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Materials and Properties of Polymer Matrix Composites

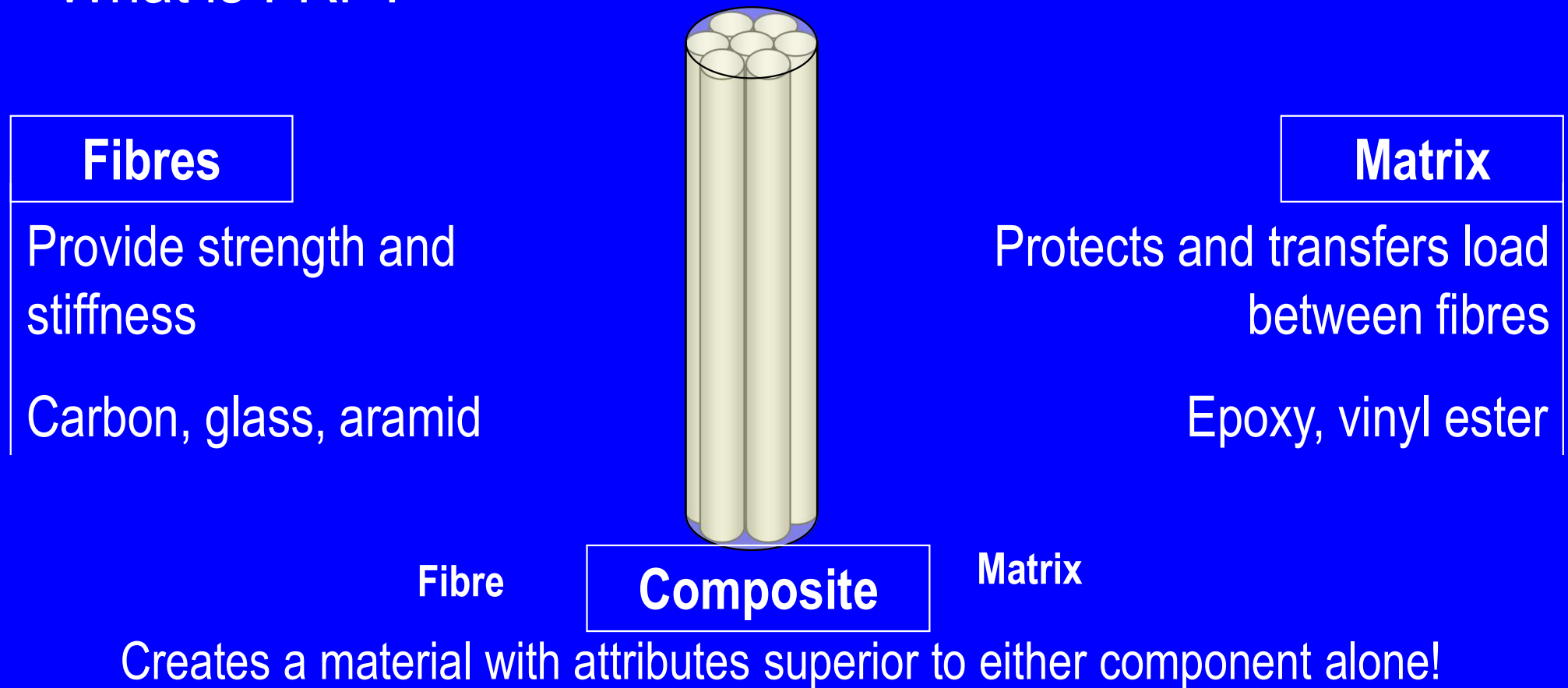
Book L. Bank, Chapter 2

Fibre Reinforced Polymers

- FRPs are ***composite materials***:
 - materials created by the combination of two or more materials, on a macroscopic scale, to form a new and useful material with enhanced properties that are superior to those of the individual constituents alone
- More familiar composite materials
 - Concrete → stone, sand, and cement paste
 - Reinforced concrete → concrete and steel
 - Wood → cellulose and lignin
 - Bone → collagen and apatite

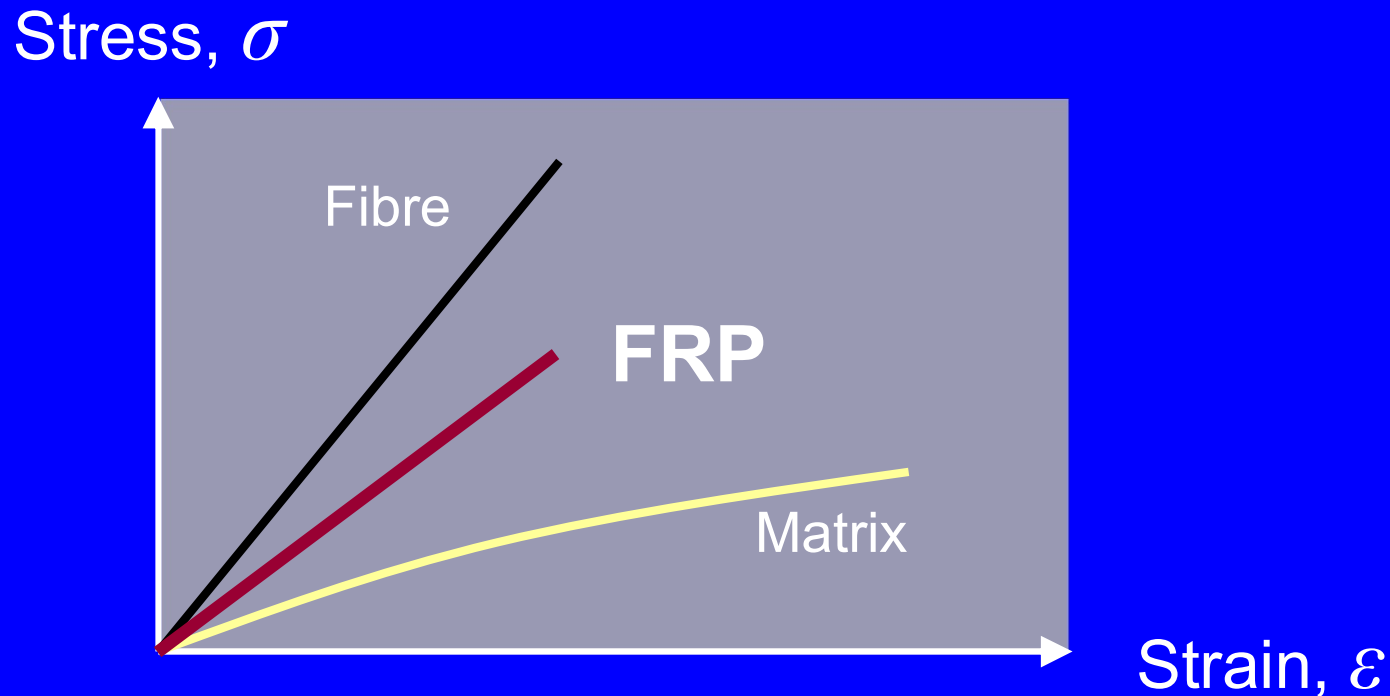
FRP Materials

- What is FRP?



Fibres and matrix both play critical roles in the composite material...

Matrix + Fibre = FRP



Combining fibres and matrix gives a composite material with superior properties

Fibers versus human hair



Hair



E-Glass



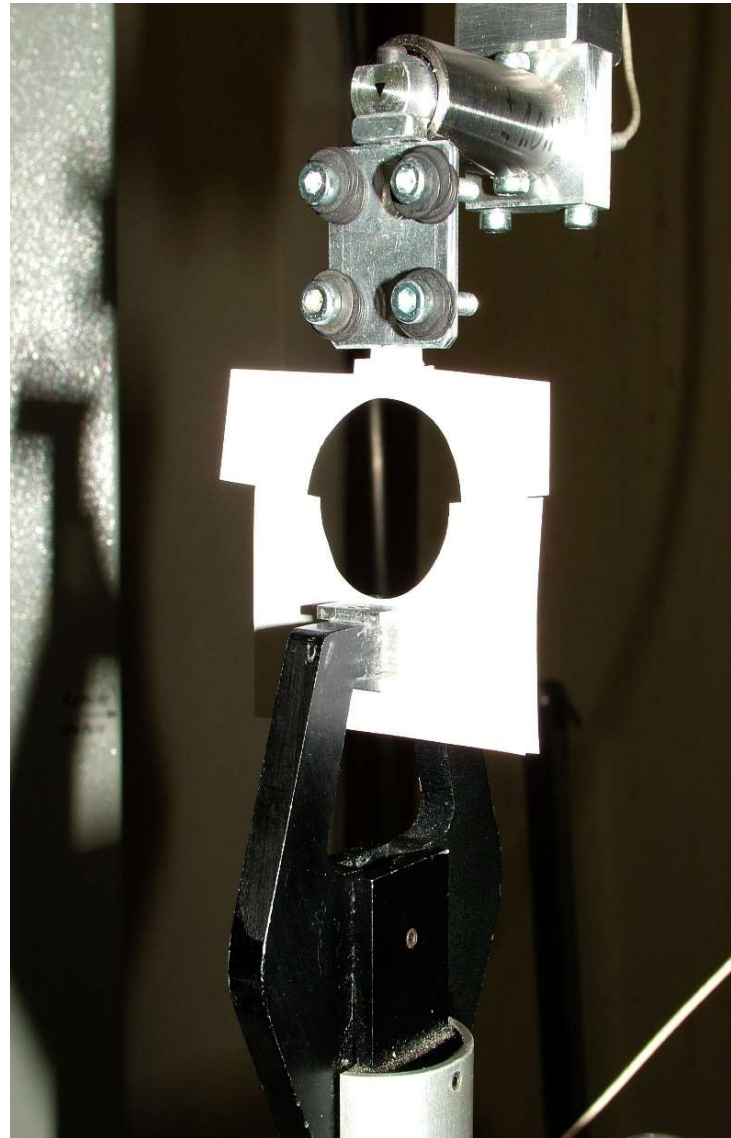
Aramid



Carbon

100 μm

Single Fibre Tests at Empa



Prüfprotokoll:

Kunde / EMPA-Nr.: Sika/449551 Prüfnorm : ISO 11566
Material-Lfd.Nr. : 3117 Probenform : Einzelfaden
Material : CF
Versuchsart : Zug

Vorlagerung : NK 23/50

Püfparameter:

Prüfmaschine : Z010 Spannabstand : 35.34 mm, L0 25 mm
Kraftaufnehmer : 1.0 N Prüfungsgeschwindigkeit: 0.1 mm/min
Wegaufnehmer : Traverse Prüfklima / Datum : NK
Probenhalter : pneum. Spannköpfe Prüfer / Visum : res117

Prüfgergebnisse:

Legende	Nr	Prb.Nr.	F-max N	ε-F max %	ε-F max 2 mm
	1	W300-25_01	0.1517	1.917	0.479

Statistik (Mittelwert):

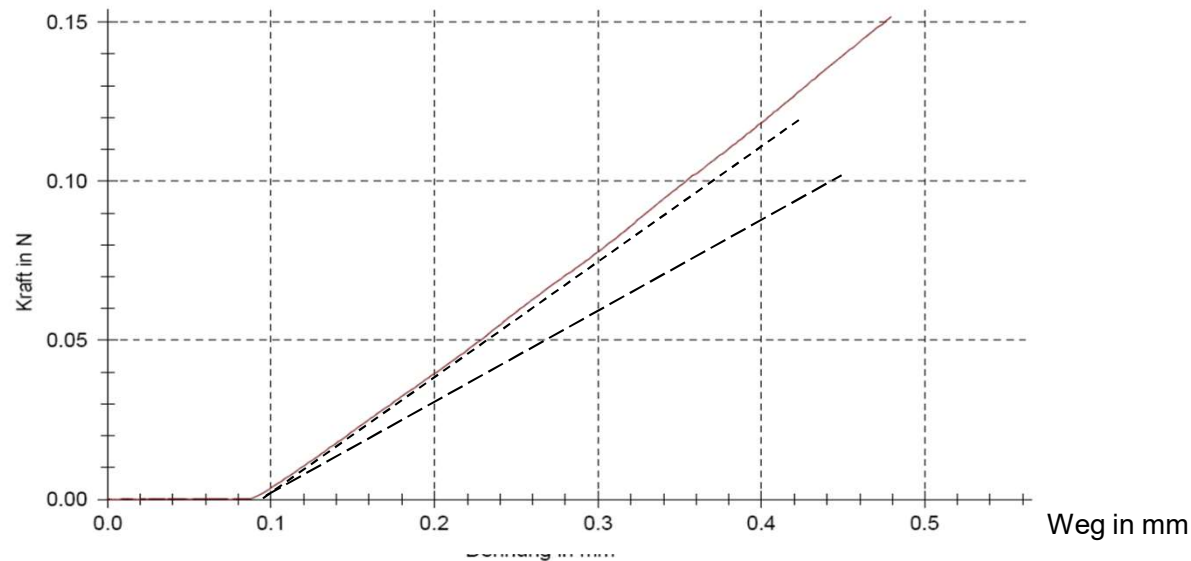
Serie n = 1	F-max N	ε-F max %	ε-F max 2 mm
x	0.1517	1.917	0.479
s	-	-	-

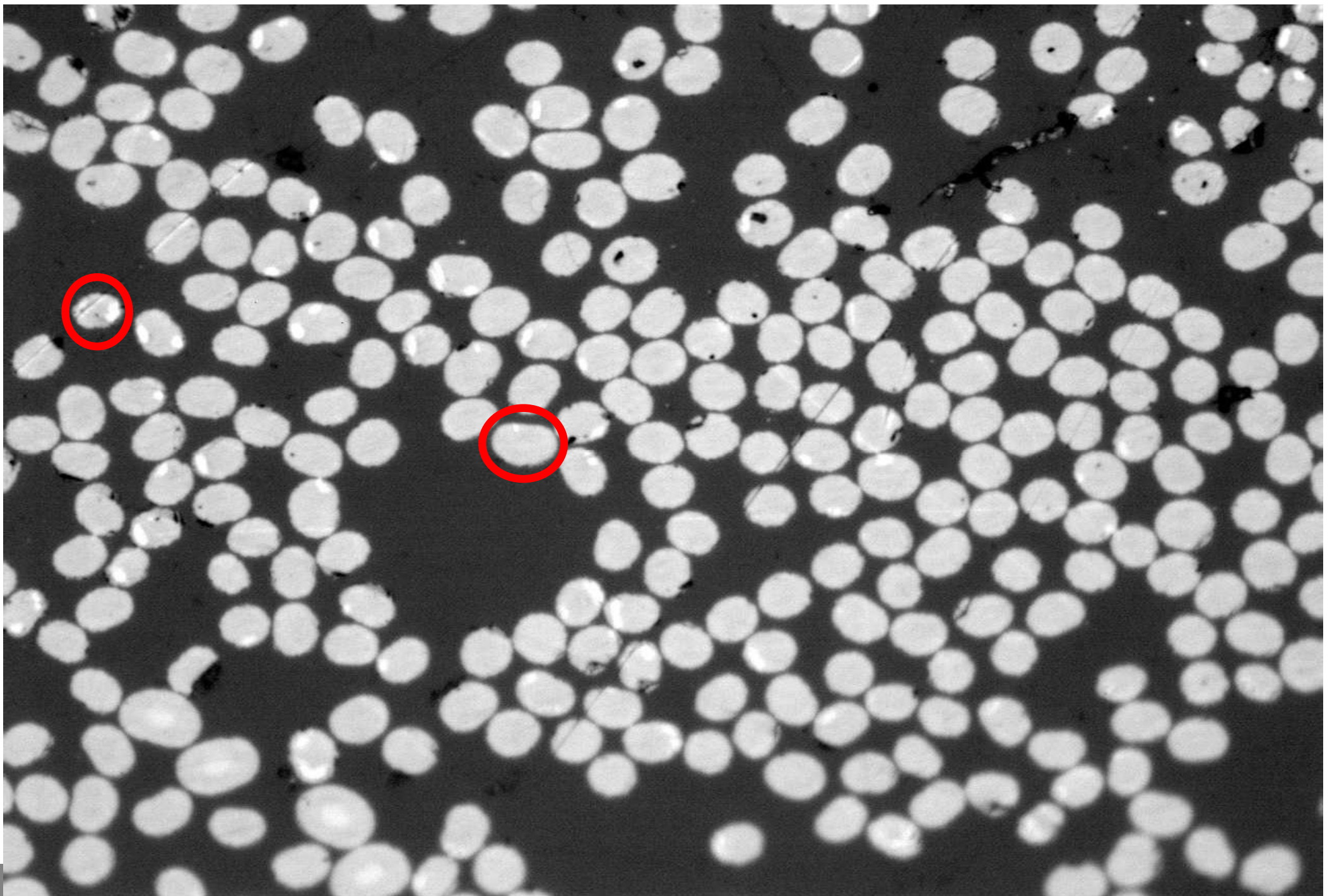
Dry Fiber Properties

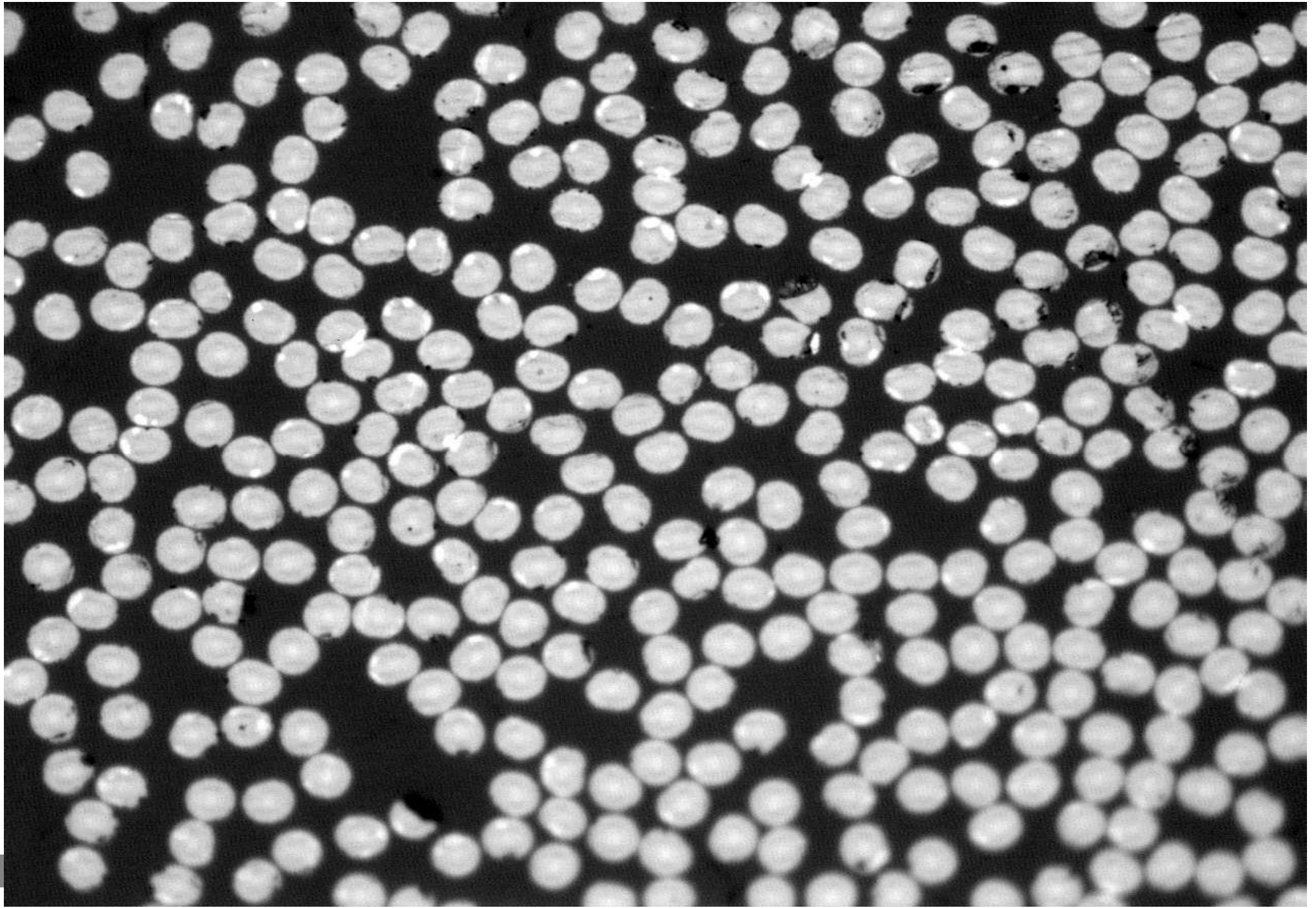
Tensile strength:
3'800 N/mm² (nominal).

