Composite Materials

Chapter 2
Reinforcements

تکلیف ۲:

یافتن و تحویل فایل حداقل ۱۰ مقاله جدید (۲۰۱۰ به بعد) مرتبط با موضوع از مجلات معتبر

موضوع تکلیف ۲			
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			۵
			۶

- زمان تحویل مقالات روی CD: تا پایان اسفند
- از بین مقالات تحویل شده، یک مقاله به عنوان مقاله محوری تکلیف اصلی درس انتخاب خواهد شد.
- زمان تحویل تکلیف اصلی تا اواخر ترم می-باشد.

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موضوع تکلیف ۲			
Self healing composites	کامپوزیت-های خود ترمیم-گر		۱
Self cleaning composites	کامپوزیت-های خود تمیزگر		۲
Self reinforcing composites	کامپوزیت-های خود تقویت-کننده		۳
Shape memory composites	کامپوزیت-های حافظه دار		۴
Foam composites	کامپوزیت-های فومی		۵
Functionally graded composites	کامپوزیت-ها مدرج تابعی (هدفمند)		۶

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- Reinforcement types:
  - Particles
  - Flakes
  - Whiskers
  - Short fibers
  - Continuous fibers
  - Continuous sheets

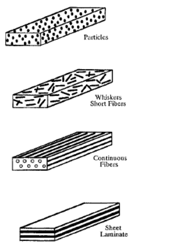
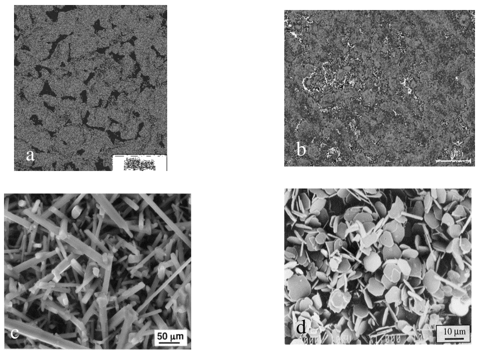


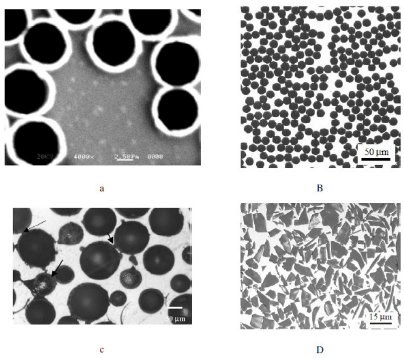
Fig. 1.1 Different types of metal matrix composites.

- Continuous fibers:
  - •Stronger and stiffer than any other form
  - •Most widely used

Metal Matrix Composites, Chawla & Chawla 2006.



a) SiC particles, b) Al_2O_3 particles, c) aluminum borate whiskers and d) Alumina flakes preforms used in pressure infiltration process



Micrographs of aluminum alloy matrix composites fabricated by pressure infiltration process. Preforms are made form a) nickel coated carbon fibers, b) Altex (γ-Al_2O_3) fibers, c) fly ash cenospheres and d) SiC particles.

Table 1.1 Typical Reinforcements Used in Metal Matrix Composites

Type	**Aspect Ratio**	**Diameter, μm**	**Examples**
Particle	1–4	1–25	SiC, Al_2O_3, BN, B_4C, WC
Short fiber or whisker	10 – 10000	1–5	C, SiC, Al_2O_3, $Al_2O_3+SiO_2$
Continuous fiber	>1000	3 – 150	SiC, Al_2O_3, C, B, W, Nb-Ti, Nb_3Sn

Table 2.1 Some important reinforcements for metal matrix composites.

Continuous Fibers	Al_2O_3, $Al_2O_3+SiO_2$, B, C, SiC, Si_3N_4, Nb-Ti, Nb_3Sn
Discontinuous Fibers	
(a) Whiskers	SiC, TiB_2, Al_2O_3
(b) Short Fibers	Al_2O_3, SiC, ($Al_2O_3+SiO_2$), vapor grown carbon fibers
Particles	SiC, Al_2O_3, TiC, B_4C, WC

Metal Matrix Composites, Chawla & Chawla 2006.

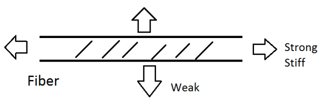
✓**Particles or discontinuously reinforced composites are important:**

- **Less expensive** than continuous fiber reinforced composites
- Use of **conventional manufacturing processes** such as casting or powder metallurgy followed by conventional secondary processing such as rolling, forging and extrusion is possible
- Relatively **isotropic property** compared to fiber reinforced composites
- Higher service temperature and thermal stability
- Improved modulus and strength
- Better wear resistance

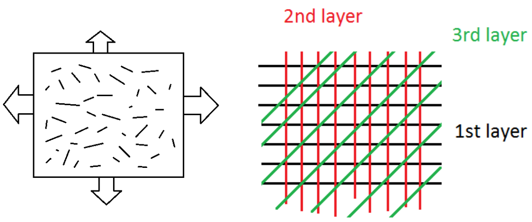
✓Composites made by liquid processes are somewhat cheaper than those made by other methods.

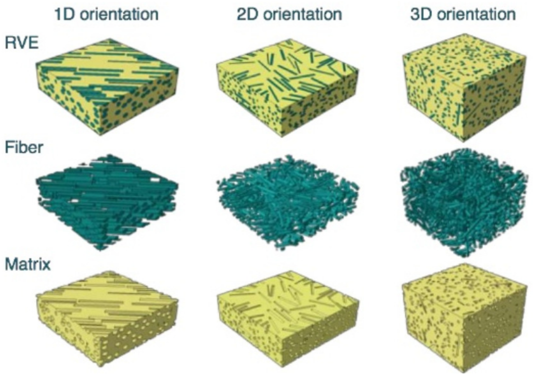
Fibrous materials

- Fiber reinforced composites are more prominent, specially in Polymer Matrix Composites (PMCs)
- Fibers must be strong, stiff and flexible for making preforms (by knitting and braiding) & small in diameter
- Fibers set anisotropic properties



- To set isotropic properties:
  - Use particles, random short fibers
  - Arrange long fibers in different directions





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Naturally occurring fibers

- Situations involving not very high stresses
- Advantage: low cost

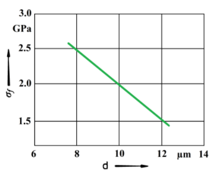
- Cellulosic fibers:
  - Cotton, flax, jute, hemp, sisal, and ramie, … used in the textile industry
  - Wood and straw ….used in the paper industry.
- Protein based natural fibers:
  - Hair, wool, and silk
  - Spider silk fibers : high work of fracture

Man-made reinforcements

- **High performance fibers:**
  - *Glass fiber*
    - The most common reinforcement for PMCs
  - *Aramid fiber*
    - 1960s, much stiffer and lighter, higher temperature resistance, …
      - Kevlar & Nomex, Du Pont's trade name for Aramid fiber
      - Twaron, Teijin Aramid trade name for Aramid fiber

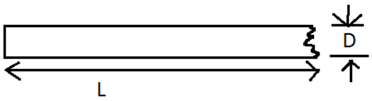
- *Gel-spun polyethylene fiber*
  - 1980s, stiffness comparable to that of Aramid fiber
- *Boron, silicon carbide, carbon, and alumina*
  - Developed in the second part of the 20^{th} century
  - High strength, high stiffness, high temperature resistnce
- *Other ceramic fibers*
  - Developed in the last quarter of the 20^{th} century
  - By novel processing techniques: Sol-gel processing and controlled pyrolysis of organic precursors

- **Fibers as high-performance engineering materials:**
  1. A small diameter with respect to its microstructural unit:
     - Size effect: the smaller the size, the lower the probability of having imperfections in the material
     - A higher fraction of the theoretical strength is attained than in a bulk form
     - Figure 2.1: General trend!
       The strength of a carbon fiber decreases as its diameter increases



2. A high aspect ratio (length/diameter)

Allows a very large fraction of the applied load to be transferred via the matrix to the fiber



- *Chapter 10:*
  - Fibers must have an aspect ratio above a critical value for load transfer to occur from matrix to fiber
  - L/D >> 10

Composite Materials, 2016, BN, IUT, Iran

3. A very high degree of flexibility

→ Can be used in a variety of techniques for making composites

Continuous glass fiber made via sol-gel

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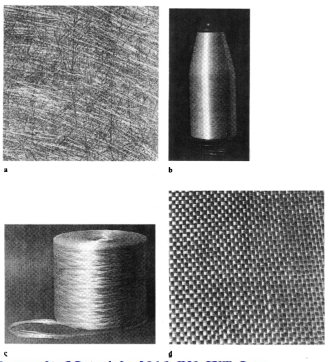
Various forms of glass fibers



a. Chopped strand mat
b. Continuous yarn
c. Roving
d. Woven fabric

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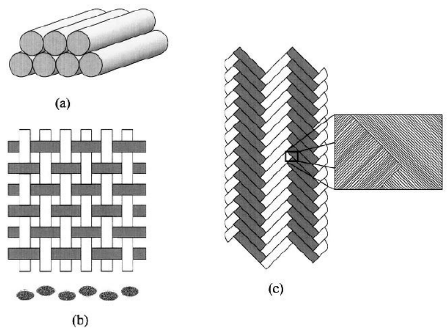
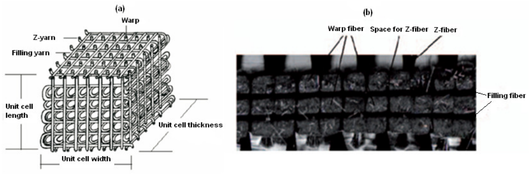
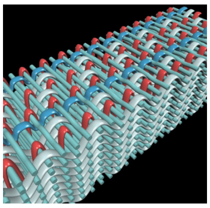


Fig. 2.1 Forms of fibrous materials (a) unidirectional fibers, (b) woven fiber fabric, and (c) fabric made of knitted fibers.

