Physical bases of dental material science

Polymers, composites

Irén Bárdos-Nagy

The simplified composition of an amalgam alloy is 45 % mercury, 40 % silver and 15 % thin. Calculate the molar percent of the components.
M_{Hg} 200,6, M_{Ag} 107,9, M_{Sn} 118,7

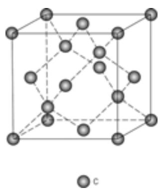
$$c_{\nu\,Ag} = \frac{\frac{40}{107{,}9}}{\frac{45}{200{,}6}+\frac{40}{107{,}9}+\frac{15}{118{,}7}}\cdot 100 = 51{,}4\%$$

$$c_{\nu\,Hg} = \frac{\frac{45}{200{,}6}}{\frac{45}{200{,}6}+\frac{40}{107{,}9}+\frac{15}{118{,}7}}\cdot 100 = 31{,}1\%$$

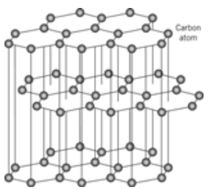
$$c_{\nu\,Sn} = \frac{\frac{15}{118{,}7}}{\frac{45}{200{,}6}+\frac{40}{107{,}9}+\frac{15}{118{,}7}}\cdot 100 = 17{,}6\%$$

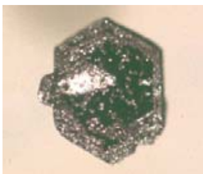
Polymers

diamond



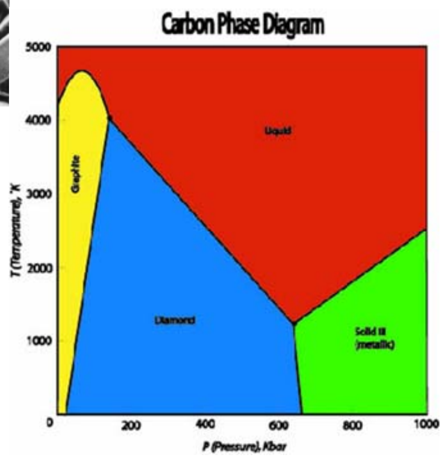
graphite



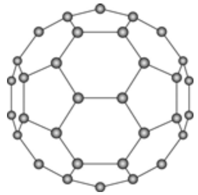


derivide from the Greek roots:

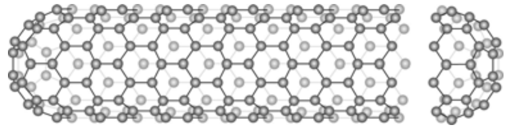
poly (many) and meros (part)

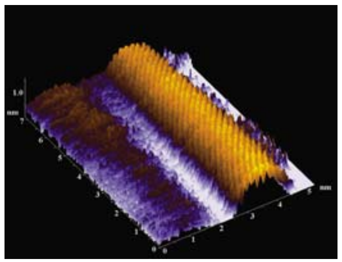


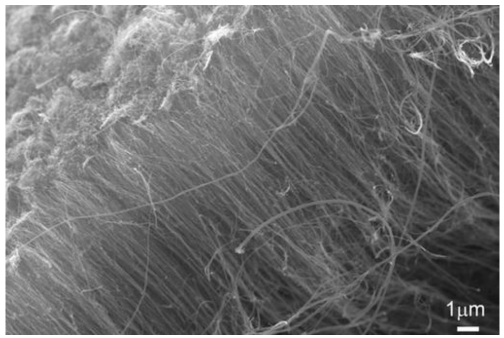
fullerene (C_{60})



nanotube

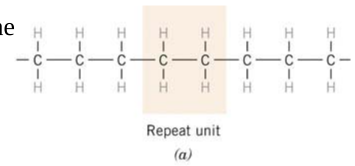






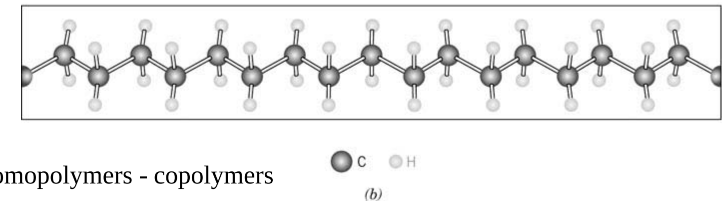
Large (macro) molecule composed of structural units connected by covalent bond

