

Composite Technology MSE 440

Constituents

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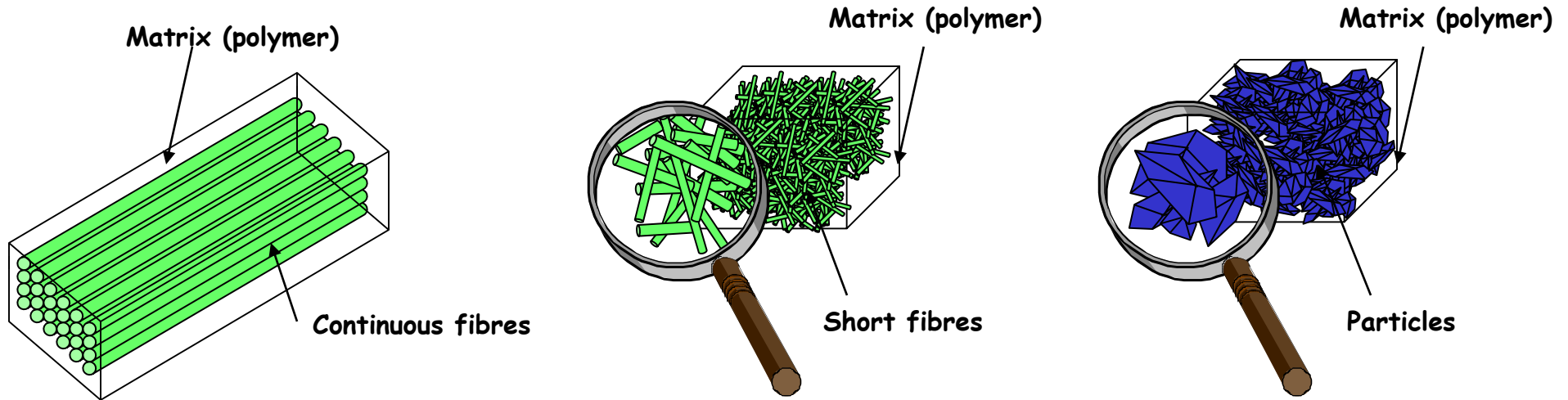
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and guest speakers

Institut des matériaux (IMX)
Ecole Polytechnique Fédérale de Lausanne (EPFL),
CH-1015 Lausanne

Composite materials



- Oriented fibres
- Unidirectional composites (UD)

• Thermoset, thermoplastic

- High mechanical performance
- Anisotropy

• Aerospace, sport, pressure vessels...

- Random distribution of
- Short fibres (< 3mm)

• Mainly thermoplastic matrices

- Isotropy
- Injection moulding

• Mechanics, microtechnology, automotive...

• Particles (1-400 μ m), silica, clay...

• Thermoset and thermoplastic

- Improvement of properties, hardness, dim. stability
- Reduction of price

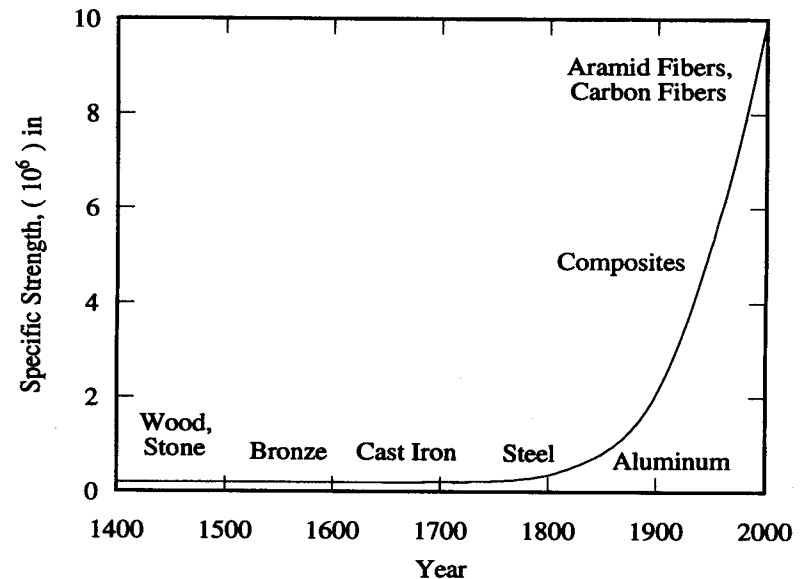
• Injection moulding, casting...

• Mechanics, microtechnology, dentistry....

Why Use Composites?

- **Advanced** design requirements
 - eg, CTE ~ 0 , reduced weight allowances with the same requirements on stiffness and strength
- Improved *specific* stiffness, *specific* strength, fatigue resistance, impact resistance

- Corrosion/environmental resistance
- **Tailorable** mechanical and physical properties
- **Integrated manufacturing** - can manufacture large parts with fewer (or one!) pieces



Specific strength as a function of time
(from Kaw, 1997)

The beauty of fibers...

1- Size effect: for brittle materials, probability of defect is reduced when volume is reduced

2- Flexibility:

Bending stiffness: $B=EI= E\pi d^4/64$

3- Shape factor L/d large \rightarrow anisotropy, even in the fiber itself

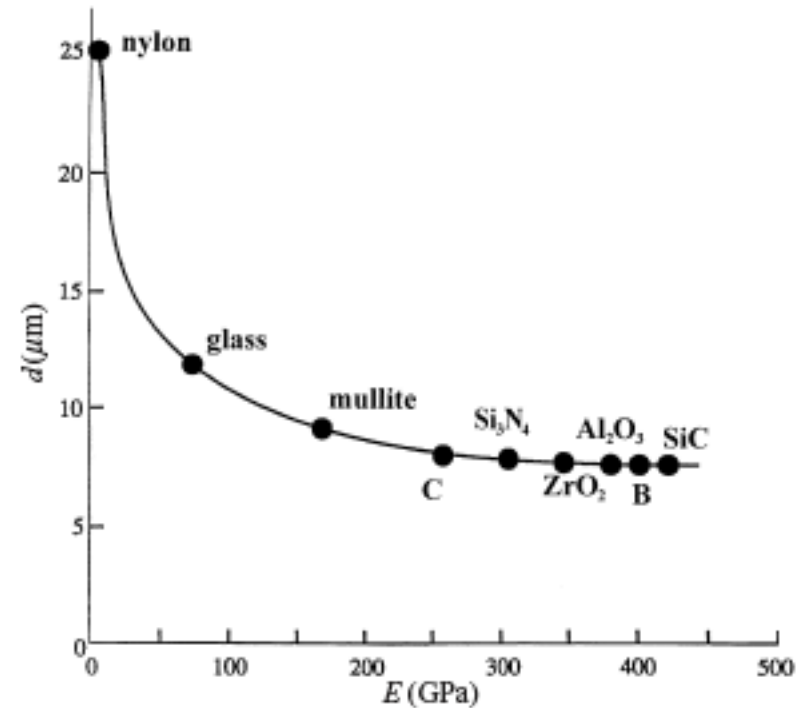


Figure 1

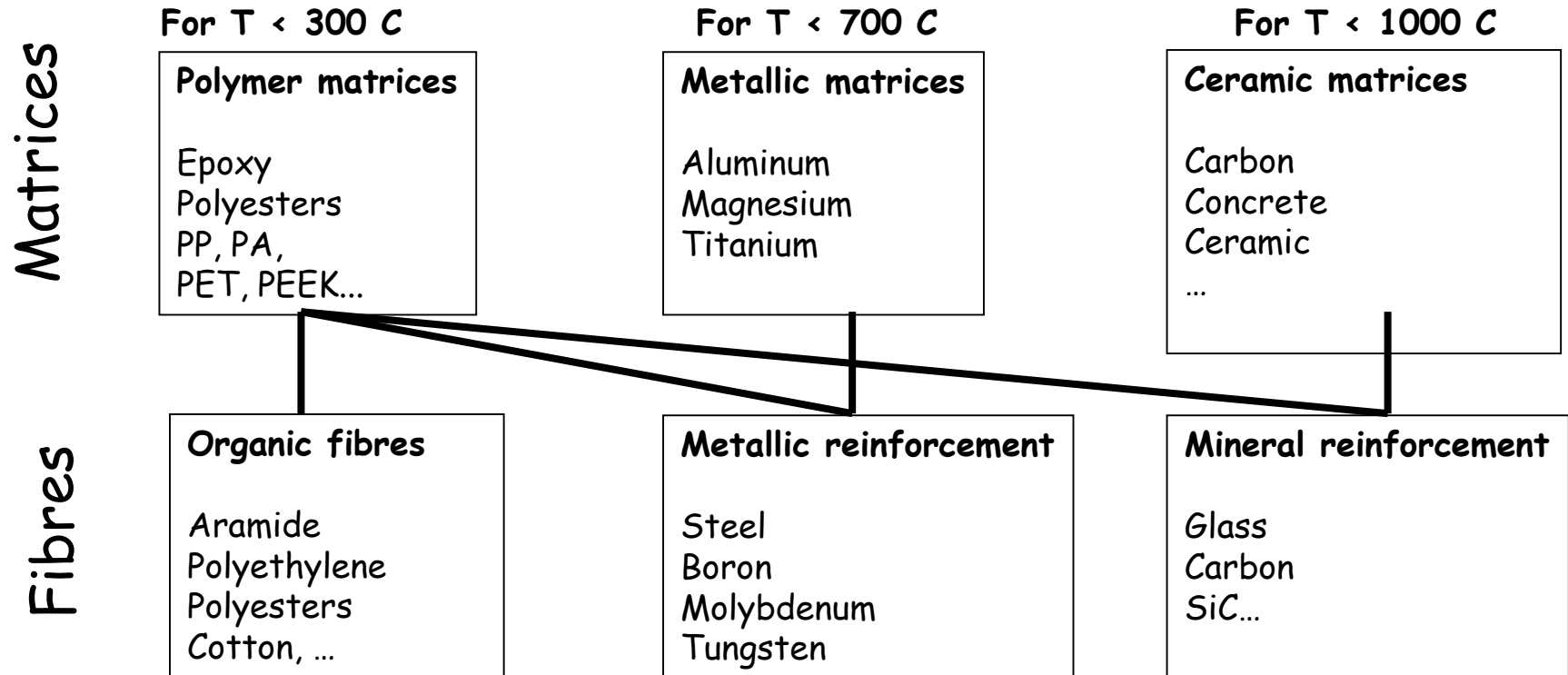
Diameter of various fibers with a flexibility equal to that of a 25 μm diameter nylon fiber. Given a sufficiently small diameter, it is possible to produce, in principle, an equally flexible fiber from a polymer, a metal, or a ceramic.