Tensile E-modulus:
242'000 N/mm² (nominal).

Elongation at break:
1.55 % (nominal).







Prüfprotokoll:

Kunde / EMPA-Nr.: 116 Prüfnorm : ISO 11566
Material-Lfd.Nr. : 3117 Probenform : Einzelfaden
Material : Haar
Versuchsart : Zug
Vorlagerung : NK 23/50
Datei : Haar_

Püfparameter:

Prüfmaschine : Z010 Spannabstand : 35.34 mm, L0 25 mm
Kraftaufnehmer : 1.0 N Prüfgeschwindigkeit: 0.1 mm/min
Wegaufnehmer : Traverse Prüfklima / Datum : NK
Probenhalter : pneum. Spannköpfe Prüfer / Visum : 17.6.08/res117

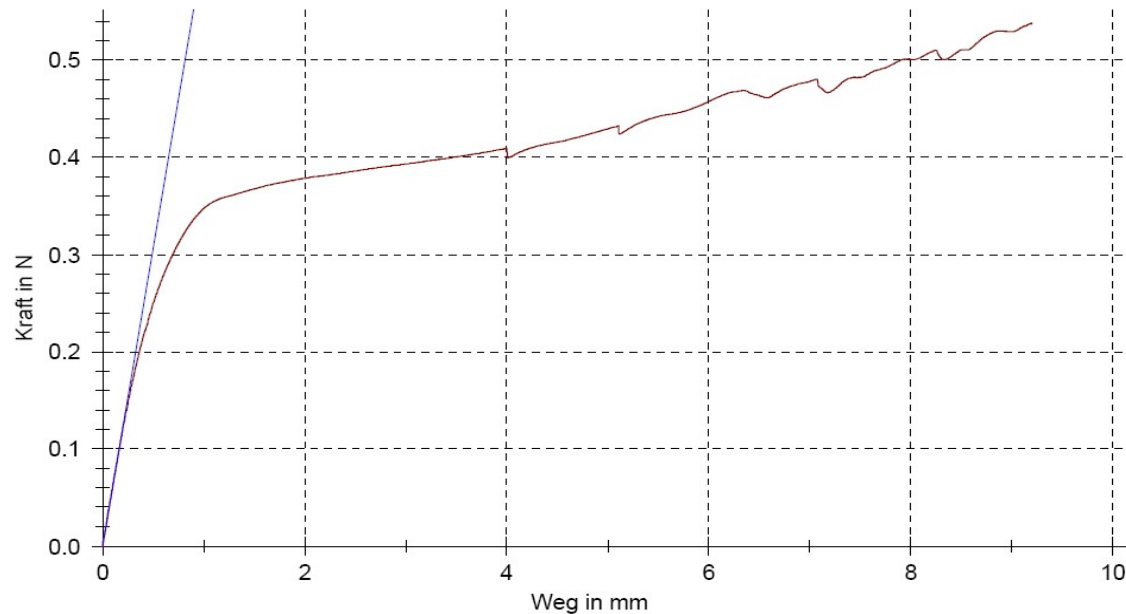
A human Hair

Prüfresultate:

Legende	Nr	Prb.Nr.	Durchmesser d0 mm	F-max N	Weg-F max %	Weg-F max 2 mm	Weg x-korr.-F max mm
	1	Haar 1	0.063	0.5380	36.775	9.194	9.19

Statistik (Mittelwert):

Serie n = 1	F-max N	Weg-F max %	Weg-F max 2 mm	Weg x-korr.-F max mm
$\bar{x}$	0.5380	36.775	9.194	9.19
s	-	-	-	-



Fiber Properties

Fiber	Fiber diameter (μm)	Density (g/cm^3)	Tensile Strength	E-Modulus
			(N/mm^2)	(N/mm^2)
Polyamid	10....40	1.14	840	2'800
E-Glas	7....10	2.55	1'800....3'000	73'000
S-Glas	7....10	2.50	3'900	87'000
C/G	7.....8	1.7...1.9	1'700...7'000	50'000...800'000
Aramid	12	1.44	2'500...3'600	70'000...130'000
Bor	100	2.60	3'000...4'000	420'000
Steel	5...250	7.80	1'800...4'200	210'000
Basalt	6...13	2.7	4'100...4'800	93'000...110'000

Fibre Component

- Fibres provide strength and stiffness
- Properties required of the fibres:
 - 1 high stiffness
 - 2 high ultimate strength
 - 3 low variation of strength between individual fibres
 - 4 stability during handling
 - 5 uniform diameter
 - 6 extremely large length-to-diameter ratio

Fibre Component

- 3 fibres commonly used in infrastructure applications
 - Glass, carbon, aramid
- Factors influencing fibre suitability:
 - ① Strength
 - ② Stiffness
 - ③ Environment and durability
 - ④ Cost
 - ⑤ Availability

Glass Fibres

- Inexpensive
- Most commonly used
- Several grades available:
 - E-Glass
 - R-Glass
 - AR-Glass (alkali resistant)
- High strength, moderate modulus, medium density
- Used in non weight/modulus critical applications

Carbon Fibres

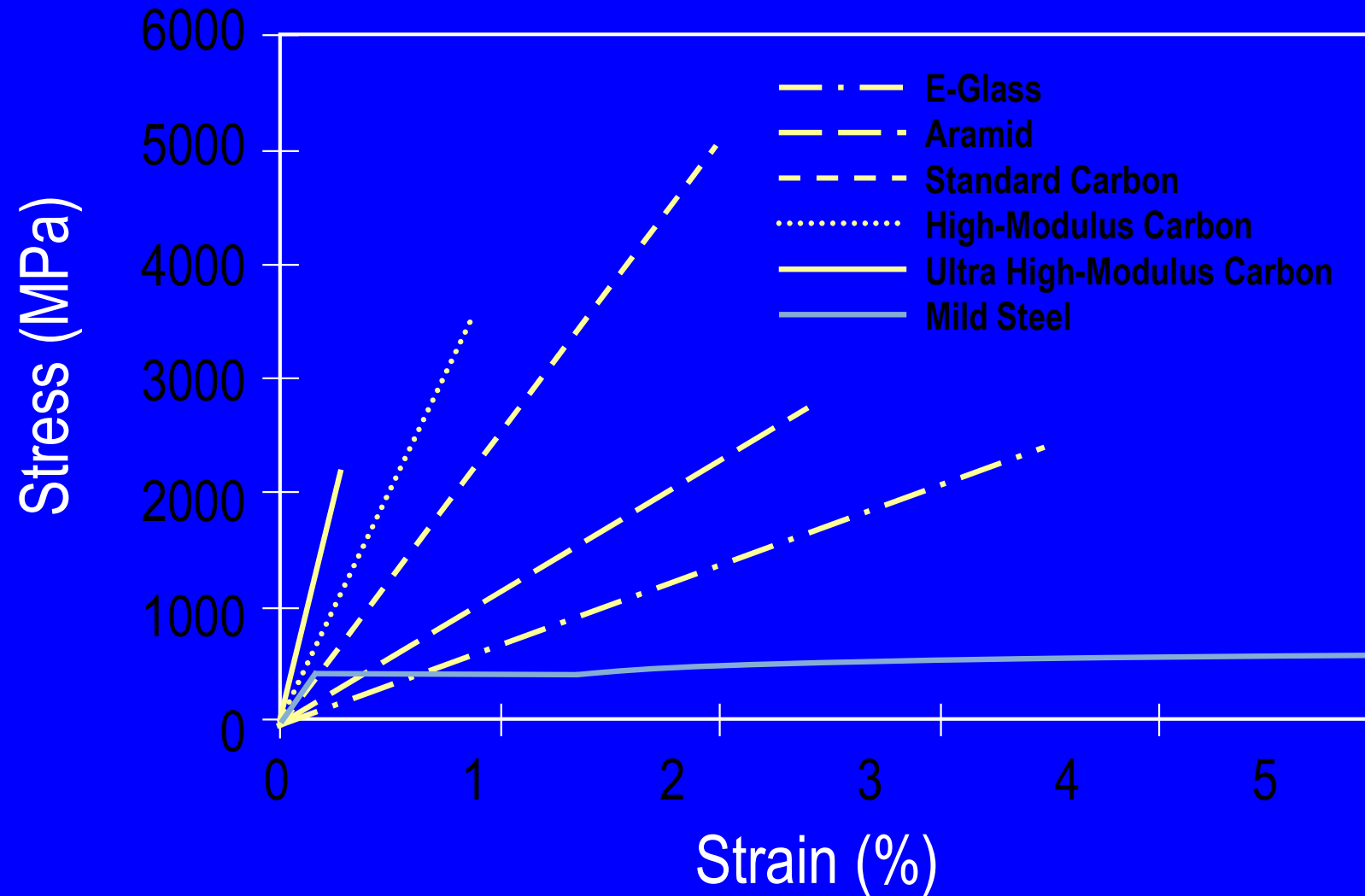
- Significantly higher cost than glass
- Several grades available:
 - Standard modulus → 250-300 GPa
 - Intermediate → 300-350 GPa
 - High → 350-550 GPa
 - Ultra-high → 550-1000 GPa
- High strength, high modulus, low density
- Superior durability and fatigue characteristics
- Used in weight/modulus critical applications

Aramid Fibres

- Moderate to high cost
- Two grades available
 - 60 GPa elastic modulus
 - 120 GPa elastic modulus
- High tensile strength, moderate modulus, low density
- Low compressive and shear strength
- Some durability concerns
 - Potential UV degradation
 - Potential moisture absorption and swelling

