Physical Foundations of Dental Materials Science 5.

Polymers, composites.

E-book Chapters: 12-13

Homework: Chapter 3.: 21, 24, 25, 27

Types of dental materials

Metallic bond

METALS

CERAMICS

Compounds of metals and non-metals

POLYMERS

Molecules composed of series of monomeric building blocks

COMPOSITES

Contains at least two of the previous three families

Polymers

Macromolecule, that is a long chain of monomers

Properties:

- low density
- liquid or solid at room temperature
- low/medium stiffness and hardness, but easily malleable
- viscoelasticity
- relatively bad heat and corrosion resistance
- relatively bad electric and heat conduction
- diverse optical properties

Structure:

- covalent bonds between monomers in the chain, but usually weaker secondary bonds between chains
- semi-crystalline or amorphous

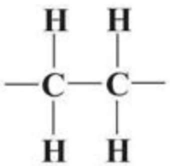
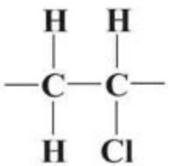
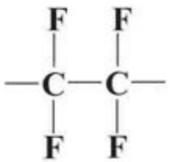
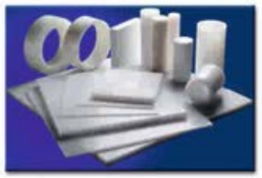
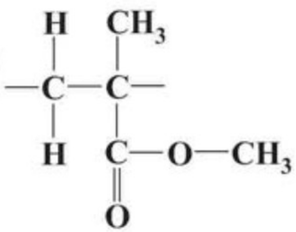
synthesis:

- addition
- condensation

Applications:

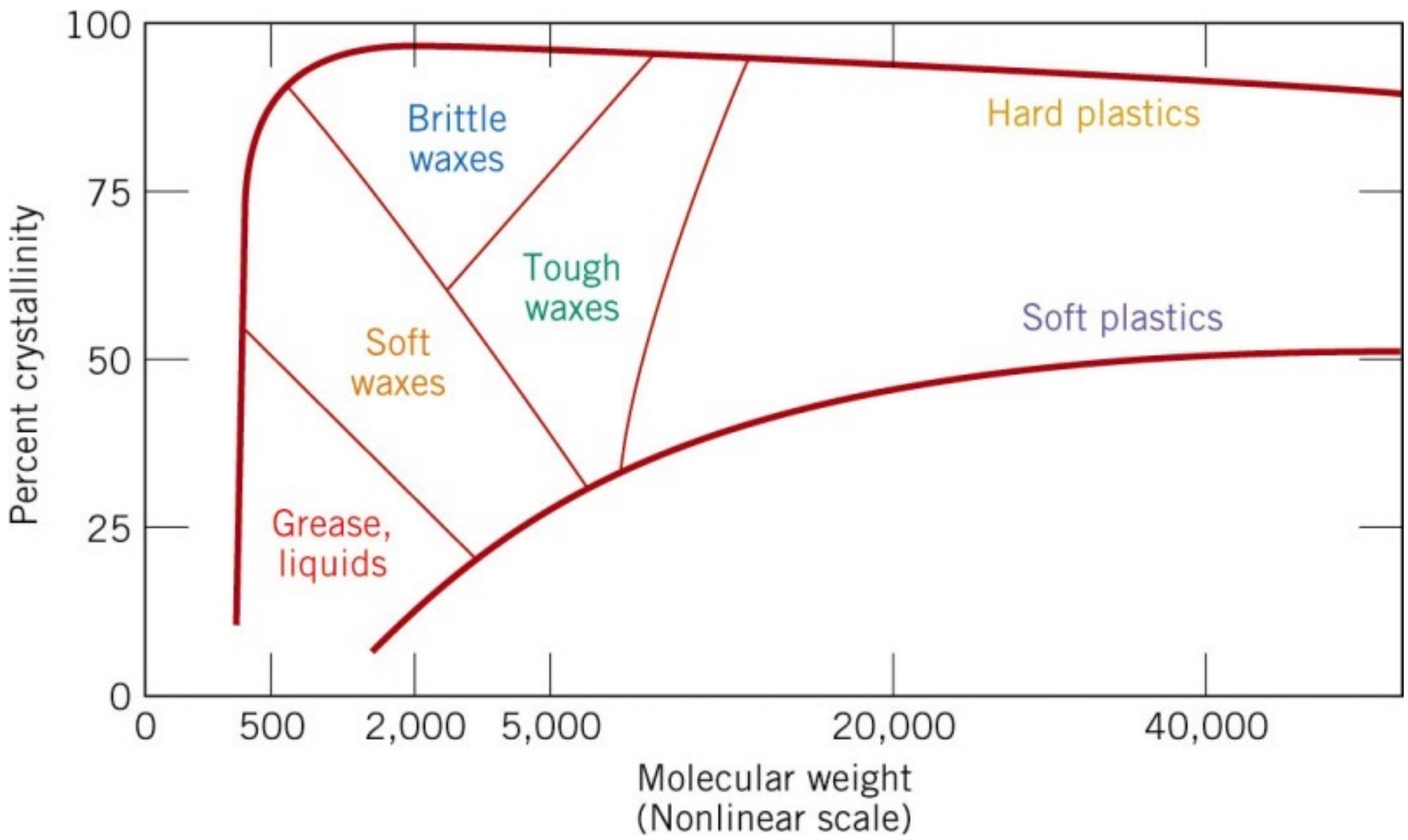
- denture
- filling
- impression materials

