Microstructure Mechanics

Polymers: Structure and Properties

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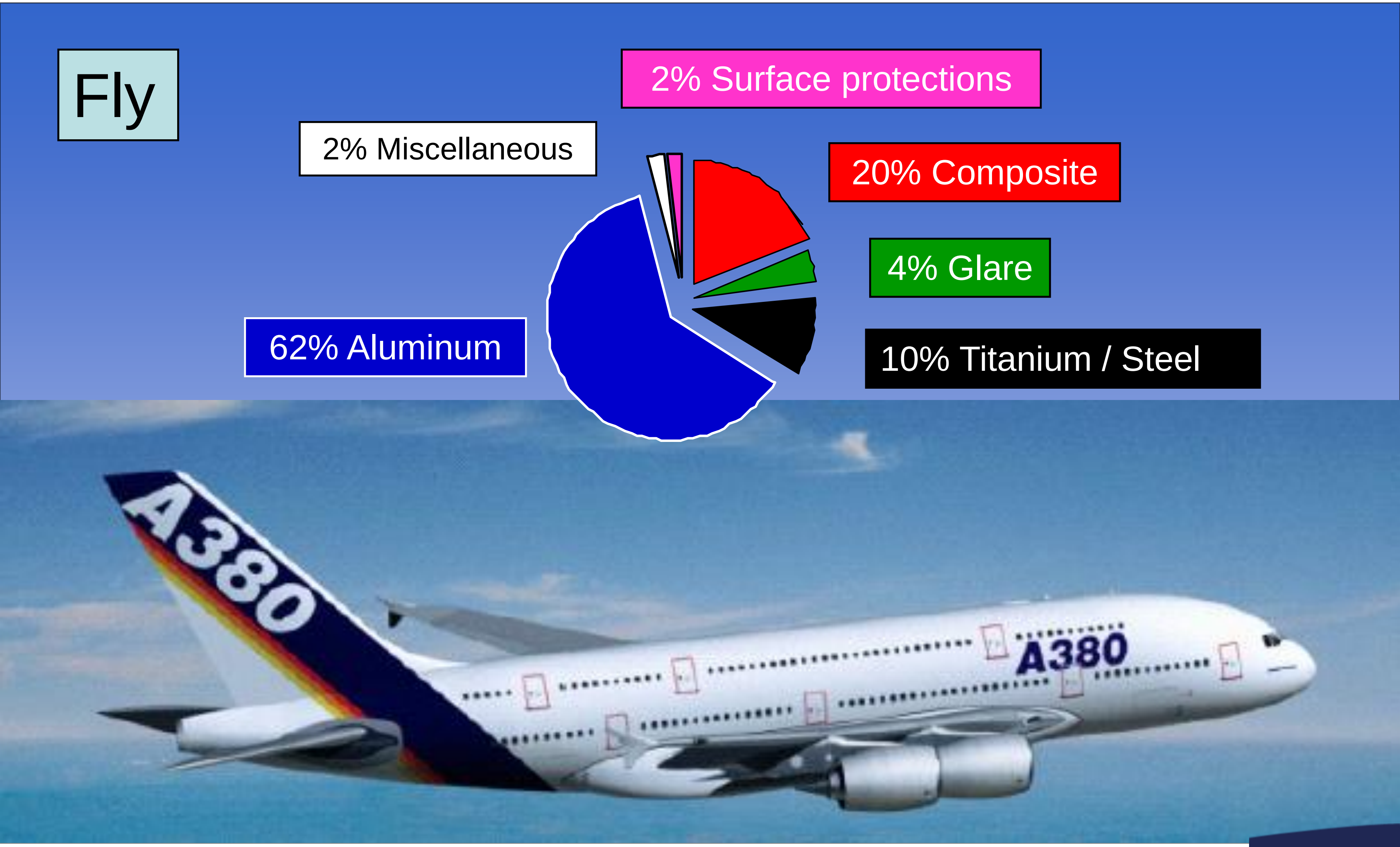
Class 2015

Technology Status A380 – Material Distribution (courtesy Airbus)



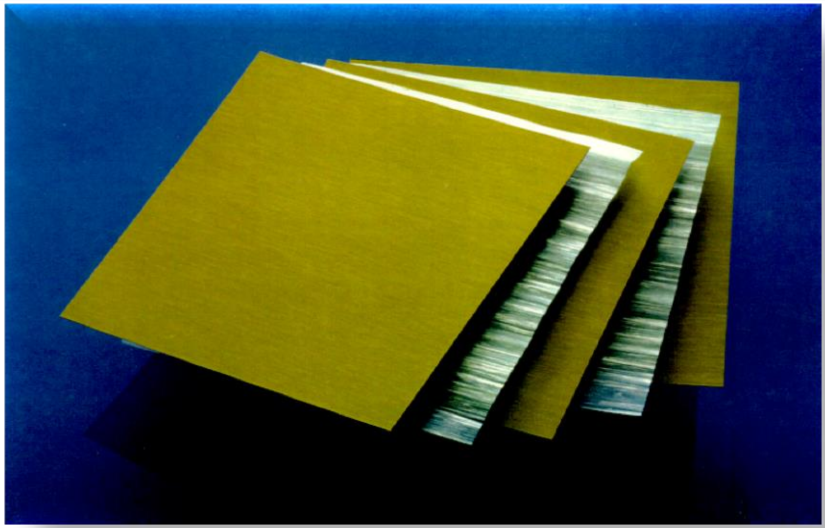
Technology Status A380 – Material Distribution (courtesy Airbus)

GLARE: "Glass Laminate Aluminium Reinforced Epoxy“

several thin layers of metal (usually aluminium) interspersed with layers of glass-fibre "pre-preg", bonded together with a matrix such as epoxy.

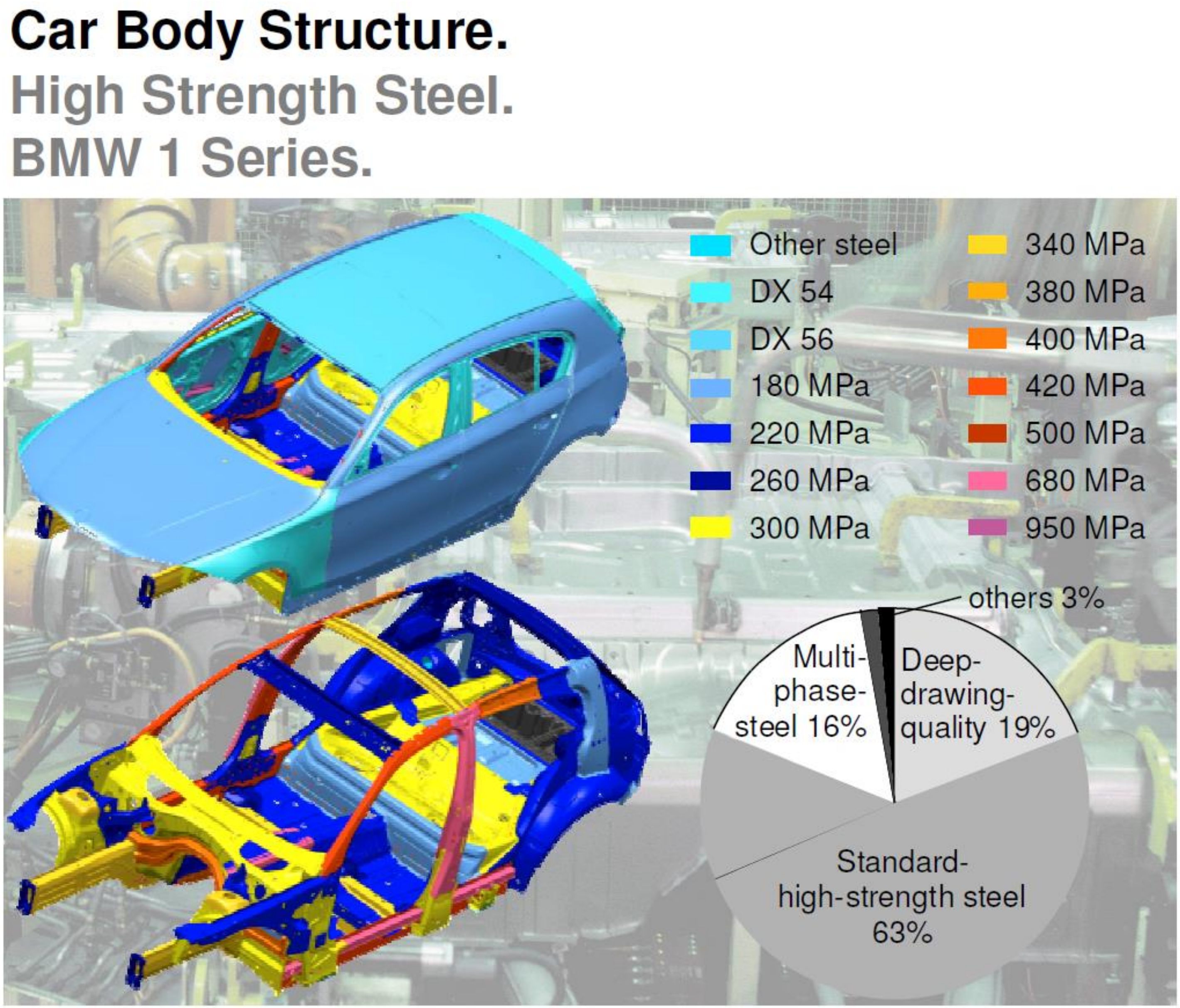
Uni-directional pre-preg layers may be aligned in different directions to suit the predicted stress conditions.

Next generation: CFK

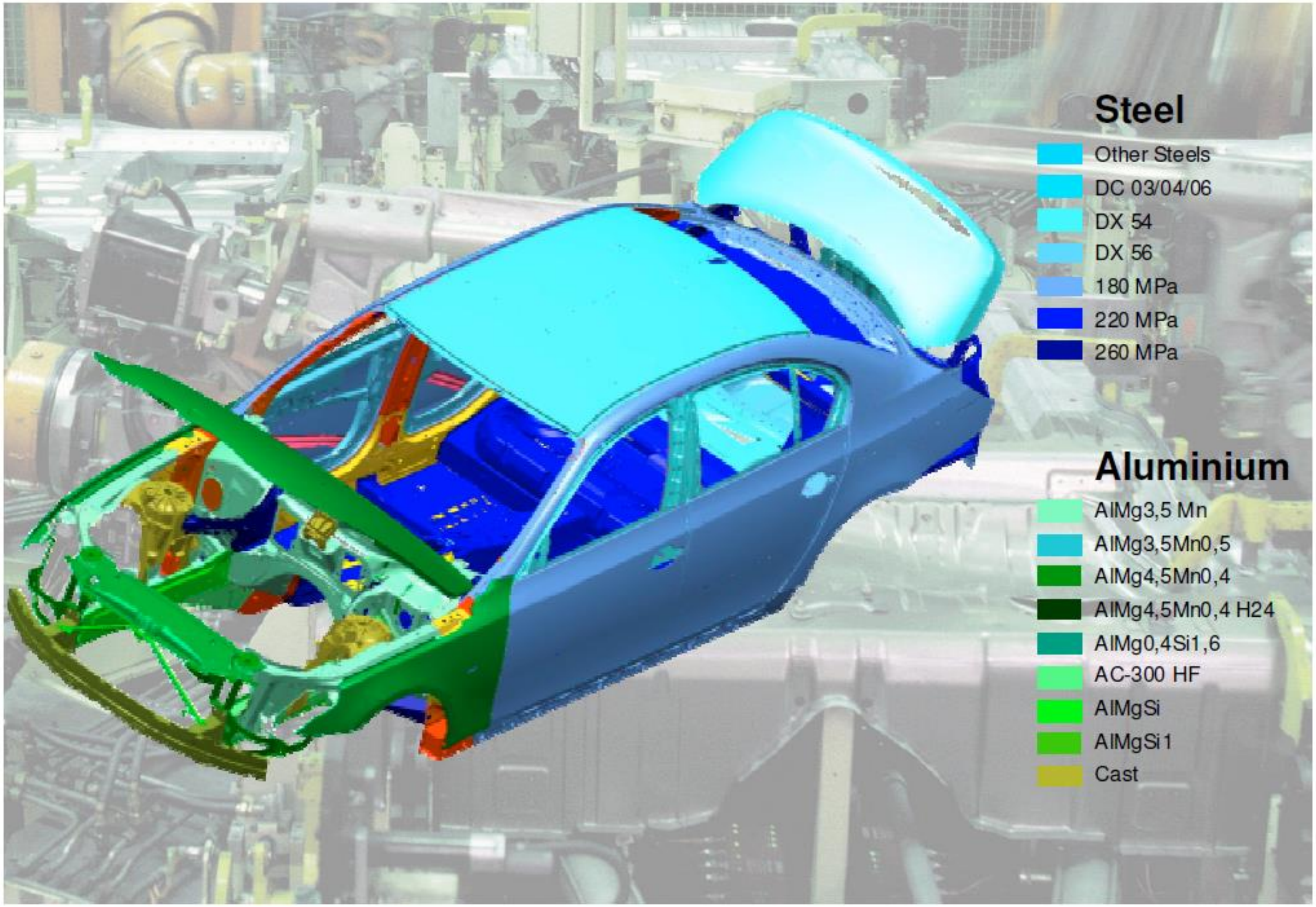


- Improved Stiffness
- Improved hot-wet shear
- Material Optimised Hybrid
- Cost reduction
- Design rules
    - *Fiber dominated*
    - *Bonded Metal laminate*

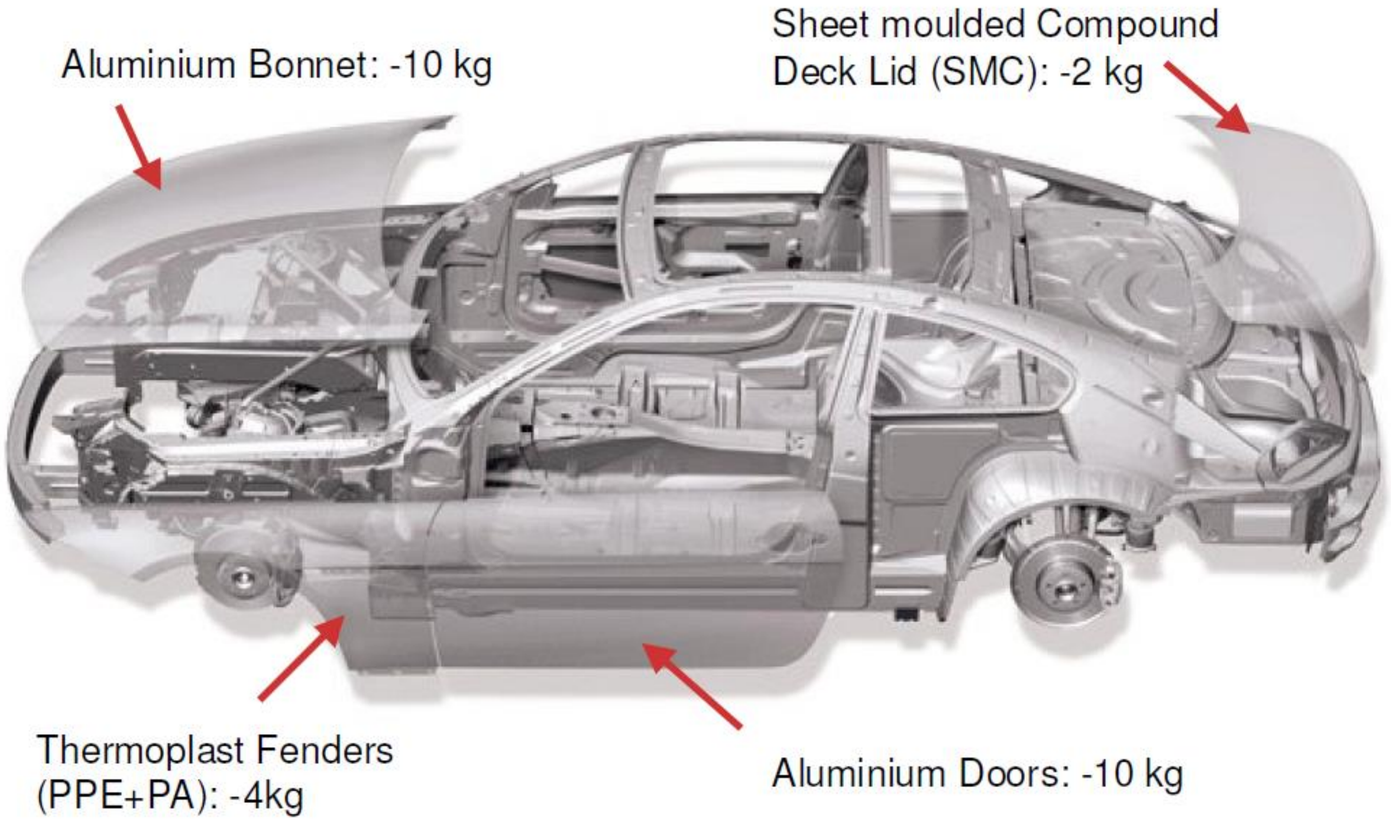
AIRBUS


Car Body Structure.
High Strength Steel.
BMW 1 Series.
Other steel
DX 54
DX 56
180 MPa
220 MPa
260 MPa
300 MPa
340 MPa
380 MPa
400 MPa
420 MPa
500 MPa
680 MPa
950 MPa
others 3%
Multi-phase-steel 16%
Deep-drawing-quality 19%
Standard-high-strength steel 63%

