

Polymerization

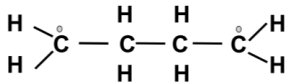
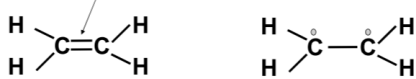
• 2 types of polymerization reactions

○ Condensation

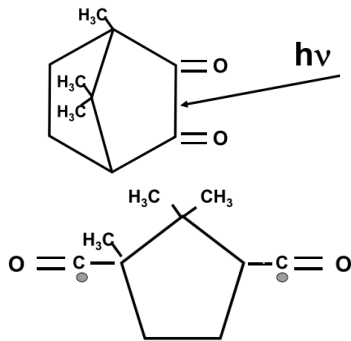
- Requires a molecule with 2+ functional groups
 - OH, -COOH, -NH₂, -X
- When bonding happens, there is a byproduct
 - OH + OH → Ester bond + water
 - COOH + OH → Ether bond + water

○ Addition

- Requires a molecule with 1+ unsaturations
 - For example, unsaturation could be C = C



- When bonding happens, there is no byproduct
- An initiator is needed to start the reaction
 - Mechanism: initiator gets activated into a free radical which is used to attack the unsaturation and start polymerization
- Activating initiators using **energy**
 - UV light
 - Heat: benzoyl peroxide's O-O bond gets broken when temperatures reach 90~100C and yields free radicals. Used in dentures
 - Visible light: camphorquinone becomes a free radical when exposed to 468 nm (see below). Used in composites.



- Activating initiators using **chemicals**
 - Benzoyl peroxide + Tertiary amine: the amine attacks the benzoyl peroxide, resulting in radical formation
- How do you know if your dental material is using energy or chemical assisted activation?
 - Energy: need to put the material in heat, under light, or shine something on it
 - Chemicals: the material comes in 2 packages and requires mixing before use

• How much initiator is good?

- High [initiator] = high chance for an initiator to meet a monomer and polymerize it. Form lots of small polymers
= Low molecular weight but fast setting time
- Low [initiator] = Initiator can only start reaction in a few areas, mostly monomer-monomer bonding
= high molecular weight but slow setting time
- In real life: camphorquinone is used at 0.2%

• Polymer classification

Linear	Branched + cross linked
2 functional groups or 1 unsaturation needed in each monomer	2+ functional groups or 1+ unsaturation needed in each monomer
Binds to other polymers via secondary bonds	Binds to other polymers via primary bonds
Susceptible to temperature changes	Not as susceptible to temperature changes

○ How to make a primarily branched polymer

- Get a mixture of monomers
 - Some with 2FG's/1UG → forms linear chains
 - Some with 2+ FG's/1+ UG → forms branches
- During the polymerization phase, the linear portions will form and attach as branches due to the cross linking monomers

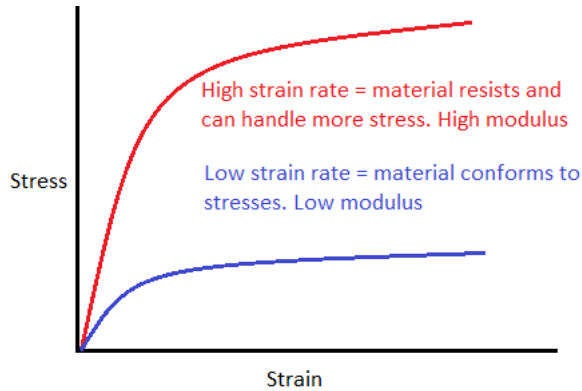
• Co-polymer classification

- Co-polymer: a polymer made up of more than 1 type of monomer (we'll use notation M₁ and M₂)
- Random copolymer
 - M₁M₂M₁M₁M₂M₁M₂ - etc
 - Random organization
- Block copolymer
 - (M₁)_x - (M₂)_y - (M₁)_z - etc
 - M₁ and M₂ are polymerized independently to form short oligomers
 - Then, they are mixed together to polymerize the blocks of oligomers
 - Used in medicine for urethanes. Linear urethanes (M₁) are flexible and aromatic urethanes (M₂) are rigid. By controlling their ratio, you can make a material with the desirable properties
- Graft copolymer
 - Long backbone of M₁ with branches of M₂ attached to it

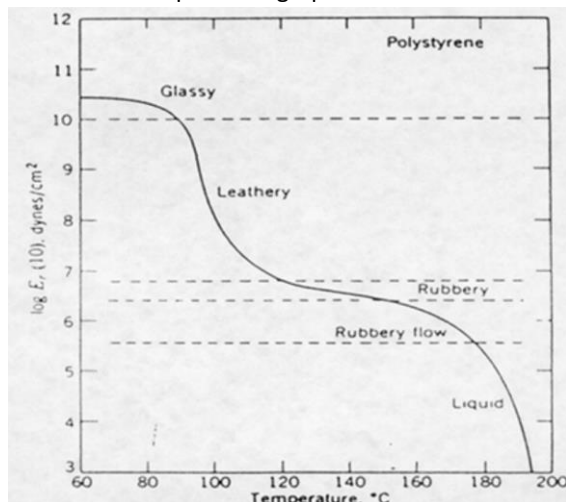
• Polymerization shrinkage

- The material contains monomers which are bound to each other by secondary bonds
- Once polymerized, these secondary bonds become primary bonds which has a significantly smaller bond length

