

Physical bases of dental material science

Polymers, composites

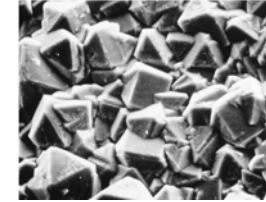
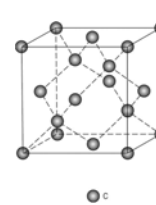
Irén Bárdos-Nagy

Polymers

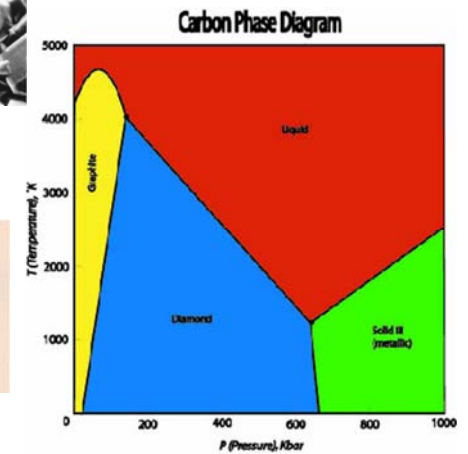
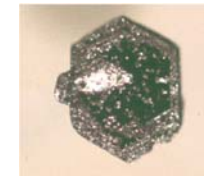
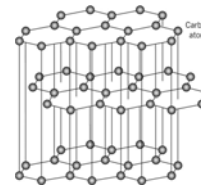
derivate from the Greek roots:

poly (many) and **meros** (part)

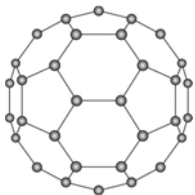
diamond



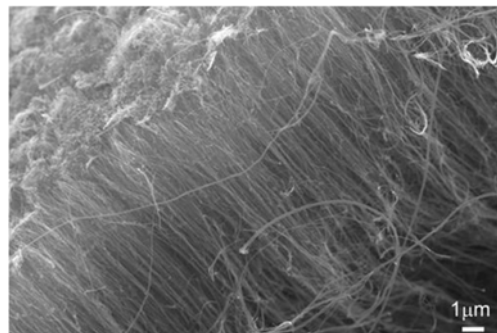
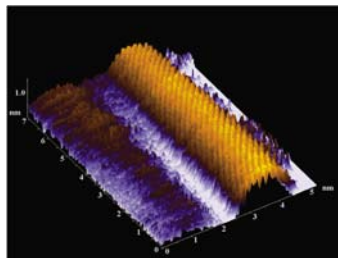
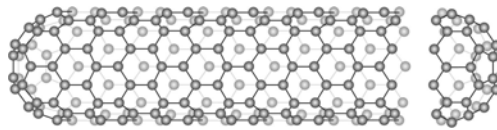
graphite



fullerene (C₆₀)

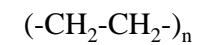
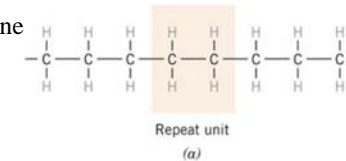