Various forms of Alumina fibers





Flexibility:

For a fiber: to what radius (R) we can bend it before it fails

$$\text{Flexibility} = \frac{1}{MR} = \frac{64}{E\pi d^4}$$

M: Bending moment
R : Radius of curvature
E : Young's modulus
d : Equivalent diameter of fiber

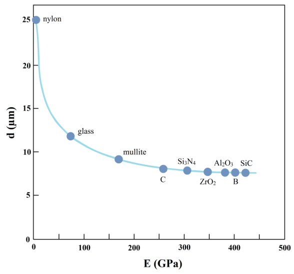
E ↓ Flexibility ↑

d ↓ Flexibility ↑

- Flexibility of a fiber is a very sensitive inverse function of its diameter, d.
- Given a sufficiently small diameter, it is possible to produce a fiber as flexible as any from a polymer, a metal, or a ceramic.
- Depending on the elastic modulus of the fiber, the fiber diameter is selected for a given level of flexibility
- Higher E ↑ Smaller d↓

- Even ceramics can have the same flexibility as a nylon fiber

Diameters required in different fibers to set the same flexibility as 25µm diameter nylon



- Obtaining such a small diameter in practice can be prohibitively expensive!

Fiber Spinning Processes

– The process of extruding a liquid through small holes in a spinneret to form solid filaments.

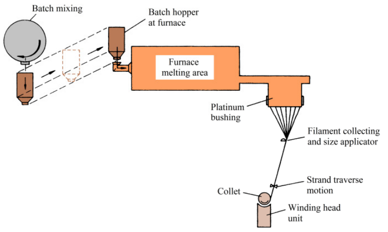
– In nature, silkworms and spiders produce continuous filaments by this process.

Important fiber spinning techniques

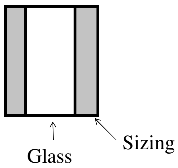
1- Melt spinning:

- The molten material is extruded through a spinneret.
- The liquid jets harden into solid filaments in air.

•Molten glass flows by gravity through the electrically heated platinum bushing to form fine continuous filaments.
•Each bushing has 200 holes at its base.
•Gathered in a strand.
•Sizing applied.



- A coating of polyvinyl acetate on Glass fibers
- Sizing protects the surface as well as binds the filaments into a strand.



- Otherwise surface cracks will damage fibers.
- Cracks extend in brittle materials leading to failure.

Important fiber spinning techniques

2- Wet spinning:

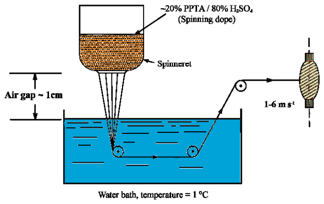
The jets of liquid freeze or harden in the coagulating bath as a result of chemical or physical changes.

3- Dry spinning:

A solution is extruded through a spinneret.

A stream of hot air evaporates the solvent and leaves the solid filaments behind.

4. Dry jet–wet spinning:
   - A special process for spinning of Aramid fibers.
   - An appropriate polymer liquid crystal solution is extruded through spinneret holes, passes through an air gap before entering a coagulation bath, and then goes on a spool for winding (Sect. 2.5.2).



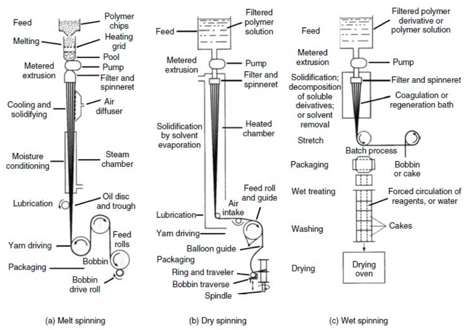


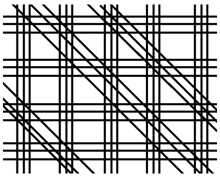
FIGURE 11.1 Three main types of spinning processes: melt spinning, dry solution spinning,

Stretching and Orientation

- Skin effect: During extrusion through a spinneret, the molecules in the surface region undergo more orientation than the ones in the interior.
- The as-spun fiber is subjected to some stretching, causing further chain orientation along the fiber axis and better tensile properties, such as stiffness and strength, along the fiber axis.
- Higher draw ratio results in a higher elastic modulus, higher degree of crystallinity, lower moisture absorption, greater chemical stability.

Glass Fibers

- In use since first quarter of 1900's
- Silica based fibers (50-60% SiO_2) + other oxides of Ca, B, Na, Al, and Fe
- Light, strong, and inexpensive material
- Common reinforcement in PMCs
  - Strand- group of 204 fibers
  - Roving- group of strands
  - Fabric



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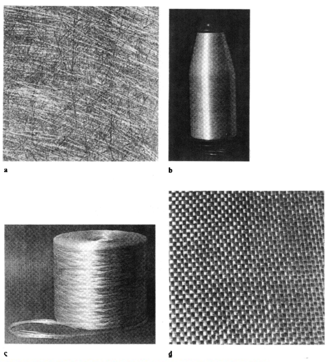
Various forms of glass fiber



a. Chopped strand mat
b. Continuous yarn
c. Roving
d. Woven fabric

Composite Materials, 2016, BN, IUT, Iran

- Stiffness is not very high
  - E_{Glass} ~ 70 GPa
  - $E_{Carbon\ fiber}$ > 200 GPa
  - $E_{Boron\ fiber}$ ~ 400 GPa
  - $E_{Al_2O_3\ fiber}$ > 150 GPa
  - $E_{SiC\ fiber}$ > 200 Gpa
- Glass is susceptible to surface damage, moisture, decrease in strength and fatigue

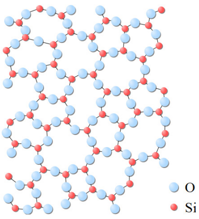
Composite Materials, 2016, BN, IUT, Iran

Table 2.1 Approximate chemical compositions of some glass fibers (wt.%)

Composition	E glass	C glass	S glass
SiO_2	55.2	65.0	65.0
Al_2O_3	8.0	4.0	25.0
CaO	18.7	14.0	–
MgO	4.6	3.0	10.0
Na_2O	0.3	8.5	0.3
K_2O	0.2	–	–
B_2O_3	7.3	5.0	–

- E Glass
  - ✓ Electrical insulator, good strength and modulus
  - ✓ More than 90% of all glass fiber produced is Eglass
- C Glass
  - ✓ Better resistance to corrosion
- S Glass
  - ✓ Higher temp glass due to higher SiO_2 and Al_2O_3 and less of low melting point oxides

- Glass fiber
  - Fabrication methods:
    - Melt spinning: Processing temperature is very high
    - Sol-gel: Processing temperature is much lower
  - Amorphous structure with no long range order
  - 3 dimensional network structure → Isotropic properties



•Oxygen atom is bonded covalently to silicon in each tetrahedron

Amorphous structure of silica-based glass

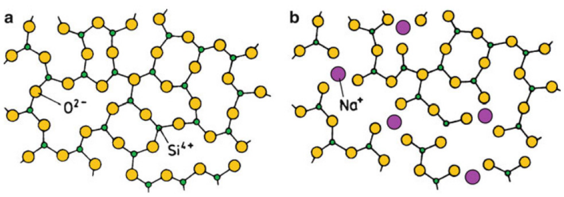


Fig. 2.6 Amorphous structure of glass: (a) a two-dimensional representation of silica glass network and (b) a modified network that results when Na_2O is added to (a). Note that Na^+ is ionically linked with O^{2-} but does not join the network directly

•Na_2O and other metal oxides change the structure and properties

Properties of E Glass

- Density 2.55 g/cm^3
- Tensile strength 1750 MPa
- Young's Modulus 70 GPa
- CTE (K^{-1}) 4.7x10^{-6}

- High strength + low density
- But modulus is not very high
  → Use of other *advanced fibers* (e.g., boron, carbon, Al_2O_3, and SiC) by the aerospace industries

- Susceptible to surface damage, moisture, and subcritical crack growth under extended loading times (static fatigue)
  →decreased strength

Applications

- ***GRP: Glass fiber reinforced plastics***

✓ Widely used in buildings and construction
  – Cladding for other structural materials, or
  – An integral part of a structural or non-load-bearing wall panels, window frames, tanks, bathroom units, pipes, ducts, …

✓ Boat hulls

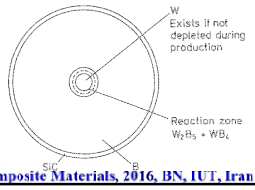
✓ In chemical industry as storage tanks, pipelines, and process vessels, …

✓ Rail and road transport industry

✓ Aerospace industry

Boron Fibers

- A brittle material
- Amorphous Boron fiber has high strength
- Density: 2.34 g cm^{-3}
- Made by CVD (chemical vapor deposition) on a substrate
- High temperatures is required for CVD process
- Choice of substrate material is limited: W or C
- It is a composite in itself!



- For 160 µm fiber with W core
  - Density is 2.6g cm^{-3}
  - Melting point 2040° C
  - CTE up to 315 °C 8.3x10^{-6} °C $^{-1}$
- Combined with Aluminum to make Al-B composites

- Boron is used in
  - Military aircraft such as F-14, F-15
  - US Space Shuttle
  - Golf Club Shafts
  - Tennis Racquet
  - Bicycle Frames
- Boron is expensive mainly due to Tungsten substrate
- Stiff competition from other advanced fibers, in particular, carbon fibers.

- Two CVD processes for obtaining Boron fiber:

1- Thermal decomposition of Boron Hydride (BH_3)

- Involves low temperatures

→ Carbon coated glass fiber can be used

Boron Hydride → Boron deposits on substrate + Hydrogen leaves

- Fibers are weak due to pores, trapped gases and poor bonding with substrate

2- Reduction of Boron Halide

- Boron Trihalide is reduced by hydrogen

$$2BX_3 + 3H_2 = 2B + 6HX$$

  - X can be Cl, Br, I
  - The temperatures involved are very high

→ A refractory metal substrate such as W is needed

  - W density = 19.3 g cm^{-3}, heavy!

