New Ideas. New Materials.

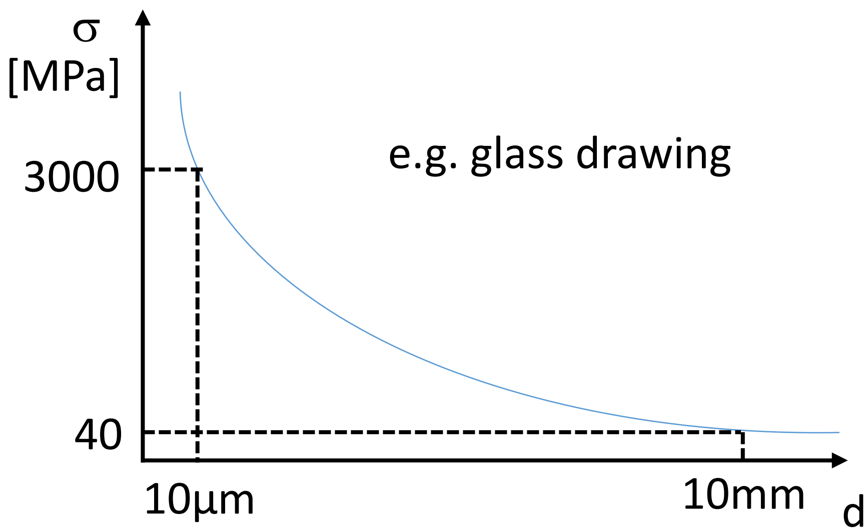
TECHNOLOGIE POLYMERE & KOMPOSITE

MC07, UdS WS 2019/2020

Chapter 4: Fibres and Composites

Why fibers? Strength and stiffness

- Strength
  - F/A … [N/mm²] … [MPa]
  - steel bar ∅ 1 cm: 450 MPa
  - steel wire ∅ 0.1 mm: 4000 MPa



- Stiffness
  - How much deforms a material elastically?
- elastic modulus
  - polymer: 3 GPa
  - glass: 70 GPa
  - steel: 200 GPa
  - carbon fibers: 200-600 GPa
  - C-nanotubes: 2000 GPa (theor.)

Reinforcement classification

- particles
- whiskers and nanofibres
- fibres
  - natural
    - asbestos (mineral)
    - cellulose (vegetal)
    - collagen and silk (animal)
- synthetic
  - organic
    - aramid
    - polyethylene
    - carbon
- inorganic
  - ceramic
    - SiC
    - SiO2
    - Al2O3
  - metallic
    - steel
    - tungsten
    - …

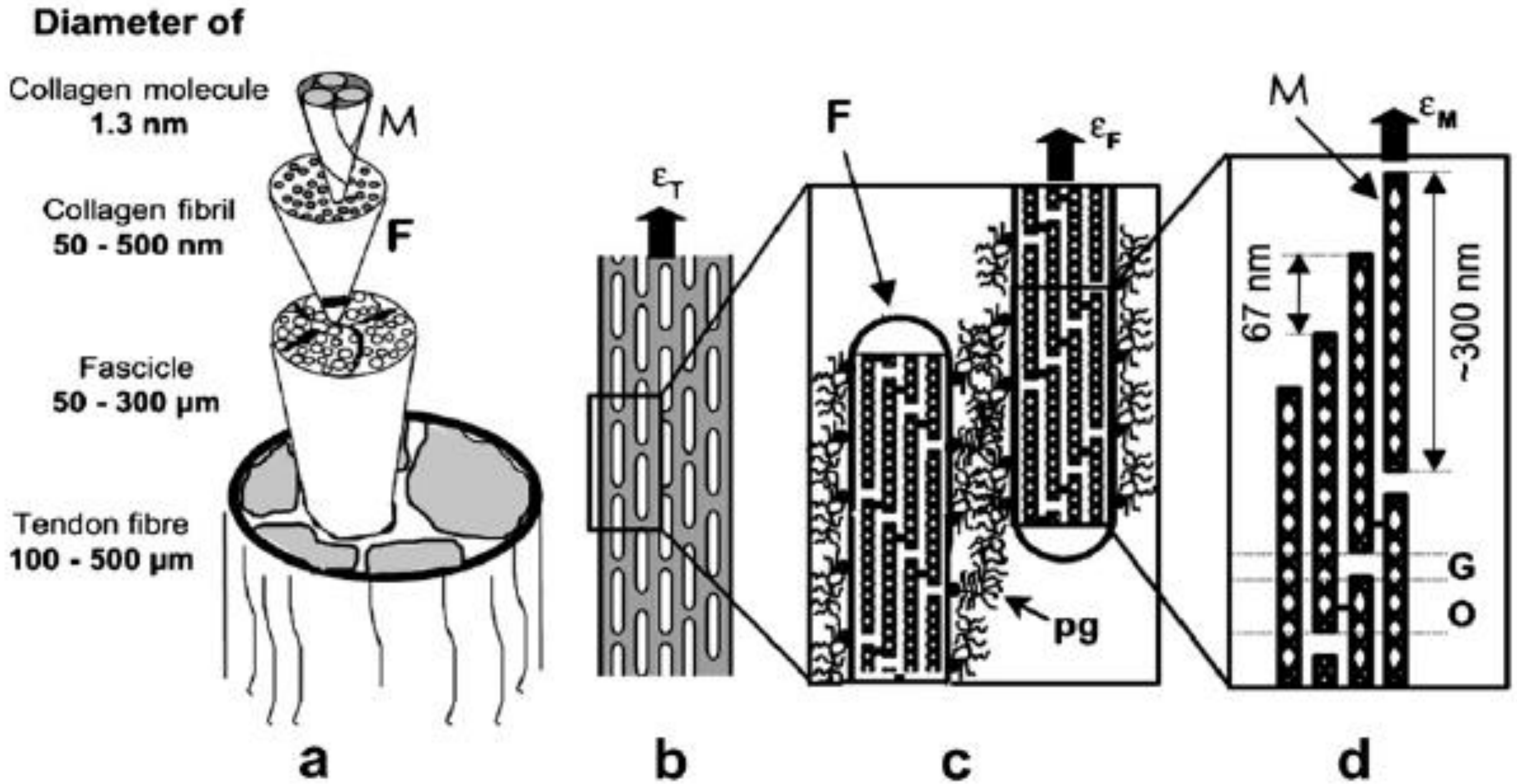
Cellulose

- polymeric fiber
- obtained from condensation reaction of glucose

$$C_6H_{12}O_6 \text{ -------> } -[C_6H_{10}O_5]- + H_2 0$$

- crystalline with polymeric chains oriented along fiber axis
  - degree of polymerisation ≈ 10^4
- fibres in plants
  - cotton
  - flax
  - hemp
  - jute
  - cellulose fibers are embedded in matrix of hemicellulose and lignin

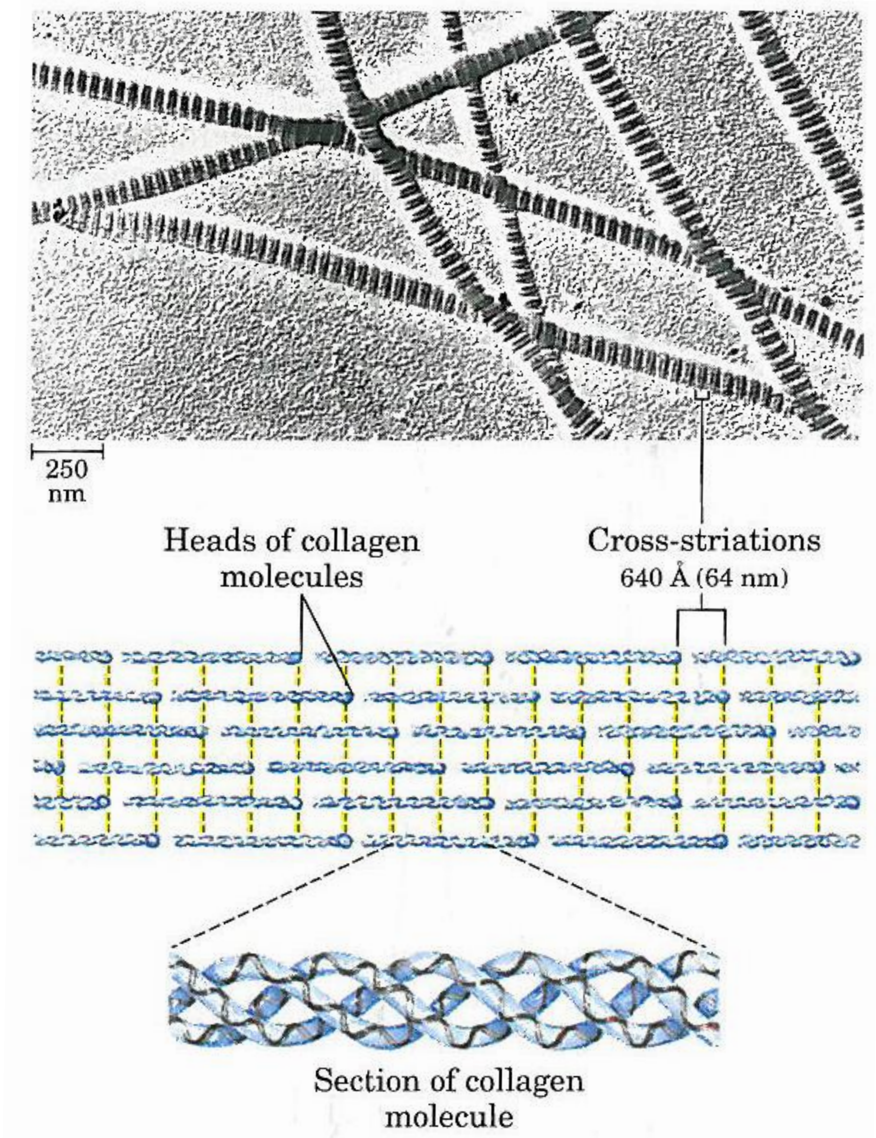
Collagen: hierarchical structure



I.M. Weiss, INM

Fratzl & Weinkamer (2007) Progr. Mat. Sci. 52,1263-1334

The collagen triple helix

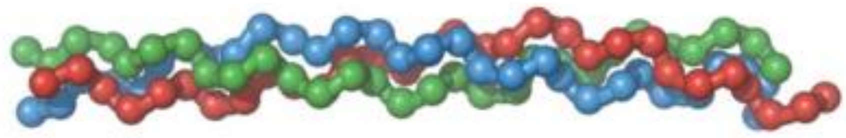


I.M. Weiss, INM

Silk

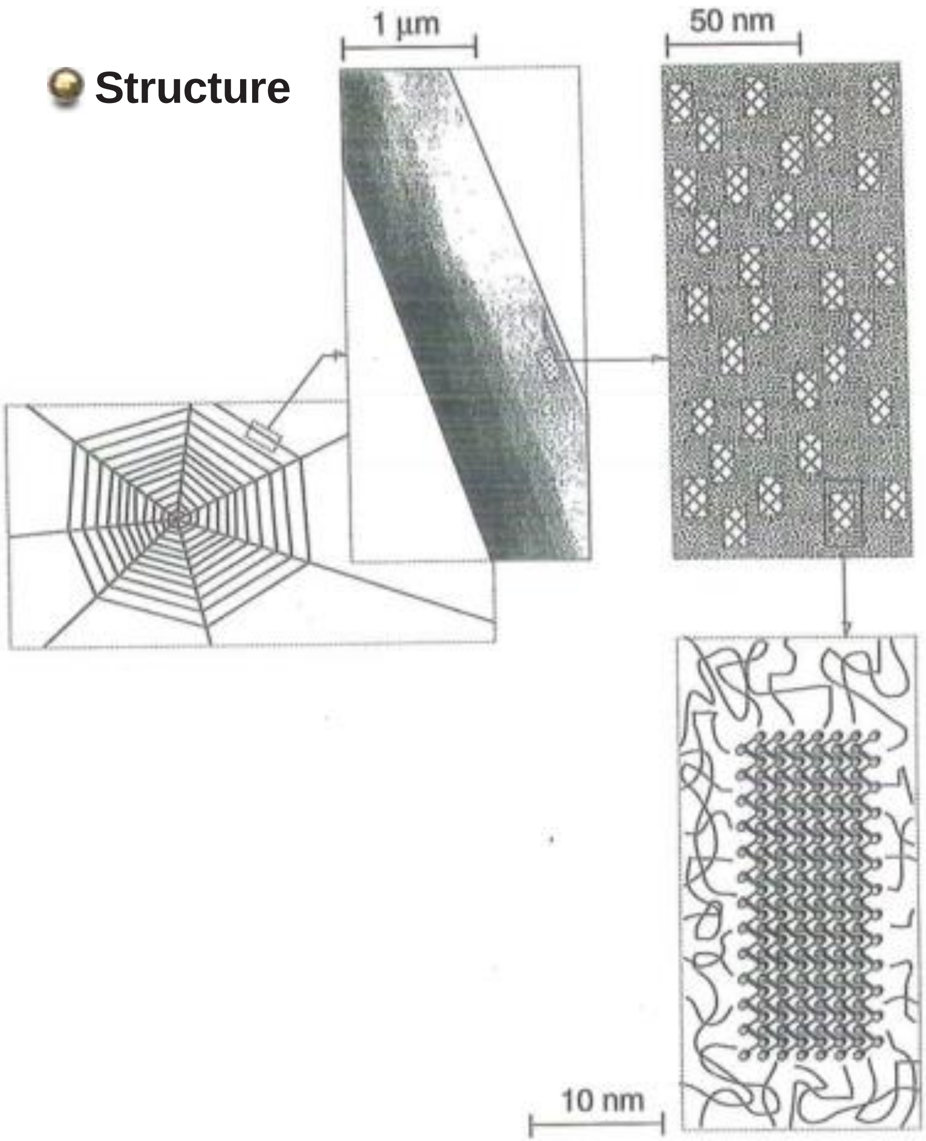
- secretory product of the spinning glands of a variety of insects and spiders
- silks are nanocomposites based on polypeptides
- nanocrystalline proteins in amorphous protein network
- outstanding mechanical properties in terms of strength and ductility

300 nm long and 1.5 nm in diameter

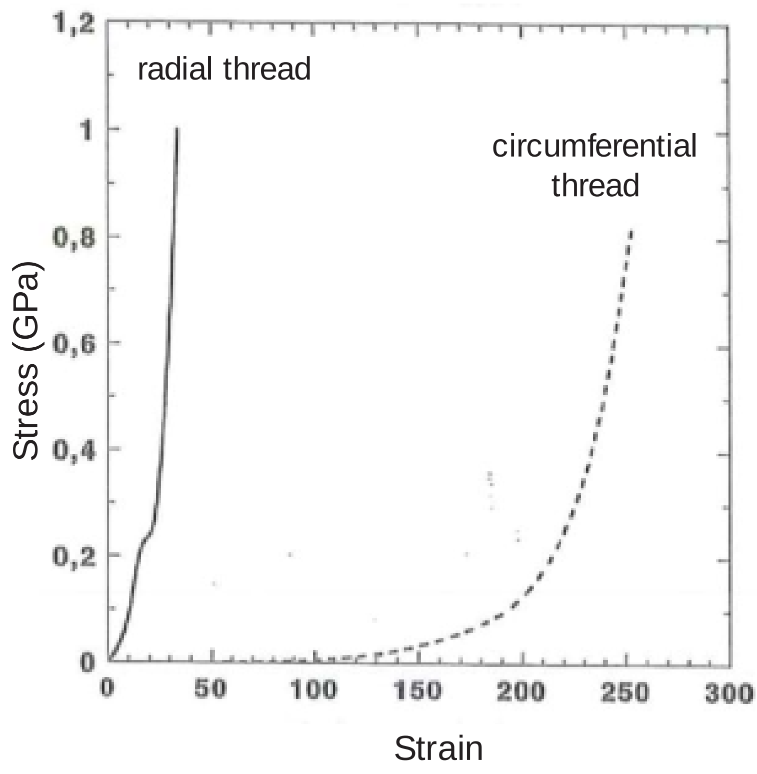


Silk

Structure



Properties



Asbestos

- fibrous mineral
- chemical composition $Mg_3(Si_2O_5)(OH)_4$
- from serpentite rocks
- several cm length
- was used
  - to improve tensile strength of cement
  - better electical insulation
  - heat and fire resistance
- currently banned because asbestos fibres lead to lung cancer

Glass fibers

- Glass fibers are amorphous fibers based on SiO_2. They are the backbone of information technology. We will focus in glass fibers for composite reinforcement.

- Raw materials to manufacture glass fibers are abundant and cheap. Processing route is unsophisticated: cheap glass fibers are readily available for reinforcement.