Monomer

name of the polymer	structure of the monomer	industrial application	dental application
polyethylene (PE)			
polyvinylchloride (PVC)			
polytetrafluoroethylene (PTFE, Teflon)			
Poly(methyl methacrylate) (PMMA, acrylic glass)			

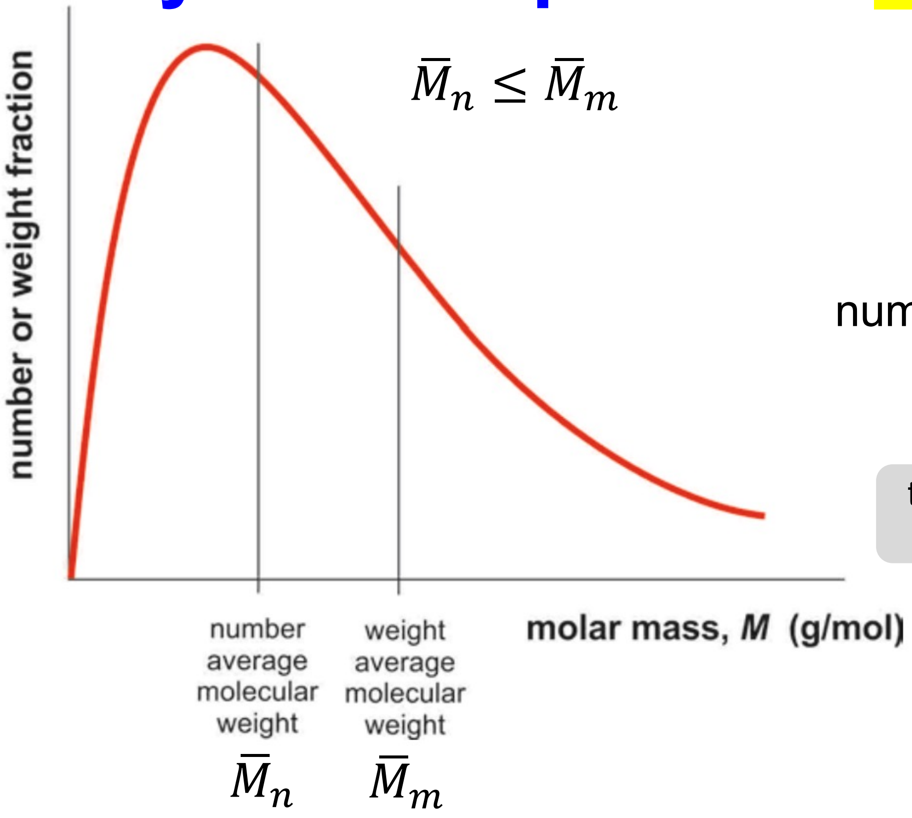
- **homopolymer:** one kind of monomer only
- **heteropolymer (copolymer):** two or more kinds of monomers

The length (molar mass) of polymer molecules and percent of crystallinity determines the physical properties:



Polymer composition

Statistics!



...of molecules with given molecular weight

number...

mass...

number ratio: $\dfrac{n_i}{n}$

mass ratio: $\dfrac{m_i}{m}$

total number of molecules

total mass of molecules

number average molecular weight ($\bar{M}_n$):

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \cdots + n_i M_i + \cdots + n_k M_k}{n_1 + n_2 + \cdots + n_i + \cdots + n_k} = \frac{\sum_{i=1}^{k} n_i M_i}{\sum_{i=1}^{k} n_i} \,.$$

weight average molecular weight ($\bar{M}_m$):