example: polyethylene



$(\text{-}CH_2\text{-}CH_2\text{-})_n$

$10.000 < n < 100.000$

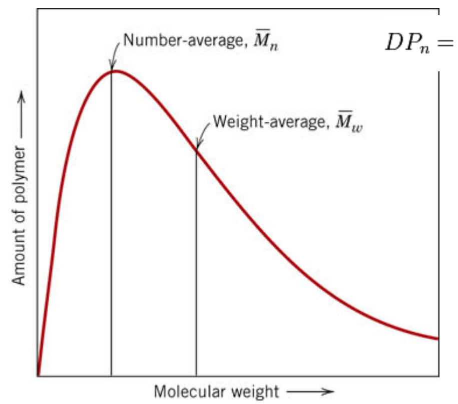


homopolymers - copolymers

1. homopolymer
2. alternating
3. statistical
4. block
5. graft

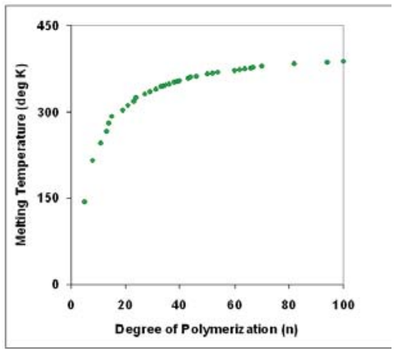
(2–5: copolymers)

Molecular weight – degree of polymerisation

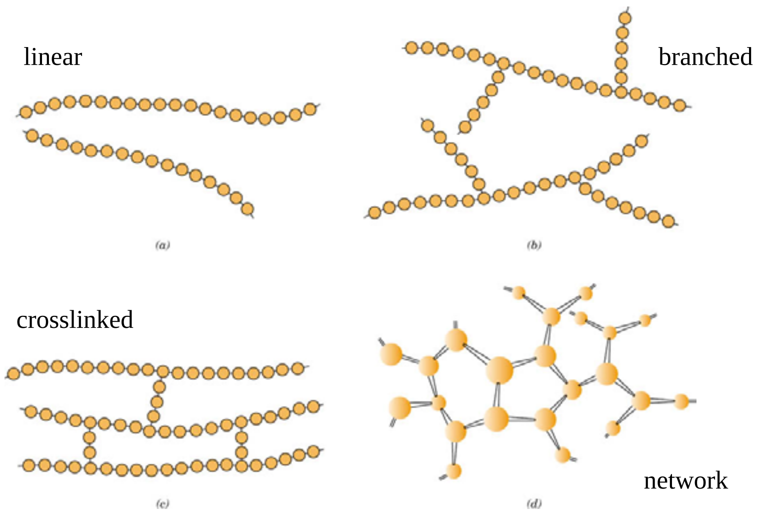


$$DP_n = \frac{\text{Total MW of the polymer}}{\text{MW of the repeating unit}} \equiv X_n = \frac{M_n}{M_0}$$