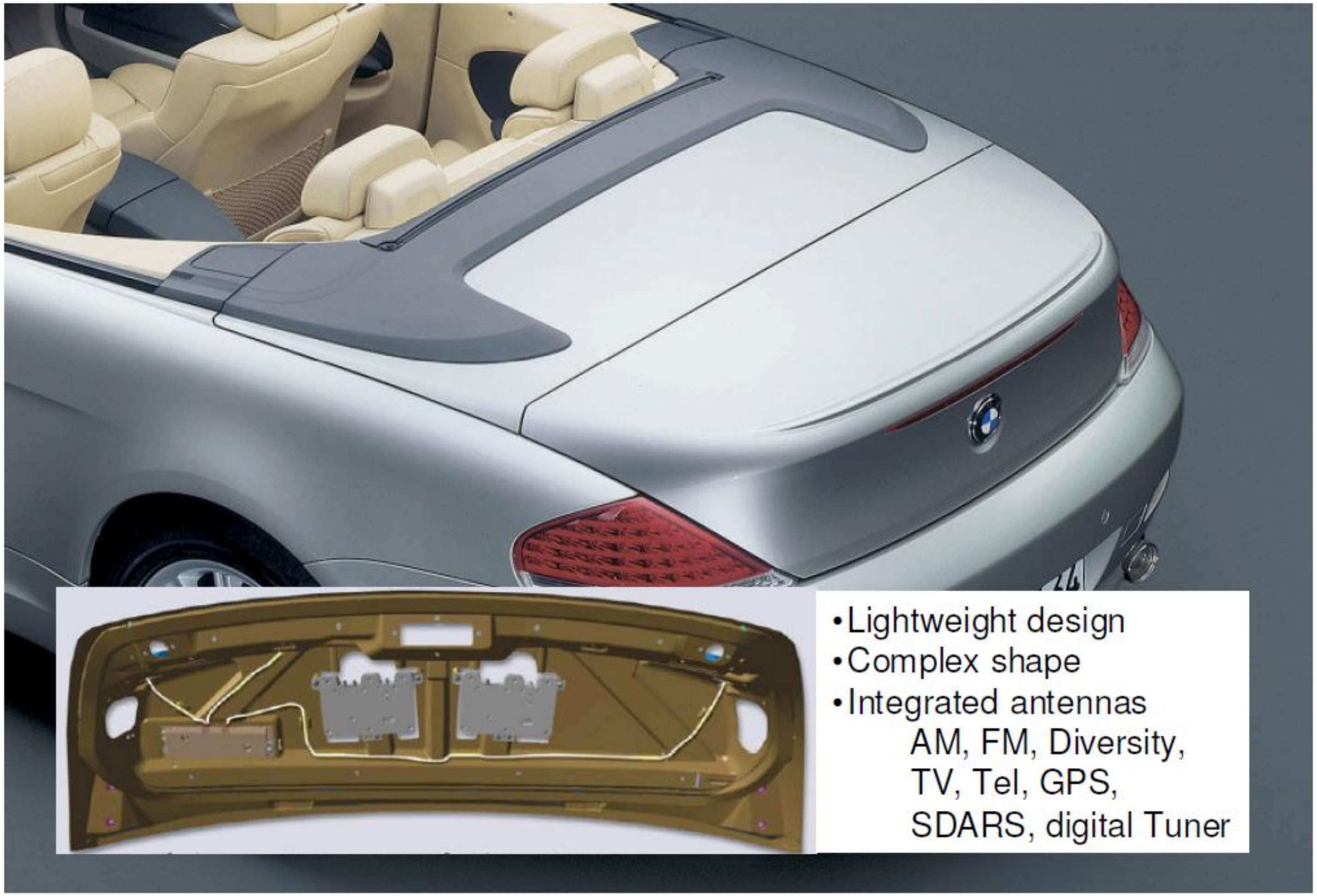
Car Body Structure.
Aluminium Front End / Steel passenger Cab.
BMW 5 Series.



Car Body Shell.
Materials for the BMW 6 Series.
Weight savings compared to Steel

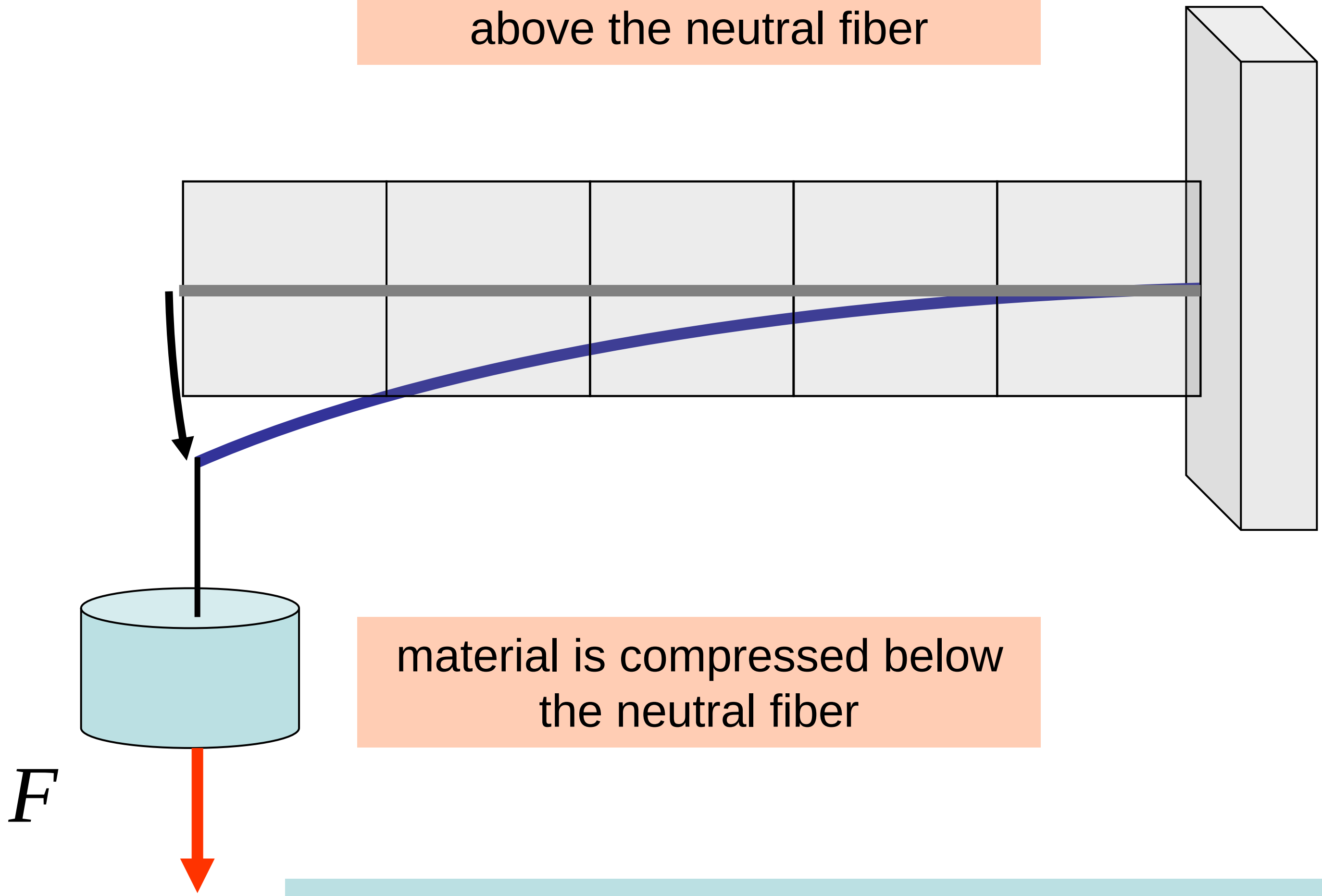


Car Body Shell.
Sheet Moulded Compound (SMC).
Deck Lid BMW 6 Series.



- Lightweight design
- Complex shape
- Integrated antennas
  AM, FM, Diversity,
  TV, Tel, GPS,
  SDARS, digital Tuner

Material is under tensile stress above the neutral fiber



material is compressed below the neutral fiber

„***Neutral Fiber*** “: Center line remains unchanged during bending

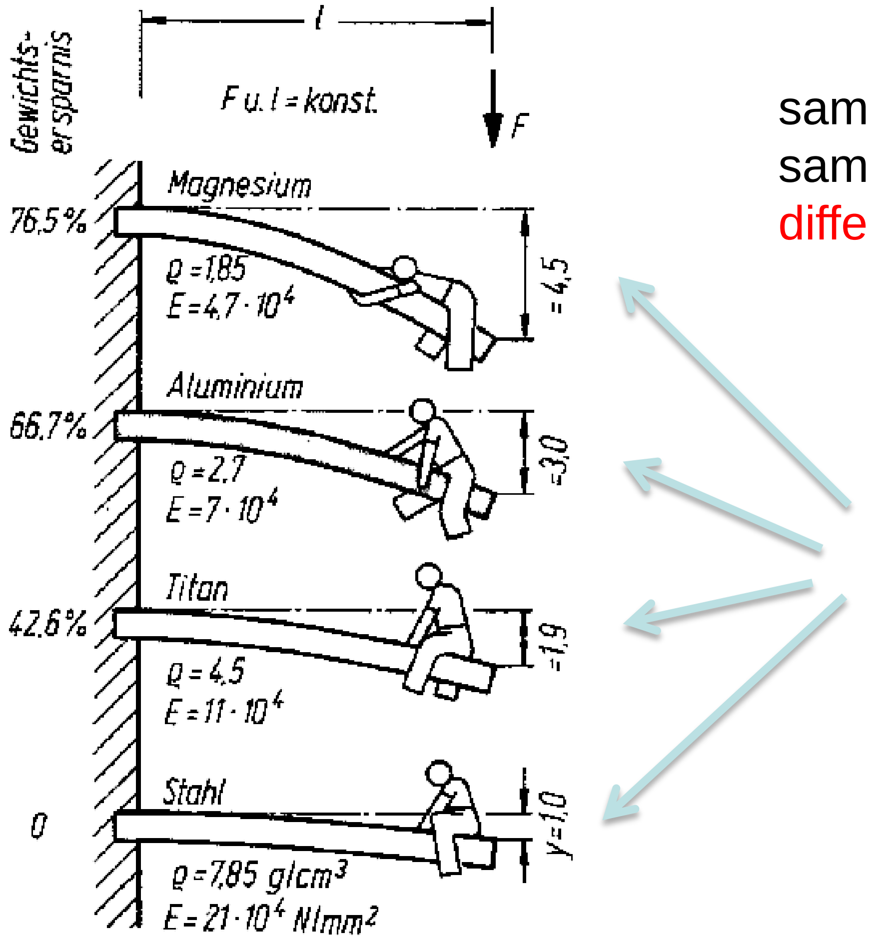
Construction stiffness: beam bending

$\Delta h = \frac{4 \cdot F \cdot l^3}{E \cdot b \cdot a^3}$	1 m	supported on one end
$\Delta h = \frac{F \cdot l^3}{4 \cdot E \cdot b \cdot a^3}$	1 m	supported on both ends
Δh	1 m	displacement
F	1 N	load
a	1 m	beam thickness
l	1 m	beam length
b	1 m	beam width
E	1 N/m^2	Elastic modulus

Beam thickness a: 3rd power against displacement, modulus acts only linear

1) Intrinsic elastic stiffness of the material (elastic modulus)

2) Dimension of the structure that is made of the material (third order increase of structure stiffness with cross section)

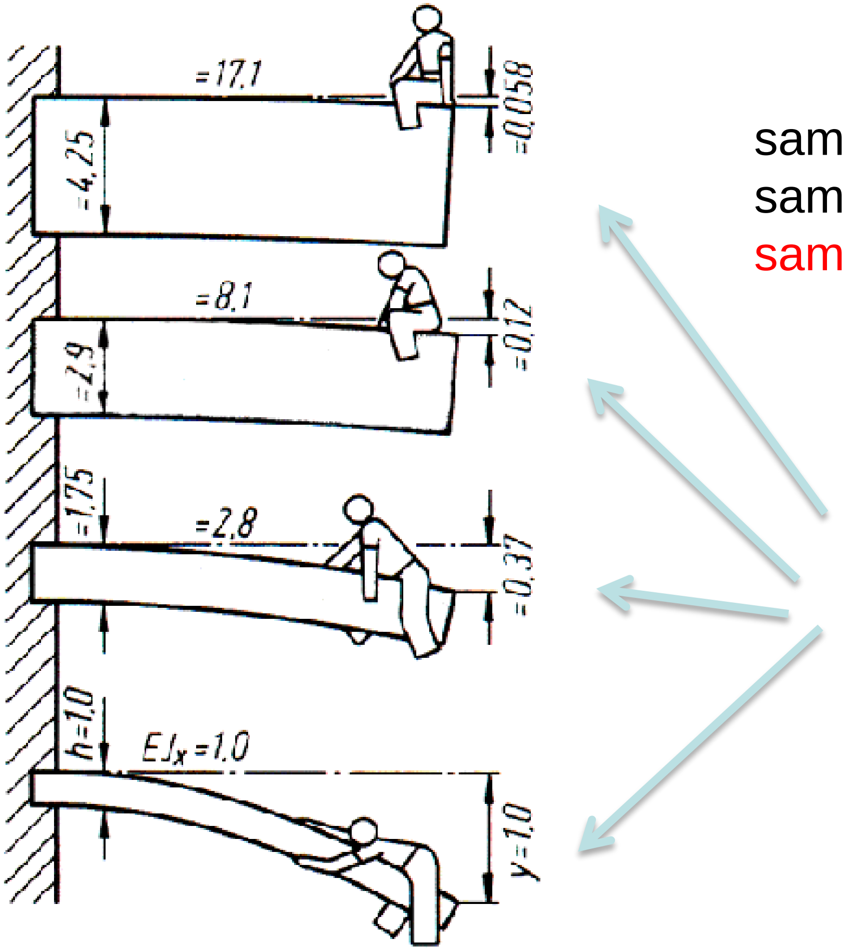


same force
same cross section
different materials

$$\Delta h = \frac{4 \cdot F \cdot l^3}{E \cdot b \cdot a^3}$$

1) Intrinsic elastic stiffness of the material (elastic modulus)