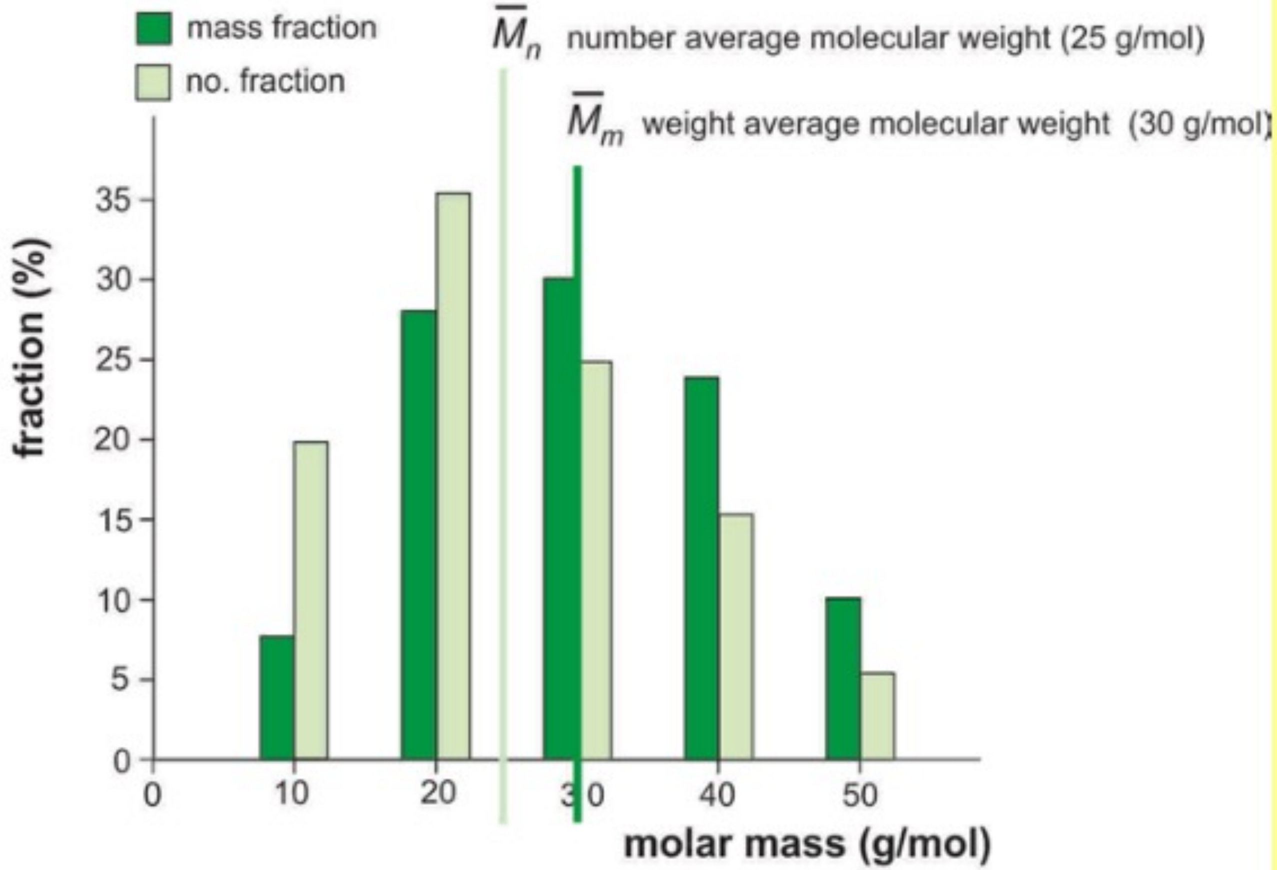
$$\bar{M}_m = \frac{m_1 M_1 + m_2 M_2 + \cdots + m_i M_i + \cdots + m_k M_k}{m_1 + m_2 + \cdots + m_i + \cdots + m_k} = \frac{\sum_{i=1}^{k} m_i M_i}{\sum_{i=1}^{k} m_i} \,.$$

An example:

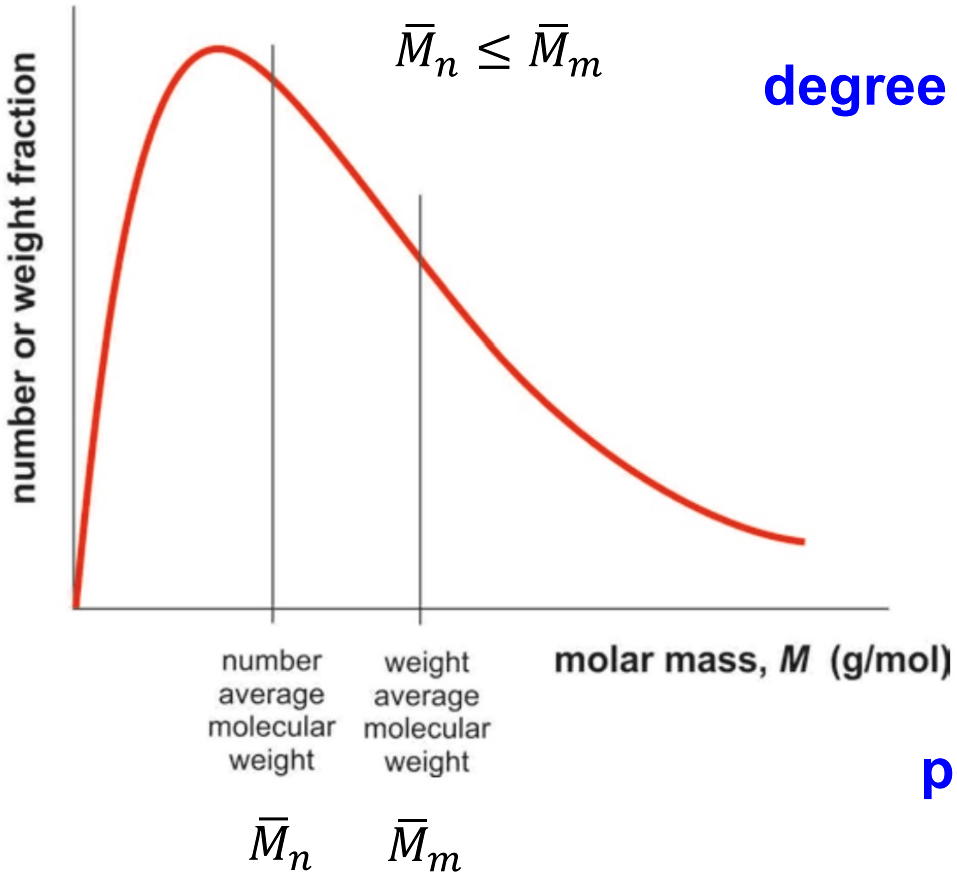
molar mass, M_i (g/mol)	n_i	number ratio n_i/n	$m_i = n_i \cdot M_i$ (g/mol)*	mass ratio m_i/m
$M_1 = 10$	$n_1 = 4$	4/20 = 0.20 = 20%	$m_1 = 4 \cdot 10 = 40$	40/500 = 0.08 = 8%
$M_2 = 20$	$n_2 = 7$	7/20 = 0.35 = 35%	$m_2 = 7 \cdot 20 = 140$	140/500 = 0.28 = 28%
$M_3 = 30$	$n_3 = 5$	5/20 = 0.25 = 25%	$m_3 = 5 \cdot 30 = 150$	150/500 = 0.30 = 30%
$M_4 = 40$	$n_4 = 3$	3/20 = 0.15 = 15%	$m_4 = 3 \cdot 40 = 120$	120/500 = 0.24 = 24%
$M_5 = 50$	$n_5 = 1$	1/20 = 0.05 = 5%	$m_5 = 1 \cdot 50 = 50$	50/500 = 0.10 = 10%
total	$n = 20$	1 = 100%	$m = 500$	1 = 100%