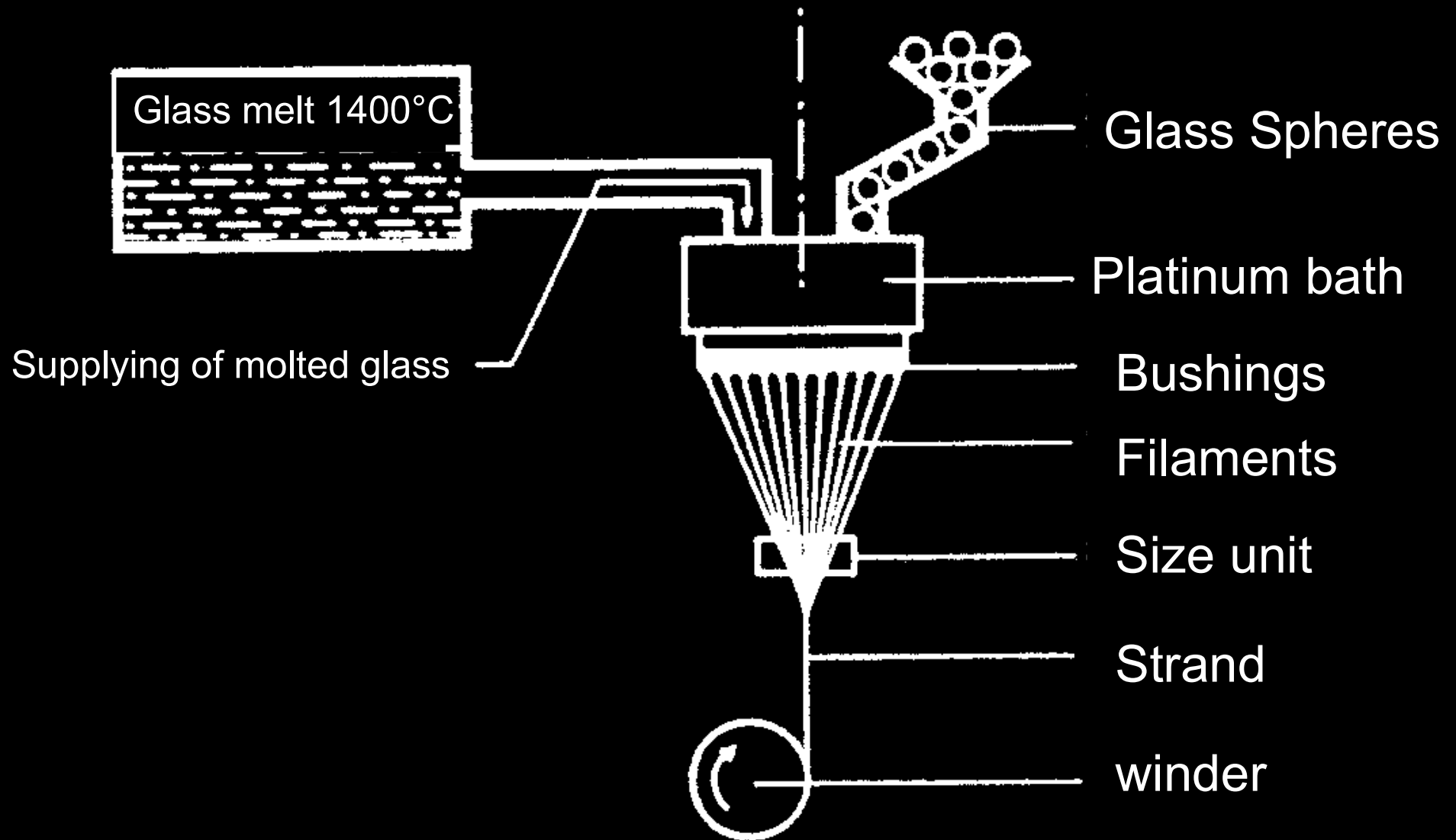
Fibre Comparison: Stress-Strain

Fibres

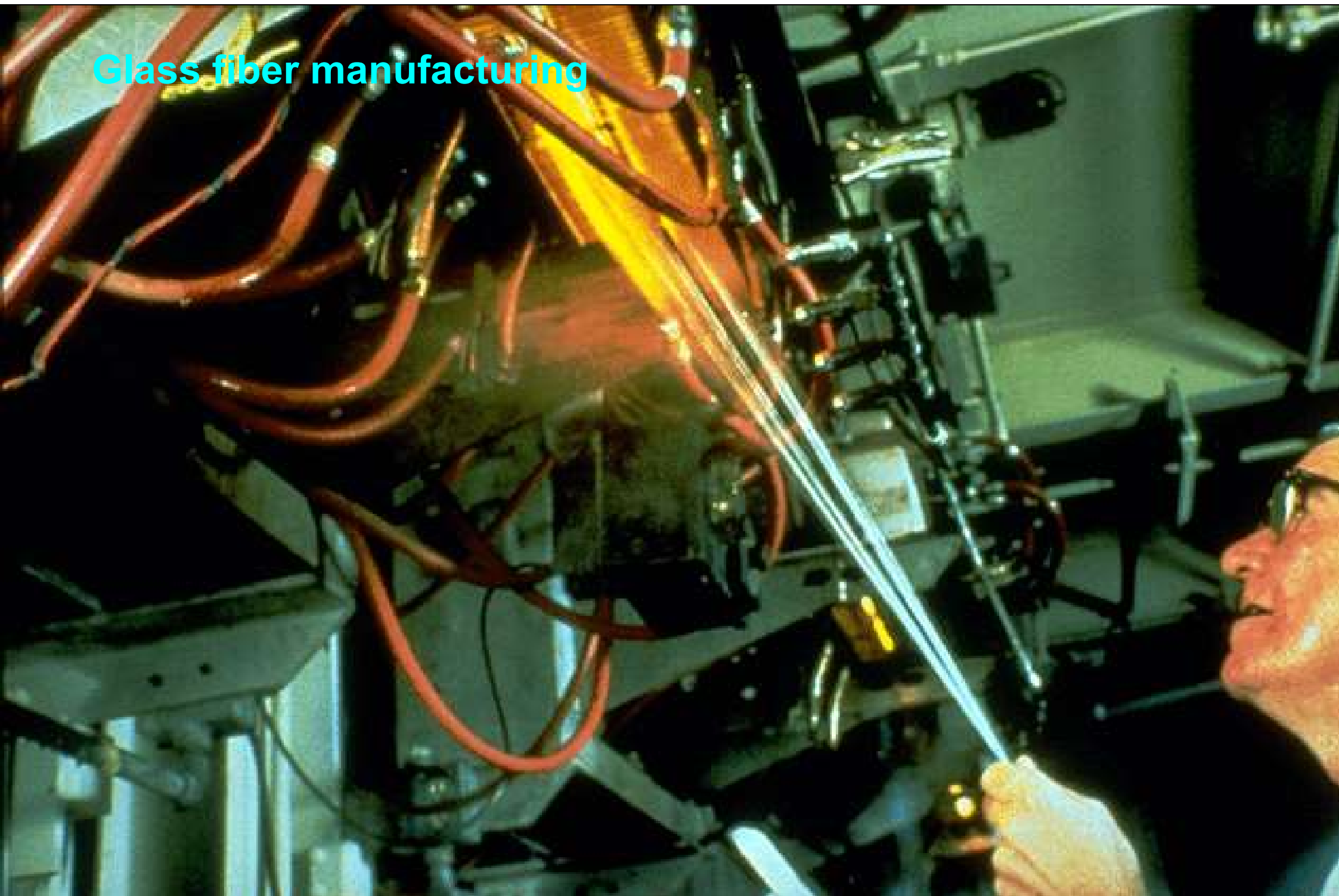


- Fibres only!
- No Matrix

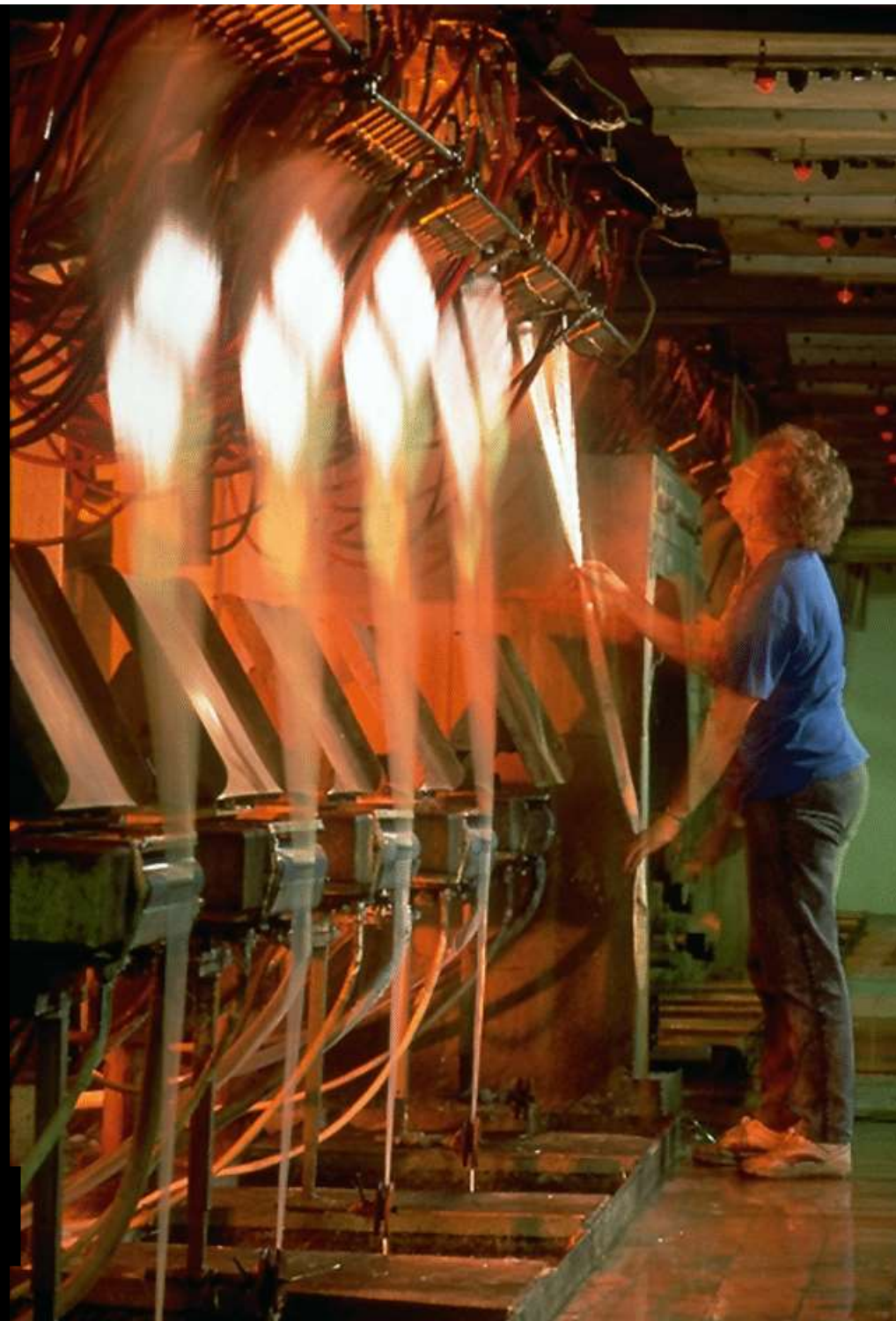
Glass fiber manufacturing



Glass fiber manufacturing



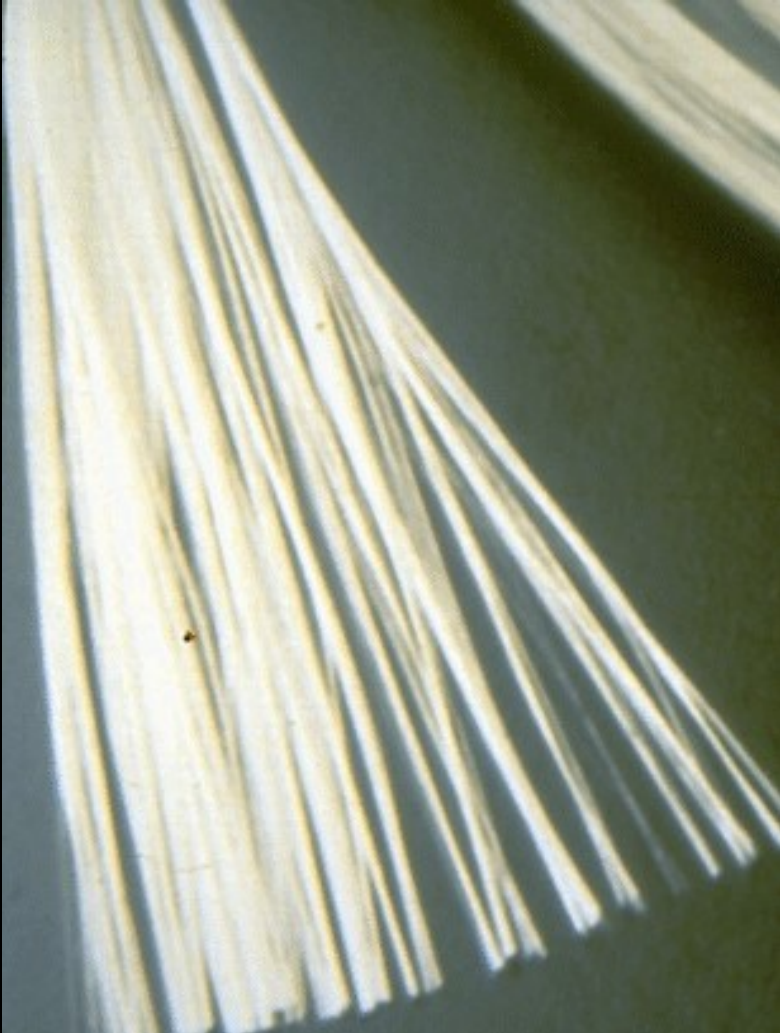
Glass fiber manufacturing



Winding



Roving, Rovings spool



Chopped Rovings, Powder



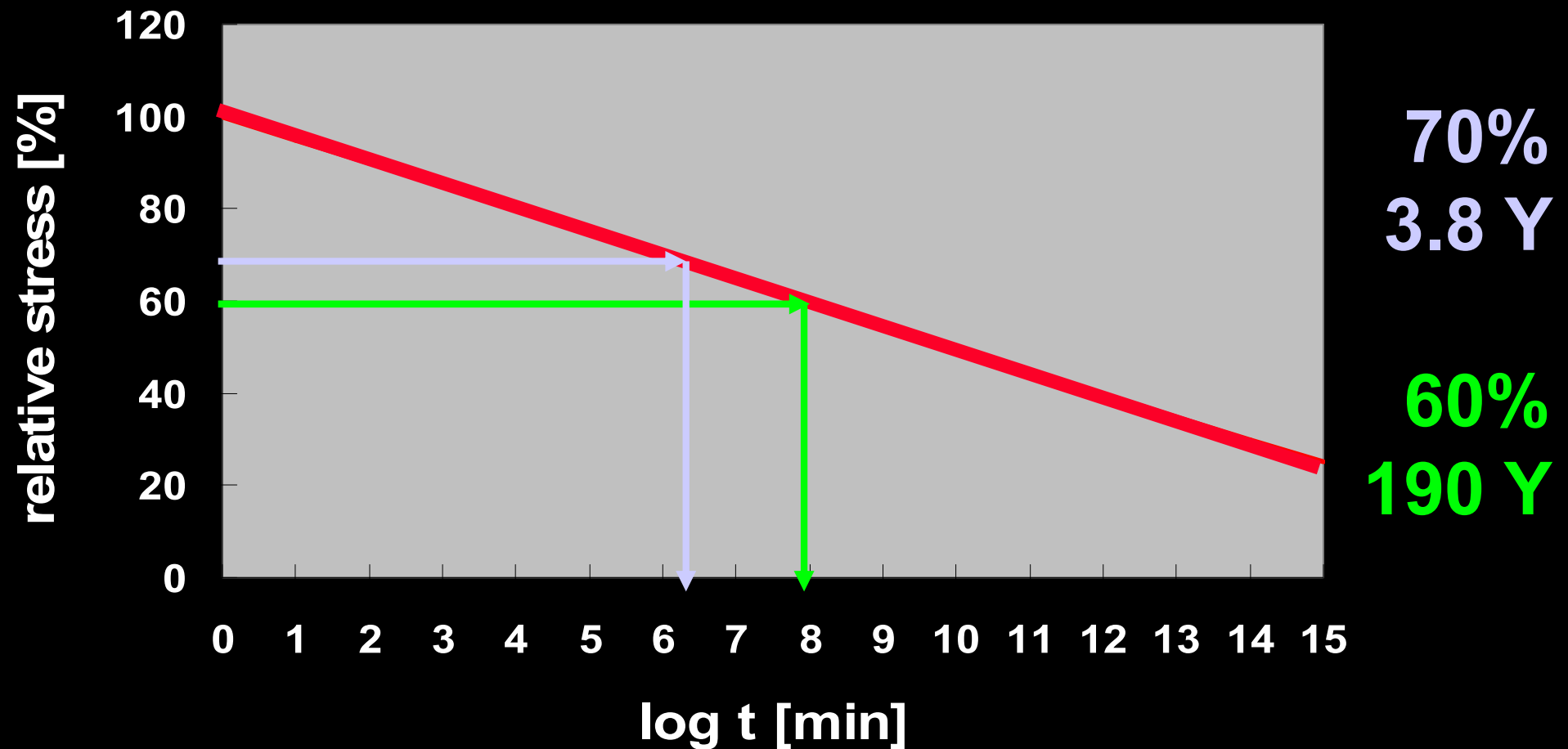
Stress Corrosion of E-Glass

5% drop per decade of time

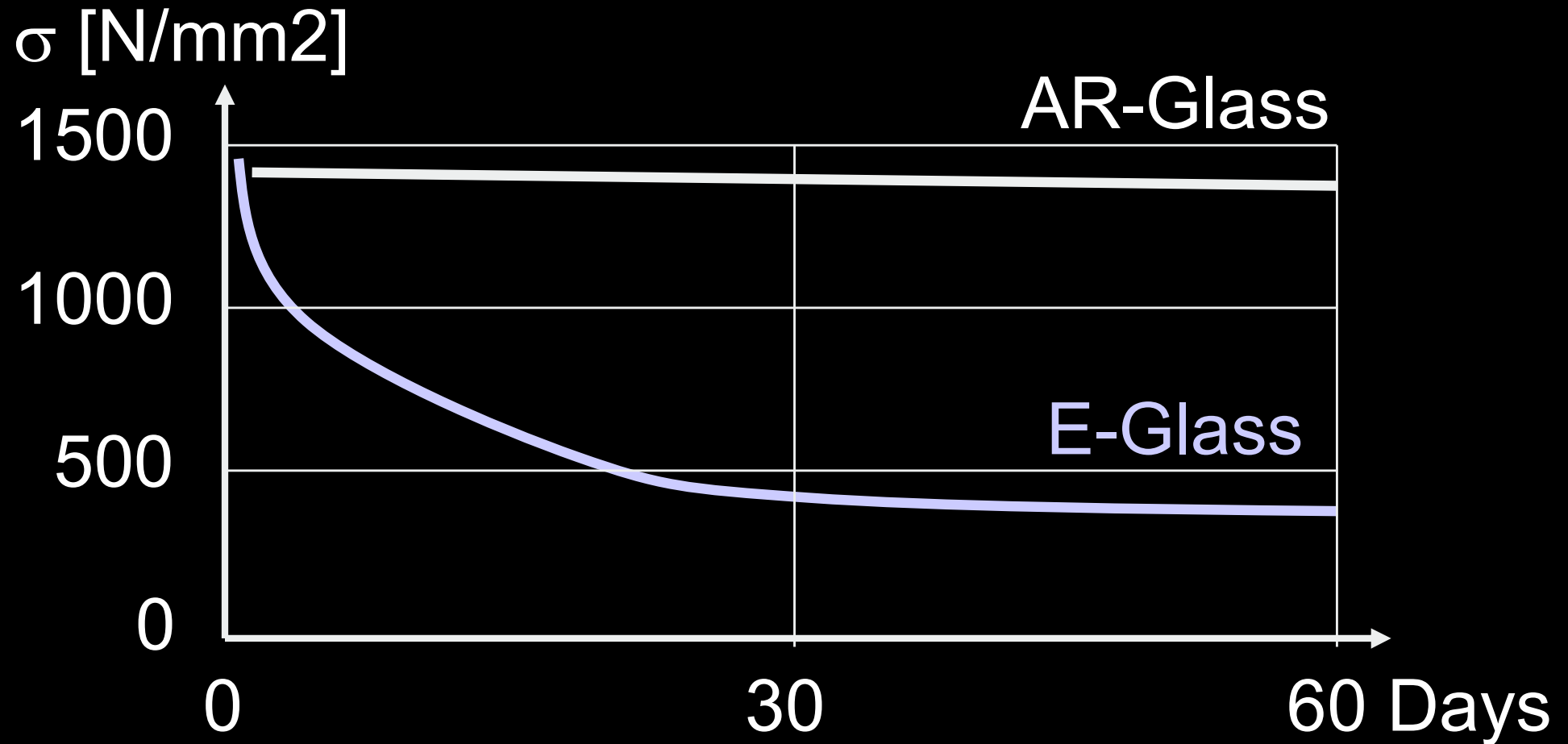
% of Failure Stress: Time to Failure [Years]:

75	.19
70	1.9
65	19
60	190

Stress Corrosion of E-Glass



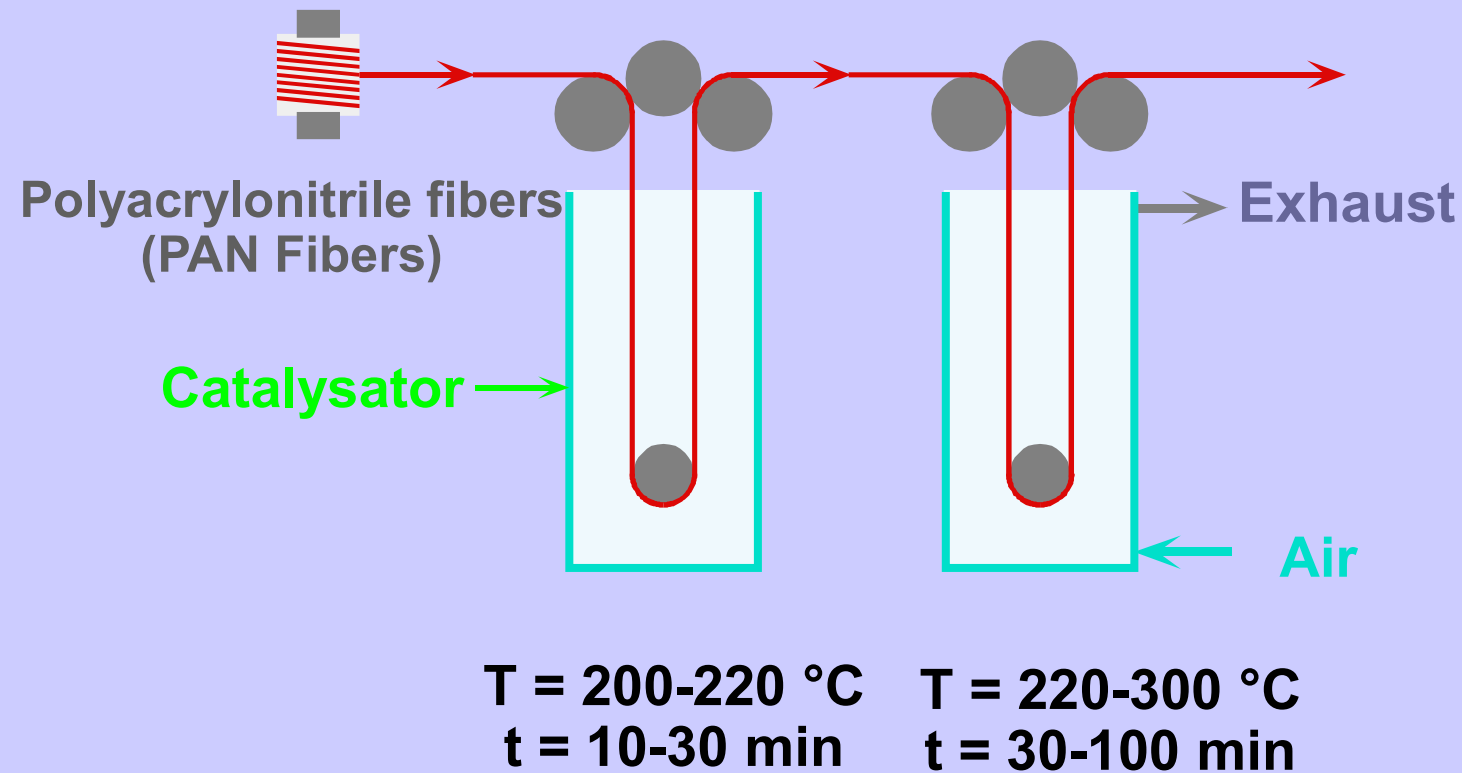
Alkali-Resistancy of glass fibers in liquide Portland-Cement solution at 20°C



