains

to failure, thermoplastics are the only matrices currently available that are suited to thermo-forming and other forms of rapid manufacture.

Thermo-loading is the most straight forward thermoplastic forming technique where a straight line is heated and folded. The process is used in volume applications like aircraft floor boards. Thermofolding operations can be carried out on solid laminate materials as well as on sandwich panels.

Press Forming process for thermoplastic composites is related to that used for metals, the difference being that the blank material is heated to a high temperature and processed within a very short time span. Applications for press forming are reinforcement ribs.

To date, applications of thermoplastic composites have ranged from small, simple, structural details such as ribs or spars up to relatively large structures. Table M3.2.3 given below lists some of these applications in aircraft industry.

Polymer Type	Applications
• PEEK	• Airbus A320 vertical stabilizer brackets • EH-101 helicopter floor • F-117 rudder assembly • F-22 weapons bay doors • F-22 access covers • OH-58d helicopter horizontal stabilizer
• Poly-phenylene-sulphide	• Airbus A320-200 rudder nose ribs • Airbus A340 aileon ribs • Airbus A340-500/600 inboard wing leading edge assemblies • Airbus A340-500/600 inboard wing access panels • Airbus A340-500/600 keel beam connecting angles • Airbus A340-500/600 keel beam ribs • AirbusA340-500/600pylon panels • Fokker50 main landing gear door
• PEI	• 737 smoke detector pans • 737/757 galleys • 747. stowage bins • 767 aircraft acoustical tiles • 767andotherBoeingaircraftbrackets • AirbusA320 bulk cargo floor sandwich structural Panels • Airbus A330 lower wing fairings • A3XX main stair case (developmental) • Beluga heavy duty entrance floor panel • Dornier 328 landing flap ribs

	• Dornier 328 ice protection plates • Fokker 50 ice protection plates • Fokker 50 trailing edge wing shroud skins • Fokker 70/100 structural floor panels • Gulfstream G-V structural floor panels • Gulfstream IV and V rudder ribs • Gulfstream IV and V rudder trailing edges • Learjet air steps • Galleys on most commercial aircraft
--	--

Table M3.2.3 Applications in aircraft industry

Amongst the thermoplastics, polypropylene and polyamides are used in applications where moderate temperatures are experienced. On the other hand, **poly-ether-imide (PEI)**, **poly-ether-sulphone (PES)** and **PEEK** are used in applications where temperature requirements are comparatively high. Characteristic temperatures of these thermoplastics along with their mechanical properties are given in Table M3.2.4:

Thermo-plastic	T _g ° C	T _m ° C	Processing Temperature (° C)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Fracture Toughness (kJ/m ²)
Poly-propylene	-10	165	200 - 240	1.1 – 1.6	30 - 40	-
Poly-amide	55	265	270 - 320	2.5 – 3.8	50 – 80	-
PEEK	143	343	380 – 400	3.1 – 3.8	90 – 100	4.0
PES	220	None	300 - 320	2.6	80	1.9
PEI	217	None	335 - 420	3.0	105	3.3

Table M3.2.4 Characteristic temperatures of these thermoplastics along with their mechanical properties

As indicated above, thermoplastics with low T_g such as polypropylene and Polyamides have lower modulus and strength. However, their fracture toughness is higher and valid data is difficult to obtain. Thermoplastics with continuous use temperature above 150°C (302°F) are of particular interest since they perform better than epoxies. Table M3.2.5 gives the temperature T_g and the heat deflection temperature (HDT) for various thermoplastics. HDT is the temperature at which a critical deflection of the sample is obtained. HDT is determined by subjecting the material to static load (typically 1.8 MPa) and slowly increasing the temperature till critical deflection takes place.

Thermo-plastic	Structure	T _g (° C)	HDT (° C)	Variation of HDT
PES	Amorphous	220	203	Below T _g
Polyamide	Amorphous	217	200	Below T _g
PEEK	Crystalline	-10	60	Above T _g

PES	Crystalline	55	75	Above T _g
PEI	Crystalline	143	160	Above T _g

Table M3.2.5 Variation of the heat deflection temperature (HDT) with respect to temperature T_g for various thermoplastics

In crystalline thermoplastics, HDT is some what higher than T_g. On the other hand, HDT is below T_g for amorphous thermoplastics. Creep effects in thermoplastics are very strong close to and above T_g. For this reason, the maximum temperature for continuous service under significant load is unlikely to exceed a temperature of 20°C (68°F) below T_g for crystalline thermoplastics. The primary advantage of crystallinity is, therefore, chemical resistance. Table M3.2.6 shows that, the crystalline thermoplastics have better chemical resistance than the amorphous ones.