$$\bar{M}_n = \frac{\sum_{i=1}^{k} n_i M_i}{\sum_{i=1}^{k} n_i}$$

$$\bar{M}_m = \frac{\sum_{i=1}^{k} m_i M_i}{\sum_{i=1}^{k} m_i}$$



$$\bar{M}_n \leq \bar{M}_m$$



degree of polymerization: $\dfrac{\bar{M}_n}{M_{\text{monomer}}}$

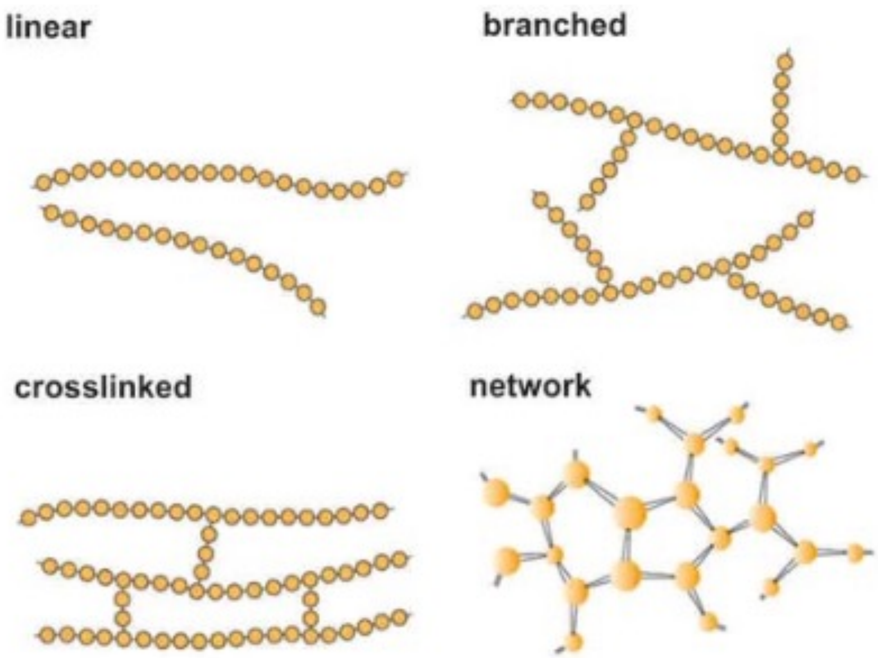
average length of polymer molecules

polydispersity index: $\dfrac{\bar{M}_m}{\bar{M}_n}$

diversity of polymer molecules

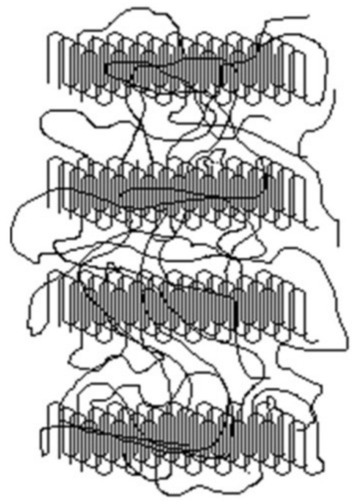
= 1: monodisperse
1< : polydisperse

Structure of polymers



- thermoplastics: *Acrylic (PMMA), Nylon, polyethylene, PVC, teflon...*
- thermosets: vulcanized rubber, bakelite, epoxy...
  - elastomers: great elasticity

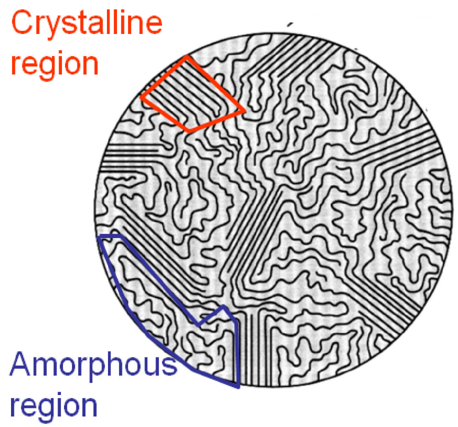
semi-crystalline



Degree of crystallinity (*x*):