Alkali-Resistancy of glass fibers in liquide Portland-Cement solution at 80°C



Manufacturing of C/G-Fibers



1. Step

Fibers are stretched to have dimensional stability

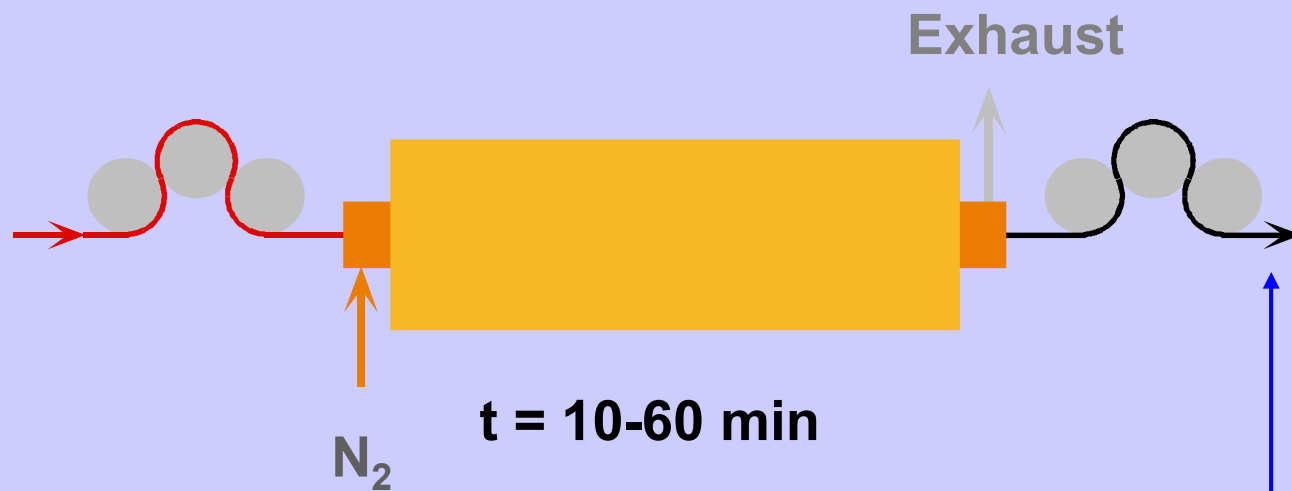
$T = 200-300\text{ }^{\circ}\text{C}$

Manufacturing of C/G-Fibers

2. Step

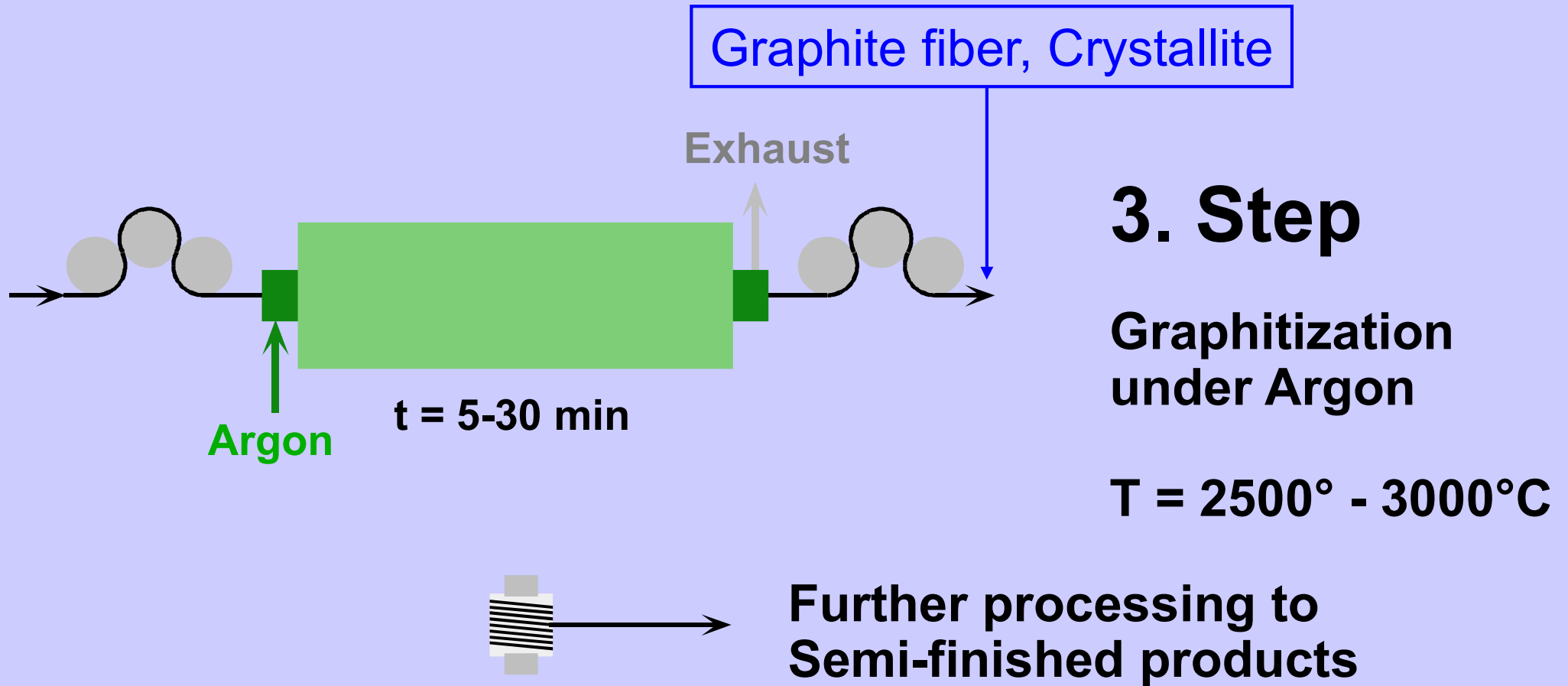
Carbonization

$T = 1500\text{ }^{\circ}\text{C}$



Carbon fiber, Semi crystallite

Manufacturing of C/G-Fibers



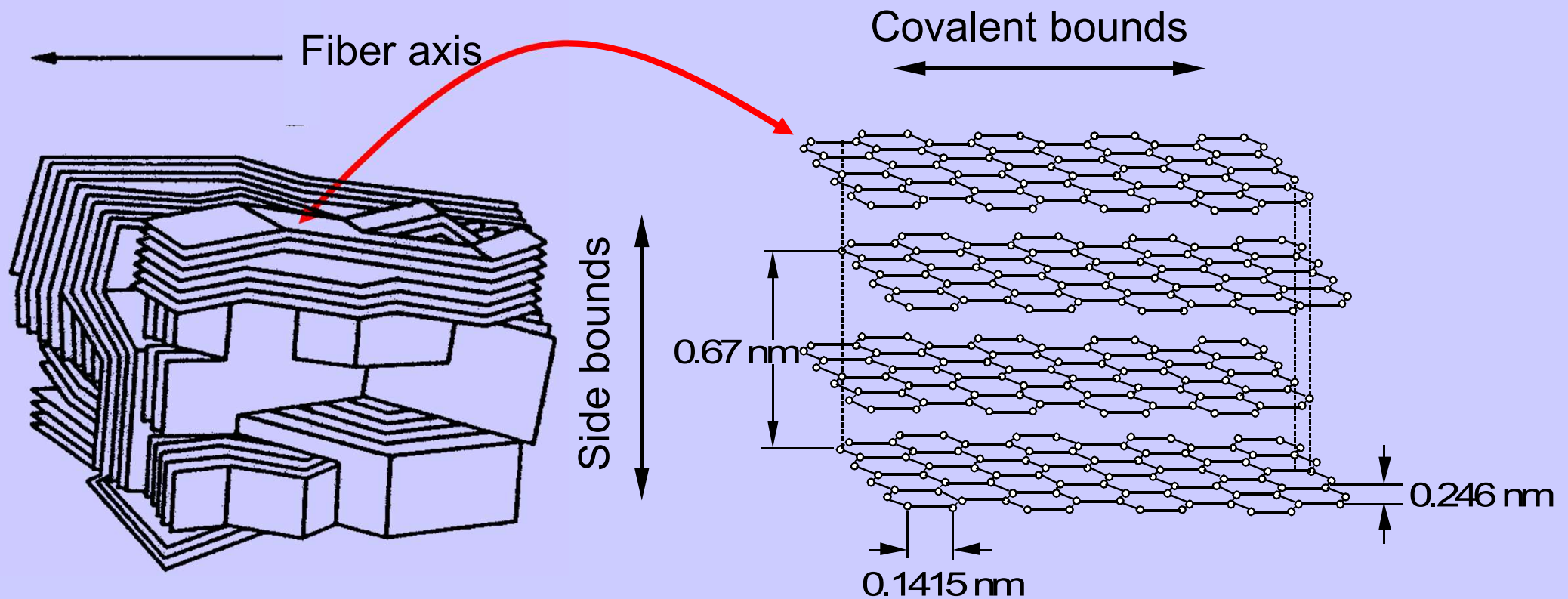
C-Fibers

EMPA

20KV

10µm
X500

Bond structure of C/G-Fibers

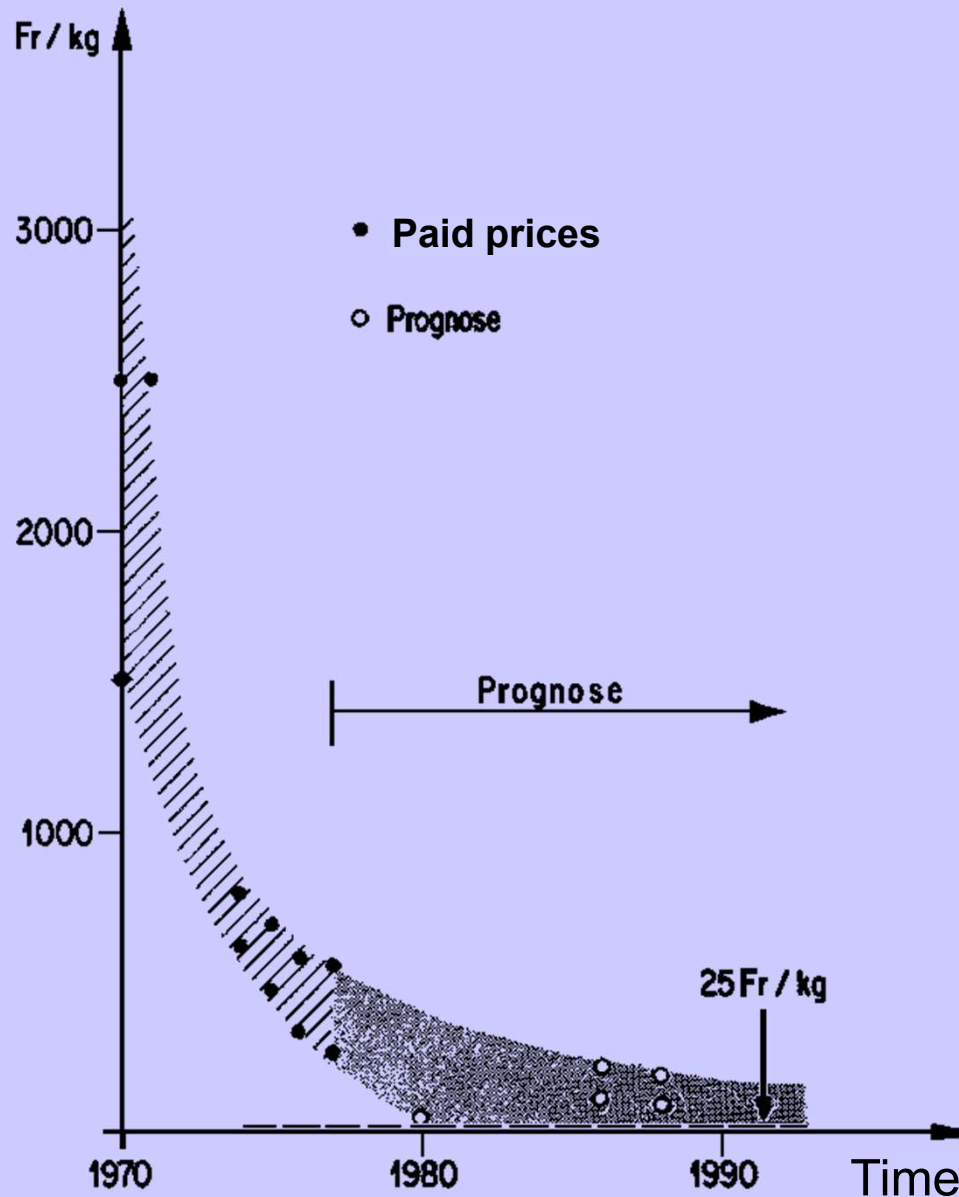


Prediction of carbon fiber prices by
Prof. Urs Meier (EMPA) in 1977.
This prediction was the basis for the
research and development project
'CFRP application in Civil Engineering'!

2500 Fr./kg

23 Fr./kg

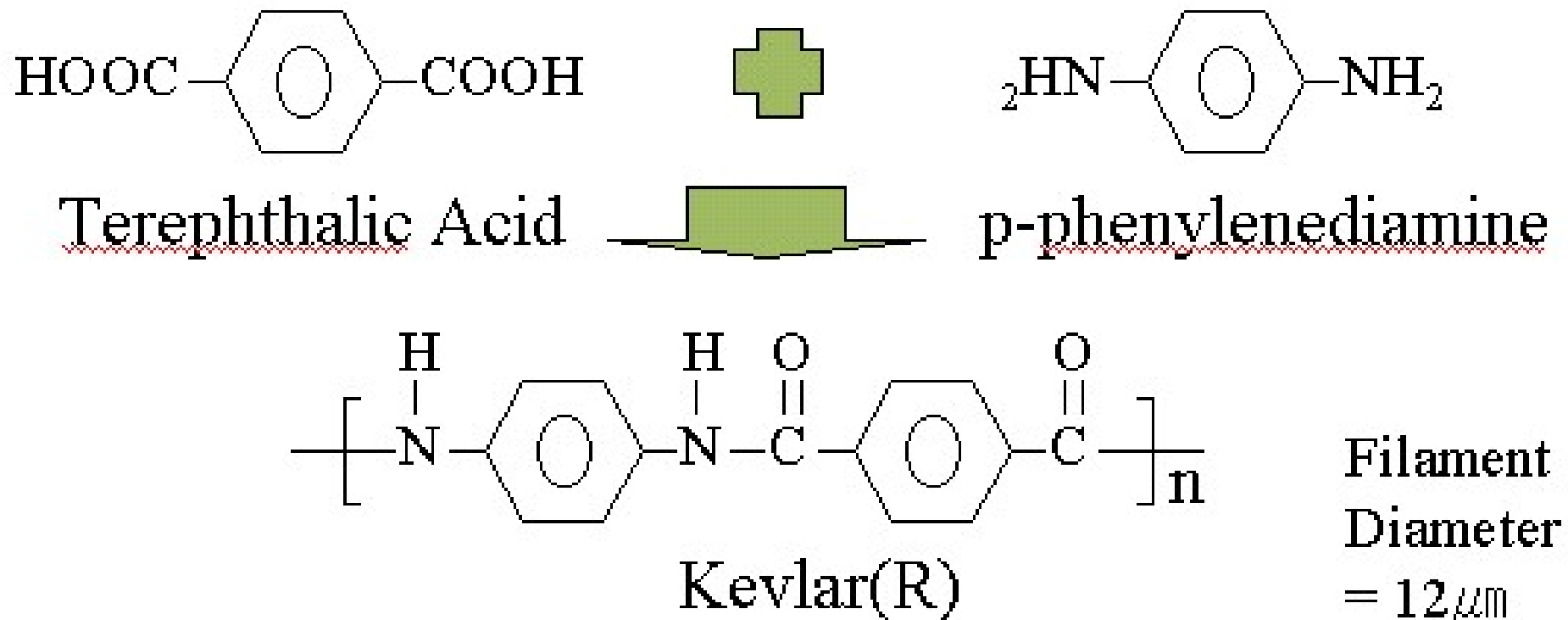
Today: 43 Fr./kg (here!!!!)



Aramid (Kevlar)