- Polymers are viscoelastic

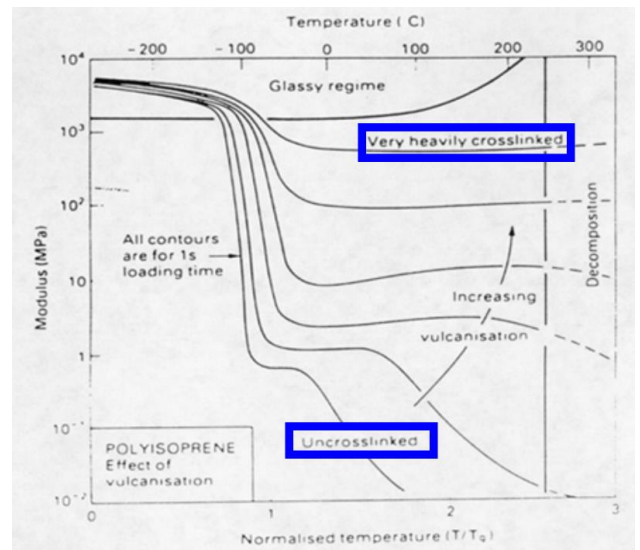


- Low strain rate = the polymers can slide past each other slowly = low modulus
 - High strain rate = polymers don't have time to untangle, hence undergoing less strain with the same stress = high modulus
 - Viscoelasticity means a material's stress-strain curve (and hence modulus) is strain rate dependent**
 - Note: the changes in modulus are far less significant in cross linked polymers compared to linear polymers**
- Because polymers are viscoelastic, they have a **glass transition temperature (T_g)**
 - Low temperature = polymers cannot break and re-form secondary bonds very easily due to low energy = the material has a high modulus = acts like glass
 - High temperature = polymers break and re-form secondary bonds with ease, conforming to the strain applied = acts like rubber
 - In between rubbery/glassy temperature, the polymer displays leathery characteristics
 - Glass transition temperature is the temperature at which the polymer transitions between the glassy and rubbery properties**
- Glass transition temperature graph



- $<90^\circ\text{C}$ = polymer is glassy therefore modulus is high
 - $120\sim 180^\circ\text{C}$ = polymer is flexible and rubbery
 - $>180^\circ\text{C}$ = polymer melts
 - Note: X axis is on a log scale, so each unit on the X axis denotes a 10x increase in modulus

- Changes to the graph due to polymer type



- When a polymer is linear, the polymers can move past each other easily once above the glass transition temperature
 - When a polymer is cross linked, the polymers still have difficulty moving past each other despite being above the glass transition temperature
 - When a polymer becomes cross linked, there is a smaller change in modulus between glassy/rubbery states (as mentioned before). The T_g does not change**

Resin composites

- Composite: material system composed of a combination of 2+ micro/macro constituents that differ in form and chemical composition and which are essentially insoluble in each other

- Main constituents

Matrix	Filler
-Polymers (BisGMA, UEDGMA)	-Silica or silica based glasses and ceramics
-Metals	-Can be organized into spheres, fibers, or flakes
-Ceramics	

- Amalgam composites are made of metal and metal
 - Resin composites use polymer for their matrix and a filler
- Minor constituents
 - Activator, inhibitors, antioxidants, coupling agents (MPTS), pigments, radiopaque components

- Types of fillers

- Fibre



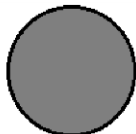
- Length is the dominant dimension
 - $E_c = kV_f E_f + V_m E_m$
 - The modulus of the composite is based on the modulus and relative volume of the filler and matrix
 - Relative volume, not relative weight
 - K = direction of the fiber
 - $K = 1 \rightarrow$ all fibers orientated in 1 direction
 - $K = 1/2 \rightarrow$ bi directional fibers
 - $K = 1/3 \rightarrow$ random in plane
 - $K = 1/6 \rightarrow$ random in 3D
 - **Fibrous fillers are not used in dental composites because it is not possible to ensure that all fibers are orientated in the same direction**

- Flake



- Surface is the dominant dimension
 - Will not be further discussed

- Sphere



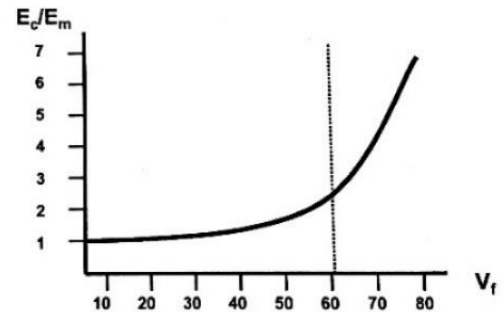
- No predominant dimension
 - This is used in dental composites
 - Calculating the modulus is discussed below

- Spherical fillers

- E = modulus of elasticity (AKA measure of stiffness)

$$E_{\text{composite}} = \frac{1}{\left(\frac{\text{Volume}_{\text{filler}}}{E_{\text{filler}}}\right) + \left(\frac{\text{Volume}_{\text{matrix}}}{E_{\text{matrix}}}\right)}$$

- Plot the formula



- X axis = % of filler used in the composite
 - Y axis = stiffness of the composite (compared to the baseline [100% matrix, 0% filler])
 - **You need more than 60% filler ($V_f > 60$) to improve the strength of the composite by 2x**
 - Plotting the same formula but with varying strengths of the fillers (X axis) and varying amounts (Y axis)

E_c/E_m	$E_f = E_m$	$E_f = 10E_m$	$E_f = 50E_m$	$E_f = 100E_m$
$V_f=10\%$	1	1.098	1.108	1.109
$V_f=30\%$	1	1.369	1.416	1.422
$V_f=50\%$	1	1.818	1.960	1.980
$V_f=70\%$	1	2.7	3.185	3.257
$V_f=85\%$	1	4.25	5.988	6.309

- Red = the filler is 100x stiffer than the matrix. This is a very good filler. However, it only makes up 10% of the composite. Therefore, there is hardly an increase in the total modulus ($\uparrow 1.1x$)
 - Blue = the filler sucks (only 10x stiffer than the matrix). But, a lot of it is used (85%) and resulted in a 4.25x increase in the composite's modulus
 - **Conclusion: the strength of the filler hardly matters. What matters is how much of it you use in your composite**
 - Even a simple calcium carbonate filler (only about 10~15x stronger than matrix) can increase the strength of the composite significantly if enough is used
 - "Best bang for your buck"