2) Dimension of the structure that is made of the material (third order increase of structure stiffness with cross section)



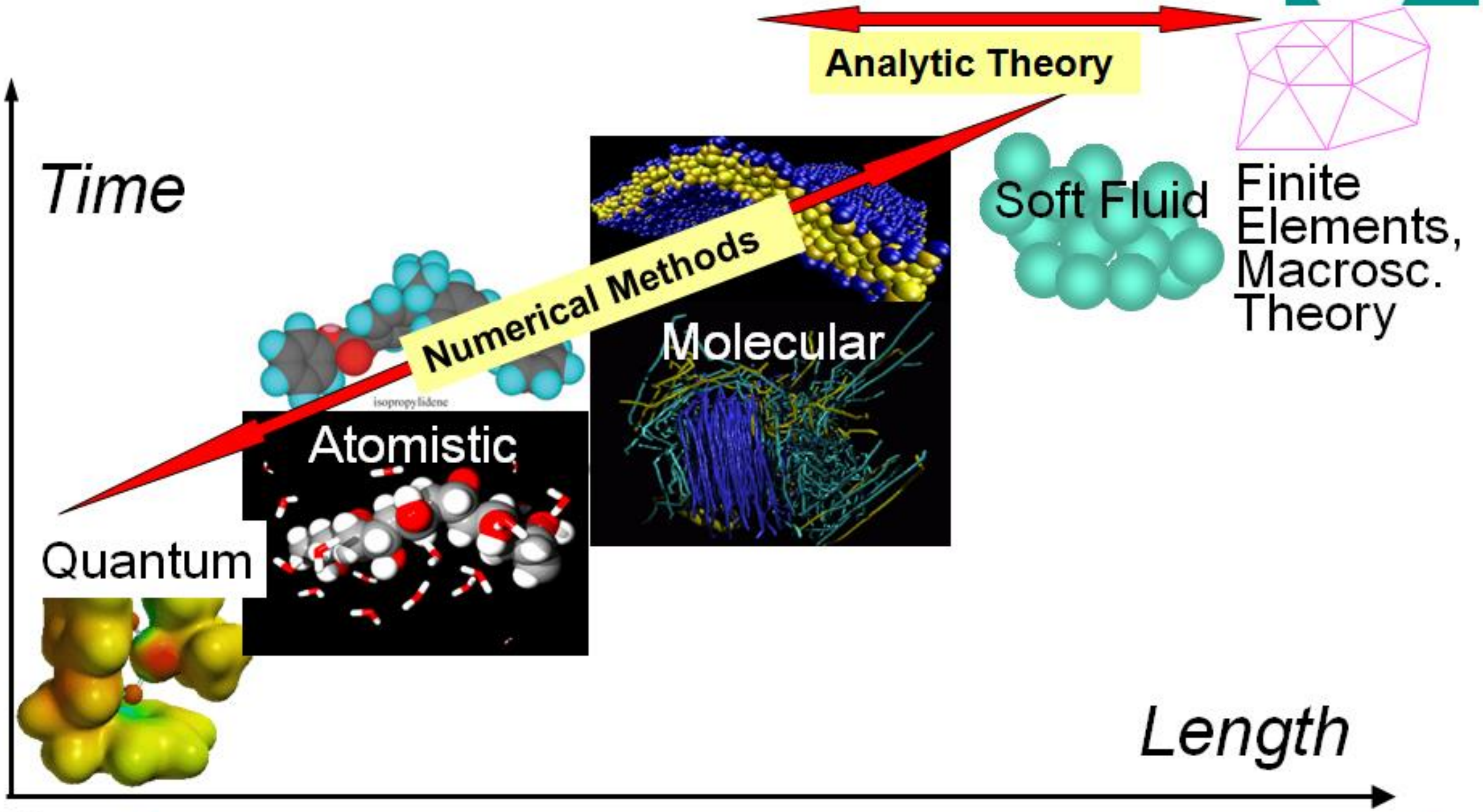
same force
same mass of beam
same material

$$\Delta h = \frac{4 \cdot F \cdot l^3}{E \cdot b \cdot a^3}$$

- **Structures**

Theory of polymers (slide with courtesy from Prof. Kurt Kremer)

Soft Matter Theory: Comprehensive Understanding of Physical and Chemical Properties



Local Chemical Properties ⇔ Scaling Behavior of Nanostructures
Energy Dominance ⇔ Entropy Dominance of Properties

Polymers: Introduction

- **Polymers** – materials consisting of *polymer molecules* that consist of repeated chemical units (`mers') joined together, like beads on a string. Some polymer molecules contain hundreds or thousands of monomers and are often called *macromolecules*.

- Polymers may be **natural**, such as leather, rubber, cellulose or DNA, or **synthetic**, such as nylon or polyethylene.

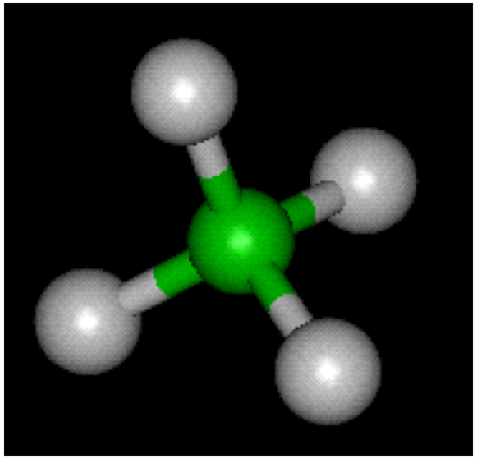
Structure of polymers

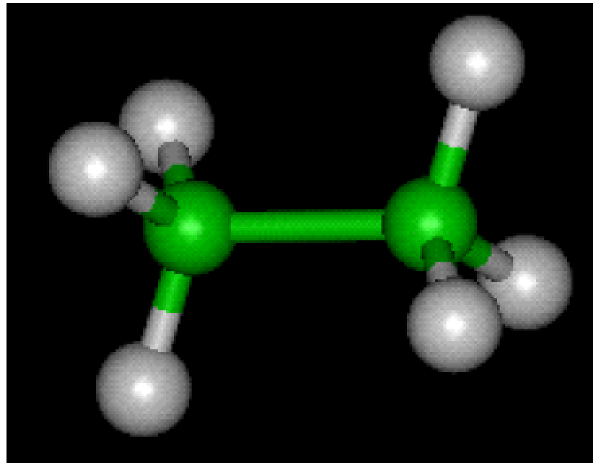
- Macromolecules are formed by linking of repeating units through covalent bonds in the main backbone

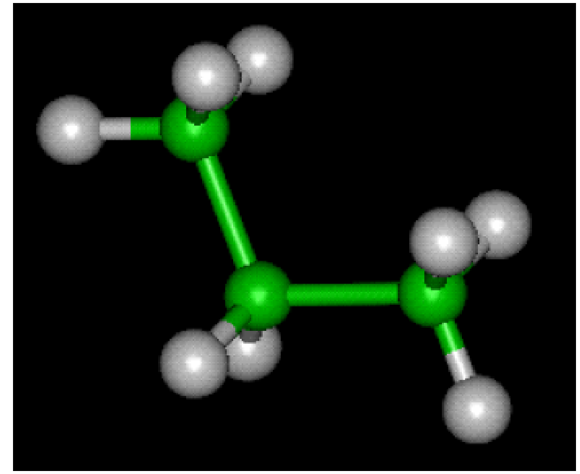
- Properties of macromolecules are determined by
  - molecular weight
  - length
  - backbone structure
  - side chains
  - crystallinity

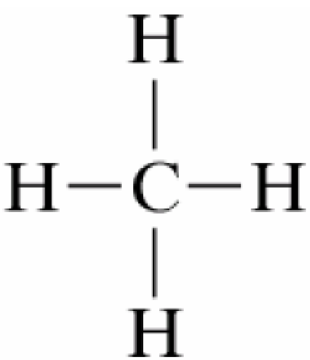
- Resulting macromolecules have huge molecular weights

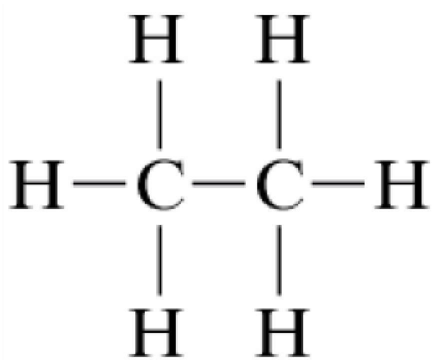
Types of polymers

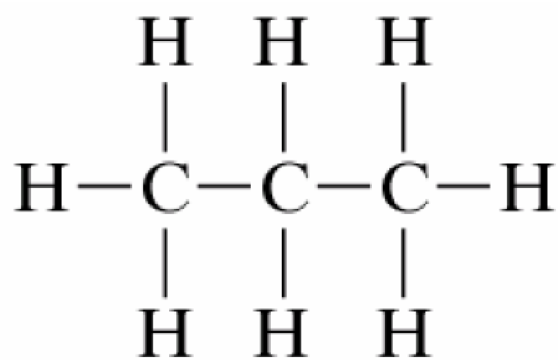












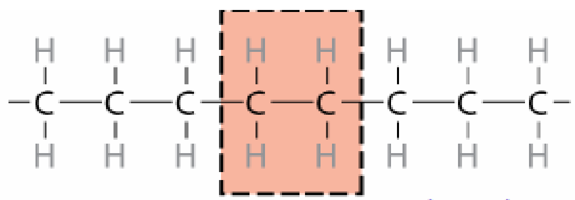
Methane, CH_4

Ethane, C_2H_6

Propane, C_3H_8

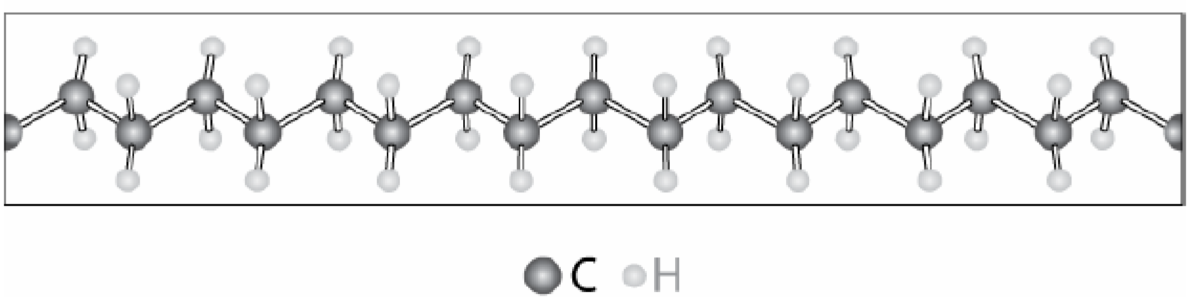
Types of polymers

- Polymer molecules can be very large (macromolecules)
- Most polymers consist of long and flexible chains with a string of C atoms as a backbone
- Side-bonding of C atoms to H atoms or radicals
- Double bonds are possible in both chain and side bonds
- Repeat unit in a polymer chain ("unit cell") is a **mer**
- Small molecules from which polymer is synthesized is **monomer**. A single mer is sometimes also called a monomer.

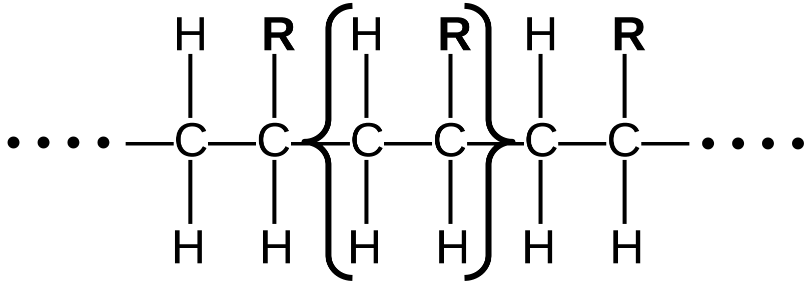


Repeat unit (mer)

polyethylene (e.g. paraffin wax for candles)

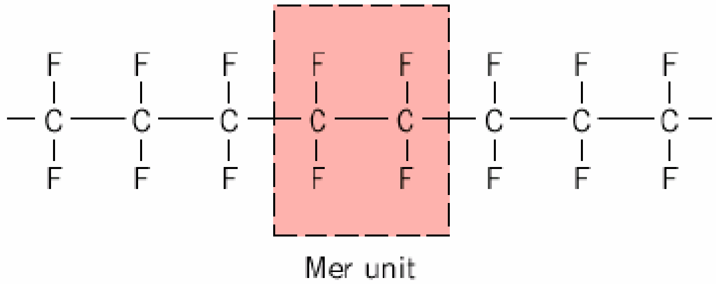


Types of polymers



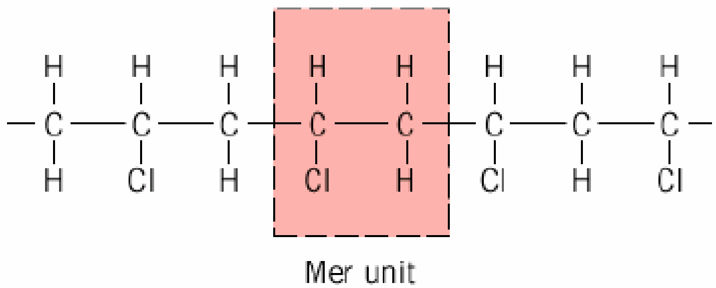
Structure	Source-Based Name	Application
R = -H	Polyethylene	Plastic
R = $-CH_3$	Polypropylene	Rope
R = -Cl	Poly(vinyl chloride)	"Vinyl"
X = -H, R = $-C_2H_5$	Poly(ethyl acrylate)	Latex paints
X = $-CH_3$, R = $-CH_3$	Poly(methyl methacrylate)	Plastic
R = -H	Polybutadiene	Tires
R = $-CH_3$	Polyisoprene	Tires
X = -F, R = -F	Polytetrafluoroethylene	Teflon®

Types of polymers



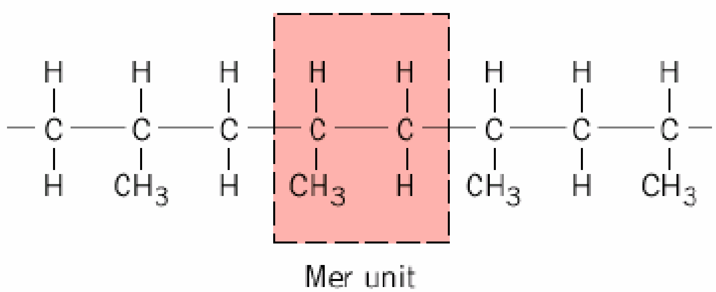
(a)

hydrogen atoms in polyethylene are replaced by fluorine: polytetraflouroethylene PTFE – Teflon



(b)

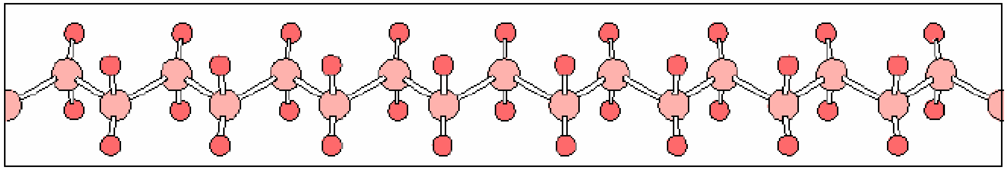
every fourth hydrogen atom in polyethylene is replaced with chlorine: poly(vinyl chloride) PVC



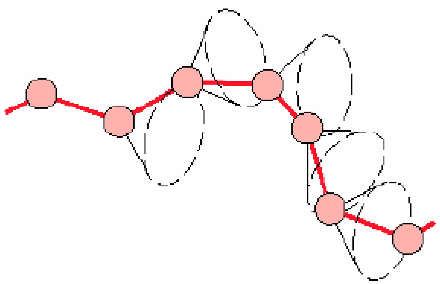
(c)

every fourth hydrogen atom in polyethylene is replaced with methyl group (CH_3): polyproplylene PP

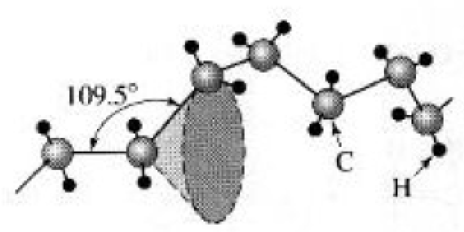
Molecular shape (conformation)

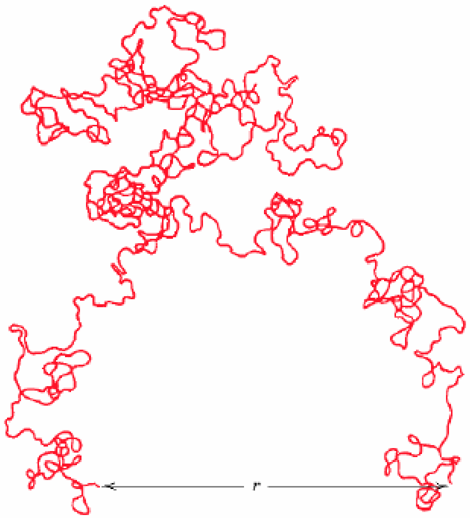


- The angle between the singly bonded carbon atoms is ~109° – carbon atoms form a zigzag pattern in a polymer molecule.
- Moreover, while maintaining the 109° angle between bonds polymer chains can rotate around single C-C bonds (double and triple bonds are very rigid).