→ The fiber is heavy, but dense and uniform in quality

Boron fiber production by CVD

$$2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$$

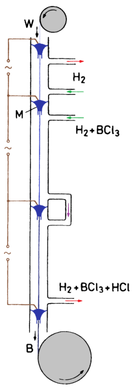
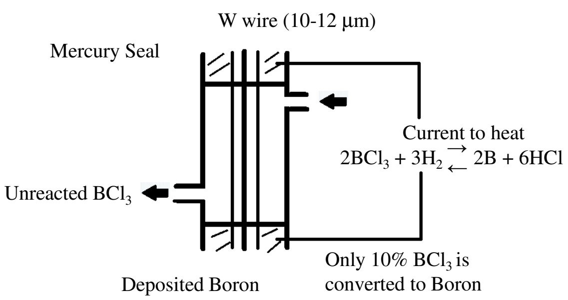
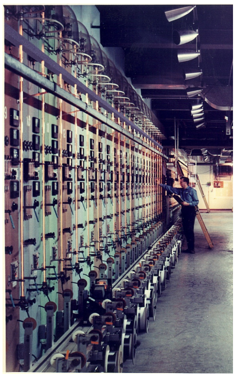
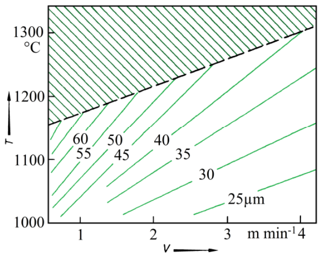


Fig. 2.7: Schematic of boron fiber production by halide decomposition on a tungsten substrate



A boron fiber production facility





•Temp. must be below a critical temperature otherwise you get crystalline Boron which has poor properties. Lower temps give amorphous nanocrystalline

•For a stationary wire the critical temperature is ~1000° C

- The more rapidly the fiber is drawn, the higher the allowed temperature
  - Boron is deposited in an amorphous state and the more rapidly the wire is drawn out from the reactor, the higher the allowed temperature is.
  - Faster speed → Higher production rate

$V \uparrow \quad T_{critical} \uparrow$

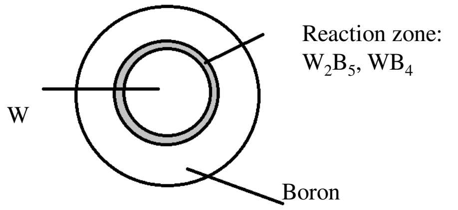
$d \uparrow \quad T \uparrow < T_{critical}$

- The structure and morphology of boron is a function of
  - conditions of deposition
  - temperature
  - composition of gases
  - instability in gas flow
  - impurity elements
  - process irregularities
  - fluctuations in electric power
  - operator-induced variables

Structure:

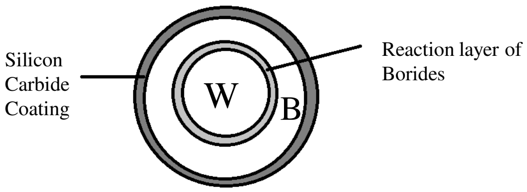
- If temp of CVD deposition is > 1300° C
  - β rhombohedral boron is deposited
- If temp of deposition is < 1300° C
  - Amorphous or α rhombohedral is deposited
- X-ray diffraction pattern shows large and diffuse halos
- Electron diffraction however confirms that it is nano-crystalline
  - Amorphous is really nanocrystalline boron with grain diameter 2 nm.

•Presence of *large microcrystalline phases,* specially at temperatures above the critical temperature, constitutes serious imperfections



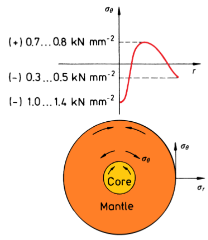
- W and B react at high temperature → form a series of compounds at the interface: W_2B, WB, W_2B_5, WB_4
- Prolonged heating, the core may be completely converted into WB_4
- Boron diffuses into Tungsten and forms Borides – fiber expands (from 12.5 µm to 17.5 µm)

- **SiC barrier coating** is used to prevent any adverse reaction between B and the matrix (such as Al) at high temperatures.



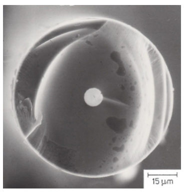
- SiC is vapor deposited onto boron using a mixture of Hydrogen and methyl-dichlorosilane

- **Residual stresses**
  - Residual stresses in Boron fiber due to CVD process
  - Boron and W_xB_y core have different coefficients of expansion
  - Boron diffuses in tungsten and reacts → forming higher volume products → residual stresses



- Compressive stresses on fiber surface due to quenching when fiber is pulled out of hot chamber
- These stresses can lead to cracks in the fiber

- Cracks initiate fracture in Boron Fibers
- Fracture can also initiate at other preexisting defects at core fiber interface or at surface
- Radial cracks can lead to a brittle fracture



•Note the radial crack. It does not extend all the way to surface of the fiber.

•This is because the surface layer of boron fiber is in compression.

- Ave. tensile strength: 3-4 GPa
  - Lower than the predicted values of ~14 GPa
  - Due to internal stresses and defects such as voids and structural discontinuities
- Young's modulus: 380-400 GPa
- Lightly etched or polished fibers
  → less surface defects → are stronger
    - Chemically polished: 4.6 GPA strength

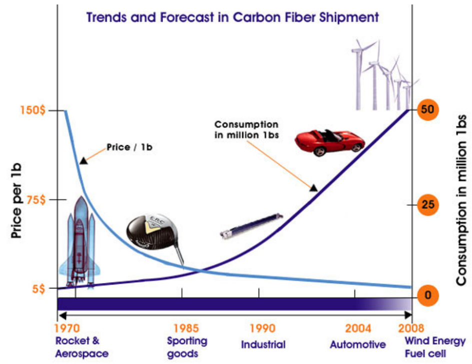
Table 2.3 Strength properties of improved large-diameter boron fibers

Diameter (μm)	Treatment	Strength Average[a] (GPa)	Strength COV[b] (%)	Relative fracture energy
142	As-produced	3.8	10	1.0
406	As-produced	2.1	14	0.3
382	Chemical polish	4.6	4	1.4
382	Heat treatment plus polish	5.7	4	2.2

[a] Gauge length = 25 mm
[b] Coefficient of variation = standard deviation/average value

- In these experiments:
  - In fibers showing strengths greater than 4 Gpa, the fracture was controlled by a tungsten boride core
  - In fibers with strengths of 4 GPa or less, the fracture was controlled by fiber surface flaws
- The high temperature treatment improved the fiber properties by putting a permanent axial compressive strain in the sheath.

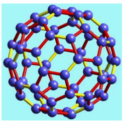
Carbon Fibers

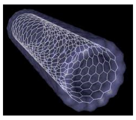


Carbon Fiber

- Light, Carbon density= 2.268 g/cm^3
- Carbon exists in a variety of crystalline forms:
  - Graphite
  - Diamond
  - Buckminster Fullerene (Bucky ball)

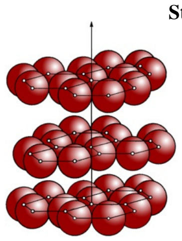
    - CNT



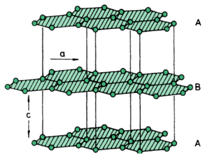


- For composites, graphite form is important
- Graphite: carbon atoms are arranged in hexagonal close pack lattices

Structure of graphite



Hexagonal layered structure formed by ABAB stacking of carbon atoms.
Note the *a* and *c* directions



↑ Weak Bond ↓ E_{th}= 35 GPA

← Strong Bond → E_{th}= 1000 GPA

- A goal of almost all carbon fiber processing techniques: Obtaining a very high degree of preferred orientation of hexagonal planes along the fiber axis.
- Raw material for carbon fiber: Special textile polymeric fibers that can be carbonized <u>without melting</u>.
- The precursor fiber consists of long-chain molecules (0.1–1 μm when fully stretched) arranged in a random manner.

- Precursor fibers:
  - Polyacrylonitrile (PAN)
  - Rayon
  - Pitch based
  - Polyvinyl alcohol based
  - Polyimides based
  - Phenolics based

- Essential steps in carbon fiber fabrication processes:
  - 1. A **fiberization** procedure to make a precursor fiber (spinning followed by some drawing or stretching).
  - 2. A **stabilization** treatment that prevents the fiber from melting in the subsequent high-temperature treatments.
  - 3. **Carbonization** that removes most non carbon elements.
  - 4. **Graphitization** that improves the properties of carbon fiber obtained in step 3 (optional).
- Rigorous controls are needed!

Processing

- Japan- First to produce high modulus carbon from polyacrylonitrile (PAN) precursor fiber, 1961, E=170 GPa
- Now you can get carbon fiber with modulus of more than 600 GPA
- Basically all methods involve **thermal decomposition** of organic fibers under **controlled heating and stretching** in selected atmospheres

Processing of ex-PAN carbon fiber

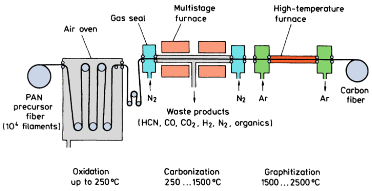
• ex-PAN carbon fiber: Carbon fiber made from PAN

•**Stabilized** in air at 250º C under tension to prevent contraction

  • Flexible PAN transforms to rigid ladder polymer, white fibers turn black

• **Carbonization**: Heating slowly in inert atmosphere to 1000-1500 °C, maintains high degree of molecular order in fiber

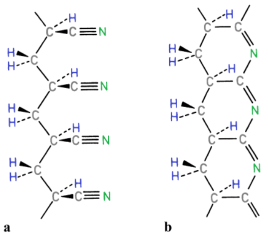
• **Graphitization**: Very short time at temperatures up to 3000 °C, improves alignment of fiber texture



Structure of PAN molecule

Stabilization:

Flexible PAN molecule → Rigid ladder (or oriented cyclic) molecule

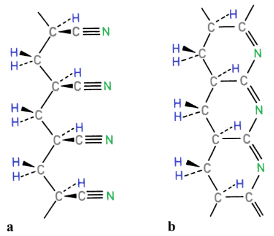


(a) Flexible polyacrylonitrile molecule and (b) Rigid ladder molecule

- High modulus is achieved by alignment of basal planes of graphite lamellas or crystals parallel to the length of the fibers
- This is done by closely controlled stretching of carbon fibers during high temperature treatment.
- Such stretching causes the basal planes to rotate parallel to the axis of stress and parallel to fiber length.
- Without alignment of basal planes the modulus is lower

- The structural changes:
  - **Stretching**: improves axial alignment of the polymer molecules.
  - **Oxidation treatment**: fibers are maintained under tension. In the absence of tensile stress, a relaxation will occur and the ladder polymer structure will become disoriented with respect to the fiber axis.
  - **Carbonization**: the remaining considerable quantities of N_2 and H_2 are eliminated
  - The carbon atoms remaining are mainly in the form of a network of extended hexagonal Ribbons.
  - These strips tend to align parallel to the fiber axis, but the degree of order of one ribbon with respect to another is relatively low.
  - **Graphitization** treatment improves the order

Structure of PAN molecule

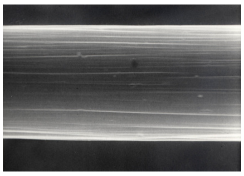


(a) Flexible polyacrylonitrile molecule.
(b) Rigid ladder (or oriented cyclic) molecule