Material	Hydraulic Fluid	Chlorinated Hydro-carbons	Ketones	Esters	H ₂ O absorption (%)
Polyamide	-	No effect	No effect	No effect	8
PEEK	No effect	No effect	No effect	No effect	0.5
PES	Absorbed	Dissolved	Absorbed	Absorbed	0.3
PEI	No effect	Dissolved	Absorbed	Absorbed	1.2

Table M3.2.6 Comparison of chemical resistance Crystalline-thermoplastics with the amorphous- thermoplastics

Due to the above advantages, PEEK is a widely used thermoplastic. As stated above, it possesses glass transition temperature of 143°C (290°F). Above this temperature, as expected, there is a drop in mechanical properties but it maintains useful properties up to its melting point of 343°C (650°F). The polymer can be reinforced to further improve properties and maintain them up to a higher temperature. Glass or carbon fibres are the commonly used reinforcements. Some of the significant properties of PEEK are as follows:

- Retention of useful mechanical properties at temperatures up to 315°C (600°F).
- PEEK exhibits a high fatigue resistance. It is also resistant to thermal fatigue when the temperature cycle is less than 150°C (300°F).
- PEEK has higher impact strength as compared to other thermoplastics but lower than most metals.
- Although there is drop in mechanical properties after glass transition temperature, PEEK is significantly stronger than most of other thermoplastics at higher temperatures.
- Many thermoplastics are vulnerable to continuously applied loads as they are susceptible to creep. PEEK exhibits higher creep over a wide range of temperature.
- Fracture toughness of PEEK is about 50-100 times higher than epoxies.
- It exhibits low water absorption characteristics, which is less than 0.5% at 23°C (73°F) compared to 4-5% for conventional aerospace epoxies.
- It offers resistance to a wide range of process chemicals.
- PEEK offers good resistance to wear and chemicals.
- It shows good resistance to gamma radiation thereby offering its use as wire covering material for control cabling within the containment area of nuclear reactors.

One of the major advantages of using thermoplastics is their ability to produce parts to finished shape and tolerance. The most common processing technique employed for thermoplastics is injection molding. However, for larger parts and short production, compression molding has proved cost effective. It is frequently possible to produce thermoplastic parts, which function more efficiently than conventionally manufactured parts. By using a thermoplastic, which can be molded to almost any shape, it is possible to produce parts to the optimum design in a single step.

M2.3.3.3 Carbon matrices

Carbon fibre reinforced carbon is a high strength composite material, which is also resistant to high temperature in a non-oxidizing atmosphere. It is composed of a carbon matrix into which reinforcing carbon fibres are embedded. Such a material was first used under extreme thermal and mechanical loads in space technology. The criteria for selection of carbon-carbon composites as a thermal protection system are based on the following requirements:

- Maintenance of reproducible strength levels at 1650°C (3002°F).
- Sufficient stiffness to resist flight loads and large thermal gradients.
- Low coefficient of thermal expansion to minimize induced thermal stresses.
- Tolerance to impact damage.

Carbon-carbon composites are used in many applications due to their following properties:

- Low specific weight.
- High heat absorption capacity.
- Resistance to **thermal shock**.
- High resistance to damage.
- Exceptional frictional properties at high energy levels.
- Resistance to high temperatures.
- Chemical inertness.

The disadvantages of carbon-carbon composites are the lack of resistance to oxidation at temperatures in excess of 500°C (930°F) and economic problems namely long manufacturing time and high production cost.

To allow the use of carbon-carbon composites in an oxidizing atmosphere, they must be compounded with materials that produce oxidation protective coatings through thermo-chemical reaction with oxygen above 2000°C (3630°F).

Important areas of use of carbon-carbon composites are aircraft brakes, brake system for high-speed trains and racing cars. Its application as braking material is due to high-energy absorption capacity, low specific weight and the fact that it does not contain any environmentally harmful elements like asbestos. Some other examples of its use include heavy duty clutches, tools for high temperature production of alloys like titanium, etc.

There are two production methods to obtain a carbon matrix reinforced with carbon fibres.

1. Chemical vapour impregnation - where a preform is compressed by deposition of carbon from a gaseous phase.
2. The liquid phase impregnation - where a carbon preform is compressed by means of multiple impregnations with resin and intermediate carbonization steps.

Carbon-Carbon Brakes:

As we know, conventional aircraft landing gear brakes are made up of three principal parts:

1. A torque tube,
2. A loading system for the heat sink, and
3. A heat sink.

The heat sink is made of **rotors** and **stators**. The stators are located around the torque tube while the rotors are fitted to the wheel. The object of the heat sink is to transform kinetic energy to thermal energy through the friction between stators and rotors. Consequently, the performance of brakes depends almost completely upon the heat sink material. The material, which can be used for a heat sink, should have the following properties:

- Very high specific heat - the higher the specific heat, the greater the amount of kinetic energy absorbed and better will be the brake efficiency.
- Good mechanical properties at high temperature - since the temperature of the heat sink can be very high, the mechanical properties of the rotors and stators should stay good enough so as to ensure a good brake torque transmission.
- Good resistance to thermal shock - at the beginning of the braking, the heat sink material is very cold and within a few seconds reaches a very high temperature due to large amount of absorbed energy. Therefore, the heat sink material should have good resistance to thermal shock.
- Good frictional characteristics at high temperatures - the brake torque should stay as smooth as possible all along the braking process- even at the end when the temperature is very high.
- Low thermal expansion to avoid deformation.
- As light as possible so as to save on weight.