nanotube

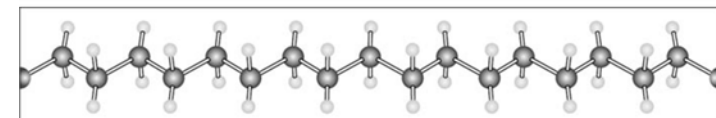


Large (macro) molecule composed of structural units connected by covalent bond

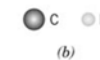
example: polyethylene



$$10.000 < n < 100.000$$



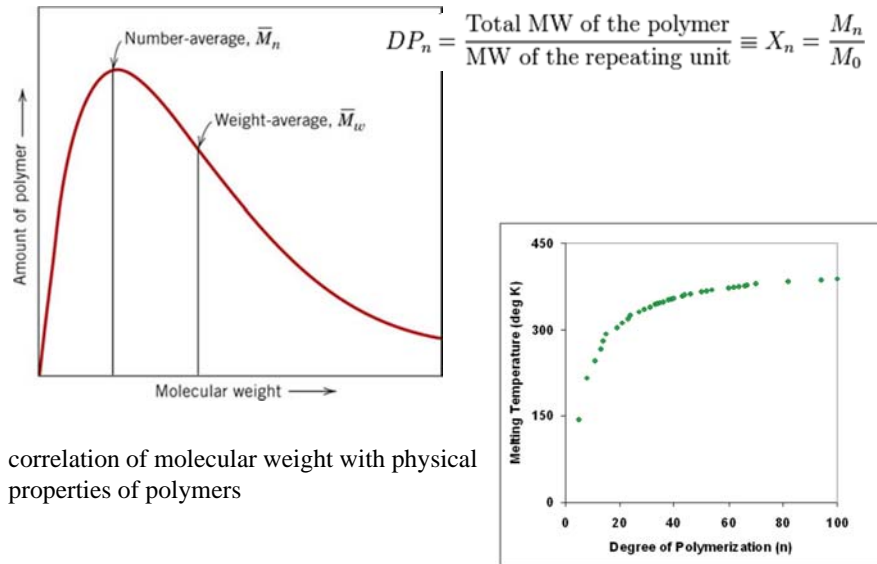
homopolymers - copolymers



- 1 ← homopolymer
- 2 ← alternating
- 3 ← statistical
- 4 ← block
- 5 ← graft

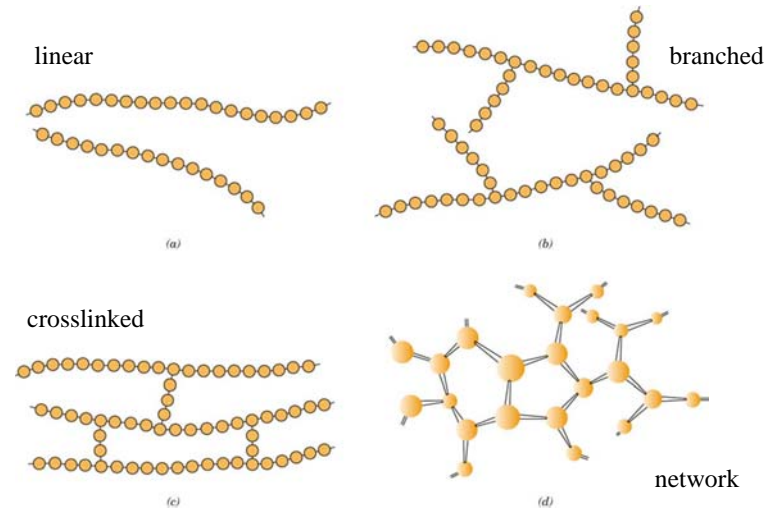
copolymers

Molecular weight – degree of polymerisation



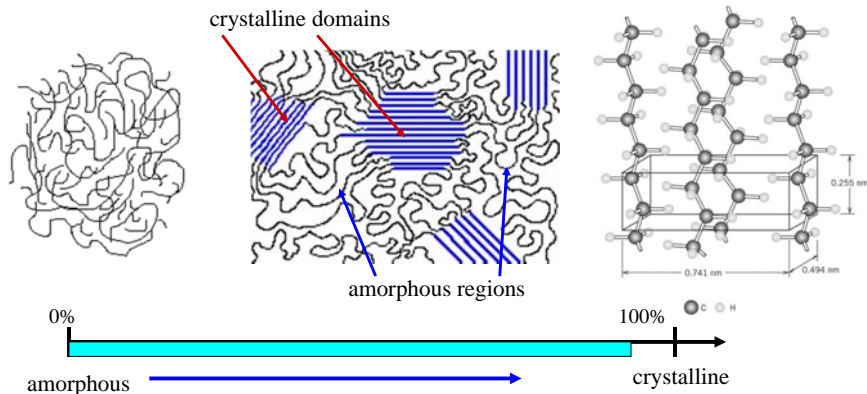
correlation of molecular weight with physical properties of polymers