Disadvantages of Composites

- Increased capabilities in some areas (strength, stiffness) may result in degraded performance in other areas (in-service temperatures, moisture, etc)
- High cost for fabrication (\$650-\$900/kg, finished)
 - Note: this is not always true!
- Increased difficulty in materials characterization, design and analysis
 - Lack of general expertise in composites
- Repair of in-service parts is neither simple or cheap
- Recycling or reuse of parts is uncommon and expensive

NONE

Matrices and reinforcements



Fibres

Fibres	Advantages	Limits
Glass	<ul style="list-style-type: none"> +++ cost ++ ratio mecha. performance / cost ++ specific strength ++ dielectric properties ++ high temperature resistance ++ low thermal conductivity and dilatation 	<ul style="list-style-type: none"> --- ageing in presence of water --- resistance to acid and bases -- density -- modulus
Carbon	<ul style="list-style-type: none"> ++++ mechanical properties +++ chemical inertia ++ density ++ high temperature resistance ++ low thermal expansion coefficient ++ good thermal conductivity 	<ul style="list-style-type: none"> --- impact resistance -- wear resistance -- galvanic corrosion when in contact with metals - high cost
Aramid (Kevlar®)	<ul style="list-style-type: none"> ++++ impact resistance ++ tension strength ++ low density ++ low thermal dilatation ++ resistance to fatigue and wear ++ chemical resistance 	<ul style="list-style-type: none"> --- cost --- machining -- compression strength -- water uptake -- adhesion to matrices - degradation at 400°C
Polyethylene (Dyneema®)	<ul style="list-style-type: none"> ++++ impact resistance +++ low density +++ chemical resistance ++ tension strength 	<ul style="list-style-type: none"> ----- melting temperature at 150° ---- adhesion to matrices - machining

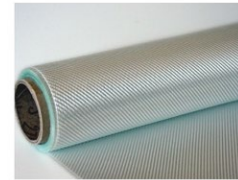
Fibre cost?

Swiss-Composite.ch/ Global tools, : on line stores
In CHF/kg, bobbins

Glass : 5-15
Kevlar: ~100
Carbon (HTS): 1k : 800
3k : 274
6k : 147
12k : 100
24k : 122
60k : 80
Basalt: 10-15

In CHF/m², fabrics

3-10 for 100 à 200g/m²
~ 30
30 to 100



des fibres de verre



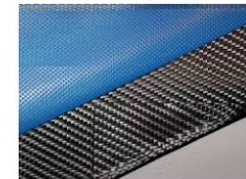
des fibres de carbone



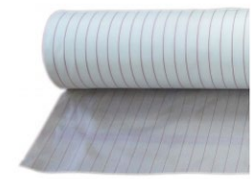
aramides



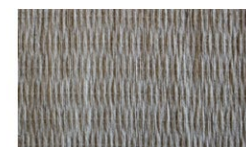
fibre mixte / hybride



Préimprégné de carbone



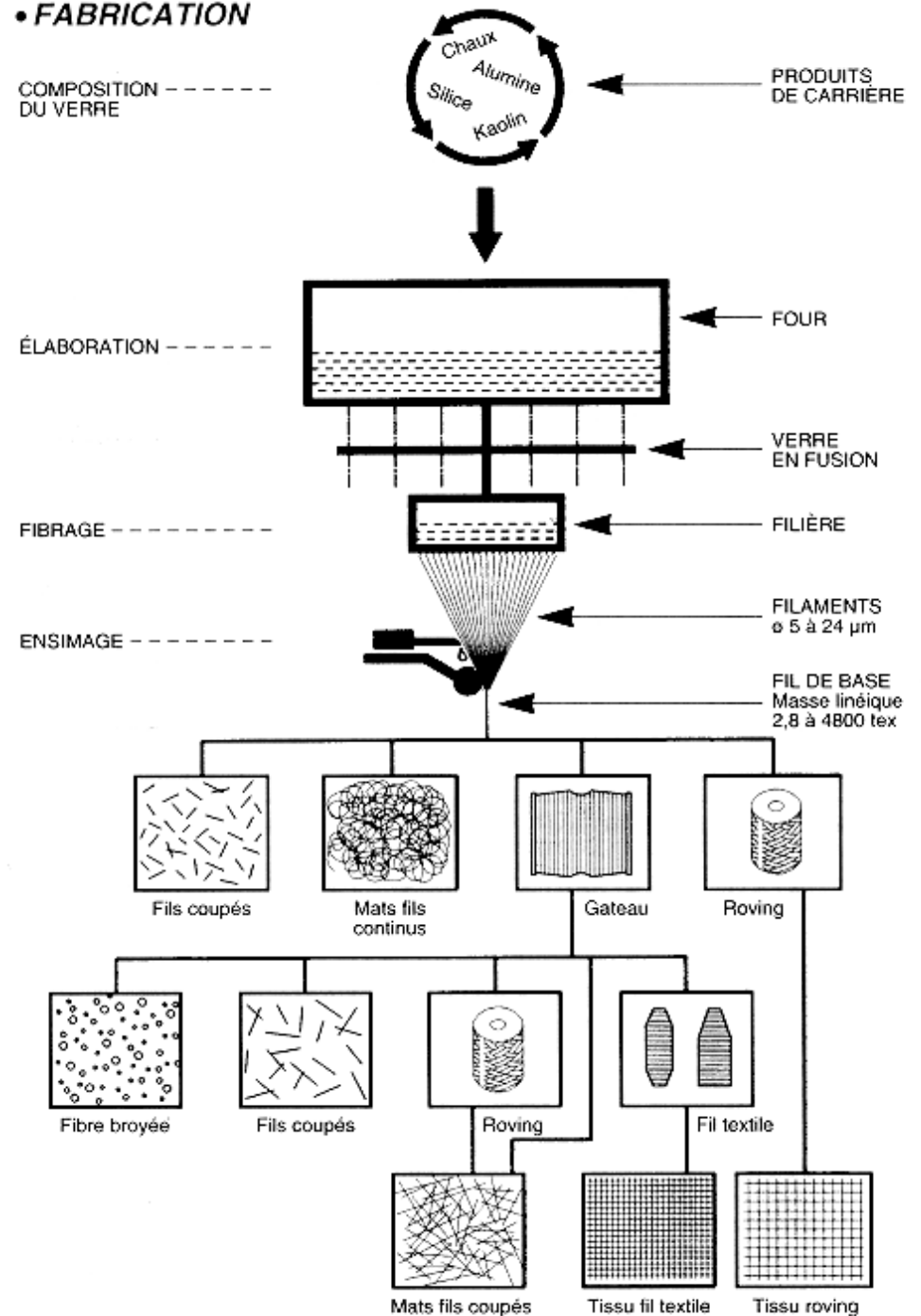
Peel ply



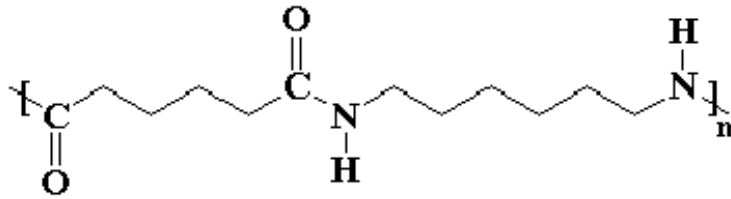
Glass fibres

- Several grades possible, most common is E-glass
- Fibers are very sensitive to scratches, the sizing (ensimage) is crucial to protect the fiber and ensure adhesion to the matrix.

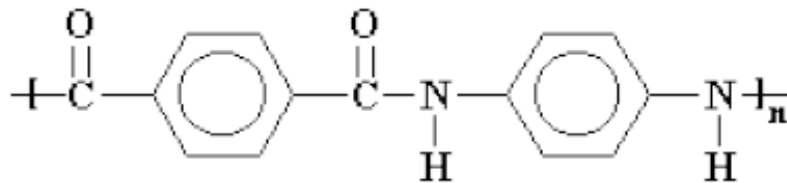
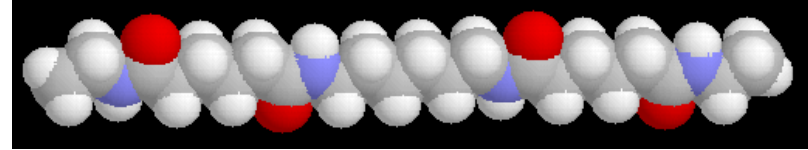
• FABRICATION