Due to the above mentioned properties of these composites, carbon-carbon brakes are able to meet the brake requirements in normal and overweight landing conditions and also during rejected take-offs. The performance of carbon-carbon brakes, therefore, is superior to that of brakes made of conventional materials. In case of a normal landing, the maximum temperature allowed is limited by the metallic parts, which are in the heat sink environment. They must not be damaged if we want to reuse the brake, which is the case after normal landing. In case of rejected take-off, the only requirement is to stop the aircraft and, therefore, the maximum allowed temperature is dependent on the heat sink material. The limit for steel is about 1000°C (1830°F) beyond which it exhibit mechanical frictional properties will no longer. Steel brakes absorb, rather than release, a great deal of heat. This eventually melt the brakes and poses safety

problems. The brakes can overheat and leave an aircraft stranded on the runway after landing. On the other hand, carbon can handle 3-4 times the amount of heat, as compared to steel, without melting. For carbon-carbon, the maximum allowed temperature is about 2000°C (3630°F). Thus if carbon-carbon brakes are used in place of steel brakes, we will have, for the same weight, a much more efficient and secure system or in other words for the same efficiency, the system will be much lighter.

Disk brakes for aircraft are the representation of a heat sink. They are composed of a number of disks, half of which are keyed to the non-rotating brake mechanism (stators), and the other half rotate with the wheel to which they are keyed (rotors). Braking is accomplished by forcing the disks together, at which time friction is converted into heat that must be dissipated. This requires a material that is resistant to thermal shock, stable at very high temperatures, and has low thermal expansion as well as good thermal conductivity. In addition, the material should have a friction coefficient of about 0.3 to 0.5 to ensure good stopping performance.

Carbon-carbon composites have all of these properties, which provide nearly four times the stopping power of copper or steel brakes. In conclusion, the advantages of the carbon-carbon brakes may be summarized as:

- Smooth braking,
- Lighter brake (carbon brakes weigh approximately 1/3rd less than the steel brakes),
- High efficiency brake,
- Increased life (nearly 2-3 times), and
- Cost effectiveness.

Carbon-carbon brakes are presently being used in number of aircraft viz. Concord, Airbus and Boeing family, etc. As an example, the weight saving by using carbon-carbon brakes on Boeing family of aircraft is as follows:

Aircraft	Weight Saving (Kg)
B-747	635
B-757	272
B-767	408

Life projection of carbon-carbon brakes and steel brakes is as follows:

Aircraft	Estimated Loading	
	Carbon-carbon	Steel
B-747	2000	800
B-757	3000	1500
B-767	3000	1500

Other application of carbon-carbon composites is the one piece, bladed turbine rotor that is coated to prevent oxidation. The rotor offers higher temperature performance without cooling. Gas turbine engine applications using carbon-carbon composites include exhaust nozzle flaps and seals, augmenters, combustors and acoustic panels. Carbon-carbon composite are being used

in products such as the nozzle in the **F-100 jet engine afterburner**, turbine wheels operating at a speed more than 40000 rpm, leading edges for missiles and for the space shuttle. Pushing the state of the art in carbon-carbon composite is the piston for internal combustion engines. The carbon-carbon pistons have exhibited reduction in weight and increase in mechanical and thermal efficiencies of the engine. The carbon-carbon piston concept features a low piston-to-cylinder wall clearance. Carbon-carbon material maintains its strength at elevated temperatures. The piston allowing to operate at higher temperatures and pressures (than those of a comparable metal piston). The high emittance and low thermal conductivity of the carbon-carbon piston should improve the thermal efficiency of the engine because less heat energy is lost to the piston and cooling system. The elimination of rings reduces friction, thus improving mechanical efficiency. Besides being lighter than conventional pistons, the carbon-carbon piston can produce cascading effects that could reduce weight of other reciprocating components such as the crankshaft, connecting rods, flywheels and balances, thus improving specific engine performance.

M2.3.3.4 Metallic Matrices

Metallic matrices are essential constituents for fabrication of **Metal Matrix Composites (MMC)**, which have potential for structural materials at high temperatures. Metal matrix has the advantage over polymeric matrix in applications requiring a long-term resistance to severe environments, such as high temperature. The yield strength and modulus of most metals are higher than those for polymers, which is an important consideration for applications requiring high transverse strength and modulus as well as compressive strength for the composite. Another advantage of using metals is that they can be plastically deformed and strengthened by a variety of thermal and mechanical treatments. However, metals have a number of disadvantages, namely, they have high specific gravities, high melting points (therefore, high process temperatures), and a tendency toward corrosion at the fibre/matrix interface.

While a variety of matrix materials has been used for making MMCs, the major emphasis has been on the development of lighter MMCs using aluminum and titanium alloys, due to the significant potential of improvement in the thrust to-weight ratio for the aerospace, space and automotive engines.

Aluminium alloy matrix composites are suited to applications below the temperatures of 400°C (750°F). For higher temperatures, titanium based alloys offer promise as matrices. For applications in excess of 900°C (1650°F), fibre reinforced super alloys are used with most promising reinforcements being tungsten alloy wires. In spite of their high density, such composites are being considered for turbine blades and vanes in aircraft and rocket motors. Compared to un-reinforced super alloys, they exhibit improved creep and fatigue strength as well as higher thermal conductivity.

Aluminium and titanium have comparatively low specific gravities and are available in a variety of alloy forms. Although magnesium is even lighter, its great affinity toward oxygen promotes atmospheric corrosion and makes it less suitable for many applications. Beryllium is the lightest of all structural metals and has a tensile modulus higher than that of steel. However, it suffers from extreme brittleness, which is the reason for its exclusion as a potential matrix material.

Nickel-and cobalt-based super alloys have also been used as matrix, however, the alloying elements in these materials tend to accentuate the oxidation of fibres at elevated temperatures.