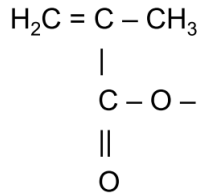
- Real life modulus values

- Dentin is 18 GPa
 - Enamel is 84 GPa
 - Resin is 1~3 GPa
 - Not even comparable to dentin, fillers needed
 - All purpose composite = 10~20 GPa
 - Anterior composite = 6~20 GPa
 - Posterior composite = 10~25 GPa

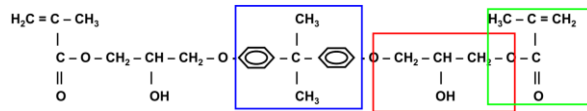
- Polymers used in dentistry

- Methacrylate

- The mother of all polymers
 - Has 1 unsaturated bond = addition reaction polymerization
 - Activated through heat (via benzoyl peroxide), UV, or visible light (via camphorquinone)

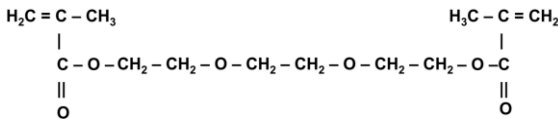


- Bis-GMA (Bis-Phenol A Glycidylmethacrylate)



- Methacrylate groups (green) → polymerizes
 - Multiple unsaturations → cross links
 - Glycerol (red) and bisphenol backbone (blue) → gives rigidity to the monomer
 - Too viscous to use in practice

- TEGDMA (Triethyleneglycol dimethacrylate)

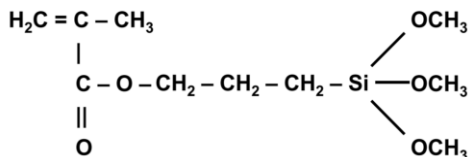


- Methacrylate groups on the ends → polymerizes
 - Ethylene glycol backbone → less rigid than BisGMA, much more flexible
 - Not as viscous
 - TEGDMA and BisGMA are combined
 - Posteriors: 25% BisGMA, 75% TEGDMA
 - Flowables: more TEGDMA

- UDMA

- Urethane based invented for dental materials
 - More flexible than BisGMA
 - Created to replace BisGMA due to safety concern

- MPTS (γ methacryloxypropyl trimethoxy silane)

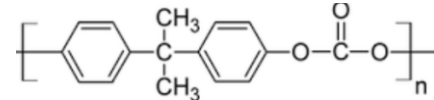


- Called a **coupler** which binds the **resin polymers** to the **SiO₂ glass filler particles**
 - Methacrylate group on one end → polymerizes
 - Silanol group on other end → bonds to silica filler
 - How is this prepared in real life?
 - Grind up glass (SiO₂) to desired size
 - Expose glass to MPTS
 - Rinse in ethanol to remove excess MPTS
 - Yields glass particles with MPTS coating which will polymerize with the resin
 - In the presence of water

$$\text{M} - \text{R} - \text{Si}(\text{OCH}_3)_3 + \text{H}_2\text{O} \longrightarrow \text{M} - \text{R} - \text{Si}(\text{OH})_3$$
 - The bonds between glass and MPTS can break because it is a weak ether link
 - Can compromise strength of composite

- Polycarbonate plastics and public health concerns

- Type of plastic made of BPA and phosgene, which is versatile and used in glasses, shields, etc



- BPA**: bisphenol A (blue part in bis-GMA)
 - Phosgene**: polycarbonate molecule

- Why is BPA such a concern?

- Molecules with benzene rings and a OH group attached are known to be xenoestrogenic
 - Xenoestrogenic compounds bind to estrogen receptors and can cause hormonal disturbance
 - BPA has 2 benzene's with OH's
 - If the bond between polycarbonate and BPA is broken, then the xenoestrogenic compound will be exposed

- Examples of BPA exposure

- Microwaving BPA plastics → heat or radiation can break the polycarbonate bonds and expose BPA
 - Baby bottles in the dishwasher → heat can break the polycarbonate bonds and expose BPA

- Dental relevance

- BisGMA

- Structure: BPA + glycerol + methacrylate
 - Does not have exposed alcohol groups because the O's on the BPA form ether bonds to glycerol
 - Esterases in the mouth can break the methacrylate bond to glycerol, but will not break the BPA + glycerol bond

- Risk of BPA exposure is minimal**

- Sealants

- Structure: BPA + methacrylate
 - There is no glycerol in sealants
 - This means mouth esterases will break the methacrylate + BPA bond and expose the OH on BPA
 - Risk is possible, but nowadays, sealants are BPA-free**

- Human exposure to bisphenol A by biomonitoring:

- Methods, results and assessment of environmental exposures. Wolfgang Dekant, Wolfgang Völkel (2008)
 - Daily tolerable intake of BPA is 50 ug/kg/day
 - Average daily human exposure to BPA is 6ug/person, which means <0.1 ug/kg/day
 - We are 500x lower than the daily limit

- Classification of composites

- Based on filler size (in μm)

- Meaningless, when talking about mechanical properties of the material
 - Manufacturers will still advertise this info though
 - However, can be useful in determining if the composite will be esthetic
 - Visible light is 450~750 nm
 - You want the particles to be $<1/2$ this wavelength because otherwise it will undergo specular reflection (looks ugly)
 - So, you want particles to be <200 nm
 - Particle size and surface area
 - As the filler particle size gets smaller, their esthetics improve but the surface area increases exponentially
 - Example: say there was 40mm^3 of filler
 - 1 big particle = 56.55mm^2 surface area
 - 10^{21} particles = 262m^2 surface area
 - \downarrow particle size = \uparrow surface area = \uparrow bonding+strength
 - However, \downarrow particle size will require more resin to interact with the increasing surface area. Thus, $\%V_f$ will have to decrease if you want the resin to be able to coat each filler particle
 - This problem is seen for micro and nano filled composites, hence their weak properties