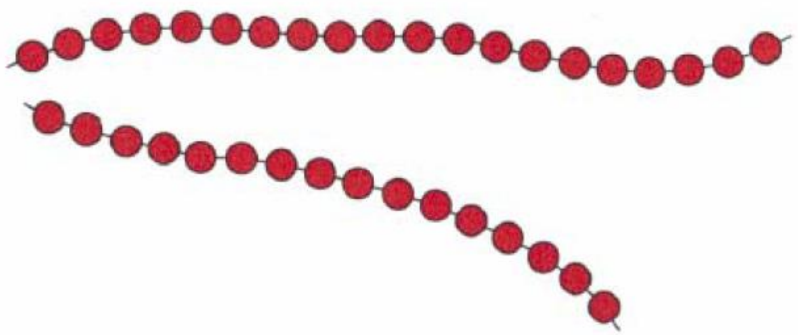


- Random kinks and coils lead to entanglement, like in the spaghetti structure:

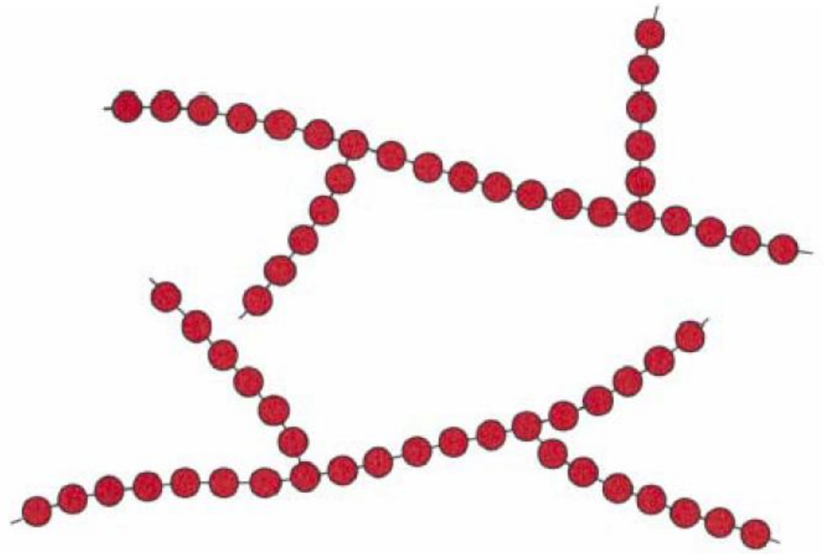




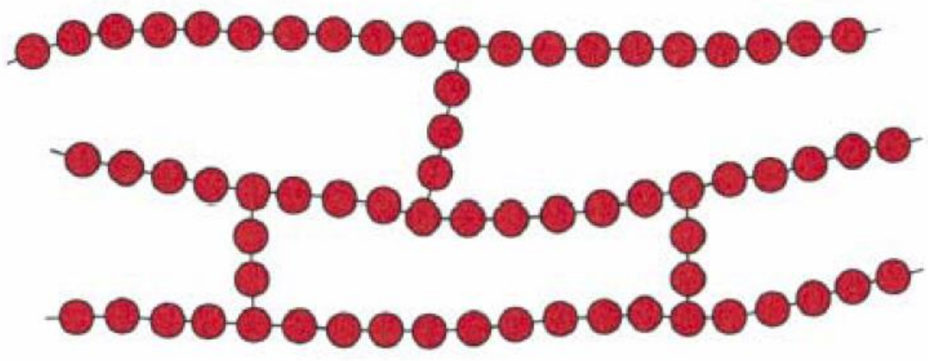
1 **Linear polymers**: Van der Waals bonding between chains. Examples: polyethylene, nylon.



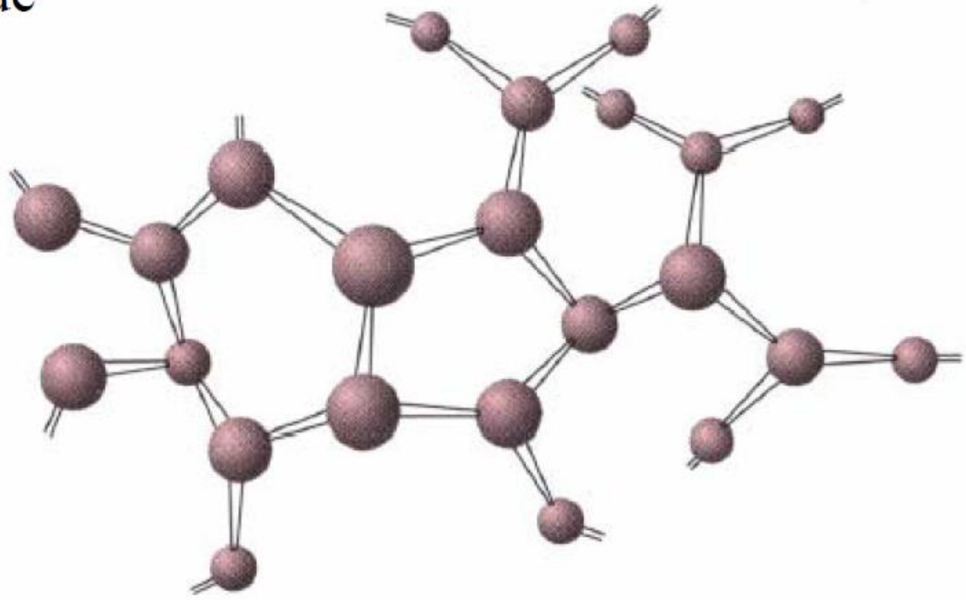
2 **Branched polymers**: Chain packing efficiency is reduced compared to linear polymers - lower density

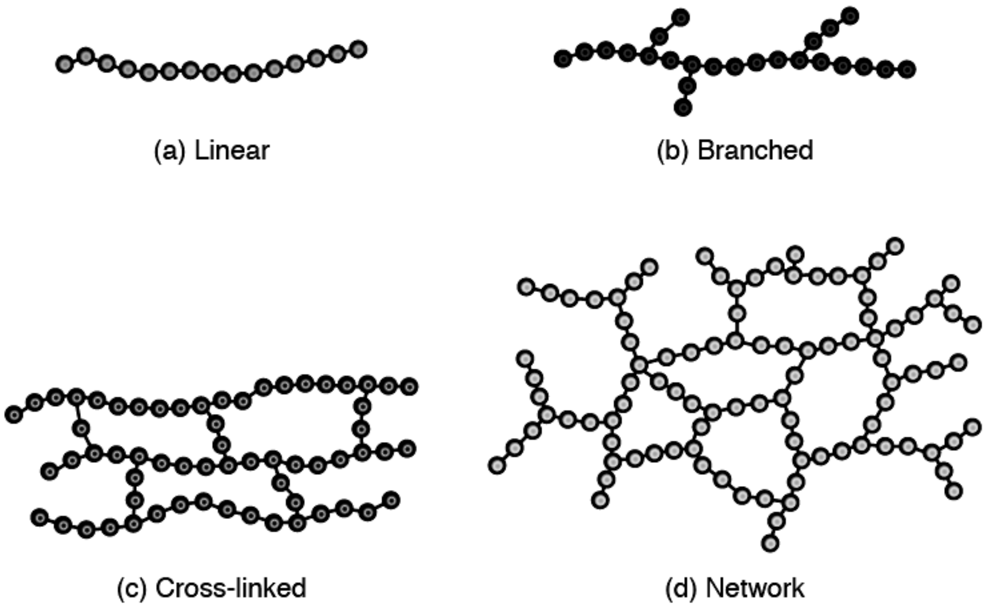


3 **Cross-linked polymers**: Chains are connected by covalent bonds. Often achieved by adding atoms or molecules that form covalent links between chains. Many rubbers have this structure.



4 **Network polymers**: 3D networks made from trifunctional mers. Examples: epoxies, phenol-formaldehyde

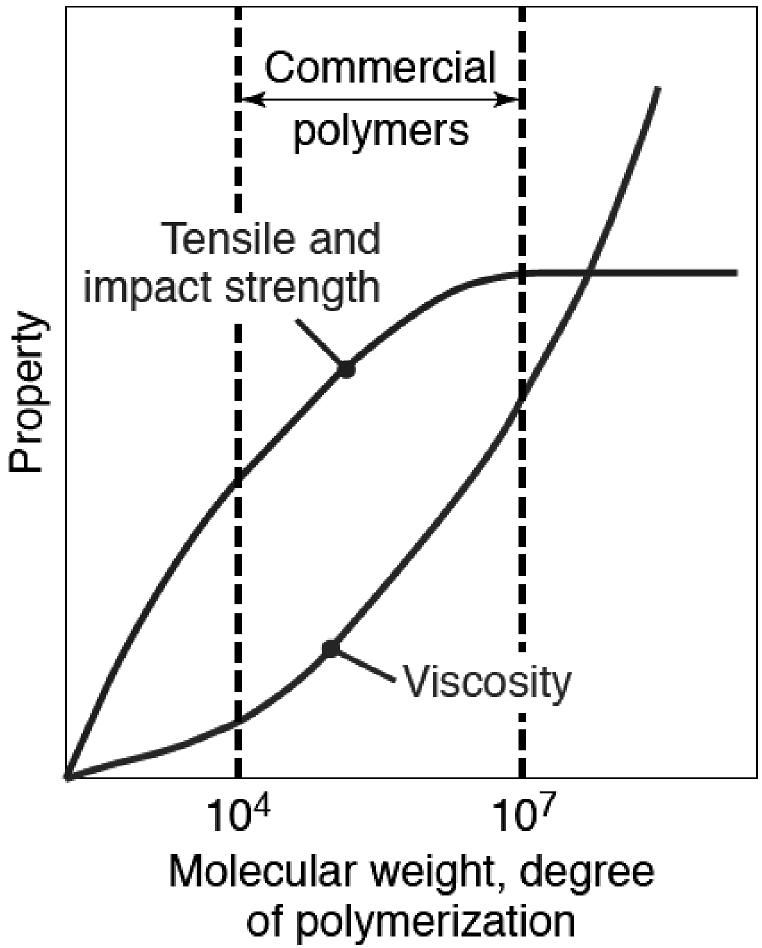




Schematic illustration of polymer chains.

(a) Linear structure; thermoplastics such as acrylics, nylons, polyethylene, and polyvinyl chloride have linear structures.
(b) Branched structure, such as polyethylene.
(c) Crosslinked structure; many rubbers and elastomers have this structure. Vulcanization of rubber produces this structure.
(d) Network structure, which is basically highly cross-linked; examples include thermosetting plastics such as epoxies and phenolics.

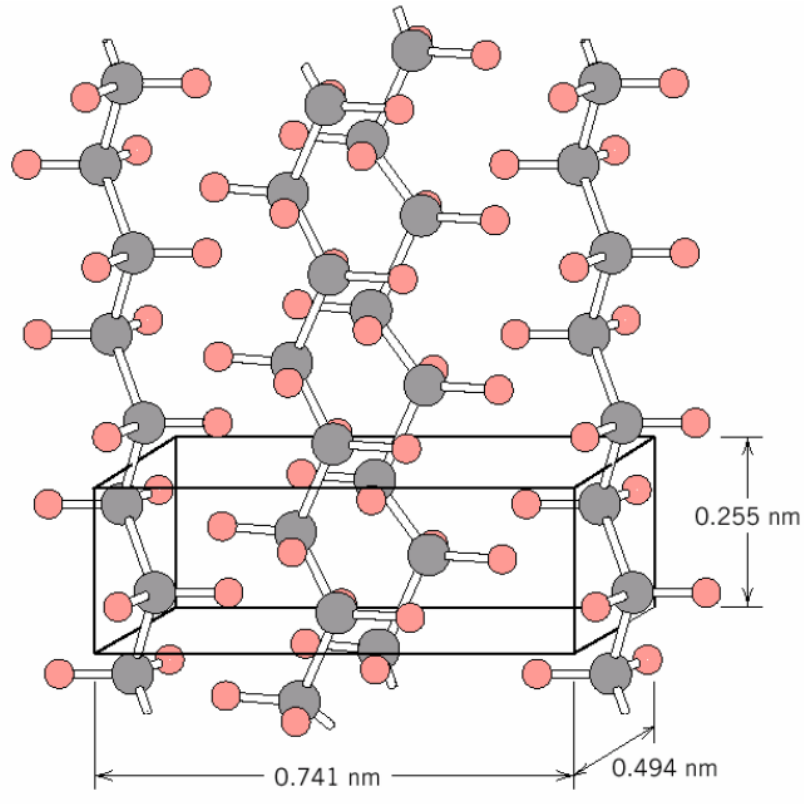
Effect of molecular weight on mechanical properties



Effect of molecular weight and degree of polymerization on the strength and viscosity of polymers.

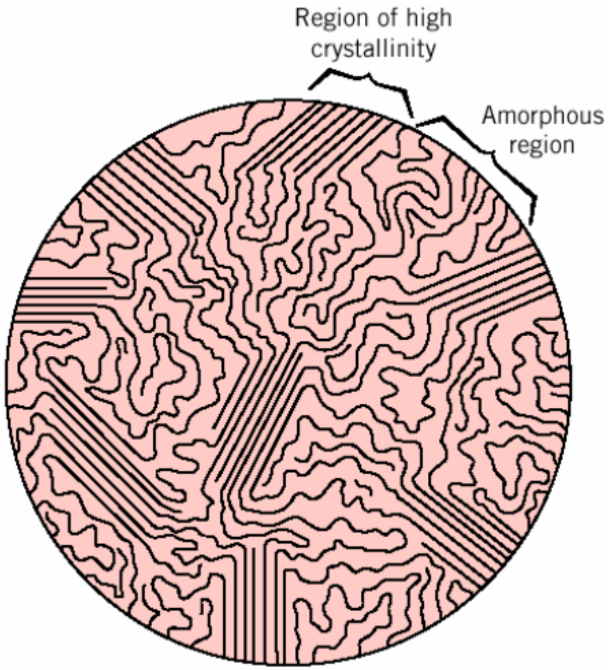
Polymer structure, crystals

Atomic arrangement in polymer crystals is more complex than in metals or ceramics (unit cells are typically large and complex).