amorphous $x = \frac{m_{crystalline}}{m_{total}} (\cdot\, 100\%)$ crystalline

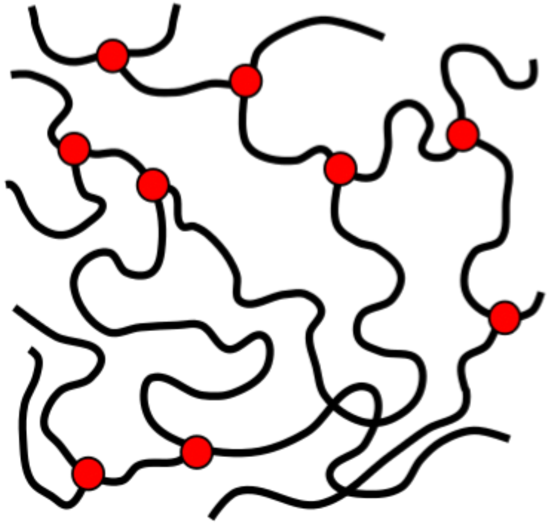
0% → 100%

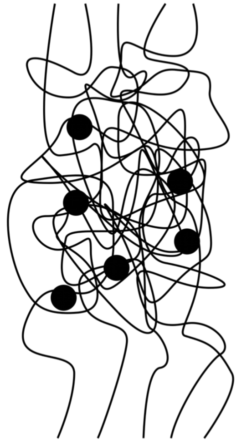


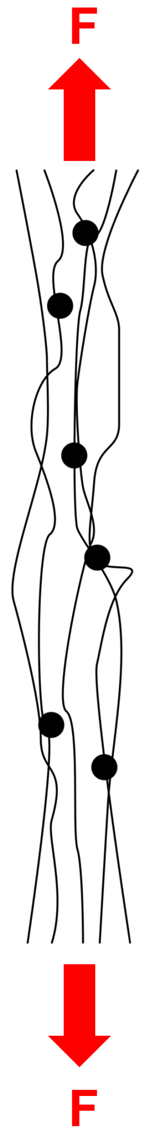
Elastomers

Elastic polymers

- Composed of long coiled chains
- Few cross-links between chains
- Network of long chains





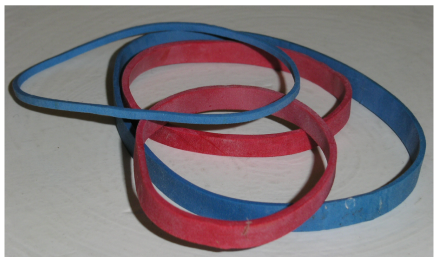


max reversible strain: 5-700%

vulcanization

(cross-links)

Rubber

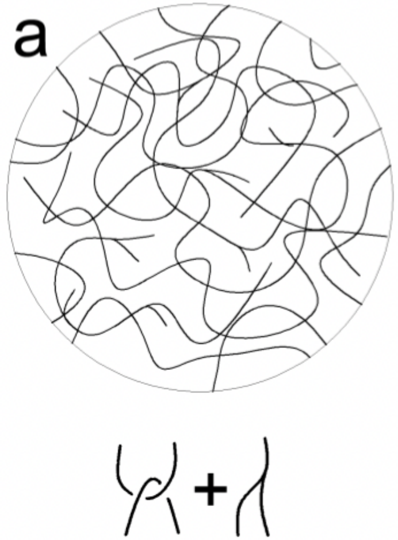


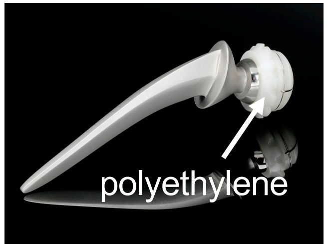
Thermoplastics

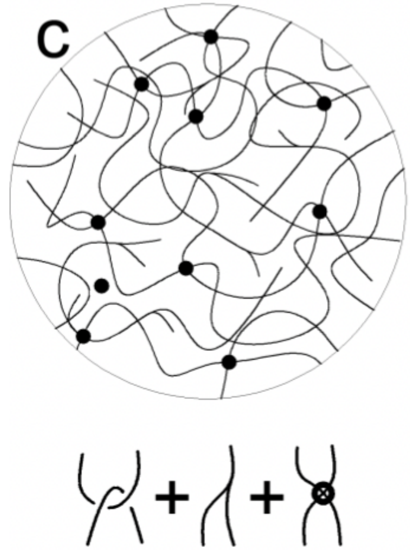
- Softens upon heating
- No cross-links between chains
- Amorphous or crystalline

Thermosets

- Strong (primary) cross-linking bonds between chains
- Network structure







Amorphous

- PVC
- PMMA

Semicrystalline

- Polyethylene
- PET

Network structure

- Epoxy resins

Composites

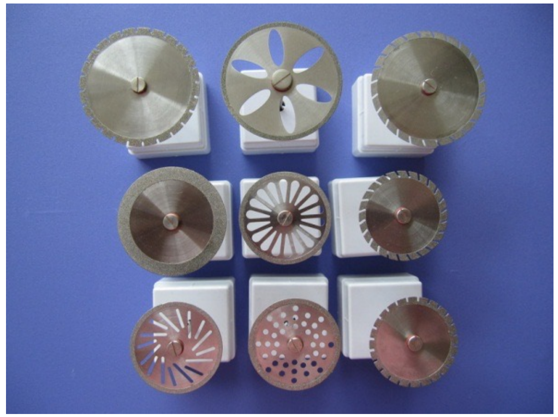
Materials of multiple, chemically different components with distinct phase boundaries

Properties:

- low density
- solid at room temperature
- combines the benefits of each of the phases
- strong, elastic and tough
- diverse optical properties