Aluminium and its alloys have attracted the most attention as matrix material in metal matrix composites. Commercially, pure aluminium has been used for its good corrosion resistance. Aluminium alloys, such as 201, 6061, and 1100, have been used for their higher tensile strength to weight ratios. Carbon fibre is used with aluminium alloys, however, at typical fabrication temperatures of 500°C (932°F) or higher, carbon reacts with aluminium to form aluminium carbide, which severely degrades the mechanical properties of the composite.

Protective coatings of either titanium boride or sodium are used on carbon fibres to reduce the problem of fibre degradation as well as to improve their wetting with the aluminium alloy matrix. Carbon fibre reinforced aluminium composites are inherently prone to galvanic corrosion, in which carbon fibres act as a cathode owing to a corrosion potential of one volt higher than that of aluminium. A more common reinforcement for aluminium alloys is Silicon Carbide (SiC).

Titanium alloys that are most useful in metal matrix composites are alpha, beta alloys (e.g. Ti-6Al-4V) and metastable beta alloys (e.g. Ti-10V-2Fe-3Al). These titanium alloys have higher tensile strength to weight ratios as well as better strength retention at 400-500°C (752-932°F) over those of aluminium alloys. The thermal expansion coefficient of titanium alloys is closer to those for reinforcing fibres, which reduces the thermal mismatch between them. One of the problems with titanium alloys is their high reactivity with boron fibres at normal fabrication temperatures. **Borsic** (boron fibres coated with silicon carbide) and SiC fibres

Show less reactivity with titanium. Improved tensile strength retention is obtained by coating boron and SiC fibres with carbon-rich layers.

Continuous silicon carbide fibre reinforced metals have been successfully applied on aerospace development programs fulfilling primary design objective of high specific strength over conventional monolithic materials. The high specific strength of silicon carbide metal matrix composites has generated significant interest for the aircraft industry. The principal areas of interest are for high performance structures such as aircraft, missiles and engines. Some of the materials in this category under consideration are:

- Silicon carbide/aluminium - Development of missile body casings. Wing structural elements
- Silicon carbide/titanium - Drive shaft for core of the engine requiring increased stiffness and increased critical vibratory speed ranges. Disks for turbine engine. Hollow fan blades.
- Silicon carbide/Copper - For high temperature missile application
- Silicon carbide/bronze - Propellers for naval application

MMC production technology is complicated and requires satisfaction of the following conditions, of which the most significant are as follows:

- Maintaining the reinforcing fibres strength.
- Ensuring a strong bond of fibres with matrices and between the matrix layers.
- Providing the correct fibre length, greater than the critical length.

- Even distribution of fibres in the matrix.
- Orientation of fibres in the direction of the applied load.
- Achieving the required shape and dimensions of the MMC.
- Obtaining MMC strength reasonably near to theoretical.

M2.3.3.5 Ceramic Matrices

While ceramic matrix composites are still in the early stages of component design, fabrication and testing, these materials, with their damage' tolerant mechanical behaviour, are considered as prime candidates for application of futuristic aircraft gas turbine engines. The selection of matrix materials for ceramic composites is strongly influenced by thermal stability and processing considerations. These include oxides, carbides, nitrides, borides and **silicides**. All these materials have melting temperatures above 1600°C (2912°F).

M2.3.3.6 Curing of Resins

Thermoset resin like polyester is cured by adding a catalyst, which causes a chemical reaction without changing its own composition. The catalyst initiates the chemical reaction of the unsaturated polyester and monomer ingredient from liquid to a solid state. When used as a curing agent, catalysts are referred to as catalytic hardeners. Proper care is required to be taken while handling the catalysts as they can cause skin burning and permanent eye damage.

Epoxy resin is cured by adding hardener. Unlike the catalytic hardeners used for curing polyester resin, epoxy resin hardener contains monomers, which contribute to the curing reaction. Proper care is required to be taken while handling the epoxy resin liquids and hardeners as they give off potentially harmful vapour causing skin rashes.

After curing, low shrinkage is desirable in order to minimize in-built stressing and distortion of the fibres and matrix. Desirable qualities for a matrix are that it should be tough, durable and thermally stable over a wide range of temperatures and that it should resist cracking, chemical attack, ultra violet light and moisture.

M2.3.3.6.1 Ingredients and Additives used in Manufacturing of Resins

Manufacturers of all types of resins use various ingredients and additives, in different proportions, to give their resins differing properties and characteristics suited to particular applications. Some general classes of additives used are as follows:

M2.3.3.6.1.1 Catalysts, Promoters, Inhibitors

In polyesters, the most important additive is catalyst or initiator. Typically, organic peroxide such as SMEKP (Methyl Ethyl Ketone Peroxide) is used for room temperature cured processes, or benzoyl peroxide is added to the resin for heat cured molding. When triggered by heat, or used in conjunction with a promoter (such as cobalt naphthenate), peroxides convert to a reactive state (exhibiting free radicals), causing the unsaturated resin to react (cross-link) and become solid. Some additives such as TBC (Tertiary Butyl Catechol) are used to slow the rate of reaction and

are called inhibitors. They are used in polyester resins to extend their shelf life. Accelerators such as DMA (Dimethyl Aniline) speed up curing process.