correlation of molecular weight with physical properties of polymers



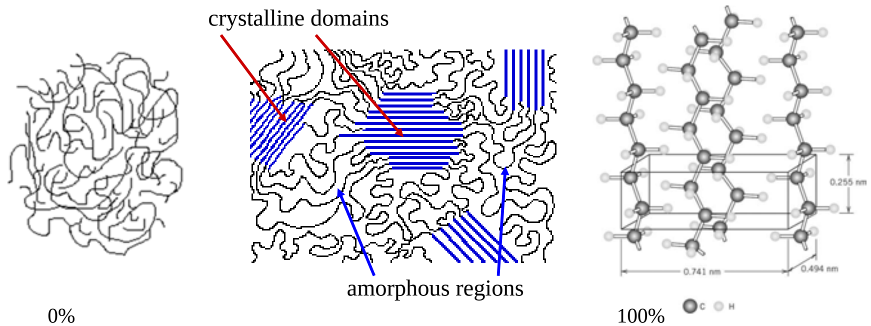
Types of the polymer chains

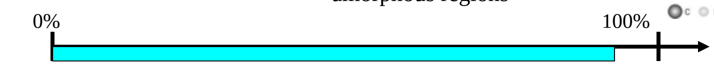


Morphology of polymers

ordered crystalline – like regions + disordered amorphous domains

semi - crystalline structure

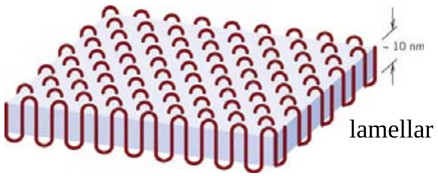




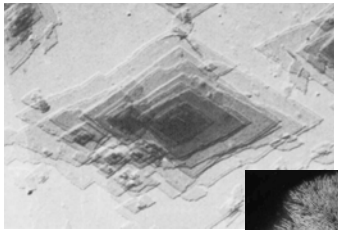
increase in rigidity, tensile strength and opacity, decrease in deformability

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

Types of structure:

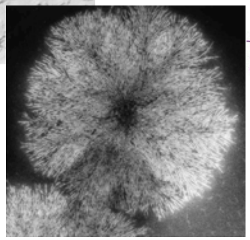


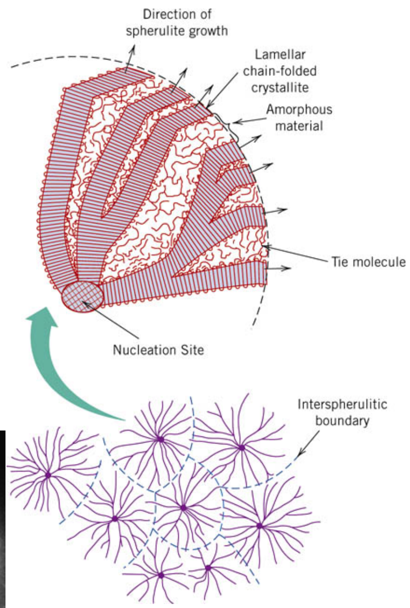
lamellar



polyethylene

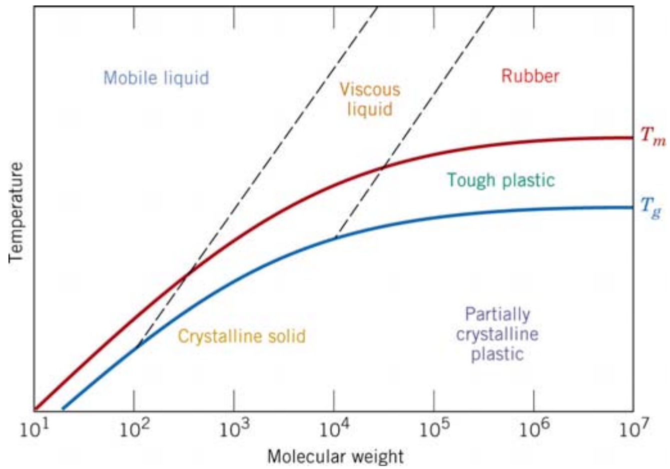
rubber





spherulitic

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



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

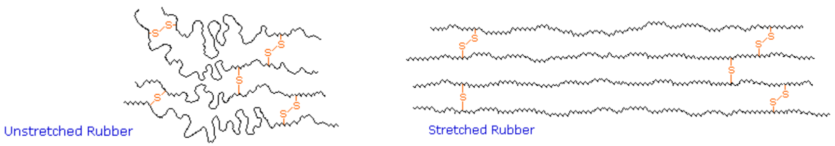
Thermoplastic polymers (thermoplasts): soften *reversibly* when heated (harden when cooled)

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 hinder bending and rotations. Thermosets are harder, more dimensionally stable, and more brittle than thermoplasts.

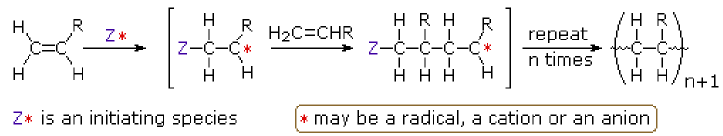
Elastomers: a group of amorphous polymers that have the ability to stretch and then return to their original shape at temperatures above Tg.