Chemical fibers

Developed in the 60s, commercialized in 1971



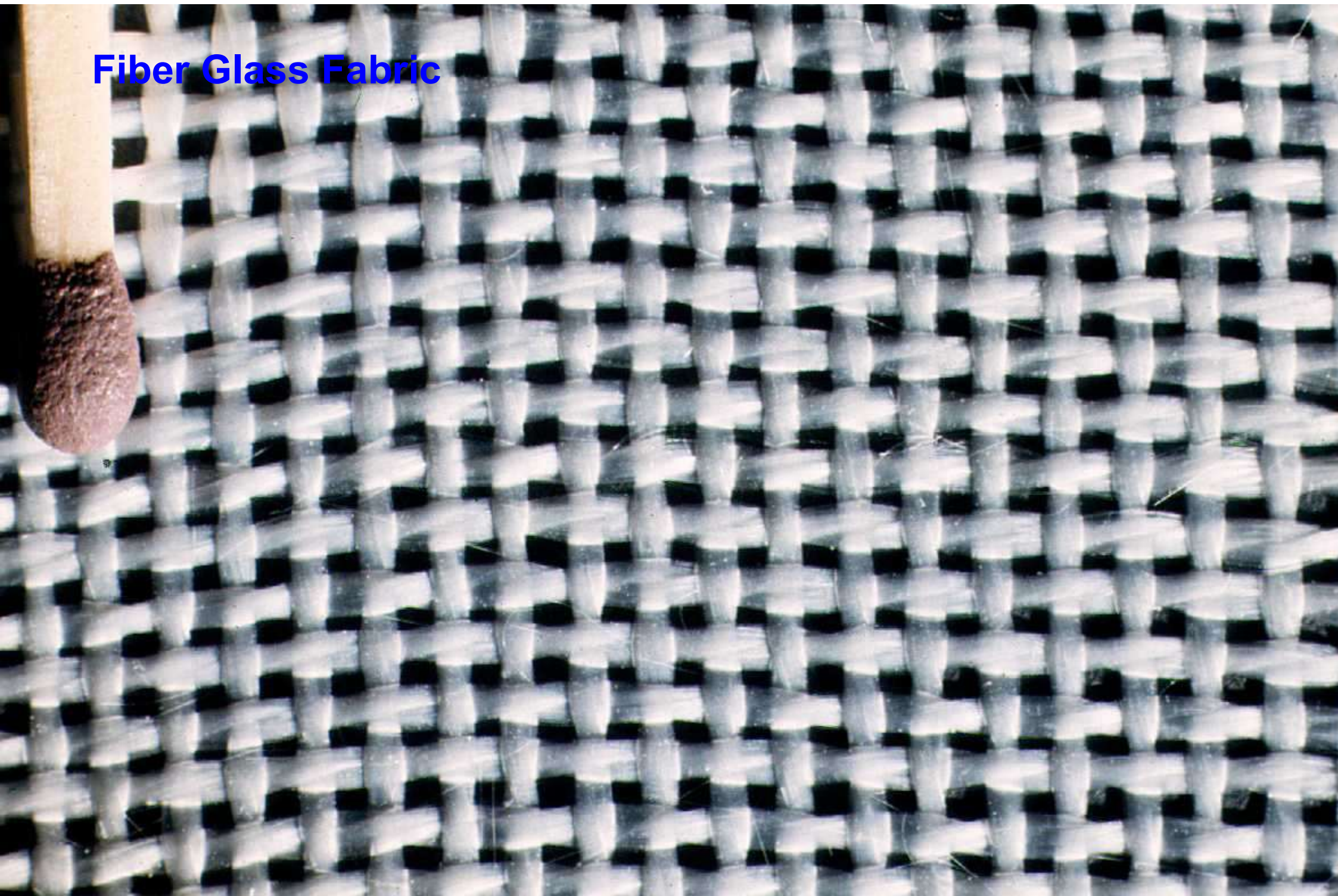
Fiber Reinforced Materials

- Mats
- Fiber Glass Fabric
- Roving Fabric
- Mesh
- Prepreg

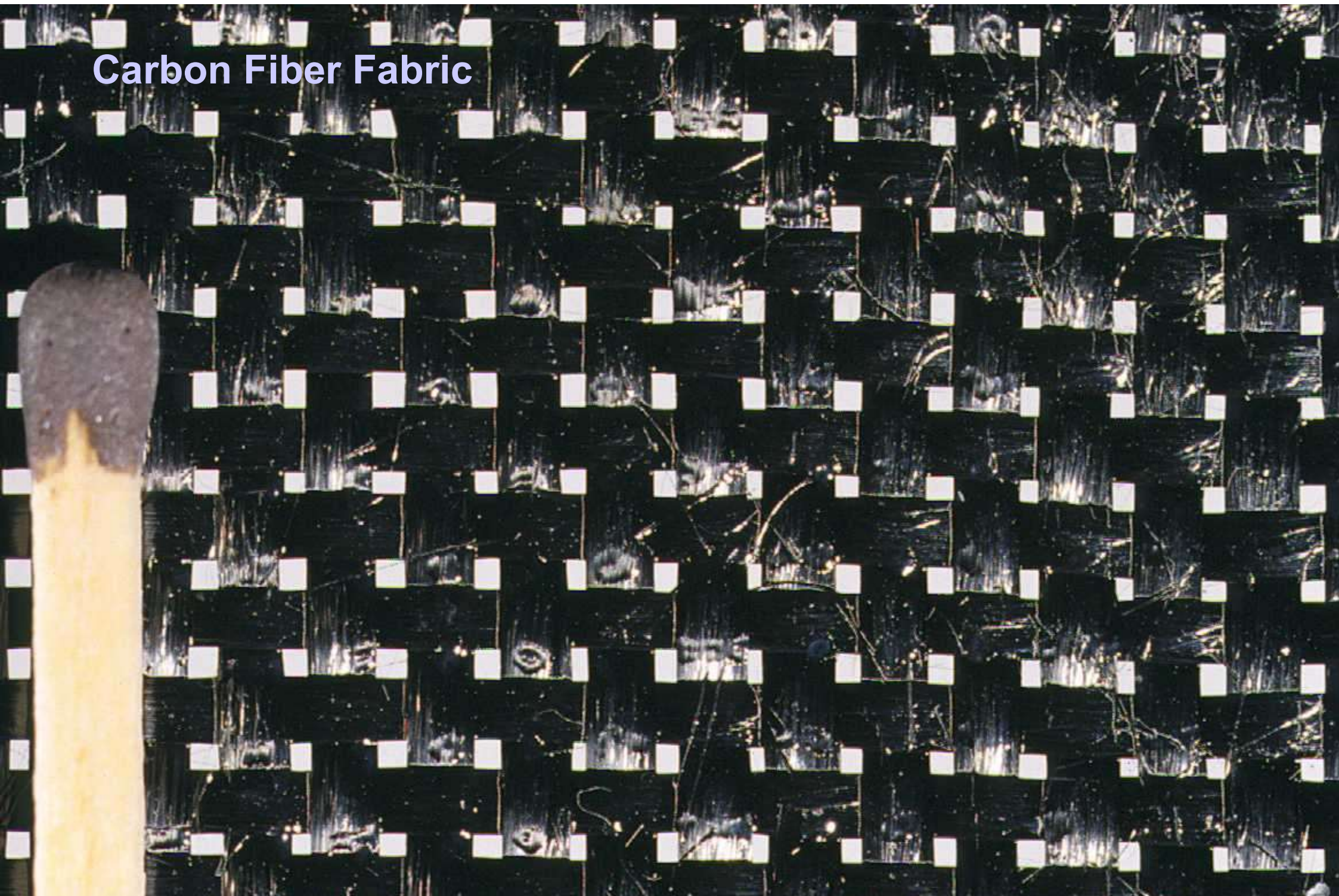
Fiber Glass Mat



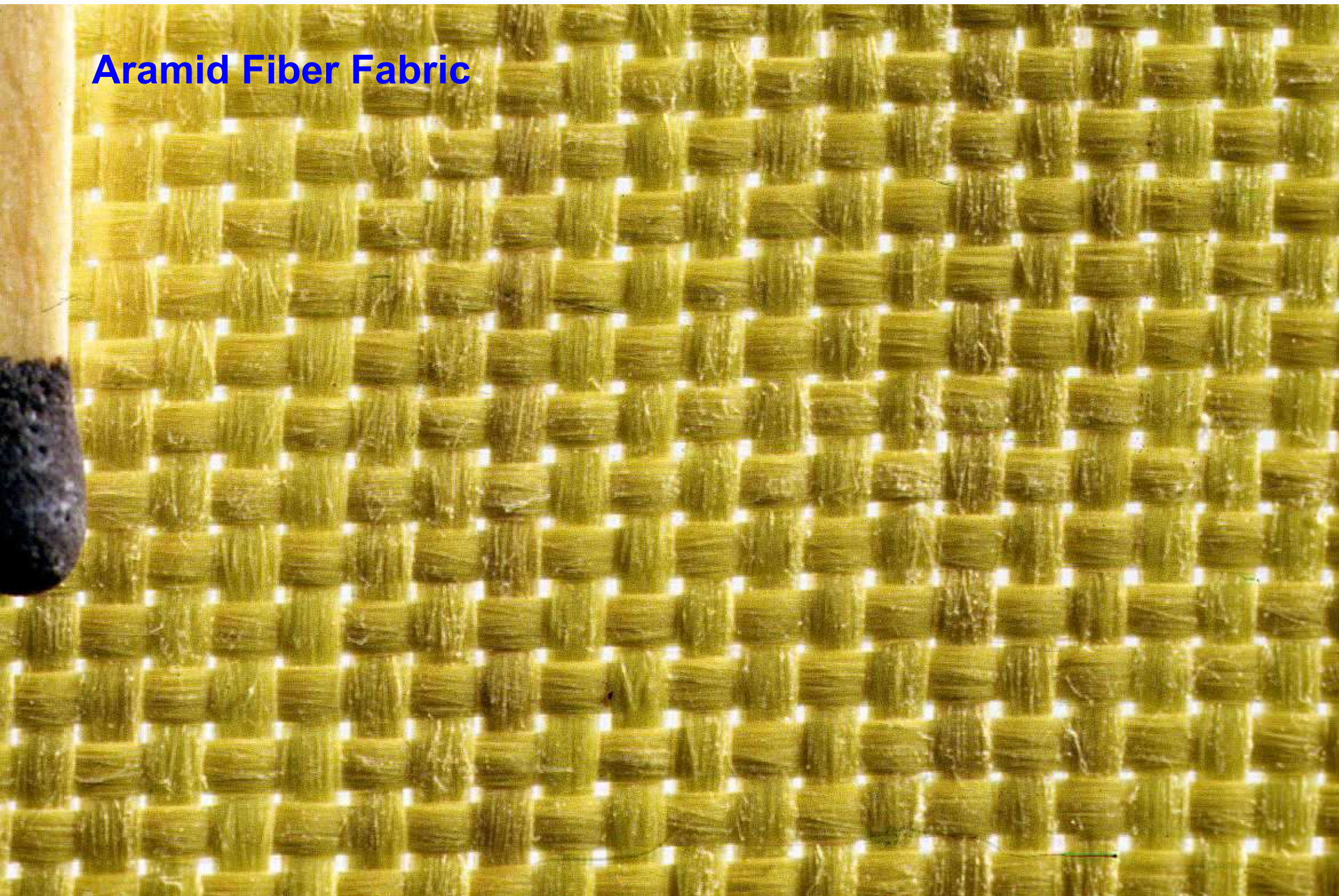
Fiber Glass Fabric



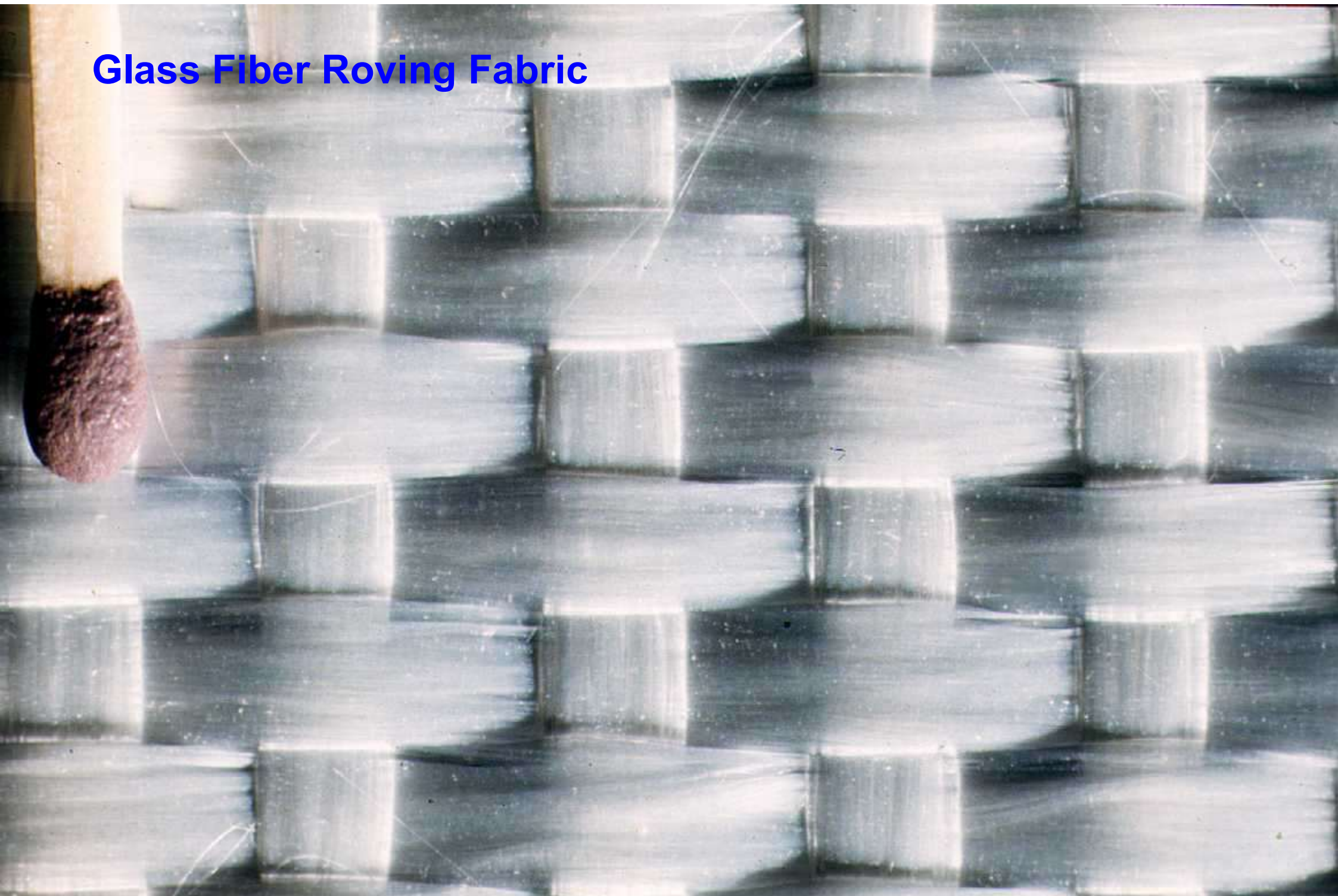
Carbon Fiber Fabric



Aramid Fiber Fabric



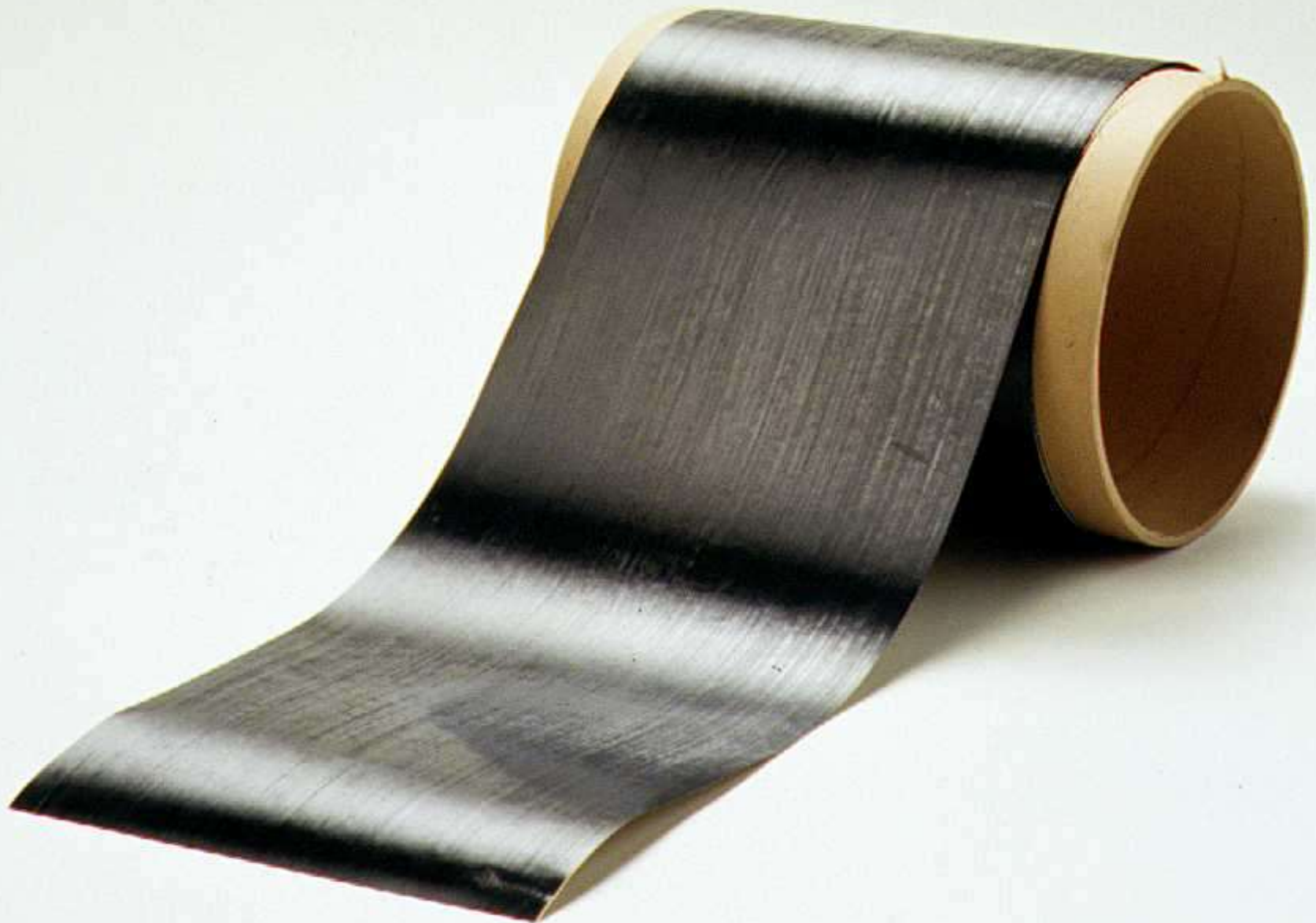
Glass Fiber Roving Fabric



Aramid Fiber Roving Fabric



**Carbon Fiber Prepreg,
unidirectional
(UD)**



Glass Fiber Prepreg (UD)



Glass Fiber Prepreg



Hybrid Mesh of Aramid and C Fibers



Aramid Fiber Mesh Hose



Polymer Matrix Component

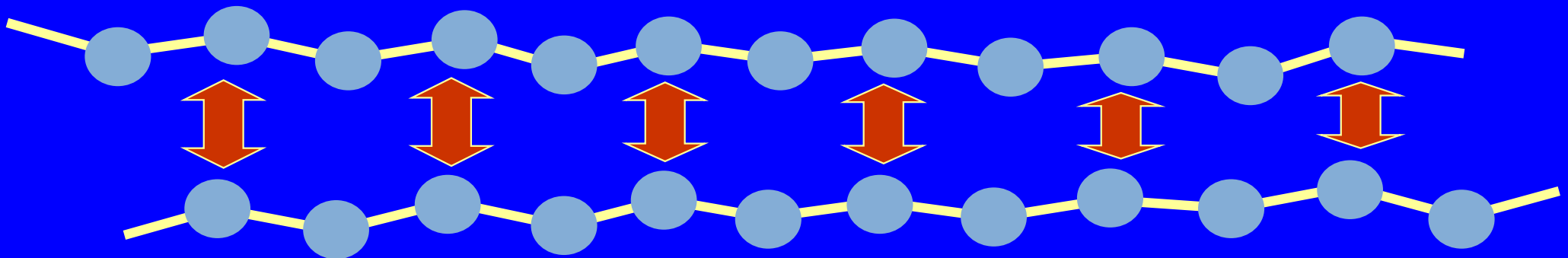
- Critical functions of the polymer matrix:
 - 1 **Bind** the fibres together
 - 2 **Protect** the fibres from environment and abrasion
 - 3 **Separate and disperse** the fibres throughout the composite
 - 4 **Transfer force** between the individual fibres

Polymers

- Polymer:
 - An **organic** compound comprised of **long-chain** molecules consisting of smaller repeated units called **monomers**
- Two types:
 - ① **Thermoplastics**
→ polyethylene, nylon, polyamide
 - ② **Thermosetting polymers**
→ polyester, vinylester, epoxy