M2.3.3.6.1.2 Additives and Modifiers

A wide variety of additives are used in composites to modify materials properties and tailor the laminates performance. Although these materials are generally used in relatively low quantity by weight compared to resins, reinforcements and fillers, they perform critical functions. Additive used in thermoset and thermoplastic composites exhibits the following properties:

- **Low shrink/low profile** - When parts with smooth surfaces are required, a special thermoplastic resin, which moderates resin shrinkage, can be added to thermoset resins.
- **Fire resistance** –Combustion resistance is improved by proper choice of resin, use of fillers or flame retardant additives. Included in this category are materials containing antimony trioxide, bromine, chlorine, borate and phosphorus.
- **Air release**- Most laminating resins, gel coats and other polyester resins might entrap air during processing and application. This can cause air voids and improper fibre wet-out. Air release additives are used to reduce such air entrapment and to enhance fibre wet-out.
- **Emission control** - In open mold applications, styrene emission suppressants are used to lower emissions for air quality compliance.
- **Viscosity control**-In many composite types, it is critical to have a low, workable viscosity during production. Lower viscosity in such filled systems is usually achieved by use of wetting and dispersing additives. These additives facilitate the wet-out and dispersion of fillers resulting in lower viscosity.
- **Electrical conductivity**- Most composites do not conduct electricity. It is possible to obtain a degree of electrical conductivity by the addition of metal, carbon particles or conductive fibres. Electromagnetic interference shielding can be achieved by incorporating conductive materials.
- **Toughness**- Toughness can be enhanced by the addition of reinforcements. It can also be improved by special additives such as certain rubber or other **elastomeric** materials.
- **Antioxidants** - Plastics are sometimes modified with antioxidants, which retard or inhibit polymer oxidation and the resulting degradation of the polymer.
- **Antistatic agents** – Antistatic agents are added to polymers to reduce their tendency to attract electrical charge. Control of static electricity is essential in processing and handling operation of certain plastics, as well as in finished products. Static charges on plastics can produce shocks, present fire hazard and attract dust. The effect of static charge in computer/data processing applications, for example, is particularly detrimental.
- **Foaming agents**- Foaming agents are added to polymers during processing to form minute cells throughout the resin. Foamed plastics exhibit lower density, decrease material costs, improves electrical and thermal insulation, increase strength to weight ratio and reduce shrinkage and part warping.
- **Plasticizers**- Plasticizers are added to compounds to improve processing characteristics and offer a wide range of physical and mechanical properties. Slip and blocking agents - They provide surface lubrication. This results in reduced coefficient of friction on part surfaces and enhances release of parts from the mold.

- **Heat stabilizers-** They are used in thermoplastic resins to inhibit polymer degradation that results from exposure to heat.
- **Ultraviolet Stabilizers-** Both thermoset and thermoplastic composites use special materials which are added to prevent loss of gloss, crazing, chalking, discoloration, changes in electrical characteristics, embitterment and disintegration due to ultraviolet (UV) radiation. Additives, which protect composites by absorbing the UV, are called ultraviolet absorbers. Materials, which protect the polymer in some other manner, are known as ultraviolet stabilizers.

M2.3.3.6.2 Fillers

Fillers are inert substances added to reduce the resin cost and/or improve its physical properties, viz., hardness, stiffness and impact strength. Commonly used fillers are calcium carbonate, hydrated alumina and clay.

Calcium carbonate is the most widely used inorganic filler. It is available in a variety of particle sizes and treatments, especially for composite applications. They assist in reducing shrinkage of the molded parts. Most common grades of calcium carbonate filler are derived from limestone or marble.

Kaolin (hydrous aluminium silicate) is commonly known as clay. Mined clays are processed either by air flotation or by water washing to remove impurities and to classify the product for use in composites. They serve to control viscosity, promote flow, and improve resistance **to cracking in molded parts**.

Hydrated alumina is frequently used when improved fire/smoke performance is required. They provide flame redundancy while maintaining good electrical properties. When exposed to high temperature, this filler gives off water, thereby reducing the flame spread and development of smoke. They are used in most electrical and construction applications.

Calcium sulphate is a major flame/smoke retarding filler. Other commonly used fillers include mica, feldspar, silica, talc, flake glass, milled glass fibres, etc.

M2.3.3.6.3 Colorants

Colorants are often used in composites to provide colour throughout the part. Additives can be mixed in as part of the resin or applied as part of the molding process (as a gel coat). Also, a wide range of coatings can be applied after molding.

M2.3.3.6.4 Release Agents

Release agents facilitate removal of parts from molds. These products can be added to the resin, applied to molds, or both. Correct selection of release agents can optimize not only cycle time, but also consistency of surface finish, minimizing post mold operation prior to painting or bonding. Zinc stearate is a popular mold release agent that is mixed into resin for compression

molding. Waxes, silicones and other release agents may be applied directly to the surface of molds.

Release agents must be used at the lowest possible concentration. Use of excessive amounts can reduce mechanical strength and affect adhesion characteristics.

Learning Unit-4: M2.4

M2.4 Fibre Reinforced Polymer (FRP) Laminated Composites

M2.4.1 Laminate Lay-up

A structural laminate is designed to have a specific lay-up or ply arrangement, based on the various design criteria imposed on it. A laminate lay-up definition refers to the fibre orientation of successive plies in a laminate with respect to an established reference coordinate system.