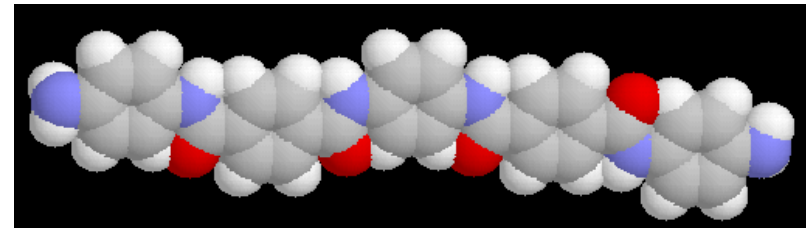
Aramid fibers



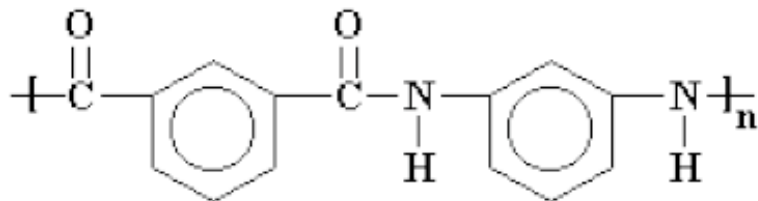
Structure chimique du PA 6.6



Structure chimique du Kevlar®



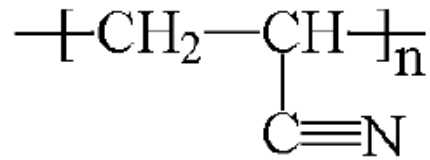
Kevlar® is an aromatic PA discovered in 1972 by DuPont
It is highly crystalline and does not melt below 500° C



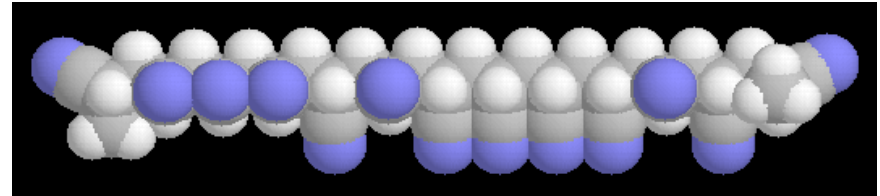
Structure chimique du Nomex®

Nomex® differ from Kevlar® because *meta*-phenylen groups
are instead of *para*-phenylen

Carbon fibers

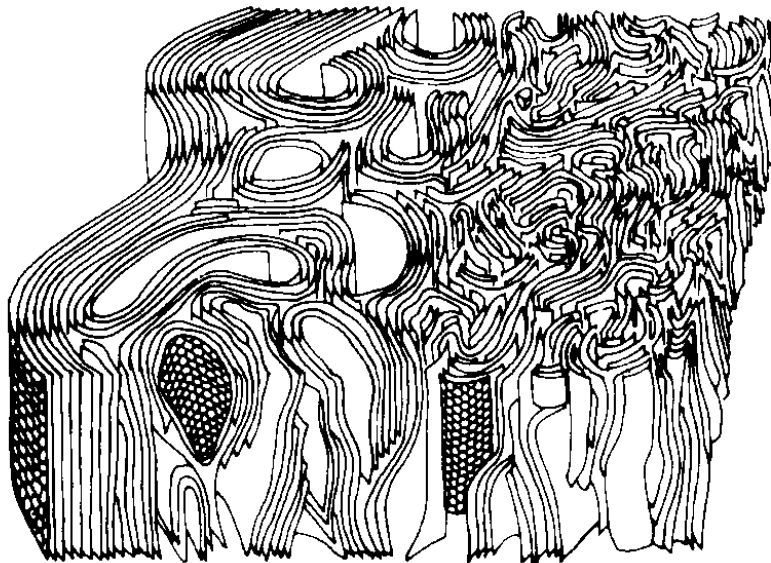


Chemical structure of PAN

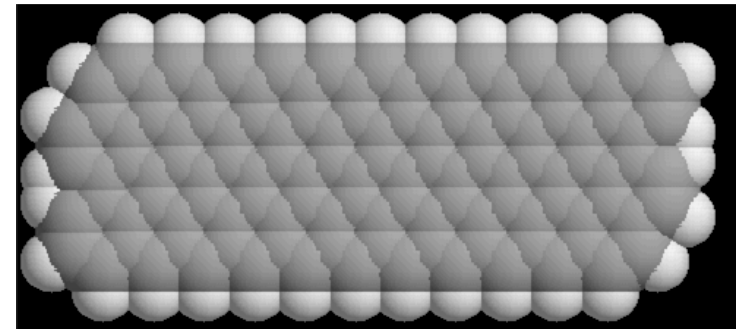


C fibers are obtained by pyrolysis of a precursor polymer (PAN:polyacrylonitrile)

Fibre axis
↑



Schematics of a carbon fiber structure



<https://www.compositesworld.com/articles/the-making-of-carbon-fiber>

CF manufacturing line

Diagram from Harper International



Precursors

Stabilization
& Oxidation

Carbonization/
Graphitization

Surface
Treatment

Spooling &
Packaging

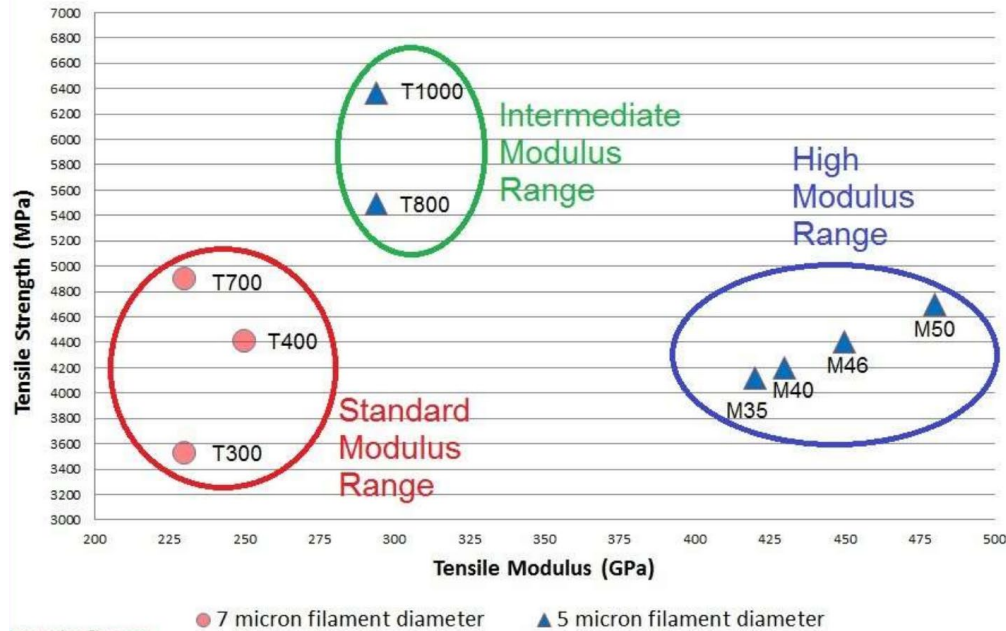
Pitch, PAN or Rayon

200-300C, 80-120 Min
Precise Stretching

1200-1800C
5-10 Min

Handleability
Resin Compatibility

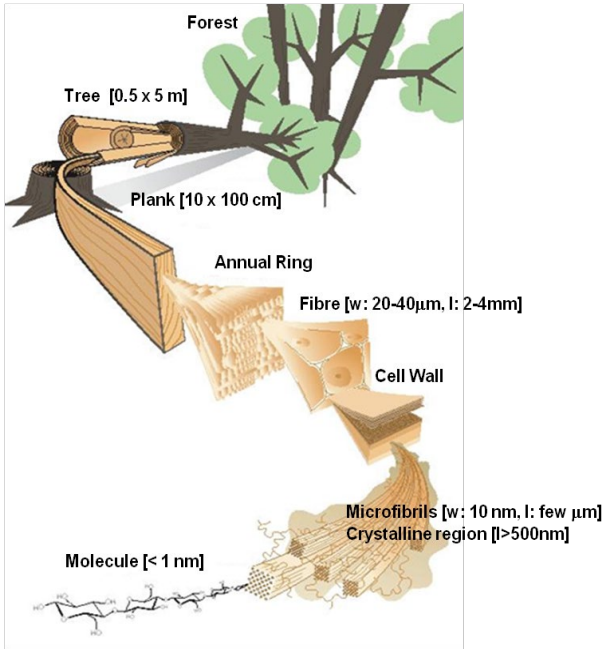
Range of Carbon Fiber Properties
(Tensile Strength & Modulus)



www.carbon-fiber.com

Natural fibers

Flax, hemp, Abaca ,sisal, jute, ...



Araldite: flax/carbon epoxy



Stöckli



Artengo: flax(5%)/carbon epoxy



Museeuw: flax/carbon epoxy



Natural fibres

<i>Fibre</i>	<i>Density(g/cm³)</i>	<i>Young's Modulus (GPa)</i>	<i>Tensile strength (MPa)</i>	<i>Failure strain (%)</i>
Synthetic:				
E-glass	2.56	76	2000	2.6
HS carbon	1.75	230	3400	3.4
Aramid	1.45	130	3000	2.3
Boron	2.6	400	4000	1
Natural:				
Flax	1.5	50-70	500-900	1.3-3.3
Hemp	1.48	30-60	310-750	2-4
Jute	1.4	20-55	200-450	2-3
Sisal	1.45	9-22	80-840	3-14
cotton	1.5	6-10	300-600	6-8

Advantages

Low density

High specific properties

Stiffness and damping, hybrid composites

Renewable resource with production requiring low CO₂ emissions

Worker-friendly processing atmosphere

Good thermal and acoustic insulating properties

Biodegradability

Current limitations

Decreasing variability

Poor moisture resistance

Poor thermal resistance

Low durability

Lack of fibre-matrix adhesion

Continuous technical fibres

Other fibers...

UHMN-PE

(Ultra High Molecular Weight PE)

Spectra® }
Dyneema® } melting point
at 150° C

Exotic Fibers

Zylon® [PBO (poly(p-phenylene-2,6-benzobisoxazole))]

Vectran® [LCP (Liquid Crystal Polymer)]

And other fibers ?