Macro filled	$>5 \mu\text{m}$	-Poor wear, cracks propagate, looks ugly
Micro filled	$0.04\sim 0.4\mu\text{m}$	-Good esthetics -Only done in low V_f
Small particle	$1\sim 3\mu\text{m}$	-Short lived, rarely used
Hybrid	$0.04\sim 3\mu\text{m}$	-Excellent mechanical properties
Micro hybrid Nano hybrid	$0.004\sim 3\mu\text{m}$	-Nice esthetics but not load bearing (weak)

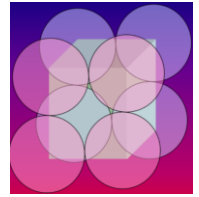
- Based on % of filler (V_f)

- Midway filled ($<60\%$) \rightarrow esthetics
 - Ultrafine ($<3\mu\text{m}$) or fine ($>3\mu\text{m}$)
 - Compact filled ($>60\%$) \rightarrow load bearing
 - Ultrafine ($<3\mu\text{m}$) or fine ($>3\mu\text{m}$)
 - This method of classification is much more useful to clinicians but it is not frequently used
 - As a clinician, you should always ask: what is the V_f and modulus of the material
 - Why can't we just keep adding filler to make composites stronger and stronger?
 - Practical limitation: the material becomes too viscous and hard to work with
 - Theoretical limitation: the amount of volume that spherical fillers can occupy has a limit. See packing efficiency

- Packing efficiency

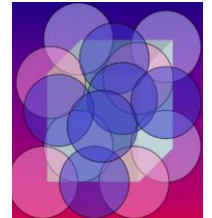
- Cubic lattice

- The matrix will be broken down into units called "cells" which are cubes
 - Each corner on the "cell" will represent the center of a sphere
 - Each corner of the cube has $1/8$ of a sphere
 - The cube has 8 corners
 - $8 \times 1/8 = 1$ sphere worth of volume per cell
 - Volume of 1 sphere is $4\pi r^3/3$
 - Volume of the cube is $(2r)^3$
 - $V_f = V_{\text{spheres}}/V_{\text{cube}} = (4\pi r^3/3) / ([2r]^3) = 0.5236$
 - If a matrix has spherical fillers organized in a cubic lattice, then 52% is the theoretical upper limit of filler possible**



- Face centered cubic lattice

- Each corner has $1/8$ of a sphere like before
 - Each face has $1/2$ of a sphere
 - $1/8 \times 8 \text{ corners} + 1/2 \times 6 \text{ faces} = 4$ spheres of volume per cell
 - Volume of 1 sphere is $4\pi r^3/3$
 - Volume of the cube is $(2.828r)^3$
 - Because the spheres have to be smaller to allow face-cubes to fit, each dimension of the cube has to be $2.828r$, not $2r$
 - $V_f = V_{\text{spheres}}/V_{\text{cube}} = [4 \times (4\pi r^3/3)] / [(2.828r)^3] = 0.74$
 - If a matrix has spherical fillers organized in a face centered cubic lattice, then 74% is the theoretical upper limit of filler possible**



- In real life

- It is not possible to reach the theoretical 74%
 - However, having hybrid sizes of particles (bimodal distribution) means that the smaller particles can squeeze between the larger spheres and get closer to the 74% limit

- Values used to determine composite strength

- Modulus of elasticity (GPa)

- How much deformation there is with a defined amount of stress**
 - Dentin is 18 GPa, Enamel is 84 GPa
 - Resin composite 18~20, Gold 77, Ceramic 70~80, Amalgam 34
 - This is the value that we should look at

- Compressive strength (MPa)

- How much stress the material can handle (does not account for deformation)**
 - Dentin is 297 MPa, Enamel is 384 MPa
 - Resin composite is 250~450
 - Compressive strength is not the limiting factor, but this is the value reported by manufacturers to give the impression that it is "comparable" to teeth strength**

- Thermal expansion

- Important because restorative material needs to expand and shrink similar to natural teeth. Major discrepancies can cause leakage of restoration or stress on tooth
- Coefficient of thermal expansion (α) in ppm/°C
 - Enamel = 11.4 Dentin = 8.3
 - Composite = 23~40 (closer to 40)
 - Amalgam = 25
- Force applied on tooth walls due to thermal expansion

$$\text{Force on tooth} = E * \alpha * \Delta\text{temp} * \text{area}$$

Amalgam	Composite
$F = 34 * 22 * \Delta\text{temp} * \text{area}$	$F = 15 * 40 * \Delta\text{temp} * \text{area}$
$F = 850 * \Delta\text{temp} * \text{area}$	$F = 600 * \Delta\text{temp} * \text{area}$

- Polymer shrinkage

- Uncured = particles adhere through secondary bonds
- Cured = particles adhere through primary bonds
- Primary bonds are much stronger and bond length is significantly reduced → will lead to shrinkage
- Configuration factor (C factor)
 - Imagine the composite glob as a cube
 - $C = \# \text{ of bonded surfaces} / \# \text{ of free surfaces}$
 - If placed on a free surface, $C = 1/5 = 0.2$
 - If placed in a "cup" (like class 1 prep), $C = 5/1 = 5$
 - ↑ C factor = ↑ stress due to shrinkage
 - To minimize C factor in restorations, place in increments
- Coefficient of H₂O resorption
 - The composite will absorb H₂O from the pulp and the environment for the next 24~48 hours
 - This compensates for the shrinkage