Synthesis of polymers - polymerization

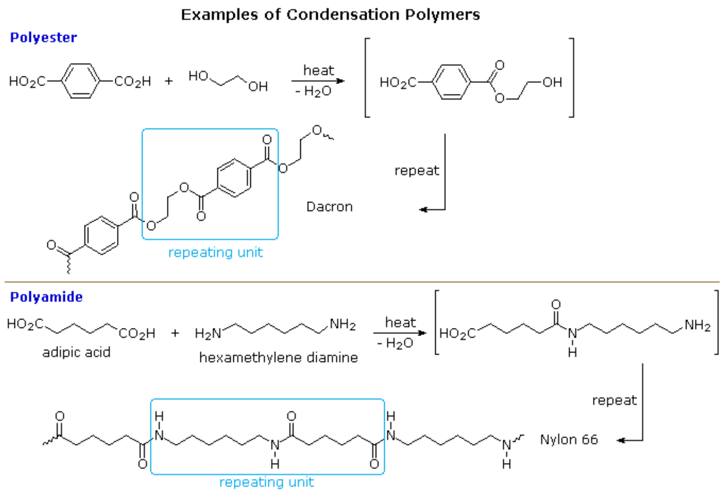
a./ Addition (chain-reaction or chain-growth) polymerization:

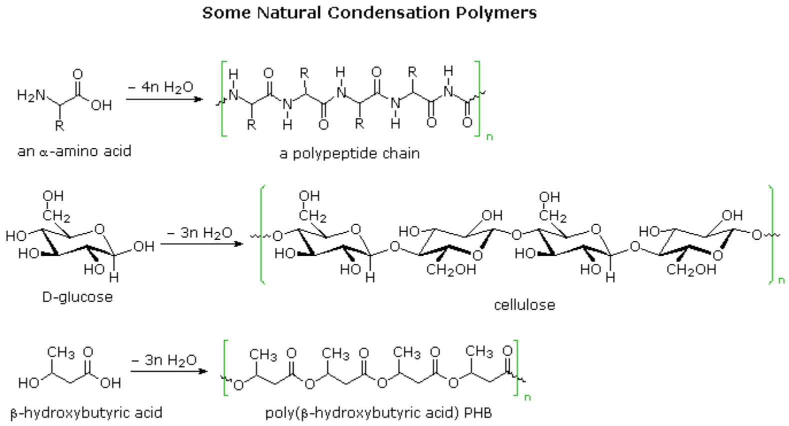
The monomer units are attached one at a time.
Has three distinct stages: initiation, propagation, and termination.



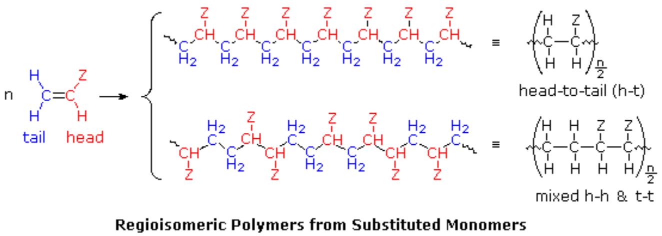
b./ Condensation (step reaction, step growth) polymerization:

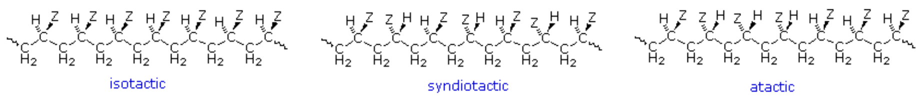
stepwise intermolecular chemical reactions that produce the mer units





Regio and stereoisomerisation in macromolecules



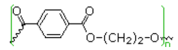
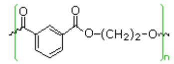
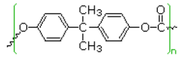
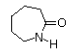
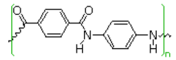
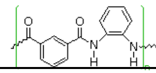
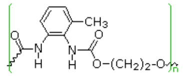
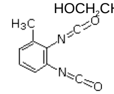