Types of the polymer chains



Morphology of polymers

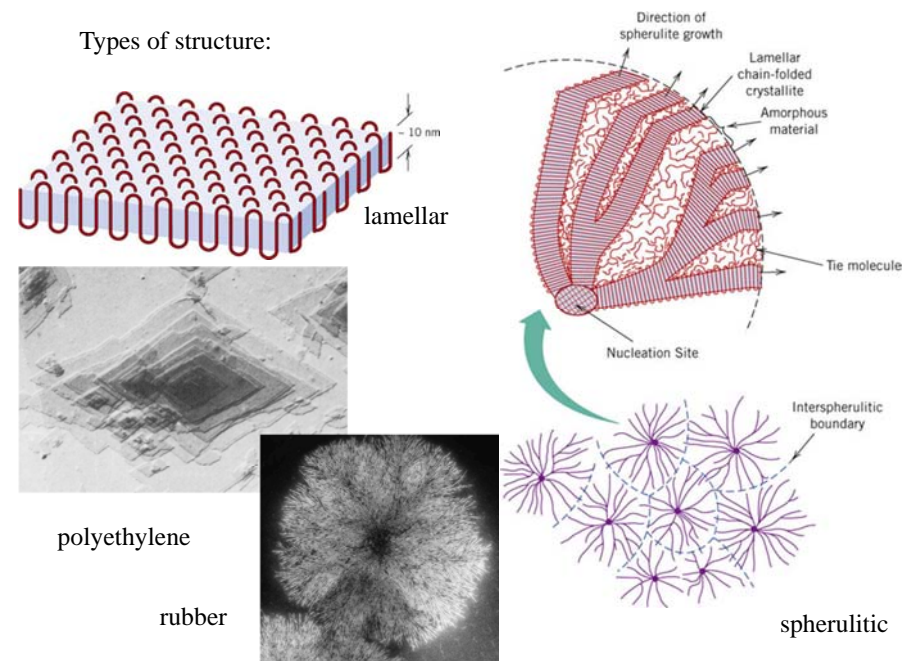
ordered crystalline – like regions + disordered amorphous domains
 semi - crystalline structure



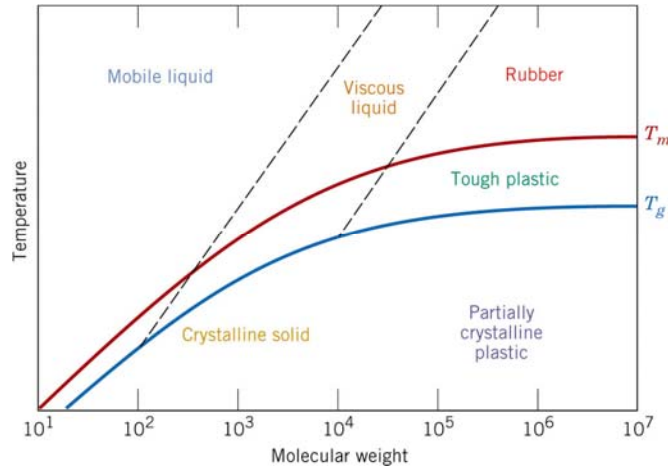
increase in rigidity, tensile strength and opacity, decrease in deformability

factors influencing the degree of crystallinity: temperature, type of the monomer,
 chain length, chain branching, interchain bonding

Types of structure:



Dependence of melting and glass transition temperatures and polymer properties on molecular weight



T_m is the temperature at which crystalline domains lose their structure, or melt. As crystallinity increases, so does T_m.
T_g is the temperature below which amorphous domains lose the structural mobility of the polymer chains and become rigid glasses.

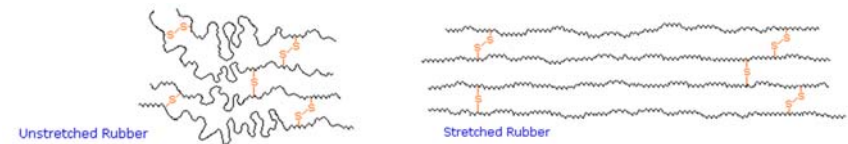
Thermoplastic polymers (thermoplasts): soften *reversibly* when heated (harden when cooled)

At elevated T inter-chain bonding is weakened allowing deformation at low stresses. Most thermoplasts are linear polymers and some branched structures.

Thermosetting polymers (thermosets): harden *permanently* when heated.

Covalent crosslinks (~ 10 - 50% of mers) formed during heating. Cross-linking hinders bending and rotations. Thermosets are harder, more dimensionally stable, and more brittle than thermoplasts.

Elastomers: a group of *amorphous polymers* that have the ability to stretch and then return to their original shape at temperatures above T_g.

