## **CL 630**

# **Composite Materials**

 $(3\ 0\ 0\ 6)$ 

- 1. Introduction—10 hours
- 2. Theory of Reinforcement—4 Hours
- 3. Polymer nanocomposite (CNT) —6 Hours
- 4. Lamination Theory—5 Hours
- 5. Mechanical behavior of composite materials—9 Hours
- 6. Composite fabrication—6 Hours

#### **Tentative Grading**

1. Assignment:	40%
2. Surprise Quiz:	10%
3. Attendance/interaction:	10%
4. MCQ:	40%



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**CL 630** 

# **Composite Materials**

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# Chapter 1 Introduction

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# **Background**

- ✓ The importance of a composite material is that two or more distinctly different materials combine together to form a composite which possesses properties that are superior to the properties of the individual components.
- ✓ The composites industry has usually been perceived as providing specially parts at premium prices.
- ✓ Today however, composites are being reclassified from "specially" to "common" industry.
- ✓ The growth of the composite material development has resulted in lower prices without loss of properties.
- ✓ As the value of fiber reinforced polymers became apparent and accepted in electrical applications and corrosive environments, these synthetic materials began to penetrate virtually every other market worldwide, from automotive and marine to primary structural elements of aircraft and bridges, medical uses, satellites and launch vehicles, specialized industrial machinery components etc.



# **Background**

- **✓** Composite is still an evolving field of material science.
- ✓ Surveying the pathways to arrive at the present position, some important development in the field is expected.
- ✓ These will be associated with new composites, design strategies, materials technology, fabrication processes, resource management etc.
- ✓ These developments will advance in parallel and with synergy to allow composite to play an increasingly important role in engineering and process industry.
- ✓ These may become the **economic barometer** while selecting the material of construction which steel and other alloy are enjoying.

# Textbooks/References

- R.M. Jones, **Mechanics of Composite Materials**, 2<sup>nd</sup> Ed., 1<sup>st</sup> Indian Reprint, Taylor & Francis, 2010.
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- B.D. Agarwal, and J.D. Broutman, **Analysis and Performance of Fiber Composites**, John Willey and Sons, New York, 1990.
- P.K. Mallick, **Fiber-Reinforced Composites: Materials, Manufacturing and Design**, 2<sup>nd</sup> Ed., Marcel and Dekker, New York, 1993.
- K.K. Arthur, Mechanics of Composite Materials, CRC Press, 1997.
- P.K. Mallick, Composite Engineering Handbook, 2<sup>nd</sup> Ed., Marcel and Dekker, New York, 1997.

## **Composite Material:**

- Two or more materials combined to form a useful third material
- Heterogeneous/distinct constituent phases with distinct interface
- Properties significantly different from constituent properties
- Some properties that can be improved:
  - Strength
  - Stiffness
  - Corrosion resistance
  - Thermal conductivity
  - Gas barrier properties
  - Membrane performance

## **Composite Materials:**

- Matrix: Continuous Phase
- Reinforcement: Discontinuous Phase

## Common Examples:

- Wood: Cellulose fibres in lignin matrix
- Bone: Collagen fibres and hydroxyapatite
- Concrete: Gravel/sand/crushed stone (aggregate) in cement
- Reinforced Concrete: Steel rods in concrete
- Plywood: Thin layers of wood glued together

#### **Reinforcement:**

- Discontinuous phase
- Usually responsible for property enhancement
- Factors that can affect properties of composites:
  - Properties of constituent materials
  - Reinforcement geometry (shape, size)
  - Concentration of reinforcement
  - Uniformity in distribution of reinforcement
  - Orientation of reinforcement
  - Interaction between reinforcement and matrix

## Classification based on Geometry of Reinforcement:

- Fibre-reinforced
   Composites (FRCs)
  - Single-layer
    - Continuous-fibre-reinforced
      - Unidirectional
      - Bidirectional
    - Discontinuous-fibre-reinforced
      - Random orientation
      - Preferred orientation
  - Multilayered
    - Laminate
    - Hybrid laminate

- Particle-reinforced Composites
  - Random orientation
  - Preferred orientation

### Particle-reinforced Composites/Particulate Composites:

- Reinforcement can be classified as particles
- Spherical, cubic, irregular-shaped, platelet but not fibrous
- Examples:
  - Tungsten-carbide particles in cobalt matrix: high surface hardness
  - Chromium-carbide particles in cobalt matrix: high corrosion and abrasion resistance
  - Carbon black particles in rubber: improve strength
  - Copper particle in epoxy (polymer): increases electrical conductivity
  - Mica flakes in glassy matrix: good insulation properties
  - Polymer-clay nanocomposites (clay platelets dispersed in polymer matrix): improve mechanical, gas barrier and flame retardant properties

# Fibre-reinforced Composites/Fibrous Composites:

- Discontinuous-fibre-reinforced composites: Short fibres, fibre length affects composite properties
  - Orientation cannot be controlled easily
  - Composite properties can be isotropic
  - □ If injection moulding is used for fabrication, fibre orientation can occur in flow direction; not isotropic.

## Fibre-reinforced Composites/Fibrous Composites:

- Reinforcement are fibres (high aspect ratio, length much longer than cross sectional dimensions)
- Flaws are minimized due to small cross sectional dimensions
- Continuous-fibre-reinforced composites: Long fibres.
  - Unidirectional composites are very strong in fibre direction but weaker in direction perpendicular to the fibre orientation. Multiple layers may be stacked in various orientations to form laminates.
  - Bidirectional reinforcement: reinforcement with woven fabric instead of linear fibres.

# **Mechanical Properties of Some Fibres:**

Material	Tensile Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm <sup>3</sup> )	Specific Modulus (GPa.cm³/g)	Specific Strength (GPa.cm³/g)
Fibres					
E-glass	72.4	3.5	2.54	28.5	1.38
S-glass	85.5	4.6	2.48	34.5	1.85
Graphite	390	2.1	1.90	205.0	1.1
Boron	385	2.8	2.63	146.0	1.1
Tungsten	414	4.2	19.3	21.0	0.22
Kevlar	130	2.8	1.50	87.0	1.87
Conventional Materials					
Steel	210	0.34-2.1	7.8	26.9	0.043-0.27
Glass	70	0.7-2.1	2.5	28.0	0.28-0.84
Tungsten	350	1.1-4.1	19.3	18.1	0.057-0.21

Fibres used as reinforcement are lightweight, strong and stiff.

Fibres are stronger than bulk material due to:

- preferential orientation of molecules along fibre direction
- reduced number of defects compared to bulk material;
   e.g. tensile modulus of bulk E-glass is 1.5 GPa, that of fibre is 3.5 GPa

Fibres show a distribution of strengths that follows the Weibull distribution.

The cumulative probability of a fibre failing with a strength less than or equal to  $\sigma$  is:

$$F(\sigma) = 1 - exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right]$$

where m is the shape parameter and  $\sigma_0$  is the scale parameter

#### Glass Fibres

- Processed from bulk glass; main constituent is silica, SiO<sub>2</sub> (46-75%)
- Hard, corrosion resistant, inert, flexible, lightweight, inexpensive
- Most common type of fibres used in low-cost applications
- Fibre diameters typically range from 0.5 to ~25 microns.
- Types:
  - E-glass fibres (E for electrical):
    - High strength, good chemical resistance, low cost
    - Typical composition: 54% SiO<sub>2</sub>, 15% Al<sub>2</sub>O<sub>3</sub>, 17% CaO, 5% MgO, 8% B<sub>2</sub>O<sub>3</sub>
    - Preferred structural reinforcement, most widely used glass fibre

#### Glass Fibres

- S-glass fibres (also S-2-glass fibres) (S for strength):
  - Highest strength among glass fibres, high cost (especially S-glass)
  - Typical composition: 64% SiO<sub>2</sub>, 25% Al<sub>2</sub>O<sub>3</sub>, 10% MgO
  - Limited applications due to high cost; aircraft components
- C-glass-fibres (C for corrosion) for corrosion-resistant applications
- D-glass fibres (D for dielectric) for electrical applications

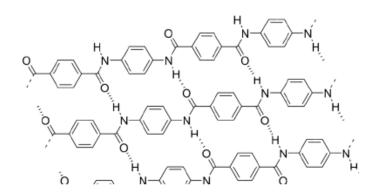
#### Carbon Fibres

- Also called graphite fibres
- Lightweight, strong, chemical resistance, high temperature performance
- High cost; used in weight-critical applications such as aerospace
- Common precursors: Polyacrylonitrile (PAN) and pitch
- PAN fibres have higher strength but are more expensive than pitch fibre
- Fabrication typically involves oxidation of precursor fibres followed by carbonization and graphitization



#### Organic Fibres: Polymeric Fibres

- Aramid Fibres: Kevlar
  - High strength-to-weight and
  - modulus-to-weight ratio
  - High impact resistance
  - Applications: Body armour, aircraft
  - Disadvantages: poor high temperature properties
- PBO (poly(p-phenylene-2,6-benzobisoxazole)) fibres: Zylan
- Polyester fibres: Vectran



#### Boron Fibre

- High stiffness, high strength, low density
- Applications: Aerospace, sporting goods
- Mechanical properties preserved at high temperatures
- High toughness, good compressive behaviour
- Produced by chemical vapour deposition on tungsten wire
- Very expensive



## INTRODUCTION

- 1. Definition, properties, classification
- 2. Use of composite materials over metals, ceramics and polymers
- 3. Structural applications
- 4. Materials

#### Structural materials:

- (a) Metals; (b) Polymers; (c) Ceramics and (d) Composite materials
- 1 (a) **Definition**: Two or more structural materials, namely, metals, polymers and ceramics, are combined in a structural unit on a macroscopic scale to form a new useful material is called composite material.