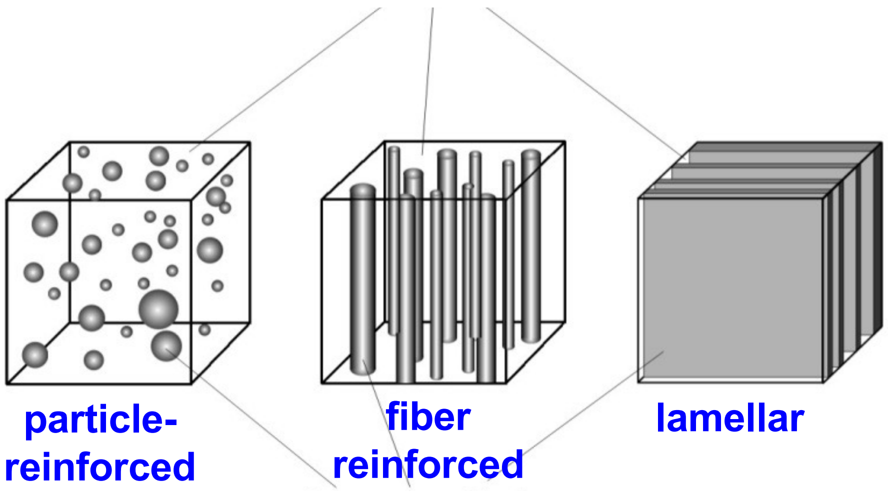
Applications:

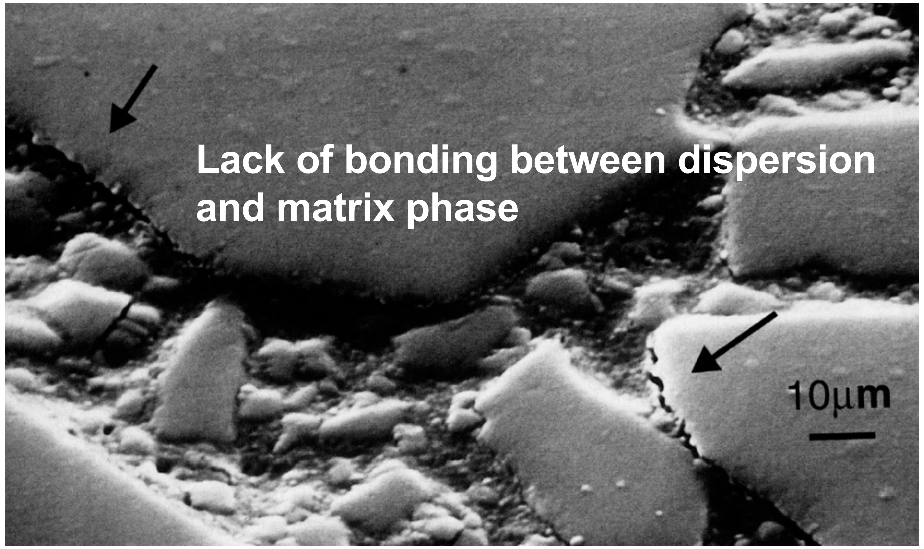
- filling
- dental tools



Structure of composites

Two-phase composite: **Matrix phase** **(polymer, metal, ceramics)**
+
dispersion phase **(ceramics, metal, ...)**
+
couplin agent! **(silanes)**