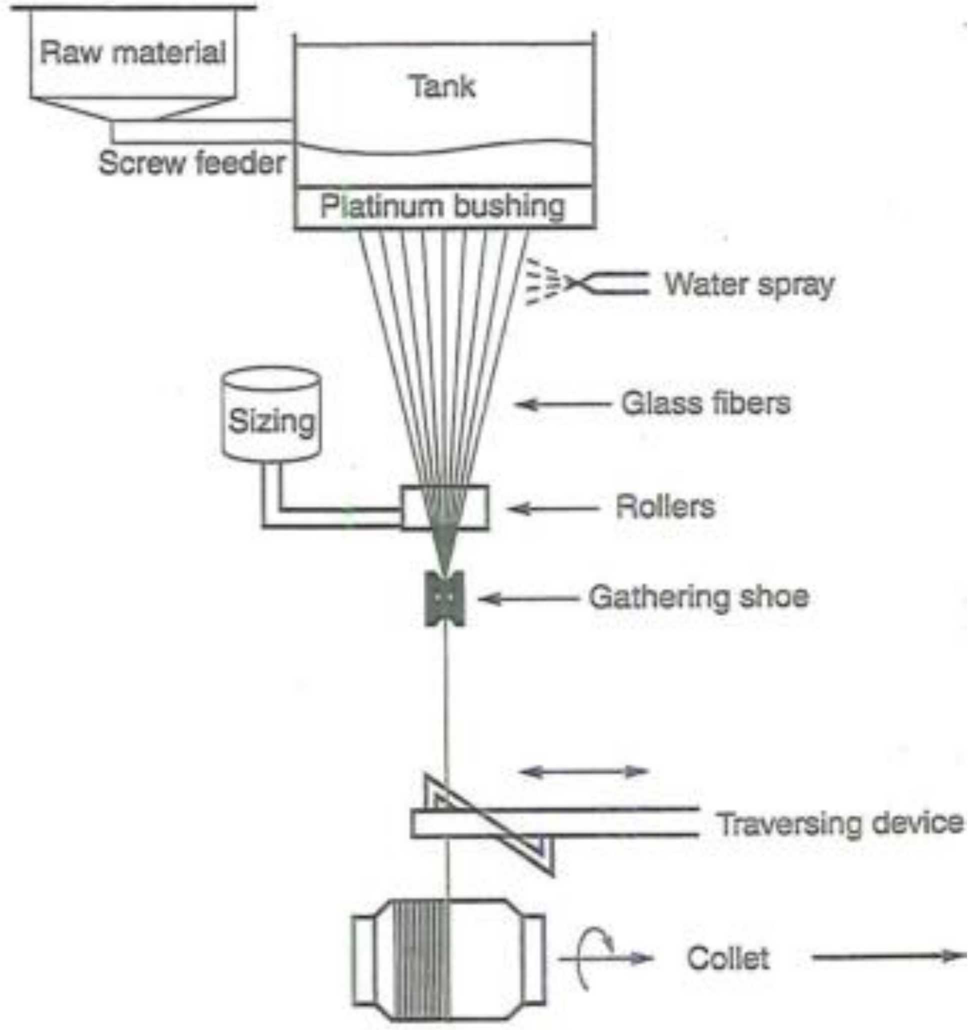
- **Structure:** glass fibers are amorphous.

- **Composition:**

- Glass fibers are based on SiO_2 (≈ 50-60%) and contain a host of other metallic oxides. Different properties can be obtained by changing the chemical composition:

  - E glass (standard): 55% SiO_2, 19 % CaO, 8% Al_2O_3, 7% Li_2O
  - C glass (corrosion resistant): 65% SiO_2, 14% CaO, 9% Na_2O, 5% Li_2O, 4% Al_2O_3
  - S glass (high strength): 65% SiO_2, 25%Al_2O_3, 10% MgO

Glass fiber production



Glass fibers

- **Properties:** glass fibers are isotropic and present isotropic properties

- The may have high strength but the stif fness is limited. Thus, the specific stiffness is low.

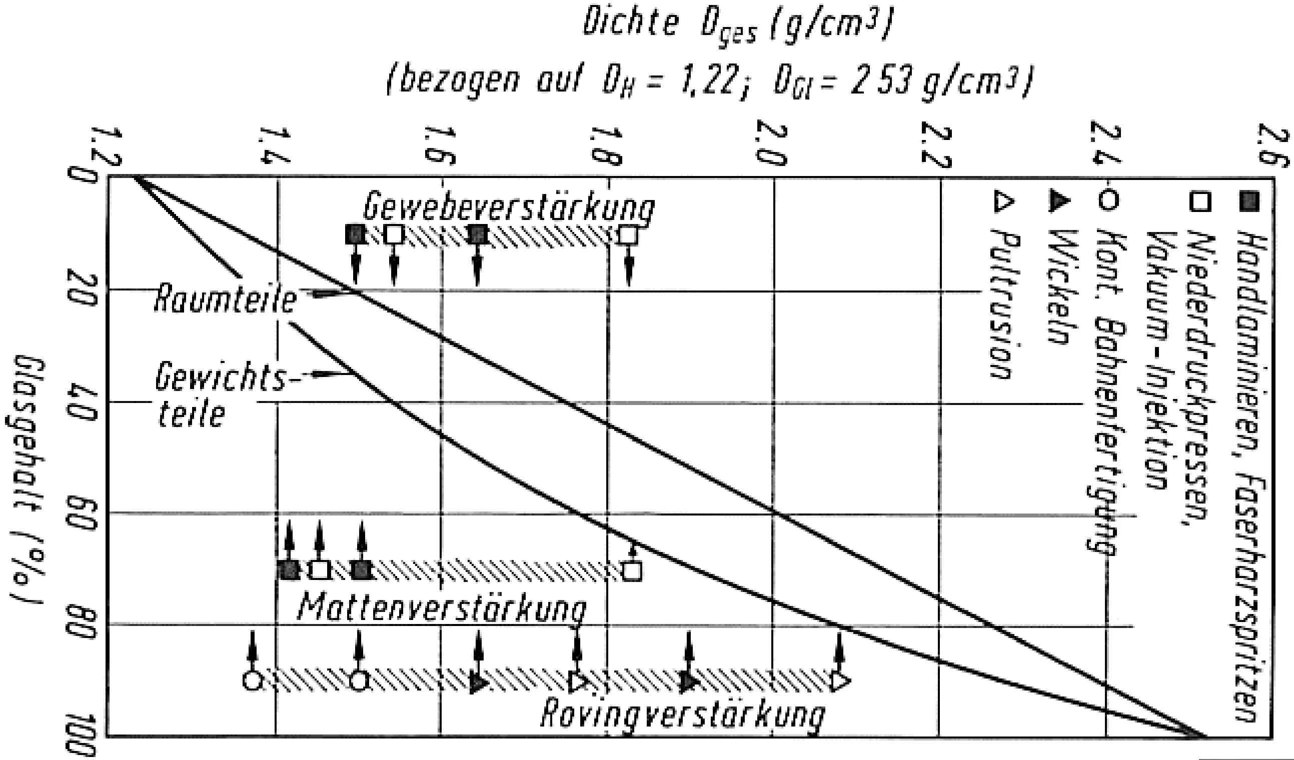
- They are resistant to fire and many chemicals but moisture (water adsorption) can lead to a important reduction in strength.

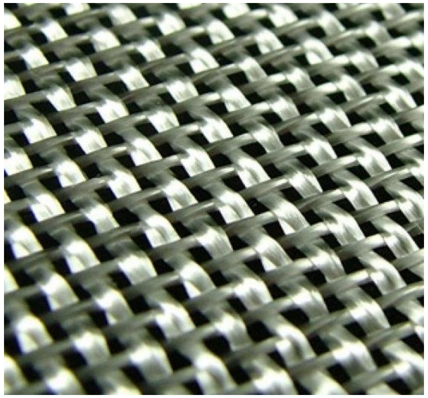
- E glass is corroded in alkaline environments (cement).

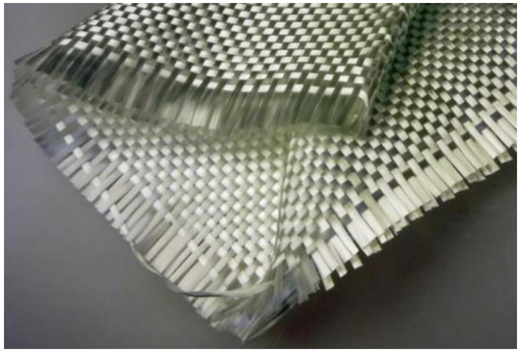
- Mechanical properties decay rapidly above 400ºC-500ºC due to melting. The melting temperature (and the viscosity) increase with the SiO_2 content.

- Glass fibers are the standard reinforcement for low-added-value composite applications in engineering which speci fic stiffness is not critical (civil construction, marine and automotive markets, etc.)

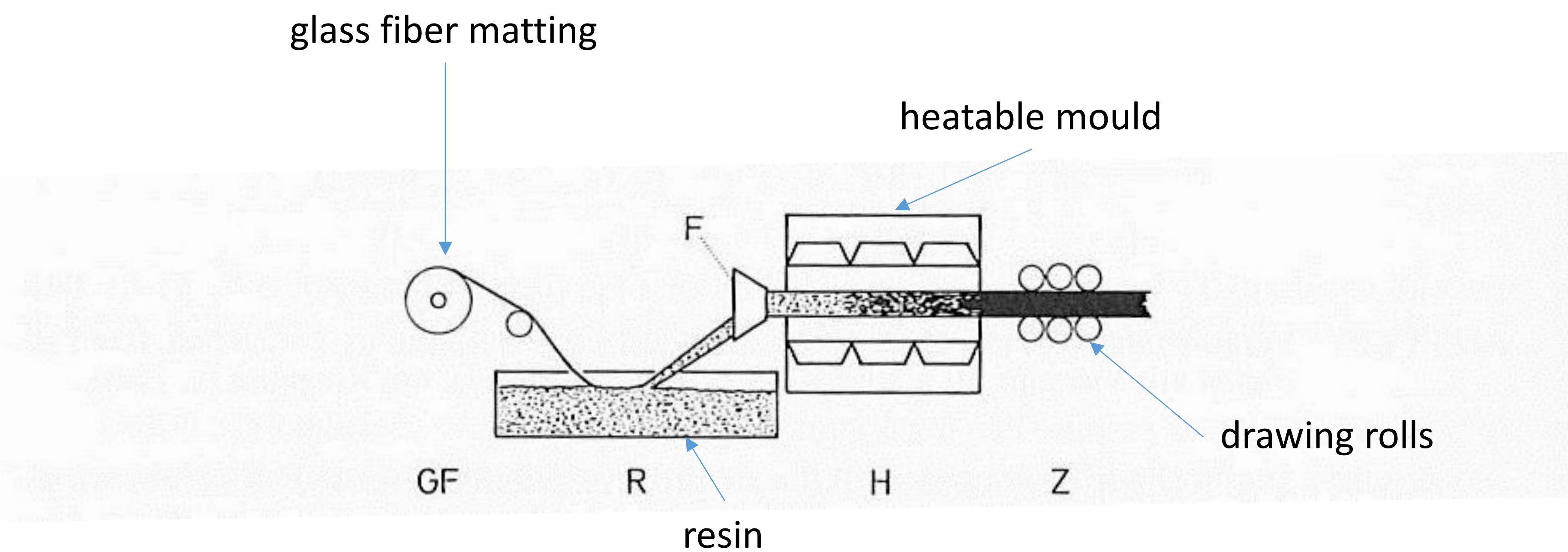
Glass fibre composites







Pultrusion of glass fiber matting



SiC fiber processing by CVD

Structure: Polycrystalline SiC fibers of ≈ 100- 150 µm in diameter are grown by CVD on a W or C fiber.

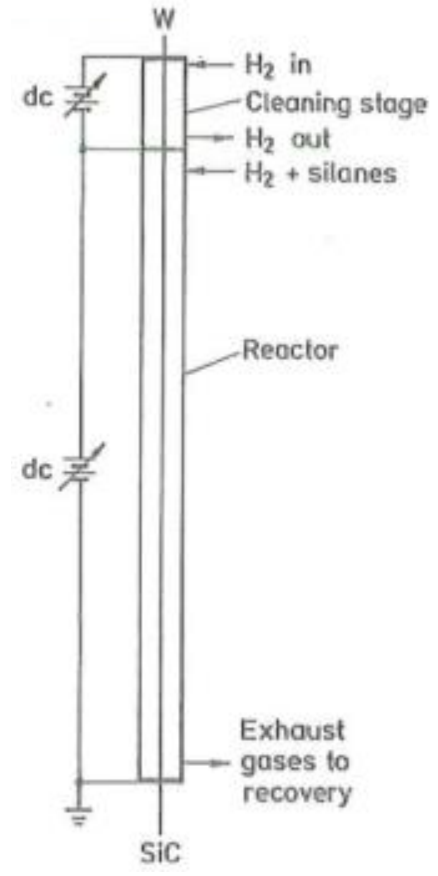
- The external fiber sheath is made up of ß-SiC with some alpha-SiC near the core. The {111} planes in SiC are parallel to the fiber axis.

Processing:

- CH_3SiCl_3 (g) ----> SiC (s) + 3 HCl (g)

- Reaction takes place at 1000ºC in an atmosphere of H_2 (70%) and CH_3SiCl_3 (30%)

- Processing of a 100 µm fiber takes 20s.



SiC fibers from polymer precursor

- **Structure:** small diameter (10-20 µm) SiC fibers can be obtained by pyrolysis of a polymer precursor

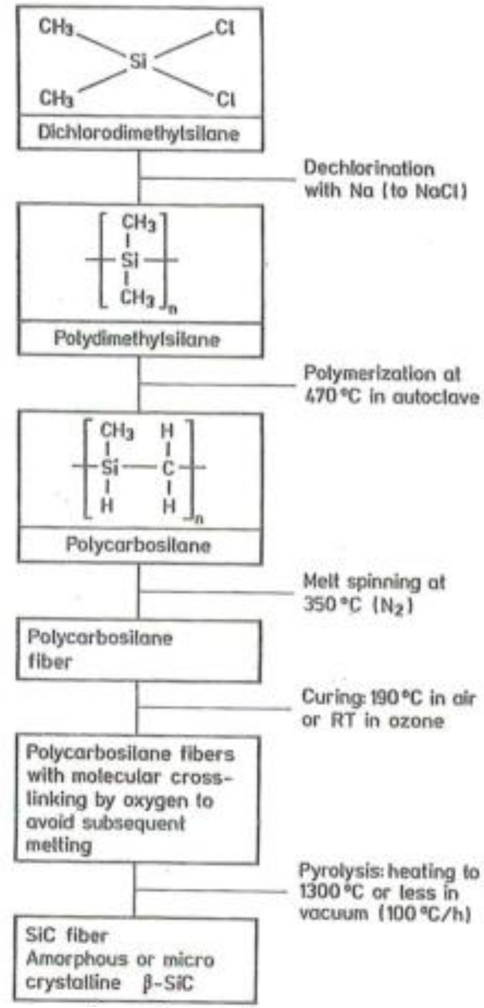
  - Fiber composition is a mixture of SiC, SiO_2 and free C. Chemical composition is 59% Si, 31% C, and 10% O

- **Processing:**

  - Polymer precursor -[CH_3-Si-CH_3]$_n$- is treated at 470°C leading to polycarbosilane with 1500 MW.

  - Polycarbosilane is melt spun at 350°C in N_2 to obtain a fiber precursor.

  - Fiber precursor is stabilized (190°C in O_2) and then pyrolyzed at 1300°C in vacuum.



Al_2O_3 fibers

- Al_2O_3 fibers are of particular interest for high temperature and/or oxidation resistant applications.

- **Structure:**

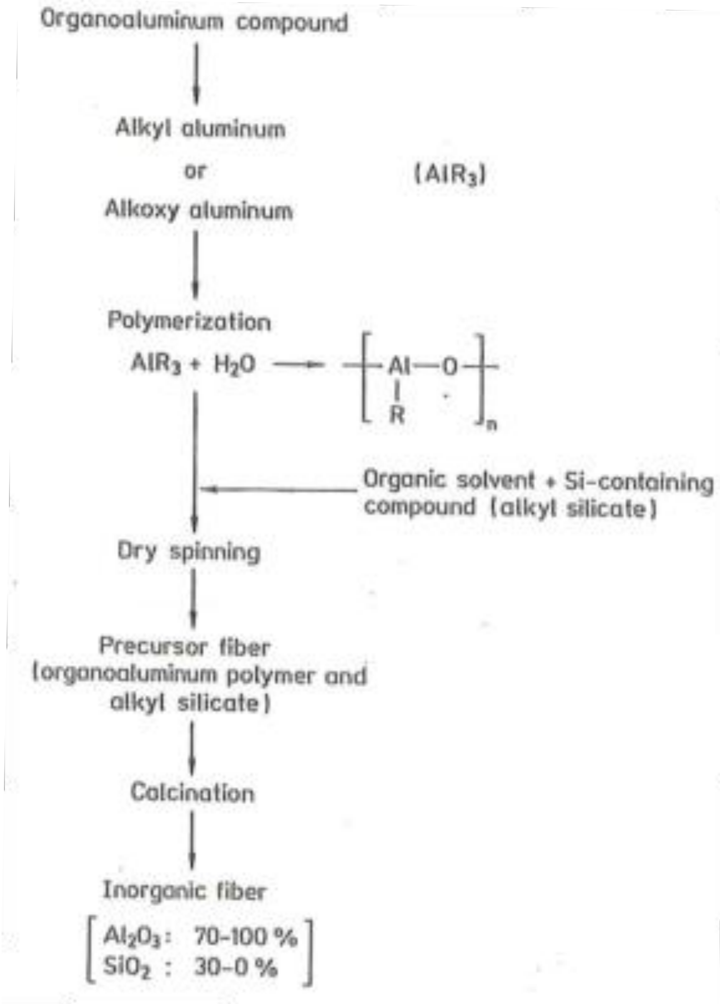
- Polycrystalline Al_2O_3 fibers of ≈ 10 µm in diameter are obtained by a sol-gel route.

- They can contain different amounts of SiO2, leading to fibers of different grade. Glassy phases are found at the grain boundaries.

- **Processing:**

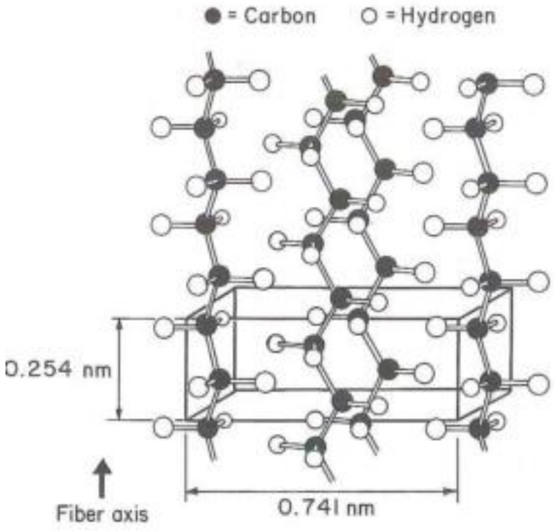
- An organic Al salt solution -starting material- is polymerized and spun to form a precursor fiber.