Composite materials have two distinct phases; (a) continuous, generally in a greater quantity—matrix (metals, polymers and ceramics) and (b) reinforcing phase for reinforcement of matrix—fibrous or particulate materials.

In general, properties of a matrix are enhanced by incorporating reinforcing phases.



1 (b) **Properties**: The following properties can be improved by forming a composite material as:

(i) Strength

(iii) Corrosion resistance

(v) Attractiveness

(vii) Fatigue life

(ix) Thermal insulation

(xi) Acoustical insulation

(ii) Stiffness

(iv) Wear resistance

(vi) Weight

(viii) Temperature dependent behavior

(x) Thermal conductivity

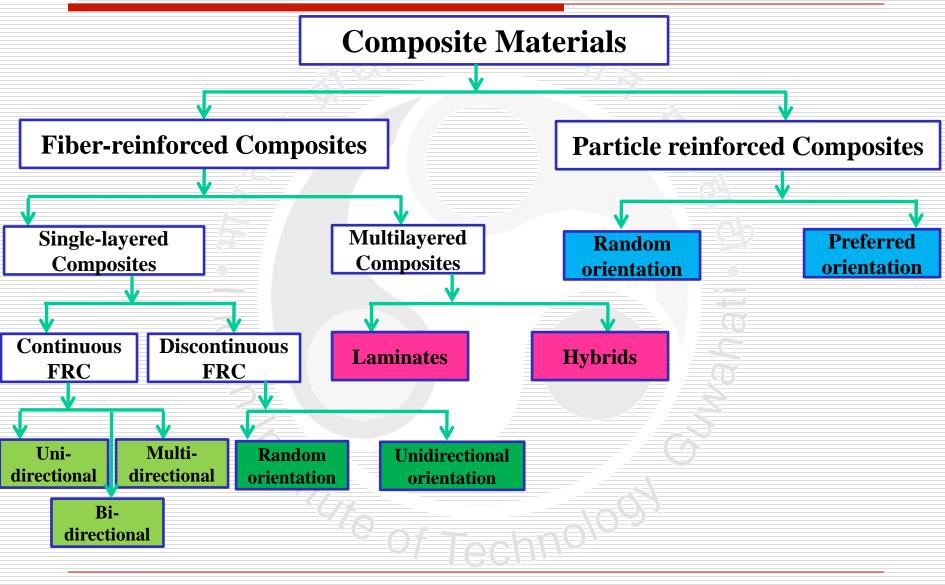
#### **NATURAL COMPOSITES:**

- (A) Wood-fibrous cellulose in lignin matrix
- (B) Bone-layered and oriented collagen fibrils in protein-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> matrix

Fiber-reinforced, resin matrix composite materials have high strength/weight and stiffness/weight for weight sensitive applications, like, aircraft and space vehicles.



#### 1 (c) Classification



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# Chapter 1 Introduction

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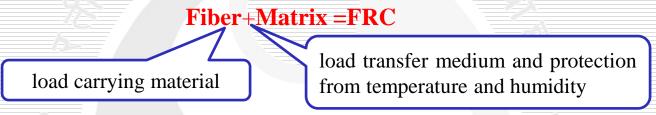


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#### (A) Fiber-reinforced composites

**Definition**: Fiber-reinforced composite materials consist of fibers of high strength and modulus embedded in or bonded to a matrix with distinct interfaces (boundaries) between them.



*Fibrous composite materials*: Long fibers are stiffer and stronger than same material in bulk form.

Example: Ordinary plate glass fractures at 2900 psi whereas, commercially available glass fibers have 4,00,000 to 7,00,000 psi and laboratory prepared form glass fibre has 10,00,000 psi tensile strength.

Fibers: Glass; Carbon; Aramid; Extended chain polyethylene; Natural Boron; Ceramic

Matrix: Polymer; Metal; Ceramics



#### Single-layer composite

$$Aspect\ ratio = \frac{Length\ of\ fiber}{Cross-section}$$

In single-layer composites, long fiber with high aspect ratio is called continuous FRC, whereas, short fibers with low aspect ratio gives discontinuous FRC.

#### **Continuous FRC**

#### Unidirectional, bidirectional and multidirectional reinforcement

All the fibers in one direction in continuous FRC are called <u>unidirectional</u>.

Fibers are in two directions, usually, normal to each other is termed as <u>bidirectional</u> (woven) reinforcement.

Fibers in more than two directions are multidirectional reinforcement.

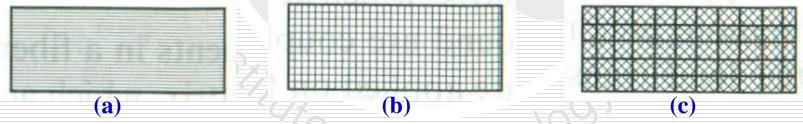


Figure: (a)Unidirectional, (b) bidirectional and (c) multidirectional reinforcement.



#### **Discontinuous FRC**

#### Random and unidirectional reinforcement



Figure: (a) Random and (b) unidirectional discontinuous reinforcement.

## Multilayered composites

#### Laminates

The most common form in which fiber-reinforced composites are used in structural applications is called laminate, stack of number of thin layers of fibers (4 to 40) and matrix.

Figure: Consolidated stack of many layers in laminate.



#### Hybrids

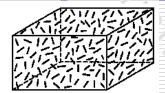
Hybrids are multilayered composites with mixed fibers. The fibers may be mixed in a ply or layer-by-layer and are designed to benefit from different properties of the fibers used. Example:

Glass+carbon fibers → polymer matrix → hybrid FRC (inexpensive, enhanced mechanical properties for stiffness of carbon)

FRC+PRC→ Hybrids

#### (B) Particle reinforced composites

These composites have approximately equal dimensions in all directions. Shape may be spherical, cubic, platelet or regular/irregular geometry. The arrangement of particulate reinforcement may be either random or preferred orientation. For practical purposes, random orientation is the majority.



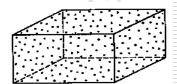


Figure: Random and preferred orientation of Particle reinforced composites.



#### 2. Use of composite materials over metals, ceramics and polymers

Commercial and industrial applications of composite materials are huge. Structural application includes, aircraft, automotive, sporting goods, marine, electrical, chemical and infrastructure. These are also used in electronics, furniture, building construction, medical industry, power industry, etc.

## Salient features

- •Superior performance and low maintenance cost
- •Same strength and stiffness as high strength steel and 70% lighter
- •Compared to Al, three times stronger 60% less weight
- •Fatigue strength and fatigue damage tolerance are excellent



## Table: Structural materials and their specific strengths

Category	Material	Tensile or Flexural strength (MPa)	Young's Modulus (GPa)	Specific Strength $\left(\frac{MPa}{\frac{g}{cc}}\right)$
Metal	SAE 1010 steel	365	207	46.4
	6060-T6 Al Alloy	310	68.9	114.4
	Nickel (20% Cr, 15% Co)	1200	204	146.7
	Titanium (2.5% Sn)	792	112	173.7
Ceramic	Alumina	332	382	85.8
	β-Sialon	945	300	290.8
	Zirconia	900	170	152
	Nylon 6.6	70	2	61.4
Polymer	Polystyrene	50	3	47.6
	PVC rigid	60	3	35.3
Composite	Carbon fiber-epoxy matrix (unidirectional)	1550	137.8	1000
	Kevlar 49 fiber-epoxy matrix	1378	75.8	998.6



## 3. Structural applications of composite materials

## (A) Aircraft and military applications

Aircraft	Component	Material	Weight reduction (%)	Commercial/ Military
Boeing 727	Elevator face sheet	Carbon fiber epoxy	25	Commercial
Boeing 737	Wing spoilers	Carbon fiber epoxy	37	Commercial
F-14 (1969)	Skin on horizontal stabilizer box	Boron fiber epoxy	19	Military
AV-8B	Wing skins and substructures, flaps	Carbon fiber epoxy	25	Military
(1982)			3	



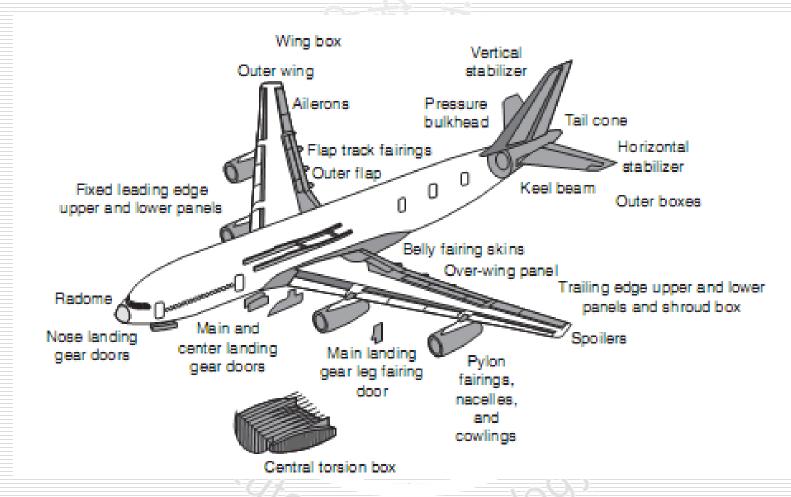


Figure: Use of fiber-reinforced composites in Airbus 380.