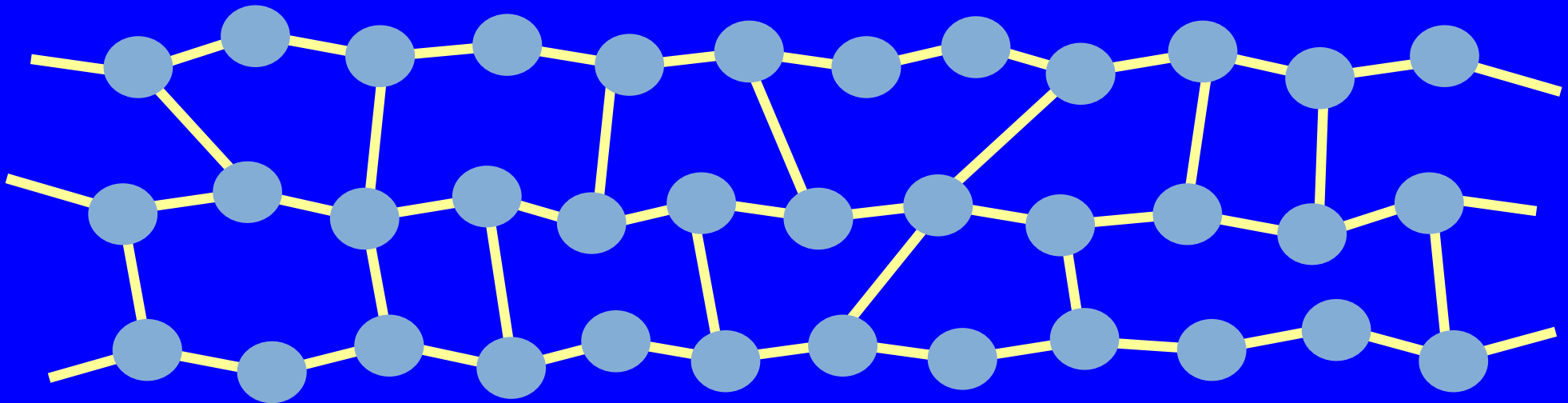
Thermoplastics

- Extremely strong bonds within chain molecules
- Chains held by weak Van der Waals Forces
 - Molecules can slide past one-another on heating
 - Polymer can be reversibly softened
- **Not currently used for FRPs in civil engineering**



Thermosetting Polymers

- Molecular chains cross-linked through chemical bonds
 - Cannot be reversibly softened → cannot be bent on site!
 - deteriorate irreversibly at elevated temperature
- Commonly used in infrastructure FRPs
 - **Epoxies, vinylesters, polyesters**



Thermosets used in Civil Engineering

- **Polyesters**
 - Widely used for FRP components (not for rebars)
 - **Inexpensive**, easy processing
- **Vinylesters**
 - Used commonly in **FRP rebars** (alkali resistance)
 - Reduced moisture absorption and shrinkage
 - More expensive
- **Epoxies**
 - Used in **wet lay-up** applications and laminate fabrication
 - Outstanding **adhesion and bonding** characteristics
 - Highest cost

Matrix Properties

Matrix		Density (g/cm ³)	Tensile Strength at 23°C (N/mm ²)	E-Modulus at 23°C (N/mm ²)
UP	Cold Cured	1.2	70	3'500
	Warm Cured	1.2	60	3'500
EP	Cold Cured	1.2	70	3'500
	Warm Cured	1.2	90	3'500
PEEK		1.3	100	3'800

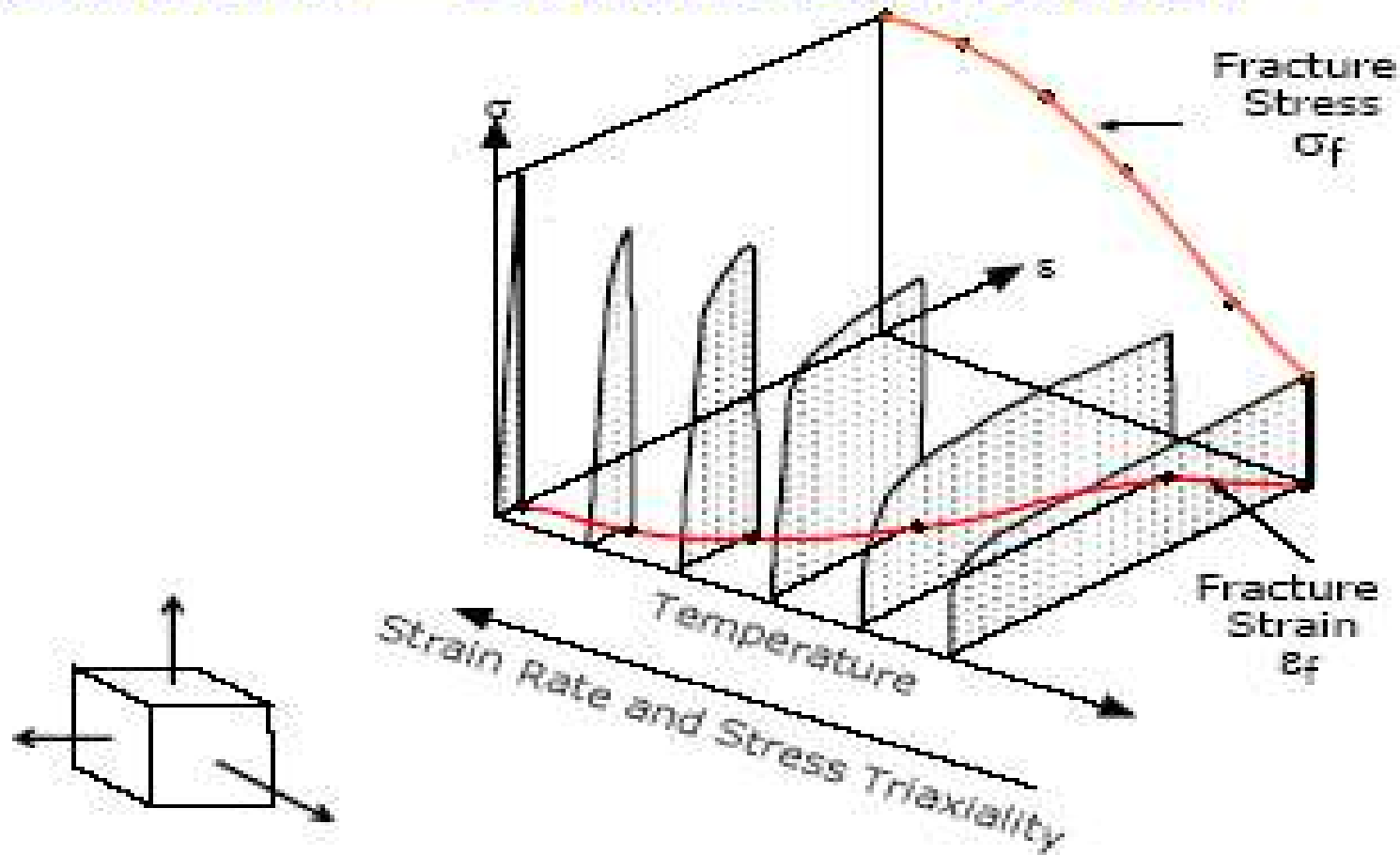
UP: Unsaturated Polyester Resin (Thermoset)

EP: Epoxy Resin (Thermoset)

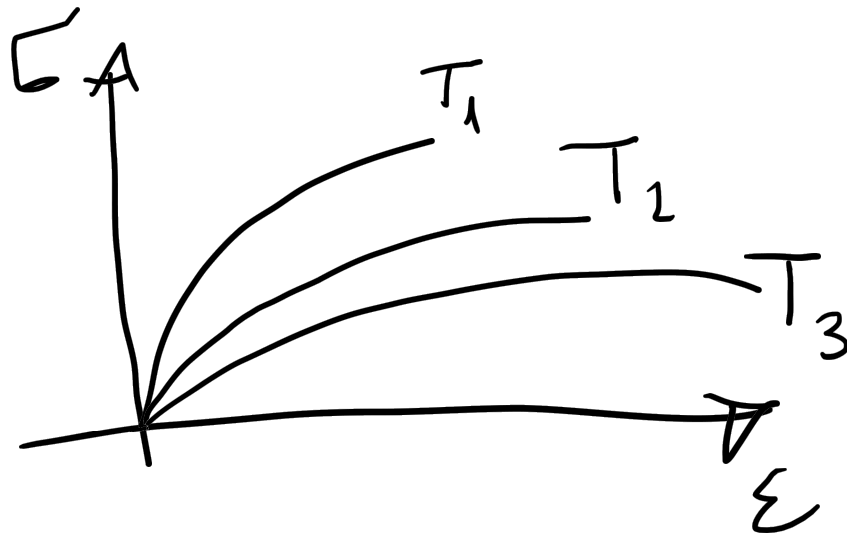
PEEK: Polyetheretherketone (Thermoplastic)

Viscoelasticity

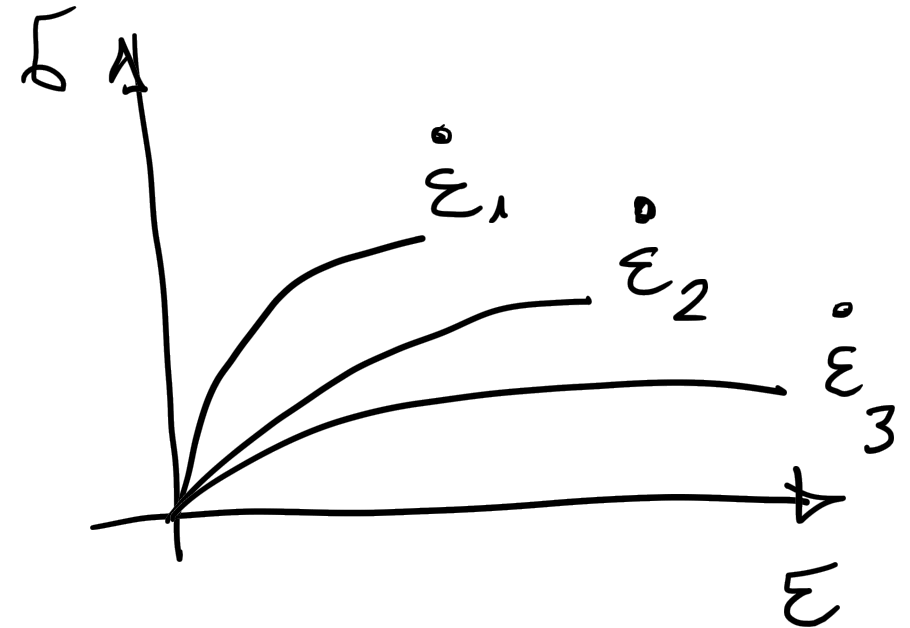
Ductile - Brittle Behavior



57



$$T_1 < T_2 < T_3$$



$$\dot{\epsilon}_1 > \dot{\epsilon}_2 > \dot{\epsilon}_3$$

Polymers at diff T and $\dot{\epsilon}$

Mechanical Properties of Polymers

- Each covalent bond in an individual molecule behaves like a spring with modulus κ . Application of a constant stress, σ , results in an instantaneous and constant strain, ϵ , according to Hooke's Law

$$\sigma = \kappa \epsilon$$

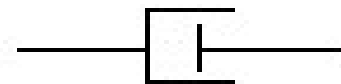


This behavior is elastic and reversible.

Mechanical Properties of Polymers

- An applied force also causes movement (slip) of chains past each other. This movement involves overcoming energy barriers (secondary forces) and is a rate process associated with viscous flow according to Newton's Law.

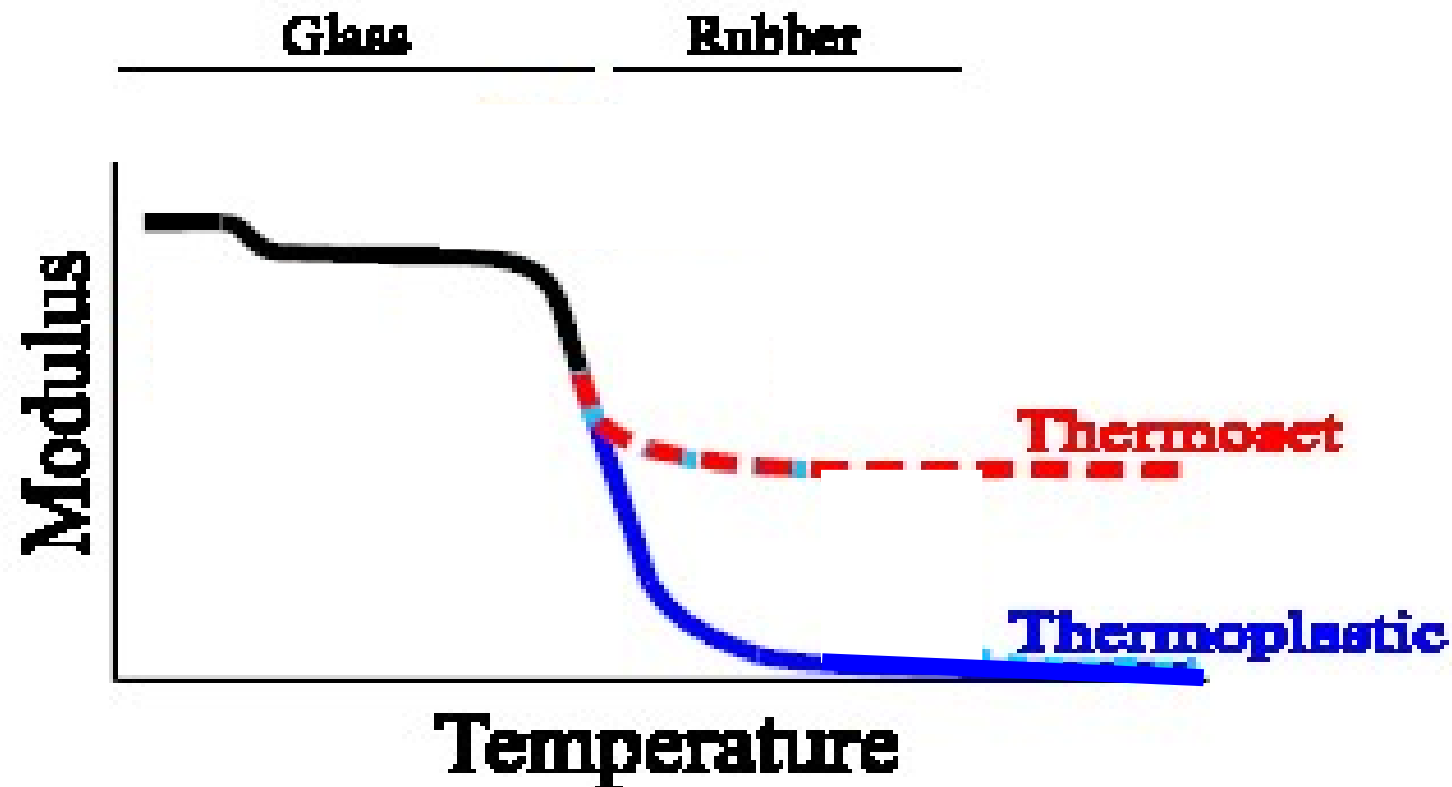
$$\sigma = \eta \frac{d\varepsilon}{dt} = \eta \dot{\varepsilon}$$



Polymer Viscoelasticity

- This combination of elastic and viscous behavior results in a time-dependent response to a constant stress or strain. This gives rise to the characteristic viscoelasticity of polymers.

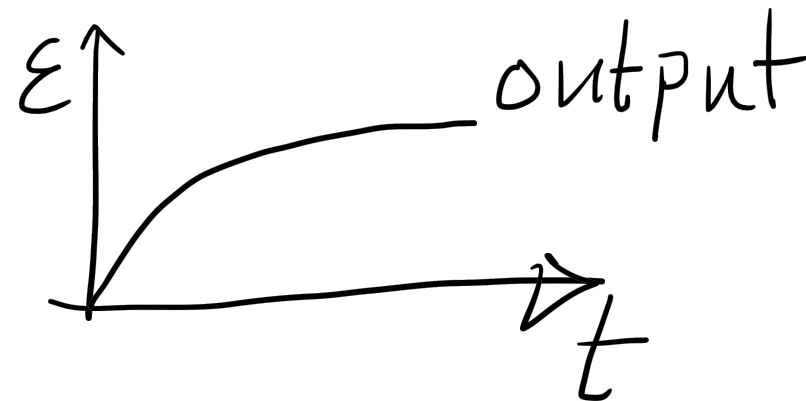
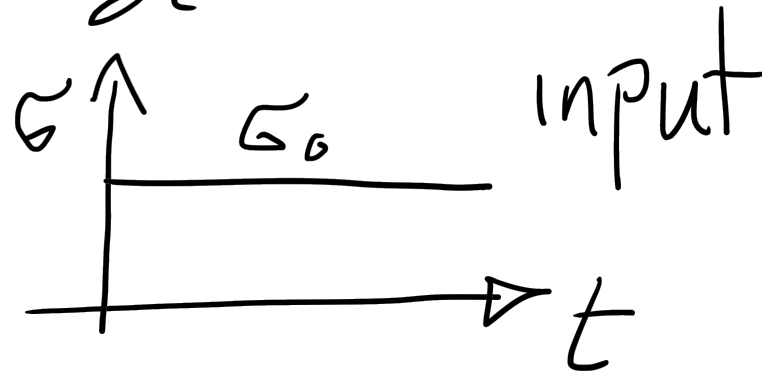
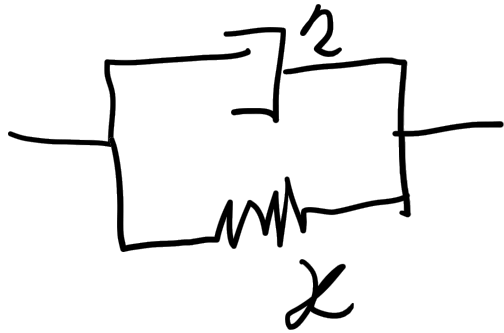
Viscoelastic Polymer Behavior