- Fiber is calcined at 1400ºC under careful conditions to obtain the inorganic fiber.



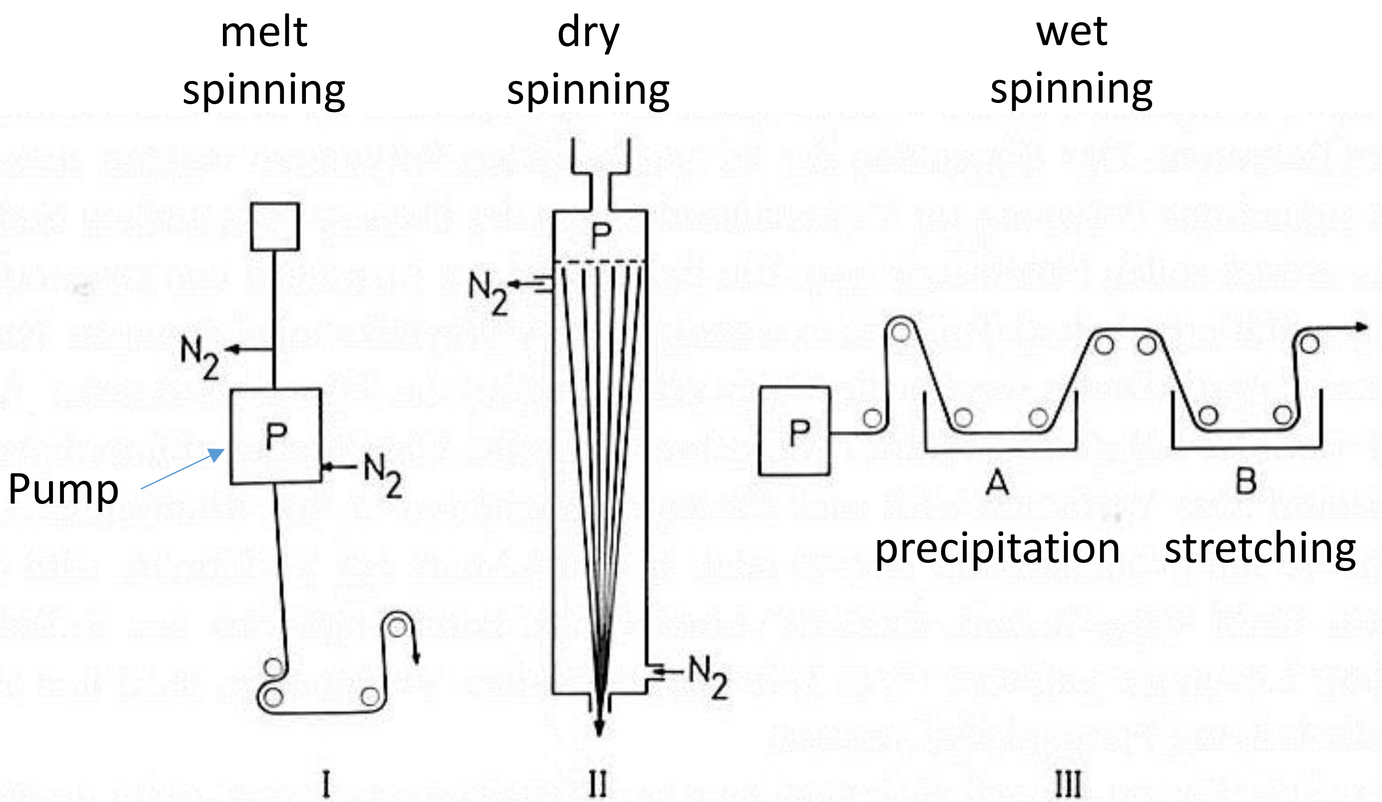
Polyethylene

- ultra-high molecular weight PE chains ($>10^6$)
- structure
  - oriented along the fibers axis
  - fiber structure is highly crystalline
  - actual density of PE fibers is very close to the theoretical one (0.998 g/cm³)
- processing
  - processed by gel-spinning
  - swollen fiber (folded chains with solvent
  - drawing temperature 120 °C
  - draw ratio up to 200
  - leading to orientation

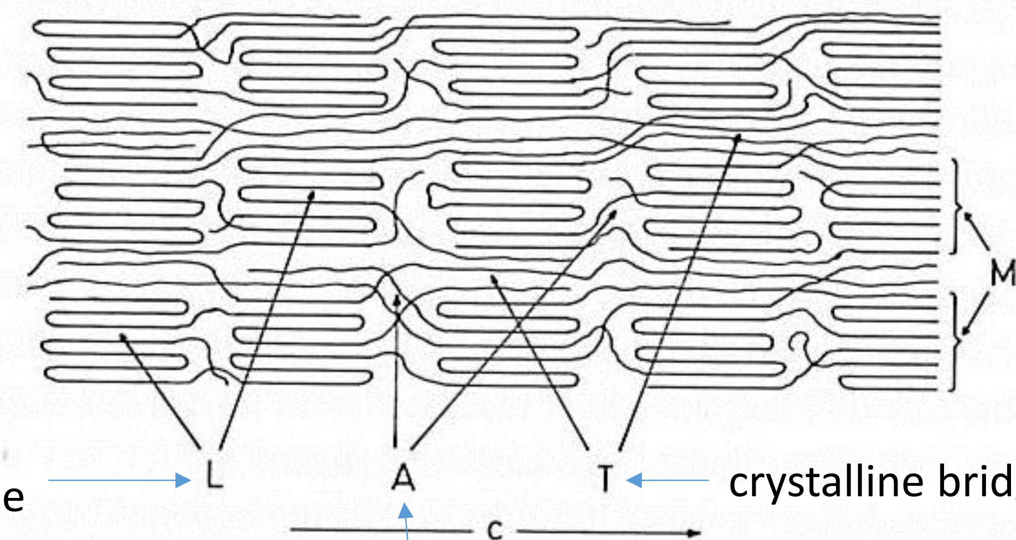


single crystal PE unit

Spinning methods



Structural model for elongated partially crystalline fibers



micro fibrillae

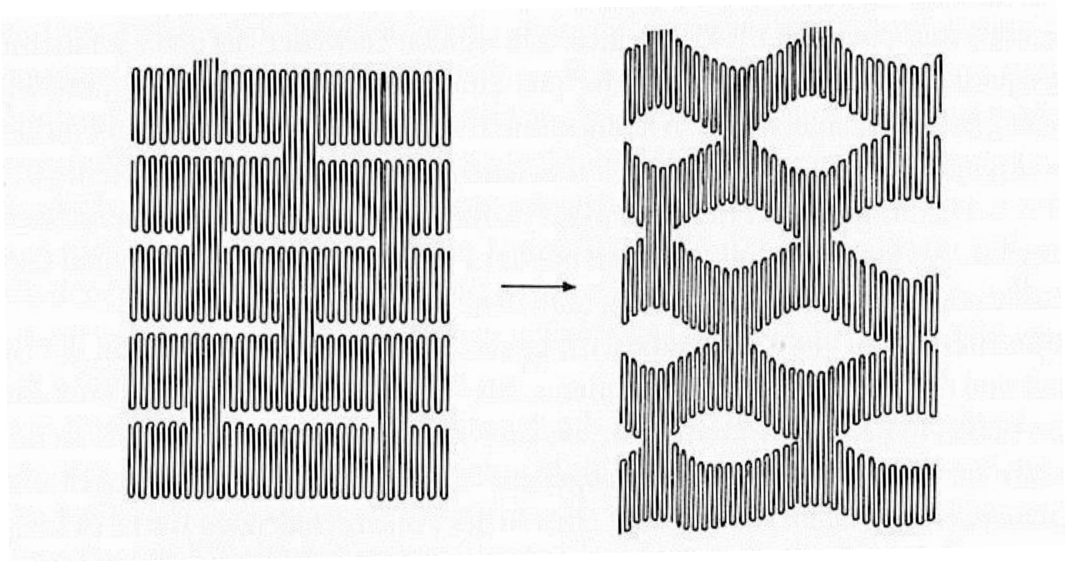
folded lamellae

crystalline bridges

interlamellar regions

Model of a hard elastic fiber

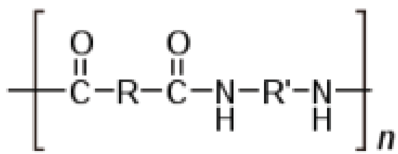
- lamellar packages are deformed
- crystalline bridges hinder delamination
- snapping back



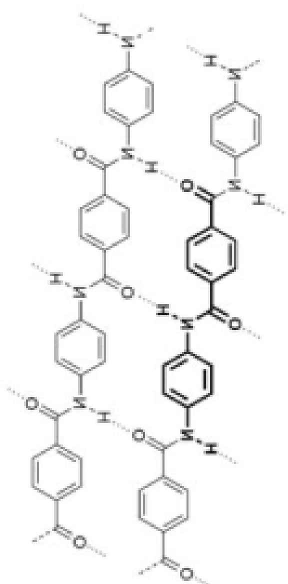
Aramid

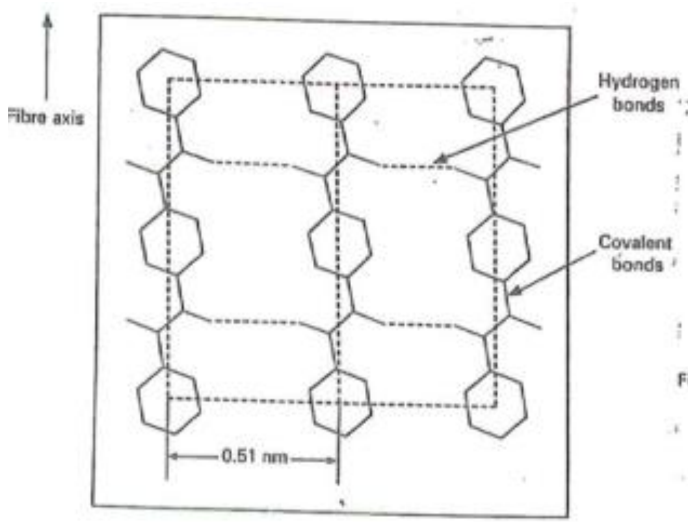
- aramid fibers based on aromatic polyamide chains
- closely related to nylon,…

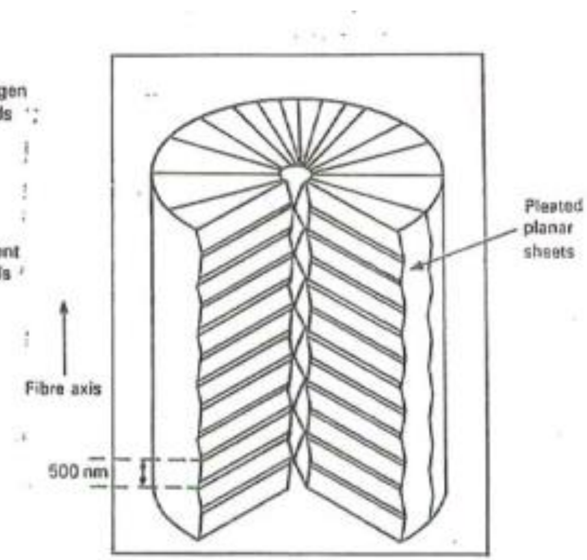
Polyamide



Nylon	R = R'= CH_2
Aramid	R = R'= aromatic ring

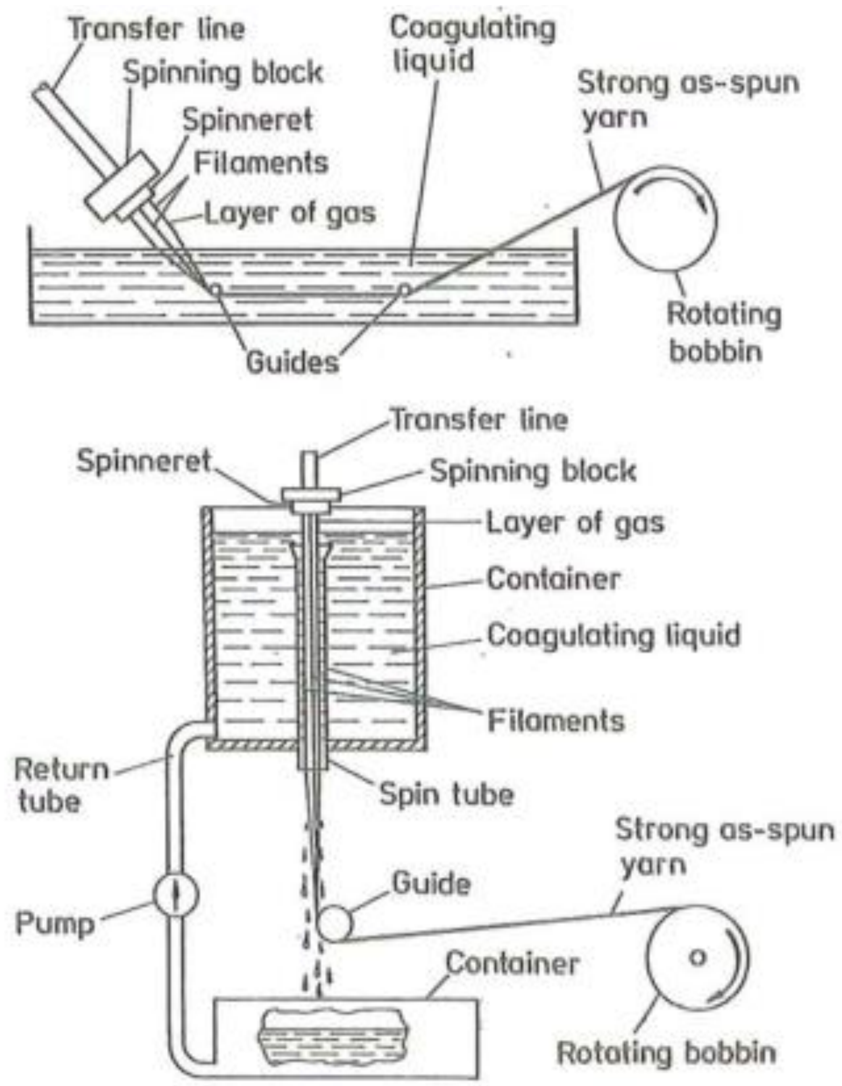






Aramid Processing

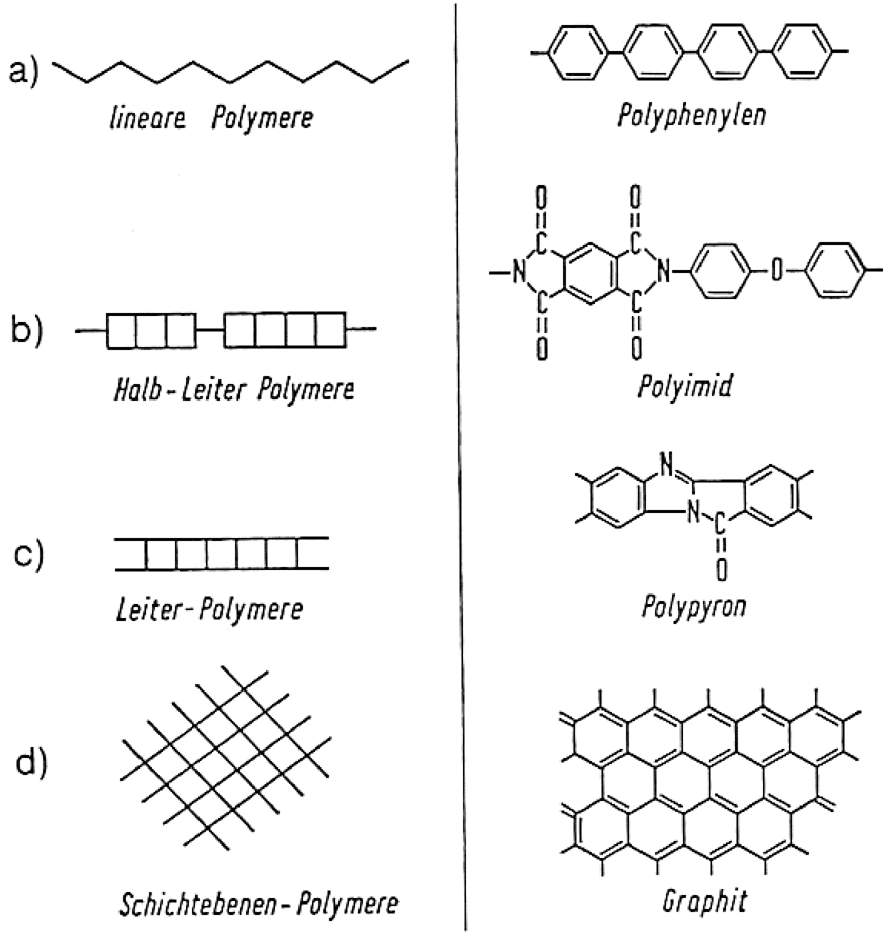
- spinning from liquid crystalline polymer solutions
- critical point: obtaining a polymer solution in which the polymer chains are ordered forming a liquid crystal
- critical conditions: 100 °C, 20 % H_2SO_4