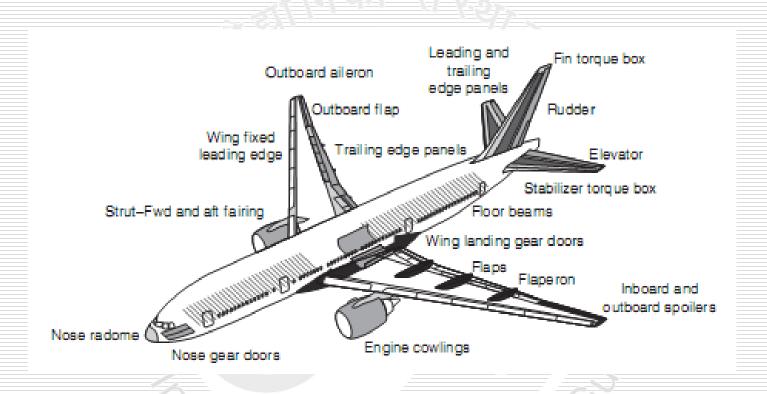


Figure: Use of fiber-reinforced composites in Boeing 777.



#### (B) Space applications

Various FRC are used in space vehicles. These include

- •mid-fuselage truss structure (Boron fiber reinforced Al tubes)
- •payload bay door (Sandwich laminate of carbon fiber reinforced epoxy face sheets and Al honeycomb core)
- •remote manipulator arm (ultrahigh-modulus caqrbon fiber-reinforced epoxy tube)
- •pressure vessels (Kevlar 49 fiber reinforced epoxy)
- •support structures for many smaller components
- •building truss structures of low earth orbit (LEO) satellites (Carbon fiber reinforced epoxy tubes)

Low weight and low coefficient of thermal expansion (TE)



#### (C) Automotive applications

There are three different components in automobiles. These are body components; chassis components and engine components.

- •Body components: Hood/body panels→high stiffness and dent resistance (damage tolerance)=> E-glass fiber-reinforced sheet molding compound (SMC)
- •Chassis components: Multileaf steel springs → Unileaf E-glass fiber-reinforced epoxy springs (80% weight reduction)
- •Engine components: Shafts can be replaced but not cost effective → non successful;

Fatigue loads at very high temperature pose challenge. High temperature polymer/metal/ceramic matrix will be used.



#### (D) Sporting goods applications

Tennis rackets, athletic shoes, bicycle frames, hockey sticks, base ball bats, archery bows, arrows and helmets are made by composites.

Advantages: Weight reduction; vibration damping; design flexibility

Woods, metals and leathers are replaced by composite materials.

#### (E) Marine applications

Boats (Sail boats; fishing boats; dinghies; life boats and yachts)

Recreational boats 

Glass FRC or Glass FR vinyl ester resins

Advantages: Weight reduction; higher cruising speed; acceleration; fuel efficiency; maneuverability (controlled change in direction)



#### (F) Infrastructure

Reinforced concrete and steels in bridge, building and other civil infra-

structures are widely replaced by FRC.

Advantages: Corrosion resistance; longer life; lower maintenance and repairing cost; light weight and hence lower dead weight; easier transportation from production factory to bridge location

(USA and Canada): The Wickwire Run Bridge in West Virginia, USA→ Glass fabric-reinforced polyester (vinyl ester) matrix.



View from the top showing round composite cross-rods inserted in the predrilled holes in composite I-bars placed in the direction of trafffic



Figure: Glass fiber-reinforced vinyl ester pultruded section in bridge construction.



#### 4. Materials

Material selection is one of the most important and critical steps in the mechanical design process. It requires the knowledge of performance requirements of the structure/component under consideration. It also requires the knowledge of

- (a) types of loading, e.g., axial, bending, torsion;
- (b) mode of loading, e.g., static, fatigue, impact, shock;
- (c) service life,
- (d) operating/service environment, e.g., temperature, humidity, presence of chemicals;
- (e) other structures or components with which the particular design under consideration is required to interact;
- (f) manufacturing process that can be used to produce the structure;
- (g) cost, manufacturing cost, assembly cost and transportation cost.
- A. Fibers: Glass; Carbon; Aramid; Extended chain polyethylene; Natural Boron; Ceramic
- **B. Particles:** (Whiskers → small single crystal) SiC
- C. Matrix: Polymer; Metal; Ceramics
- **D. Fillers and additives: CaCO**<sub>3</sub>



## A. Fibers

These materials occupy the largest volume fraction in a composite and share the major portion of the load acting on a composite structure. Fibers influence the following characteristics:

- (a) density
- (b) tensile strength and modulus
- (c) compressive strength and modulus
- (d) fatigue strength and fatigue failure mechanism
- (e) electrical and thermal conductivities
- (f) cost.

Proper selection of fiber depends on (i) fiber type; (ii) fiber volume fraction; (iii) length and orientation.

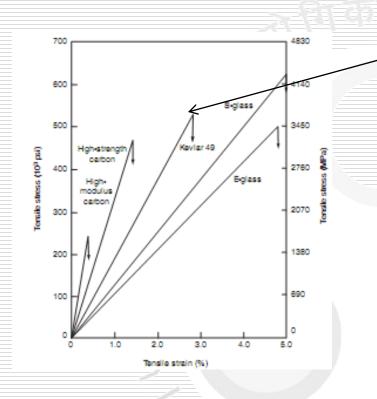
A bundle of large number of continuous filaments with small diameter may be *untwisted* or *twisted*.

Untwisted: i) Strand/end→ Glass and Kevlar fibers

ii) Tow→ Carbon fibers

Twisted: Yarn





Upto point of failure

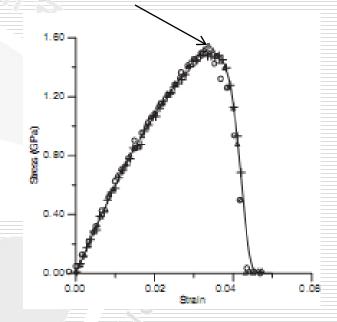


Figure: Tensile stress-strain diagram for single filament test.

Figure: Tensile stress-strain diagram for 300 filaments of untwisted E glass fibers.



Tensile strength, 
$$\sigma_f = \frac{F_u}{A_f}$$

where,  $F_u$ =Force at failure and  $A_f$ =Average filament cross-sectional area.

Tensile modulus, 
$$E_f = \frac{L_f}{C.A_f}$$

where,  $L_u$ =Gage length and C=True compliance, (speed, loading rate and system compliance).

Both non-linearity and progressive failure occur due to statistical distribution of strength. Weaker filaments fail at low stresses and surviving filaments continue to carry the tensile load.



#### **GLASS FIBERS**

Glass fibers are the most common of all reinforcing fibers for polymeric matrix composites (PMC).

Advantages: Low cost, high tensile strength, high chemical resistance, excellent insulating resistance

**Disadvantages:** Low tensile modulus, high density, sensitivity to abraision during handling (decreases tensile strength) low fatigue resistance, high hardness (causes excessive wear on molding dies and cutting tools)

**Types:** E-glass-lowest cost

S-glass-highest tensile strength (aircraft, missile casing)

C-glass-Chemical applications (corrosion resistant)

S-2-glass-Lower cost version of S-glass to acid resistant



## **Table: Chemical composition of glass fibers**

Type	SiO <sub>2</sub>	Al <sub>2</sub> O	CaO	MgO	$B_2O_3$	Na <sub>2</sub>	Total
E- glass	54.5	14.5	17.0	4.5	8.5	0.5	100
SiQ $_2$ $\rightarrow$ P Al $_2$ O $_3$ an N $_2$ las $\rightarrow$ 0	d61,0,	<b>-2</b> ∕000d	ify hetv	vdfk(st nprove	ructure s work:	of <b>©iO</b> ability	<sub>2</sub> 100

Glass fibers are amorphous and isotropic.



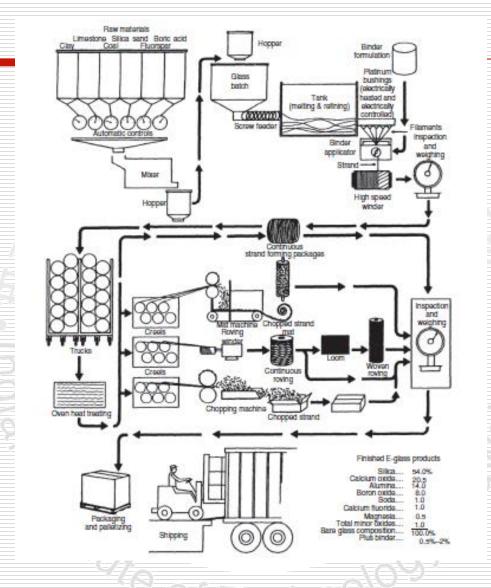


Figure: Flow diagram for glass fiber manufacturing.



#### **Manufacturing process**

The manufacturing process for glass fibers is presented in above Figure.