Carbon

Metallic

Boron

Glass fibers

Silica
Quartzel®

Ceramic
Nextel® 312
Fiber FP
Fiber PAD 166

Aramid
Kevlar® 49
Kevlar® 149 ?
Twaron®
Nomex®

Basalt (basaltex)

High-performance
Fibers

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graph TD; HPF[High-performance Fibers] --> UHMN-PE[UHMN-PE (Ultra High Molecular Weight PE)]; HPF --> Exotic[Exotic Fibers]; HPF --> Carbon[Carbon]; HPF --> Metallic[Metallic]; HPF --> Boron[Boron]; HPF --> Glass[Glass fibers]; HPF --> Silica[Silica Quartzel®]; HPF --> Ceramic[Ceramic Nextel® 312, Fiber FP, Fiber PAD 166]; HPF --> Aramid[Aramid Kevlar® 49, Kevlar® 149?, Twaron®, Nomex®]; HPF --> Basalt[Basalt (basaltex)];
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Synthetic fibers

Fibre Type & Initial producer	Repeat Unit in the Macromolecule	Maximum Elastic Modulus (GPa)	Melting pt. or decomp. temp. °C
Polyamide 6 [Nylon 6] I.G.Farben	$\left[\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO} \right]_n$	4	230
Polyamide 6/6 [Nylon 6.6] Du Pont	$\left[\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO} \right]_n$	~5	260
Polyethylene terephthalate [Polyester] ICI	$\left[\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2 \right]_n$	~15	260
Poly(m-phenylenediamine-isophthalamide) Nomex Du Pont	$\left[\text{NH}-\text{C}_6\text{H}_3(\text{NH}-\text{CO})-\text{C}_6\text{H}_3(\text{NH}-\text{CO})-\text{CO} \right]_n$	17	400
Poly-paraphenylene/3,4-diphenylether terephthalamide [Technora] Teijin	$\left[\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_m \left[\text{NH}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_n$	70	500
Poly(p-phenylene terephthalamide) [Kevlar] Du Pont	$\left[\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_n$	135	550
Poly(p-phenylene benzobisoxazole) PBO [Zylon] Toyobo	$\left[\text{C}_6\text{H}_4-\text{N}(\text{O})-\text{C}_6\text{H}_2(\text{N},\text{O})-\text{N}(\text{O})-\text{C}_6\text{H}_4 \right]_n$	280	650
Poly{2,6-dimidazo [4.5-b:4'.5'-e] pyridinylene-1,4 (2,5-dihydroxy) phenylene} (PIPD) M5 AKZO	$\left[\text{C}_6\text{H}_2(\text{OH})_2-\text{N}(\text{O})-\text{C}_6\text{H}_2(\text{N},\text{O})-\text{N}(\text{O})-\text{C}_6\text{H}_2(\text{OH})_2 \right]_n$	330	650

Fiber selection criteria

Product requirements:



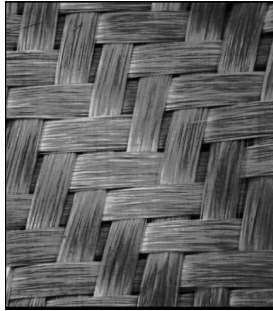
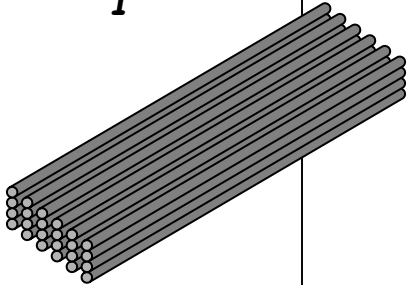
- compromise stiffness/mass/cost
- failure strain
- use temperature
- impact resistance, compression, shear resistance...
- resistance to chemicals, UV, corrosion
- electrical and thermal conductivity
- thermal expansion coefficient of the part
- compatibility with the polymer matrix
- choice of the processing method
- assembly issues with other materials

Reinforcement potential

Material

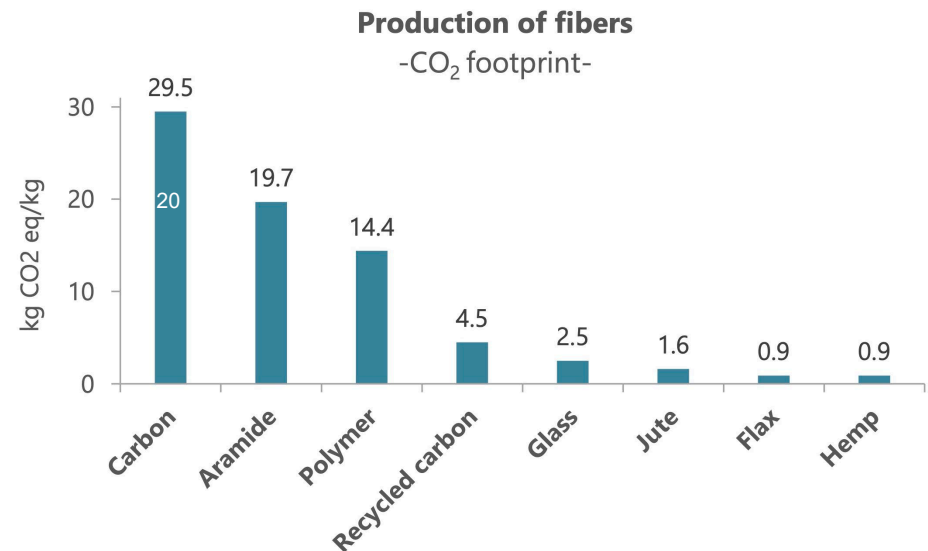
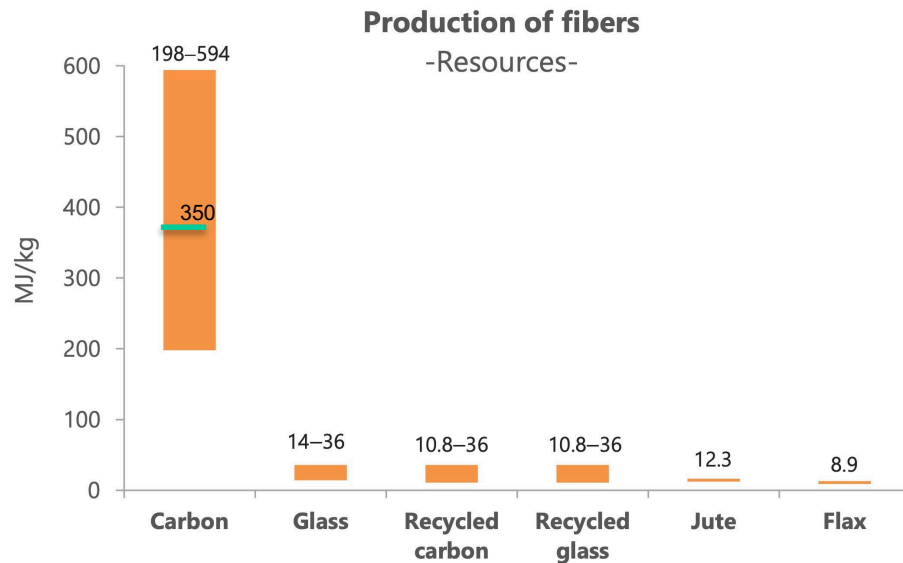
Shape

Configuration

	Glass	Aramid	Steel	Carbon
	<hr/>			
	0	<i>E Modulus (Gpa)</i>		400
	<hr/>			
	Particles	Short fibres	Long discontinuous fibres	Continuous fibres
	<hr/>			
	1	<i>Aspect ratio L/d</i>		∞
	<hr/>			
	Random	Knit	Woven	UD
	<hr/>			
	0	<i>Orientation</i>		1
				

Some data on environmental impact

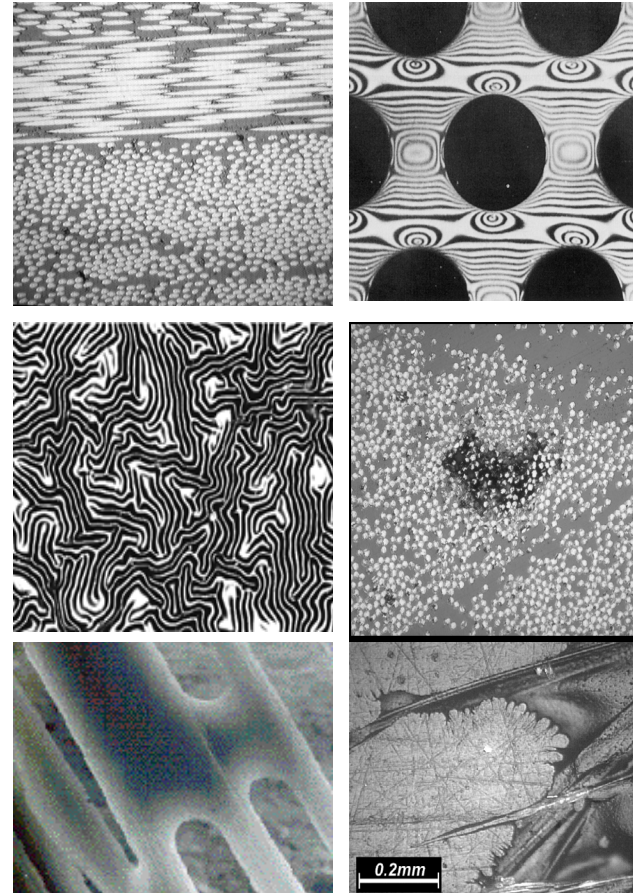
Main fibers, resources needed and CO₂ footprint for producing 1kg of fibers



Sources: Ecoinvent database; JEC observer 2021: Current trends in the global composite industry 2020-2050; Niels de Beus, Michael Carus, Martha Barth. 2019: Carbon footprint and sustainability of different natural fibres for biocomposite and insulation material, Teijin website, Dyneema website
New data for carbon in 2022: <https://www.carbonfiber.gr.jp/english/tech/lci.html>

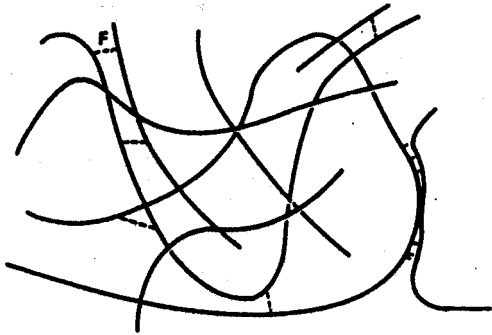
Roles of a matrix

- Transfer and distribution of stresses between fibres (mechanical properties, adhesion, damage and failure mechanisms...)
- Interface with environment, surface performance (temperature, humidity, acids, UV....)
- Influence processing (shrinkage, low viscosity...)