Aramid

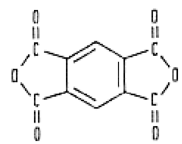
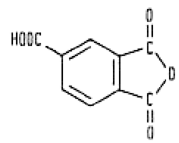
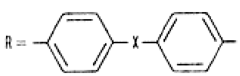
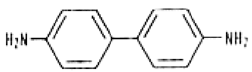
- strong, stiff fiber
  - high elongation at break (3.5-4.0 % in Kevlar 29)
  - suitable for protection against impact
- compressive strength is about 1/8 of the tensile strength due to anisotropic structure
- good damping properties
- sensitive to UV radiation
  - leads to breakage of chemical bonds and degradation of mechanical properties

Structural types of aromatic polymers



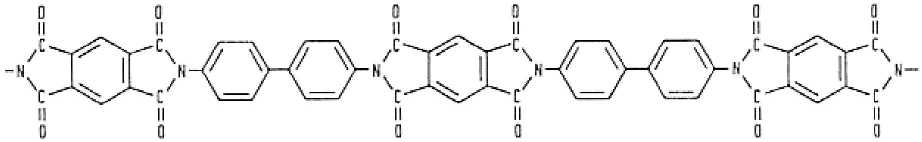
Aromatic polymers

Tafel 4.81. Aufbaureaktionen für Polyimide

(A)			
 (1) Pyromellitsäure-Anhydrid	 (2) Trimellitsäure-Anhydrid	 (3) Bismaleinimid 	 (4) Benzidin

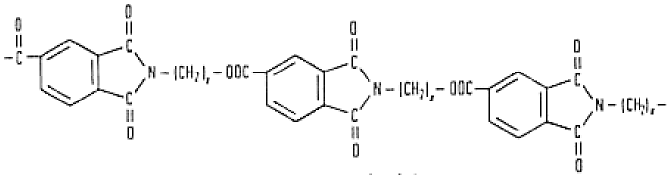
(B) Polykondensation unter H_2O-Abspaltung von

(B1) 1 + 4



Polyimide

(B2) 2 + Amino-alkohol

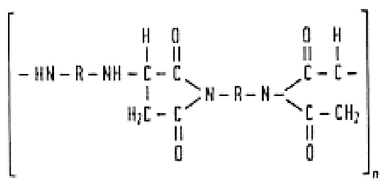


Polyesterimide

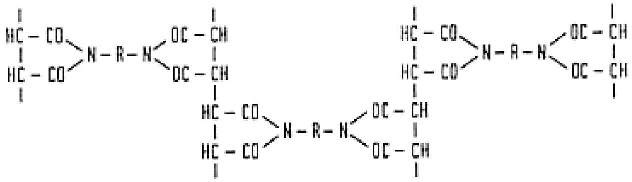
Typical monomer units in polyimides

(C) Stufen-Polymerisation

von
3 + p-Diamin

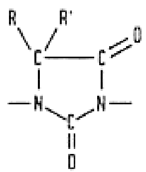


Polybismaleinimid
(thermopl. Zwischenprodukt)

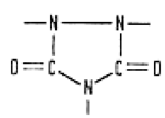


Vernetzungsreaktion
(schematisch)

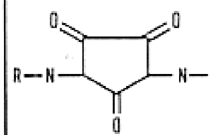
(D) Einige andere wichtige Heterocyklen



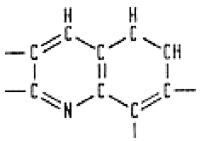
Hydantoin



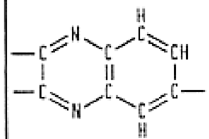
Urazol



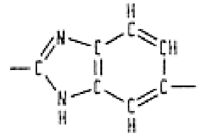
Parabansäure



Chinolin

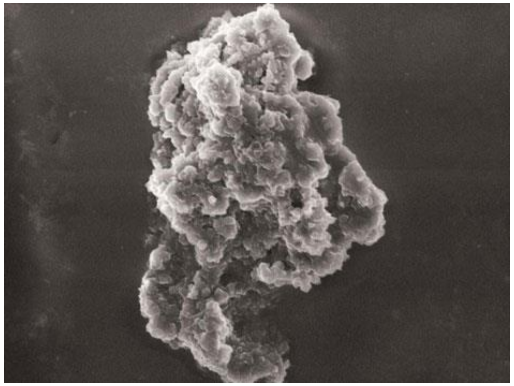


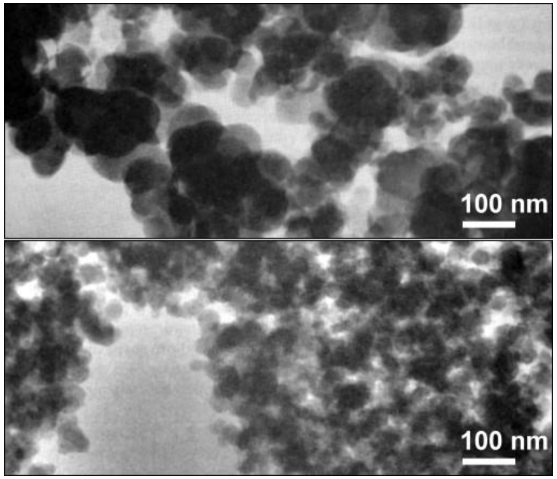
Chinoxalin

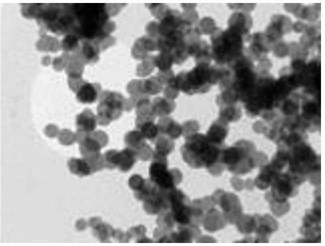


Benzimidazol

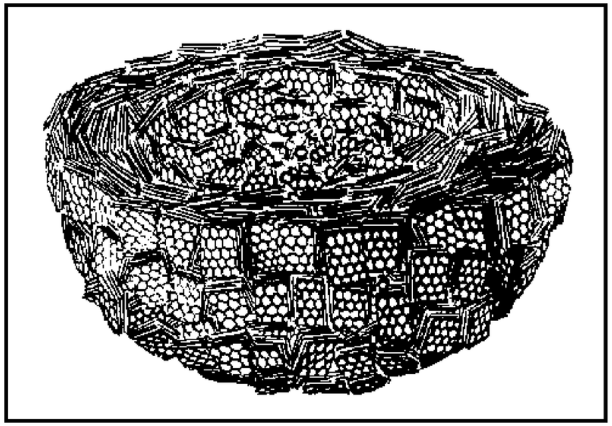
Carbon black



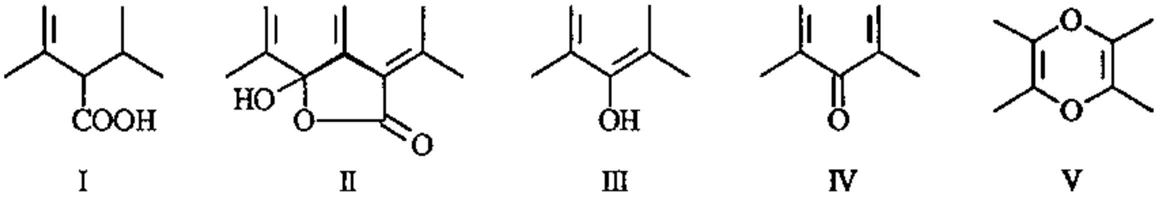




primary particle cross section

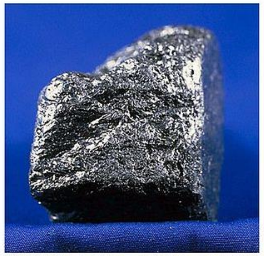


typical functional groups

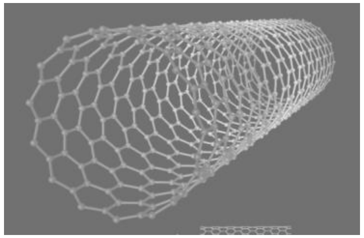


Allotropic forms ofcarbon

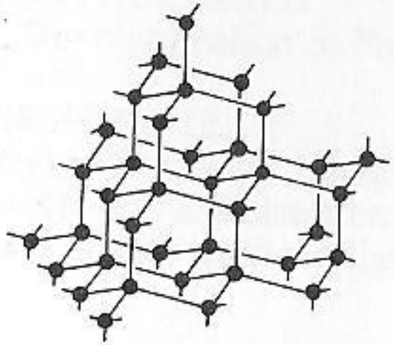
diamond



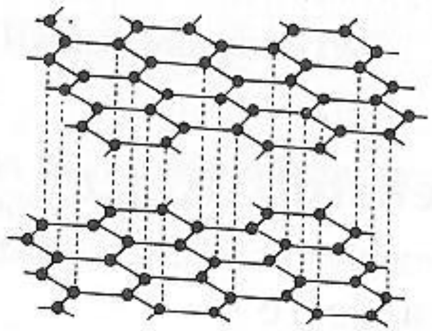
graphite



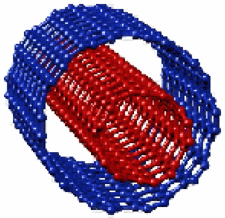
carbon nanotubes



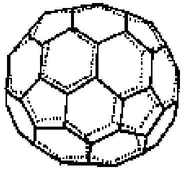
D



G



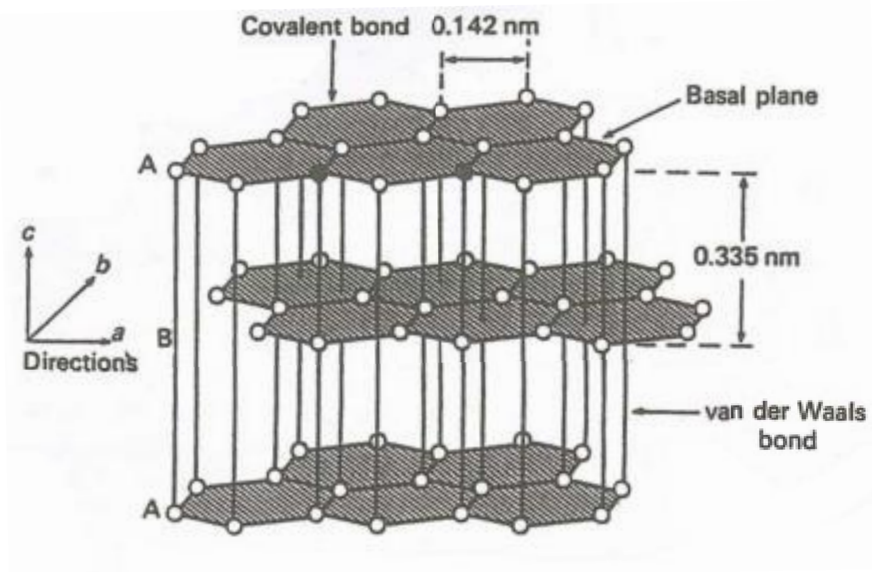
C_{60}



C_{70}

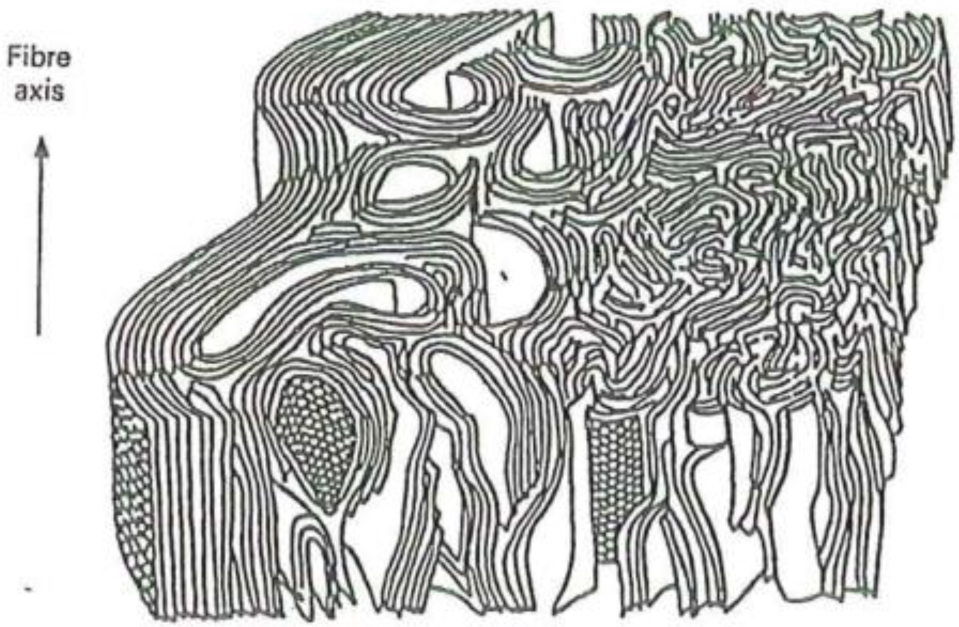
fullerenes

Carbon



- carbon fibers are based on the unusual properties of graphite, one of the allotropic forms of carbon
- basal planes with hexagonal C structures based in very strong C-C-bonds (≈ 525 kJ/m²)
- basal planes are linked by weak Van der Waals forces (< 10 kJ/m²)leading to ABAB… structure
- extreme anisotropy in stiffness (≈ 1000 GPa / ≈ 35 GPa)
- high thermal and electrical conductivity along the graphene sheets

Carbon



- main feature: orientation of the graphitic sheets along the fiber direction
- degree of alignment depends on the processing route
  - nature of precursor
  - heat treatment temperature
  - …
- graphitic ribbons are oriented more or less parallel to the fibers axis
- random interlinking of the layers

Carbon

- **Processing:** C fibers are processed by controlled pyrolysis (followed by graphitization) of an organic fiber precursor. There are always four mains steps:

  - Transformation of the original organic precursor into a small diameter fiber by extrusion or spinning of a polymer melt or solution.

  - *Stabilization* of the organic fiber precursor by means of heat treatment (200ºC-450ºC) in oxidizing atmosphere. This leads to the formation of lateral bonds between polymeric chains and renders the precuror fiber infusible during subsequent high temperature treatments.

  - *Carbonization* of stabilized fiber by means of pyrolysis (heat treatment at 1000ºC-2000ºC in N_2 atmosphere). Elements dif ferent from C are removed from the fiber and the C content reaches 85-95%.

  - *Graphitization* by means of a high treatment at very high temperature (2400ºC-3000ºC) in an inert atmosphere to generate graphitic structures oriented along the fiber axis.

- Main processing routes are based on P AN or Pitch precursors.

Carbon

Processing based on pitch: Pitches are low cost by products coming from petroleum cracking. Main sources are pitch are petroleum asphalt, coal tar and PVC. They are made up by a complex mixture of high molecular weight aromatic hydrocarbons.

- The first step is the spinning pitch filaments from a mesophase pitch with a nematic (liquid crystalline) structure. Centrifugal and jet spinning are often used to obtain a better alignment of the crystalline domains. Final steps include stabilization, carbonization and graphitization, as usual.

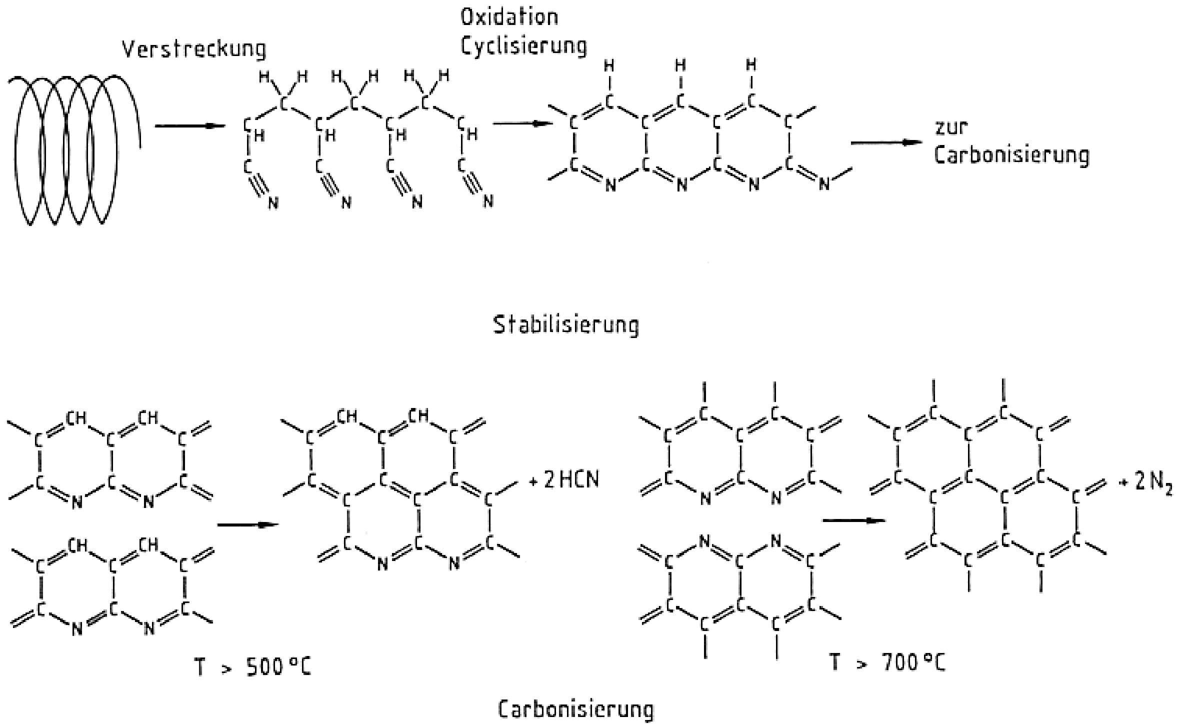
- Pitch is a cheap source of precursors but the variations in the composition may lead to variability of the final properties.

Sizing: Commercial C fibers have a *size*, protective surface coating to provide ease of handling (rubbing of fibers can lead to defect formation) and to improve adhesion with polymeric matrices.