M2.4.2 Ply Orientation definition

The ply orientation symbol is shown in Figure M2.4.1. It designates the tape fibre direction or the warp direction, as applicable.

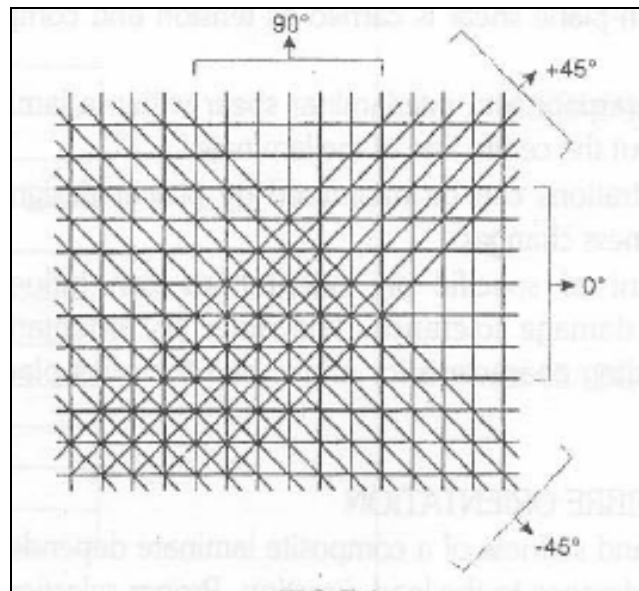


Figure M2.4.1 Ply orientation symbol

It is important that for positive and negative angles should be consistent with the coordinate system chosen.

One of the advantages of using a modern composite is its potential to orient the fibres to respond to the load requirements. This means that the composite designer must take into consideration the

characteristics of the material including the aspects of the fibre orientation in each ply and how the plies are arranged.

Each **ply (lamina)** is defined by a number representing the direction of the fibre in degrees with respect to the reference (x) axis. 0° fibres of both tape and fabric are oriented at angles equal in magnitude but opposite in sign, (+) and (-) are used. Each (+) or (-) sign represents one ply.

M2.4.2.1 Criteria used during Ply Orientation

Following criteria should be used during ply orientation:

- Attention to ply orientation on strength controlled laminates can prevent matrix and stiffness degradation. The 0° ply orientation is used to carry the longitudinal loading, the 90° ply orientation is suited to the transverse loading and the $\pm 45^\circ$ ply orientation is for shear loading.
- In order to minimize the in-plane shear, place the $\pm 45^\circ$ and -45° plies together; the in-plane shear is carried as tension and compression in the 45° plies.
- To minimize warpage and interlaminar shear within a laminate, maintain the symmetry about the centre line of the laminate.
- Stress orientation can be minimized by proper designing or by stepped laminate thickness changes.
- The placement of specific ply orientations can influence the buckling strength and damage tolerance. The outer ply orientations influence the laminate bending characteristics more than plies placed at or near the laminate bending characteristics more than the plies placed at or near the neutral axis.

M2.4.3 Influence of Fibre Orientation

Strength and stiffness of a composite laminate depends on the orientation of the plies with reference to the load direction. Proper selection of ply orientation is necessary to provide a structurally efficient design. As stated above, a composite part might require 0° plies to react to the axial loads, $\pm 45^\circ$ to react to the shear loads and 90° plies to react to the side loads. For example, a lay-up of 50% of 0° plies and 50% of $\pm 45^\circ$ plies will have strength and stiffness equivalent to those of aluminium when loaded in the 0° direction.

M2.4.4 Laminate Lay-up Code

Laminate lay-up code must be able to specify the following:

- The orientation of each ply relative to the reference axis;
- Number of plies, with orientation;
- Exact geometric sequence of plies;
- Adjacent plies oriented at angles equal in magnitude but opposite in sign, appropriate positive or negative signs should be assigned.

Laminate lay-up definition codes are given below:

M2.4.4.1 Total Lay-up code

Fibre orientation of all the plies is sequentially written. Subscript 'T' outside the bracket denotes total laminate definition code, and $\pm$ sign denotes fibre orientation.

Laminate Lay-up	Code
• 45°	[45/0/-60 ₂ /30] _T
0°	
-60°	
-60°	
30°	
• 45°	[±45/-30/+30/0] _T
-45°	
-30°	
30°	
0°	

Table M2.4.1 Total Lay-up code

M2.4.4.2 Symmetric Lay-up Code

In a laminate with symmetric lay-up code, every ply above the mid-plane has an identical ply below the mid-plane. One half of the laminate, from the first ply to the mid-plane, is written sequentially within brackets. A subscript 'S' outside the bracket denotes **symmetrical laminate** definition code. The laminate mid-plane divides a physical ply into a case of symmetric laminate with odd number of plies.

Laminate Lay-up	Code
• 90°	[90/0] _s
0°	
0°	
90°	
• 0°	[0/45/90/ $\overline{90}$] _s
45°	
90°	
90°	
90°	
45°	
0°	

Table M2.4.2 Symmetric Lay-up Code

M2.4.4.3 Hybrid Laminate Code

A hybrid laminate includes plies of different materials within its lay-up. In this case, every ply is identified by its fibre orientation angle and a subscript on the angle identified the type or material.

