Composite Materials

Reinforcement materials

Reinforcements

Imbedded phase is most commonly one of the following shapes:

- *Fibers*
- *Particles*
- *Flakes*

In addition, the secondary phase can take the form of an infiltrated continuous phase in a skeletal or porous matrix

Example: a powder metallurgy part infiltrated with polymer

Reinforcements

In composites, the general rule is that mechanical properties such as strength and stiffness increase as reinforcement length increases

Particulates are the limit of short fibers

In theory whiskers should have superior properties because of their higher aspect ratio. However they tend to break up into shorther lengths during processing.

Another disadvantage of using whisker reinforcement is that they may become oriented by some processes like rolling and extrusion, producing composites with anisotropy

It is also more difficult to pack whiskers than particulate (lower reinforcement/matrix ratio)

Basic Definitions

Fibers are filaments of reinforcing material, usually circular in cross-section

Fiber diameters range from less than 2.5 micrometers to 130 micrometers

Particulates are second common shape ranging in size from microscopic to macroscopic

Flakes are two-dimensional particles like small flat platelets

The distribution of particles in the composite matrix is random so the properties of the composite are usually isotropic

Fibers and flakes are usually oriented so the properties of the composites are anisotropic

Fibers

- *Filaments provide greatest opportunity for strength enhancement of composites*
- *The filament form of most materials is significantly stronger than the bulk form*
- *As diameter is reduced, the material becomes oriented in the fiber axis direction and probability of defects in the structure decreases significantly*
- *Continuous fibers - very long; in theory, they offer a continuous path by which a load can be carried by the composite part*
- *Discontinuous fibers (chopped sections of continuous fibers) - short lengths (L/D <100)*
- Whiskers are important type of discontinuous fiber
  - hair-like single crystals with diameters down to about 1 microns with very high strength

Commercially available forms of fibers

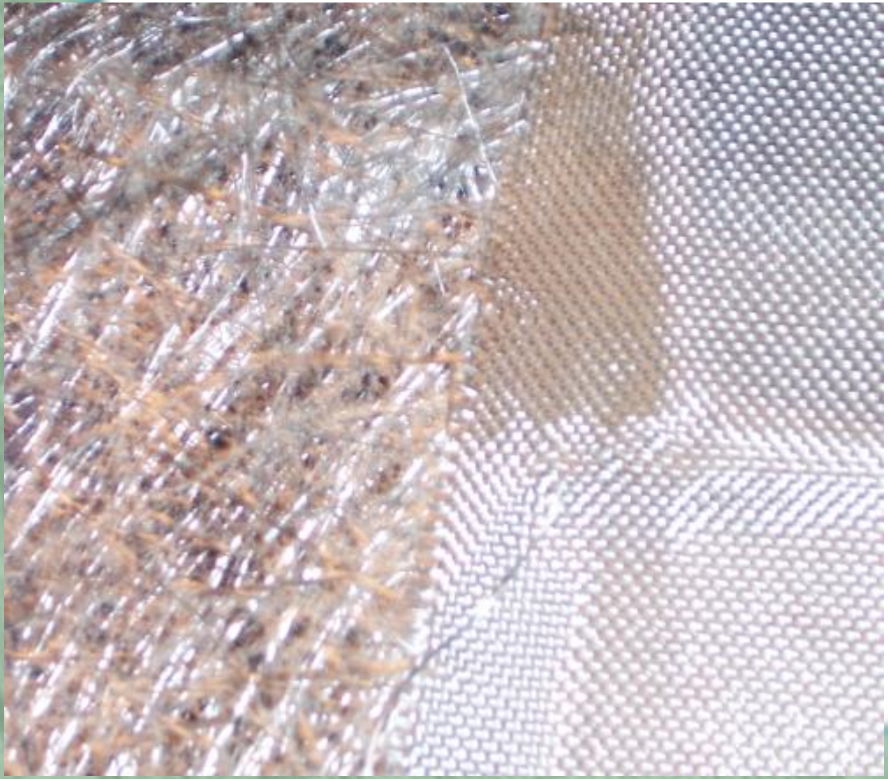
- *Filament: a single thread like fiber*
- *Roving: a bundle of filaments wound to form a large strand*
- *Chopped strand mat: assembled from chopped filaments bound with a binder*
- *Continuous filament random mat: assembled from continuous filaments bound with a binder*
- *Many varieties of woven fabrics: woven from rovings*