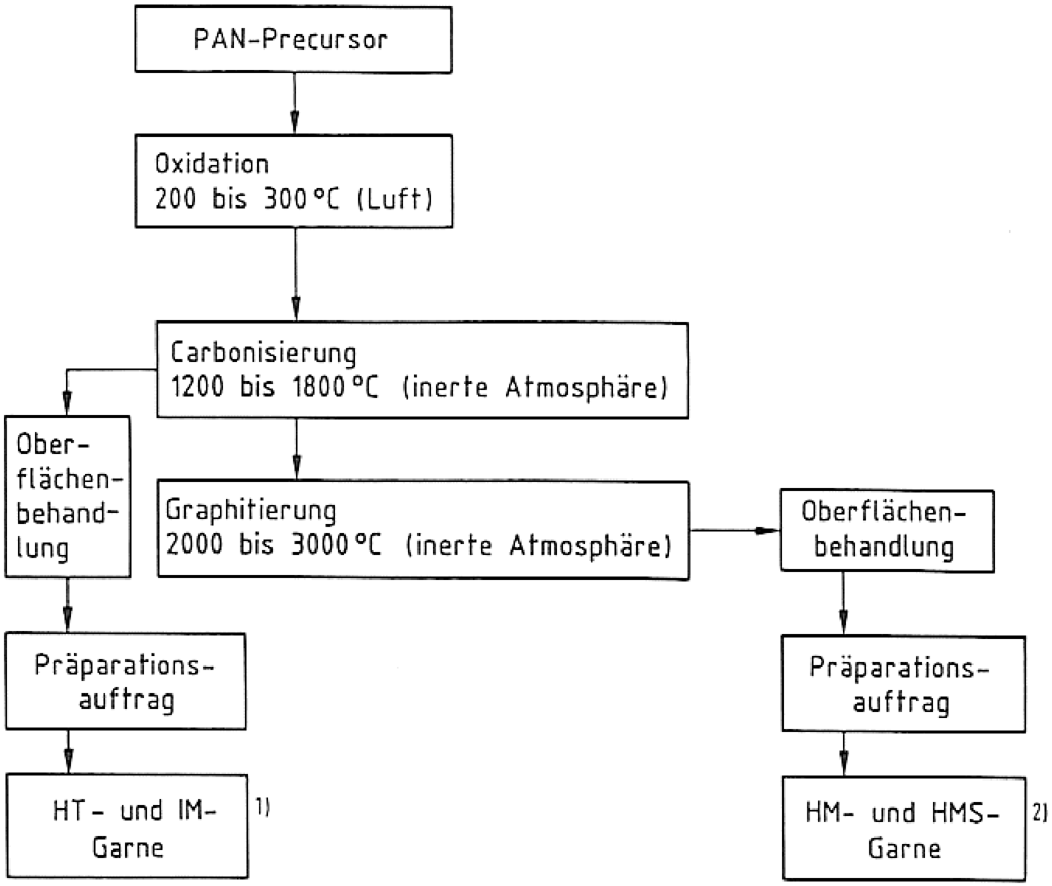
- Low-molecular weight epoxy resins are commonly used for sizing.

- Oxidative treatments are also given to increase roughness and improve adhesion

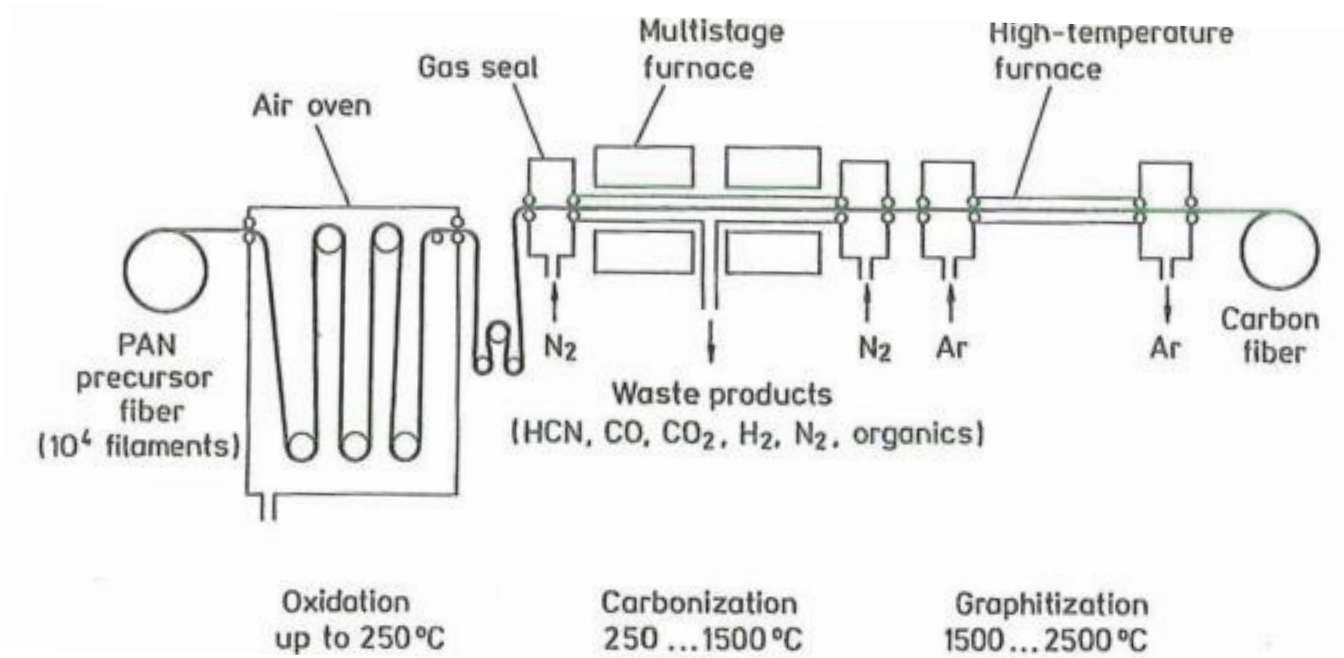
Graphitisation of PAN



C-fibers from PAN precursor



Processing based on PAN



C- fibers properties

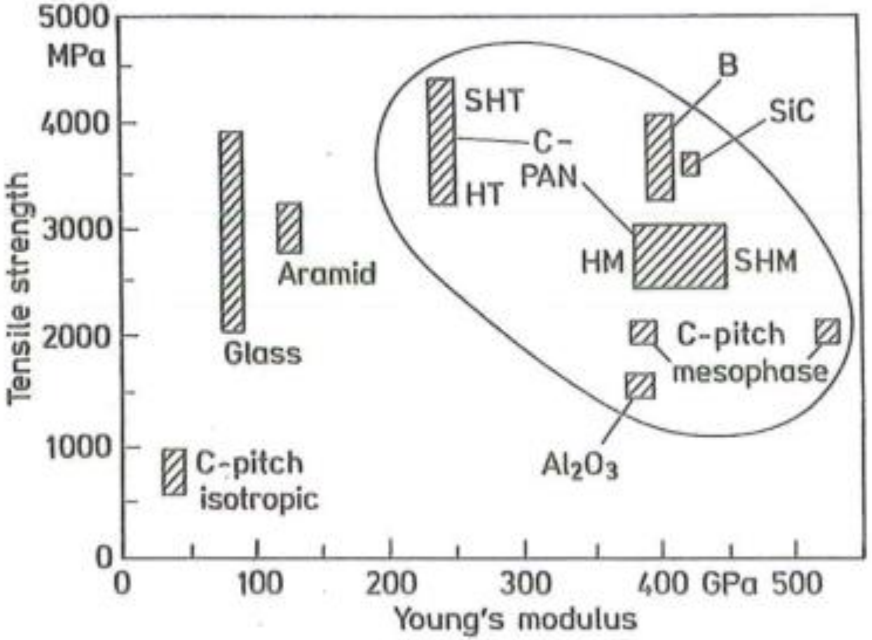
- C fibers are very anisotropic due to their graphitic structure. They are very strong and stiff in the fiber direction, and the properties depend on the amount of graphite and the orientation of the basal planes along the fibers. This leads to a variety of fibers

- Strength of C fibers is controlled by the presence of defects (inclusions, void).

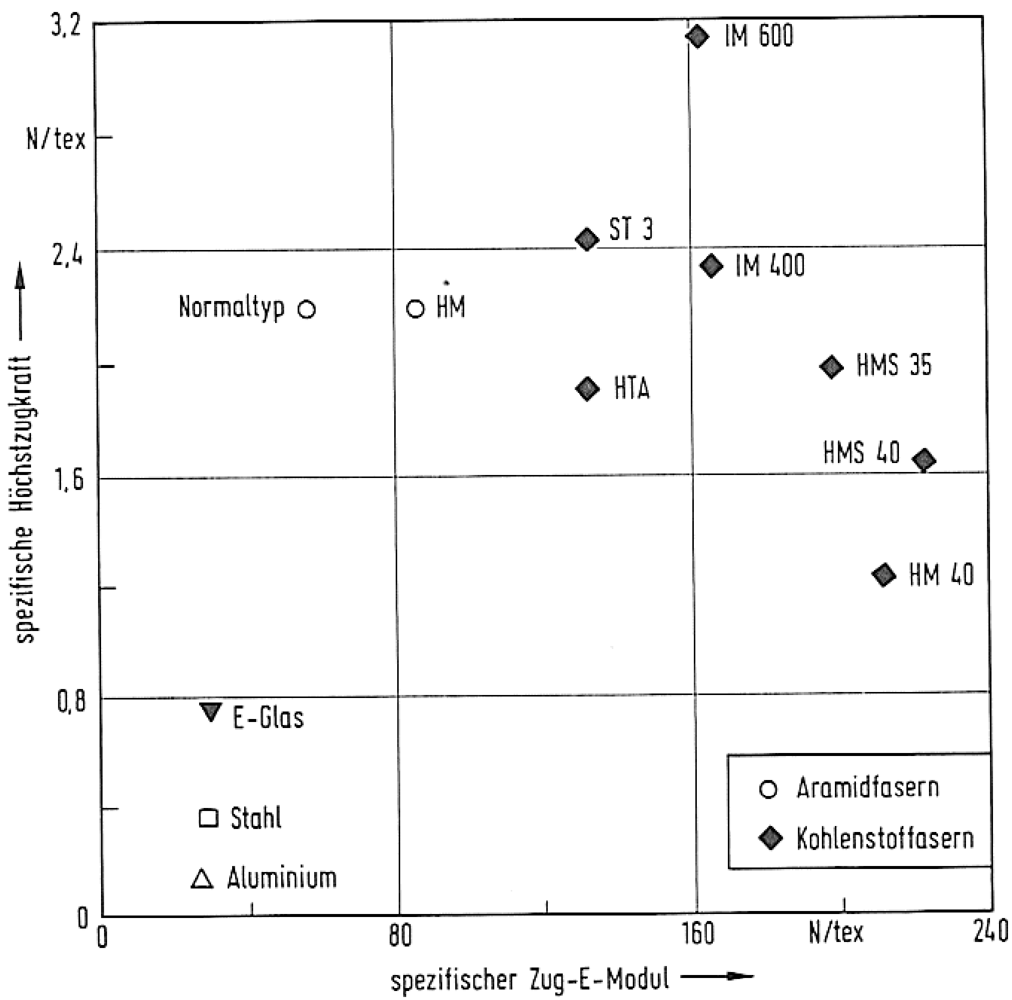
- C fibers have good thermal and electrical conductivity and negative CTE in the fiber direction.

- High Modulus fibers are more sensitive to defects and have lower strength. They present higher conductivity along the fiber and lower (more negative) CTE.

- Transverse properties of C fibers are very different: E≈20-40 GPa, CTE = 10^{-5}°C^{-1}.



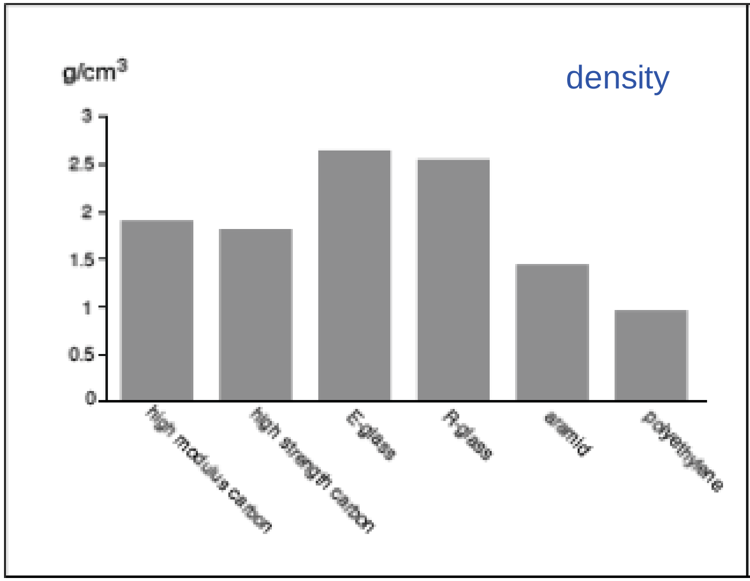
C-fibres properties

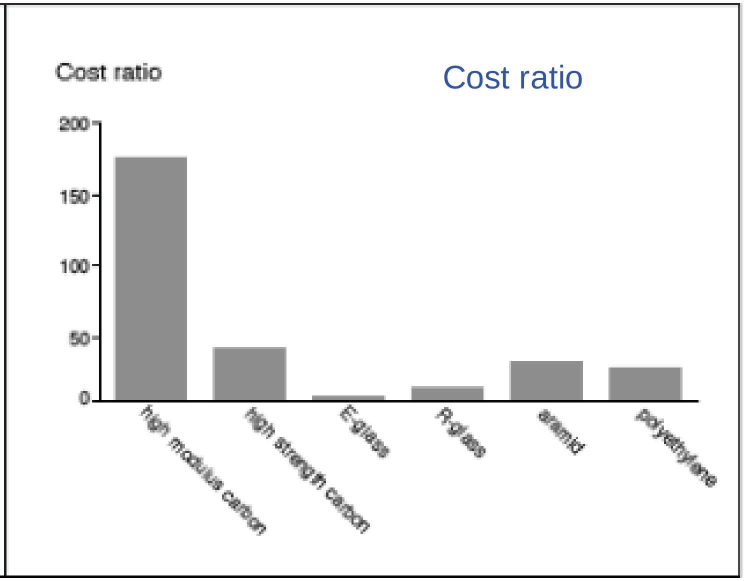


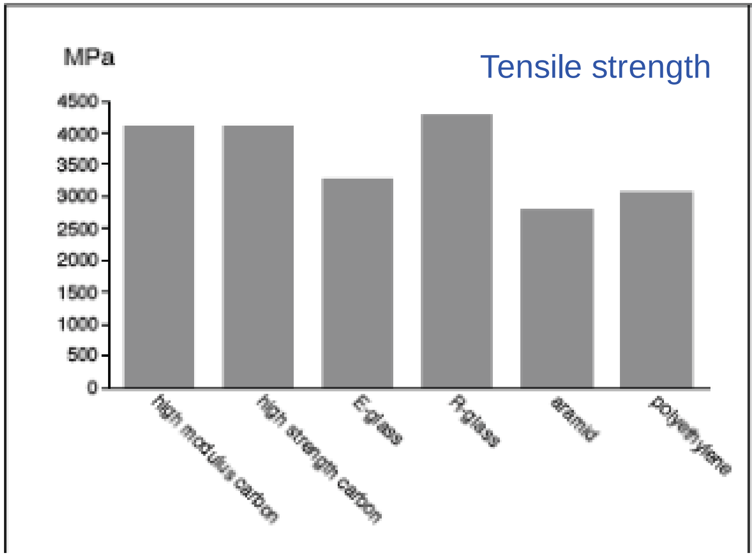
Summary of fiber properties

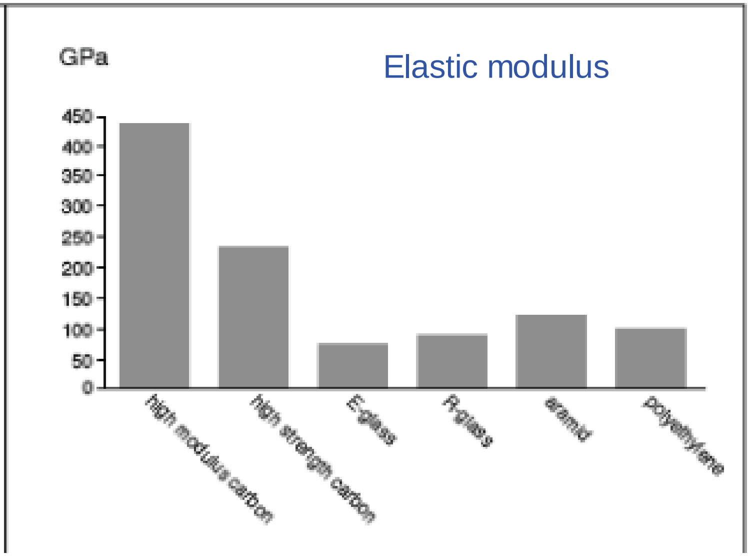
Fiber	Diameter (μm)	Density (g/cm^3)	Strength (GPa)	Failure Strain (%)	Elastic Mod. (GPa)	CTE ($10^{-6}K^{-1}$)	Melt. Temp. (K)	Thermal Cond. (W/m K)
Aramid (Kevlar 49)	12	1.45	2.8	2.8	125	-5.0	700	0.04
Polyethylene	38	0.97	2.6	3.5	120		400	
Spider Silk (dragline)	2-5	1.3	0.8-1.5	20-40	5-8		400	
Carbon PAN (HS)	7-8	1.80	5.0	2.0	230	-0.7	3950	8
Carbon PAN (HM)	7-10	1.86	2.7	0.7	390	-0.5	3950	70
Carbon Pitch	10	2.00	2.0	0.4	380	-0.9	3950	100
Glass (E)	8-15	2.6	3.4	2.6	76	4.9	1000	13
SiC (CVD)	100-150	3.0	3.5	0.9	400	4.0	3000	10
SiC (polymer)	10-20	2.6	2.2	1.0	200	6.5	2313	10
Al_2O_3	10	3.3	2.0	0.7	300	7.0	2288	5
Be	130	1.85	1.3	0.5	300	11.6	1550	150
W	25-250	19.3	3.8	1.1	360	4.5	3673	168
0.9% Carbon steel	100	7.8	4.3	2.5	210	11.8	1573	29
Stainless steel	50-250	8.0	0.7-1.0	0.5	200	18.0	1573	29
Mo	25-125	10.2	2.5	0.9	310	6.0	2873	145