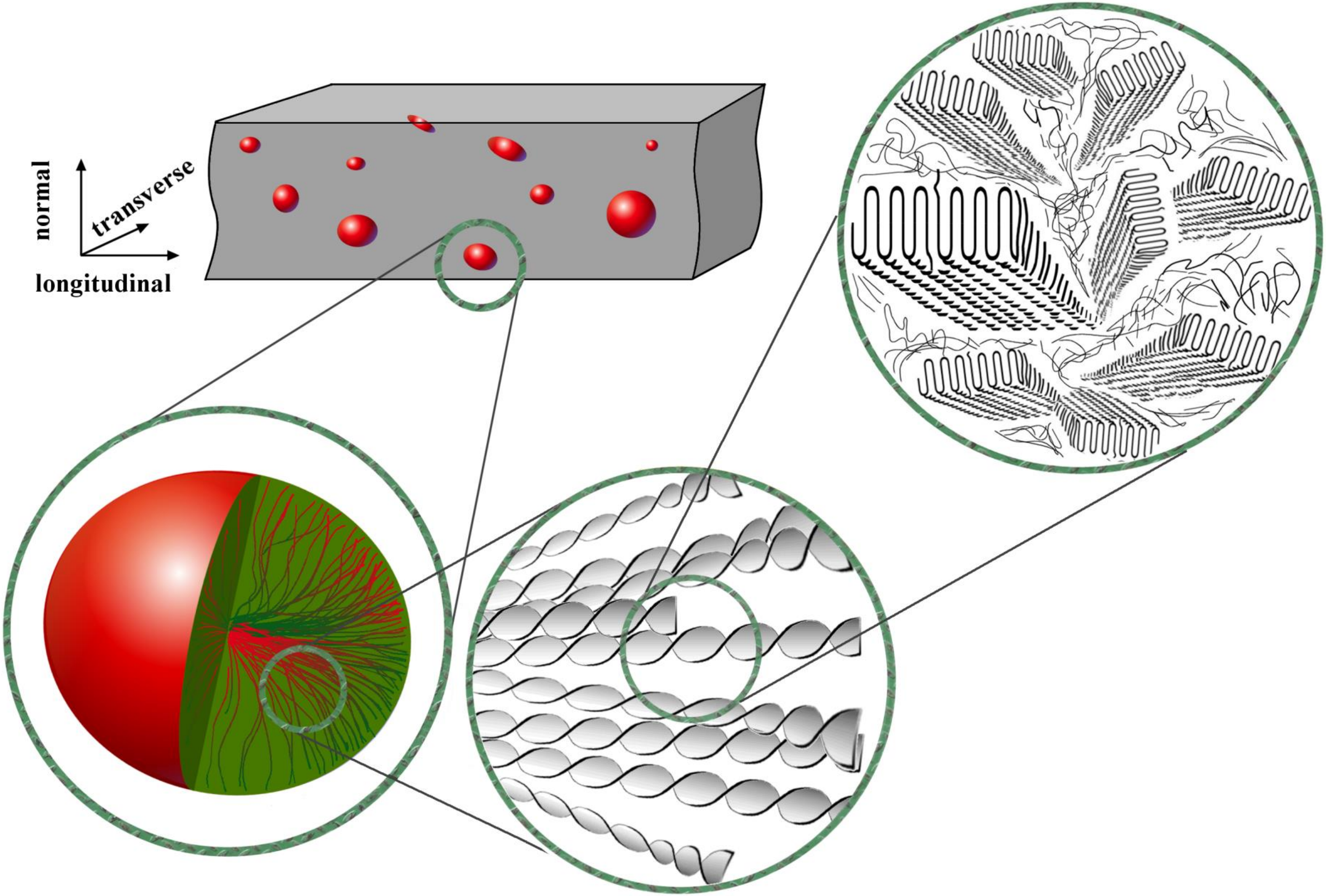
Polyethylene

Polymer structure, crystals and amorphous structure

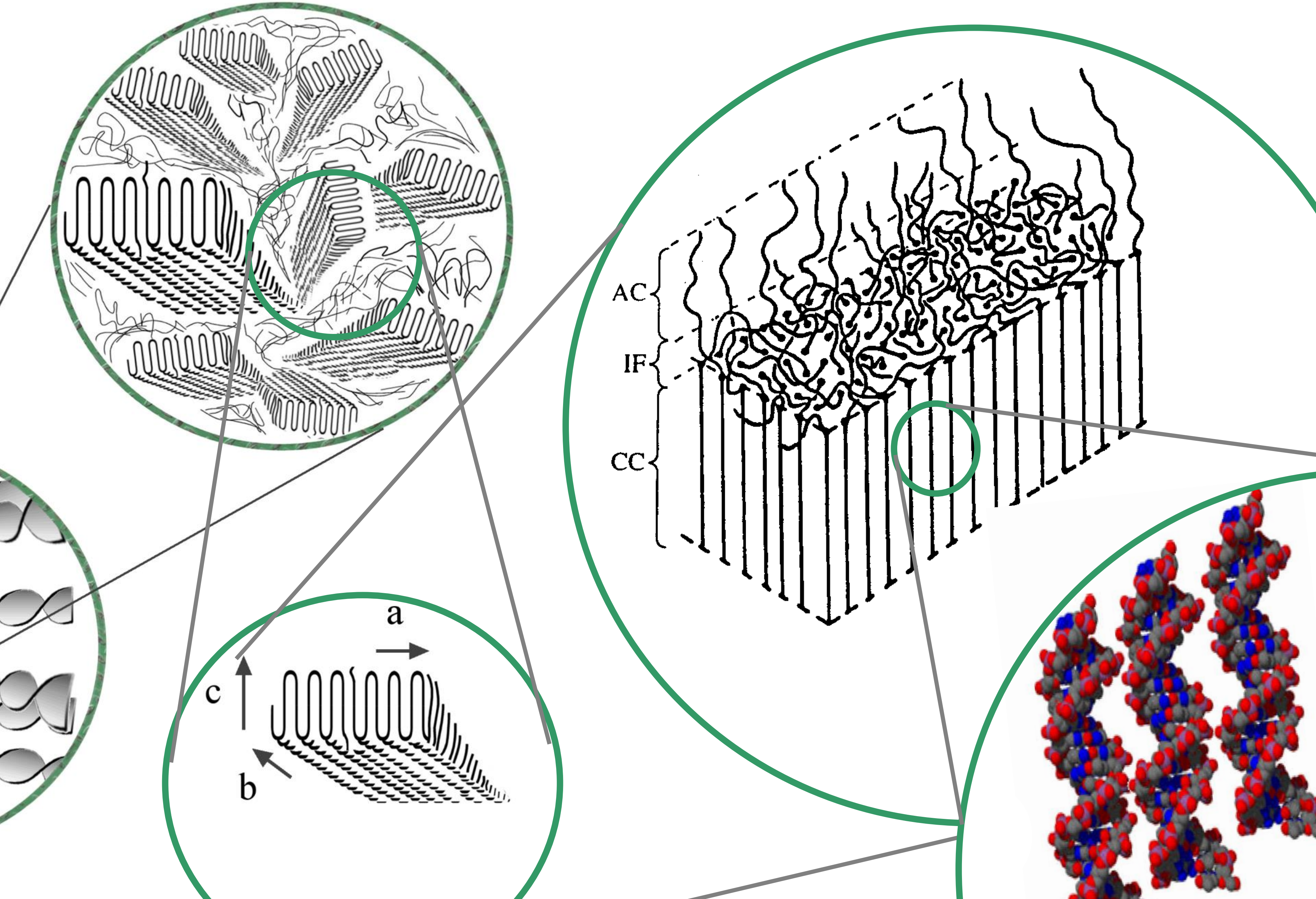


Polymer molecules are often partially crystalline (semi-crystalline), with crystalline regions dispersed within amorphous material.

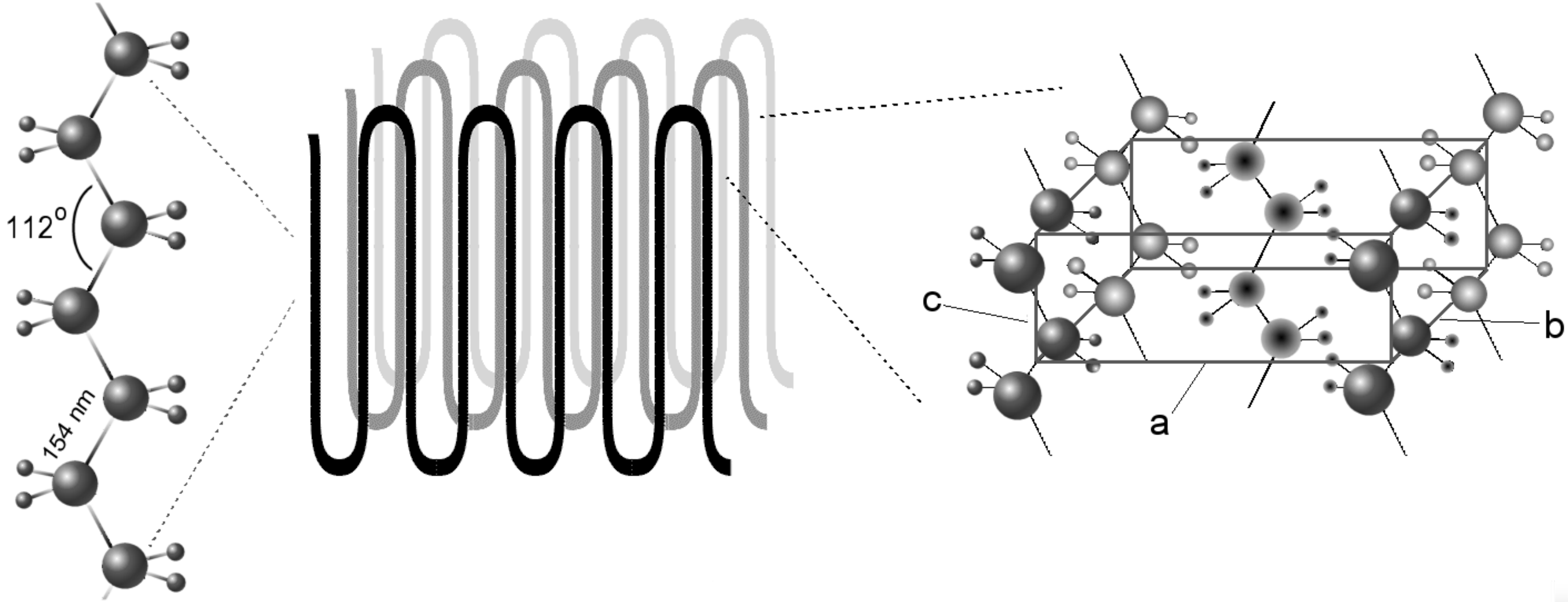
Structure, scales, partially crystalline polymers

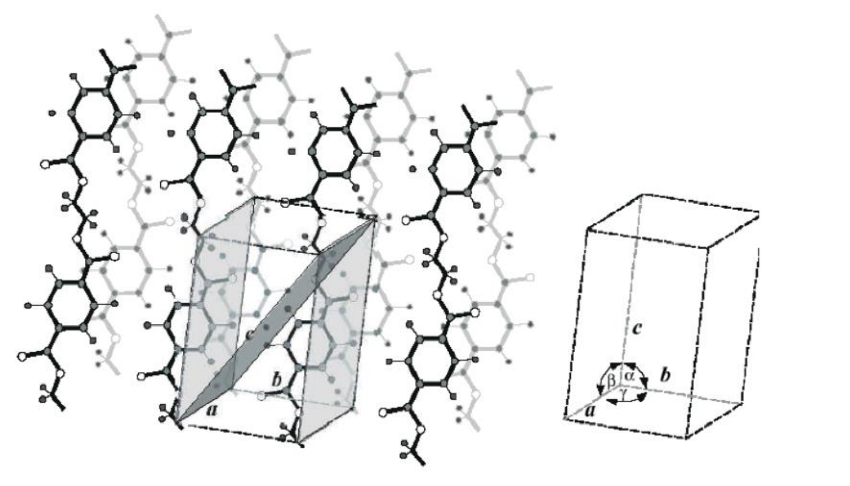


Structure, scales, partially crystalline polymers



Structure, scales, partially crystalline polymers

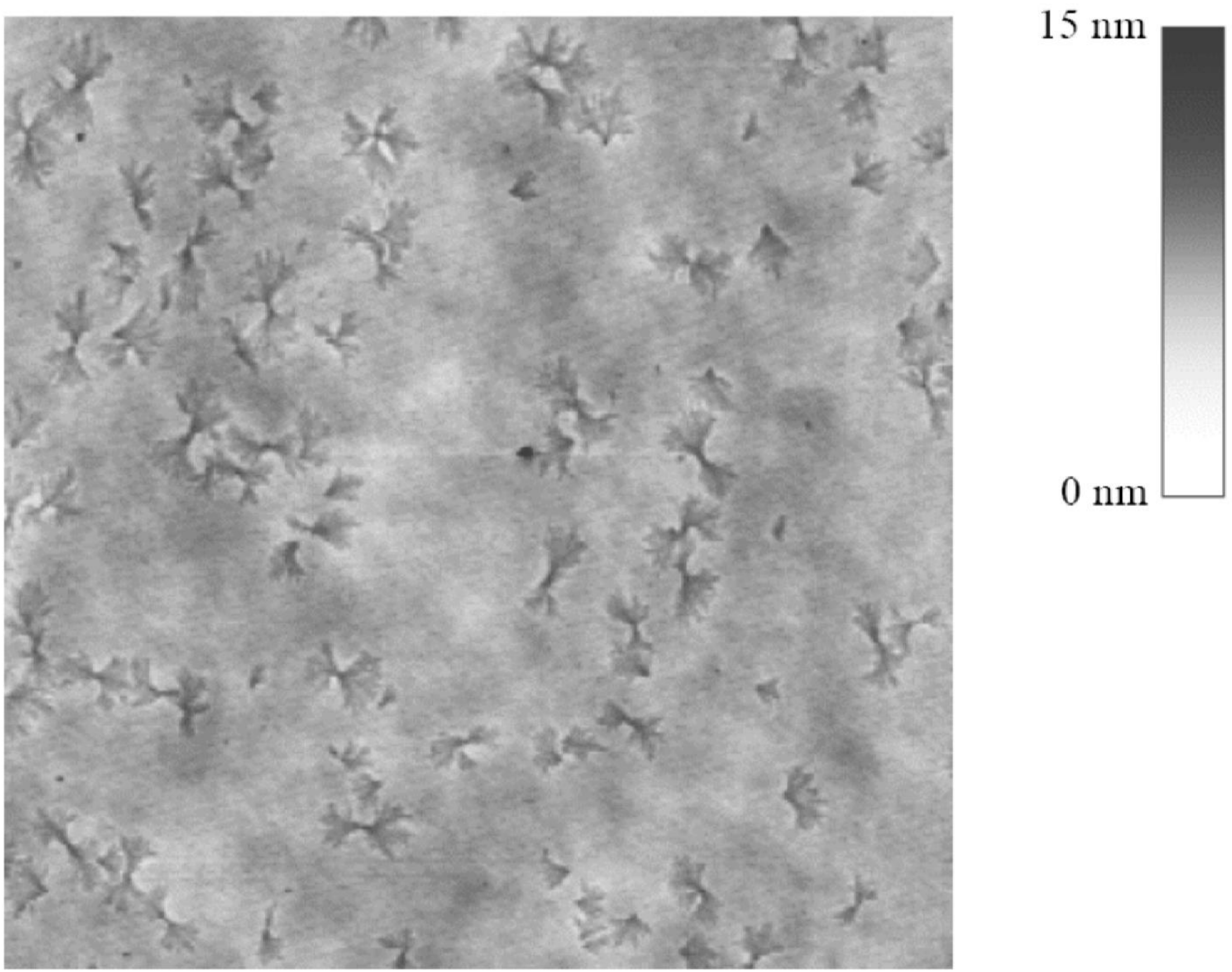




The crystalline unit cell for PET (a = 4.56 Å, b = 5.94 Å, c = 10.75 Å; α = 98.5°, β = 118°, γ = 112°),