- Light curing

- Goal is to activate the photoinitiator
 - Example: camphorquinone (needs 468 nm light)
 - Halogen lights emit in a wide spectrum = can cure various composites
 - LED's are monochromatic = can't cure all composites
- Energy of the light decreases exponentially with distance, it is crucial to be as close to the composite as possible
- Light intensity can be weak on the edges of the curing unit
- Polymerization is measured by degree of conversion
- Cannot achieve 100% conversion, deal with it

- Alternative composite materials

- Compomers (composite ionomer)**

- Resin matrix contains carboxylic groups
- Also called polyacid modified composites (PAMC)
- No H₂O involved like GIC
- Low Vf and questionable filler-matrix bonding
- Like composite, but worse properties

- Packable composite**

- Viscous characteristics to mimic amalgam
- No advantages

- Polymer ceramic**

- Not a ceramic – misnomer
- Used for indirect restorations, lab processed
- May contain ceramic-like components, but it is nowhere comparable to the strength of a ceramic
- Some manufacturers will advertise that they use ceramic fillers, but remember that filler strength has a very small influence on overall strength of the composite. The Vf matters the most

- Flowable composite**

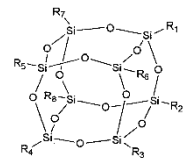
- Low viscosity with low Vf
- Questionable mechanical properties
- May be suitable as liners, but avoid exposure to occlusal/oral environment
- Modulus = 9 GPa
- Useful when you are trying to pack composite into the preparation. Adhesive is slippery and the composite will stick to your instrument. Applying a thin layer of flowable can help with this, and preserve the thin adhesive layer

- 3M ESPE Nanocomposite**

- Fillers are silane treated to provide cross link to surrounding resin
- Broad filler distribution → high Vf
- Due to so much surface area, they can get very viscous
- Cannot be silanated completely and coupled to bond to the matrix
- Long term behaviour is concerning
- Water could seep in

- Polyhedral oligomeric silsesquioxane (POSS)**

- 1 silicon : 1 oxygen ratio
- Has a cage
- After 10% filler, properties sucked
- Comes out in literature, but be aware its success is not that great



- Silorane composites**

- Uses epoxy groups which open up once polymerized and prevents polymer shrinkage
- Mechanically, not that great

- Thiol polymers (came out in 2014!)**

- Promised 90~95% degree of conversion
- Currently no long term studies

Impression materials

- Characteristics desirable in an impression material
 - Pleasant odour, taste, and aesthetic colour
 - Free of toxic or irritant constituents
 - Adequate shelf life for requirements of storage and distribution
 - Economically commensurate with the results obtained
 - Easy to use with minimum equipment
 - Setting characteristics that meet clinical requirements
 - Satisfactory consistency and texture
 - Readily wets oral tissues
 - Elastic properties that doesn't permanently deform after being strained
 - Will not break upon removal from mouth
 - Dimensionally stable over humidity/temperature changes for a long enough time to cast or die
 - Compatibility with cast or die materials
 - Accuracy in clinical use
 - Readily disinfected without loss of accuracy

Classification of impression materials

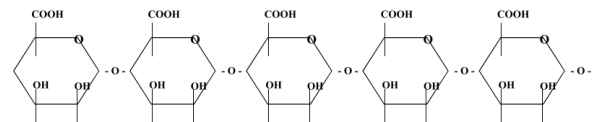
	Rigid	Elastic
Irreversible	-Plaster (gypsum) -Zinc oxide eugenol	-Elastomers (polysulfide, polyether, polysilicone) -Alginate
Reversible	-Compound -Wax	-Hydrocolloid agar

- Rigid = for edentulous patients
 - Note: being rigid does not mean that the material cannot be elastic. The material is more resistant to deformation
 - High E
 - Elastic = for dentulous patients
 - Used in dentulous patients to conform around the undercuts of the teeth
 - Low E
 - Reversible = the material sets based on temperature changes, and can revert back to its original state
 - Irreversible = sets by chemical reaction
- Old people and people with implants have weakly attached teeth
 - They can fall out during impressions
 - Always lubricate teeth that are mobile
 - Always lubricate implants
 - It will not affect impression clarity

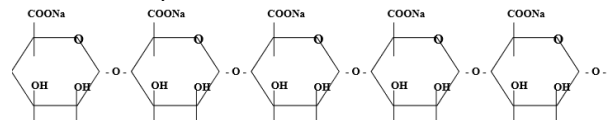
Alginates

- Properties of alginates
 - Elastic**
 - E value is low
 - Needed to conform around the teeth
 - Hydrocolloid**
 - What is a colloid?
 - Suspensions: >500 nm sized particles
 - Colloids: 200~500 nm sized particles
 - Solutions: atomic sized particles
 - Colloids and suspensions will distort light because they are >1/2 the wavelength of light
 - The dispersing medium is called an aerosol (if it is air), and hydrosol (if it is water)
 - The dissolved material is called the dispersed phase
 - Properties of colloids
 - Undergoes a reversible reaction of liquefying (Sol) and solidifying (Gel)
 - Sol \leftrightarrow Gel
 - Temperature dependent
 - Alginate hydrocolloid
 - Considered an irreversible hydrocolloid because in clinical use, we never reach the temperatures needed to trigger the reversible reaction (Sol \leftrightarrow Gel)
 - Goes into the gel phase via a chemical reaction rather than via a temperature reaction

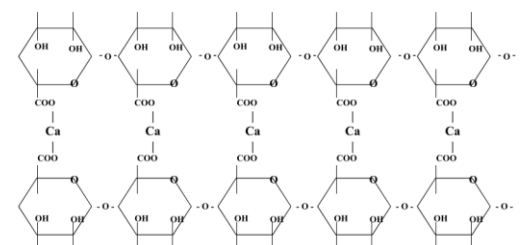
Irreversible



- Alginate acid – not soluble in water, so not very useful. Reacted with sodium



- Sodium alginate – soluble in water and this is the “white powder” that we see



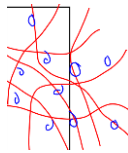
- Calcium alginate – insoluble in water. This is the set form of alginate, which is irreversible