Comparison of fiber properties



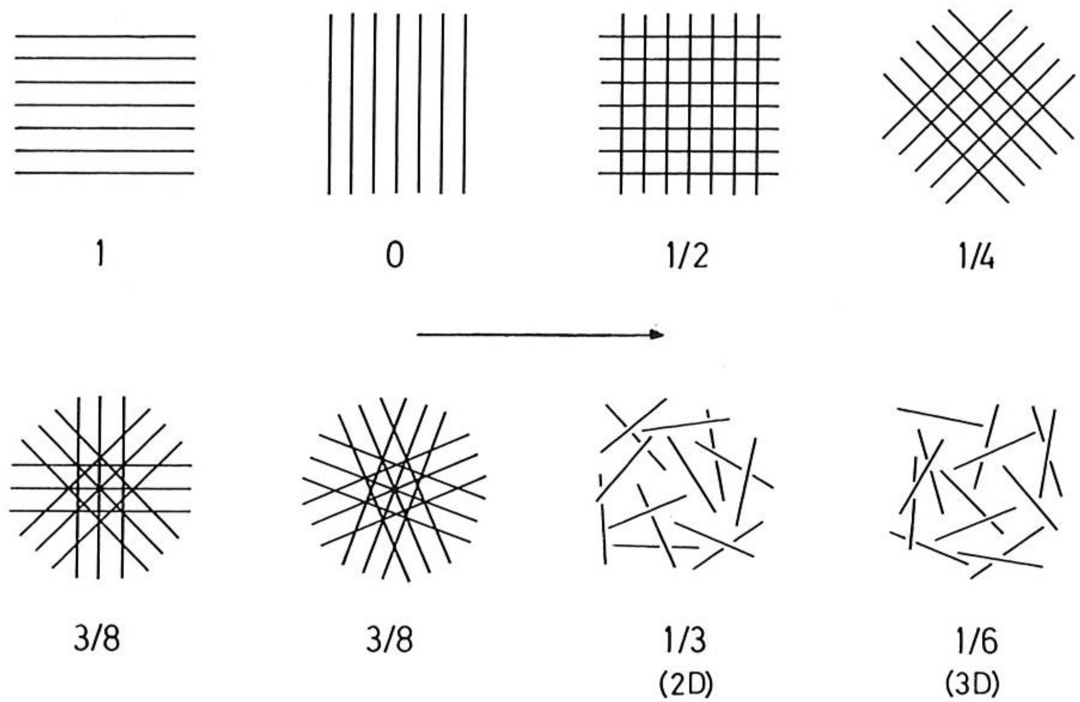






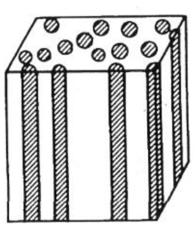
Orientation factors of long fibres

orientation factors of long fibres for different orientation modes



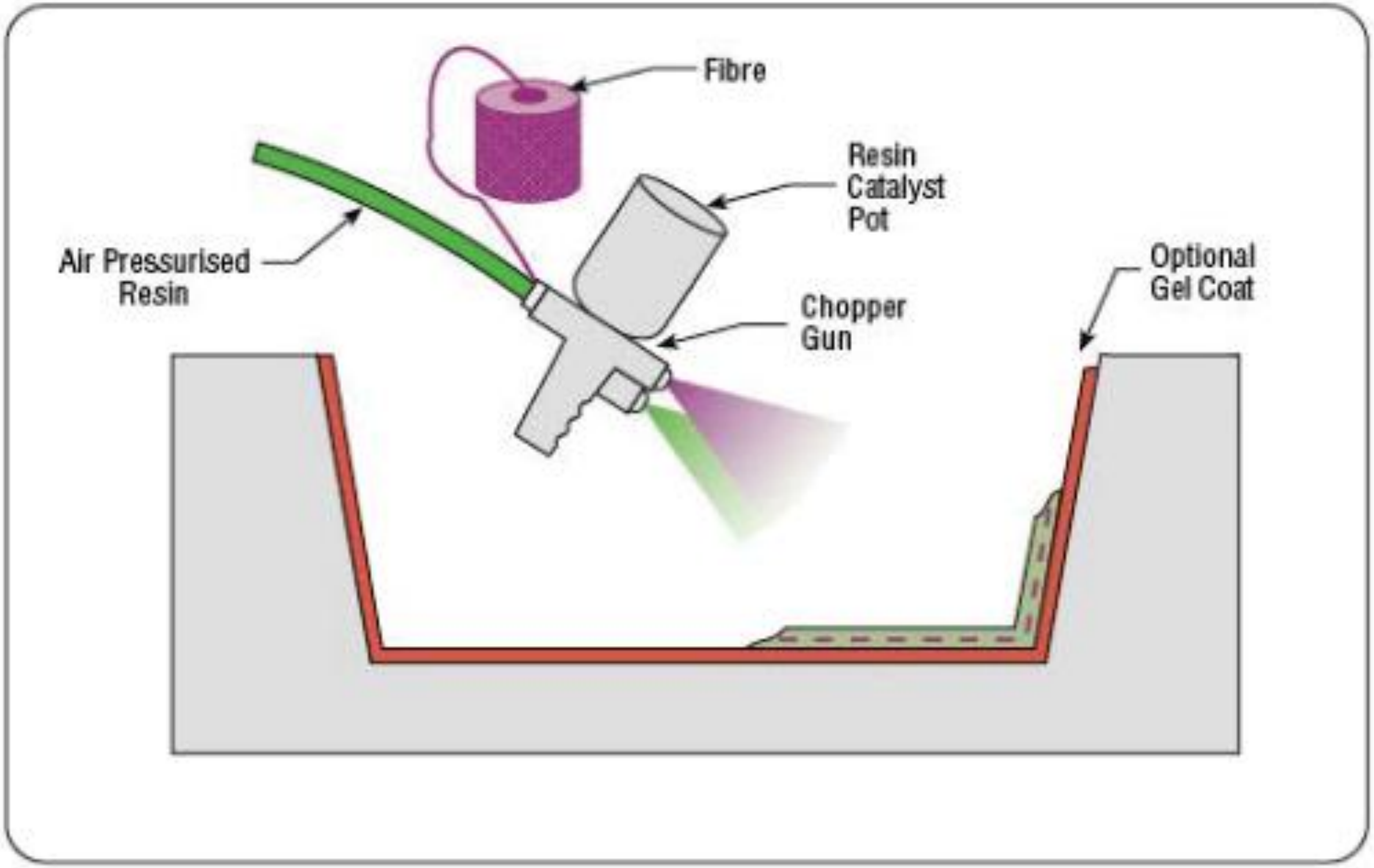
random
2-dimensional

random
3-dimensional



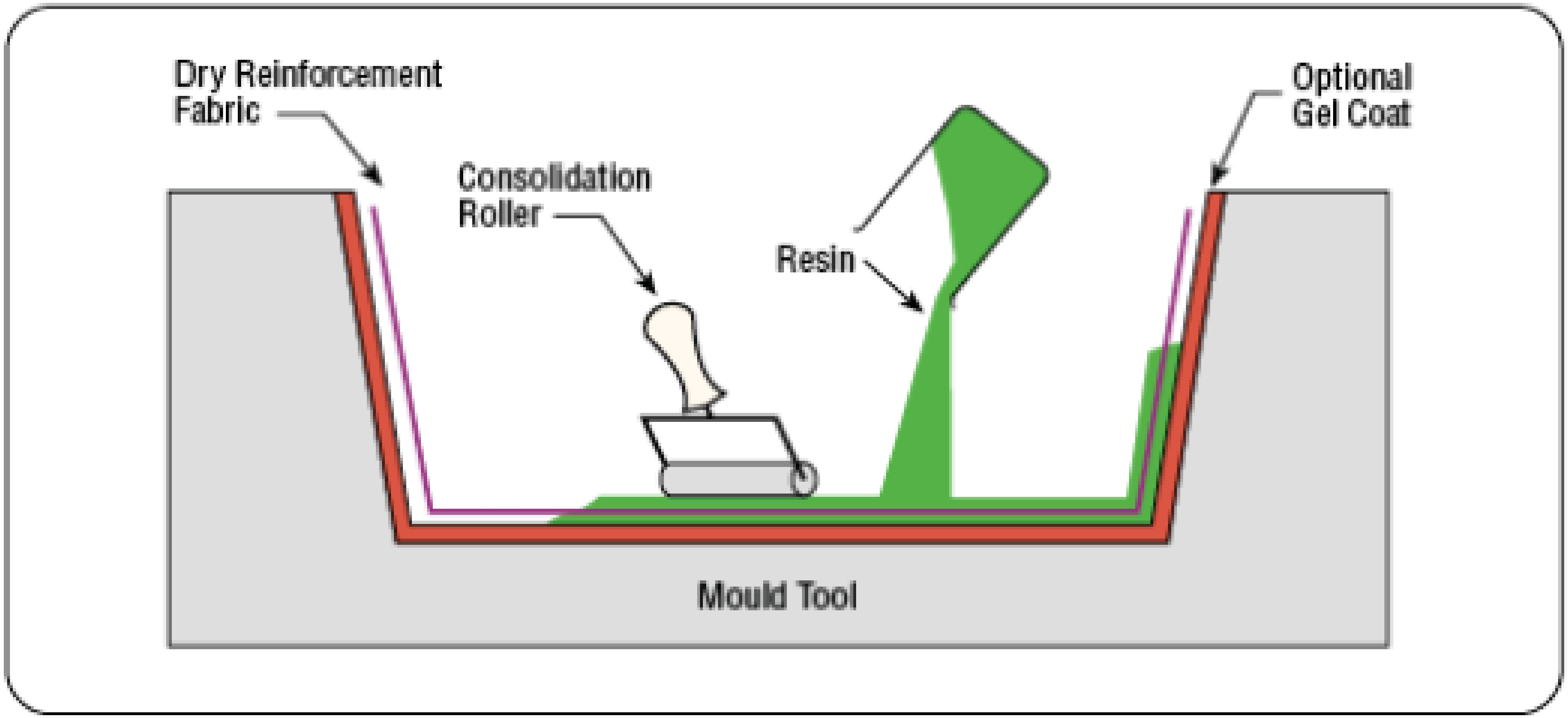
Prepreg = fiber matts impregnated with uncured resin