M Durell (2002)

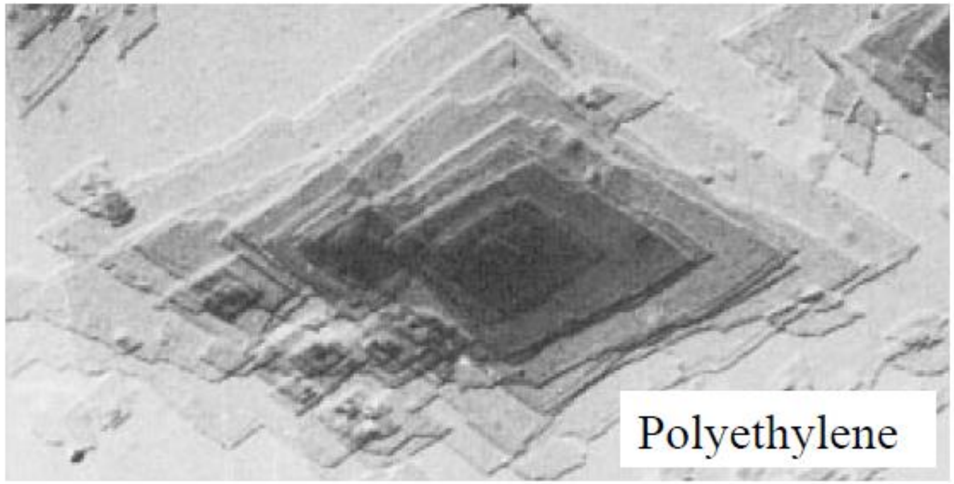
Polymer structure: spherulite growth

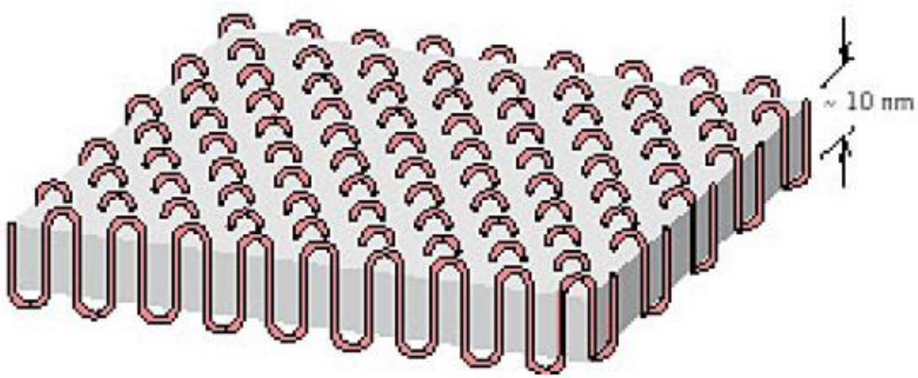


PET / AFM: M Durell, J E Macdonald, D Trolley, Europhysics Letters (2002)

Polymer structure: spherulite growth

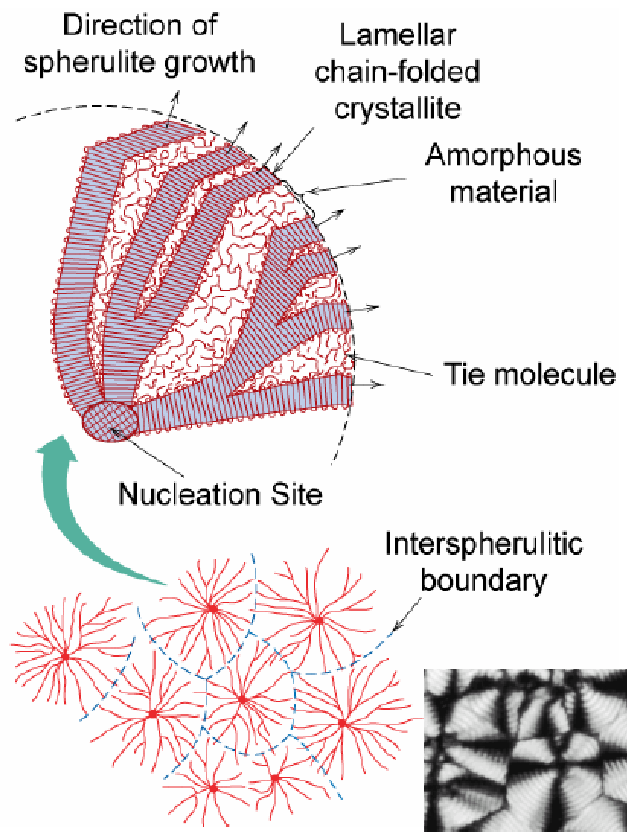
Thin crystalline platelets grown from solution - chains fold back and forth: chain-folded model



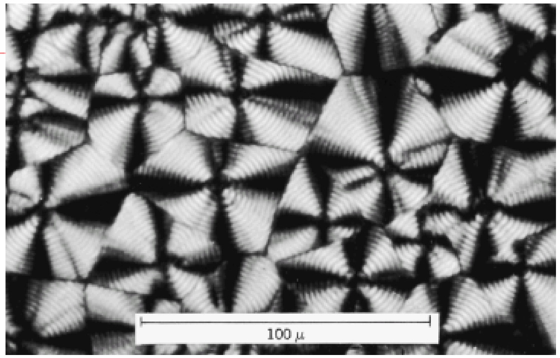


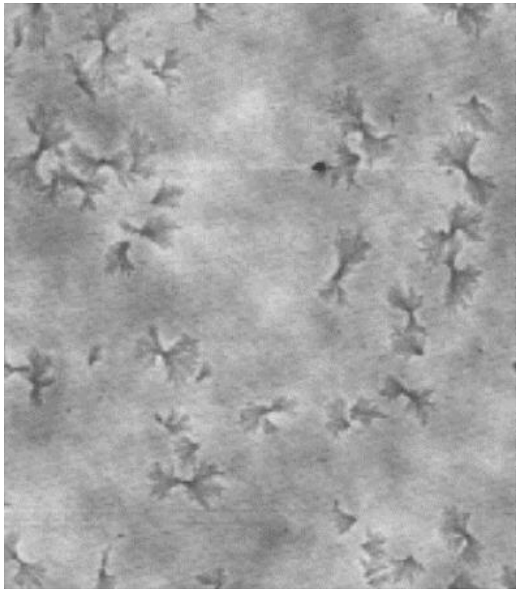
The average chain length can be much greater than the thickness of the crystallite

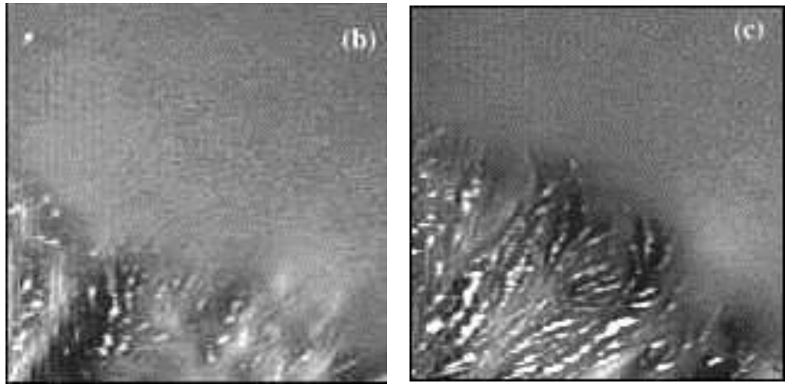
Spherulites: Aggregates of lamellar crystallites ~ 10 nm thick, separated by amorphous material. Aggregates are formed upon solidification from a melted state and are approximately spherical in shape.



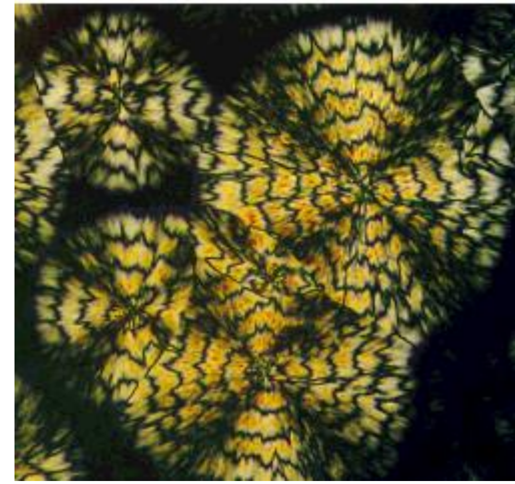
Photomicrograph of spherulite structure of polyethylene







1 micron square, AFM



1 millimeter square, OM

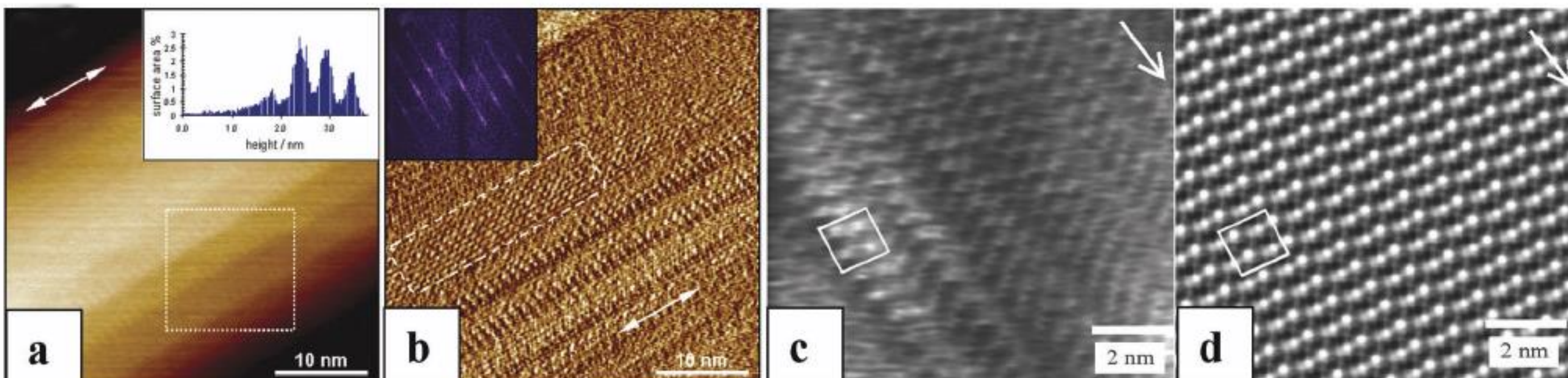
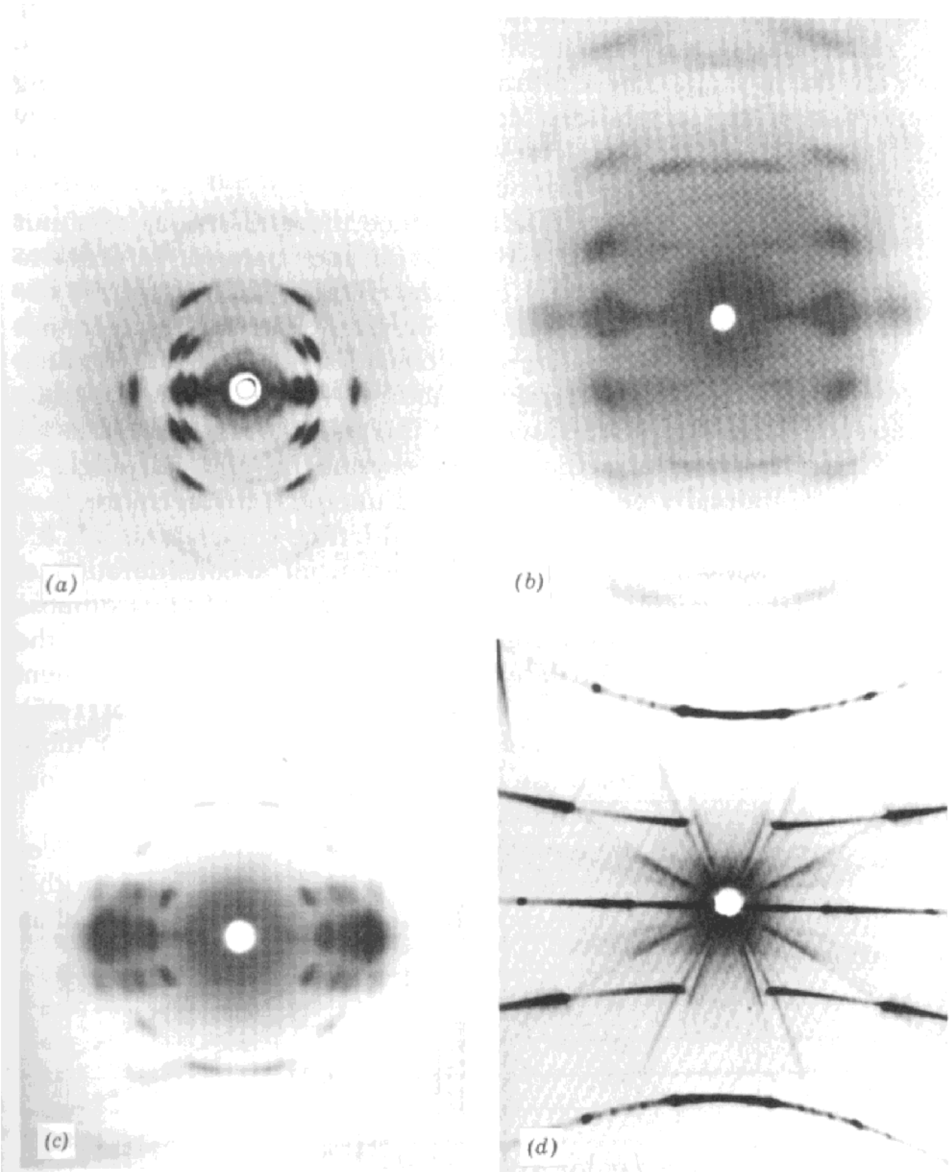
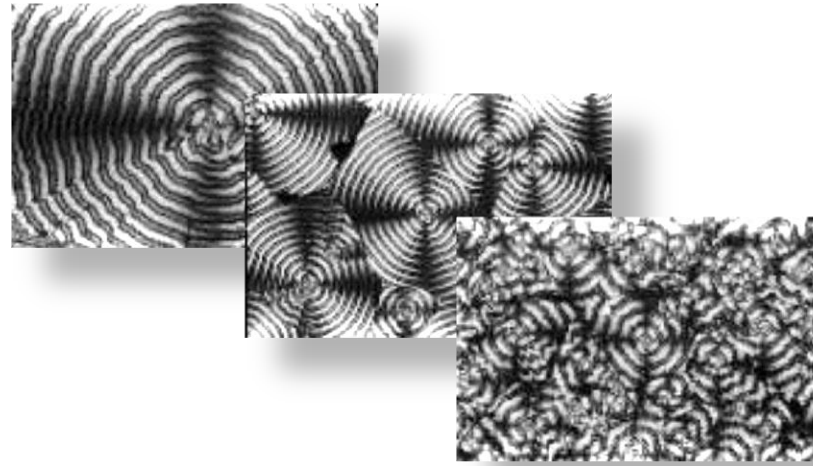


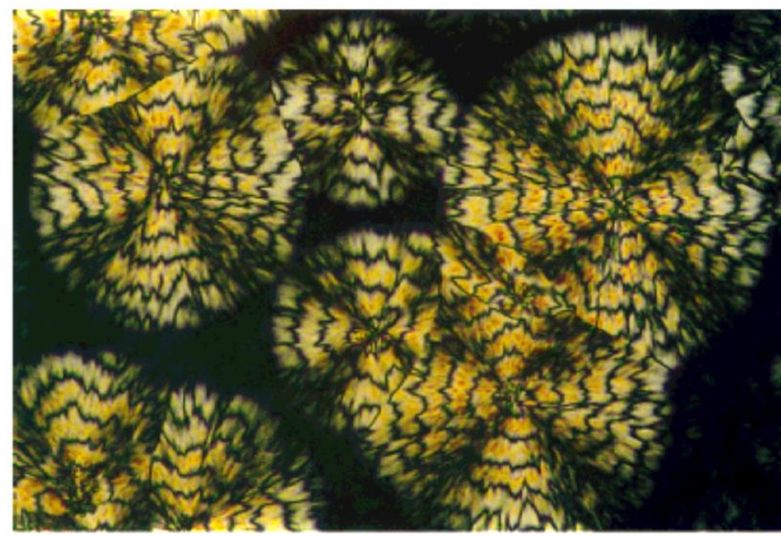
Fig. 2 AFM contact mode images. Cellulose molecules in micro-fibril crystal: (a) topographic image; and (b) error-signal image. Polybutene-1 molecules: (c) topographic image; and (d) simulated AFM image based on crystallographic data.