- Setting reaction of alginates

- Chains of sodium alginate are reacted with calcium
 - Since calcium is divalent, it will want to bind to 2 things to satisfy the octet
 - Replacing the Na on 1 alginate chain will only satisfy 1 bond, so calcium binds to 2 alginate chains
 - Cross linking of alginate chains solidifies the material and this is the set form of the impression material
- Source of calcium
 - Calcium is provided by gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which is called the “reactor”
- This reaction is very quick
 - The material will set too quickly to be useful
 - A “retardant” is needed to slow the reaction
 - Retardant can be K_3PO_4 or Na_3PO_4
 - PO_4 ions have a strong affinity for calcium, so they scavenge and compete for free Ca ions
 - Sodium alginate will not cross link until all of the PO_4 ions are depleted
- In clinical practice, this all appears as a white powder
- Always put powder into water to reduce formation of aggregates and having dry alginate stick to the bowl

- Molecular structure

- Referred to as a “brush heap” structure
- Water is entrapped between the polymer strands

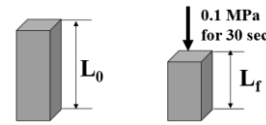


- Mechanical properties

- Viscoelasticity – the modulus of the alginate depends on the strain rate
 - If load is applied slowly, the water can slowly ooze out and deform the structure. Low modulus
 - If load is applied quickly, the structure retains its original form as water cannot displace as much
- Imbibition and syneresis
 - The relative humidity of the oral cavity is about 80% and the temperature is about 32°C
 - When the alginate sets, it sets in equilibrium in this environment
 - When removed from the oral cavity, the environment humidity and temperature changes
 - This can deform the alginate, in one of 2 possible ways
 - Imbibition: swelling and absorption of H_2O due to higher relative humidity
 - Syneresis: shrinkage due to loss of H_2O
 - Reintroducing a material that underwent syneresis back into water will not restore its original shape**
 - To preserve the accuracy of the impression, a moist towel and Ziploc bag is recommended

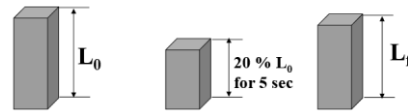
- Desirable mechanical properties of alginate

- Compressive strain



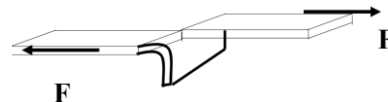
- Apply 0.1 MPa for 30 seconds
- The change in dimension L is calculated as ϵ
 - $\epsilon = (L_f - L_0) / L_0$
 - $5\% < \epsilon < 20\%$

- Elastic recovery



- The material is compressed by 20% for 5 seconds
- The material should recover to at least 95% of its original size
- Elastomers recover by 96.5%

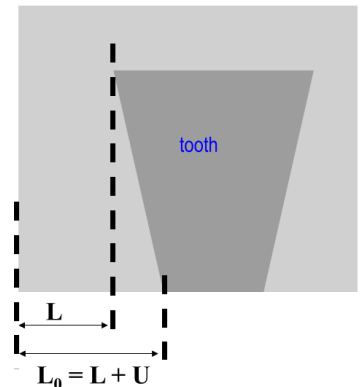
- Tear strength



- Force required to tear the material

- How to improve accuracy of impressions in the undercut areas of the teeth

- L_0 = thickness of the alginate in the area of the undercut
- U = thickness of the undercut
- L = how much the alginate needs to compress in order for the impression to be removed



- Compressive strain

- ϵ (compressive strain) is proportional to σ (stress), so **we want to minimize ϵ**
 - $\epsilon = (L - L_0) / L_0$
 - Substitute $L+U$ for L_0
 - $\epsilon = (L - (L+U)) / (L+U)$
 - $\epsilon = -U / (L+U)$
- We want to minimize ϵ , but U cannot be modified. Therefore, L is the only variable we can influence
- To minimize ϵ , L has to be as big as possible
- Conclusion: the thicker the alginate (L), the less strain/stress that the impression undergoes**
 - Use stock trays to ensure proper thickness all the way around the arch