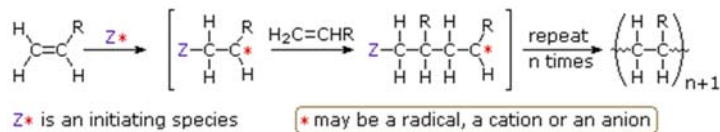


Synthesis of polymers - polymerization

a./ Addition (chain-reaction or chain-growth) polymerization:

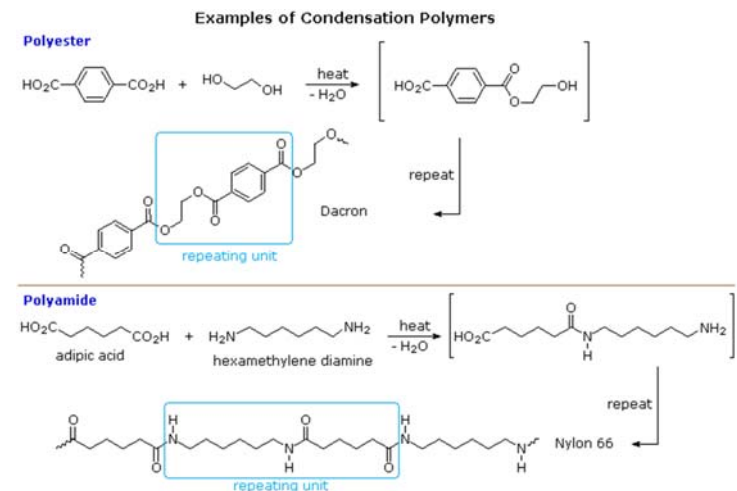
The monomer units are attached one at a time.

Has three distinct stages: initiation, propagation, and termination.

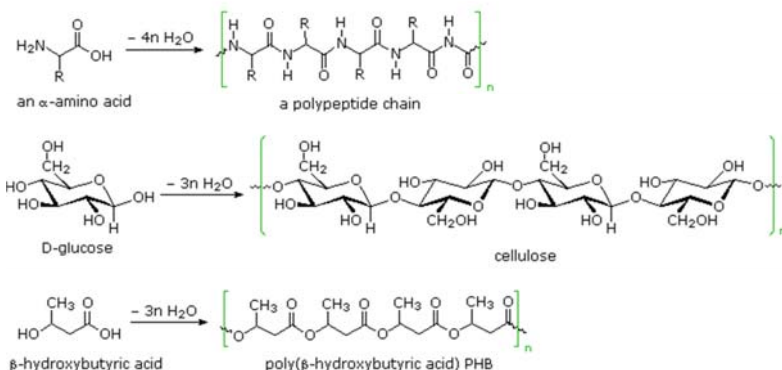


b./ Condensation (step reaction, step growth) polymerization:

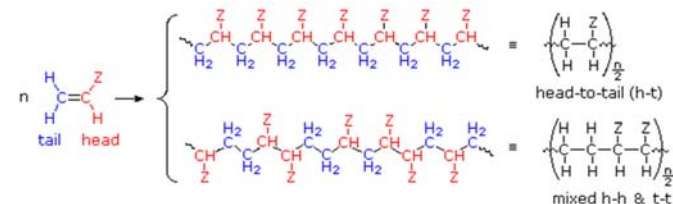
stepwise intermolecular chemical reactions that produce the mer units



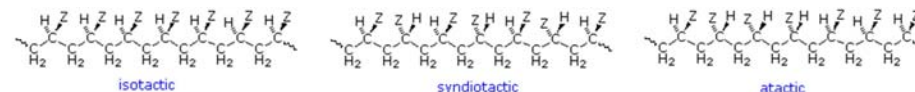
Some Natural Condensation Polymers



Regio and stereoisomerisation in macromolecules



Regioisomeric Polymers from Substituted Monomers



Polymer	T _g atactic	T _g isotactic	T _g syndiotactic
PP	-20 °C	0 °C	-8 °C
PMMA	100 °C	130 °C	120 °C

Some examples of common addition polymers

Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	ethylene $\text{CH}_2=\text{CH}_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	ethylene $\text{CH}_2=\text{CH}_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$-(\text{CH}_2-\text{CH}(\text{CH}_3))_n-$	propylene $\text{CH}_2=\text{CHCH}_3$	<u>atactic</u> : soft, elastic solid <u>isotactic</u> : hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$-(\text{CH}_2-\text{CHCl})_n-$	vinyl chloride $\text{CH}_2=\text{CHCl}$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$-(\text{CH}_2-\text{CCl}_2)_n-$	vinylidene chloride $\text{CH}_2=\text{CCl}_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$-(\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5))_n-$	styrene $\text{CH}_2=\text{CHC}_6\text{H}_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)