M. Miles, M. Antognozzi, H. Haschke, J. Hobbs, A. Humphris, T. McMaster
H.H. Wills Physics Laboratory, University of Bristol, Materials Today, Feb. 2003

Polymer structure: spherulite growth



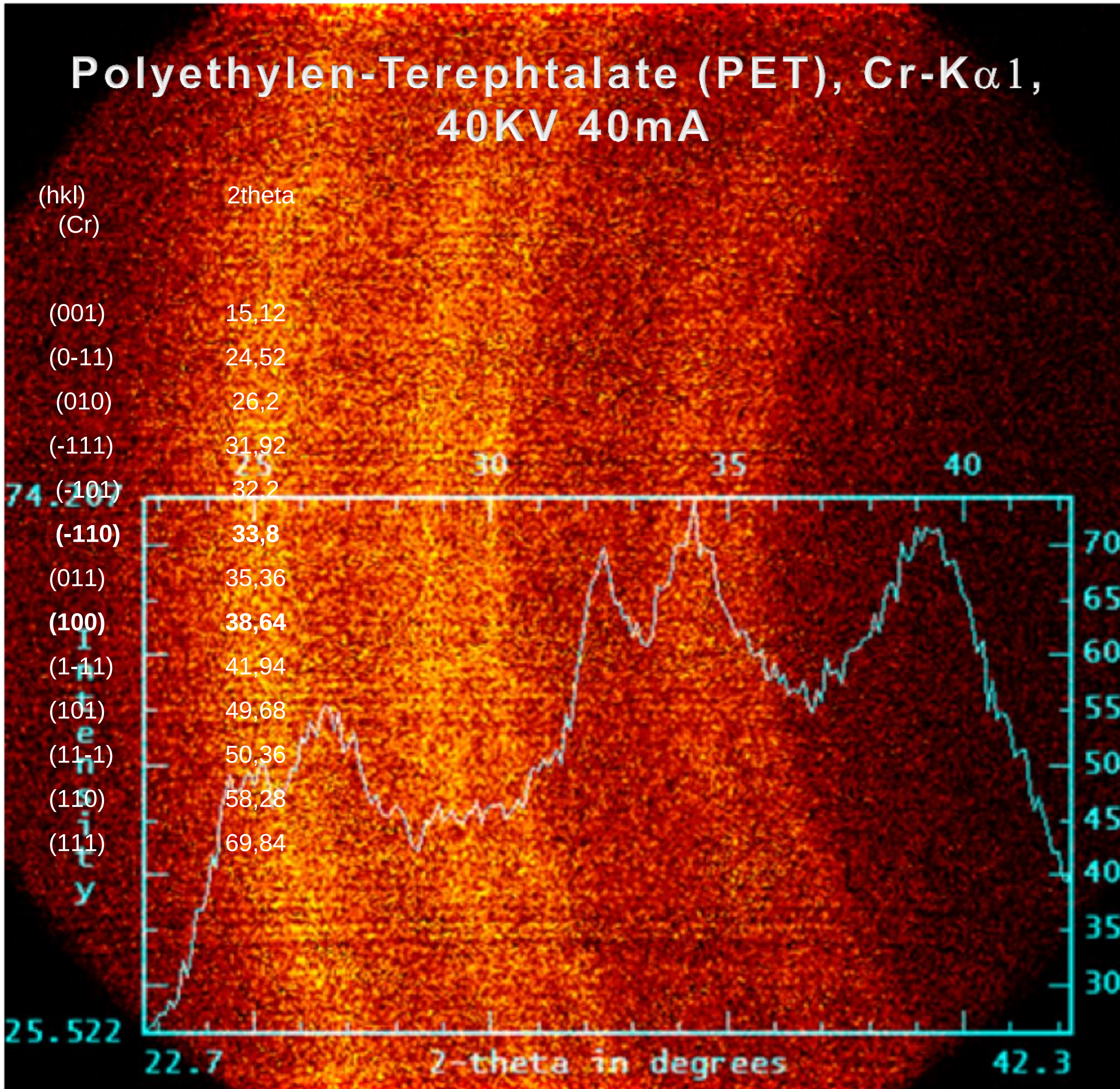




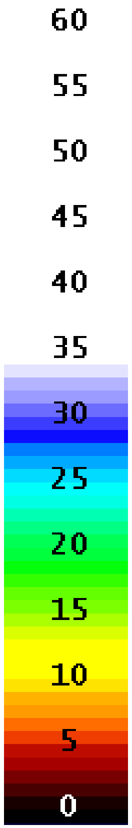
1 millimeter square, OM

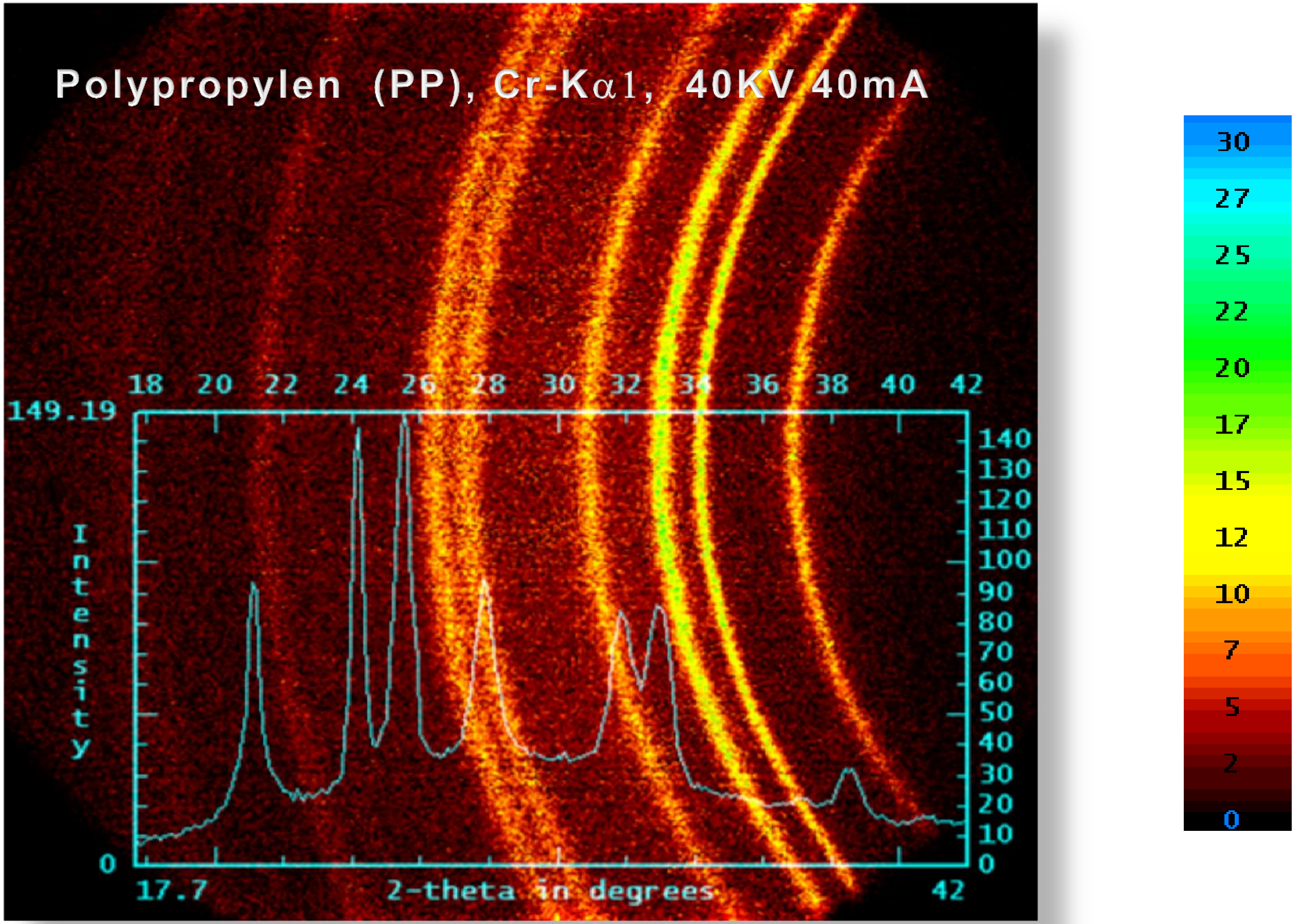
Bamford, Nature 173 (1954) p. 27;   Astbury, Endeavor 1(1942) p. 70

Polymer structure: PET: XRD



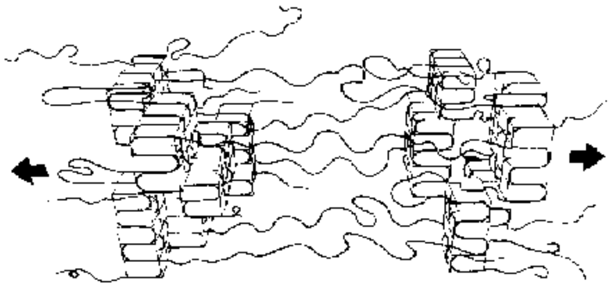
(hkl) (Cr)	2theta
(001)	15,12
(0-11)	24,52
(010)	26,2
(-111)	31,92
(-101)	32,2
(-110)	**33,8**
(011)	35,36
(100)	**38,64**
(1-11)	41,94
(101)	49,68
(11-1)	50,36
(110)	58,28
(111)	69,84



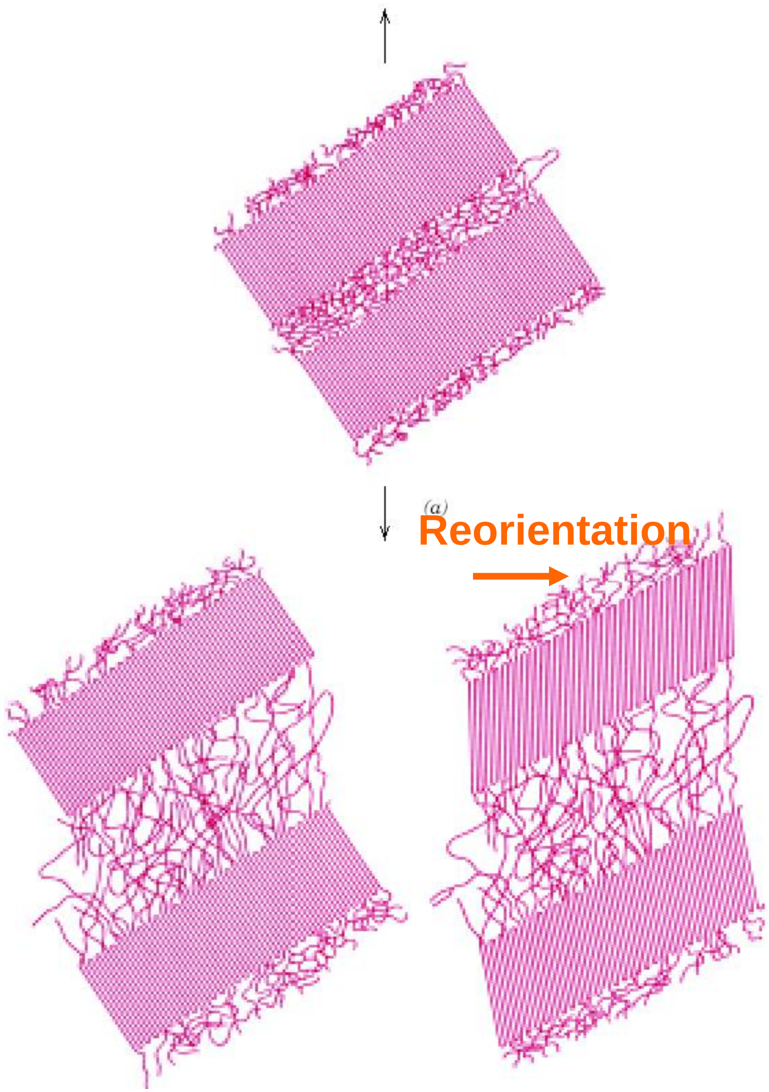

Polypropylen (PP), Cr-Kα1, 40KV 40mA
18 20 22 24 26 28 30 32 34 36 38 40 42
149.19
Intensity
0
17.7
2-theta in degrees
42
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
30 27 25 22 20 17 15 12 10 7 5 2 0

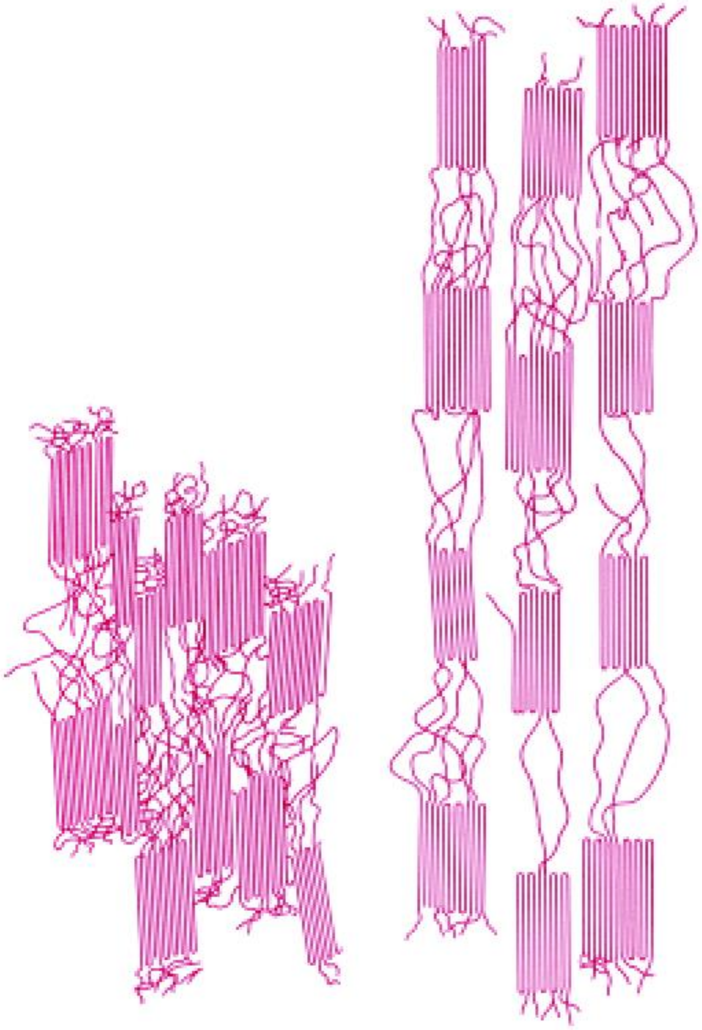
Structure of semicrystalline polymers on a molecular scale can be approximated as consisting of two phases:
(a) crystalline regions
(b) disordered quasi-amorphous interlamellar (IL) regions.