Flexible PAN molecule
↓
Stabilization: Rigid ladder molecule
↓
Still loses hydrogen and nitrogen at 1000-1500 ºC, extended hexagonal ribbons
↓
Heating at 3000º C aligns the ribbons with respect to each other

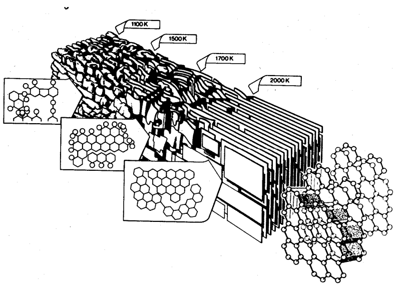
- Yield: 50 weight%
- Hot stretching above 2000 °C: plastic deformation of carbon fibers → improvement in E

Surface structure of ex-PAN carbon fiber

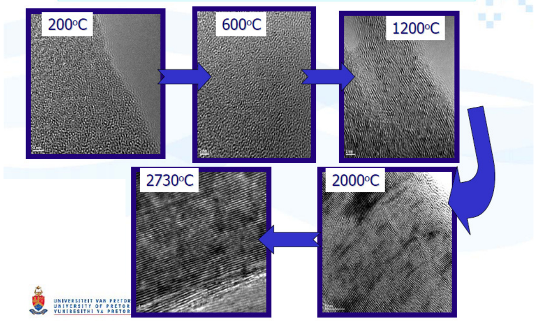


Fiber diameter = 8 µm
The surface markings stem from the fiber drawing process

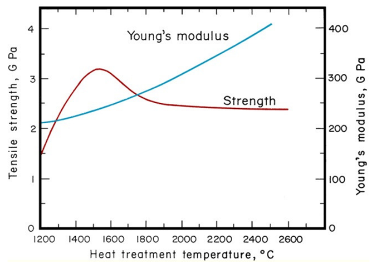
- The degree of order and the modulus in the fiber axis direction, increases with increasing graphitization temperature.



High Resolution Images of a Graphitisation Series



B. Rand, "Graphite structure, properties and manufacture", Nuclear Graphite Materials Technology, 2009



Strength and modulus of carbon fiber as a function of final heat treatment temperature

Ex-Cellulose Carbon Fibers

- **Cellulose:** a natural polymer, frequently fibrous
- **Cotton fiber**
  - The first cellulose fiber carbonized
  - Decomposes before melting ☑
  - Rather low degree of orientation along the fiber axis
    ⟹ low modulus carbon fiber ☒
  - Not available as a tow of continuous filaments ☒
  - Expensive ☒

- **Rayon**: A thermoset polymer, extracted from wood pulp → cheap
  - Continuous filament tows are produced by wet spinning

- Conversion into carbon fiber:
  - **Fiberize**
  - **Stabilize** (in air or oxygen, T<400 °C) →release of H_2O, CO, CO_2, tar
    - Chain fragmentation (depolymerization) occurs
      - Stabilizing under tension does not work!
  - **Carbonize**: ~ 1000 °C in nitrogen, (T<1500 °C)
  - **Graphitize**: ~ 2800 °C under stress (T>2500°C) → Plastic deformation

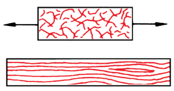
- Yield : 15-30weight%

Composite Materials, 2016, BN, IUT, Iran

Rayon-based carbon fiber production

Rayon precursor ↓ Stabilize ↓ Carbonize ↓ Graphitize

Stress orient



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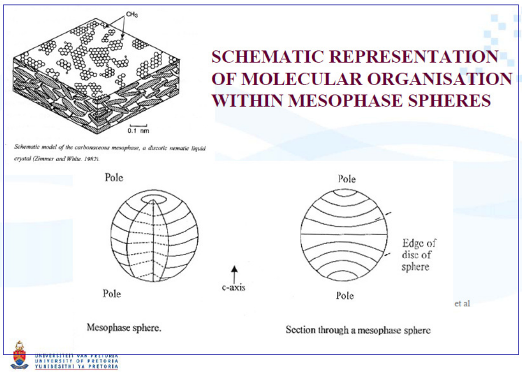
Ex-pitch carbon fiber

- Pitch: Thermoplastic polymer
- Sources: Polyvinylchloride (PVC), petroleum asphalt, and coal tar
  - Cheap
  - High yield of carbon
  - Highly oriented carbon fiber can be obtained
- ***Isotropic pitch*:** Orientation of molecules is obtained by melt spinning at high strain rates and quenching to give highly oriented pitch precursor fiber
- *Conversion of pitch precursor fiber to carbon fiber:*
  - Stabilization (oxidation): removes non-carbon elements in the form of gases and forms non-melting cross linked structure
  - Carbonization
  - Graphitization: 2500-3000 °C

Composite Materials, 2016, BN, IUT, Iran

- Prolonged heating above 350º C leads to formation of highly oriented optically anisotropic liquid crystalline phase called *mesophase* (intermediate phase)
- Mesophase: microspheres floating in isotropic pitch liquid
- ***Mesophase pitch*** can be melt spun into a precursor for carbon fiber pitch
  - Spinning involves high shear and elongation in fiber axis direction
  - A high degree of preferred orientation is achieved
- Orientation is further developed during carbonization
- Very high values of Young's modulus can be obtained
- More details is available in the text book.

Composite Materials, 2016, BN, IUT, Iran



B. Rand, "Graphite structure, properties and manufacture", Nuclear Graphite Materials Technology, 2009

Composite Materials, 2016, BN, IUT, Iran

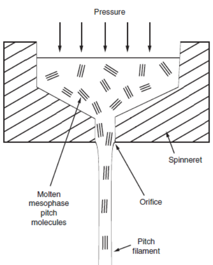
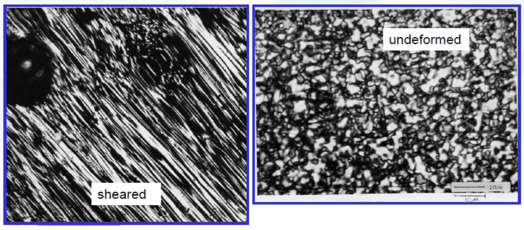


FIGURE 2.17 Alignment of mesophase pitch into a pitch filament. (After *Commercial Opportunities for Advanced Composites, ASTM STP*, 704, 1980.)

Fiber reinforced composite materials: Manufacturing and design, P.K. Mallick, 2008

Composite Materials, 2016, BN, IUT, Iran



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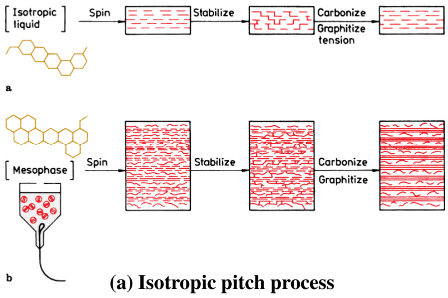
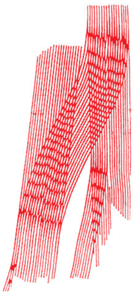


(a) Isotropic pitch process
(b) Mesophase pitch process

- The decomposition of the precursor fiber results in a weight loss and a decrease in fiber diameter.
- The weight loss: 40 to 90 %, depending on the precursor and treatment
- At the microscopic level, carbon fibers possess a rather heterogeneous microstructure.

• Many models for structure of carbon fibers



2D representation of PAN-based carbon fiber

3D representation of PAN-based carbon fiber

•A carbon fiber consists of many graphitic lamellar ribbons oriented roughly parallel to the fiber axis with a complex interlinking of layer planes both longitudinally and laterally

•The fiber surface is better oriented

Properties

- Density of carbon fiber: 1.6 – 2.0 g/cm^3 (function of precursor and thermal treatment)
- Density of precursor: 1.14-1.19 g/cm^3
- Impurities in the precursor, misoriented layer planes, voids and other flaws affect the mechanical property of carbon fiber.
- A mechanism of tensile failure of carbon fiber based on the presence of misoriented crystallites is shown in Fig. 2.23

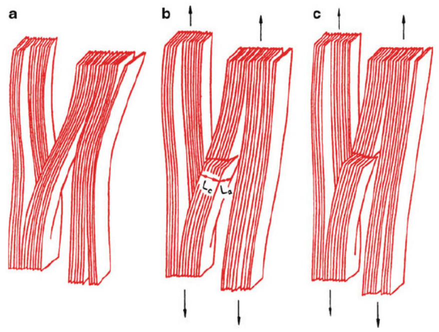
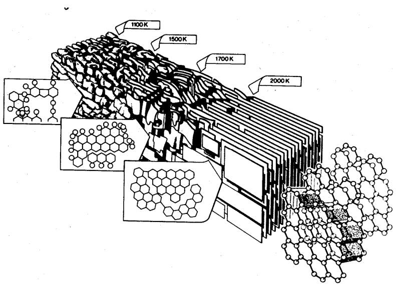


Fig. 2.23 Model for tensile failure of carbon fiber: (a) a misoriented crystallite linking two crystallites parallel to the fiber axis, (b) basal plane rupture under the action of applied stress, (c) complete failure of the misoriented crystallite [from Bennett et al. (1983), used with permission]

Properties

- The degree of order and the modulus in the fiber axis direction, increases with increasing graphitization temperature.



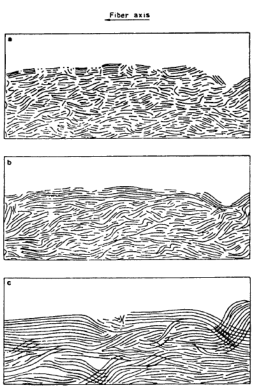


Figure 3.10 Schematic representation of the development of a skin from PAN-based carbon fibers heat-treated at (a) 1 000°C, (b) 1 500°C, and (c) 2 500°C. From Ref. 6.

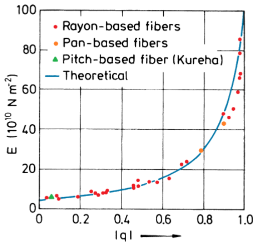
Properties

- Modulus = *f* (orientation, porosity)

Orientation ↑ Modulus ↑
Porosity ↓ Modulus ↑

•q= An orientation parameter

q = 0 → isotropic
q = 1 → anisotropic



•Modulus corrected for porosity shows good fit with experimental data

Composite Materials, 2016, BN, IUT, Iran

Properties

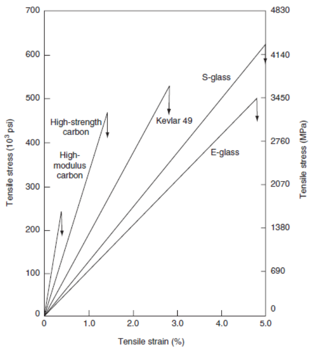


FIGURE 2.5 Tensile stress–strain diagrams for various reinforcing fibers.