Spray Lay-up

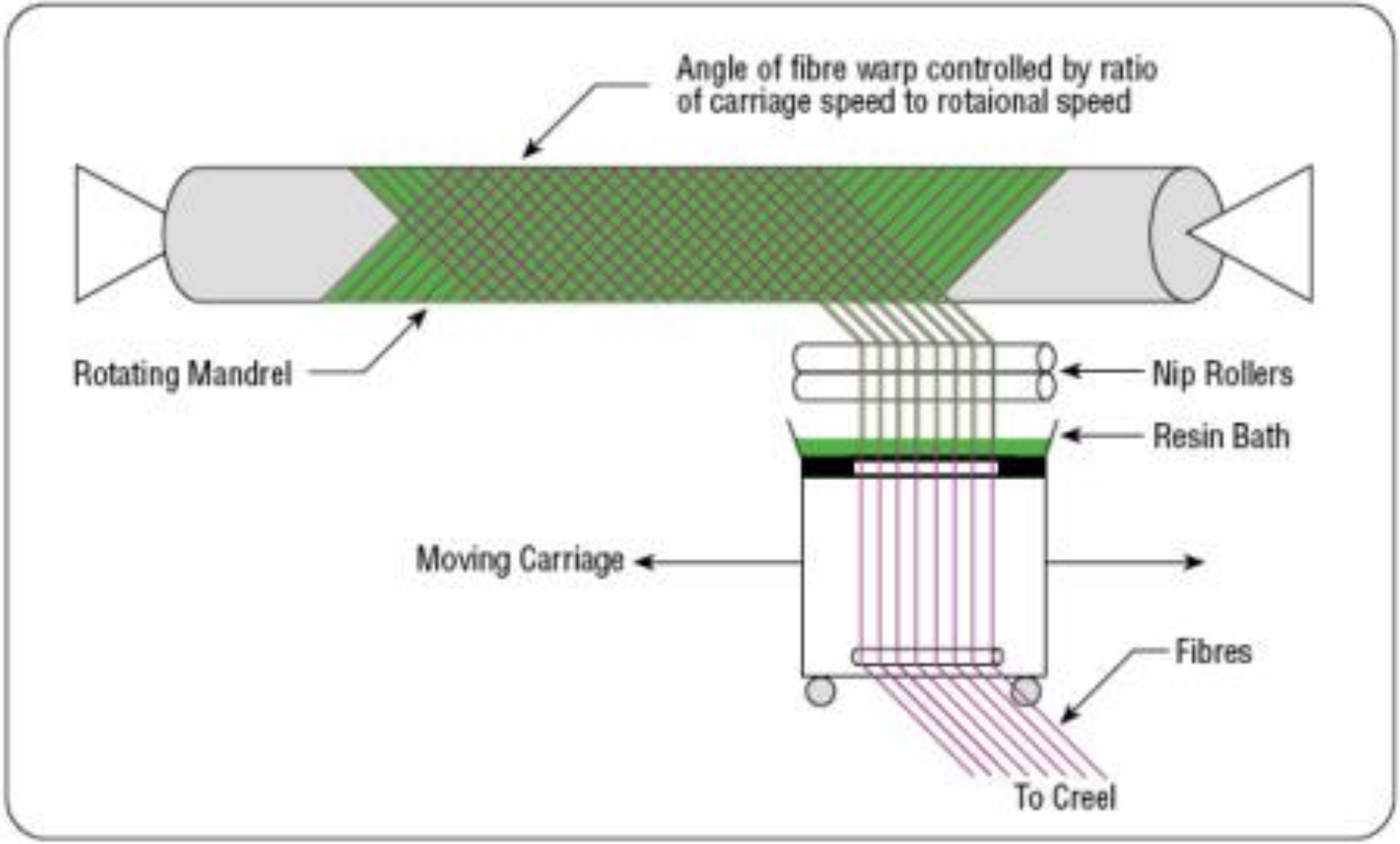


Fibre
Resin
Catalyst
Pot
Air Pressurised
Resin
Chopper
Gun
Optional
Gel Coat

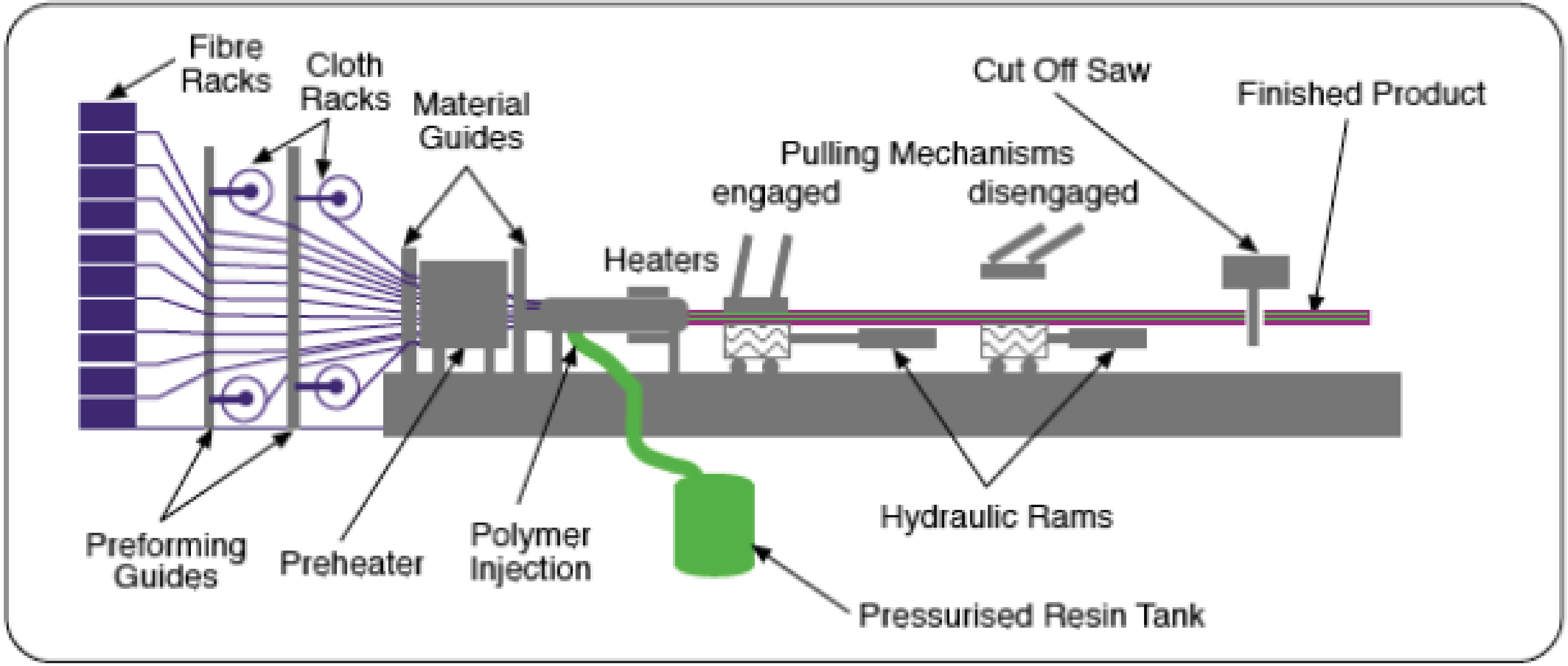
Wet Lay-up / Hand Lay-up



Filament Winding

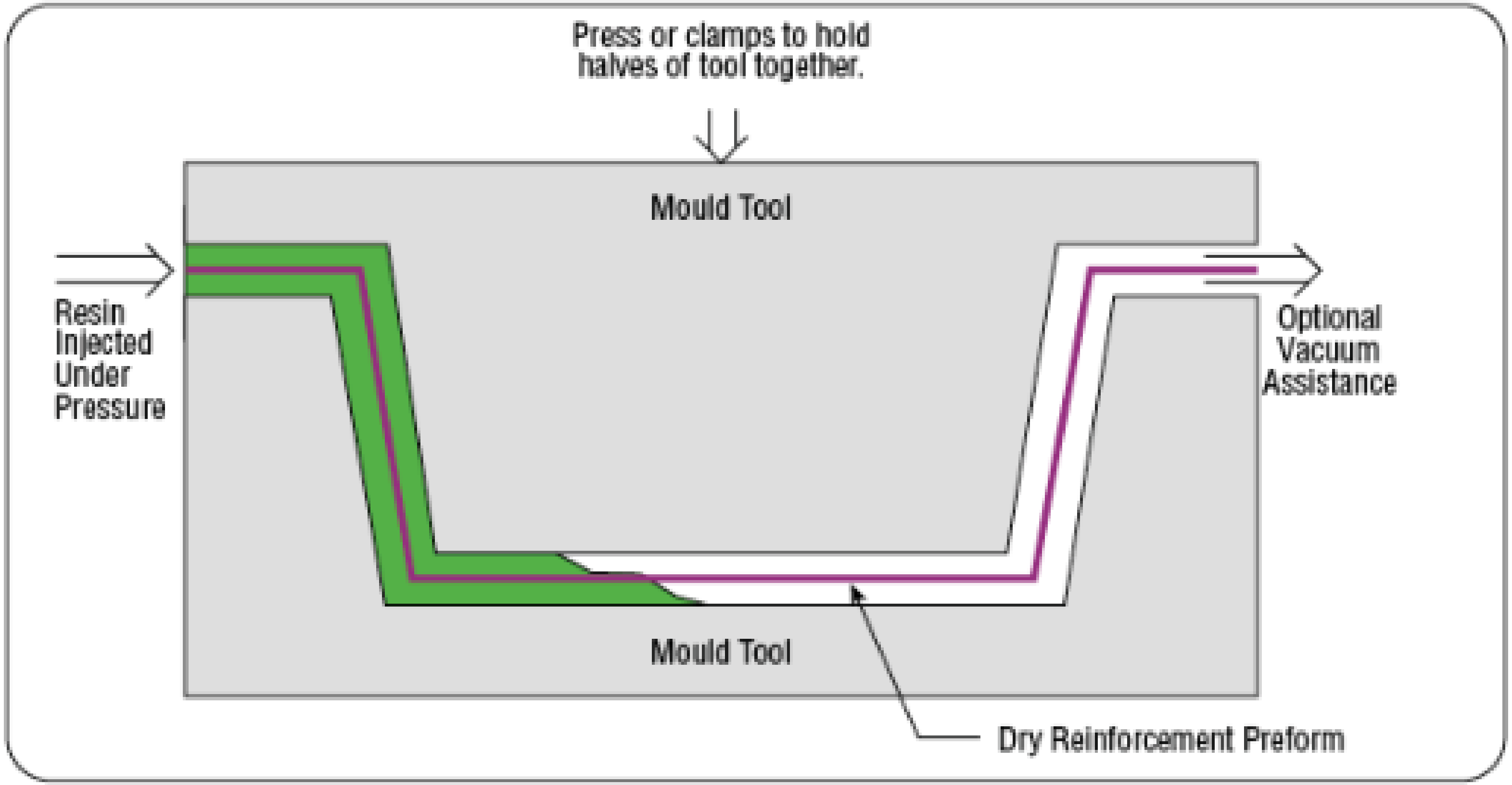


Pultrusion

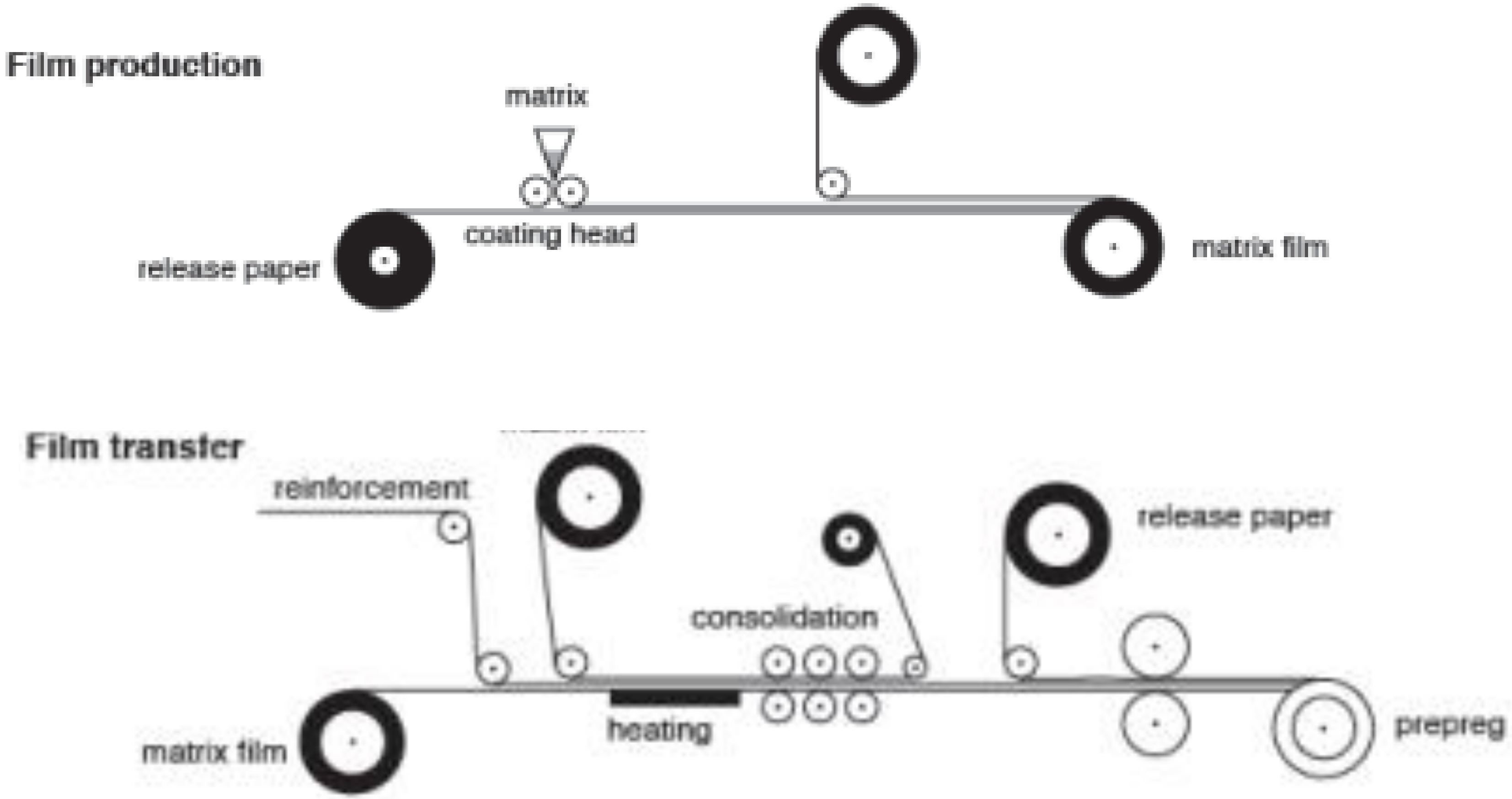


Fibre Racks
Cloth Racks
Material Guides
Pulling Mechanisms
engaged
disengaged
Cut Off Saw
Finished Product
Heaters
Preforming Guides
Preheater
Polymer Injection
Hydraulic Rams
Pressurised Resin Tank

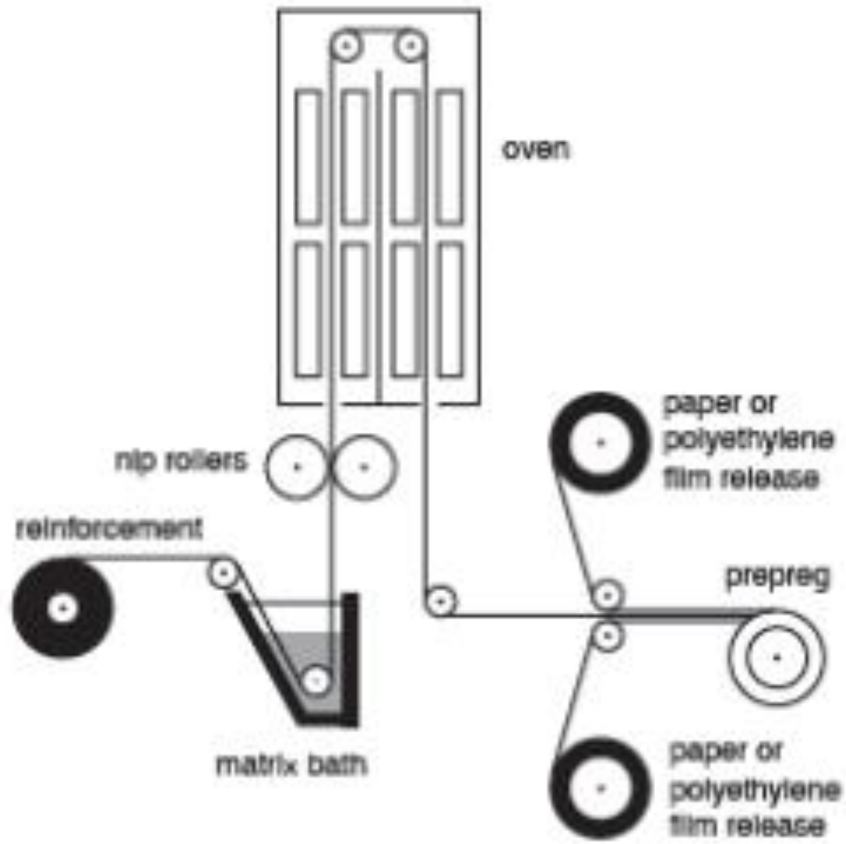
Resin Transfer Moulding



Manufacturing of Prepregs: Film Route



Manufacturing of Prepregs: Liquid Route

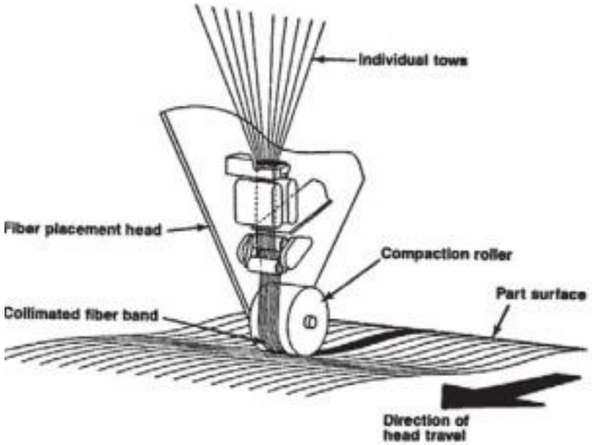


Prepreg Morphology

- Thickness: 80 - 250 µm
- Resin content: 25-45 %
- Width: up to 1500 mm

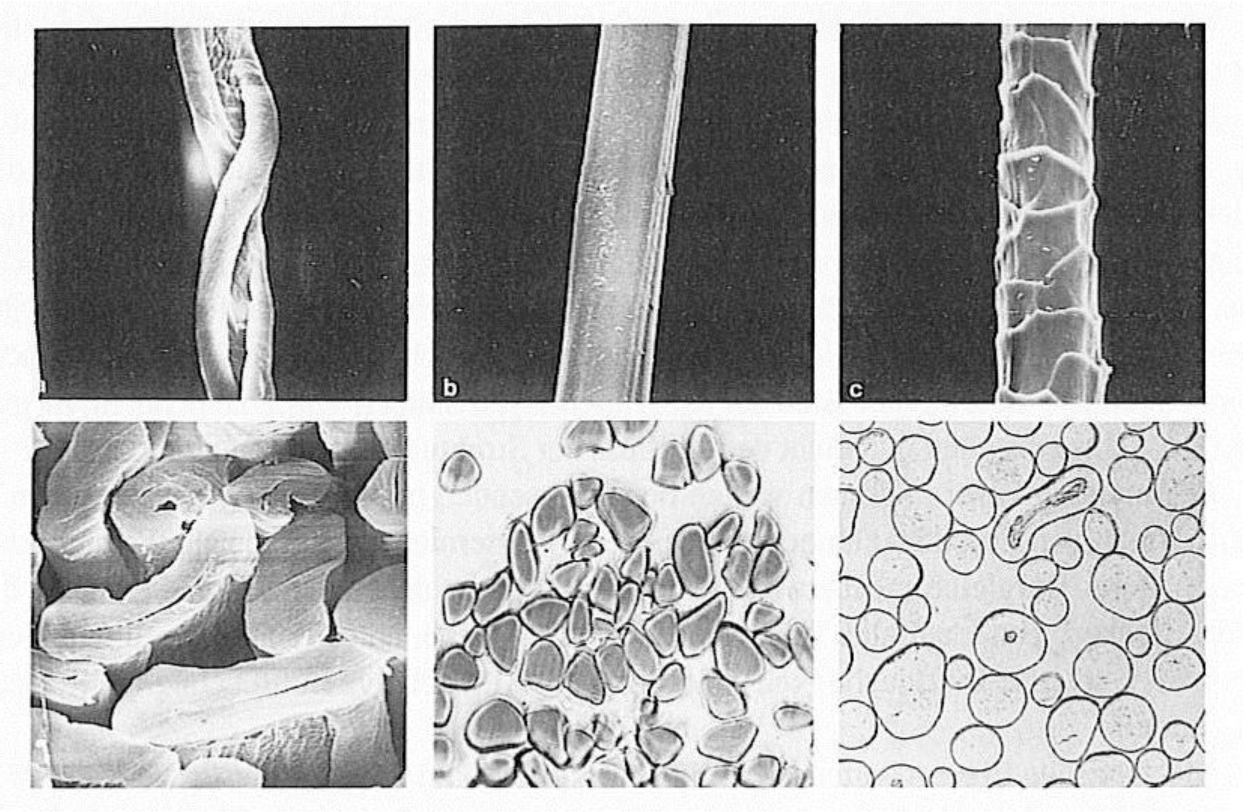
Lamination

- Advanced fiber placement robot (AFP)