Filaments

Close up of a roving

Commercially available forms of fibers

- *Random mat and woven fabric (glass fibers)*

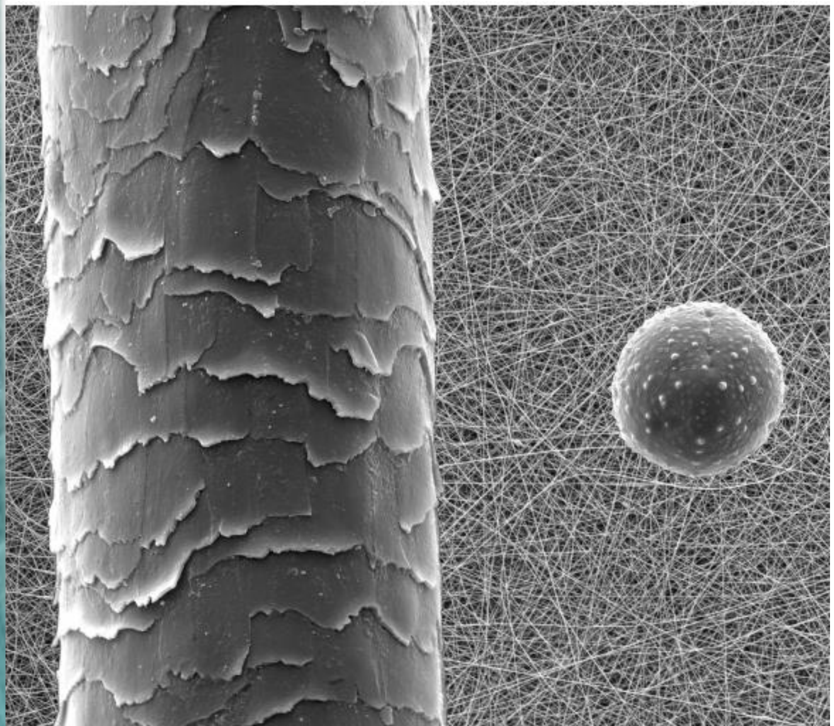


Commercially available forms of fibers

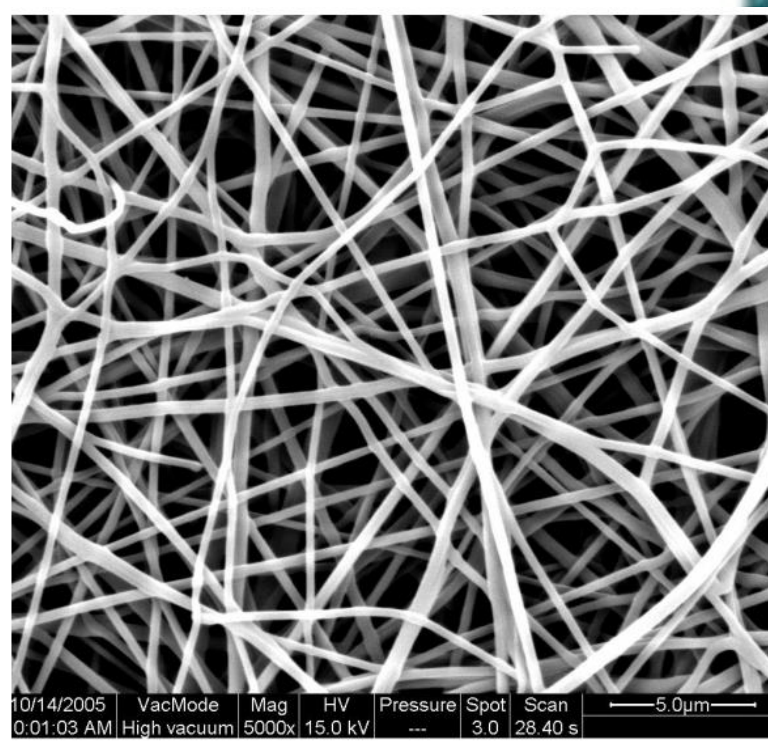
- *Carbon fiber woven fabric*

New forms of fibers

- *Nanofibers*



Comparison - human hair, pollen grain, nanofibers



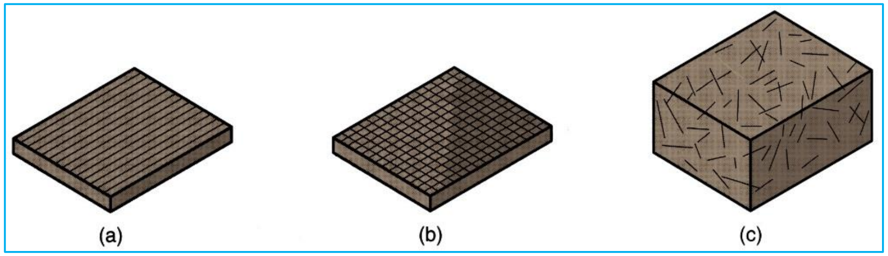
Nanofibers (PA6) - 5000x magnified

Fibers

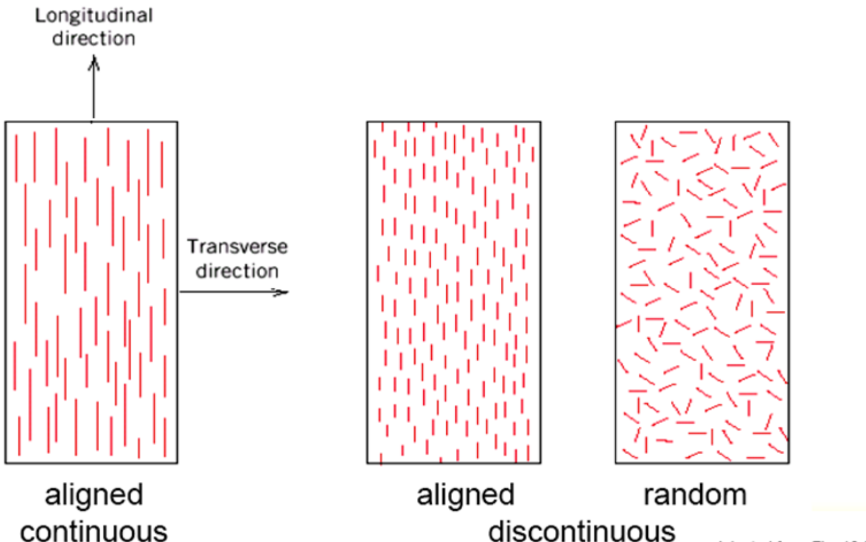
- *The fibers may be oriented randomly within the material, but it is possible to arrange for them to be oriented preferentially in the direction expected to have the highest stresses.*
- *Control of anisotropy is an important means of optimizing the material for specific applications*
- *At a microscopic level, the properties of these composite are determined by the orientation and distribution of the fibers, as well as by the properties of the fiber and matrix materials*
- *One-dimensional reinforcement, by which maximum strength and stiffness are obtained in the direction of the fiber*
- *Planar reinforcement is commonly in the form of a two-dimensional woven fabric*
- *Random or three-dimensional reinforcement by which the composite material tends to possess isotropic properties*

Fiber orientation

Fiber orientation in composite materials: (a) one-dimensional, continuous fibers; (b) planar, continuous fibers in the form of a woven fabric; and (c) random, discontinuous fibers



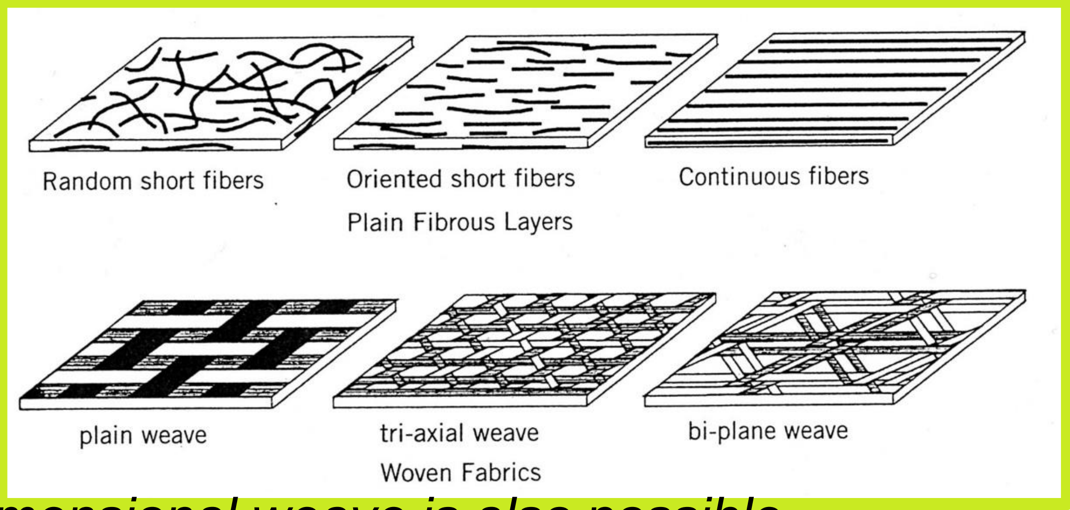
Strongest, but anisotropic



Adapted from Fig. 16.8, *Callister 7e.*

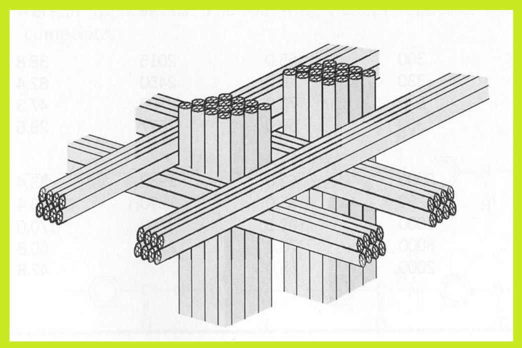
Weaker, but isotropic

Fiber orientation



A three dimensional weave is also possible

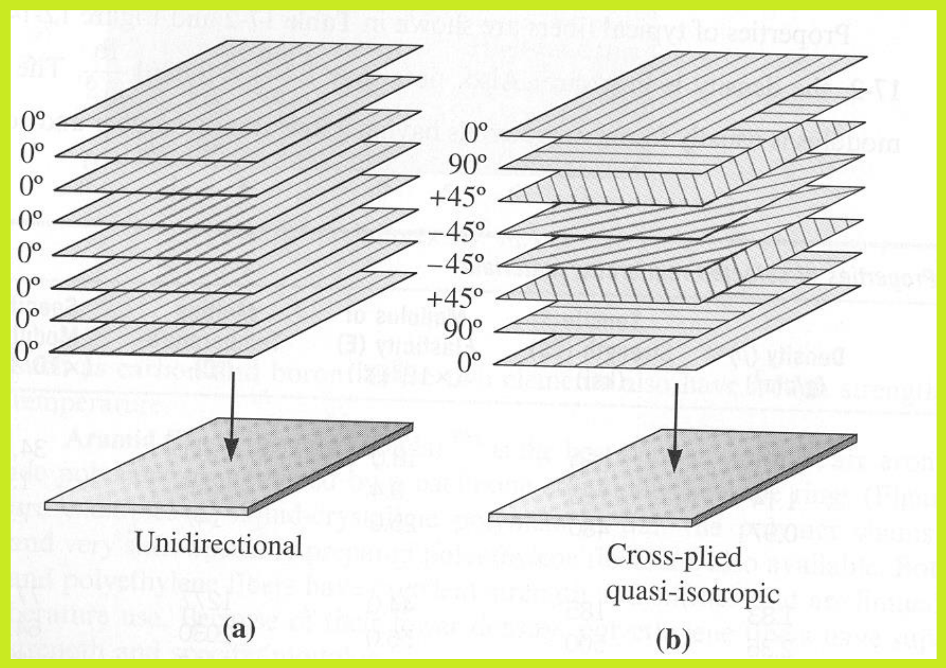
This could be done when fabrics are knitted or weaved together



Fiber orientation

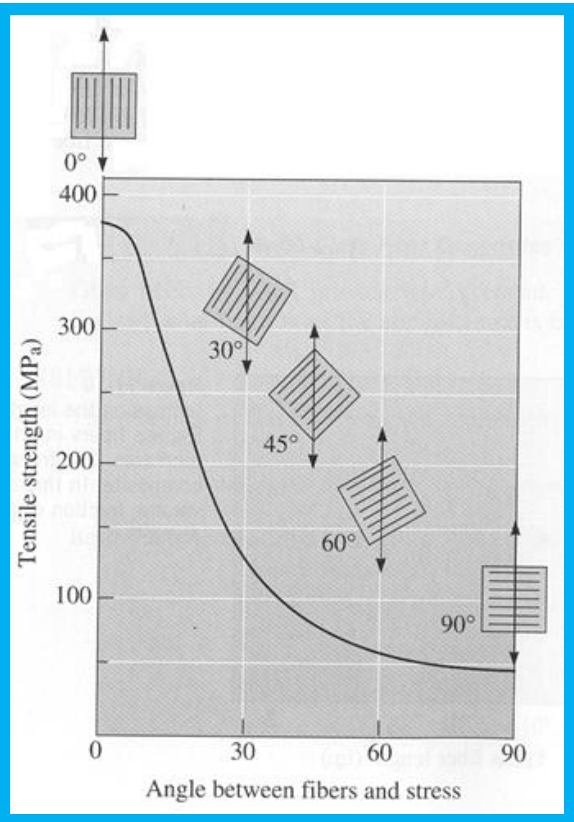
The properties of fiber composites can be tailored to meet different loading requirements