Courtesy: D. Hunston

$$\dot{\epsilon} = \frac{\partial \epsilon}{\partial t}$$

Kelvin



$$\left\{ \begin{array}{l} \sigma_s = \lambda \epsilon_s \end{array} \right.$$

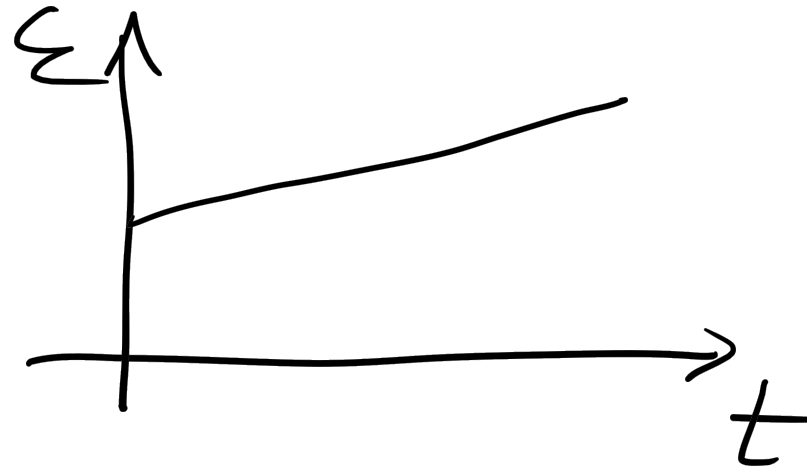
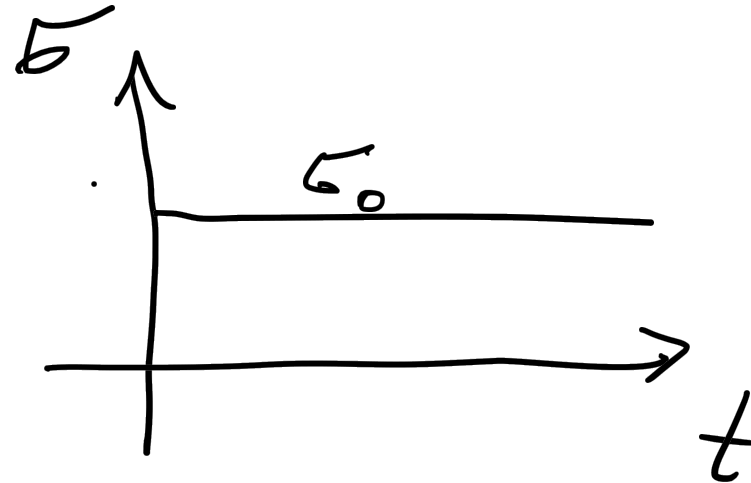
$$\left\{ \begin{array}{l} \sigma_D = \eta \dot{\epsilon}_D \end{array} \right.$$

$$\left\{ \begin{array}{l} \bar{\sigma} = \sigma_s + \sigma_D \\ \epsilon = \epsilon_s = \epsilon_D \end{array} \right.$$

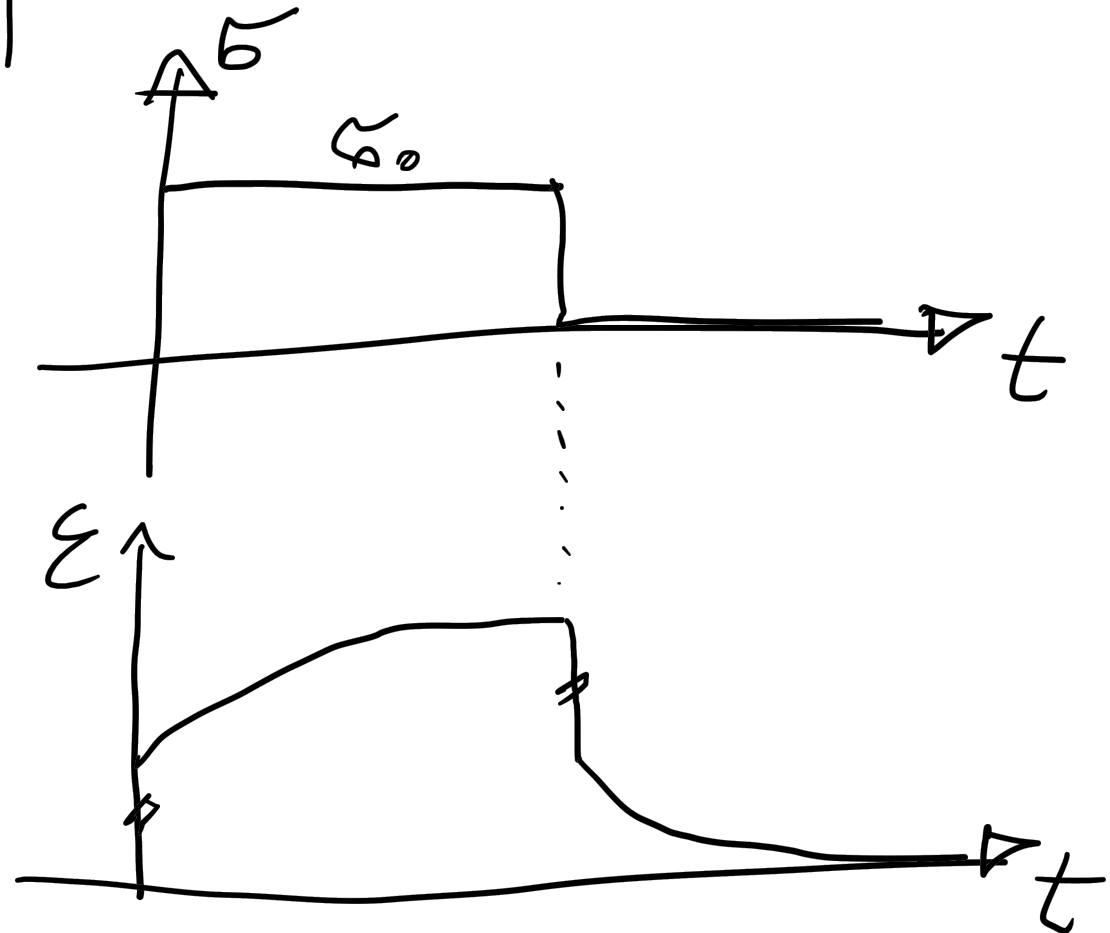
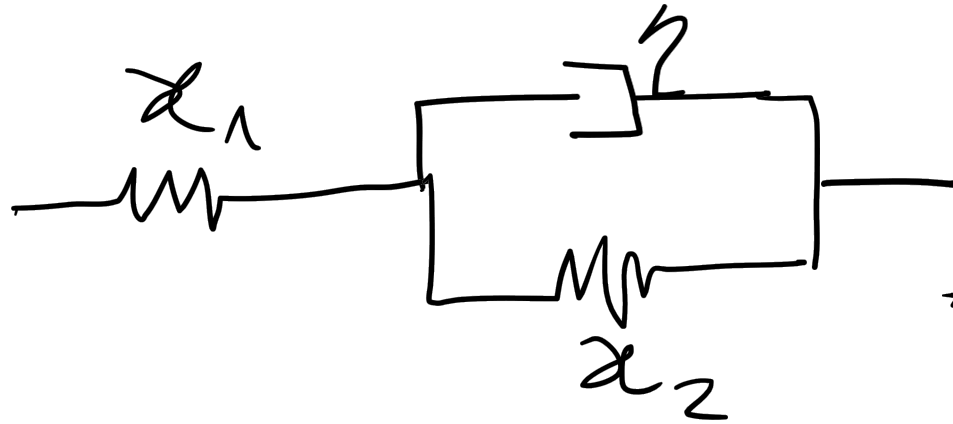
Maxwell



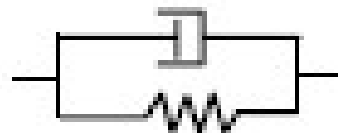
$$\begin{cases} \sigma = \sigma_s = \sigma_D \\ \epsilon = \epsilon_s + \epsilon_D \end{cases}$$



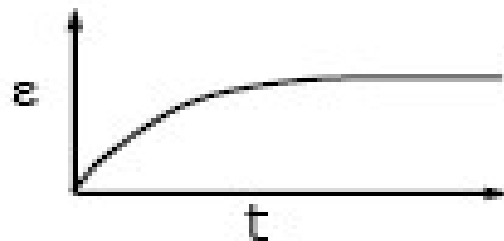
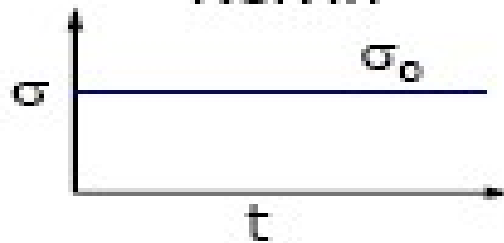
3-Parameter Solid



Linear Viscoelasticity



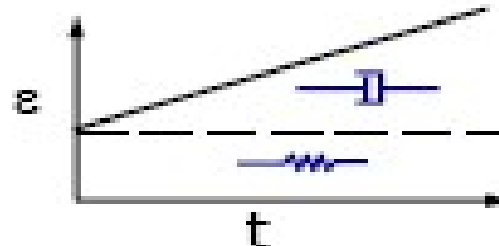
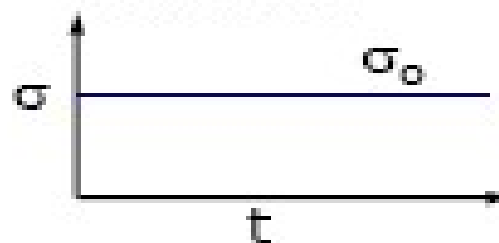
Kelvin



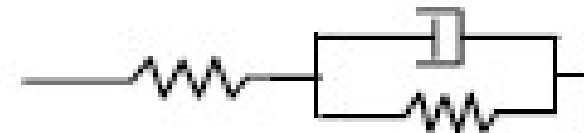
- No instantaneous response
- Solid



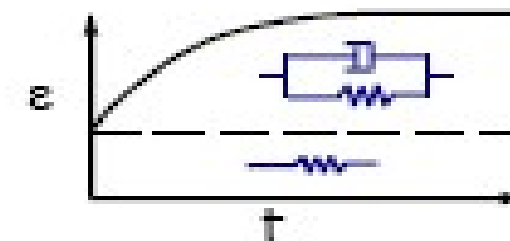
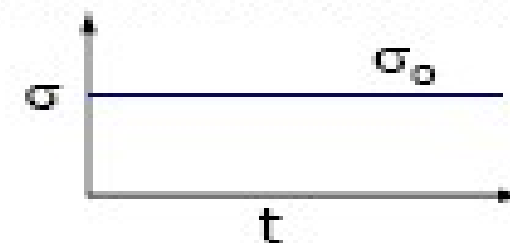
Maxwell



- Instantaneous response
- Fluid

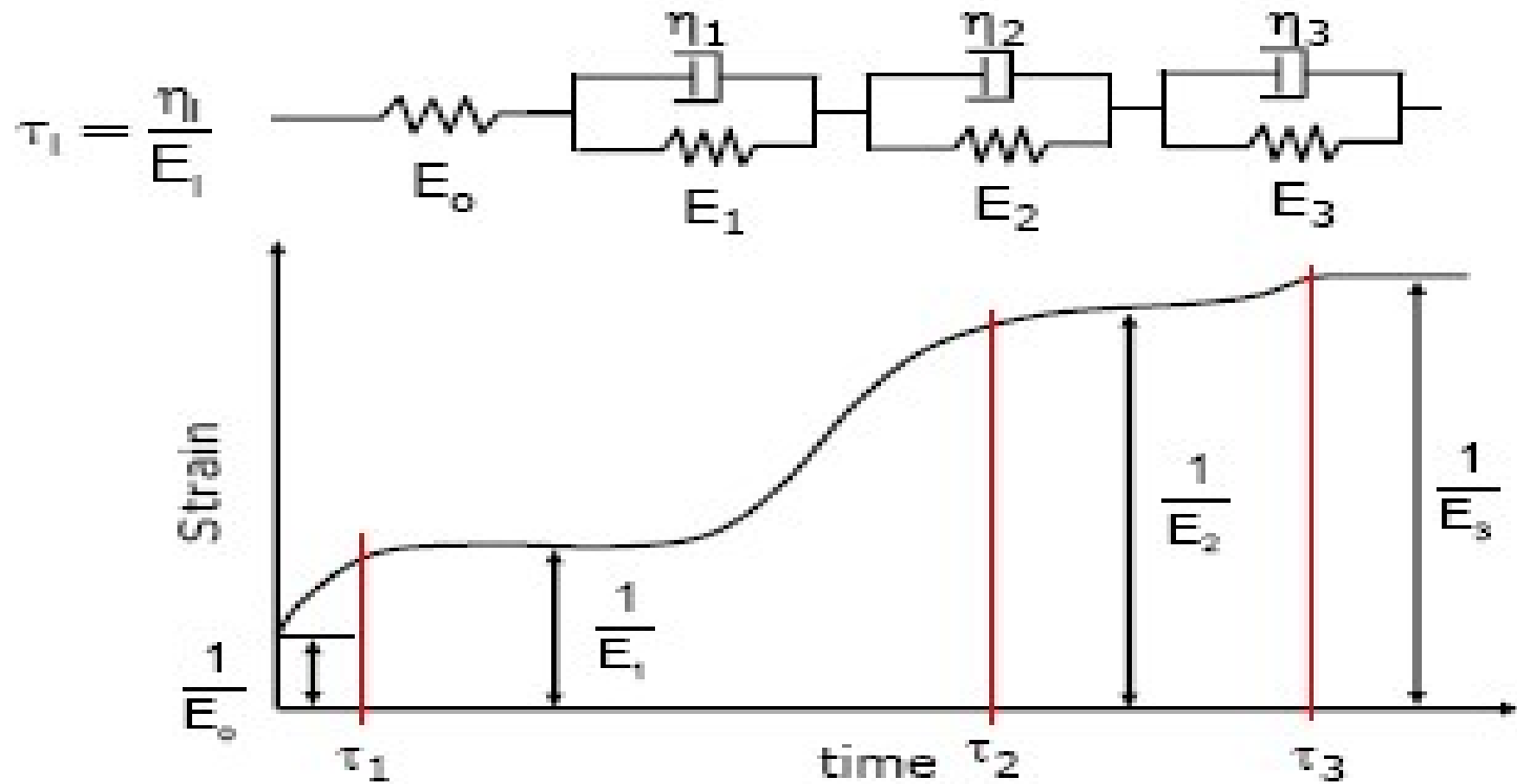


3-Parameter Solid

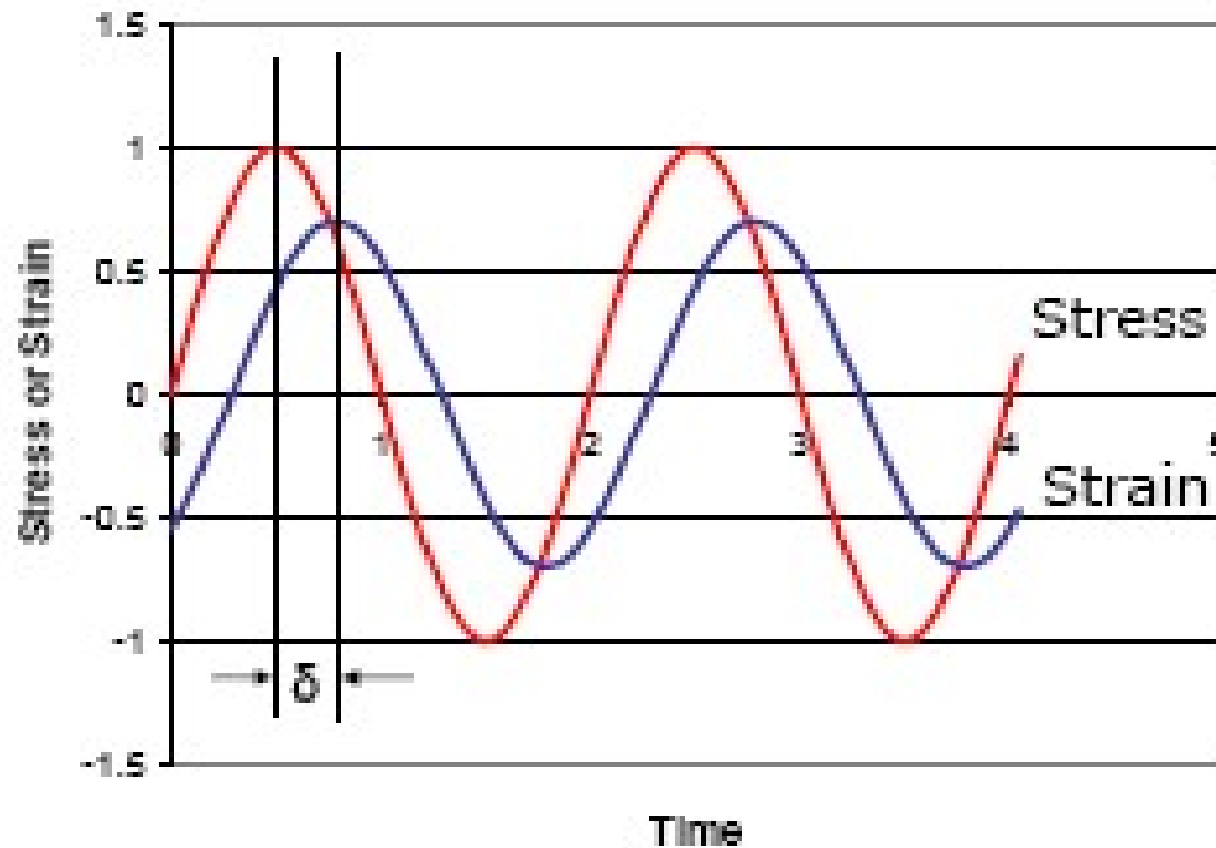


- Instantaneous response
- Solid

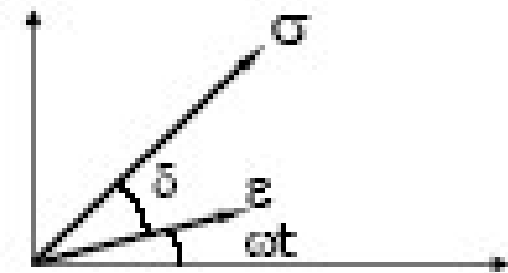
Modeling the Linear Viscoelastic Response



Viscoelasticity

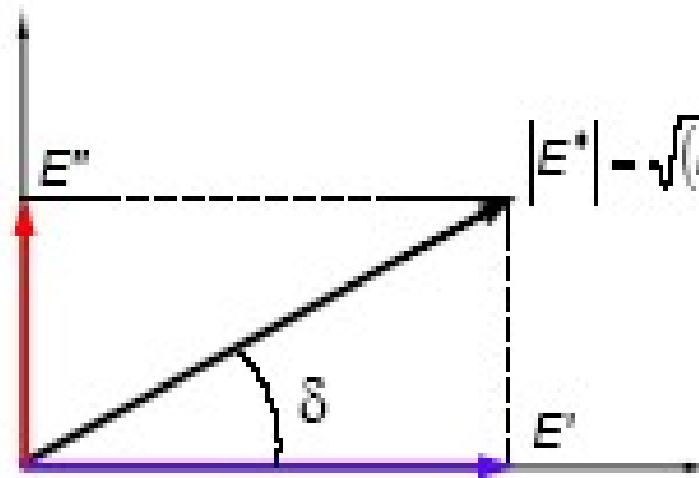


$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$
$$\epsilon(t) = \epsilon_0 \sin(\omega t)$$



Viscoelastic materials: the strain lags the applied stress

Complex Modulus



E' - Storage Modulus

E'' - Loss Modulus

$$\tan(\delta) = \frac{E''}{E'}$$

$$\sigma(t) = \varepsilon |E^*| \cos(\omega t + \delta)$$

Spring



$$\delta = 0^\circ$$

Dashpot



$$\delta = 90^\circ$$

Viscoelasticity: Nomenclature

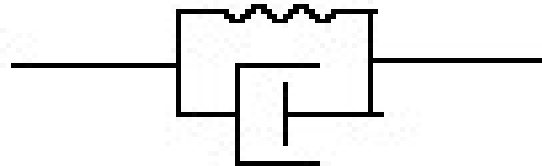
- Time-dependent strain that results from a constant applied stress is called *creep*.
- Time-dependent stress that results from a constant applied strain is called *stress relaxation*.
- The result (stress or strain) of removing a strain or stress is called *recovery*.