Polymer	T_g atactic	T_g isotactic	T_g syndiotactic
PP	–20 ºC	0 ºC	–8 ºC
PMMA	100 ºC	130 ºC	120 ºC

Some examples of common addition polymers

Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$–(CH_2\text{-}CH_2)_n–$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$–(CH_2\text{-}CH_2)_n–$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$–[CH_2\text{-}CH(CH_3)]_n–$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$–(CH_2\text{-}CHCl)_n–$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$–(CH_2\text{-}CCl_2)_n–$	vinylidene chloride $CH_2=CCl_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$–[CH_2\text{-}CH(C_6H_5)]_n–$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)

Polyacrylonitrile (PAN, Orlon, Acrilan)	$–(CH_2\text{-}CHCN)_n–$	acrylonitrile $CH_2{=}CHCN$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$–(CF_2\text{-}CF_2)_n–$	tetrafluoroethylene $CF_2{=}CF_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$–[CH_2\text{-}C(CH_3)CO_2CH_3]_n–$	methyl methacrylate $CH_2{=}C(CH_3)CO_2CH_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$–(CH_2\text{-}CHOCOCH_3)_n–$	vinyl acetate $CH_2{=}CHOCOCH_3$	soft, sticky solid	latex paints, adhesives
cis-Polyisoprene natural rubber	$–[CH_2\text{-}CH{=}C(CH_3)\text{-}CH_2]_n–$	isoprene $CH_2{=}CH\text{-}C(CH_3){=}CH_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$–[CH_2\text{-}CH{=}CCl\text{-}CH_2]_n–$	chloroprene $CH_2{=}CH\text{-}CCl{=}CH_2$	tough, rubbery solid	synthetic rubber oil resistant

Formula	Type	Components	T_g ºC	T_m ºC
$\sim[CO(CH_2)_4CO\text{-}OCH_2CH_2O]_n\sim$	**polyester**	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	< 0	50
	**polyester** Dacron Mylar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	70	265
	**polyester**	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	50	240
	**polycarbonate** Lexan	$(HO\text{-}C_6H_4\text{-})_2C(CH_3)_2$ (Bisphenol A) $X_2C{=}O$ (X = OCH_3 or Cl)	150	267
$\sim[CO(CH_2)_4CO\text{-}NH(CH_2)_6NH]_n\sim$	**polyamide** Nylon 66	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $H_2N\text{-}(CH_2)_6\text{-}NH_2$	45	265
$\sim[CO(CH_2)_5NH]_n\sim$	**polyamide** Nylon 6 Perlon		53	223
	**polyamide** Kevlar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ para $H_2N\text{-}C_6H_4\text{-}NH_2$	---	500
	**polyamide** Nomex	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ meta $H_2N\text{-}C_6H_4\text{-}NH_2$	273	390
	**polyurethane** Spandex	$HOCH_2CH_2OH$ 	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:

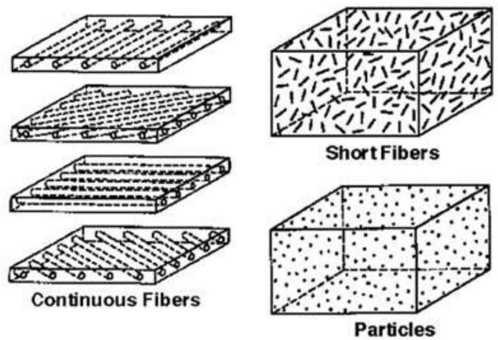
- molecular mass (chain length)
- structure
- degree of crystallinity

Dental application of polymers

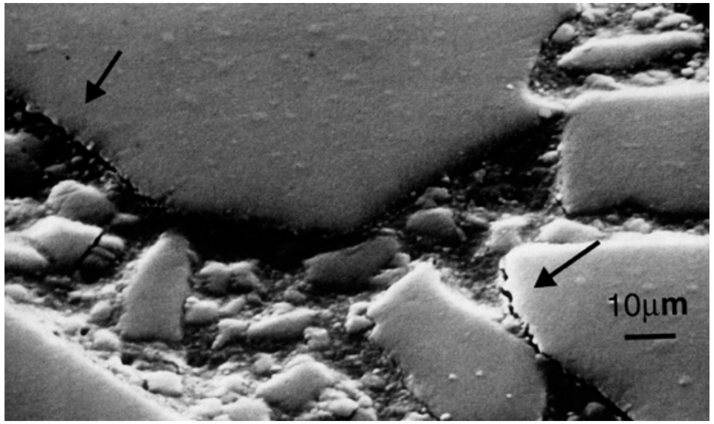
- impression materials
- bases, liners and varnishes for cavities
- prosthesis