Composite Materials, 2016, BN, IUT, Iran

Types of Carbon Fibers (ex-PAN)

- **HT** fiber: High tensile strength, medium young's modulus (200-300 GPa)
- **HM** fiber: High Modulus (400 GPa)
  - HT type show a much higher strain-to-failure value than HM type
- **SHT** fiber: Super high strength
- **SHM** fiber: Super high modulus

Composite Materials, 2016, BN, IUT, Iran

Types of Carbon Fibers (ex-PAN)

Table 2.2 Properties of PAN-based carbon fiber (strand data) (after Riggs, 1985).

Characteristic	High Strength[a]	Super High Strength[b]	High Modulus[c]
Filament diameter, μm	5.5–8.0	5.4–7.0	8.4
Density, g/cm^3	1.75–1.80	1.78–1.81	1.96
Carbon content, wt%	92–95	99–99$^+$	99$^+$
Tensile strength, MPa	3100–4500	2400–2550	1865
Tensile modulus, GPa	25–260	360–395	520
Strain at fracture, %	1.3–1.8	0.6–0.7	0.38
Electrical resistivity, μΩm	15–18	9–10	6.5
Thermal conductivity, W(mK)$^{-1}$	8.1–9.3	64–70	120

[a] Thornel T-300, T-500, T-600, T-700; Celion 3000, 6000, 1200; AS2, AS4, AS6, IM6; [b] Thornel T-50, Celion G-50, HMS; [c] Celion GY-70

Table 2.3 Properties of mesophase pitch-based carbon fiber (after Singer, 1981)

Property	Thornel P555	Thornel P755	Thornel P200
Filament diameter, μm	10	10	10
Density, g/cm^3	2.02	2.06	2.15
Carbon content, wt. %	99	99	99$^+$
Tensile strength, MPa	1895	2070	2240
Tensile modulus, GPa	380	517	690
Strain at fracture, %	0.5	0.4	0.3
Electrical resistivity, μΩm	7.5	4.6	2.5
Thermal conductivity, W/mK	110	185	515

- Mesophase pitch-based C fibers: used for reinforcement,
- Isotropic pitch-based C fibers (very low modulus): used as insulation! and fillers.

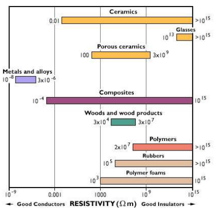
Table 2.4 Comparison of properties of different carbon fibers

Precursor	Density (g/cm^3)	Young's modulus (GPa)	Electrical resistivity (10^{-4} Ω cm)
Rayon[a]	1.66	390	10
Polyacrylonitrile[b] (PAN)	1.74	230	18
Pitch (Kureha)			
LT[c]	1.6	41	100
HT[d]	1.6	41	50
Mesophase pitch[e]			
LT	2.1	340	9
HT	2.2	690	1.8
Single-crystal[f] graphite	2.25	1,000	0.40

[a] Union Carbide, Thornel 50
[b] Union Carbide, Thornel 300
[c] *LT* low-temperature heat-treated
[d] *HT* high-temperature heat-treated
[e] Union Carbide type P fibers
[f] Modulus and resistivity are in-plane values

- Carbon has good electrical conductivity

Extreme concern!: Airborne carbon fibers can cause short circuiting (during manufacture or service).



- For high-temperature applications: oxidation resistance of carbon fibers must be taken into account
- Oxidation resistance increases with the modulus value
- The modulus increases with the final heat treatment temperature

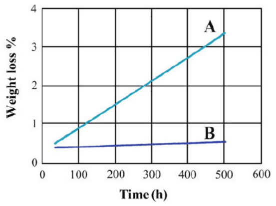
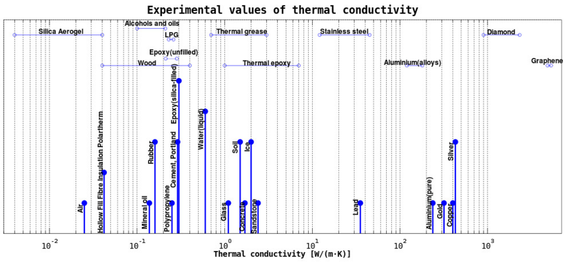


Fig. 2.25 Oxidation resistance, measured as weight loss in air at 350 °C, of carbon fibers having different moduli: (A) Low modulus Celion 3000 (240 GPa) and (B) High modulus Celion G-50 (345 GPa) [after Riggs JP (1985) Encyclopedia of polymer science and engineering, 2e, vol 2, John Wiley and Sons, New York, reprinted with permission]

Composite Materials, 2016, BN, IUT, Iran

- Ex-mesophase pitch carbon fiber can have extremely high thermal conductivity.
- A suitably oriented microstructure can have thermal conductivity as high as 1,100 W/mK.
- The thermal conductivity for an ex-PAN carbon fiber is generally less than 50W/mK.



Composite Materials, 2016, BN, IUT, Iran

- Carbon Fibers are anisotropic in terms of expansion coefficient:
  - α_l = 5.5 - 8.4 x 10^{-6} K^{-1}
  - α_t = -0.5 - – 1.3x 10^{-6} K^{-1}

α_l: longitudinal or parallel to the fiber axis

α_t: transverse or perpendicular to the fiber axis

- Compressive strength is about half their tensile strength!
  - ✓ Still, an order of magnitude better than aramid-type fibers

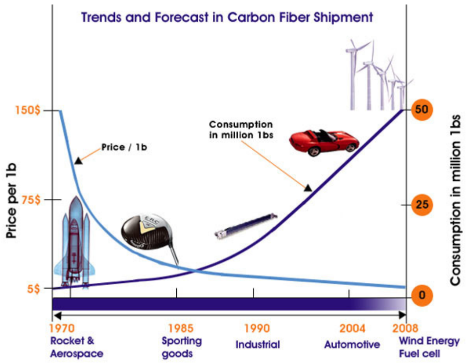
Composite Materials, 2016, BN, IUT, Iran

Table 1.3 Cost of PAN-based, mesophase pitch-based, and isotropic pitch-based carbon fibers. From Ref. 6.

	Cost of precursor ($/kg)	*Cost of carbon fibers ($/kg)*
PAN-based	0.40	60
Mesophase pitch-based	0.25	90
Isotropic pitch-based	0.25	22

- D. D. L. Chung, Carbon Fiber Composites, 1994

Carbon Fiber Applications

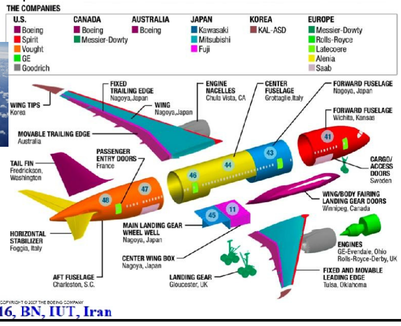


Carbon Fiber Applications

- Aerospace
- Space shuttle:
  - Cargo bay doors and booster rocket casings are made of carbon fiber reinforced epoxy composites.

Carbon Fiber Applications

- Commercial aircraft:
  - Boeing 787 (Dreamliner): fuselage and wings made of carbon fiber/epoxy composites.



Carbon Fiber Applications

- Various machinery items:
  - Turbine, Compressor and windmill blades, Flywheels
- Sport goods:
  - Tennis rackets, golf clubs, bicycles, …
- Medicine:
  - Implant materials, Ligament replacement

Organic Fibers

- Organic fibers: Such as *Polyethylene* and *Aramid* fibers, Low temperature applications (<150º C)
- Normal polymeric chains have the so-called cooked-spaghetti structure (a random coil configuration).

Organic Fibers

- Carbon-carbon bond is very strong → linear chain polymers such as polyethylene can be potentially strong and stiff
- But the macromolecular chains are neither aligned in one direction nor stretched out.
- They have predominantly weak van der Waals interactions rather than strong covalent interactions →low strength and stiffness
- Conventional polymers: E ≤ ~10 Gpa

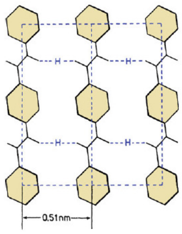


Fig. 2.34 Strong covalent bonding in the fiber direction and weak hydrogen bonding (indicated by *H*) in the transverse direction

Organic Fibers

- High-stiffness and high-strength polymers: must extend the polymer chains and pack them in a parallel array.
- Need to achieve molecular orientation by tensile drawing, die drawing or extrusion
- Highly drawn polymers: E of about 70 GPa can be obtained easily.
- The chemical nature and processing route control the orientation of the polymer chains with respect to the fiber axis and their order and crystallinity.
- Stronger and stiffer organic fibers: Oriented + fully extended chains

Organic Fibers

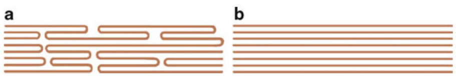
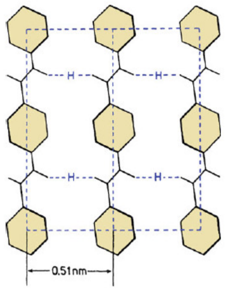


Fig. 2.26 Two types of molecular orientation: (**a**) oriented *without* high molecular extension and (**b**) oriented *with* high molecular extension [from Barham and Keller (1985), used with permission]

- E of a polymeric fiber increases linearly with the deformation ratio
- Macroscopic elongation results in a corresponding elongation at a molecular level.
- To get E>70 GPa, one needs rather high draw ratios, i.e., a very high degree of elongation at molecular level

Organic Fibers

Fig. 2.34 Strong covalent bonding in the fiber direction and weak hydrogen bonding (indicated by *H*) in the transverse direction



Organic Fibers

Table 2.5 Properties of polyethylene fibers[a]

Property	Spectra 900	Spectra 1000
Density (g/cm^3)	0.97	0.97
Diameter (μm)	38	27
Tensile strength (GPa)	2.7	3.0
Tensile modulus (GPa)	119	175
Tensile strain to fracture (%)	3.5	2.7

[a]Manufacturer's data; indicative values

Table 2.6 Properties of Kevlar aramid fiber yarns[a]

Property	K 29	K 49	K 119	K 129	K 149
Density (g/cm^3)	1.44	1.45	1.44	1.45	1.47
Diameter (μm)	12	12	12	12	12
Tensile strength (GPa)	2.8	2.8	3.0	3.4	2.4
Tensile strain to fracture (%)	3.5–4.0	2.8	4.4	3.3	1.5–1.9
Tensile modulus (GPa)	65	125	55	100	147
Moisture regain (%) at 25 °C, 65 % RH	6	4.3	–	–	1.5
Coefficient of expansion (10^{-6} K^{-1})	−4.0	−4.9	–	–	–

[a]All data from Du Pont brochures. Indicative values only. 25-cm yarn length was used in tensile tests (ASTM D-885). *K* stands for Kevlar, a trademark of Du Pont

Organic Fibers

High stiffness, high strength polymeric fibers

- **Polyethylene:** Linear molecule
- **Aramid**: Rigid rod molecule

- Two different routes to obtain *oriented and extended* chain structure:
  - Gel-spinning for PE
  - Liquid crystal route for Aramid

Organic Fibers

1- Gel-spinning for PE

Drawing the conventional flexible-chain polymers at suitable temperatures to convert the original folded chain structure into an oriented, extended chain structure.