### **Steps:**

- 1. Various ingredients are *dried*, *mixed* and *melted* in a refractory furnace at about 1370°C.
- 2. The molten glass is extruded through a number of orifices and rapidly drawn into filaments of around 10 µm diameter.
- 3. A protective coating is applied in individual filaments before these are gathered together into a strand and wound on a drum. The coating is a mixture of lubricants (prevent abrasion), antistatic agents (reduce static friction), and a binder. It may contain small percentage of coupling agent to promote adhesion between fiber and polymer matrix.



Basic commercial form is <u>strand</u> (bundle of filaments), collection of parallel filaments numbering 204 and above.

<u>Roving</u> is a group of untwisted parallel strands (also called <u>ends</u>) wound on a cylindrical package.

<u>Chopped strands</u> are made by cutting continuous strands into short lengths.

3.2 mm to 12.7 mm lengths chopped strands are used in **injection molding operation**.

Longer strands upto 50.8 mm are used to form chopped strand mats (CSM).

The tensile strength of glass fibers is reduced in presence of water or under sustainable loads. Water bleaches out the alkali present in the surface. Under sustainable loads, the growth of surface flaws is accelerated owing to stress corrosion by atmospheric moisture.

Tensile strength of glass fibers is decreased with increasing time of load duration.



#### **CARBON FIBERS**

- Carbon fibers are not new technology. These were produced by Thomas Edison as filaments for his electric light bulb.
- But in the 1960s carbon fibers were the first "high-strength, high modulus" fibers, developed for structural composites for the space and defense applications.
- Since the initial introduction of those fibers, the quality and performance have increased significantly and the price has gone down dramatically.
- As a result, carbon fibers are now used in a wide variety of commercial, industrial and consumer applications, such as sporting goods (golf clubs, tennis rackets, bicycle frames, arrows) composite hulls for boats, aircraft brakes, automobile components, industrial rollers and storage tanks, furnace insulation, electronic component shielding, and windmill blades for wind energy systems.



Carbon fibers are available with a variety of tensile modulus ranging from 207 GPa to 1035 GPa. *In general, low modulus fibers have lower density, lower cost, higher tensile strength, higher compressive strength, and higher tensile strain/failure than high modulus fibers.* 

#### Advantages:

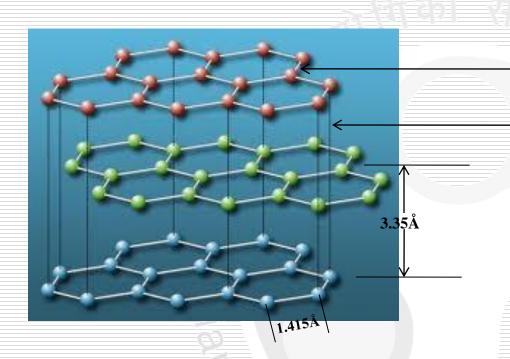
- i) Exceptionally high tensile strength/weight ratio
- ii) High tensile modulus/weight ratio
- iii) Zero or negative coefficient of thermal expansion: This is an effect of the graphite crystal structure which is oriented along the axis. The degree of crystallization and orientation directly determines the axial thermal expansion. Carbon fibers with a high degree of crystallinity and alignment have negative axial thermal expansions. The negative axial thermal expansion of the carbon fibers is used in composites to produce low expansion components for use in mirrors and precision alignment devices.
  - iv) High fatigue strength
  - v) High thermal conductivity (higher than copper)

#### Disadvantages:

- i) Low tensile strain/failure
- ii) Low impact resistance
- iii) High electrical conductivity (causes shorting in unprotected electrical machinery)
- iv) High cost



#### Structure of carbon fibers



Strong covalent bonds present between carbon atoms in a plane but weak van der Waals type force exists between two planes. Hence, anisotropic physical and mechanical properties are observed for carbon fibers (properties depend on direction).

Figure: Orientation of carbon atoms in graphite crystal.



#### **Manufacturing process**

Commercial carbon fibers are produced by a two step process - the spinning of an organic precursor and a thermal conversion to carbon.

There are three types of precursors used on a commercial basis to manufacture carbon fibers: rayon, polyacrylonitrile (PAN), and pitch.

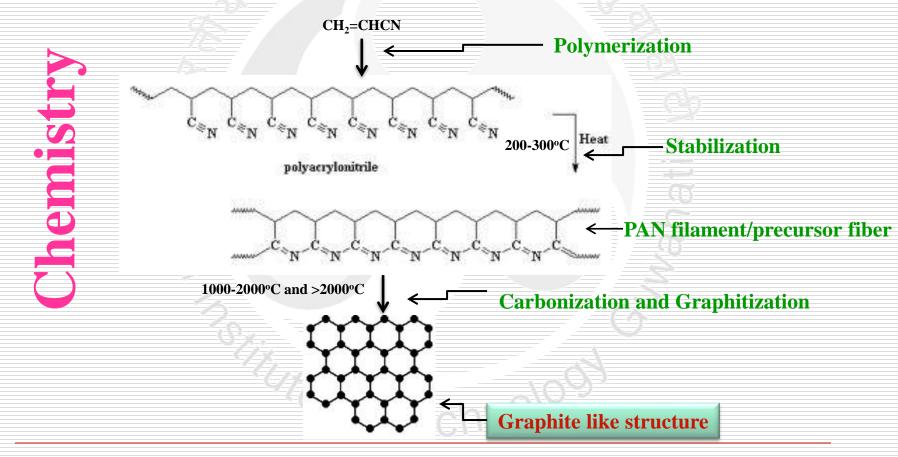
Rayon, the raw material used for the first high-performance carbon fibers, was the dominant precursor material in the 1960s and early 1970s.

However, because of its low carbon yield (2~30%), high processing cost, and limited physical properties, today rayon precursor is used for less than 1% of commercial carbon fibers.



#### PAN-based Carbon Fibers

PAN-based carbon fibers are derived from polyacrylonitrile or acrylic copolymers. Normally, a solution of the polymer is either wet or dry spun into PAN precursor fibers that are ultimately converted into carbon fibers.





#### Carbon fiber manufacture from PAN

## **Steps**

- 1. Polymerization: Acrylonitrile to polyacrylonitrile
- 2. Wet spinning: Dilute solution of acrylic polymer is extruded into a coagulation bath
- 3. Stabilization of PAN: Heating the fiber in air to temperatures ranging from 200 to 300°C for approximately 1-2 hours
- 4. Carbonization: In an inert atmosphere at 1000 to 2000°C for 30 min
- 5. Graphitization: Heating above 2000°C with or without stretching upto 3000°C
- 6. Surface treatment: Oxidation of the fiber surface to promote adhesion to the matrix resin in the composite
- 7. Sizing: Continuous carbon or graphite fiber is coated with sizing agent to promote handleability and wettability of the fiber with the matrix resin



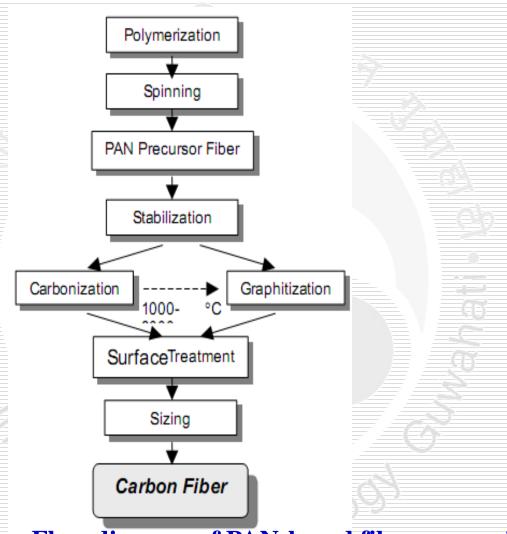


Figure: Flow diagram of PAN-based fiber processing.



#### Pitch-based Carbon Fibers

The production of high-modulus, pitch-based carbon fiber begins by heat treating a petroleum or coal tar pitch feedstock to produce a liquid crystal precursor, termed "mesophase".

The liquid crystal material is melt spun into a precursor fiber that is converted into a carbon fiber in a process similar to that used for PAN-based carbon fiber.



## Pitch-based Carbon Fibers

## **Steps**

- 1. Pitch purification: By-product of petroleum refining/coal coking is purified
- 2. Mesophase formation: Heating the pitch at 300 to 500°C
- 3. Melt spinning, drawing followed by heat stabilization: Generation of pitch filaments by passing through spinneret die
- 4. Carbonization: In an inert atmosphere at 1000 to 2000°C for 30 min
- 5. Graphitization: Heating above 2000°C with or without stretching upto 3000°C
- 6. Surface treatment: Oxidation of the fiber surface to promote adhesion to the matrix resin in the composite
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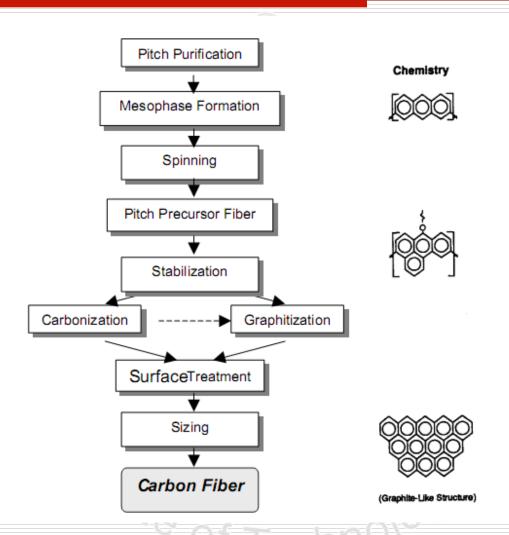


Figure: Pitch-based fiber processing.