Quasi-isotropic materials may be produced by using combinations of different fiber orientation



Fiber orientation

Maximum strength is obtained when long fibers are oriented parallel to the applied load



Common fiber materials

Metals – Steel

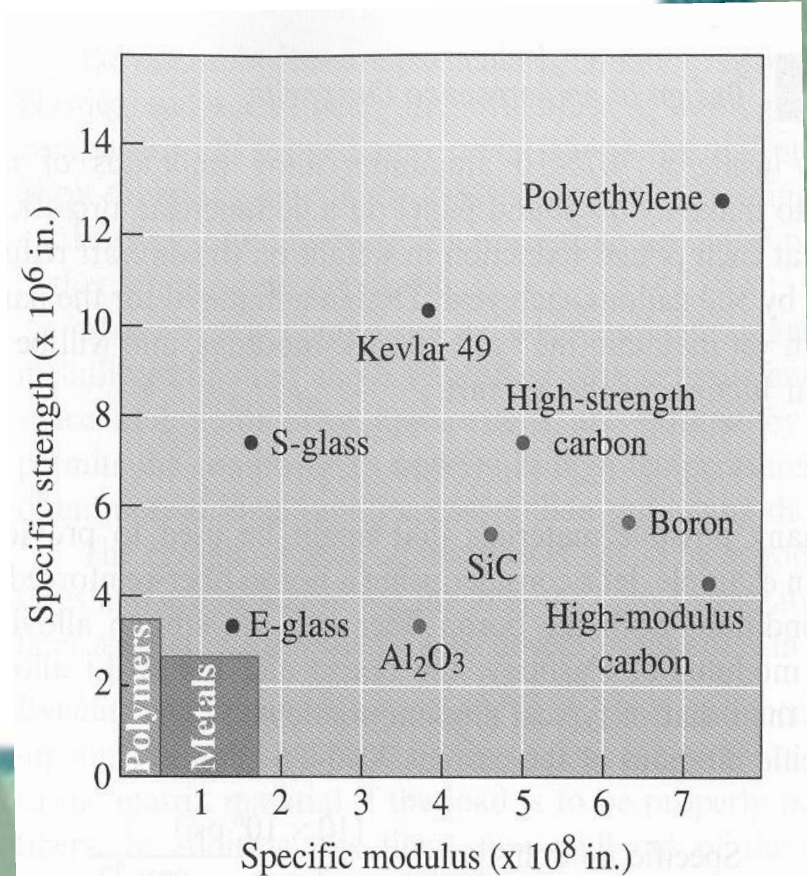
Polymers – Kevlar, UHMWPE

Ceramics – SiC and Al_2O_3

Carbon – High elastic modulus

Boron – Very high elastic modulus

Glass – Most widely used filament



Glass fibers

Fiberglass refers to a group of products made from individual glass fibers combined into a variety of forms.

Glass fibers can be divided into two major groups according to their geometry: continuous fibers used in yarns and textiles, and the discontinuous (short) fibers used as mats, blankets, or boards for insulation and filtration.

Fiberglass can be formed into yarn much like wool or cotton, and woven into fabric. Fiberglass textiles are commonly used as a reinforcement material for molded and laminated plastics. Fiberglass wool, a thick, fluffy material made from discontinuous fibers, is used for thermal insulation and sound absorption. It is commonly found in ship and submarine bulkheads and hulls; automobile engine compartments and body panel liners; in furnaces and air conditioning units; acoustical wall and ceiling panels; and architectural partitions.

Glass fibers

Fiberglass properties vary somewhat according to the type of glass used.

The major ingredients are silica sand, limestone, and soda ash. Other ingredients may include calcined alumina, borax, feldspar, magnesite, and kaolin clay

In general glass has several well–known properties that contribute to its great usefulness as a reinforcing agent:

- *Tensile strength*
- *Chemical resistance*
- *Moisture resistance*
- *Low coefficient of thermal expansion*
- *Electrical properties*

Glass fibers

There are a variety of types of glass, they are all compounds of silica with a variety of metallic oxides

Alumina addition improves mechanical and chemical performance

Borax reduces liquidus temperature

Soda and alkali oxides improve fluidity by lowering the melting temperature

The most commonly used glass is E-glass due to its low cost

Letter designation and compositions of commercial glass fibers (Gupta, 1988; Dockum, 1987).

Designation	Composition (%)						
	SiO_2	Al_2O_3	B_2O_3	CaO	Na_2O	MgO	Other
A (Alkali)	72	0.6–1.5	–	10	14.2	2.5	0.7% SO_3
C (Chemical durability)	65	4	6	14	8	3	
D (Low dielectric constant)	74	0.3	22	0.5	1.0	–	0.5% LiO_2
E (Low electrical conductivity)	52–56	12–16	5–13	16–25	0–2	0–6	0–1.5% TiO_2
E-CR	58–63	10–13	1.0–2.5	21–23	0–1.2	–	1–2.5% TiO_2, 0–3.5% ZnO
M (High modulus)	53.7	–	–	12.9	–	9.0	2.0% ZrO_2, 8% BeO 8% TiO_2, 3% CeO_2
S (High strength)	65	25	–	–	–	10	
Z or AR (High zirconia or alkali resistant glass)[a]	71	1	–	–	11	–	16% ZrO_2, 2% TiO_2

Glass fiber properties

A-glass: soda-lime glass, poor water resistance

C-glass: soda-lime-borosilicate glass, excellent resistance to acids

D-glass: low density, good electrical properties, poor water resistance

E-glass: calcia-alumina-borosilicate glass, good balance of properties, high electric resistance, poor resistance to acids and alkaline

S-glass: magnesium-alumina-silicate glass, higher stiffness and strength than E-glass

Properties of commercial glass fiber reinforcements.

Type of Fiber	Diameter	Specific gravity	Coef. therm. expansion ($\times 10^{-6}\,°C^{-1}$)	Young's modulus (GPa)	Tensile strength (GPa)	Strain at failure	Poisson's ratio	Softening temp.
E	12	~2.54	~5.0	72.4–76	3.6	~2%	0.21	845
AR	12	2.68	7.5	70–80	3.6	~2%	0.22	–
M	12	2.89	5.7	110	3.5	–	–	–
S	12	~2.48	2.9–5.0	~86	4.6	–	–	968

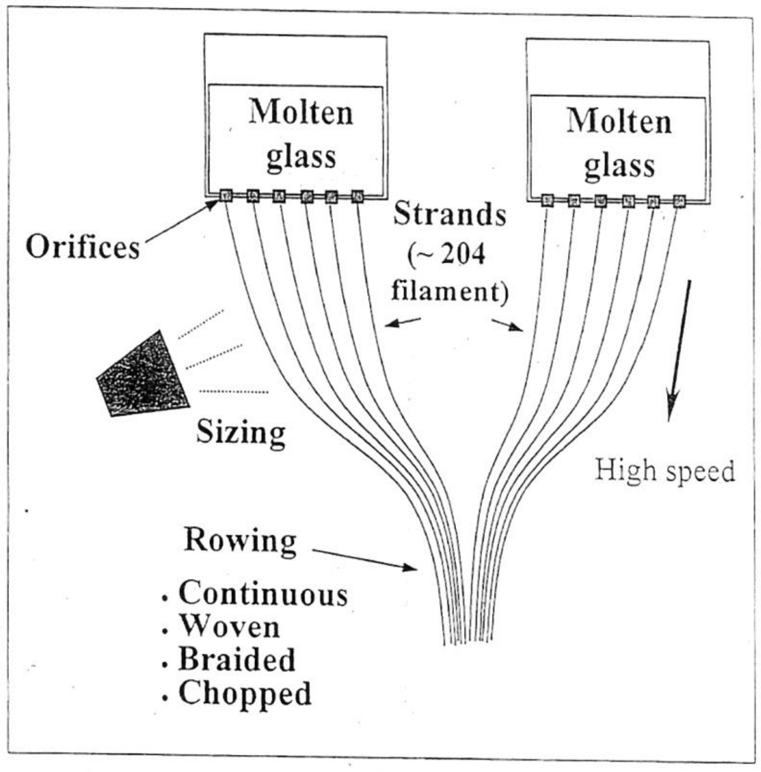
Glass fibers - summary

- *Most widely used fiber due to low cost*
- *Uses: piping, tanks, boats, sporting goods*
- *Advantages*
  - *Low cost*
  - *Thermal properties*
  - *Corrosion resistance*
- *Disadvantages*
  - *Relatively low strength*
  - *High elongation*
  - *Moderate strength/weight*

E glass" (electrical, borosilicate glass) is the cheapest and most common. "R glass" and "S glass" are more expensive but more corrosion resistant, stronger.