Simple Models to Represent Behavior

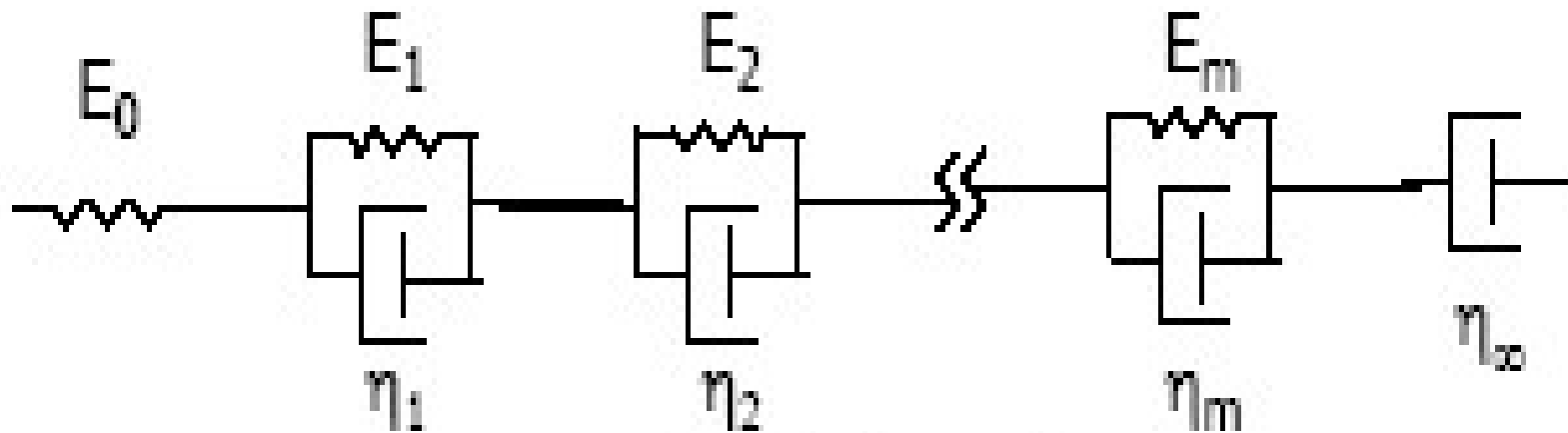
- Based on combinations of Hookean springs and Newtonian dashpots
- Series models (Maxwell fluid)



- Parallel models (Voigt or Kelvin solid)

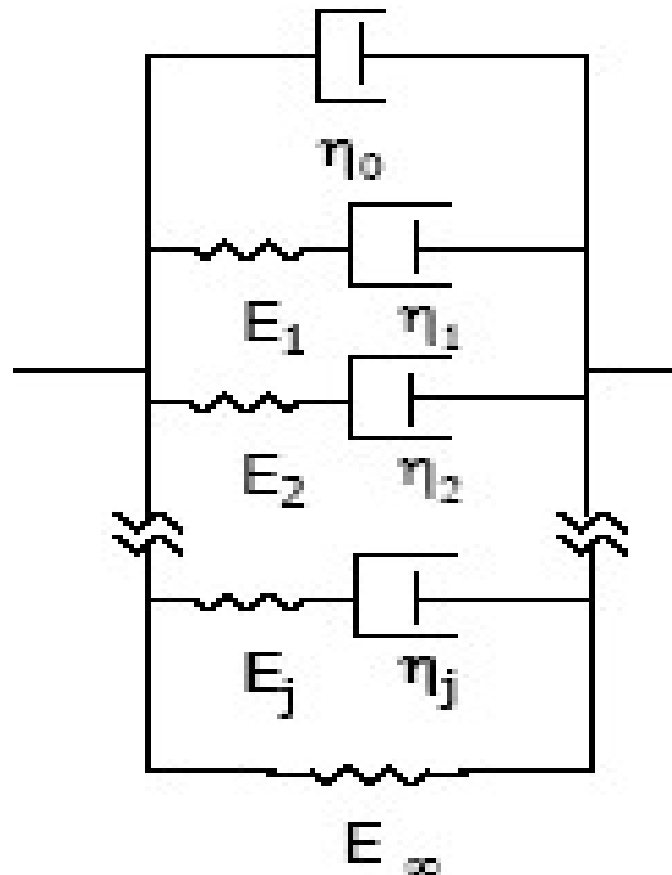


Generalized Models



Generalized Kelvin Chain

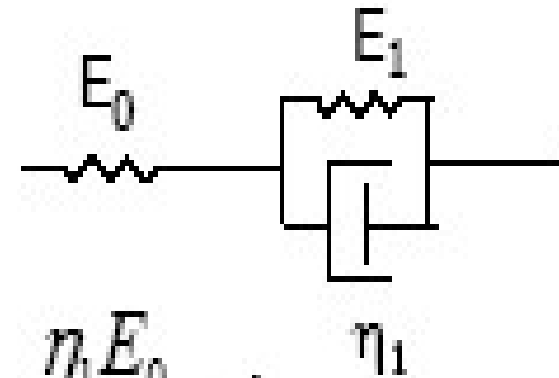
Generalized Models



Generalized Maxwell Model

Dynamic Response of Viscoelastic Materials

Example: Three-parameter solid



$$\text{GDE: } \sigma + \frac{\eta_1}{E_0 + E_1} \dot{\sigma} = \frac{E_0 E_1}{E_0 + E_1} \varepsilon + \frac{\eta_1 E_0}{E_0 + E_1} \dot{\varepsilon}$$

FRP

- Fibres + Matrix = **FRP**
 - Overall FRP properties depend on:
 - Mechanical properties of matrix
 - Mechanical properties of fibres
 - Fibre volume fraction
 - Fibre cross sectional area
 - Orientation of fibres within matrix
 - Interaction between fibres and matrix
 - Method of manufacturing
- **Key Factor**

Influence of Fibre Orientation

- FRPs are ***Orthotropic*** materials

- Properties are directionally dependent

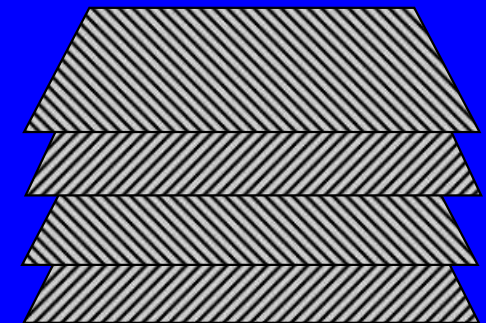
- Unidirectional FRPs

- Fibres in one direction only
- Aligned along longitudinal axis
- Stronger and stiffer in fibre direction



- Multidirectional FRPs (laminates)

- Fibres in various directions (fibre architecture)
- Properties can be tailored
- Behaviour can approach isotropy



- Unidirectional FRPs used in infrastructure applications

Examples of FRPs

Unidirectional
glass FRP bar

Carbon FRP
prestressing
tendon



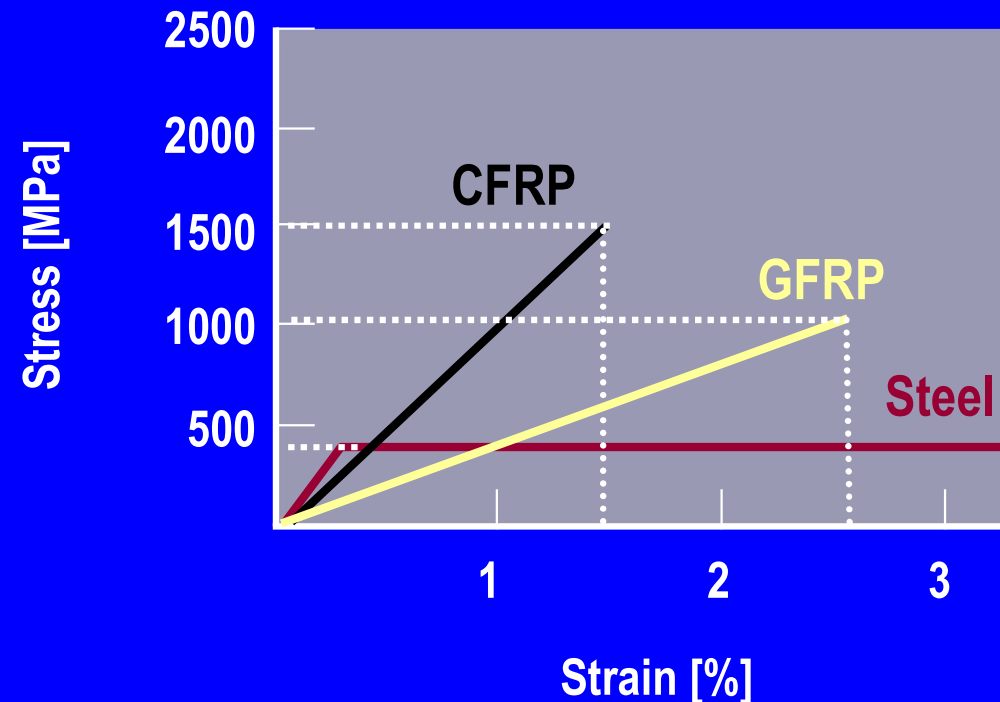
Glass FRP
grid

Glass fibre
roving

Carbon fibre
roving

FRP vs. Steel

- FRP properties
(in general versus steel):
 - Linear elastic behaviour to failure
 - No yielding
 - Higher ultimate strength
 - Lower strain at failure
 - Comparable modulus (carbon FRP)



Quantitative Comparison

Typical Mechanical Properties*

Material	Ultimate Strength	Elastic Modulus	Failure Strain
Glass FRP	517-1207 MPa	30-55 GPa	2-4.5 %
Carbon FRP	1200-2410 MPa	147-165 GPa	1-1.5 %
Aramid FRP	1200-2068 MPa	50-74 GPa	2-2.6 %
Steel	483-690 MPa	200 GPa	>10 %

* Based on 2001 data for specific FRP rebar products

Qualitative Comparison

Typical Mechanical Properties

Criterion	Fibre Type		
	Carbon	Aramid	Glass
Tensile Strength	Very Good	Very Good	Very Good
Modulus of Elasticity	Very Good	Good	Adequate
Long Term Behaviour	Very Good	Good	Adequate
Fatigue Behaviour	Excellent	Good	Adequate
Bulk Density	Good	Excellent	Adequate
Alkaline Resistance	Very Good	Good	Adequate
Price	Adequate	Adequate	Very Good

Fatigue

- **Fatigue:** degradation or failure of a structural material or element after repeated cycles of loading and unloading
- **Carbon FRPs** display outstanding fatigue behaviour
- **Glass FRPs** display intermediate/satisfactory fatigue resistance
- **Aramid FRPs** are sensitive to fatigue

Creep and Creep-Rupture

- **Creep:** a condition of increasing strain under a sustained (constant) level of stress
- Fibres are relatively insensitive to creep
- Matrix polymers are *visco-elastic* and will creep
- For Unidirectional FRPs loaded in the fibre direction
 - Creep not a significant concern if the sustained stresses are limited, as follows:
 - Glass FRP, 20%
 - Aramid FRP, 30%
 - Carbon FRP, 50%

Environmental Durability

Primary advantage of FRPs

Will not corrode electrochemically

Some durability concerns do exist...

Potentially damaging effects resulting from:

→ Temperature

→ Moisture

→ UV Radiation

→ Alkalinity

→ Fire

Temperature

- Elevated temperature causes deterioration of mechanical and bond properties
 - Due primarily to degradation of the polymer matrix
- Service temperatures must therefore be limited:
 - **Epoxy:** 20°C less than the glass transition temperature (GTT), usually less than 100°C
- Low temperatures are not generally a concern

Temperature

- **Other temperature effects:**

Temperature  = Creep 

Temperature  = Moisture or chemical ingress 

Potential for development of thermal stresses due to differential thermal expansion

Potential for damage due to thermal cycling

Moisture

- Polymers absorb moisture to varying degrees
 - continues until saturation point is reached
 - depends on FRP composition and properties
- Unidirectional composites are relatively unaffected by moisture uptake
 - Properties depend on fibres rather than matrix
- Moisture-induced swelling is a concern for aramid

Ultra-Violet Radiation

- Aramid fibres
 - UV degradation of mechanical properties
- Carbon and glass fibres
 - Insensitive to effects of UV radiation
- Polymer matrices
 - slight degradation and discolouration
- UV protection options
 - matrix additives, pigmented gel coats, painting

Alkalinity

- FRP reinforcement of concrete is becoming more common
 - pH inside concrete is normally 12-13.5
 - Glass fibres
 - Reduced toughness
 - Reduced strength
- 
- Alkalinity-induced embrittlement**
- Thus, use alkali-resistant polymer matrices

Fire

- All polymers soften at elevated temperatures
- Potential concerns during fire:



Reduced strength



Reduced stiffness



Loss of bond



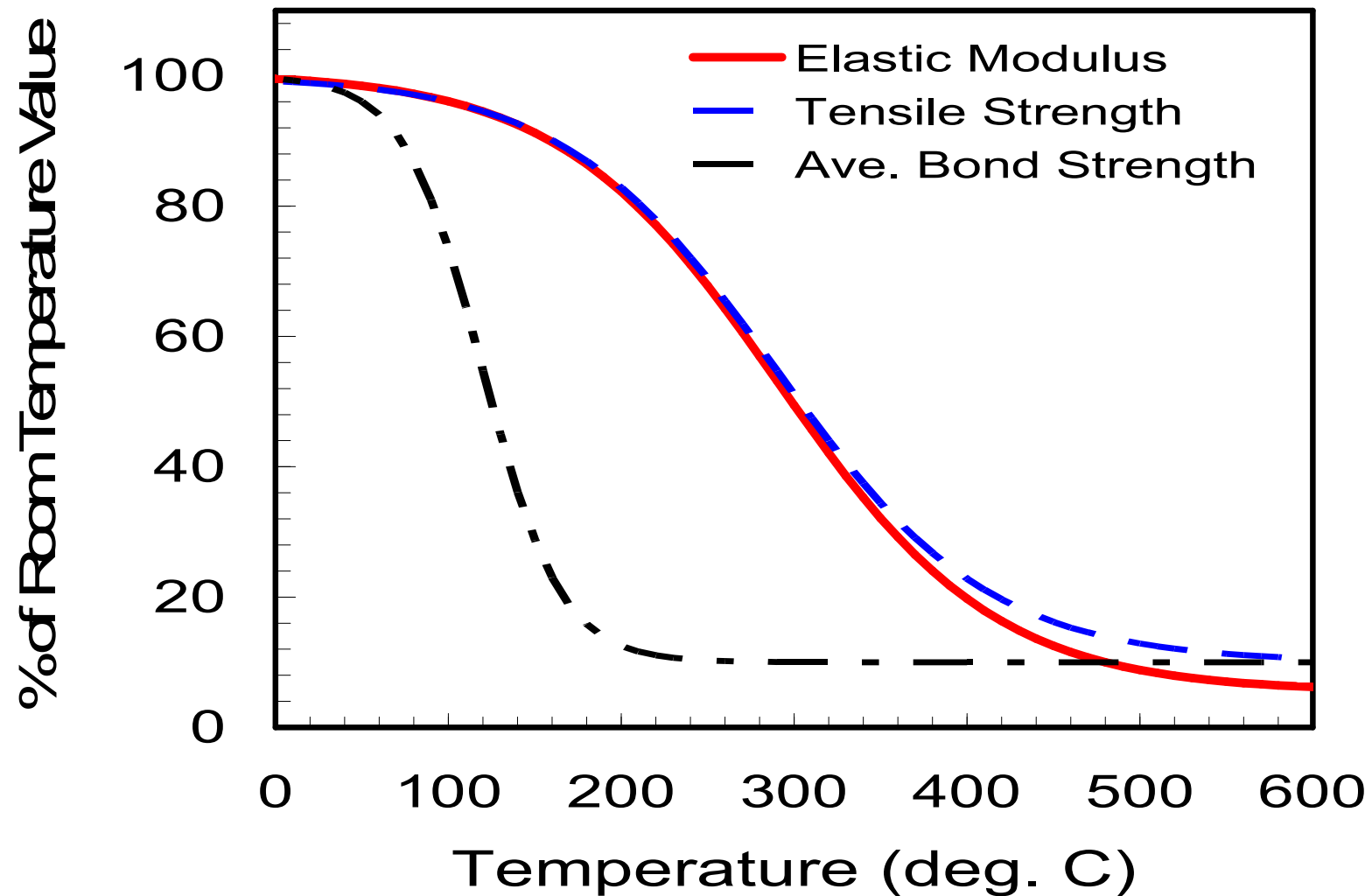
Flame spread



Toxic smoke generation

- Research is ongoing in this area...

Schematic showing typical deterioration in mechanical and bond properties for unidirectional glass FRP bars (reproduced after Bisby, 2003).



< Materials and properties of Polymer Matrix Composites >

List of symbols

$E_0, E_1, \dots$

: E-modulus of springs

$\eta_1, \eta_2, \dots$

: viscosity ratio of dashpots

E^*

: Complex modulus

E', E''

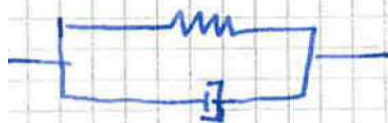
: Storage modulus, Loss modulus

T_G

: glass transition temperature



: Maxwell model



: Kelvin model