## Table: Comparison between PAN-based and Pitch-based carbon fibers

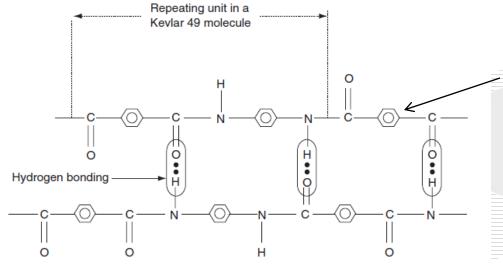
Properties	PAN carbon fiber	Pitch carbon fiber	
Thermal conductivity	Lower	Higher	
<b>Electrical conductivity</b>	Lower	Higher	
Carbon content (%)	68	93	
Cost	Higher	Lower	
Specific modulus (tensile modulus/density)	Lower	Higher	
Axial coefficient of thermal expansion	Higher	Lower	
Tensile strength	40-50% higher	40-50% lower	
Compressive strength	Higher	One third	



#### **ARAMID FIBERS**

Aramid fibers are highly crystalline aromatic polyamide fibers that have the lowest density and the highest tensile strength/weight ratio among the current reinforcing fibers. Kevlar 49 is the trade name of one of the aramid fibers.

**Application:** Marine and aerospace applications



The aromatic rings give highest chain stiffness as well as better chemical and thermal stability over other fibers or polymers.

Figure: The molecular structure of Kevlar 49.



#### **Manufacturing of Kevlar 49**

Kevlar 49 filaments are manufactured by extruding an acidic solution of a proprietary precursor (a polycondensation product of terephthaloyol chloride and p-phenylene diamine) from a spinneret.

During the filament drawing process, Kevlar 49 molecules become highly oriented in the direction of the filament axis.

Weak hydrogen bonds between hydrogen and oxygen atoms in adjacent molecules hold them together in the transverse direction.

The resulting filament is highly anisotropic, with much better physical and mechanical properties in the longitudinal direction than in the radial direction.



#### Salient features of Kevlar 49 fiber

Kevlar 49 fibers do not melt or support combustion but will start to carbonize at about 427°C.

The maximum long term use temperature recommended for Kevlar 49 is 160°C. They have very low thermal conductivity, but a very high vibration damping coefficient.

Except for a few strong acids and alkalis, their chemical resistance is good.

However, they are quite sensitive to ultraviolet lights. Prolonged direct exposure to sunlight causes discoloration and significant loss in tensile strength. The problem is less pronounced in composite laminates in which the fibers are covered with a matrix.

Ultraviolet light-absorbing fillers can be added to the matrix to further reduce the problem.



Kevlar 49 fibers are hygroscopic and can absorb up to 6% moisture at 100% relative humidity and 23°C.

The equilibrium moisture content is directly proportional to relative humidity and is attained in 16–36 h.

Absorbed moisture seems to have very little effect on the tensile properties of Keylar 49 fibers.

However, at high moisture content, they tend to crack internally at the preexisting micro-voids and produce longitudinal splitting.



## Kevlar 149

A second-generation Kevlar fiber is **Kevlar 149**, which has the highest tensile modulus of all commercially available aramid fibers.

The tensile modulus of Kevlar 149 is 40% higher than that of Kevlar 49; however, its strain-to-failure is lower.

Kevlar 149 has the equilibrium moisture content of 1.2% at 65% relative humidity and 22°C, which is nearly 70% lower than that of Kevlar 49 under similar conditions.

Kevlar 149 also has a lower creep rate than Kevlar 49.



#### EXTENDED CHAIN POLYETHYLENE FIBERS

Extended chain polyethylene fibers, commercially available under the trade name **Spectra**, are produced by gel spinning a high-molecular-weight polyethylene.

Gel spinning yields a highly oriented fibrous structure with exceptionally high crystallinity (95%–99%) relative to melt spinning used for conventional polyethylene fibers.

Spectra polyethylene fibers have the highest strength-to-weight ratio of all commercial fibers available to date.

Two other outstanding features of Spectra fibers are their low moisture absorption (1% compared with 5%–6% for Kevlar 49) and high abrasion resistance, which make them very useful in marine composites, such as boat hulls and water skis.



### **EXTENDED CHAIN POLYETHYLENE FIBERS**

The melting point of Spectra fibers is 147°C; however, since these exhibit a high level of creep above 100°C, the application temperature is limited to 80°C–90°C.

The safe manufacturing temperature for composites containing Spectra fibers is below 125°C, since these exhibit a significant and rapid reduction in strength as well as increase in thermal shrinkage above this temperature.

Spectra fibers have poor adhesion with resin matrices.

Spectra fibers provide high impact resistance for composite laminates even at low temperatures.

However, their use in high-performance aerospace composites is limited, unless they are used in conjunction with stiffer carbon fibers to produce hybrid laminates with improved impact damage tolerance than all-carbon fiber laminates.

## **CL 630** Composite Materials

(3006)

- 1. Introduction—10 hours
- 2. Theory of Reinforcement—4 Hours
- 3. Polymer nanocomposite (CNT) —6 Hours
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1. Assignment:	40%
2. Surprise Quiz:	10%
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## **Composite Materials**

(3006)

# Chapter 1 Introduction

By Dr. Chandan Das



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## Recap

CARBON FIBERS-PAN, Pitch

ARAMID FIBERS-Kevlar 49, 149

• EXTENDED CHAIN POLYETHYLENE FIBERS-Spectra



#### **BORON FIBERS**

The most prominent feature of boron fibers is their extremely high tensile modulus, which is in the range of 379–414 GPa.

Coupled with their relatively large diameter, boron fibers offer excellent resistance to buckling, which in turn contributes to high compressive strength for boron fiber-reinforced composites.

The principal disadvantage of boron fibers is their high cost, which is even higher than that of many forms of carbon fibers. For this reason, its use is at present restricted to a few aerospace applications.

Boron fibers are manufactured by **chemical vapor deposition** (**CVD**) of boron into a heated substrate (either a tungsten wire or a carbon monofilament).

Boron vapor is produced by the reaction of boron chloride with hydrogen:  $2BCl_3 + 3H_2 = 2B + 6HCl$ 



#### **BORON FIBERS**

The most common substrate used in the production of boron fibers is tungsten wire, typically 0.0127 mm in diameter.

It is continuously pulled through a reaction chamber in which boron is deposited on its surface at 1100°C–1300°C.

The speed of pulling and the deposition temperature can be varied to control the resulting fiber diameter.

Currently, commercial boron fibers are produced in diameters of 0.1, 0.142, and 0.203 mm, which are much larger than those of other reinforcing fibers.

During boron deposition, the tungsten substrate is converted into tungsten boride by diffusion and reaction of boron with tungsten.

Near the outer surface of the boron layer, a state of biaxial compression exists, which makes the boron fiber less sensitive to mechanical damage.

The adverse reactivity of boron fibers with metals is reduced by chemical vapor deposition of SiC on boron fibers, which produces borsic fibers.



#### **CERAMIC FIBERS**

Silicon carbide (SiC) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) fibers are examples of ceramic fibers notable for their high-temperature applications in metal and ceramic matrix composites.

Table: Comparison of properties between SiC and Al<sub>2</sub>O<sub>3</sub> fibers

Property	Silicon carbide	Aluminum oxide	
	(SiC) fibers	(Al <sub>2</sub> O <sub>3</sub> ) fibers	
Melting point (°C)	2830	2045	
Retention of strength upto temp °C	650	1370	
Thermal conductivity	Higher	Lower	
Electrical conductivity	Higher	Lower	
Coefficient of thermal expansion	Lower	Higher	



#### **CERAMIC FIBERS**

SiC: (1) Monofilament; (2) Multifilament and (3) Whisker

**Al<sub>2</sub>O<sub>3</sub>:** (1) Fiber FP; (2) Nextel 610; (3) Nextel 720; (4) Fiberfrax and (5) Saffil

Silicon carbide fibers are available in three different forms:

1. Monofilaments that are produced by chemical vapor deposition of β-SiC on a 10–25 μm diameter carbon monofilament substrate.

The carbon monofilament is previously coated with ~1 µm thick pyrolitic graphite to smoothen its surface as well as to enhance its thermal conductivity.

β-SiC is produced by the reaction of silanes and hydrogen gases at around 1300°C. The average fiber diameter is 140 μm.



#### **CERAMIC FIBERS**

2. **Multifilament** yarn is produced by melt spinning of a polymeric precursor, such as polycarbosilane, at 350°C in nitrogen gas.

The resulting polycarbosilane fiber is first heated in air to 190°C for 30 min to cross-link the polycarbosilane molecules by oxygen and then heat-treated to 1000°C–1200°C to form a crystalline structure.

The average fiber diameter in the yarn is 14.5 µm and a commercial yarn contains 500 fibers.

Yarn fibers have a considerably lower strength than the monofilaments.



3. Whiskers, which are 0.1–1 μm in diameter and around 50 μm in length.

#### **Manufacturing of Whiskers:**

These are produced from rice hulls, which contain 10–20 wt% SiO<sub>2</sub>.