Polymer types

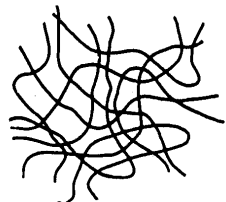
Thermoplastic



Long chains, linear or entangled,
Weak interaction between chains
Melts, reversibly

Amorphous

(transparents)



Ex: PS, PMMA

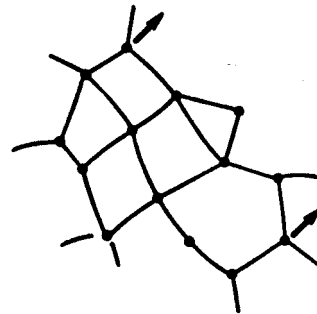
Semicrystalline

(opaques)



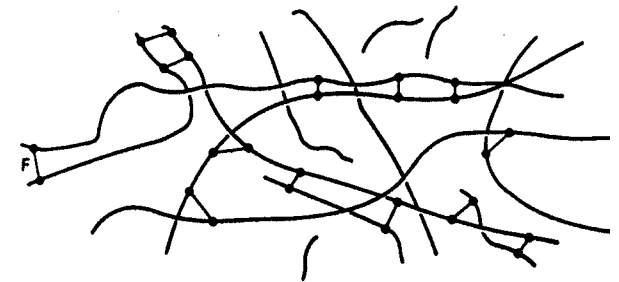
Ex: PA, PP

Thermoset



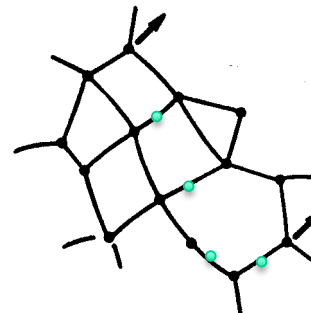
Tridimensional network
Forms by chemical reaction
Irreversible, cannot melt

Elastomer



Chemical reaction
during vulcanisation
Few bonds,
irreversible

New: vitrimers



Tridimensional network with covalent
adaptable bonds
Forms by chemical reaction
Bonds can dissociate and reassociate
above a certain temperature

Polymer matrices

Thermosets

Advantages

- + liquid at room temperature
- + ease to process (EP, UP)
- + curing between 5° and 180° C (EP)
- + cost
- + range of formulation
- + good adhesion to fibres
- + resistance to temperature variation

Limits

- volatiles, toxicity, allergy
- resistance to humidity
- impact resistance
- tailoring of chemical resistance

Thermoplastics

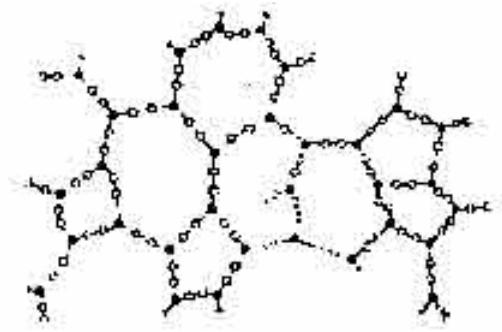
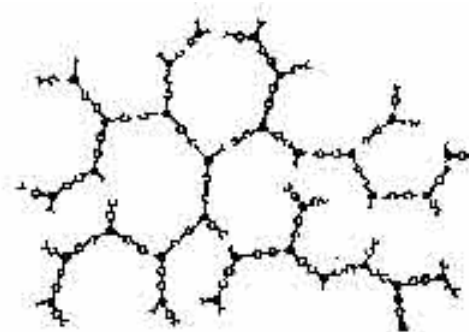
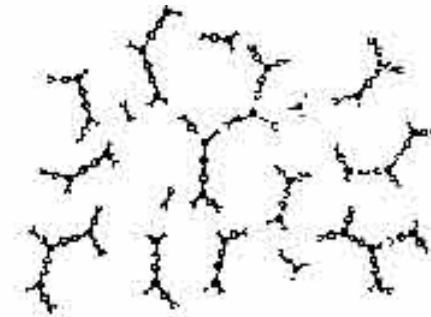
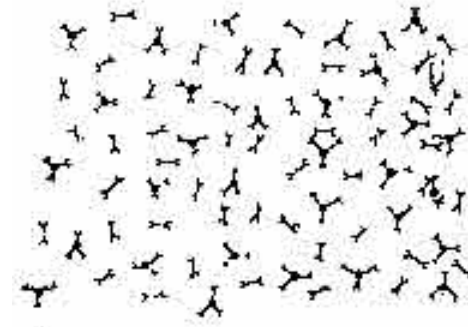
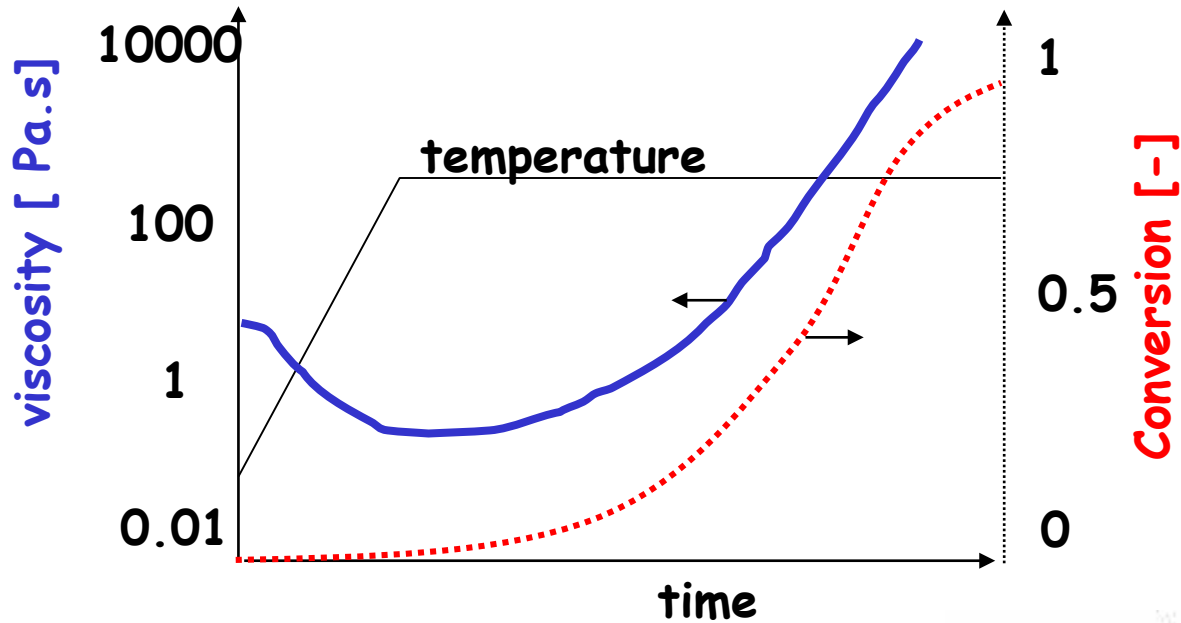
Advantages

- + rapid processing by increasing temperature
- + Processing techniques of thermoplastics are used with short fibres
- + resistance to humidity

Limits

- Often not resistant to high temperature
- Molding shrinkage
- Bad chemical resistance (amorphous)
- Adhesion to fibres
- Creep

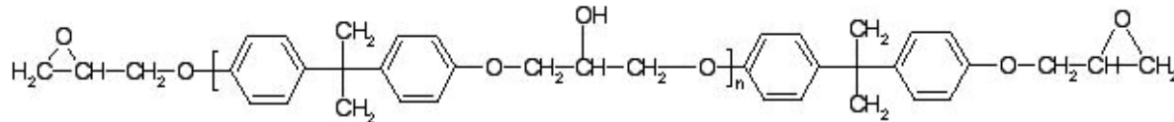
Thermoset matrices



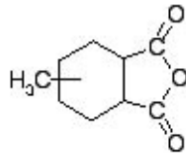
Thermoset matrices

Example of an epoxy resin, with an anhydride hardener and an amine accelerator.