Elastomers

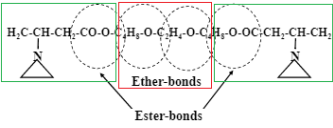
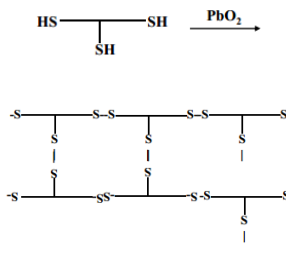
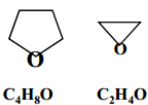
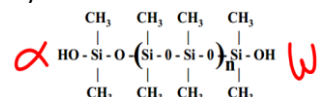
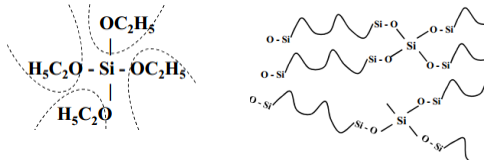
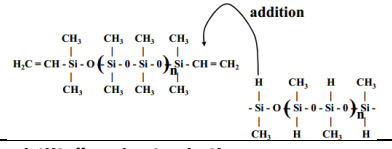
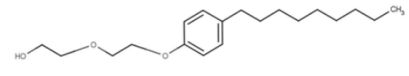
	Polysulfides	Polyethers	Polysilicones (siloxanes)						
Background	<ul style="list-style-type: none">-Originated from “isoprene”-Mostly used for crown and bridge impressions-Rotten egg smell-Possible lead exposure	<ul style="list-style-type: none">-Newest elastic elastomer-Used in edentulous or implant patients (high accuracy needed)-Expensive	<ul style="list-style-type: none">-Most popular impression materials, with polysiloxanes being more popular-Can be stored, repoured, etc-VERY dimensionally stable (few/no byproducts)						
Properties	<ul style="list-style-type: none">-Polysulfides don’t wet very well (has a high contact angle). Slightly hydrophillic-Viscoelastic (remove from patient swiftly)-Some shrinkage as water is a byproduct (can evaporate)	<ul style="list-style-type: none">-The only hydrophilic elastomeric material (low contact angle)-Expensive-Early polyethers were stiff (high E) → hard to remove-Shelf life not as good as siloxanes	Condensation silicones <ul style="list-style-type: none">-Because this is a condensation reaction (EtOH is a byproduct), shrinkage will happen-Inherently hydrophobic – dry mouth before use						
			Addition silicones <ul style="list-style-type: none">-Uses a platinum catalyst (expensive)-If there is residual water or some of the silicone monomers contain OH instead of vinyls, then there will be H₂ bubbling during setting due to Pt-Inherently hydrophobic – dry mouth before use						
Structure	$-R-S-S-R-$	 <p>(This is the monomer)</p>	<table><tr><th>Poly dimethyl siloxanes</th><th>Polymethyl siloxanes</th><th>Polysiloxanes</th></tr><tr><td>$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$</td><td>$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \end{array}$</td><td>$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$</td></tr></table>	Poly dimethyl siloxanes	Polymethyl siloxanes	Polysiloxanes	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
Poly dimethyl siloxanes	Polymethyl siloxanes	Polysiloxanes							
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{H} \quad \text{CH}_3 \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$							
Polymerization reaction	<ul style="list-style-type: none">-Functional group is the R-SH group (called the mercaptan or thiol group)-Undergoes oxidation reaction $2R-S^0H^0 + Pb^{IV}O_2 \rightarrow R-S^0-S^0-R + Pb^{II}O + H^1_2O$ <ul style="list-style-type: none">-Lead gets reduced (Pb^{IV} → Pb^{II}), so it is the oxidizing agent-Hydrogen gets oxidized (H⁰ → H¹)-Lead is commonly mistakenly called a catalyst, but it is not <ul style="list-style-type: none">-Each monomer needs to contain more than 1 SH group to allow cross linking 	Making the monomer <ul style="list-style-type: none">-Starts with aziridine attached to butanoic acid $\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CH}_2-\text{COOH} \\ \\ \text{N} \end{array}$ <p>3-(N-aziridine)-butanoic acid</p> <ul style="list-style-type: none">-The COOH group is reacted with the ether groups in tetrahydrofuran (left) or ethyleneoxide (right)  <p>C₄H₈O C₂H₄O</p> <ul style="list-style-type: none">-This yields the monomer seen below $\begin{array}{c} R-(R-O-R)_n-R \\ \quad \\ \text{N} \quad \text{N} \end{array}$ Making the polymer <ul style="list-style-type: none">-The aziridine ring is under a lot of stress. When reacted with an aromatic sulfonate ester, the ring breaks open and reveals a cationic carbon $\begin{array}{c} R-(R-O-R)_n-R \\ \quad \\ R^+N \quad NR^+ \\ \quad \\ ^+CH_2-H_2C \quad CH_2-CH_2^+ \end{array}$ <ul style="list-style-type: none">-The cation will attack the N on the next aziridine ring-This is cationic polymerization	Condensation silicones <ul style="list-style-type: none">-Monomer is α,ω-hydroxy-poly dimethyl siloxane. Alone, this monomer only has 2 functional groups so it will only form linear chains  <ul style="list-style-type: none">-It is reacted with tetraethyl orthosilicate which has 4O's to allow cross linking  Addition silicones <ul style="list-style-type: none">-Monomer is α,ω-vinyl-poly (dimethyl siloxane) Or α,ω-vinyl-poly (methyl siloxane) $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{H}_2\text{C}=\text{CH}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{CH}=\text{CH}_2 \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ <p>α,ω</p>  “Hydrophillic” polyvinyl siloxanes  <ul style="list-style-type: none">-New on the market-1 end is hydrophobic, 1 end is hydrophilic-Acts as a surfactant-Does not chemically bind to polymer						

Table 19.7 Comparison of the properties (qualitative) of elastometric impression materials.

Property	Polysulphides	Condensation silicones	Addition silicones	Polyethers
Viscosity	Available in three viscosities (no putty)	Available in four viscosities including putty	Available in four viscosities including putty	Available in a single viscosity (regular) + diluent + putty
Tear resistance	Adequate	Adequate	Adequate	Adequate
Elasticity	Viscoelastic material	Very good	Very good	Adequate
Accuracy	Good with special trays	Acceptable with stock trays	Good with stock trays	Good with special trays*
Dimensional stability	Adequate, but pouring of models should not be delayed [†]	Models should be poured as quickly as possible [†]	Very good [†]	Very good in low humidity conditions

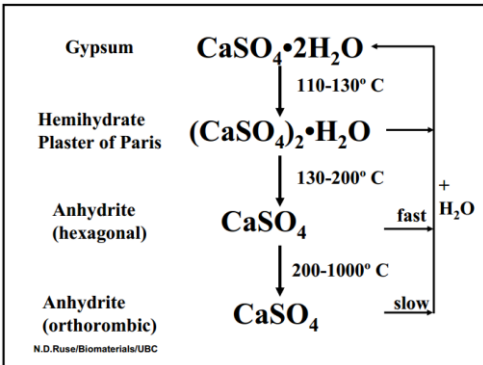
* Can give good accuracy with stock trays, with care.

[†] Some manufacturers recommend a *short* delay in pouring models for these materials, either to allow elastic recovery to occur or to allow gaseous products to escape which would otherwise cause pitting of the model surface.