Rice hulls are first heated in an oxygen-free atmosphere to 700°C–900°C to remove the volatiles and then to 1500°C–1600°C for 1 h to produce SiC whiskers according to the following reaction:

The final heat treatment is at 800°C in air, which removes free carbon.

The resulting SiC whiskers contain 10 wt% of SiO<sub>2</sub> and up to 10 wt% Si<sub>3</sub>N<sub>4</sub>.

The tensile modulus and tensile strength of these whiskers are reported as 700 GPa and 13 GPa, respectively.



#### Different aluminum oxide fibers

One aluminum oxide fiber, but not currently available in the market, is called the **Fiber FP**. It is a high-purity (>99%) polycrystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fiber.

**Nextel 610** and **Nextel 720** are available in the market now. Both fibers are produced in continuous multifilament form using the sol–gel process.

Nextel 610 contains greater than 99%  $Al_2O_3$  and has a single-phase structure of  $\alpha$ -  $Al_2O_3$ .

The average grain size is 0.1 μm and the average filament diameter is 14 μm.

Because of its fine-grained structure, it has a high tensile strength at room temperature; but because of grain growth, its tensile strength decreases rapidly as the temperature is increased above 1100°C.



Nextel 720, which contains 85% Al<sub>2</sub>O<sub>3</sub> and 15% SiO<sub>2</sub>, has a lower tensile strength at room temperature, but is able to retain about 85% of its tensile strength even at 1400°C.

Nextel 720 also has a much lower creep rate than Nextel 610 and other oxide fibers at temperatures above 1000°C.

The structure of Nextel 720 contains  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> grains embedded in mullite grains.

Another ceramic fiber, Fiberfrax, contains almost 50% Al<sub>2</sub>O<sub>3</sub> and 50% silica (SiO<sub>2</sub>).

The fiber diameter is 2–12 µm and the fiber aspect ratio (length to diameter ratio) is greater than 200.

It is manufactured either by a melt blowing or by a melt spinning process.



**Saffil**, produced by Saffil Ltd., is also a discontinuous aluminosilicate fiber, containing 95% Al<sub>2</sub>O<sub>3</sub> and 5% SiO<sub>2</sub>.

Its diameter is  $1-5 \mu m$ .

It is produced by blow extrusion of partially hydrolyzed solution of aluminum salts with a small amount of SiO<sub>2</sub>.

It contains mainly  $\delta$ - Al<sub>2</sub>O<sub>3</sub> grains of 50 nm size, but it also contains some larger size  $\alpha$ - Al<sub>2</sub>O<sub>3</sub>.

Fiberfrax and Saffil fibers are mostly used for high temperature insulation.



## **B. Particles:** (Whiskers → small single crystal) SiC

The range of materials available in particulate form is extensive than fibers as because production is so simpler-almost any material can be ground into a powder from the bulk.

The powders may also be produced by precipitation from solution, gas atomization, sol-gel processing. *Silicon carbide, SiC*, will be taken to illustrate the parameters that need to be considered when selecting either whisker/particulate reinforcement.

The morphology and dimensions of whiskers are variable when produced by same process but these are 20 to 30 µm in length and less than 1 µm in diameter.

[The manufacturing process is discussed in Ceramic fibers-SiC]



#### **B. Particles:** (Whiskers → small single crystal) SiC

Whiskers, which are 0.1–1 μm in diameter and around 50 μm in length.

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The tensile modulus and tensile strength of these whiskers are reported as 700 GPa and 13 GPa, respectively.

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#### C. Matrix: Polymer; Metal; Ceramics

The roles of the matrix in a fiber-reinforced composite are:

- (1) to keep the fibers in place,
- (2) to transfer stresses between the fibers,
- (3) to provide a barrier against an adverse environment, such as chemicals and moisture, and
- (4) to protect the surface of the fibers from mechanical degradation (e.g., by abrasion).

The matrix plays a minor role in the tensile load carrying capacity of a composite structure.

However, selection of a matrix has a major influence on the compressive; inter laminar shear.

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#### C. Matrix: Polymer; Metal; Ceramics

The matrix provides lateral support against the possibility of fiber buckling under compressive loading, compressive strength of the composite material.

The inter-laminar shear strength is an important design consideration for structures under bending loads, whereas the in-plane shear strength is important under torsional loads.

The interaction between fibers and matrix is also important in designing damagetolerant structures.

Finally, the processing and defects in a composite material depend strongly on the processing characteristics of the matrix.

For example, for epoxy polymers used as matrix in many aerospace composites, the processing characteristics include the liquid viscosity, the curing temperature, and the curing time.

# THANK YOU

# Next class Matrix Fillers and Additives

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(3006)

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#### **Composite Materials**

(3006)

# Chapter 1 Introduction

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# Recap

#### **BORON FIBERS-CVD**

## **CERAMIC FIBERS-** SiC and Al<sub>2</sub>O<sub>3</sub>

- SiC: (1) Monofilament; (2) Multifilament and (3) Whisker
- Al<sub>2</sub>O<sub>3</sub>: (1) Fiber FP; (2) Nextel 610; (3) Nextel 720; (4) Fiberfrax and (5) Saffil

Particles: (Whiskers→ small single crystal) SiC

Matrix: Polymer; Metal; Ceramics



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Finally, the processing and defects in a composite material depend strongly on the processing characteristics of the matrix.

For example, for epoxy polymers used as matrix in many aerospace composites, the processing characteristics include the liquid viscosity, the curing temperature, and the curing time.



#### **Table: Matrix Materials**

	Matrix	Category		Application	
Ī		Thermoset	Epoxides	In aerospace and aircraft applications	
		Polyesters, vinyl esters Co		Commonly in automotive, marine, chemical,	
				and electrical applications	
			Phenolics	In bulk molding compounds	
			Polyimides, polybenzimidazoles (PBI),	For high-temperature aerospace applications	
			polyphenylquinoxaline (PPQ)	(temperature range: 250°C–400°C)	
			Cyanate ester	Electronics, printed circuit boards, satellite	
	Polymer	Polymer		and aerospace structural composites, and low-	
				dielectric and radar applications	
		Thermoplastic	Nylon 6, nylon 6,6, PET, PBT),	With discontinuous fibers in injection-molded	
			polycarbonate (PC), polyacetals	articles	
			Polyamide-imide (PAI), polyether ether	Suitable for moderately high temperature	
			ketone (PEEK), polysulfone (PSUL),	applications with continuous fibers	
			polyphenylene sulfide (PPS),		
			polyetherimide (PEI)		
	Metallic	Aluminum and its alloys, titanium alloys, magnesium		Suitable for high-temperature applications	
		alloys, copper-based alloys, nickel-based		(temperature range:300°C–500°C)	
		superalloys, stainless steel			
	Ceramic	Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> ), carbon, silicon carbide (SiC),		), Suitable for high-temperature applications	
		silicon nitride (Si <sub>3</sub> N <sub>4</sub> )			



#### **POLYMER MATRIX**

#### **Polymer Matrix**

A polymer is defined as a long-chain molecule containing one or more repeating units of atoms, joined together by strong covalent bonds.

A polymeric material (commonly called a plastic) is a collection of a large number of polymer molecules of similar chemical structure (but not of equal length).

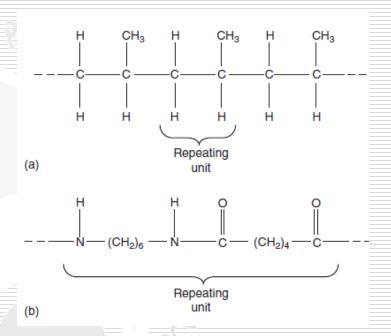


Figure: Examples of repeating units in polymer molecules. (a) A polypropylene molecule, (b) A nylon 6,6 molecule.

On a submicroscopic scale, various segments in a polymer molecule may be in a state of random excitation.



In the solid state, these molecules are frozen in space, either in a random fashion in amorphous polymers or in a mixture of random fashion and orderly fashion (folded chains) in semi-crystalline polymers.

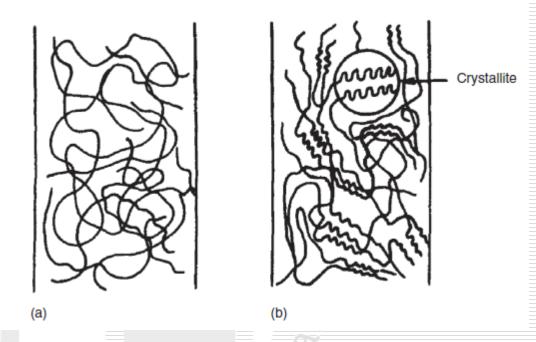


Figure: Arrangement of molecules in (a) amorphous polymers and (b) semi-crystalline polymers.

The frequency, intensity, and number of these segmental motions increase with increasing temperature, giving rise to the temperature-dependent properties of a polymeric solid.



#### Polymer categorization: Thermoplastics and Thermosets

Polymers are divided into two broad categories:. thermoplastics and thermosets

In a <u>thermoplastic polymer</u>, individual molecules are not chemically joined together.

They are held in place by weak secondary bonds or intermolecular forces, such as van der Waals bonds and hydrogen bonds.