Glass fibers - summary

- *Modulus ranges from 70- 90 GPa.*
- *Strength ranges from 1.7-5 GPa*
- *Breaking strain from 2 to 5%*
- *Density ~ 2.5 gm/cm3*
- *Manufacturing method:*



Sizing is applied to protect fibers against abrasion and degradation during handling,

Improve wetting and adhesion by polymer matrix

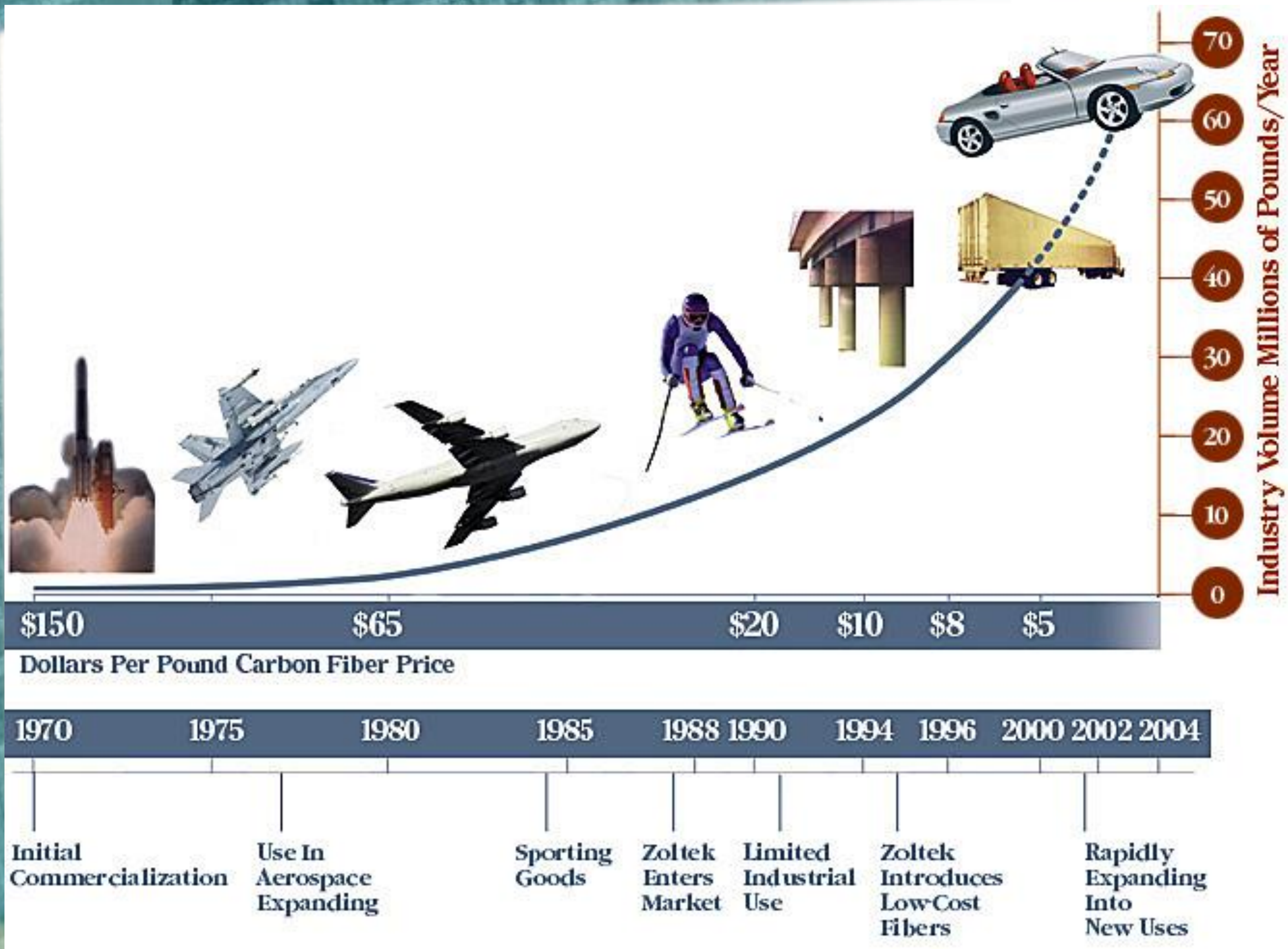
Sizing is a mixture of a coupling agent, film former, surfactant and lubricant

Carbon fibers

Carbon fiber composites are five times stronger than 1020 steel yet five times lighter. In comparison to 6061 aluminum, carbon fiber composites are seven times stronger and two times stiffer yet still 1.5 times lighter

Initially used exclusively by the aerospace industry, they are becoming more and more common in fields such as automotive, civil infrastructure, and paper production

Carbon fibers have gained a lot of popularity in the last two decades due to the price reduction


Industry Volume Millions of Pounds/Year
70
60
50
40
30
20
10
0
$150
$65
$20
$10
$8
$5
Dollars Per Pound Carbon Fiber Price
1970
1975
1980
1985
1988
1990
1994
1996
2000
2002
2004
Initial Commercialization
Use In Aerospace Expanding
Sporting Goods
Zoltek Enters Market
Limited Industrial Use
Zoltek Introduces Low Cost Fibers
Rapidly Expanding Into New Uses

Carbon fibers

Types of carbon fiber vary in strength with processing

Trade-off between strength and modulus

- *Intermediate modulus*

Fiber precursor PAN (Polyacrylonitrile) heated and stretched to align structure and remove non-carbon material

- *High modulus*

Made from petroleum pitch precursor at lower cost much lower strength

PAN-based carbon fiber is more expensive to produce, hence, limiting its use to high end applications, (used primarily by aerospace and sporting equipment industries)

High-E carbon fibers

Sources of pitch: PVC, coal tar, asphalt, petroleum

Conversion of organic precursors to carbon fibers involves three main stages:

Oxidation

Carbonization

Graphitization

Steps of carbon fiber synthesis from pitch:

1. *Pitch is spun and drawn into continuous fibers*
2. *Oxidation: T>70 C and up to 300 C to produce cross-linked structure*
3. *Carbonization: up to 1350 C in Nitrogen atmosphere*
4. *Graphitization*

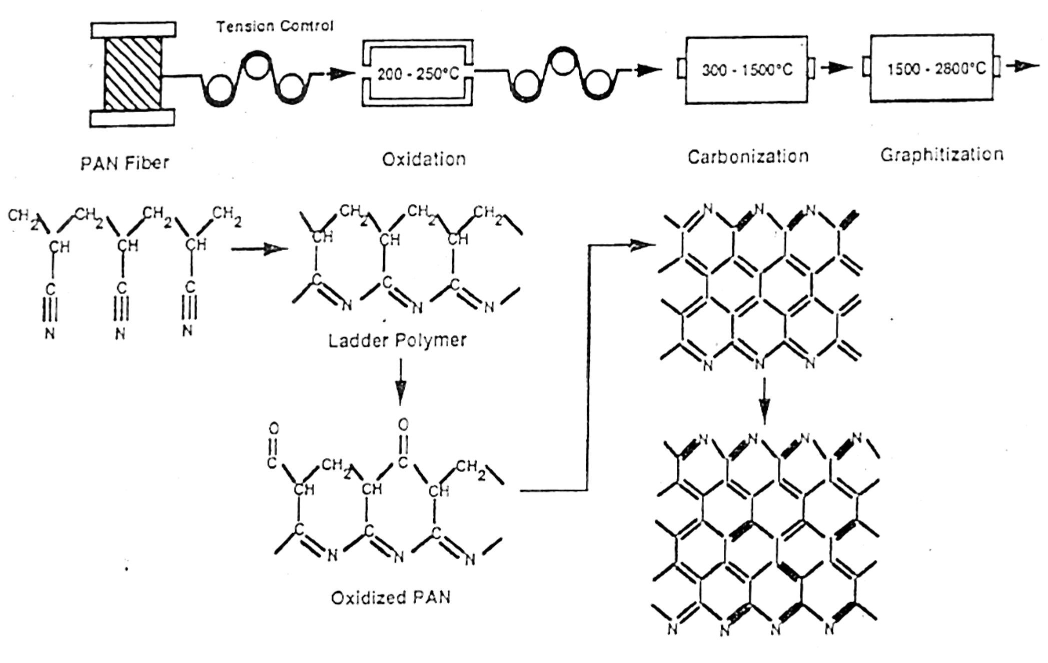
High-strength carbon fibers

Polyactylonitrile contains highly polar nitrile (-C=N) groups

Steps of carbon fiber synthesis from PAN:

- *PAN is spun into fiber form by melt spinning*

Main stages of conversion of PAN polymer to C fiber



Carbon fibers

The most common carbon-fiber type is PAN, primarily for structural reinforcement because of its high tensile strength