Laminate Lay-up	Code
0°_{B}	$[0_{\text{B}}/\pm 45_{\text{GR}}/90_{\text{GR}}]_{\text{S}}$
45°_{GR}	
-45°_{GR}	
90°_{GR}	
90°_{GR}	
-45°_{GR}	
-45°_{GR}	
0°_{B}	
0°_{B}	

Table M2.4.3 Hybrid Laminate Code

M2.4.4.4 Quasi Symmetric Lay-up Code

A laminate lay-up is quasi symmetric when every ply above the mid-plane has a correspondence ply below the mid-plane, with a change in the sign of its fibre orientation angle.

Laminate Lay-up	Code
45°	$[45/0/90]_{2\text{S}}$
0°	
0°	
-45°	

Table M2.4.4 Quasi Symmetric Lay-up Code

M2.4.4.5 Set Identification Code

In this case, sets of plies repeat within a laminate lay-up. These are identified by including them within parenthesis. An integer prefix to the subscript 'S' refers to the laminate mid-plane.

Laminate Lay-up	Code
45°	$[45/0/90]_{2\text{S}}$
0°	
90°	
45°	
0°	
90°	
90°	
0°	
45°	
90°	
0°	
45°	

Table M2.4.5 Set Identification Code

In addition to the above, following additional stacking sequences are also used design consideration points of view:

M2.4.5 Special classification of Laminates

The laminates also classified based on the symmetricity of Reinforced fibres, viz:

- Symmetric laminates
- Anti-symmetric laminates
- Non-symmetric laminates

M2.4.5.1 Symmetric laminates (Simplification of Analysis)

M2.4.5.1.1 Mid-plane Symmetric laminates

The geometric mid-plane is the reference surface for determining if a laminate is symmetrical or not. In a mid-plane symmetric laminate, identical plies are located is above and below the mid-plane, at locations that are mirror reflections of each about the fibre orientation. In general, in order to reduce out-of-plane strains, coupled bending and stretching of the laminate and complexity of analysis; laminates should be used. The in-plane response and the bending response of a mid-plane symmetric laminate are uncoupled or independent of each other because all the B_{ij} terms are zero. This means that there is no coupling between in-plane loads and curvature or between the bending loads and in-plane deformations. The in-plane load (N_x , N_y , and N_x) will only cause in-plane strains (ϵ_x° , ϵ_y° , γ_{xy}°), and will not cause the laminate to bend (the mid-plane curvature is equal to zero). A laminate that is not mid-plane symmetric has non-zero B_{ij} terms that couple the membrane and bending response. In this case, an in-plane load will cause the laminate to bend (a response that is unique in laminates and is not seen in metals). Likewise, an applied bending moment will cause the laminate mid-plane to be strained. Almost all the structural laminates are designed to be mid-plane symmetric so as to avoid the generally undesirable coupling between membrane and bending reactions.

M2.4.5.1.2 Balanced Laminates

All laminates should be balanced to achieve in-plane orthotropic behaviour. A laminate is considered balanced when there are equal number of off-axis plies in the $+ \theta$ and $- \theta$ directions with equal thickness and same material properties. If the laminate contains only 0° and/or 90° layers, it satisfies the requirements for balance. Laminates may be mid-plane symmetric but not balanced and vice versa. In a balanced laminate, $A_{16}=A_{26}=0$. In this case, an in-plane (membrane) normal load will only induce mid-plane normal strains and will not induce any mid-plane shear strains. Likewise, an applied shear load will only induce a mid-plane shear strain with no accompanying normal strain. Thus, there is no coupling between extension loads and shear strain. If, in addition, these $+ \theta$ and $- \theta$ plies are at the same distance from the mid-plane, then the corresponding B and D-matrix coefficients tend towards zero. When the balanced laminate is also mid-plane symmetric, its response emulates the behaviour of metals.

M2.4.5.1.3 Angle Ply Laminates

An angle ply laminate has a lay-up where successive plies alternate between $+\theta$ and $-\theta$ in fibre orientation. Based on this definition, angle ply laminates with an odd number of plies are mid-plane symmetric but are not balanced and angle ply laminates with an even number of alternating $+\theta$ and $-\theta$ plies above the mid-plane. A $[\pm 45]_s$ lay-up is an example.

The mechanical response of angle ply laminates provides an explanation for the use of $\pm 45^\circ$ plies at structural locations that require large shear stiffness. A set of $\pm 45^\circ$ plies increase the shear stiffness to a great extent. In the axial stiffness, 90° plies are selected to maximize the transverse stiffness and $\pm 45^\circ$ plies are selected to maximize the shear stiffness of the laminates.

M2.4.5.1.4 cross-ply Laminates

Cross-ply laminates contain only 0° and 90° plies. In a cross-ply laminate, $A_{16}=A_{26}=B_{16}=B_{26}=D_{26}=0$. Mid-plane symmetric cross-ply laminates are also referred to as orthotropic laminates. Their in-plane normal and shear behaviors are uncoupled and their pure bending and twisting behaviors are also uncoupled. This means that N_x and N_y induce only ε_x° , ε_y° ($\gamma_{xy}^\circ=0$) and M_x , M_y induce only K_x and K_y ($K_{xy}=0$). Likewise, N_{xy} induce only γ_{xy}° ($\varepsilon_x^\circ, \varepsilon_y^\circ=0$) and K_{xy} ($K_x = K_y=0$).