With the application of heat, these secondary bonds in a solid thermoplastic polymer can be temporarily broken and the molecules can now be moved relative to each other or flow to a new configuration if pressure is applied on them.

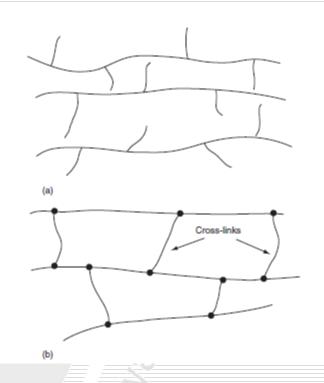


Figure: Schematic representation of (a) thermoplastic and (b) thermoset polymer.



#### **Polymer categorization: Thermoplastics and Thermosets**

On cooling, the molecules can be frozen in their new configuration and the secondary bonds are restored, resulting in a new solid shape.

Thus, a thermoplastic polymer can be heat-softened, melted, and reshaped (or postformed) as many times as desired.

In a <u>thermoset polymer</u>, on the other hand, the molecules are chemically joined together by cross-links, forming a <u>rigid</u>, three-dimensional network structure. Once these cross-links are formed during the polymerization reaction (also called the curing reaction), the thermoset polymer cannot be melted by the application of heat.

However, if the number of cross links is low, it may still be possible to soften them at elevated temperatures.



#### Selection of Matrix: Thermosets vs. Thermoplastics

The primary consideration in the selection of a matrix is its basic mechanical properties. For high-performance composites, the most desirable mechanical properties of a matrix are

- 1. High tensile modulus, which influences the compressive strength of the composite
- 2. High tensile strength, which controls the intraply cracking in a composite laminate
- 3. High fracture toughness, which controls ply delamination and crack growth

For a polymer matrix composite, there may be other considerations, such as good dimensional stability at elevated temperatures and resistance to moisture or solvents.

The former usually means that the polymer must have a high glass transition temperature  $T_g$ .

In practice, the glass transition temperature should be higher than the maximum use temperature.

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#### Selection of Matrix: Thermosets vs. Thermoplastics

Resistance to moisture and solvent means that the polymer should not dissolve, swell, crack (craze), or otherwise degrade in hot—wet environments or when exposed to solvents, namely, jet fuels, deicing fluids, and paint strippers.

- •Traditionally, thermoset polymers (also called resins) have been used as a matrix material for fiber-reinforced composites.
- •The starting materials used in the polymerization of a thermoset polymer are usually low-molecular-weight liquid chemicals with very low viscosities.
- •Fibers are either pulled through or immersed in these chemicals before the polymerization reaction begins.
- •Since the viscosity of the polymer at the time of fiber incorporation is very low, it is possible to achieve a good wet-out between the fibers and the matrix without the aid of either high temperature or pressure.
- •Fiber surface wetting is extremely important in achieving fiber—matrix interaction in the composite, an essential requirement for good mechanical performance.



#### **Comparison: Thermosets vs. Thermoplastics**

	TENN A N	
	Thermoset polymers	Thermoplastic polymers
	1. Fiber surface wetting	1. High impact strength
	2. Thermal stability	2. High fracture resistance
	3. Chemical resistance	3.Excellent damage tolerance
7	4. Less creep and stress relaxation	4. Higher strain-to-failure, i.e., resistance to matrix
		micro cracking
dvantages		5. Unlimited storage (shelf) life at room temperature
5		6. Shorter fabrication time
7		7. Post-formability (e.g., by thermoforming)
4		8. Ease of joining and repair by welding, solvent
		bonding
		9. Ease of handling (no tackiness)
		10. Can be reprocessed and recycled
74	1. Limited storage life (before the	1. The development of matrix is much slower
٥٥	final shape is molded) at room	2. Because of high melt or solution viscosities,
1 2	temperature	incorporation of continuous fibers into the matrix is
5	2. Long fabrication time in the mold	difficult.
	(curing reaction to transform the	3. Commercial engineering polymers, such as nylons
Disadvantages	liquid polymer to a solid polymer)	and polycarbonate, are of very limited interest in
	3. Low strain-to-failure that	structural applications because they exhibit lower
	contributes to low impact strengths	creep resistance and lower thermal stability.



### Table: Maximum Service Temperature for Selected Polymeric Matrices

				1
	Polymer	Tg, °C	Maximum Service Temperature,	
			°C	
	Thermoset matrix			
	DGEBA epoxy	180	125	
	TGDDM epoxy	240-	190	
		260	/a	
	Bismaleimides (BMI)	230-	232	
		290		
	Acetylene-terminated polyimide	320	280	
	(ACTP)			
	PMR-15	340	316	
	Thermoplastic matrix			
	Polyether ether ketone (PEEK)	143	250	
	Polyphenylene sulfide (PPS)	85	240	
	Polysulfone	185	160	
Rec	entlyPalyqthanheideoPEhermoplastic 1	<del>obly</del> mer	Shave been developed that p	ossess
	high Palyamide imide (PAI) and these ar			
	K-III polyimide	250	225	
	LARC-TPI polyimide	265	300	

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#### **Polymer Matrix Composites**

• Polymer matrix (epoxies, phenolics, polyester etc.) reinforced with fibres (glass, aramids, carbon, boron etc.)

#### • Advantages:

- Low cost
- High specific strength (e.g. graphite/epoxy composite five times stronger than steel per unit weight)
- Simple manufacturing

#### Disadvantages:

- High melt and solution viscosities
- Low operating temperature
- Susceptible to moisture absorption and dimensional change

#### **Polymer Matrix Composites : Typical Properties**

Property	Glass/Epoxy	Graphite/Epoxy	Aluminium	Steel
Specific Gravity	1.8	1.6	2.6	7.8
Ultimate Tensile Strength (MPa)	1062	1500	234	648
Young's Modulus (GPa)	38.6	181	69	207
Coefficient of Thermal Expansion (µm/m/°C)	8.6	0.02	23	11.7

#### **Polymer Matrix Composites**

#### **Polyesters:**

- Advantages:
  - Low cost
  - Can be made translucent

#### **Phenolics:**

- Advantages:
  - Low cost
  - Good service temperature

- Disadvantages:
  - Low service temperatures
  - Brittleness
  - High shrinkage during curing
- Disadvantages:
  - High void content

#### **Polymer Matrix Composites**

#### **Epoxies: Most commonly used resins**

- Advantages:
  - High mechanical strength
  - Good adherence to metals and glasses
  - Low shrinkage and volatility during cure

- Disadvantages:
  - High cost
  - Processing more difficult

#### Bisphenol-based epoxy resin:

Bisphenol-A

Epichlorohydrin

Bisphenol A diglycidyl ether (BADGE or DGEBA)

#### **Polymer Matrix Composites: Epoxies**

#### **Bisphenol-based epoxy resin:**

Bisphenol-A

Epichlorohydrin

Bisphenol A diglycidyl ether (BADGE or DGEBA)

Bisphenol-A

**DGEBA** 

Higher molecular weight diglycidyl ethers  $(n \ge 1)$ 

Curing Agents or Hardeners: Typically Polyamines



#### **METAL MATRIX**

*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, and this 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 *densities*, *high melting points* (*therefore*, *high process temperatures*), and a *tendency toward corrosion* at the fiber–matrix interface.

The two most commonly used metal matrices are based on **aluminum** and **titanium**.

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#### **METAL MATRIX**

Both of these metals have comparatively low densities 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 bring out the oxidation of fibers at elevated temperatures.

**Aluminum** and its alloys have attracted the most attention as matrix material in metal matrix composites.

Commercially, pure aluminum has been used for its good corrosion resistance.

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# THANK YOU

#### **Next Class:**

Metal Matrix, Ceramic matrix, Fillers

#### **CL 630** Composite Materials

(3006)

- 1. Introduction—10 hours
- 2. Theory of Reinforcement—4 Hours
- 3. Polymer nanocomposite (CNT) —6 Hours
- 4. Lamination Theory—5 Hours
- 5. Mechanical behavior of composite materials—9 Hours
- 6. Composite fabrication—6 Hours

#### **Tentative Grading**

1. Assignment:	40%
2. Surprise Quiz:	10%
3. Attendance/interaction:	10%
4. MCQ:	40%



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#### **Composite Materials**

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# Chapter 1 Introduction

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# Recap

C. Matrix: Polymer; Metal; Ceramics
Polymer Matrix Composites

Why some thermoplastic polymers are used above their glass transition temperatures?

Ans: Above Tg, in the rubbery state, they are soft and flexible.



#### **METAL MATRIX**

**Aluminum alloys**, such as 201, 6061, and 1100, have been used for their higher tensile strength—weight ratios.

Carbon fiber is used with aluminum alloys; however, at typical fabrication temperatures of 500°C or higher, carbon reacts with aluminum to form aluminum carbide (Al<sub>4</sub>C<sub>3</sub>), which severely degrades the mechanical properties of the composite.

Protective coatings of either titanium boride (TiB<sub>2</sub>) or sodium has been used on carbon fibers to reduce the problem of fiber degradation as well as to improve their wetting with the aluminum alloy matrix.

Carbon fiber-reinforced aluminum composites are inherently prone to galvanic corrosion, in which carbon fibers act as a cathode owing to a corrosion potential of 1 Volt higher than that of aluminum.

A more common reinforcement for aluminum alloys is SiC.