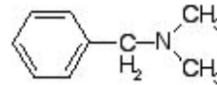
Diglycidyl ether of bisphenol A - DGEBA



Methyl-hexahydrophthalic anhydride - MHHPA

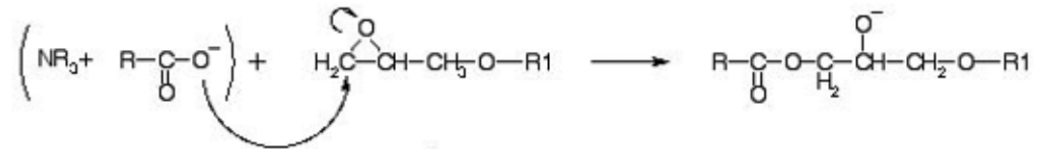
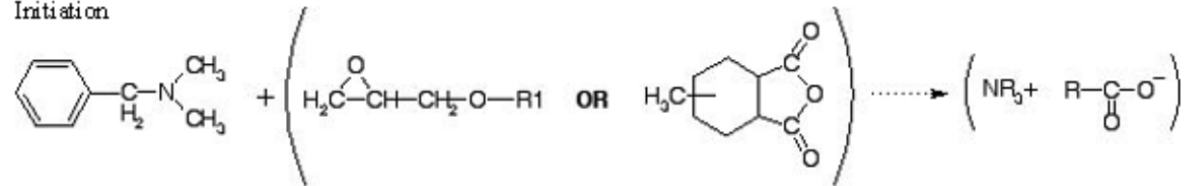


Benzyltrimethylammonium chloride - BDMA

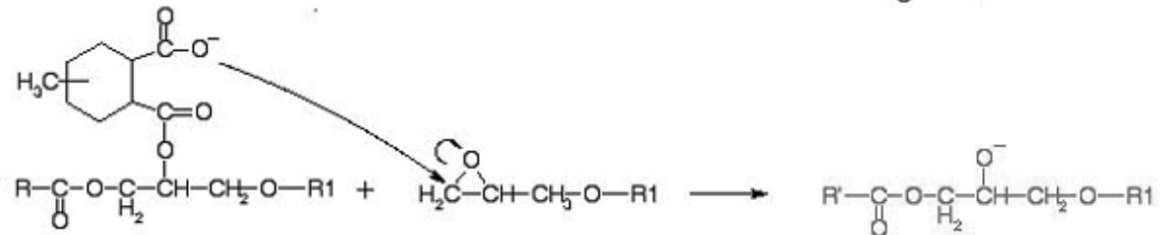
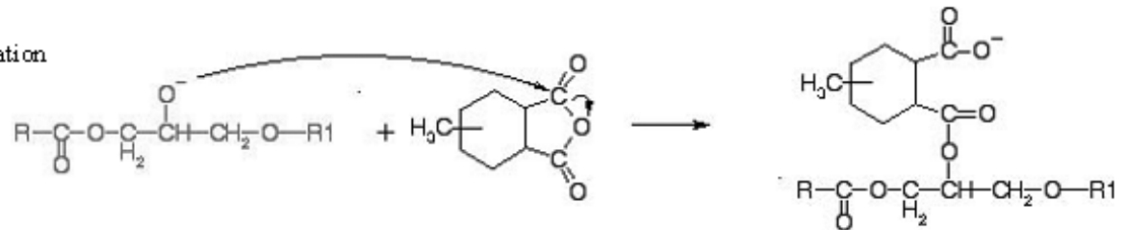


Chemical reaction

Initiation



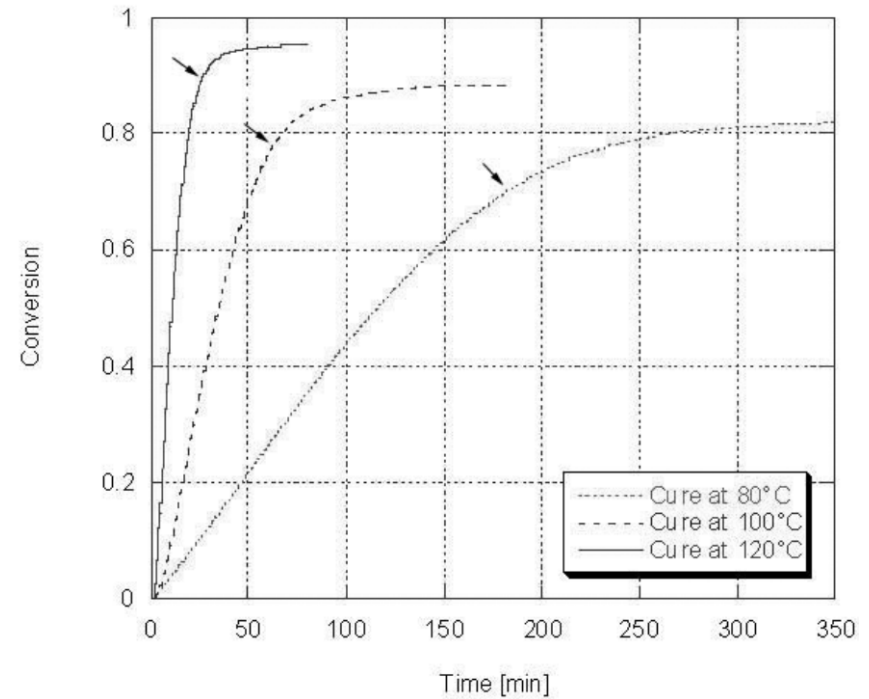
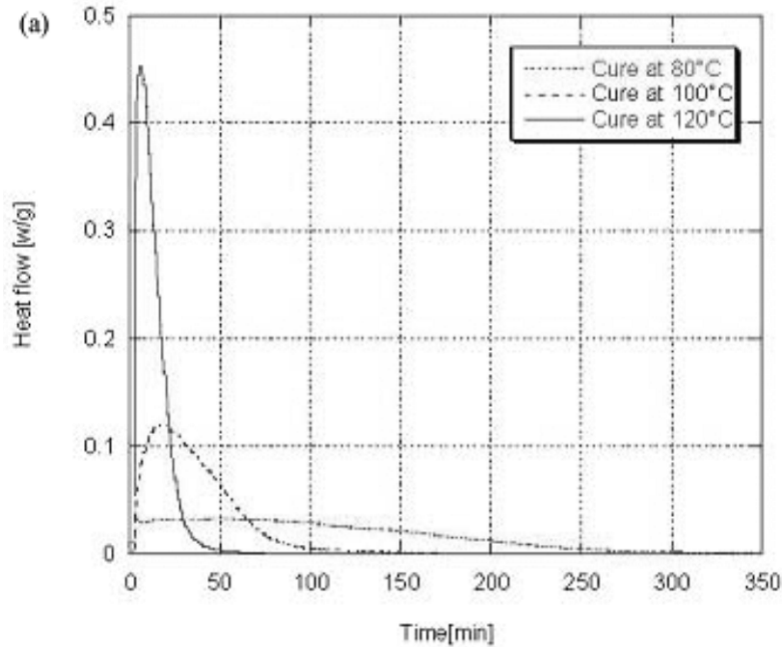
Propagation



Termination

Several terminations could be envisioned such as the formation of an ammonium ion or a transfer reaction as suggested by Steinmann [15].

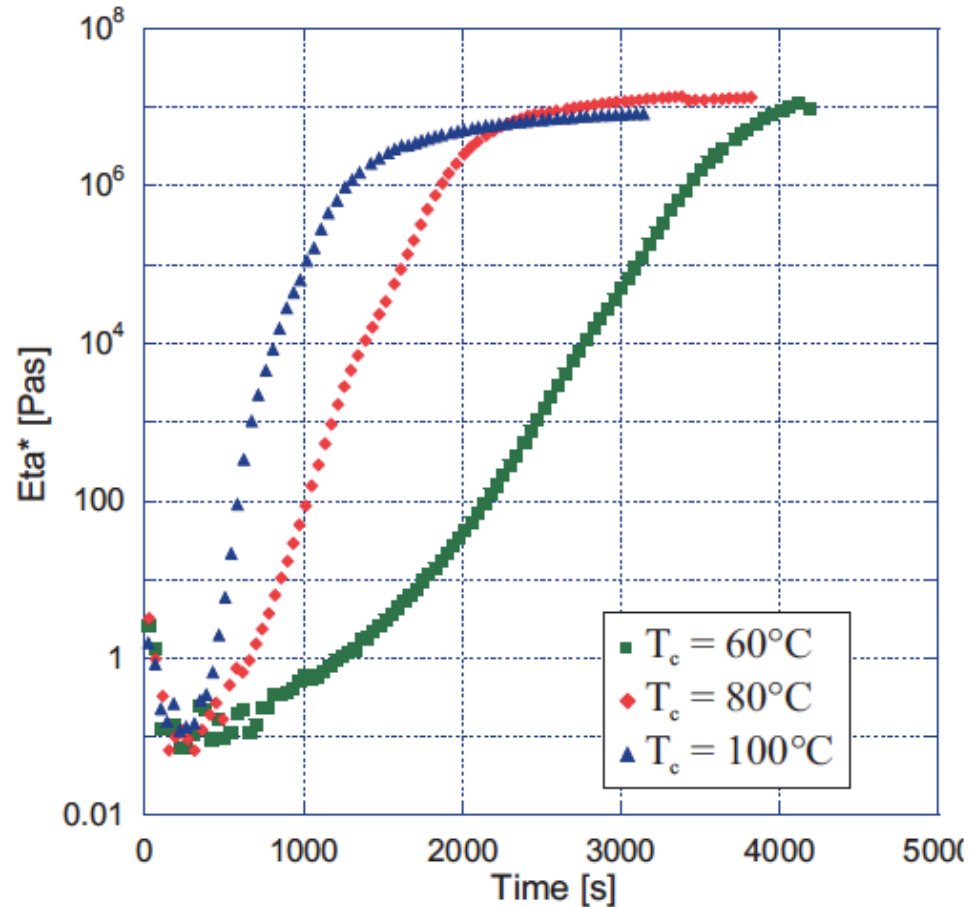
Exothermicity



reaction rate:

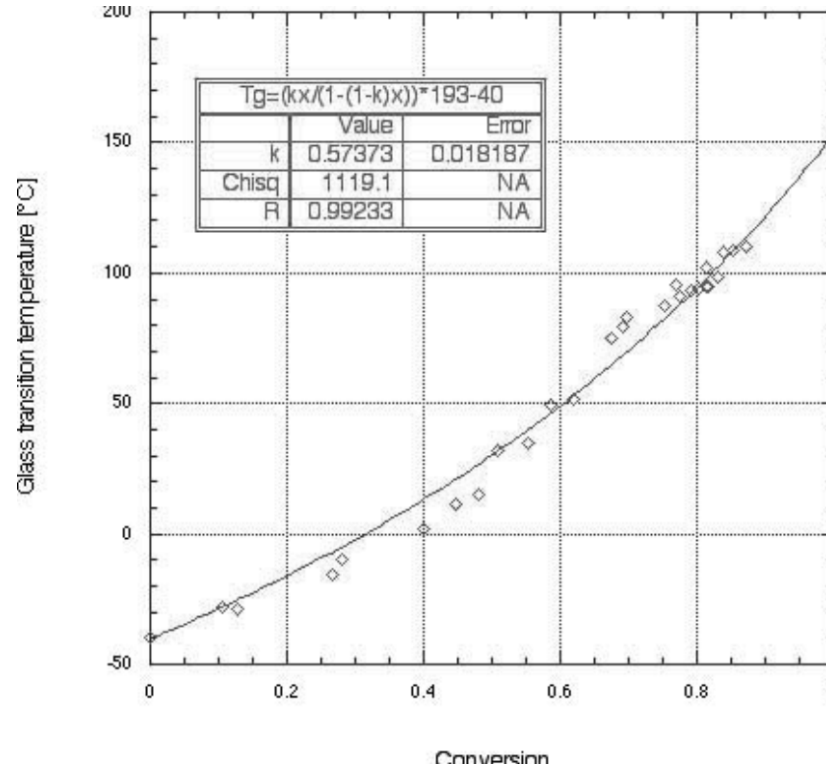
$$\alpha = \frac{\Delta H(t)}{\Delta H_{Tot}}$$

Viscosity change



(for another epoxy resin)

Tg change with conversion



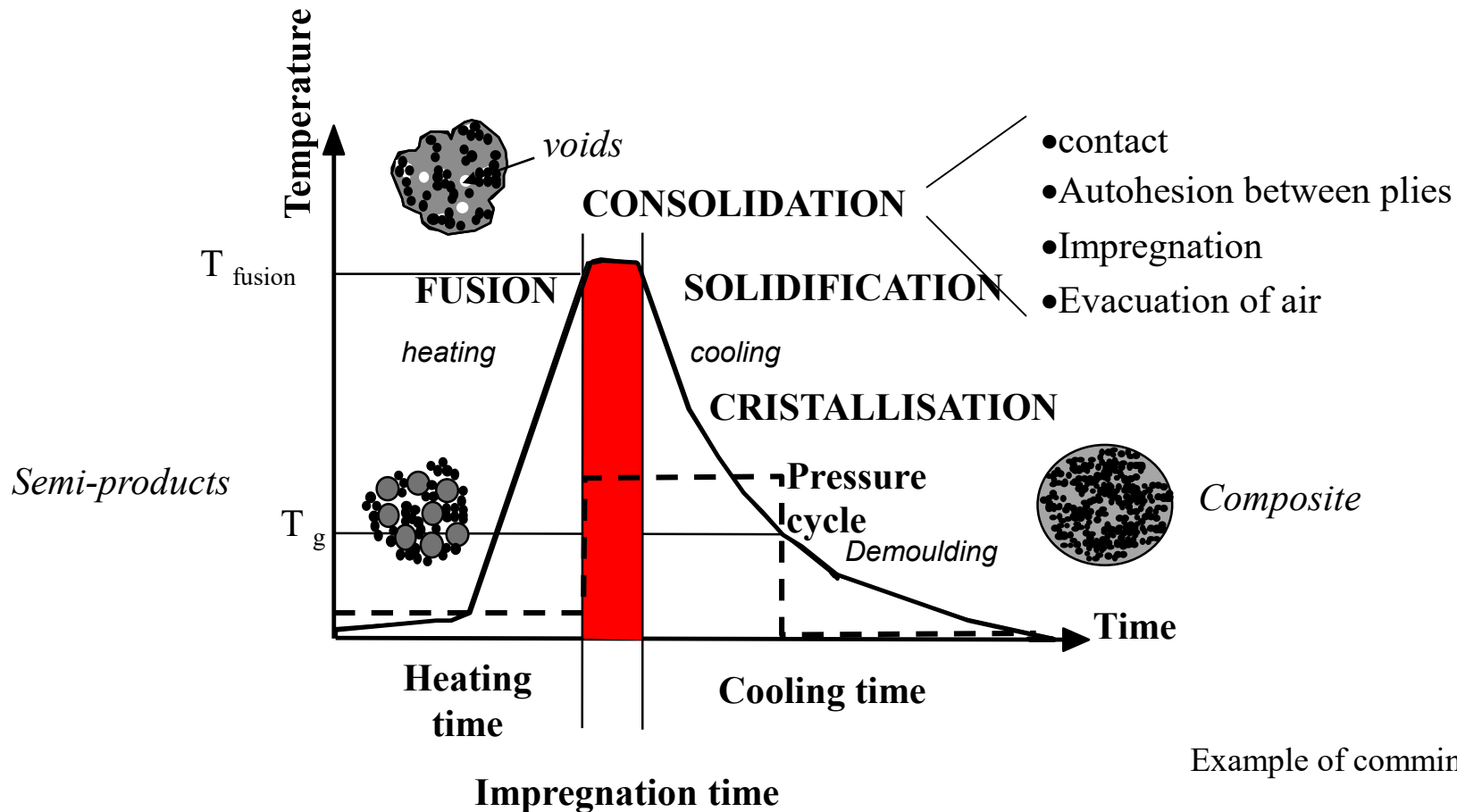
Tg, glass transition temperature, evolves with conversion

Thermoset transformation

Practical issues:

- storage in separate containers, mix when processing, or store the mix at low temperature
- at gel point, viscosity rises sharply :
limit for flow, impregnation time limited.
- demoulding when the part has reached T_g
- possibility to process in several steps (B-stage, cure, post-cure)
as long as the reaction is not complete.
- exothermicity: problem for thick parts, limitation of heating ramps,
risk of blowing up the mixed resin.
- Polymerisation shrinkage (5 to 10%)
- Dangerous reactive products: styrene, amines, ...and volatiles!

Thermoplastic matrices



Semi-crystalline and amorphous resins

Semi-crystalline

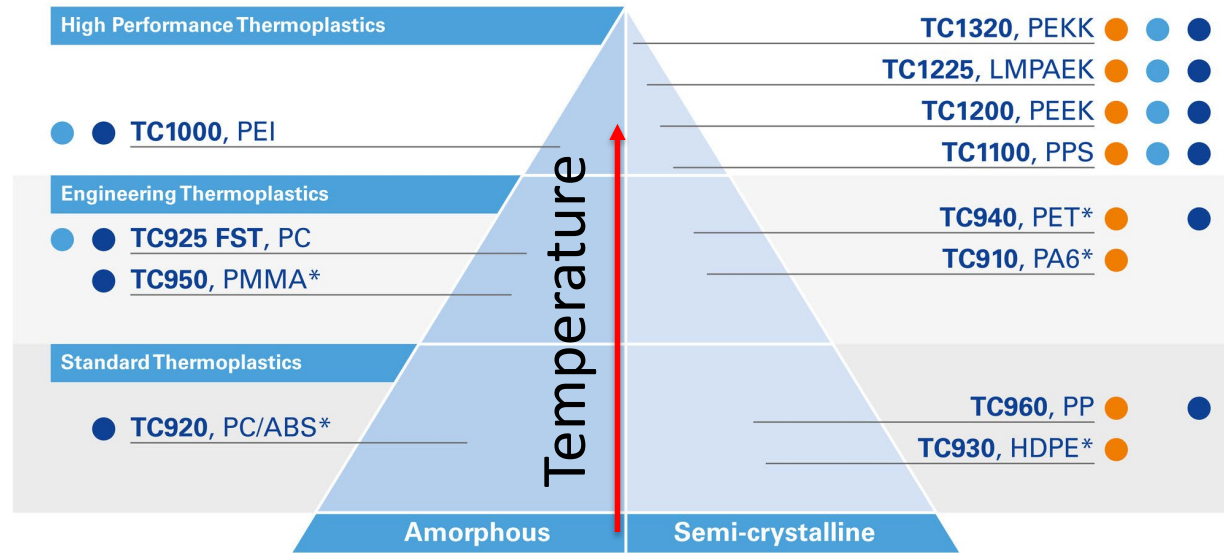
- Some areas amorphous and others are closely packed in a crystal lattice
- % crystallinity based on the type of the polymer and the cooling rate utilized in forming that part
- both Tg and melt temperature Tm, a point at which the crystalline structure breaks down.