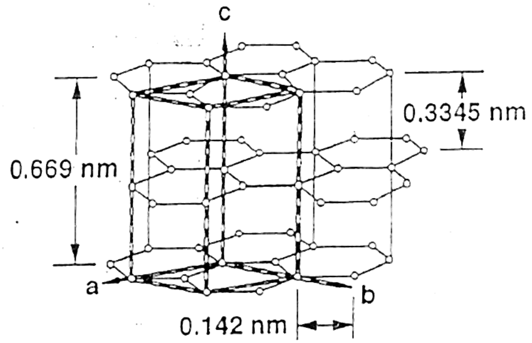
Pitch based fibers have a higher modulus, or stiffness than conventional PAN fibers, are *intrinsically more pure electrochemically. They* also possess higher thermal and electrical conductivity, and different friction properties

Internal structure consists of radially-aligned graphite platelets, which leads to some anisotropy in properties in the fibers. Both thermal and electrical conductivity are generally good

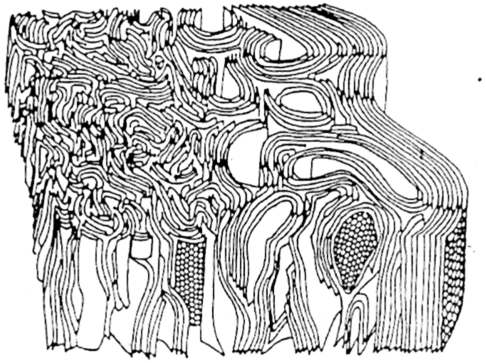
The stacking sequence in the hexagonal structure is ABAB

The structure gives high anisotropy such that

E_{11}=1060 GPa, E_{33}=37 GPa, E_{44}=4 GPa



The hexagonal structure of graphite (from Johnson, 1985).



A three-dimensional structural model for carbon fiber showing a skin-core structure (from Bennett and Johnson, 1979).

Carbon fibers

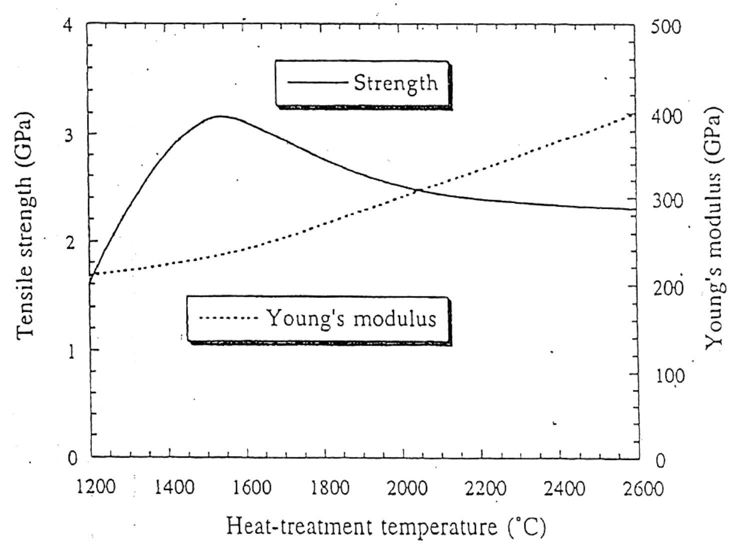
Global demand for high-strength, light-weight and durable fiber is growing; typical applications in:

- *Portable power*
- *Rechargeable batteries and fuel cell electrodes*
- *Fiber reinforced plastics, FRP*
- *Energy production; windmill blades*
- *Building and construction materials: concrete and asphalt reinforcements, soil erosion barriers*
- *Electronics, composite materials for automotives & general transportation,*
- *Specialty and niche markets*

Carbon fibers - summary

Selected PAN-based carbon fibers and their properties (Donnet and Bansal, 1990; Thorne, 1985).

Manufacturer	Designation	Filament count	Density (g/cm^3)	Tensile strength (GPa)	Modulus (GPa)	Ultimate strain (%)
AVCO, U.S.A.	Avcarb G-160	160 K	1.75	2.8	220	–
Celanese, U.S.A.	Celion 3000	3 K	1.77	3.6	–	–
	Celion 6000	6 K	1.77	3.6	234	–
	Celion 12000	12 K	–	2.5	227	1.77
	Celion ST	3 K, 6 K, 12 K	–	~4.3	~230	–
Courtaulds, U.K.	Grafil XAHS	6 K, 12 K	1.79	~3.0	220–240	~1.3
	Grafil XAHP	6 K, 12 K	1.79	3.3–3.6	220–240	~1.4
	Grafil HM	6 K, 10 K	1.86	2.3–2.6	330–350	0.7
Great Lakes Carbon, U.S.A.	Fortafil 3	40 K, 160 K	1.73	2.7	207	–
	Fortafil 5	40 K, 160 K	1.80	2.4	330	–
Hercules, U.S.A.	Magnamite AS-1	10 K	–	3.1	228	1.3
	Magnamite AS-4	3 K, 6 K, 12 K	–	3.6	235	1.5
	Magnamite HMS	10 K	–	2.2	365	0.6
	Magnamite HTS	10 K, 12 K	–	2.9	270	–
Union Carbide, U.S.A.	Thornel 300	1 K, 3 K, 6 K	1.75	3.1	231	–
	Thornel 400	3 K	1.79	4.5	238	–
Nippon Carbon, Japan	Carboton	3 K, 6 K, 12 K	–	~3.0	230	–
Toray, Japan	Torayla 300	1 K, 3 K, 6 K, 12 K	~1.45	~3.5	230	1.7
	Torayla 800	12 K	1.80	5.0	294	1.7
	Torayla M40	1 K, 3 K, 6 K	1.80	2.2–2.4	392	0.6



Effect of heat-treatment temperature on the strength and Young's modulus of carbon fibres produced from a PAN precursor. (From Moreton *et al.* 1967).

Organic fibers

Common properties:

- *Extremely high tensile strength and Young’s modulus*
- *Oriented, extended chain structure*
- *Low density*
- *High toughness*
- *Good chemical resistance*

Disadvantages:

- *Low compressive and shear properties*
- *High anisotropic structure*
- *Low operating temperature (<300 C)*

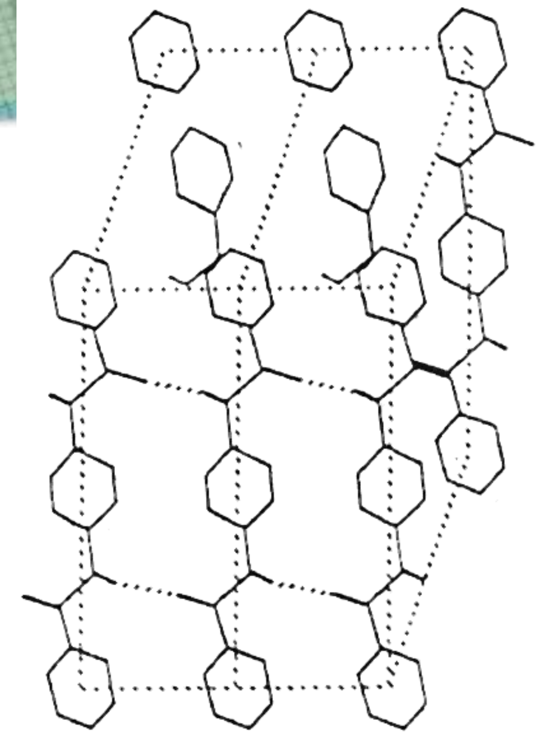
Organic fiber: Aramid

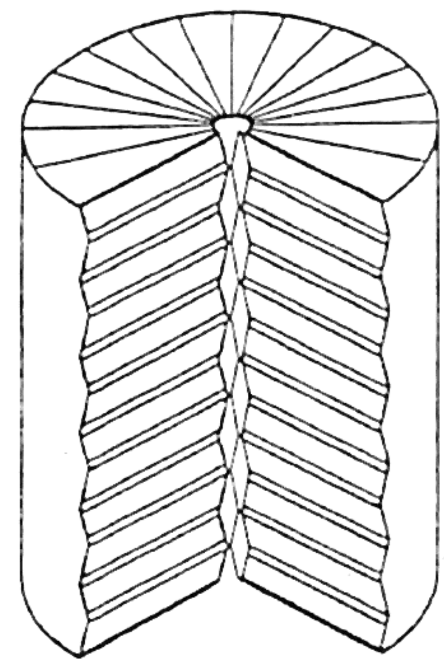
- *Highly crystalline state*
- *Poly-phylene terephtalamide (PPTA) molecules form plane sheets linked together by hydrogen bonds*
- *Sheets are stacked together radially to form Kevlar structure*

These fibers offer superior blast, fragmentation, explosive and small arms ballistic protection

They are commonly used when a degree of impact resistance is required such as in ballistic armour

They have the highest level of specific strength of all the common fibers

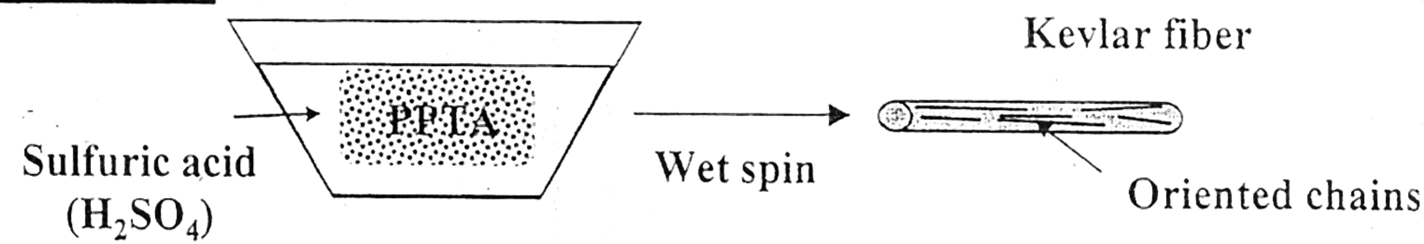




Organic fiber: Aramid

- *Very rigid extended chain structure*
- *Resistant to rotation due to Aromatic rings, amide (-NH-) and carbonyl (-CO-) bonds*
- *T_g>250 C, T_m=550 C*
- *Kevlar (USA) and Technora (Japan) are the two types*

Synthesis:



Application: Tire

Kevlar / rubber

Other organic fibers

- *Flexible chains:*

UHMW polyethylene (highly oriented, extended chain structure)

Properties of gel-spun crystalline polyethylene fibers (Calundann et al., 1988).