# Table: Comparison of the properties of various Metal Matrix

Metal Matrix	Properties	
Aluminum	Low densities and are available in a good corrosion resistance	
Titanium	Low densities and are available in a variety of alloy forms.	
Magnesium	Lighter than Ti, its great affinity toward oxygen promotes	
	atmospheric corrosion and makes it less suitable for many	
į.	applications	
Beryllium	It is the lightest of all structural metals and has a tensile modulus	
- Co	higher than that of steel but it suffers from extreme brittleness	
Nickel- and	These tend to bring out the oxidation of fibers at elevated	
cobalt-based	temperatures	
<b>Titanium alloys</b>	These have higher tensile strength-weight ratios as well as better	
7	strength retentions at 400°C–500°C over those of aluminum alloys	
	but high reactivity with boron and Al <sub>2</sub> O <sub>3</sub> fibers at normal	
*	fabrication temperatures	
<b>Aluminum alloys</b>	These have been used for <b>Aluminum alloys</b> , such as 201, 6061, and	
(201, 6061, and	1100, have been used for their higher tensile strength—weight ratios	
1100)		

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### **METAL MATRIX**

**Titanium alloys** that are most useful in metal matrix composites are  $\alpha$ ,  $\beta$  alloys (e.g., Ti-6Al-9V) and metastable  $\beta$ -alloys (e.g., Ti-10V-2Fe-3Al).

These titanium alloys have higher tensile strength—weight ratios as well as better strength retentions at 400°C–500°C over those of aluminum alloys.

The thermal expansion coefficient of titanium alloys is closer to that of reinforcing fibers, which reduces the thermal mismatch between them.

One of the problems with titanium alloys is their high reactivity with boron and  $Al_2O_3$  fibers at normal fabrication temperatures.

Borsic (boron fibers coated with silicon carbide) and silicon carbide (SiC) fibers show less reactivity with titanium.

Improved tensile strength retention is obtained by coating boron and SiC fibers with carbon-rich layers.

### **Metal Matrix Composites**

- Matrix is metal; e.g. aluminium, magnesium, titanium.
- Typical reinforcements are fibres of carbon and silicon carbide (SiC).
- Addition of fibres such as SiC to a metal matrix can
  - increase strength and stiffness,
  - reduce thermal expansion coefficient and electrical conductivity
- Advantages over conventional metals:
  - Higher specific strength and modulus
  - Lower coefficient of thermal expansion
  - Strength at high temperatures

- Disadvantages over conventional metals:
  - Ductility may be reduced
  - Fracture toughness may be lower

## **Metal Matrix Composites : Typical Properties**

Property	Aluminium	SiC/Aluminium	Graphite/Aluminium
Specific Gravity	2.6	2.6	2.2
Ultimate Tensile Strength (MPa)	234	1206	448
Young's Modulus (GPa)	69	117	124
Coefficient of Thermal Expansion (µm/m/°C)	23	12.4	18

### **Metal Matrix Composites**

- Advantages over polymer matrix composites:
  - Higher strength and modulus
  - Higher service temperature
  - Higher thermal and electrical conductivities
  - Better moisture resistance
  - Better wear and fatigue resistance

- Disadvantages over polymer matrix composites:
  - Higher density
  - Higher processing temperature

#### **Metal Matrix Composites**

- Applications
  - Space: Boron/aluminium (in space shuttle fuselage, lower mass and lower thermal conductivity)

Carbon/aluminium (space telescope)

- Military: SiC/aluminium good dimensional stability
- Transportation: Automotive engines, gas turbine engines



### **CERAMIC MATRIX**

Ceramics are known for their high temperature stability, high thermal shock resistance, high modulus, high hardness, high corrosion resistance, and low density.

However, these are brittle materials and possess low resistance to crack propagation, which is manifested in their low fracture toughness.

The primary reason for reinforcing a ceramic matrix is to increase its fracture toughness. Structural ceramics used as matrix materials can be categorized as either oxides or nonoxides.

**OXIDES:** Alumina  $(Al_2O_3)$  and mullite  $(Al_2O_3-SiO_2)$  are the two most commonly used oxide ceramics.

They are known for their thermal and chemical stability.

**NONOXIDES:** The common nonoxide ceramics are silicon carbide (SiC), silicon nitride (Si<sub>3</sub>N<sub>4</sub>), boron carbide (B<sub>4</sub>C), and aluminum nitride (AlN).



### **CERAMIC MATRIX**

Of these, **SiC** has found wider applications, particularly where high modulus is desired. It also has an excellent high temperature resistance.

Si<sub>3</sub>N<sub>4</sub> is considered for applications requiring high strength and AlN is of interest because of its high thermal conductivity.

The reinforcements used in ceramic matrix composites are SiC, Si<sub>3</sub>N<sub>4</sub>, AlN, and other ceramic fibers.

Of these, SiC has been the most commonly used reinforcement because of its thermal stability and compatibility with a broad range of both oxide and nonoxide ceramic matrices.

The forms in which the reinforcement is used in ceramic matrix composites include whiskers (with length to diameter ratio as high as 500), platelets, particulates, and both monofilament and multifilament continuous fibers.



### **Table: Comparison of different Ceramic Matrix**

Ceramic Matrix	<b>Properties</b>	
Oxides		
Alumina (Al <sub>2</sub> O <sub>3</sub> )	High thermal and chemical stability	
Mullite (Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub> )	High thermal and chemical stability	
Nonoxides		
Silicon carbide (SiC)	High tensile modulus, excellent temperature	
<u> </u>	resistance, thermal stability and compatibility	
3	with a broad range of both oxide and nonoxide	
	ceramic matrices	
Silicon nitride (Si <sub>3</sub> N <sub>4</sub> )	High tensile strength	
Boron carbide (B <sub>4</sub> C)	Extreme hardness, difficult to sinter to high	
(C)x	relative densities without the use of sintering	
The state of the s	aids, good chemical resistance, low density	
Aluminum nitride (AlN)	High thermal conductivity	

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### **Ceramic Matrix Composites**

- Matrix is ceramic such as alumina, calcium aluminosilicate (CAS);
  - typically reinforced by carbon or SiC fibres
- Ceramics have poor fracture toughness; reinforcing improves this property

#### Advantages:

- High strength and hardness
- Very high service temperatures
- Chemical inertness
- Low density (compared to metals)
- Better wear and fatigue resistance

#### • Applications:

 Good for applications requiring high mechanical properties especially at high service temperatures and/or in oxidizing environments. E.g. cutting tool inserts.

## **Ceramic Matrix Composites: Typical Properties**

Property	Aluminium	SiC/CAS	SiC/LAS
Specific Gravity	2.6	2.6	2.2
Ultimate Tensile Strength (MPa)	234	400	496
Young's Modulus (GPa)	69	121	90
Coefficient of Thermal Expansion (µm/m/°C)	23	4.5	3.6

## **Carbon-Carbon Composites:**

Carbon fibres in a carbon matrix

### Advantages:

- Good tensile and compressive strength
- Can withstand high temperatures
- High fatigue resistance
- High thermal conductivity
- Reinforcement improves fracture toughness

### Disadvantages :

- High cost
- Susceptibility to oxidation at high temperatures

### **Carbon-Carbon Composites: Typical Properties**

Property	Aluminium	Carbon/Carbon
Specific Gravity	2.6	1.7
Ultimate Tensile Strength (MPa)	234	36
Young's Modulus (GPa)	69	13.5
Coefficient of Thermal Expansion (µm/m/°C)	23	2.0

### **Carbon-Carbon Composites:**

### Applications:

Nose cones of space shuttles:

Low weight, high specific heat, high thermal conductivity, high thermal shock resistance

#### Aircraft brakes:

High durability, high specific heat, low braking distance, low weight (compared to metals)



## **D.** Fillers and additives: CaCO<sub>3</sub>

Fillers are added to a polymer matrix for one or more of the following reasons:

- 1. **Reduce cost** (since most fillers are much less expensive than the matrix resin)
- 2. Increase modulus
- 3. Reduce mold shrinkage
- 4. Control viscosity
- 5. Produce smoother surface
- ✓ The most common filler for polyester and vinyl ester resins is calcium carbonate (CaCO₃), which is used to reduce cost as well as mold shrinkage.
- ✓ Examples of other fillers are clay, mica, and glass microspheres (solid as well as hollow).
- ✓ Although fillers increase the modulus of an unreinforced matrix, they tend to reduce its strength and impact resistance.



## **D.** Fillers and additives: CaCO<sub>3</sub>

Impact strength and crack resistance of brittle thermosetting polymers can be improved by mixing them with small amounts of a liquid <u>elastomeric</u> toughener, such as, carboxyl-terminated polybutadiene acrylonitrile (CTBN). In addition to fillers and tougheners, <u>colorants</u>, <u>flame retardants</u>, and <u>ultraviolet</u> (UV) absorbers may also be added to the matrix resin.

**Table: Properties of Calcium Carbonate-Filled Polyester Resin** 

Property	Unfilled	<b>Polyester filled with</b>
	Polyester	30% CaCO <sub>3</sub>
Density (g/cc)	1.3	1.48
Heat deflection temperatures HTD	79	83
(°C) [ASTM test method D648]		A)
Flexural strength (MPa)	121	62
Flexural modulus (GPa)	4.34	7.1

# THANK YOU

## **Next Class:**

Theory of Reinforcement