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)



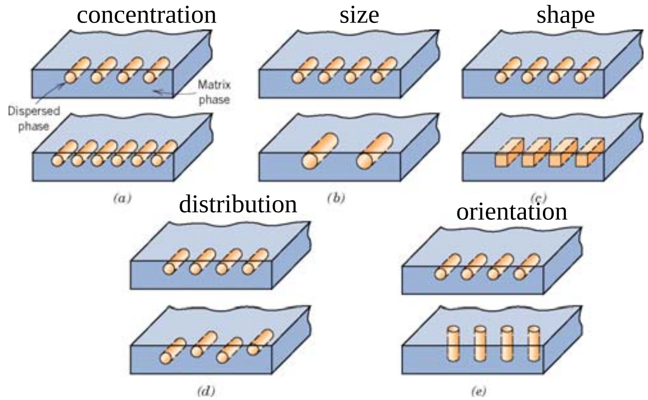
Bonding of matrix and disperse component



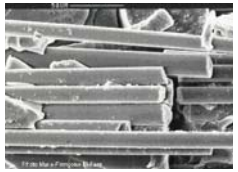
continuous phase (matrix) — dispersed phase (reinforcement)

metal, ceramic, polymer — ceramic, glass, metal…

Parameters acting on properties:

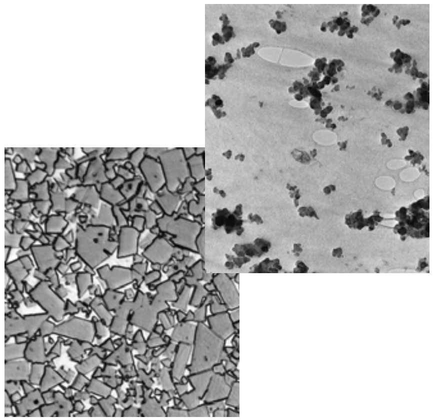


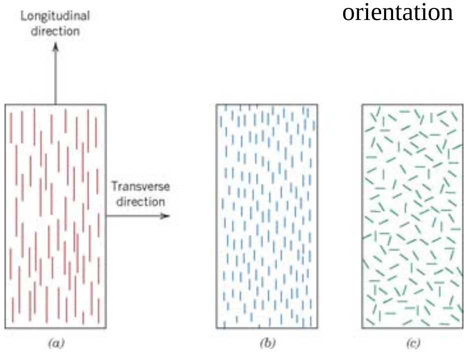
Types of composites



particle reinforcement
- rough (large size)
- fine (small size)

fiber reinforcement
- continuous one direction
- short
  - one direction
  - no definite orientation





Properties!!

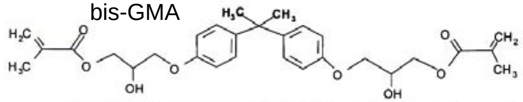
Dental application of composites:

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

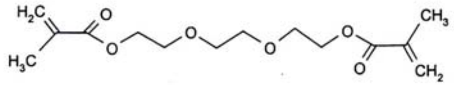
Dental composites:

Matrix: polymer (resin)
Reinforcement: ceramic, quartz, glass, polymer,
+ pigment + UV absorber

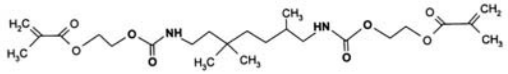
bis-GMA



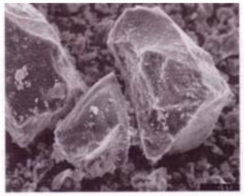
TEGDGMA



UDMA



rough grains
(0,1-100 mm)



micrograins
(≈ 40 nm)