Designation	Producer	Density (g/cm^3)	Young's modulus (GPa)	Tenacity (GPa)	Elongation (%)
Spectra 900	Allied Fibers	0.97	119	2.6	3.5
Spectra 1000	Allied Fibers	0.97	175	3.0	2.7
Dyneema SK60	DMS/Toyobo[a]	0.97	50 – 125	2 – 3.5	3 – 6
Tekilon	Mitsui Petrochem	0.96	60 – 100	1.5 – 3.5	3 – 6

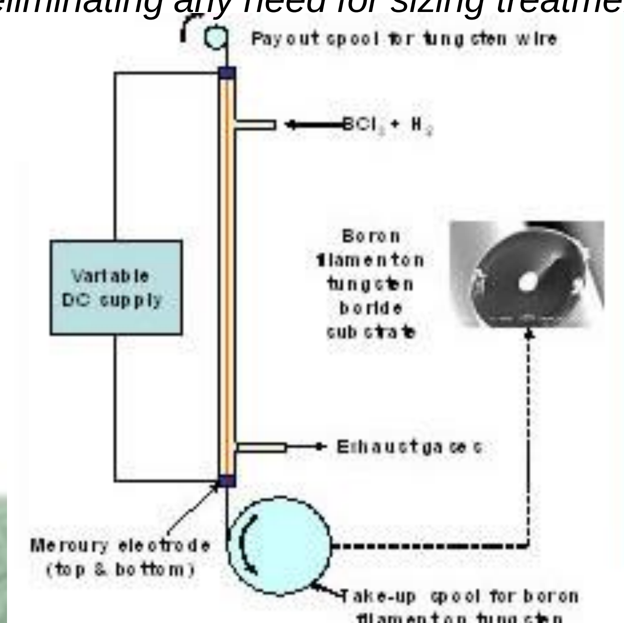
- *Semi-rigid:*
  - *Polyester fibers (E=90 GPa)*
- *Rigid:*
  - *HMW heteroyclic polymers*
  - *Polybenzobisthiazole (E=200 GPa)*

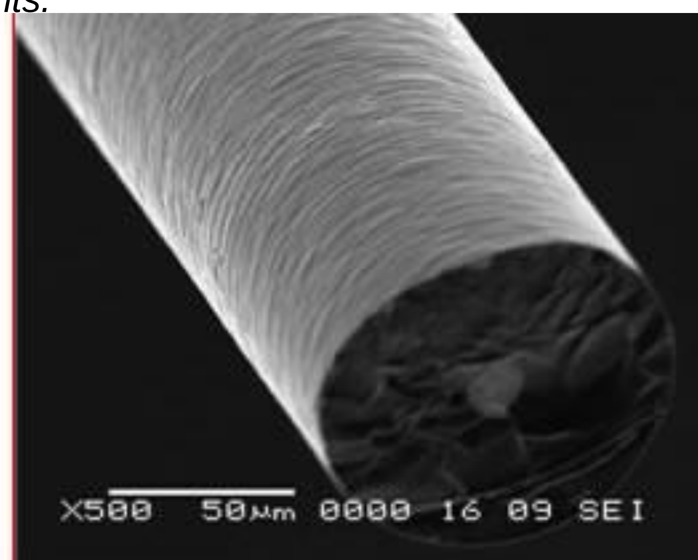
Ceramic fibers

- *Very high temperature applications (e.g. engine components)*
- *They are brittle and flaw-sensitive*
- *Their strength decrease as their length increase (size effect)*
- *Ceramic matrix is suitable so thermal shock resistance is not compromised*
- *Infrequent use*
  - *Alumina*
  - *Silicon carbide*
  - *Silica*
  - *Alumina-Silica*
  - *Zirconia*
  - *Magnesia*
  - *Boron (elemental, nitride, carbide)*

Boron fibers

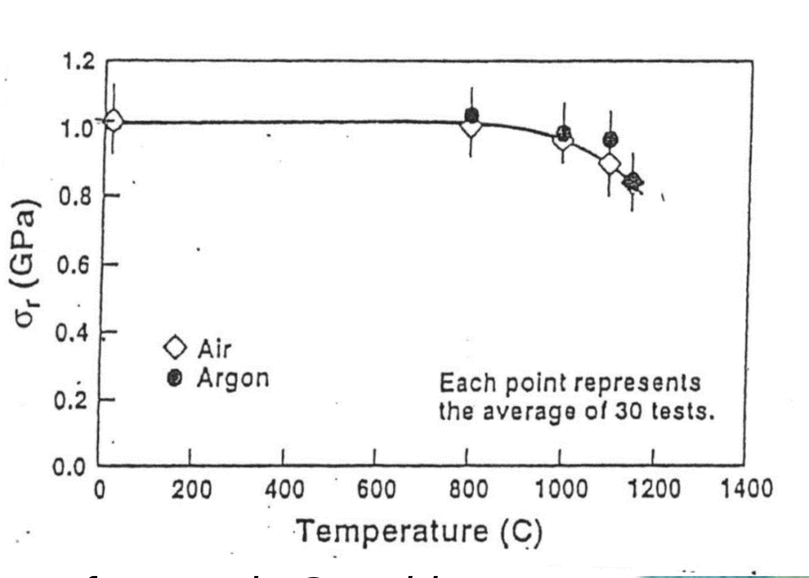
- *High stiffness, very high cost*
- *Large diameter > 100 microns*
- *Good compressive strength*
- *In the production process, elemental boron is deposited on an even tungsten wire substrate which produces diameters between 102 microns and 142 microns. It consists of a fully borided tungsten core with amorphous boron*
- *The textured surface provides an excellent interface in resin-matrix composites, eliminating any need for sizing treatments.*





Ceramic fibers: Alumina

- *Excellent high temperature stability in air*
- *High modulus*
- *Moderate strength*
- *Electrically insulating*



Types:

Monocrystalline continuous alpha alumina grown from melt: Sapphire

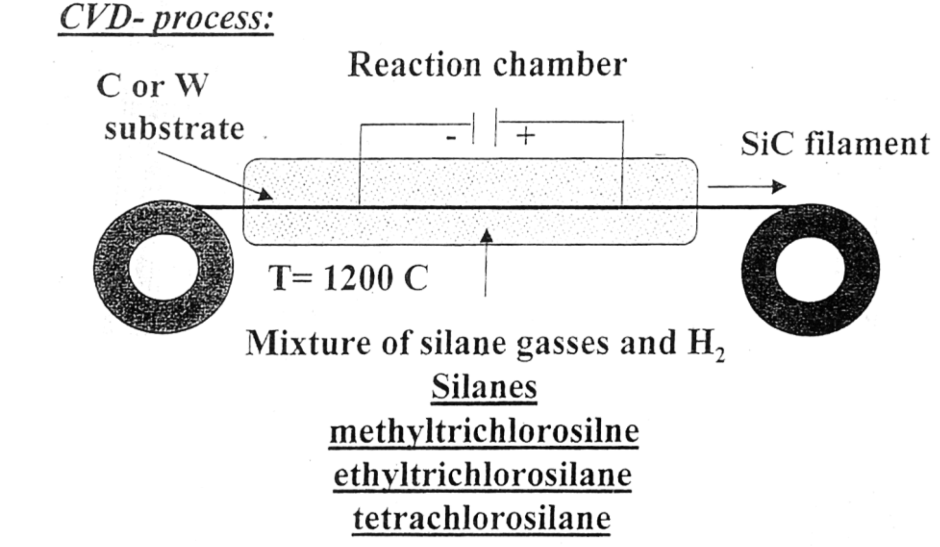
Polycrystalline alpha alumina fiber by solution spinning:

Sumika (85% Al_2O_3, 15% SiO_2), very small crystallites of Gamma alumina imbedded in amorphous silica

Nextel (Al_2O_3, SiO_2, B_2O_3)

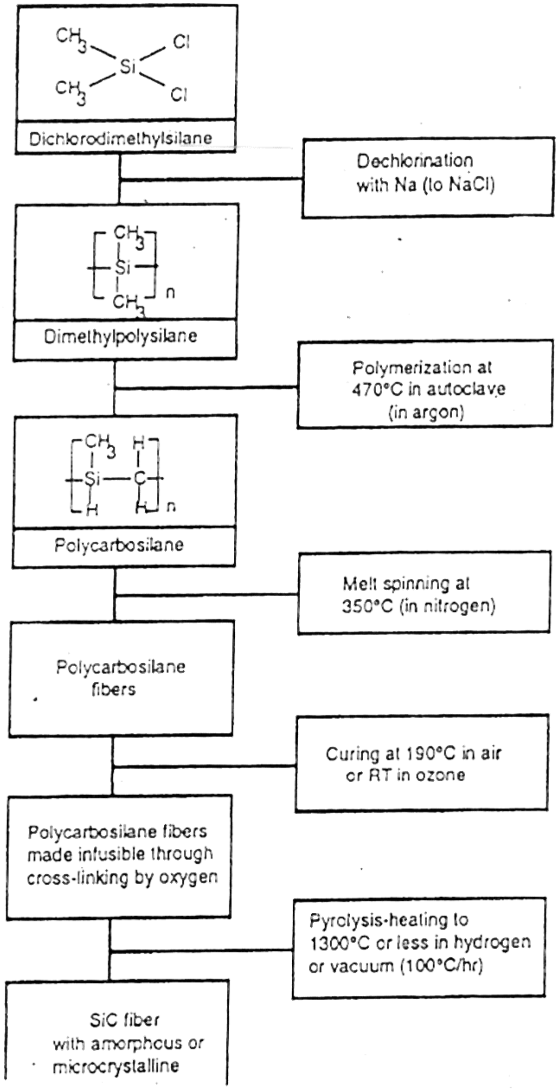
Ceramic fibers: Silicon Carbide

- *Excellent for reinforcing ceramics and some metals*
- *High stiffness and strength*
- *Good thermomechanical stability*
- *Low density*
- *Low thermal expansion coefficient*
- *Chemical vapor deposited from polymers*



Ceramic fibers: Silicon Carbide

Polymer-derived process:



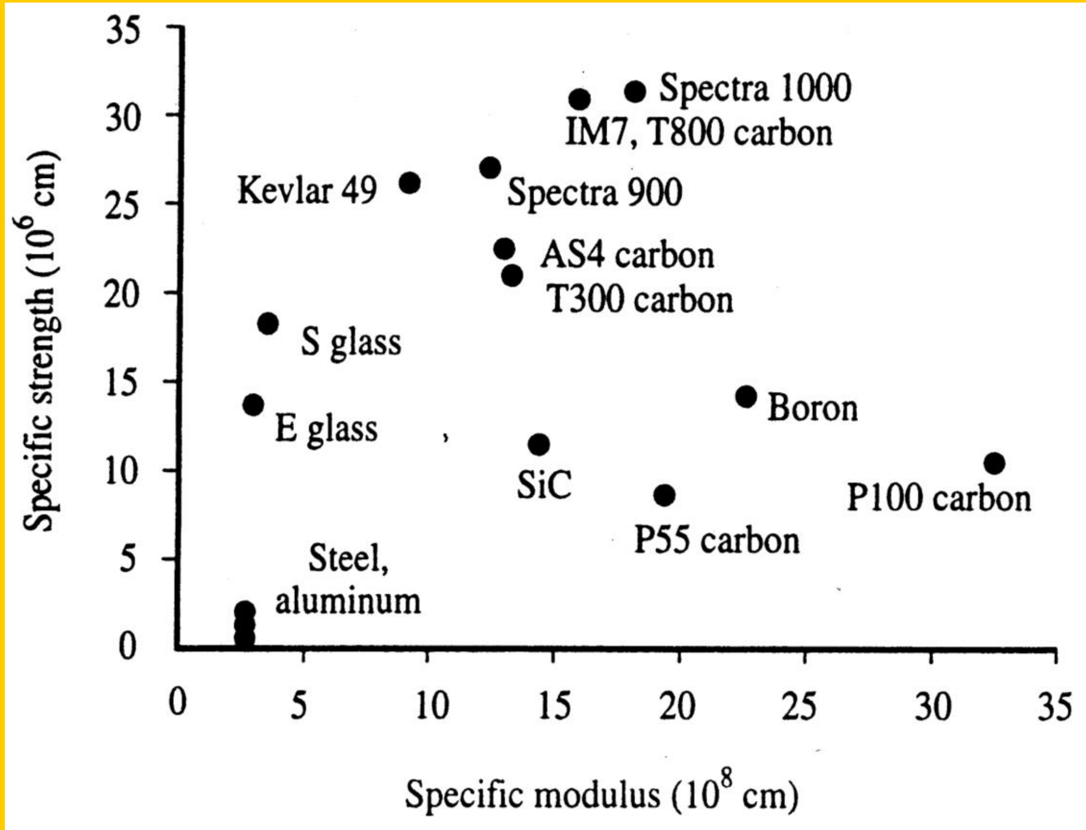
Comparison of fiber properties

Mechanical Properties of Typical Fibers

Fiber	Fiber Diameter (μm)	Fiber Density (lb/in³)	Fiber Density (g/cc)	Tensile Strength (ksi)	Tensile Strength (GPa)	Tensile Modulus (Msi)	Tensile Modulus (GPa)
E-glass	8–14	0.092	2.54	500	3.45	10.5	72.4
S-glass	8–14	0.090	2.49	665	4.58	12.5	86.2
Polyethylene	10–12	0.035	0.97	392	2.70	12.6	87.0
Aramid (Kevlar 49)	12	0.052	1.44	525	3.62	19.0	130.0
HS Carbon, T300	7	0.063	1.76	514	3.53	33.6	230
AS4 Carbon	7	0.065	1.80	580	4.00	33.0	228
IM7 Carbon	5	0.065	1.80	785	5.41	40.0	276
XUHM Carbon	—	0.068	1.88	550	3.79	62.0	428
GY80 Carbon	8.4	0.071	1.96	270	1.86	83.0	572
Boron	50–203	0.094	2.60	500	3.44	59.0	407
Silicon Carbide		0.115	3.19	220	1.52	70.0	483

- *Steel: density (Fe) = 7.87 g/cm³; TS=0.380 GPa; Modulus=207 GPa*
- *Al: density=2.71 g/cm³; TS=0.035 GPa; Modulus=69 GPa*

Comparison of fiber properties



Fiber	Cost ($/lb)
Boron	320
Silicon Carbide	100
Carbon	30
Alumina	30
Kevlar	20
E-Glass	3

Comparative cost of fiber reinforcement

Fiber reinforced composites

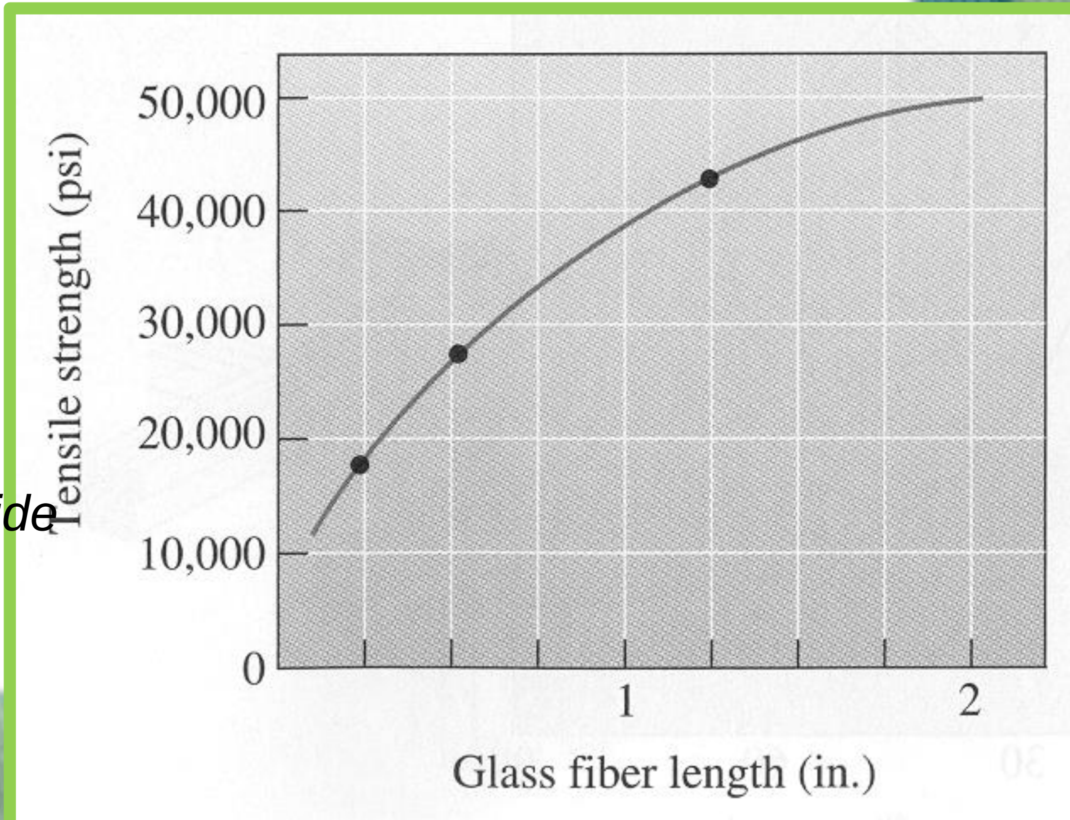
Some commonly used fibers for polymer matrix composites:

- *Glass fibers*
- *Carbon fibers*
- *Aramid fibers*

Some commonly used fibers for metal matrix composites:

- *Boron fibers*
- *Carbon fibers*
- *Oxide ceramic and non-oxide ceramic fibers*

Data for a chopped E-glass-epoxy composite



Strength of fibers

- *Stiff fibers are generally brittle due to the presence of flaws*
- *Strength depends on the concentration of flaws*
- *So it is not a single-value property but a statistical variable*
- *The statistical distribution is described by Weibull model:*

The distribution is based on the weakest link theory in which failure of the most serious flaw leads to the catastrophic fracture of the entire material.

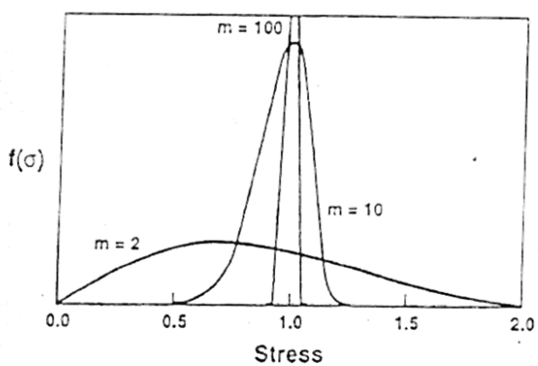
The model assumes that flaws are homogeneously distributed throughout the material, the strength along a fiber has the same distribution with all individual fivers and fracture is perfectly brittle

Strength of fibers

Failure probability density function

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

$$\ln\{-\ln[1 - P(\sigma)]\} - \ln L = m \ln(\sigma) - m \ln(\sigma_0)$$



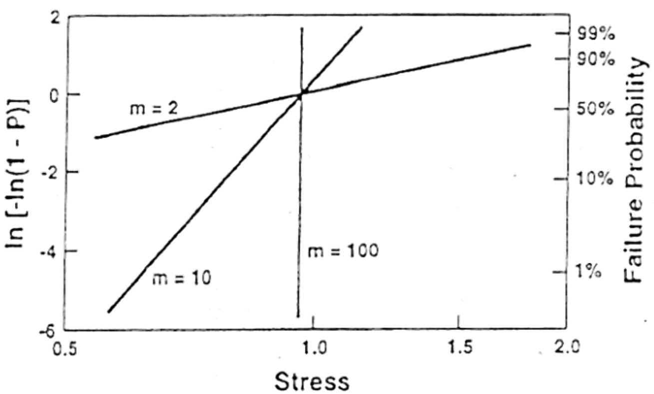
Plots of the Weibull probability density function for various values of the Weibull modulus (from van der Zwaag, 1989).

The mean fiber strength

$$\bar{\sigma} = \int_0^\infty \sigma\, p(\sigma)\, \mathrm{d}\sigma = \frac{\sigma_0}{L^{1/m}} \Gamma\left(1 + \frac{1}{m}\right)$$

Γ gamma function

1 - P(σ) denotes probability of survival



Plots of Eq. (2-8) for various values of the Weibull modulus (from van der Zwaag, 1989).

Strength of fibers

BEVITORI, A. B. et al . Diameter dependence of tensile strength by Weibull analysis: Part II jute fiber.

Table 1: Weibull parameter σ_n the jute fiber strength in different diameter interval.

Diameter Interval (mm)	Weibull Modulus β	Characteristic Strength θ	Precision Adjustment R^2	Average Tensile Strength (MPa)	Statistical Deviation (MPa)
0.04-0.06	1.82	364.1	0.949	323.7	184.7
0.06-0.08	2.20	228.0	0.938	201.9	96.7
0.08-0.10	2.53	144.8	0.860	128.5	54.4
0.10-0.12	2.15	119.5	0.933	105.8	52.6
0.12-0.14	1.88	97.5	0.959	86.6	47.8
0.14-0.16	1.48	67,7	0.964	61.2	42.1
0.16-0.18	1.77	66.9	0.967	59.6	34.7

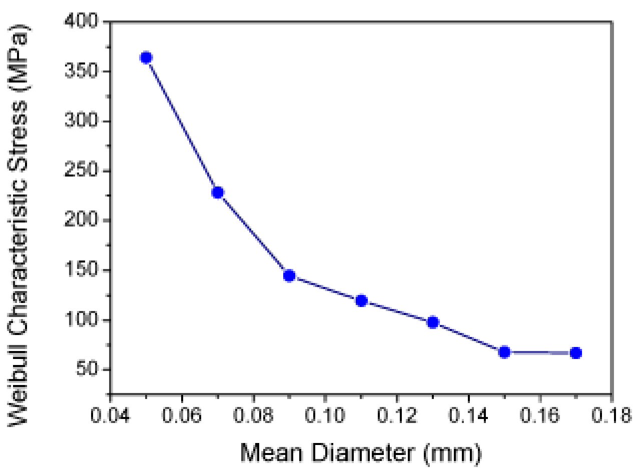


Figure 4: Variation of the characteristic stress with the mean diameter for each interval.

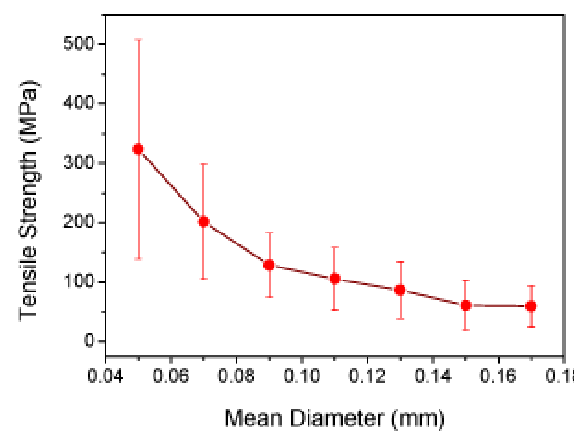


Figure 5: Variation of the average tensile strength with the mean diameter for each interval.

Coatings for fibers

- *Fiber/matrix interface coatings provide improved composite properties*
- *Especially important for metal matrix composites, coatings prevent undesirable reactions, improve the strength of the fibers and the bond strength between fiber and matrix*
- *A reaction barrier is needed for some fiber/matrix combinations when the composite is exposed to high temperatures in processing or service*

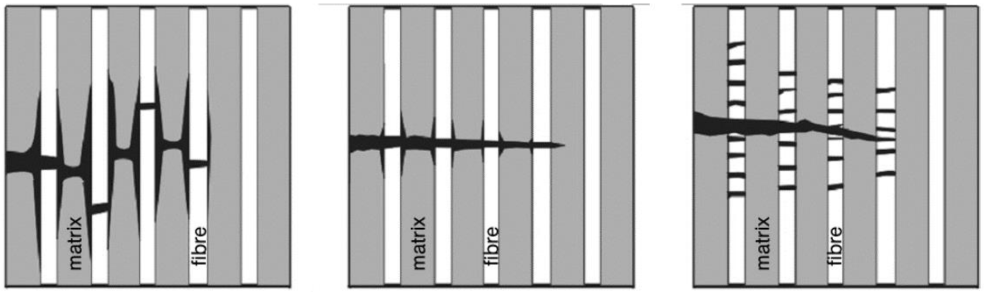
Example – Boron fibers coated with boron carbide and silicon carbide to prevent diffusion and chemical reactions with the matrix phase.

- Alumina fibers coated with silica to improve tensile strength

Coatings for fibers

- *The bond strength between the fiber and matrix determines the mechanical properties of the composite.*

- *If adhesion between fiber and matrix is too good, cracks in the matrix propagate through the fibers, making the composite brittle*



a) poor adhersion b) medium adhesion c) good adhesion

- *Coatings can enhance crack deflection at the interface and lead to higher energy absorption during fracture by reducing the bond strength*

- *Coatings can also promote wetting between the matrix and the fiber to achieve a good bond*

Example – Titanium diboride coating on graphite fiber promotes wetting