Amorphous

- Tg, but does not form crystalline structure
- Reduced solvent resistance

Cetex[®]

OUR HIGH PERFORMANCE THERMOPLASTIC POLYMERS AND PRODUCT FORMS



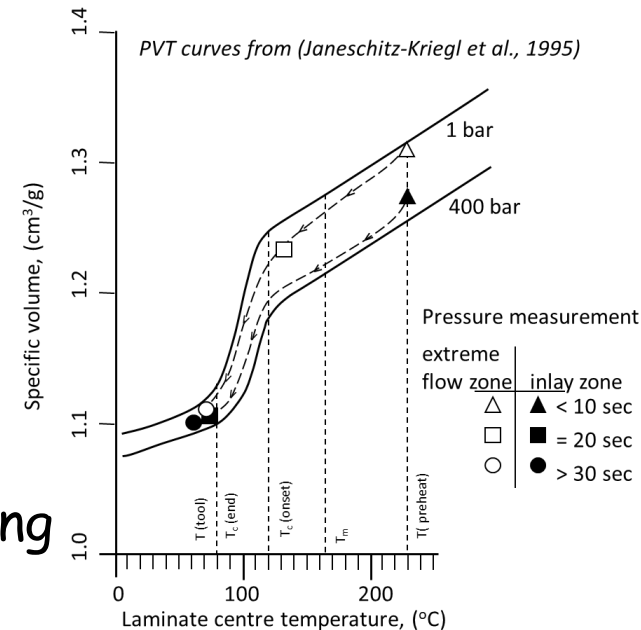
● UD Tape
 ● Woven Prepreg
 ● Laminate
 * Laminate Parts



Thermoplastic processing

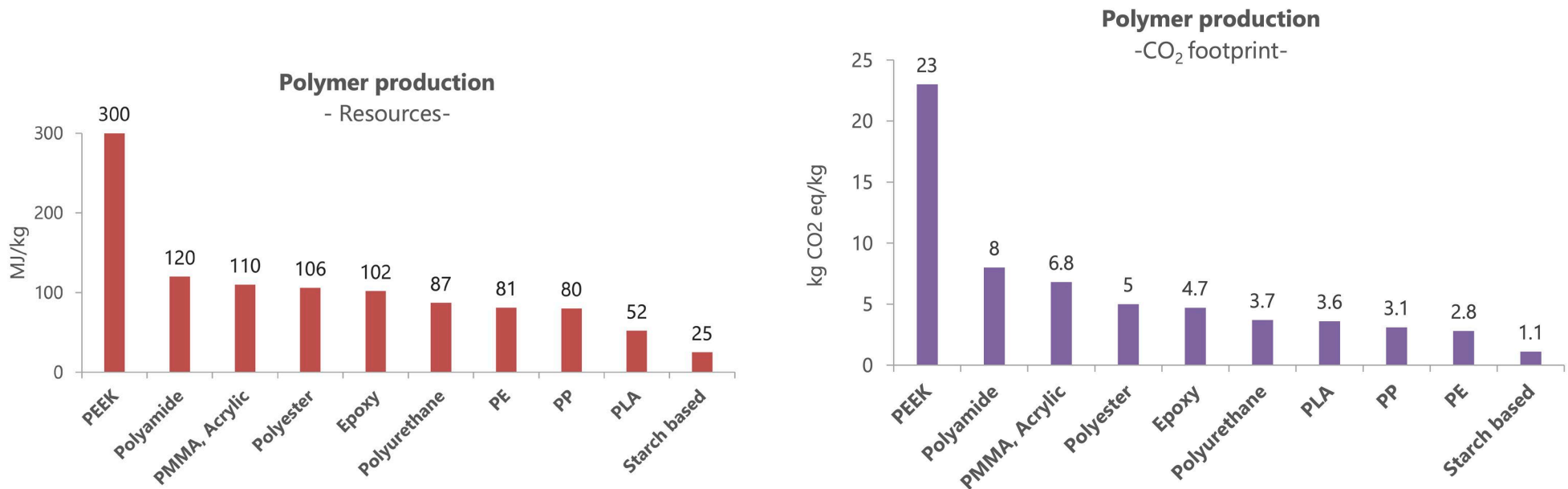
Practical processing issues :

- No chemistry problem, except degradation.
- Possibility to heat and reheat several times, for post-forming, shaping, welding...
- Process temperatures generally above T_m or T_g (so above service temperature)
- Higher melt viscosities: changes vs. shear rate, temperature and molecular weight
- Impregnation: lamination, powder, solvent, commingling
- Crystallisation shrinkage (up to 30%!), PVT behaviour



Some data on environmental impact

Main matrices, resources needed and CO₂ footprint for 1kg of polymer



Sources: Ecoinvent database; Ashby, Materials and sustainable development

Composite market

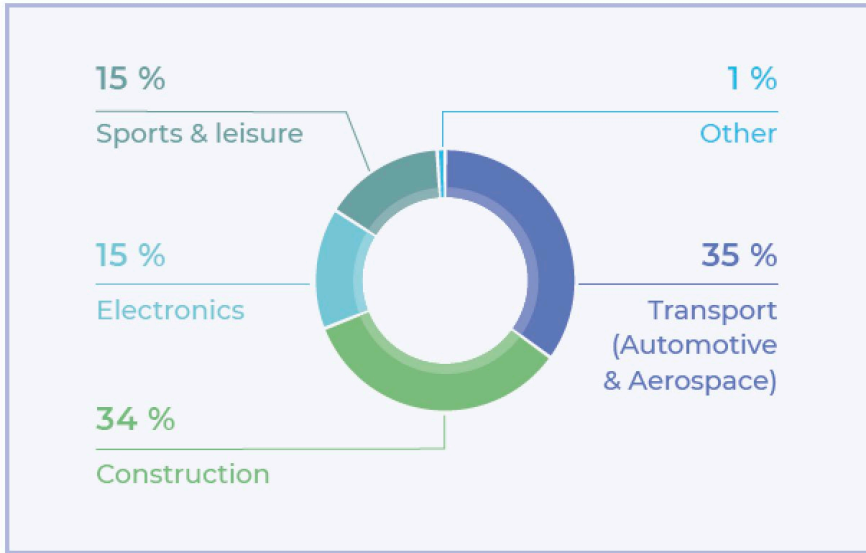


Figure 3. Composites production in Europe by type of application

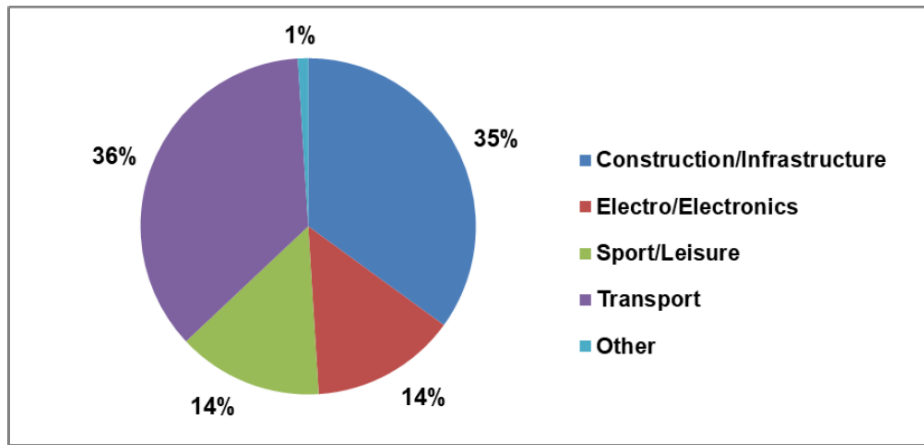


Fig. 15: GRP production in Europe by application industry (year: 2018 = estimated)

Carbon fiber reinforced

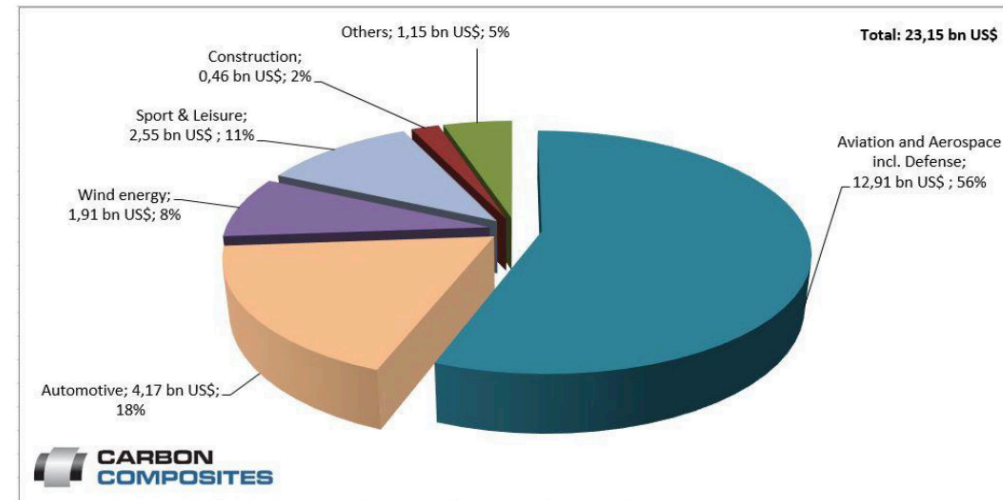


Figure 10: Global CC-Turnover in Thsd. Tons by application (11/2018).

Sources: CC Schweiz, Suschem report

Constituents/Process/Markets

Main innovations in 2019 – Volume ~11,7 Mt
 – Value⁽¹⁾ ~86 B\$ / 73 B€

Next generation cars will drive market growth



- Autonomous cars penetration in 2040
- Natural gas vehicles CAGR (2000-2030)
- Hydrogen vehicles CAGR (2015-2030)

Global adjacent market amounts to ~22 Mt⁽²⁾



Composites are popular in transportation and construction (Breakdown by application)



Thermosets are the main resin used for composite materials

(Breakdown by resin type)



Glass Fibre is the most popular reinforcement

(Breakdown by Fibre type)



China, & North America are the main composites markets

(Breakdown by geography)



Note:
 (1) Value for end products with composites; (2) Including composite market; (3) Wood-Plastic Composites; (4) Ceramic Matrix Composites; (5) Metal Matrix Composites; Source: JEC & Co. Interviews, analysis and estimates

Constituents/Process/Markets

Overview of the global composites' material market in 2019⁽¹⁾

Glass fibre

Top players



Top applications



Top regions for production 2019



Thermoset resin

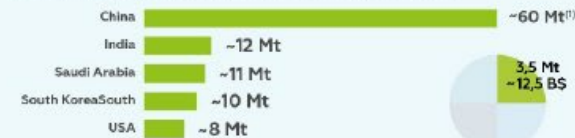
Top players



Top applications



Top regions for production 2019



Carbon fibre

Top players



Top applications



Top regions for production 2019



Thermoplastic resin

Top players



Top applications



Top regions for production 2019



Note:
 (1) Production of material for all applications, composites and other applications
 Sources: Exin & Co interviews, analysis and estimates

Conclusions

- Baseline data on the main constituents for composites for those who never had any intro to composite courses.
- Further info can be found in reference books on composites, or the encyclopedia of composites.