2- Liquid crystal route for Aramid

Synthesis, followed by extrusion of "liquid crystal polymers" with a rigid-rod molecular chain structure to obtain highly ordered, extended chain fibers.

Composite Materials, 2016, BN, IUT, Iran

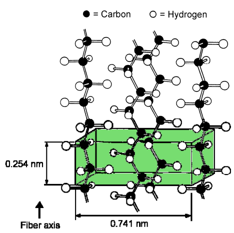
Organic Fibers

Polyethylene

- PE: a simple linear macromolecule

$$[-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-]_n$$

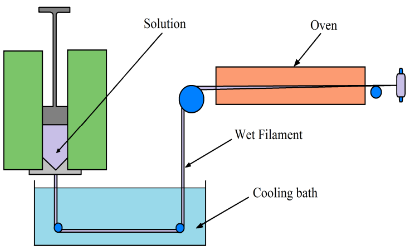
- Compared to other polymers, it is easier to obtain an extended and oriented chain structure in polyethylene.
- Solution and gel spinning of very high molecular weight polyethylene ($>10^6$): moduli as high as 200 GPa.



Composite Materials, 2016, BN, IUT, Iran

Organic Fibers

PE: gel spinning and hot drawing



1. Solution preparation
2. Spinning of gel
3. Quenching in air and a cooling bath
4. Hot drawing

Composite Materials, 2016, BN, IUT, Iran

Organic Fibers

Gelation/crystallization of as-spun PE fibers

- Use a dilute (5–10%) solution of polymer in a solvent (paraffin oil, paraffin wax, …) at about 150 °C.
  Dilute solution → lesser chain entanglement → easier orientation of the final fiber
- Spinning followed by air quenching → A polyethylene gel is produced.
- Cooling in a bath: Fiber has a structure consisting of folded chain lamellae with solvent between them and a swollen network of entanglements.

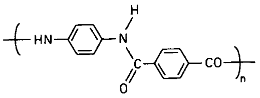
→ the as-spun fiber can be drawn to draw ratios as high as 200.

- Removal of remaining solvent and drawing are done at 120 °C
- Low spinning rates of 1.5 m/min!

Organic Fibers

Aramid or aromatic polyamide fibers

- Consists of oriented para-substituted aromatic units, which makes them rigid rod like polymers.



Chemical structure of aramid fiber.

Aramid fiber:

- Trade names: *Kevlar*, *Twaron* , *Nomex*
  - Poly (p-phenylene terephthalamide) or PPTA,
  - Poly (m-phenylene isophthalamide)

Organic Fibers

- Extended-chain polyamides have **Nematic liquid crystal** order.
- The fibers are spun from liquid crystalline polymer solutions by dry jet-wet spinning.

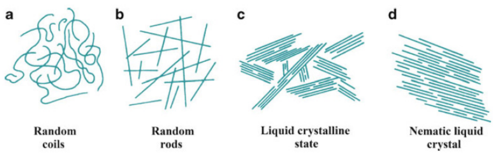


Fig. 2.28 Various states of polymer in solution: (**a**) two-dimensional, linear, flexible chains (random coils), (**b**) random array of rods, (**c**) partially ordered liquid crystalline state, and (**d**) nematic liquid crystal (randomly distributed parallel rods)

Organic Fibers

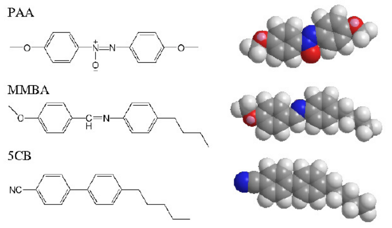
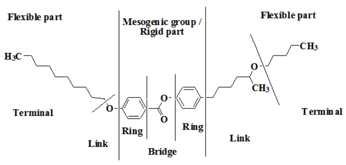
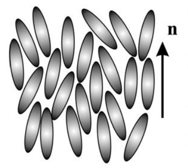


Figure 3: Typical compounds forming nematic mesophases: (PAA) *p*-azoxyanisole. From a rough steric point of view, this is a rigid rod of length ~ 20Å and width ~ 5Å. The nematic state is found at high temperatures (between 116°C and 135°C at atmospheric pressure). (MMBA) *N*-(*p*-methoxybenzylidene)-*p*-butylaniline. The nematic state is found at room temperatures (between 20°C to 47°C). Lacks chemical stability. (5CB) 4-pentyl-4'-cyanobiphenyl. The nematic state is found at room temperatures (between 24°C and 35°C).

Organic Fibers





Orientation of the molecules in nematic phase

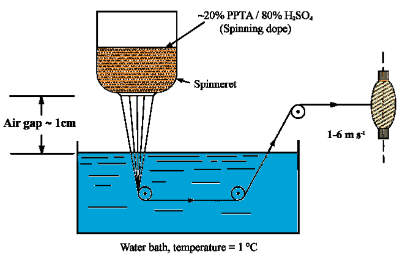
•Increasing concentration of rodlike molecules → forming regions of partial order

•This partially ordered state is called a *liquid crystalline* state (Fig. 2.28c).

•*Nematic* liquid crystal: When the rod like chains become approximately arranged parallel to their long axes, but their centers remain unorganized or randomly distributed (Fig. 2.28d).

Organic Fibers

Aramid: dry jet-wet spinning



Organic Fibers

Spinning: Nematic LC vs. conventional polymer

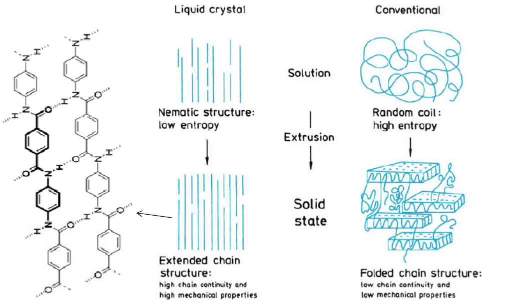


Fig. 2.32 Comparison of dry jet–wet spinning of nematic liquid crystalline solution and conventional spinning of a polymer [reprinted from Jaffe and Jones (1985), p 349, courtesy of Marcel Dekker, Inc.]

Organic Fibers

Table 2.5 Properties of polyethylene fibers[a]

Property	Spectra 900	Spectra 1000
Density (g/cm^3)	0.97	0.97
Diameter (μm)	38	27
Tensile strength (GPa)	2.7	3.0
Tensile modulus (GPa)	119	175
Tensile strain to fracture (%)	3.5	2.7

[a]Manufacturer's data; indicative values

Table 2.6 Properties of Kevlar aramid fiber yarns[a]

Property	K 29	K 49	K 119	K 129	K 149
Density (g/cm^3)	1.44	1.45	1.44	1.45	1.47
Diameter (μm)	12	12	12	12	12
Tensile strength (GPa)	2.8	2.8	3.0	3.4	2.4
Tensile strain to fracture (%)	3.5–4.0	2.8	4.4	3.3	1.5–1.9
Tensile modulus (GPa)	65	125	55	100	147
Moisture regain (%) at 25 °C, 65 % RH	6	4.3	–	–	1.5
Coefficient of expansion (10^{-6} K^{-1})	−4.0	−4.9	–	–	–

[a]All data from Du Pont brochures. Indicative values only. 25-cm yarn length was used in tensile tests (ASTM D-885). *K* stands for Kevlar, a trademark of Du Pont

• *More information in the Text book.*

2.6. Ceramic Fibers

- Continuous ceramic fibers are very attractive for reinforcing polymer, metal, and ceramic matrices.
- They combine high strength and elastic modulus with high temperature capability and good environmental resistance.
- → Attractive as reinforcements in high temperature structural materials
- Methods to make ceramic fibers:
  - Chemical vapor deposition
  - Polymer pyrolysis: SiC, Si_3N_4, B_4C, BN
  - Sol-gel techniques: Al_2O_3

- Polymer pyrolysis:
  - Controlled heating of polymers containing carbon, silicon, nitrogen and boron (similar to pyrolysis of carbon-based polymers to produces carbon fiber)
- Sol–gel process:
  - Conversion of fibrous gels, drawn from a solution at a low temperature, into ceramic fibers at several hundred degrees Celsius
  - The sol–gel method using metal alkoxides consists of preparing an appropriate homogeneous solution, changing the solution to a sol, gelling the sol, and converting the gel to ceramic by heating
    - Nextel fibers: A series of alumina and silica-alumina fibers produced by the 3M Company from metal alkoxide solutions

2.6.1. Oxide fibers

- Most widely used: Al_2O_3
- γ, δ, η and α allotropic forms. α-alumina is the most stable form.
- Alumina-based continuous fibers made by sol–gel processing are available commercially.
- Common steps to all fibers:
  - Formulate sol
  - Concentrate to form a viscous gel
  - Spin the precursor fiber
  - Calcine to obtain the oxide fiber

Table 2.8 Composition and properties of some oxide fibers[a]