Crystal regions typically consist of crystal lamellae by regular folding chains.
Within the IL regions four types of molecules are present
(a)- tails with one free end;
(b)- loops, which start and end in the same lamellae;
(c)- bridges (**tie molecules**) which join up two lamellae
(d)- floating molecules which are unattached to any lamella

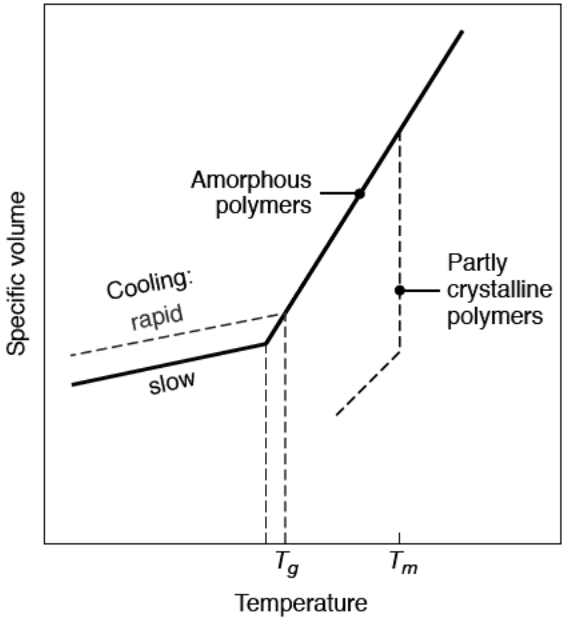


Polymer structure: deformation of semi-crystalline polymers





Polymer structure: deformation of semi-crystalline polymers

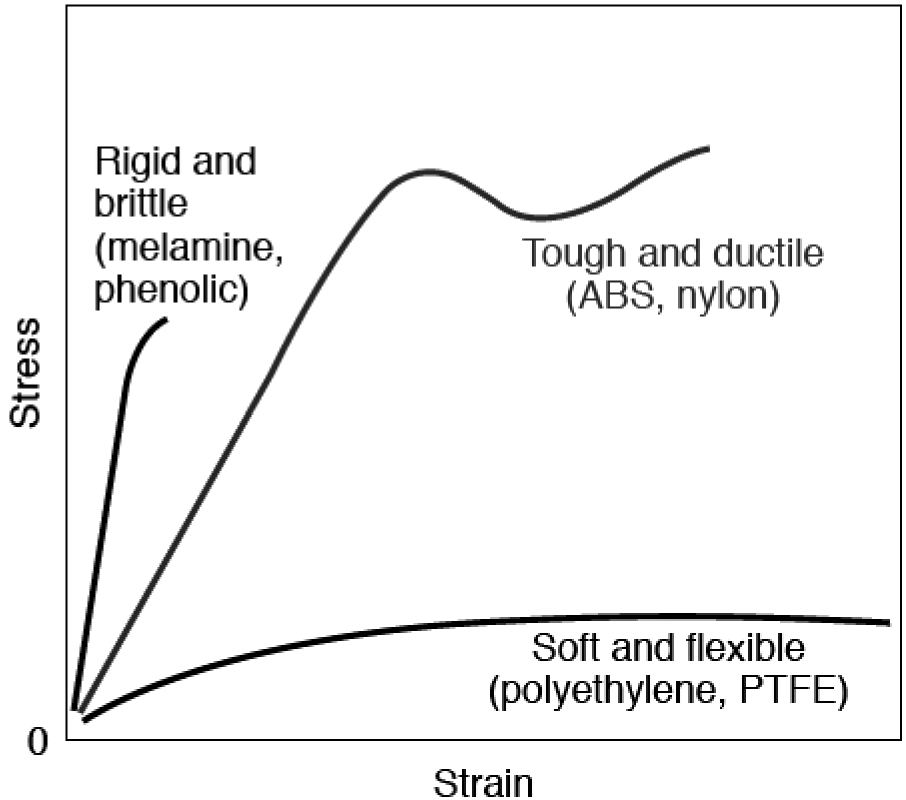


Material	T_g (°C)	T_m (°C)
Nylon 6,6	57	265
Polycarbonate	150	265
Polyester	73	265
Polyethylene		
High density	-90	137
Low density	-110	115
Polymethylmethacrylate	105	–
Polypropylene	-14	176
Polystyrene	100	239
Polytetrafluoroethylene (Teflon)	-90	327
Polyvinyl chloride	87	212
Rubber	-73	–

Specific volume of polymers as a function of temperature. Amorphous polymers, such as acrylic and polycarbonate, have a glass-transition temperature, *Tg, but do not have a specific melting* point, *Tm. Partly crystalline polymers, such as* polyethylene and nylons, contract sharply at their melting points during cooling.

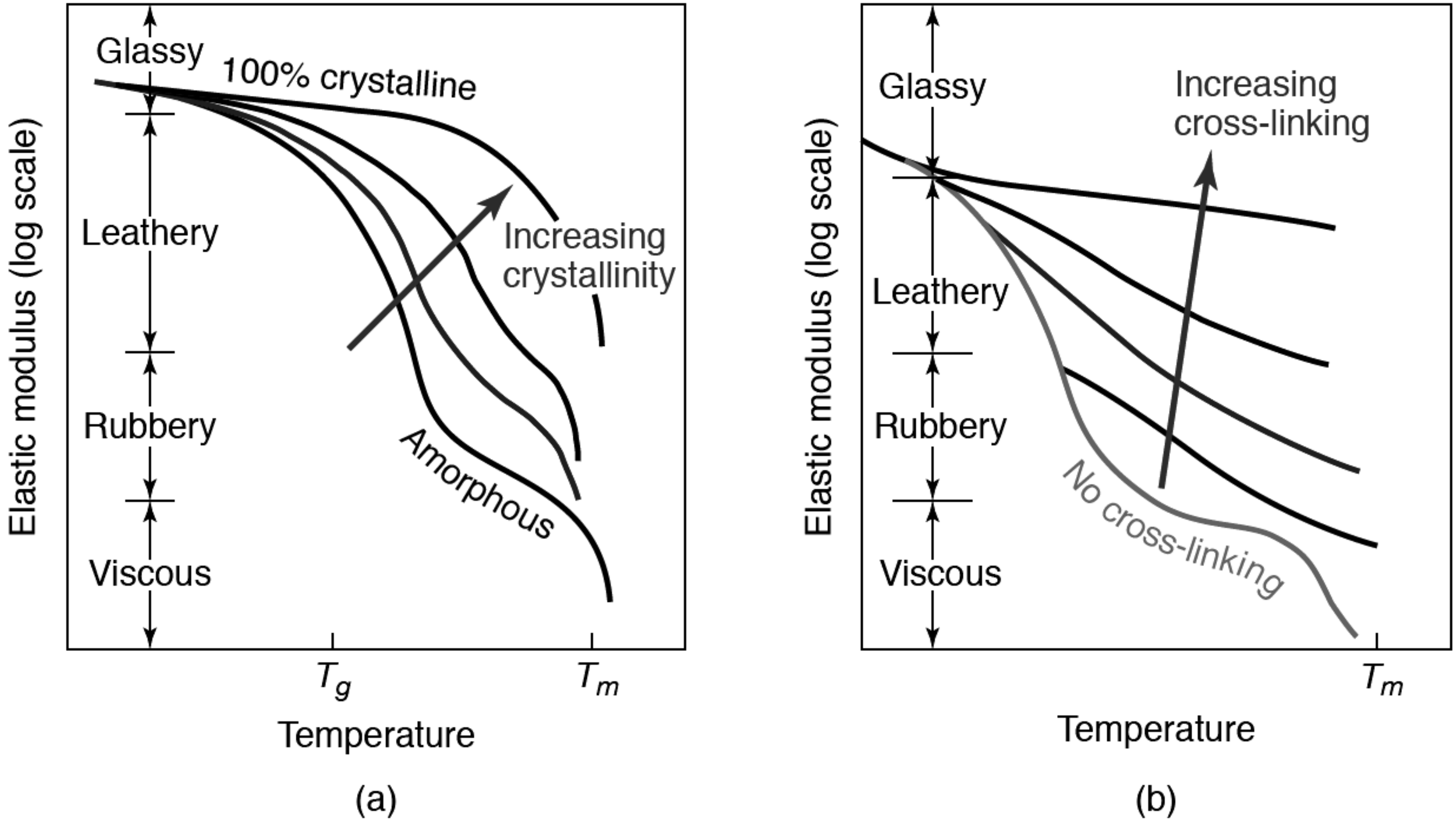
Glass-Transition and Melting Temperatures of Selected Polymers

Polymers: mechanical properties – trends

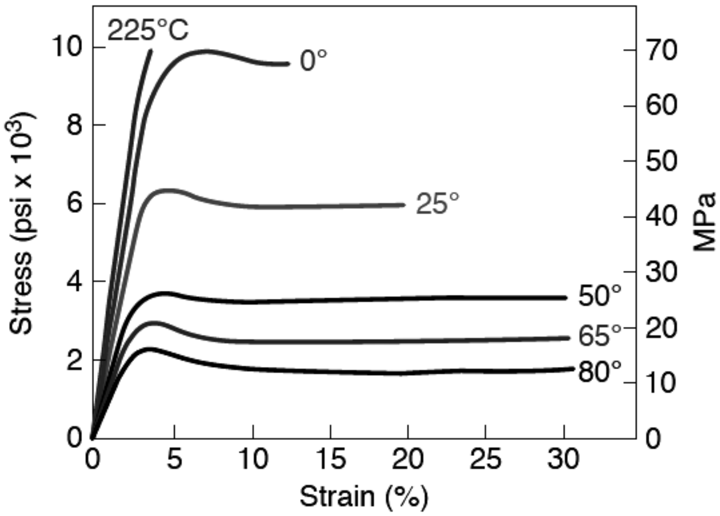


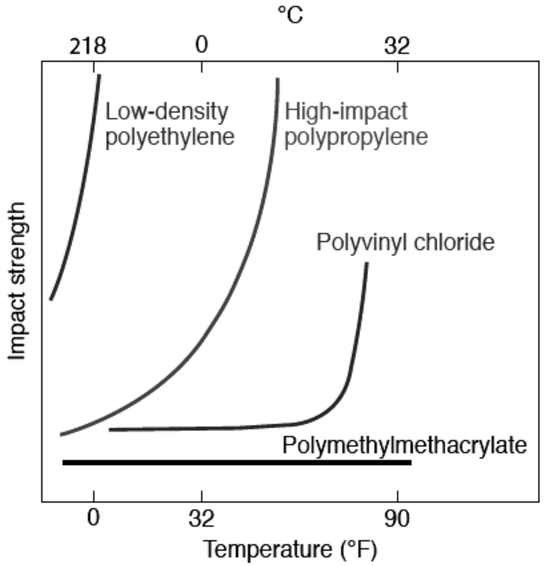
General terminology describing the behavior of three types of plastics. PTFE is polytetrafluoroethylene (Teflon, a trade name). *Source: After R.L.E. Brown.*

Polymers: mechanical properties – the influence of temperature



Behavior of polymers as a function of temperature and (a) degree of crystallinity and (b) crosslinking. The combined elastic and viscous behavior of polymers is known as viscoelasticity.





Effect of temperature on the stressstrain curve for cellulose acetate, a thermoplastic. Note the large drop in strength and increase in ductility with a relatively small increase in temperature. *Source: After T.S. Carswell and H.K.* Nason.

Effect of temperature on the impact strength of various plastics. Note that small changes in temperature can have a significant effect on impact strength. *Source: P.C.* Powell.

Durability of polymer composites

Polymer composites change with time and most significant factors are

- Elevated temperatures
- Fire
- Moisture
- Adverse chemical environments
- Natural weathering when exposed to sun's ultra-violet radiation

Polymer composites: mechanical properties

MATERİAL	Relative density	Diameter thickness ratio (microns)	Length (mm)	E (GPa)	Tens. Str. (MPa)	Failure strain (%)	Volume in composite (%)
Mortar matrix	1.8-2.0	300-5000	-	10-30	1-10	0.01-0.05	85-97
Concrete matrix	1.8-2.4	10000-20000	-	20-40	1-4	0.01-0.02	97-99.5
Asbestos	2.55	0.02-30	5-40	164	200-1800	2-3	5-15
Carbon	1.16-1.95	7-18	3-cont.	30-390	600-2700	0.5-2.4	3-5
Glass	2.7	12.5	10-50	70	600-2500	3.6	3-7
Polyethylene							
HDPE filament	0.96	900	3-5	5	200	-	2-4
High modulus	0.96	20-50	Cont.	10-30	> 400	> 4	5-10
Polypropylene (Monofilament)	0.91	20-100	5-20	4	-	-	0.1-0.2
Polyvinyl alcohol (PVA)	1-3	3-8	2-6	12-40	700-1500	-	2-3
Steel	7.86	100-600	10-60	200	700-2000	3-5	0.3-2.0

Performance is controlled by

- **vol. fraction of fibers**
- **properties of fibers and matrix**
- **bond between the two**

Polymer composites: mechanical properties

Material	UTS (MPa)	E (GPa)	Elongation in 50 mm (%)	Poisson's ratio (ν)
ABS	28–55	1.4–2.8	75–5	–
ABS (reinforced)	100	7.5	–	0.35
Acetals	55–70	1.4–3.5	75–25	–
Acetals (reinforced)	135	10	–	0.35–0.40
Acrylics	40–75	1.4–3.5	50–5	–
Cellulosics	10–48	0.4–1.4	100–5	–
Epoxies	35–140	3.5–17	10–1	–
Epoxies (reinforced)	70–1400	21–52	4–2	–
Fluorocarbons	7–48	0.7–2	300–100	0.46–0.48
Nylon	55–83	1.4–2.8	200–60	0.32–0.40
Nylon (reinforced)	70–210	2–10	10–1	–
Phenolics	28–70	2.8–21	2–0	–
Polycarbonates	55–70	2.5–3	125–10	0.38
Polycarbonates (reinforced)	110	6	6–4	–
Polyesters	55	2	300–5	0.38
Polyesters (reinforced)	110–160	8.3–12	3–1	–
Polyethylenes	7–40	0.1–0.14	1000–15	0.46
Polypropylenes	20–35	0.7–1.2	500–10	–
Polypropylenes (reinforced)	40–100	3.6–6	4–2	–
Polystyrenes	14–83	1.4–4	60–1	0.35
Polyvinyl chloride	7–55	0.014–4	450–40	–

Approximate range of mechanical properties for various engineering plastics at room temperature.

Type	Tensile Strength (MPa)	Elastic Modulus (GPa)	Density (kg/m^3)	Relative Cost
Boron	3500	380	2600	Highest
Carbon				
High strength	3000	275	1900	Low
High modulus	2000	415	1900	Low
Glass				
E type	3500	73	2480	Lowest
S type	4600	85	2540	Lowest
Kevlar				
29	2800	62	1440	High
49	2800	117	1440	High
129	3200	85	1440	High
Nextel				
312	1630	135	2700	High
610	2770	328	3960	High
Spectra				
900	2270	64	970	High
1000	2670	90	970	High

Note: These properties vary significantly, depending on the material and method of preparation. Strain to failure for these fibers is typically in the range of 1.5% to 5.5%.

Typical properties of reinforcing fibers