Polyacrylonitrile (PAN, Orlon, Acrilan)	$-(\text{CH}_2-\text{CHCN})_n-$	acrylonitrile $\text{CH}_2=\text{CHCN}$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$-(\text{CF}_2-\text{CF}_2)_n-$	tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$-(\text{CH}_2-\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3)_n-$	methyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$-(\text{CH}_2-\text{CHOCOCH}_3)_n-$	vinyl acetate $\text{CH}_2=\text{CHOCOCH}_3$	soft, sticky solid	latex paints, adhesives
cis-Polyisoprene natural rubber	$-(\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2)_n-$	isoprene $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$-(\text{CH}_2-\text{CH}=\text{CCl}-\text{CH}_2)_n-$	chloroprene $\text{CH}_2=\text{CH}-\text{CCl}=\text{CH}_2$	tough, rubbery solid	synthetic rubber oil resistant

Formula	Type	Components	T _g °C	T _m °C
$\sim[\text{CO}(\text{CH}_2)_x\text{CO}-\text{OCH}_2\text{CH}_2\text{O}]_n\sim$	polyester	$\text{HO}_2\text{C}-(\text{CH}_2)_x-\text{CO}_2\text{H}$ $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$	< 0	50
	polyester Dacron Mylar	para $\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$	70	265
	polyester	meta $\text{HO}_2\text{C}-\text{C}_6\text{H}_3-\text{CO}_2\text{H}$ $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$	50	240
	polycarbonate Lexan	$(\text{HO}-\text{C}_6\text{H}_4)_2\text{C}(\text{CH}_3)_2$ (Bisphenol A) $\text{X}_2\text{C}=\text{O}$ (X = OCH ₃ or Cl)	150	267
$\sim[\text{CO}(\text{CH}_2)_x\text{CO}-\text{NH}(\text{CH}_2)_y\text{NH}]_n\sim$	polyamide Nylon 66	$\text{HO}_2\text{C}-(\text{CH}_2)_x-\text{CO}_2\text{H}$ $\text{H}_2\text{N}-(\text{CH}_2)_y-\text{NH}_2$	45	265
$\sim[\text{CO}(\text{CH}_2)_5\text{NH}]_n\sim$	polyamide Nylon 6 Perlon		53	223
	polyamide Kevlar	para $\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ para $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$	---	500
	polyamide Nomex	meta $\text{HO}_2\text{C}-\text{C}_6\text{H}_3-\text{CO}_2\text{H}$ meta $\text{H}_2\text{N}-\text{C}_6\text{H}_3-\text{NH}_2$	273	390
	polyurethane Spandex	$\text{HOCH}_2\text{CH}_2\text{OH}$ 	52	---

Physical properties of polymers (summary)

- low rigidity
- good ductility and viscoelasticity
- fragility (mainly the thermosets)
- chemical environment and temperature sensitivity
- low density
- large resistivity against the corrosion
- low resistivity against the heat

strongly depend on:

- molecular mass (chain length)
- structure
- degree of crystallinity

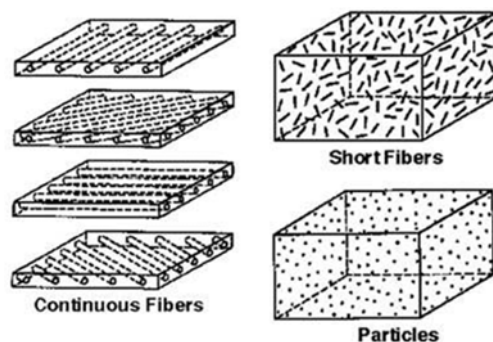
Dental application of polymers

- impression materials
- bases, liners and varnishes for cavities
- prosthesis

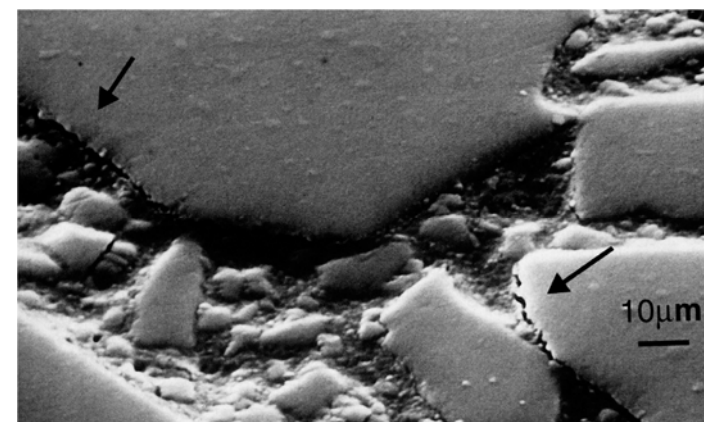


Composites

Composite materials (or composites) are made from two or more constituent materials with significantly different physical or chemical properties and which remain separate and distinct within the finished structure.(on microscopic and macroscopic scales)