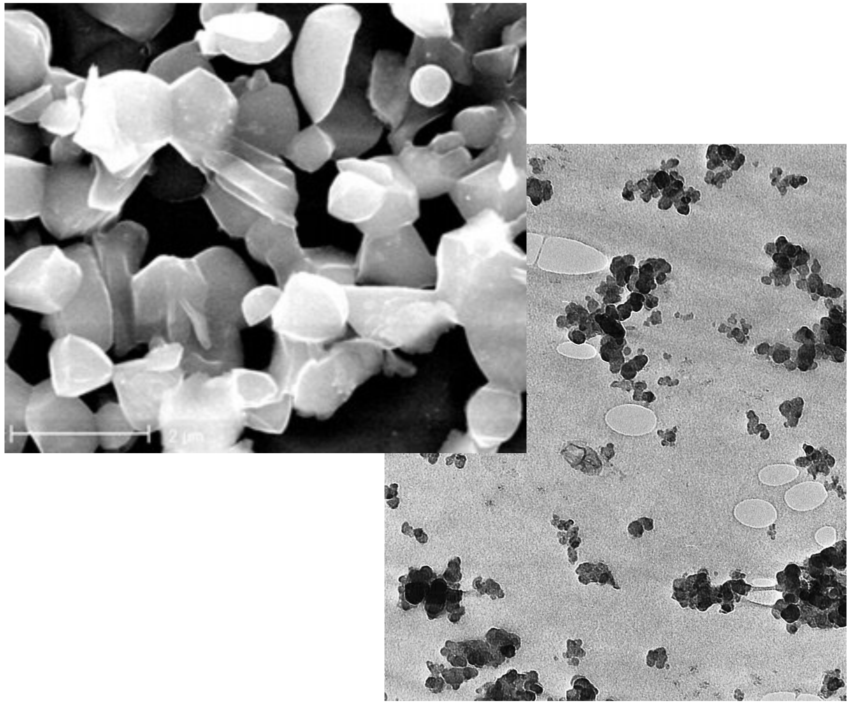




Hybrid composites: multiple dispersion phases particle-reinforced

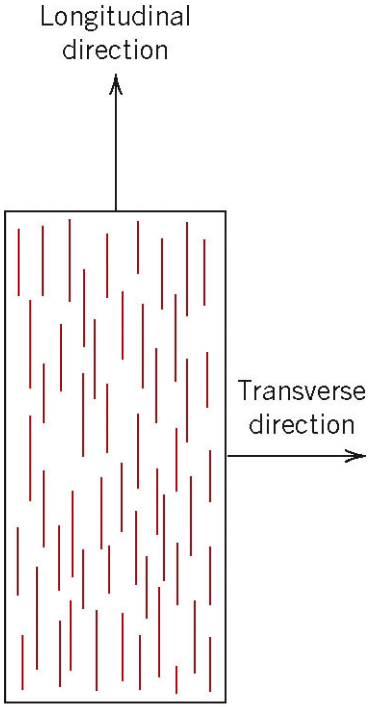
large particles

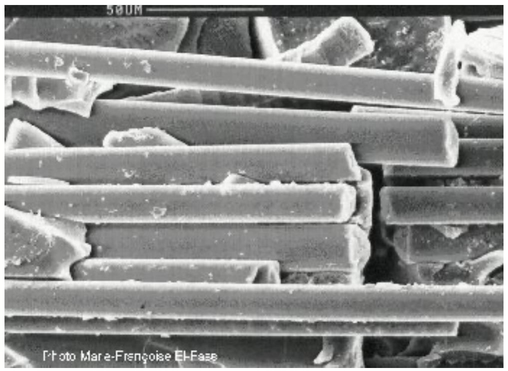
fine particles



fiber-reinforced

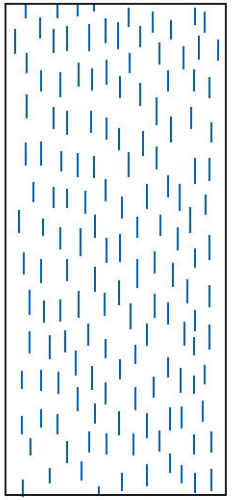
long unidirectional



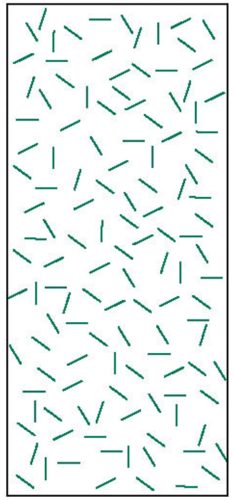


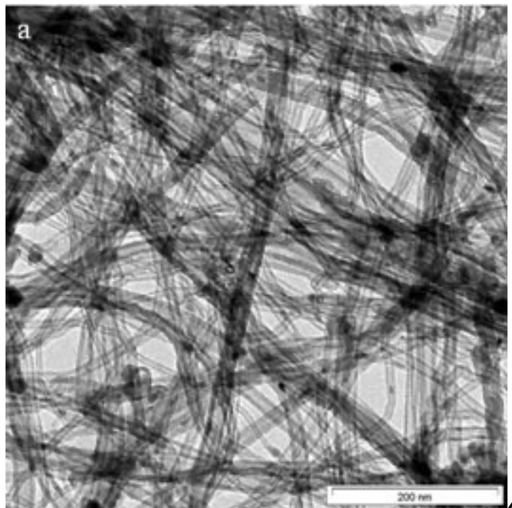
short fiber

unidirectional

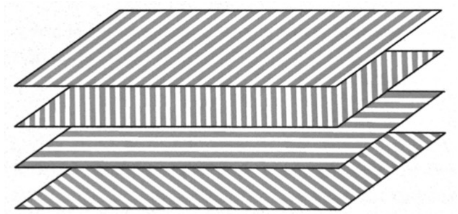


randomly oriented

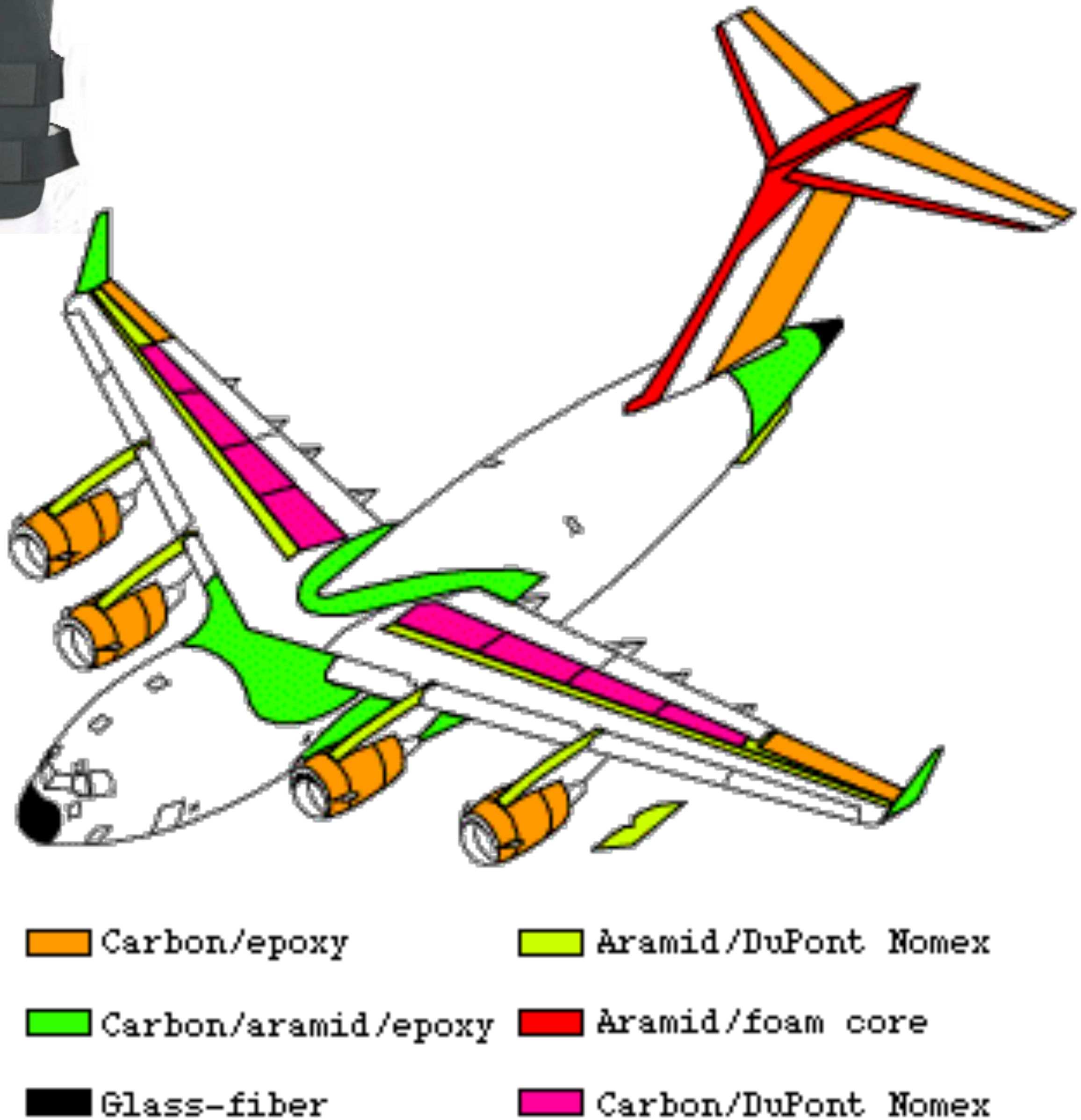




Structural compsites