Natural fibers

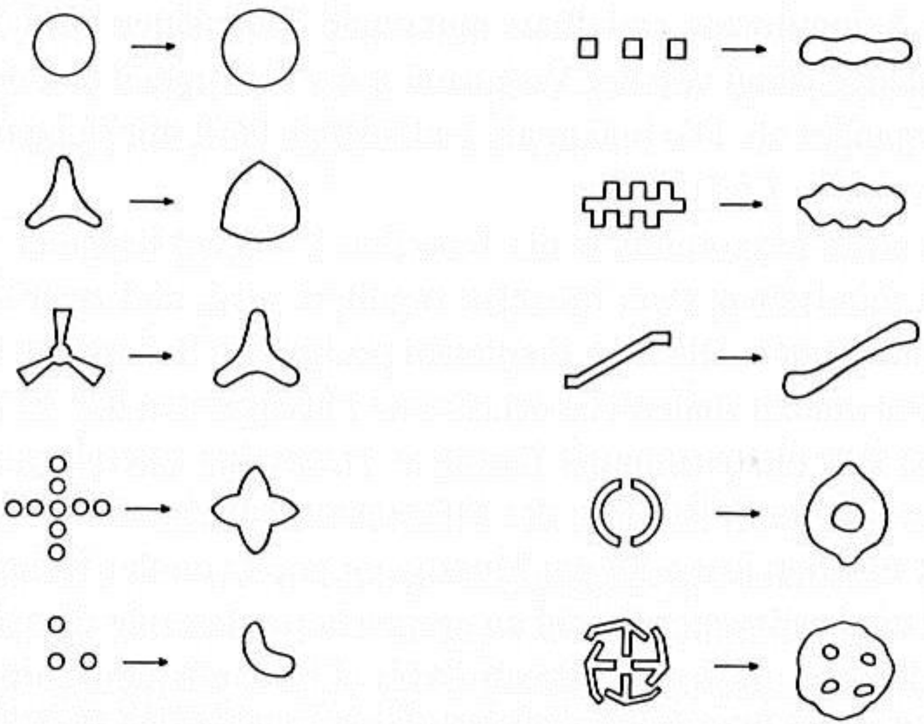
cotton | silk | lamb‘s wool



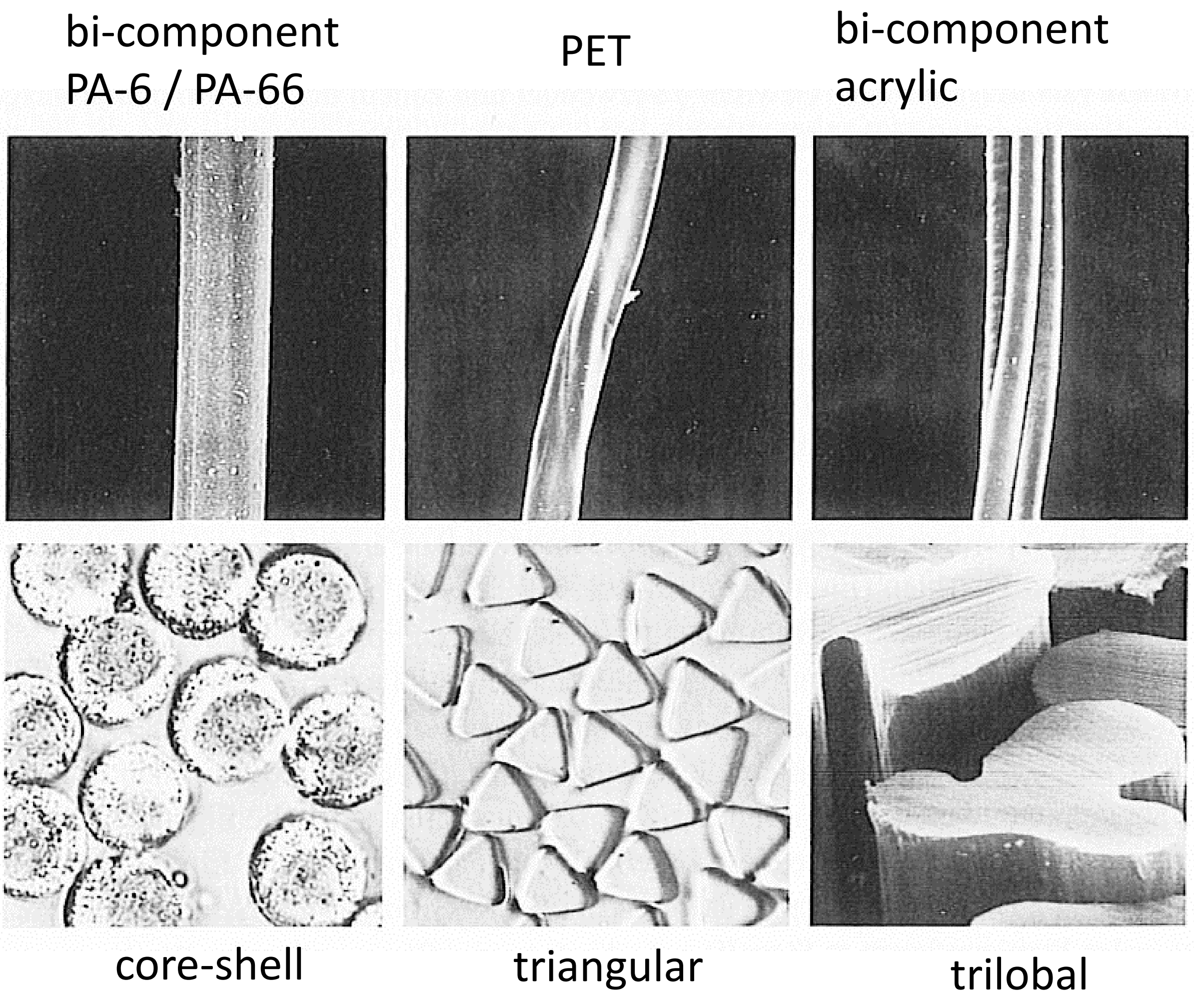
hollow | triangle | scabby

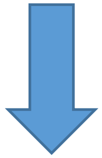
IAM-FHG

Nozzles and resulting fiber cross sections



Synthetic fibers





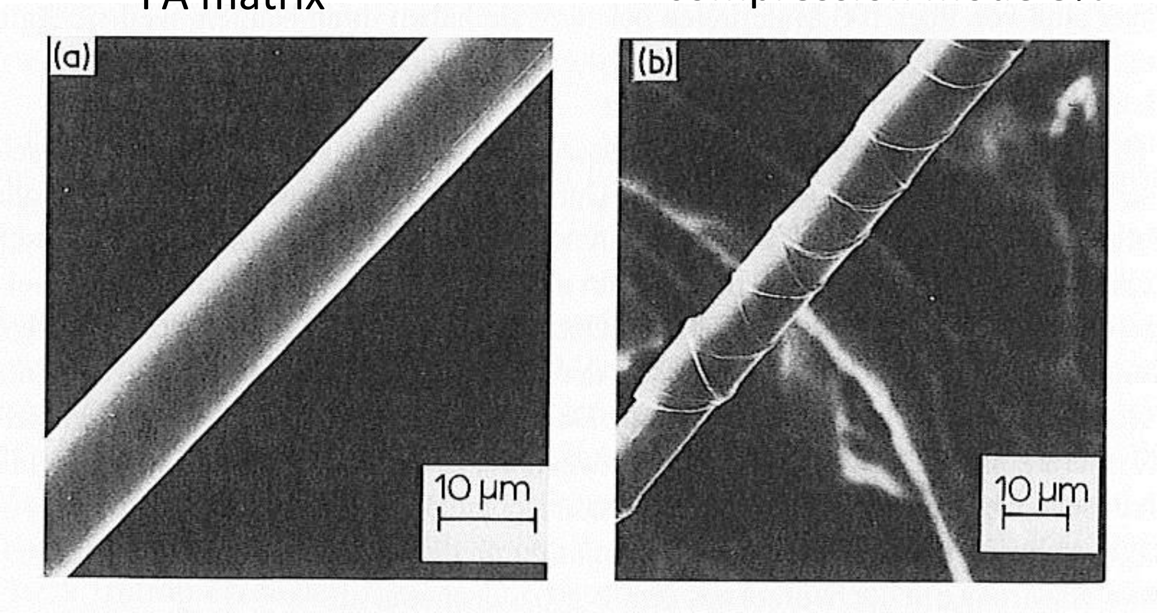
dependence on the nozzle geometry and the cooling process

IAM-FHG

Kevlar fibers with core shell structures from spinning

Kevlar fiber in PA matrix

deformation zones in compression mode 3%

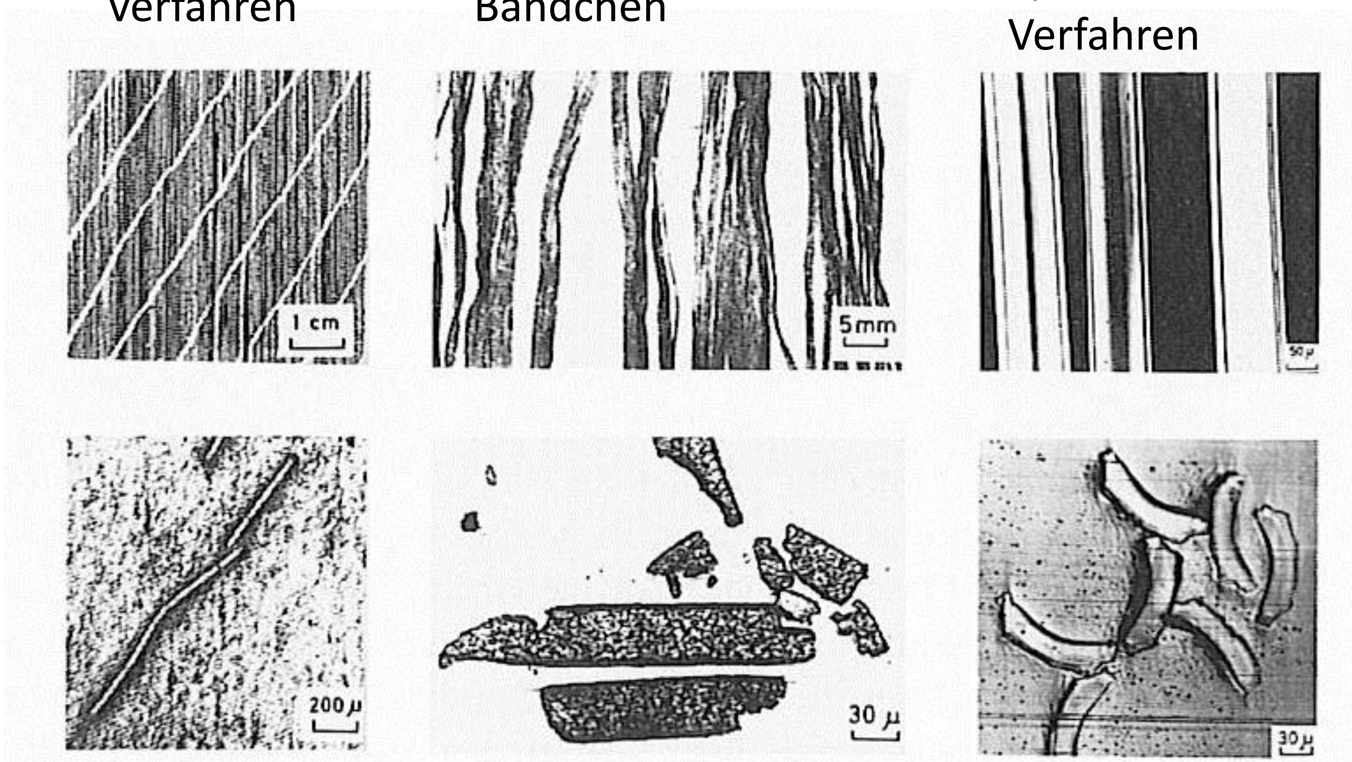


Different fiber types based on i-PP

Nadelwalz-verfahren

Zwirnen von PP-Bändchen

Lenzinger Spaltfaser-Verfahren

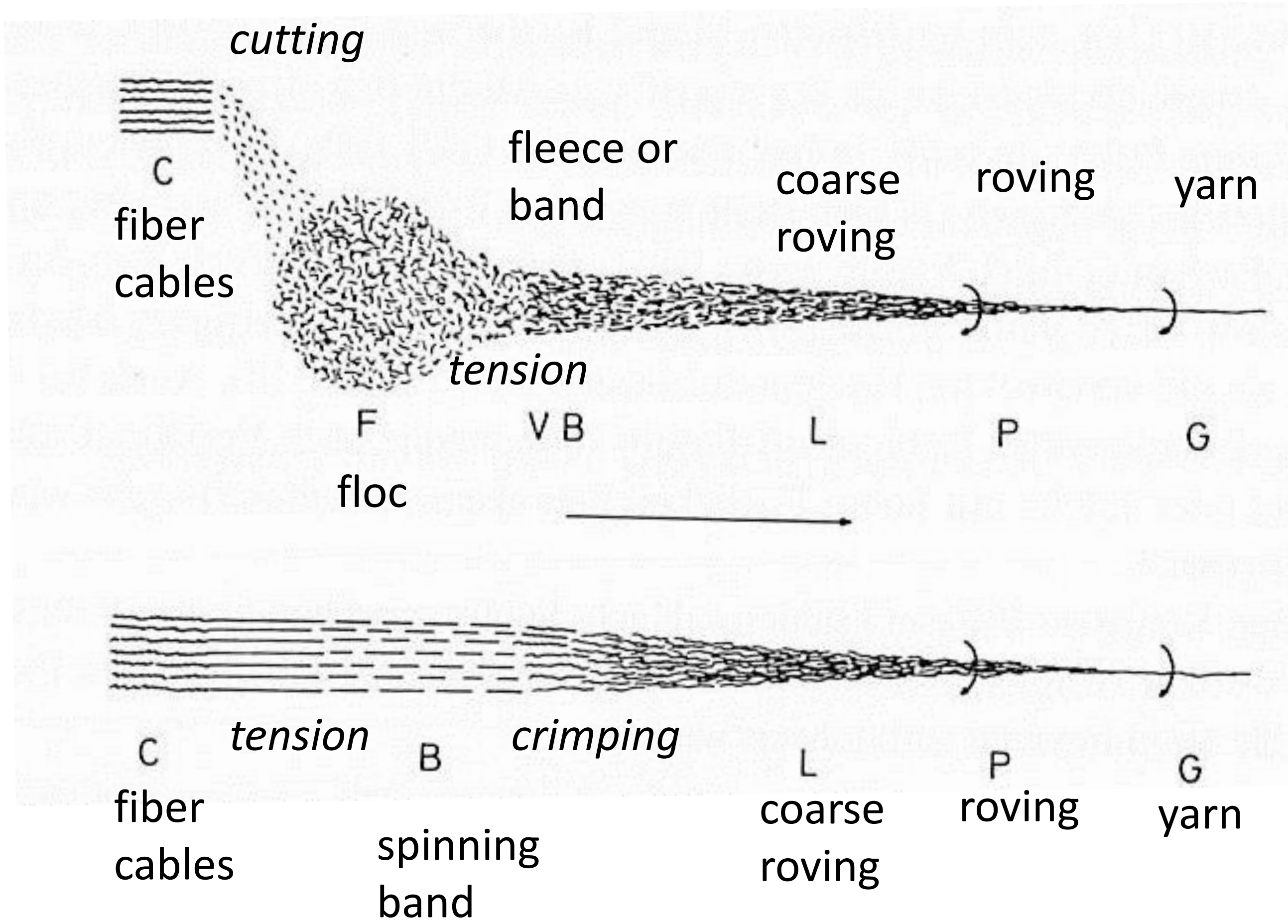


Spaltfasern

Splitfasern

Spaltfasern

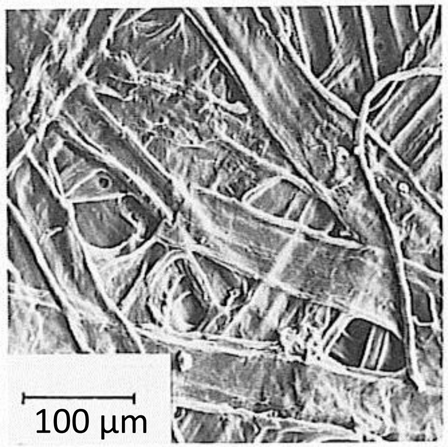
Spinning protocols for synthetic fibers



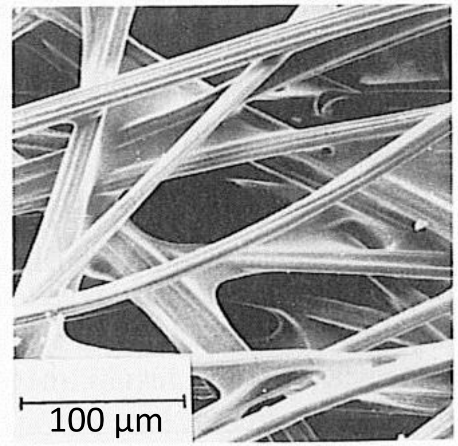
W. Albrecht

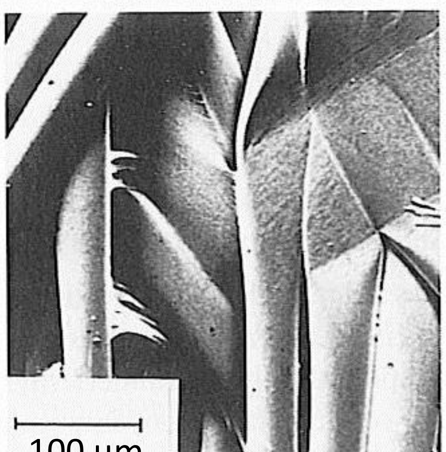
Paper and textile composites

paper from pine

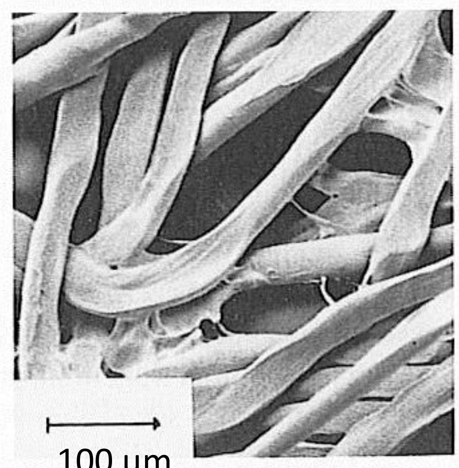


latex-bonded non-woven fabric from rayon fiber





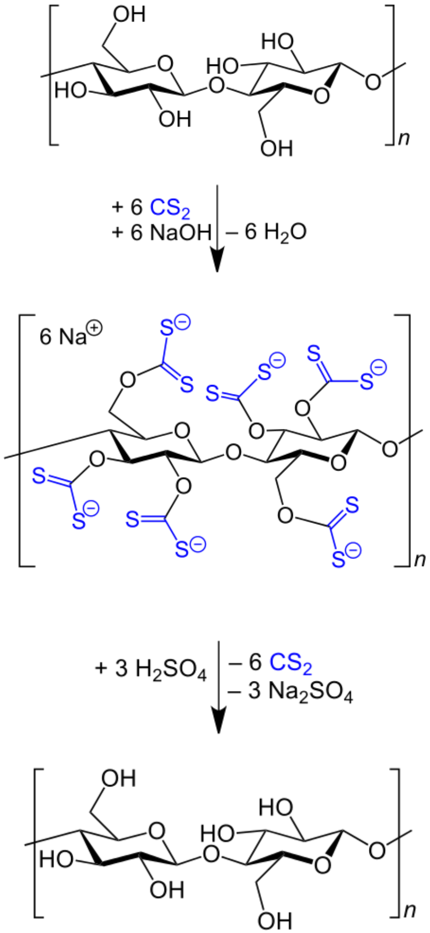
spunbonded PE



thermoplastic bonded PP fibers

E. Treiber

Rayon (= Viscose)



cellulose

cellulose - xanthogenate

wet-spinning process

- through nozzle: „rayon“ fiber
- through slit: „cellophan“ foil

fabric

Commingled Yarns