Fiber type	Composition (wt.%)	Diameter (μm)	Density, (g/cm^3)	Tensile strength (GPa)	Young's modulus (GPa)
Nextel 312	Al_2O_3-62.5, SiO_2-24.5, B_2O_3-13	10–12	2.70	1.7	150
Nextel 440	Al_2O_3-70, SiO_2-28, B_2O_3-2	10–12	3.05	2.0	190
Nextel 550	Al_2O_3-73, SiO_2-27	10–12	3.03	2.0	193
Nextel 610	Al_2O_3-99+	10–12	3.9	3.1	370
Nextel 650	Al_2O_3-89, ZrO_2-10, Y_2O_3-1	10–12	4.10	2.5	358
Nextel 720	Al_2O_3-85, SiO_2-15	10–12	3.40	2.1	260
Saffil	Al_2O_3-96, SiO_2-4	3	2.3	1.0	100
Saphikon	Single Crystal Al_2O_3	75–250	3.8	3.1	380
Sumitomo	Al_2O_3-85, SiO_2-15	9	3.2	2.6	250

[a]Manufacturer's data

Nextel fibers: 3M Co. , $Al_2O_3+SiO_2+B_2O_3$
- Fine diameter (10-12 µm), imparts flexibility to an inherently brittle material
- Sol-gel process
- Starting materials: Metal alkoxides

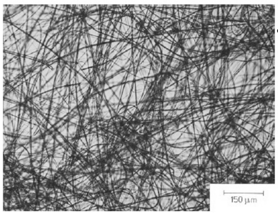


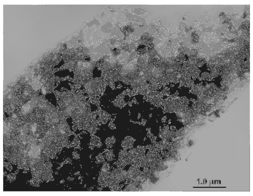
Fig. 2.37 Optical micrograph of Nextel 312 ($Al_2O_3 + B_2O_3 + SiO_2$) fiber

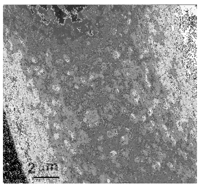
- Metal alkoxides :
  - $M(OR)_n$ type compounds
    - M: the metal
    - n: the metal valence
    - R: an organic compound

- M-OR bonds are broken and MO-R is obtained to give the desired oxide ceramics.
- *More details in the text book*

Characteristics of Nextel 610 Fiber

Fiber	Composition	Diameter (µm)	Density (g/cm^3)	Microstructure
Nextel 610	99% Al_2O_3, 0.2-0.3% SiO_2, 0.4-0.7% Fe_2O_3	10-12	3.9	Single phase α-Al_2O_3 grains (~0.1 µm)





Surface of alumina fiber

- **Sumitomo fibers:**
  - Sumitomo Chemical Co. produces a fiber that is a mixture of alumina and silica.
  - Fig. 2.38.
  - Starting from an organo-aluminum (poly-aluminoxanes or a mixture of poly-aluminoxanes and one or more kinds of Si-containing compounds)

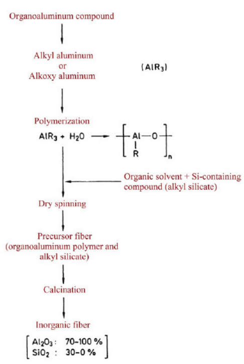


Fig. 2.38 Flow diagram of an alumina + silica fiber production

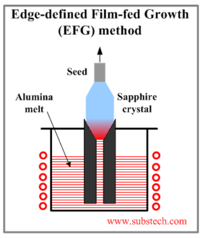
- **Saffil fiber**: δ Al_2O_3
- **Saphikon fiber**:
  - Continuous monocrystalline sapphire (Al_2O_3) fiber
  - Edge-defined Film-fed Growth (EFG) technique

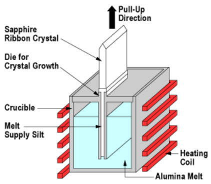
•Edge-defined Film-fed Growth (EFG) technique

- To make continuous monocrystalline sapphire (Al_2O_3) fiber
- A modified Czochralski puller
- Fiber growth rates as high as 200 mm/min
- A sapphire seed crystal is used to control the orientation of the single crystal fiber.

•A Molybdenum die

•A capillary supplies a constant liquid level at the crystal interface.





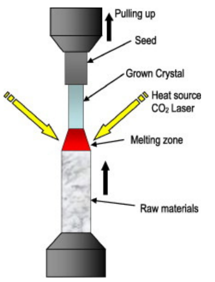
• Laser-heated floating zone method

• A variety of ceramic fibers: Al_2O_3, Y_2O_3, $MgAl_2O_4$, Na_2O_3, TiC, TiB_2

•A CO_2 laser
•A source rod
•A seed crystal to control the orientation.

•The diameter is a function of the feed rate/pull rate ratio.

•The fiber purity is determined by the purity of the starting material.



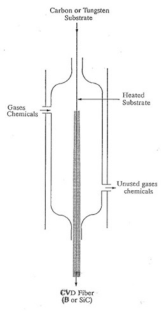
2.6.3. Nonoxide fibers

- The most widely used: SiC fibers
  - Conventional production method: **CVD**
  - Non-conventional production method: Controlled **pyrolysis** of polymeric precursors

CVD process for SiC fiber:

- Substrate: tungsten or carbon.
- Heated to around 1300 ºC.
- Reactive gaseous mixture: hydrogen and alkyl silanes
- A gaseous mixture (70% hydrogen and 30% silanes) is introduced at the reactor top (Fig. 2.39).
- CVD is done on the tungsten substrate (~13 µm diameter), which enters the reactor.
  - 100 µm SiC monofilament in about 20 s

CVD process for SiC fiber



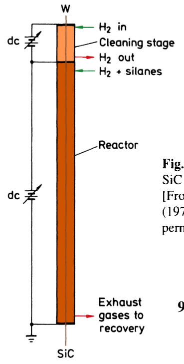


Fig. 2.39 CVD process for SiC monofilament fabrication [From J.V. Milewski et al. (1974), reproduced with permission]

95 % unused silanes!

CVD process for SiC fiber

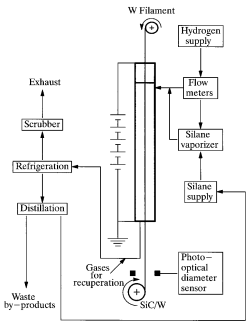
- Methyl trichloro silane (MTS)-CH_3SiCl_3 is an ideal raw material to make SiC.
- One Si and one C atom → A stoichiometric SiC can be deposited.
- Chemical reaction:

$$CH_3SiCl_3\ (g) \xrightarrow{(H_2)} SiC\ (s) + 3\ HCl\ (g)$$

- The exhaust gases contains 95 % of the original mixture + some HCl.
- It is passed around a condenser to recover the unused silanes.

CVD process for SiC fiber

- An optimum amount of hydrogen is required.
- If the hydrogen is less than sufficient, MTS will not be reduced to Si and free carbon will be present in the mixture.
- If too much hydrogen is present, the excess Si will form in the end product.
- Generally, solid (free) carbon and solid or liquid silicon are mixed with SiC.



CVD process for SiC fiber

Table 2.9 Properties of CVD SiC monofilament

Composition	Diameter (μm)	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)
β-SiC	140	3.3	3,500	430

- The final monofilament (100-150 μm) consists of a sheath of mainly β-SiC (cubic crystal structure) with some α-SiC (Hexagonal crystal structure) on the tungsten core.
- This large diameter fiber is not flexible.

Silicon Carbide Fibers

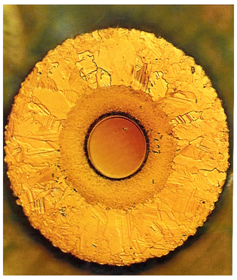
•**SCS**: A series of surface-modified silicon carbide fibers available
  •Have a complex through the thickness gradient structure.

•**SCS-6**: Diameter=142 mm
  •Produced by CVD of Si and C containing compounds onto a pyrolytic graphite-coated carbon fiber core.

  •The carbon monofilament + pyrolytic graphite coating: 37 μm
  •The final SiC monofilament: 142 μm diameter

•Special concentration gradient at and near the surface

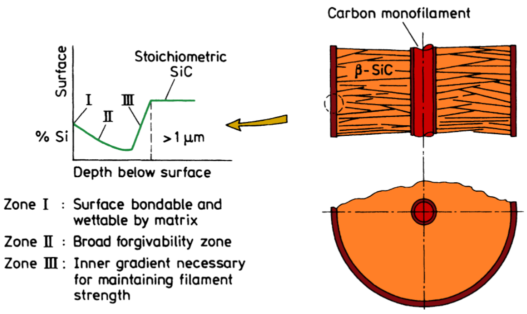
SiC monofilament: SCS-6 fiber



140 μm

SiC monofilament: SCS-6 fiber

The few micrometer thick surface coating consists of C-doped Si.



Nonoxide Fibers via Polymers

- Need for fine, continuous, and *flexible* fiber!
- Mid 1970s: Prof . Yajima, Japan

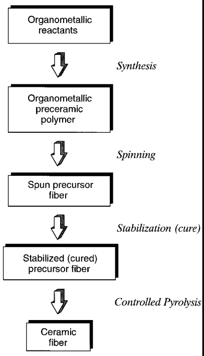
Polymer route

- Synthesis and characterization of a suitable starting Si based polymer

- Melt spinning the polymer into precursor fiber

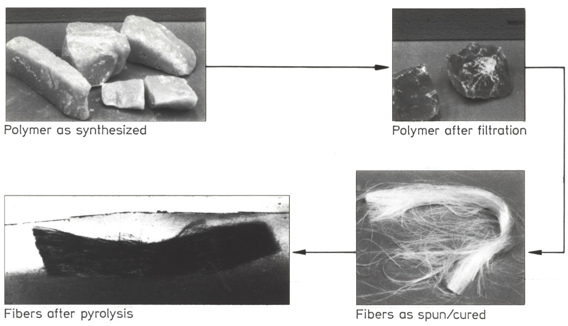
- Curing the precursor fiber to crosslink the molecular chains making it infusible during the subsequent pyrolysis

- Controlled pyrolysis



Ceramic fiber from a polymeric precursor

Ceramic fiber from a polymeric precursor



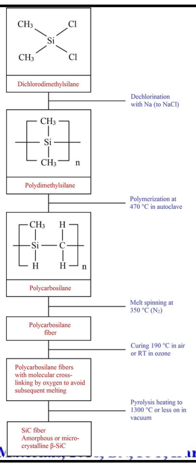


Fig. 2.42: Yajima process for SiC (Nicalon) production

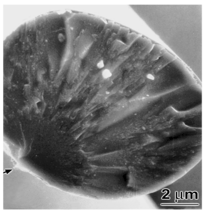
Table 2.10 Properties of some fine-diameter SiC type fibers[a]