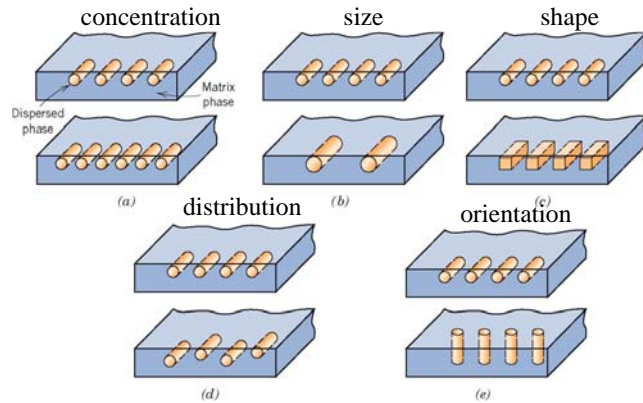
Bonding of matrix and disperse component



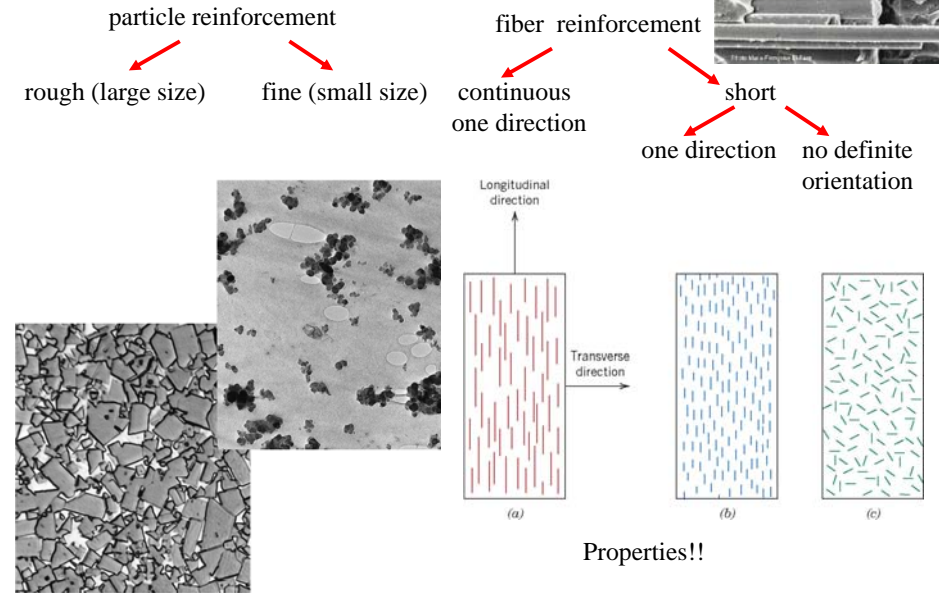
continuous phase (matrix)
metal, ceramic, polymer

dispersed phase (reinforcement)
ceramic, glass, metal...

Parameters acting on properties:



Types of composites



Dental application of composites:

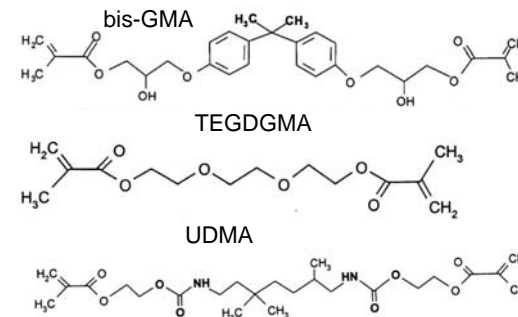
- fillings
- veneers
- restoration
- temporary crowns
- surface shaping and contouring



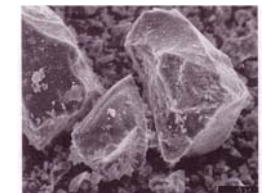
Dental composites:

Matrix: polymer (resin)

Reinforcement: ceramic, quartz, glass, polymer,
+ pigment + UV absorber



rough grains
(0,1-100 mm)



micrograins
(≈ 40 nm)