Applications

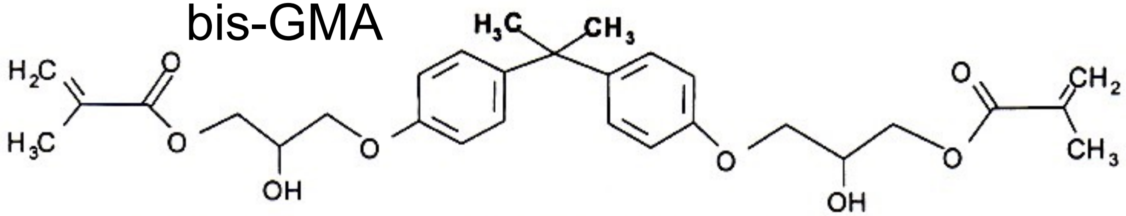


Dental composites

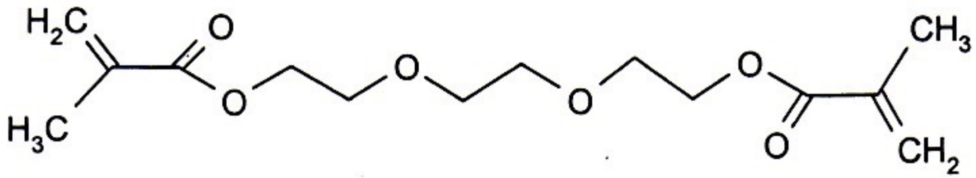
matrix: polymer (dimethacrylate)

dispersion material: glass (silica), ceramic crystal (i.e. quartz), polymer, + pigment, + UV absorbent (photoinitiator), ...

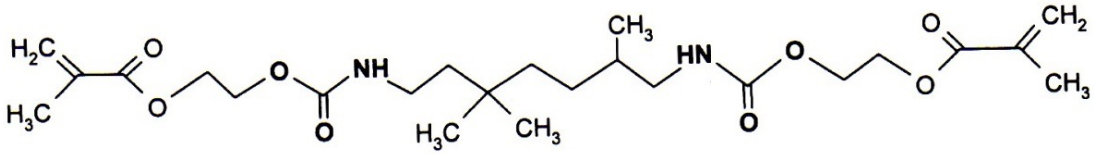
bis-GMA



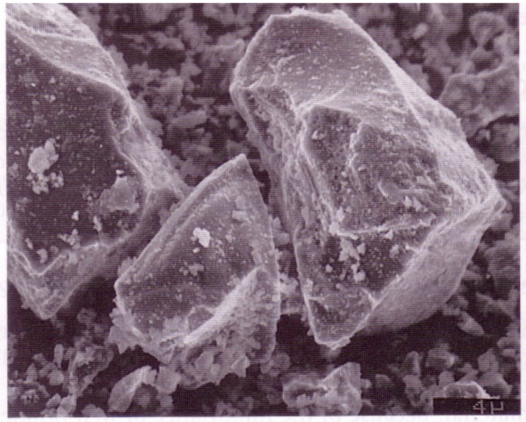
TEGDGMA



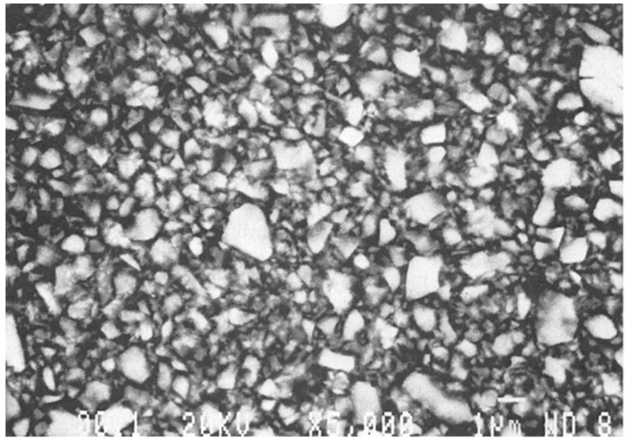
UDMA



large-grained (0,1-100 μm)



micrograined (≈ 40 nm)



shrinkage during polymerization may cause secondary caries