Fiber	Tensile strength (GPa)	Young's modulus (GPa)	Coefficient of thermal expansion (10^{-6} K^{-1})
Nicalon 200	2	200	3.2
Hi–Nicalon	2.8	270	3.5
Hi–Nicalon S	2.5	400	–
Sylramic iBN	3.5	400	5.4
Tyranno SA3	2.9	375	–

[a]After A. R. Bunsell and A. Piant (2006)

- **Nicalon fibers** manufactured by Nippon Carbon Co. using this process
- Diameter: 10-20 µm

• Other types of SiC fiber are available, e.g. Sylramic



Fracture initiation in Nicalon fiber

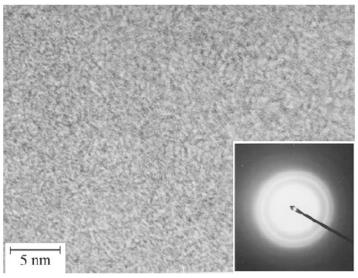
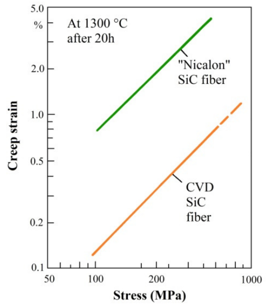


Fig. 2.43 High-resolution transmission electron micrograph of Nicalon fiber showing its amorphous structure [courtesy of K. Okamura]

- The microstructural analysis shows that SiC fibers contain some SiO_2 and free carbon → lower density than CVD β-SiC

• Creep properties



CVD SiC fiber:
Mostly β SiC, has higher density and lower creep strain

Nicalon fiber:
A mixture of SiC, SiO_2, and free carbon.

SiC Whiskers

- Almost monocrystalline, short fibers
- Extremely high strength
  - Absence of crystalline imperfections such as dislocations, grain boundaries, etc
- Diameter: a few micrometers
- Length: a few millimeters → L/D: 50-10,000
- Disadvantages:
  - Diameter and length varies
  - Very large spread in properties
  - Alignment of whiskers in a matrix is difficult
  - Whiskers can be hazardous

SiC Whiskers

- Produced by:
  - Vapor-liquid-solid growth
  - Vapor phase growth
  - Pyrolysis of rice hulls, 1970s
- Rice hulls contain cellulose, silica, and other organic and inorganic materials
- The dissolved silica from soil is deposited in the cellulosic structure of the hulls by liquid evaporation
- *Coking* at about 700 °C in the absence of oxygen to drive out the volatile compounds
- Coked rice hulls are heated in inert or reducing atmosphere (flowing N_2 or NH_3 gas) at 1,500-1,600 °C for about 1 h

$$3C + SiO_2 \rightarrow SiC + 2CO$$

SiC Whiskers

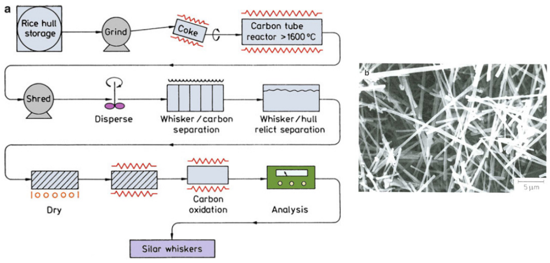


Fig. 2.45 (a) Schematic of SiC whisker production process starting from rice hulls. (b) Scanning electron micrograph of SiC whiskers obtained from rice hulls [courtesy of Advanced Composite Materials Corporation (formerly Arco)]

Composite Materials, 2016, BN, IUT, Iran

SiC Whiskers

- VLS process: **V**apor feed gases, **l**iquid catalyst, and **s**olid crystalline whiskers, 1985

$$SiO_2(g) + C(s) \rightarrow SiO(g) + CO(g)$$

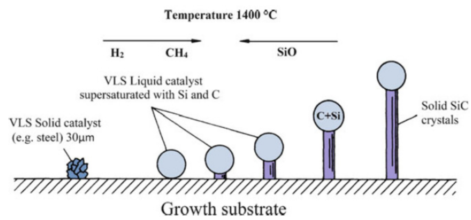


Fig. 2.46 The VLS process for SiC whisker growth [after Milewski et al. (1985), used with permission]

Composite Materials, 2016, BN, IUT, Iran

SiC Whiskers

- The catalyst forms a liquid solution interface with the growing crystalline phase, while elements are fed from the vapor phase through the liquid–vapor interface.
- The catalyst must take in solution the atomic species of the whisker to be grown.
- For SiC whiskers, transition metals and iron alloys meet this requirement

Composite Materials, 2016, BN, IUT, Iran

- Whisker lengths: ~10 mm
- Ave. equivalent circular diameter: ~6 µm.

- Exceptionally strong and stiff SiC whiskers
  - Ave. tensile strength: 8.4 GPa (1.7-23.7 GPa)
  - Ave. modulus: 581 GPa

- An extremely slow process

.

Other Non-oxide Reinforcements

- **Silicon Nitride (Si_3N_4) fibers**:

✓ CVD on a C or W substrate
  - Using volatile silicon compounds such as $SiCl_4$
    $3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$
  - Large diameter , expensive

✓ Polymer route:
  - Pyrolysis of silicon–nitrogen containing polymer precursors (organosilazane polymers with methyl groups on Si and N)
  - Give SiC bearing silicon nitride fibers

- **Boron Nitride (BN) fiber:**
  ✓ Melt spun Boric Oxide is nitrided with ammonia
  $B_2O_3 + 2NH_3 \rightarrow 2BN + 3H_20$

Other Non-oxide Reinforcements

- **Boron Carbide (B_4C) fiber:**
  $4BCl_3 + 6H_2 + C_{Fibers} \rightarrow B_4C_{Fibers} + 12HCl$

- **Metallic fibers:** made by wire drawing
  - Beryllium: low density, high modulus
  - Tungsten: high modulus and refractory
  - Steel: high strength, low cost
  - Copper/tungsten: electrical contacts
  - Ni/ Co base alloys

- **Metallic glasses (amorphous ribbons or wires):**
  - Pd77.5 Cu6 Si16.5
  - Fe80 P16 C3 B1
  - Fe60 Cr6 Mo6 B28

Other Non-oxide Reinforcements

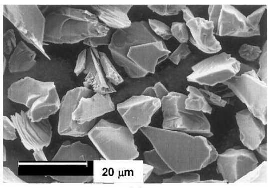
- **Particulate SiC**
- ✓ Silica sand and coke, react at 2,400 °C in an electric furnace, form large SiC granules, crushed to the desired size
- ✓ Cheap, abundant
- **Particulate Tungsten Carbide (WC)**
- ✓ Carburization of (W+ carbon black) powder in the presence of hydrogen at 1,400-2,650 °C

  Carbon black + hydrogen →gaseous hydrocarbons

  $W + CH_4 \rightarrow WC + 2H_2$
- ✓ Deagglomeration by milling
  - ✓ Angular particles
  - ✓ Size: 0.5 to 30 mm

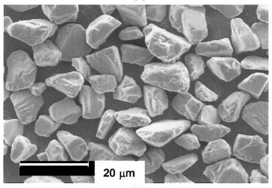
SEM micrograph of SiC particulate reinforcement:

(a) angular morphology



(a)

(b) rounded morphology



(b)

Effect of High-temperature exposure on ceramic fibers

- **Carbon fiber:**
  - Excellent at high temp. in an inert atmosphere
  - Starts oxidizing in air at temp. above 400-450 °C
- **SiC and Si_3N_4**: Only suitable candidates for reinforcement at very high temperatures (1,200–1,300 °C) and in air.
- SiC starts oxidizing above 1,300–1,400 °C in air
- High-temperature strength of SiC-type fibers is limited by oxidation (CO evaporation), internal void formation, and β-SiC grain growth
- **Oxide fibers**: Inherent stability in air (even at temp. >1,300 °C), but poor creep properties!

➢ Any glassy phase leads to softening (SiC, Boron fibers, Oxide fibers)

Comparison of fibers

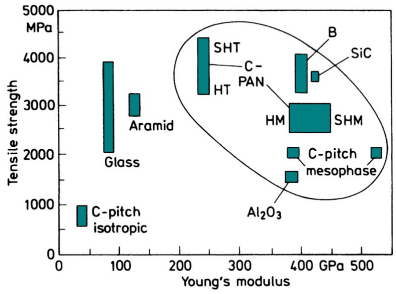


Table 2.11 Properties of reinforcement fibers

Characteristic	PAN-based carbon HM	PAN-based carbon HS	Kevlar 49	E glass	SiC CVD	SiC Nicalon	Al_2O_3	Boron (W)
Diameter (μm)	7–10	7.6–8.6	12	8–14	100–200	10–20	20	100–200
Density (g/cm^3)	1.95	1.75	1.45	2.55	3.3	2.6	3.95	2.6
Young's modulus (GPa)								
Parallel to fiber axis	390	250	125	70	430	180	379	385
Perpendicular to fiber axis	12	20	–	70	–	–	–	–
Tensile strength (GPa)	2.2	2.7	2.8–3.5	1.5–2.5	3.5	2	1.4	3.8
Strain to fracture (%)	0.5	1.0	2.2–2.8	1.8–3.2	–	–	–	–
Coefficient of thermal expansion (10^{-6} K^{-1})								
Parallel to fiber axis	−0.5–0.1	0.1–0.5	−2–5	4.7	5.7	–	7.5	8.3
Perpendicular to fiber axis	7–12	7–12	59	4.7	–	–	–	–

Fibers

–Low density

–Mostly covalently bonded- strong bonds

–High Young's modulus

–Small diameter for high flexibility

–Some have anisotropic properties, e.g.:

- Carbon
- Any single-crystal fiber or whisker, e.g., alumina single-crystal fibers, …

–Low strains to fracture (2-3%)

–Fibers carry major load in composites

–Matrix transmits the load to fibers in addition to acting as a binder

End of Chapter 2

تکلیف ۴: سوالات (2.1, 2.4, 2.6, 2.8, and 2.9) از صفحه ۷۱ کتاب

مسئله 2.4 را برای فیبر K49 در جدول 2.6 حل کنید.
در حل مسئله از روابط صفحه ۹ کتاب و رابطه زیر می توانید استفاده نمایید.

$$\sigma = \frac{MY}{I}$$

σ = استحکام
M= ممان خمشی فیبر
Y = فاصله محور خنثی فیبر تا سطح آن = شعاع فیبر
I = ممان اینرسی فیبر