M2.4.5.1.5 Quasi-Isotropic Laminates

Quasi-isotropic laminates behave like isotropic materials at the laminate level though their individual plies are orthotropic or anisotropic with respect to the reference coordinates. In case of quasi-isotropic laminates, only the elastic in-plane properties are isotropic. The strength properties, however, will vary with direction.

The goal of composite design is to achieve the lightest as well as most efficient structure by aligning most of the fibres in the direction of the load. Many times there is a need; however, to produce a composite, which has some isotropic properties, similar to metal, because of multiple or unified load paths. A quasi-isotropic laminates lay-up accomplishes this for the x- and y-planes only; the z- or through-the-laminate-thickness plane is quite different and lower. Laminates with plies distributed every 45° are called $\Pi/4$ laminates (plies can be in the 0° , 45° , 90° and -45° directions). Another class of laminates (plies can be in the 0° , 60° , or -60° directions). In both cases, an equal percentage of plies in each of the pre-selected orientations result in a quasi-isotropic laminate. Most laminates produced for aircraft applications have been, with few exceptions, quasi-isotropic. For a quasi-isotropic laminate, the following are the main design requirements:

- It must have three layers or more.
- Individual layers must have identical stiffness matrices and thickness.

The layers must be oriented at equal angles. For example, if total number of layers is 'n', the angle between two adjacent layers should be $360^\circ/n$. If a laminate is constructed from identical sets of three or more layers each, the condition on orientation must be satisfied by the layers in each set, for example, $(0^\circ \pm 60^\circ)_S$ or $(0^\circ \pm 45^\circ/90^\circ)$.

M2.4.5.2 Anti-symmetric Laminates

Symmetry of a laminate about the mid-plane is often desirable to avoid coupling between bending and extension. However, many physically applications design requirements. An even number of plies may be necessary at orientations that alternate from ply to ply i.e. $-\theta/+ \theta/ \theta/+ \theta$. Thus, symmetry about the mid-planes is destroyed and the characteristics of a laminate can be changed from that of the symmetric case. The laminate is not symmetric but anti-symmetric about the mid-plane. The general class of anti-symmetric laminates must have an even number of plies. Further, each ply should have same thickness.

An anti-symmetric cross-ply laminate consists of an even number of plies with principal material directions alternating at 0° and at 90° to the laminate axes. The thickness of the plies is also the same.

An anti-symmetric angle ply laminate has plies orientated at $+\theta^\circ$ to the laminate coordinate axes on one side of the mid-plane and corresponding equal thickness ply orientated at $-\theta^\circ$ on the other side.

Anti-symmetric Laminates

The general class of anti-symmetric laminates must have a number of layers. In such laminates, $A_{16}=A_{26}=D_{16}=D_{26}=0$. The coupling stiffness B_{ij} vary for different classes of anti-symmetric laminates.

In case of anti-symmetric cross-ply laminates, $A_{16}=A_{26}=B_{16}=B_{26}=D_{16}=D_{26}=0$. As the number of layers in a laminate increases, coupling stiffness B_{11} also approaches zero.

In case of anti-symmetric angle ply laminates, $A_{16}=A_{26}=B_{11}=B_{12}=B_{66}=D_{16}=D_{26}=0$. As the number of layers in a laminate increases; the coupling stiffness B_{16} and B_{26} also approaches zero.

The designer should, therefore, take advantage of the orthotropic nature of the fibre composite ply in order to –

- Orient the individual plies as per the above criteria.
- Intersperse the ply orientation. If a design requires a laminate with 16 plies at $\pm 45^\circ$, 16 plies at 0° , and 16 plies at 90° , use the intersperse design $(90_2/\pm 45_2/0_2)_{4S}$ rather than $(90_8/\pm 45_8/0_8)_S$ design. Concerning plies at nearly the same angle provides the opportunity for large matrix cracks to form thereby producing lower laminate allowable. Even if a design requires all 0° plies, some 90° plies and some off-angle plies should be interspersed in the laminate to provide some biaxial strength and stability and also to accommodate unplanned loads. This improves handling characteristics of the laminates

and serves to prevent large matrix cracks from forming. Ensure that the laminate has sufficient fibre orientations to avoid dependence on the matrix for stability.

- Use multiple ply angles. Typical composites are constructed from multiple unidirectional or fabric layers which are positioned at angular orientations in a specified stacking sequence. The multiple layers are usually oriented in at least two different angles, and possibly three or four; $(\pm\theta^\circ/0^\circ/\pm\theta^\circ)$ or $(0^\circ/\pm\theta^\circ/90^\circ)$ cover most of the applications with θ between 30° and 60° . Unidirectional laminates are rarely used except when the basic composite material is only mildly orthotropic or when the load path is absolutely known or carefully oriented parallel to the reinforcement.

M2.4.5.3 Spirally Stacked Laminates/Non-symmetric laminates

It has been shown by experiments that inter-laminar stresses are less in a spirally stacked laminate as compared to any other laminate with similar fibre orientation. Inter-laminar stresses arise out of the difference between the angles of two adjacent plies- smaller difference is better than larger difference.

Most laminates used today are symmetric so as to eliminate or reduce any tendency of the structure to warp unexpectedly. Most laminates are also balanced, often because it is erroneously thought to be preventing the structure from warping. A balanced laminate is really necessary in situations with reversible shear loading conditions.