- Exists in light body, medium body, heavy body, and putty states
 - Each state has an increasing amount of filler and hence higher modulus
 - Light body is applied first
 - Low amount of filler and thus low viscosity
 - Used to secure critical areas of your impression where you need the greatest amount of accuracy and detail (eg. around a crown prep and on occlusal surfaces of teeth)
 - Use a syringe to apply this material so that you can place it exactly where you want and avoid air bubbles
 - Then stiffer elastomers are applied over top
 - Better mechanical properties and thus are used in conjunction with light body to give strength to the impression
 - This technique where you use light body to get details and higher viscosity material to give strength is called the “wash” technique
 - So these different “bodies” are just different consistencies, the chemistry of all of them is the same
- Custom trays or stock trays?
 - Alginates have poor mechanical properties
 - So, stock trays are used when taking alginate impressions to ensure adequate wall thickness when removing the impression
 - Elastomers have better mechanical properties
 - Thickness of the walls is less of a concern
 - Custom trays can be used which results in thinner walls
 - Saves material (elastomers are expensive)

Gypsum

- Gypsum products
 - Normally, gypsum is in the form of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$
 - Water is incorporated into the crystalline structure
 - With a changes in temperature and/or pressure, gypsum can be changed into different compounds

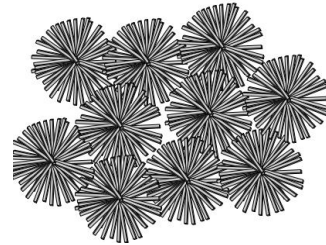


- Hemihydrate (Plaster of Paris)
 - This is the form of gypsum that is sold in stores
 - There is less water, but not completely absent
 - Comes in 2 forms: α and β hemihydrate
 - Chemically, they are the same
 - They differ in terms of crystalline structure
 - Alpha has more desirable characteristics

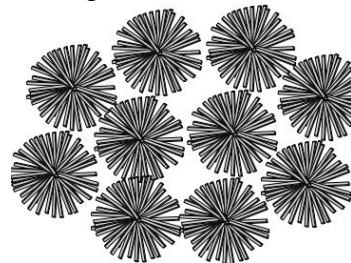
	β hemihydrate	α hemihydrate
How it is made (starting from gypsum)	-Calcination -130°C -Atmospheric temperature	-Autoclaving -Higher pressure -Higher temperature
Structure	 <ul style="list-style-type: none"> -Poor crystallinity -High porosity -Irregular shape 	 <ul style="list-style-type: none"> -Crystalline -Non porous -Regular shape
Properties	-Weaker	-Stronger
Use	-Plaster	-Stone -Die stone

- Setting reaction when water is re-introduced
 - $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 - Clinically, slightly add more water than this stoichiometric ratio
- Anhydrite
 - Formed when gypsum is continually heated past the hemihydrate stage
 - All the water is removed
 - Like the hemihydrate stage, there are 2 types of anhydrites
 - Hexagonal and orthorhombic
 - They differ in their reactivity to water

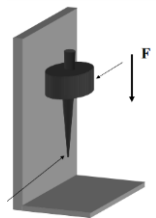
- Gypsum additives
 - Potassium sulfate \rightarrow accelerator
 - Sodium sulfate \rightarrow accelerator
 - Borax \rightarrow inhibitor
- Volumetric change in gypsum as it sets
 - Theoretically** (determined by math)
 - $V_f = 0.935 V_o$
 - 6.5% volumetric shrinkage
 - 2.2% linear shrinkage
 - There should be an overall shrinkage
 - Realistically**
 - Gypsum crystallizes in multiple spheres
 - As the crystals grow, they impinge on each other
 - Lots of space between the crystals



- Gypsum expands, does not shrink
- In the presence of extra water, even more expansion happens due to hygroscopic expansion
 - This is seen more in plasters than gypsums because plasters are more porous, hence needing more water

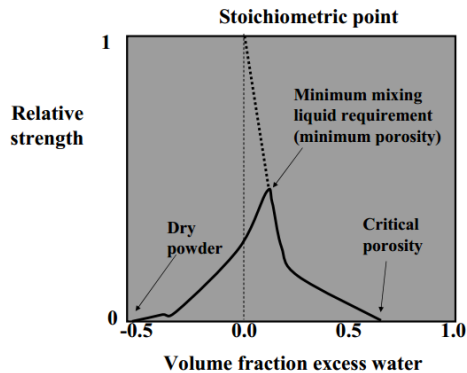


- Gilmore needle
 - Needle with a weight attached
 - Placed on setting gypsum
 - Used to calculate the strength of gypsum or determining its exact setting time
- Setting time
 - Water is consumed
 - Initially appears glossy
 - Turns to matte and dry looking
 - Loss of gloss = indicates initial setting time
 - Can detect this far before the increase in temperature associated with gypsum setting
- Gauging volume
 - Volume fraction of pores in the bulk powder
 - Measure of free space
 - You have to add enough water to gypsum to allow it to set, as well as fill in the pores (gauging volume) to let the material be plastic enough to handle



- Gypsum strength when **rehydrated**

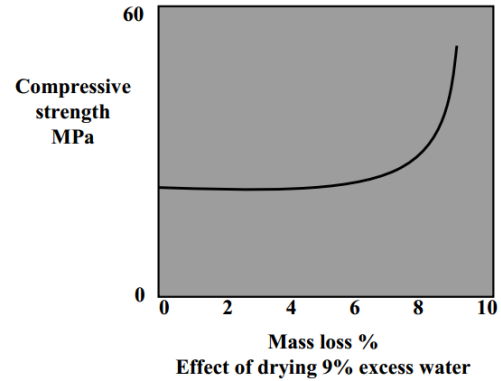
- When water is added to hemihydrate, gypsum will form. If there is any excess water, it will form micro porosities
 - More porosities = weaker gypsum
- This table will be on the exam



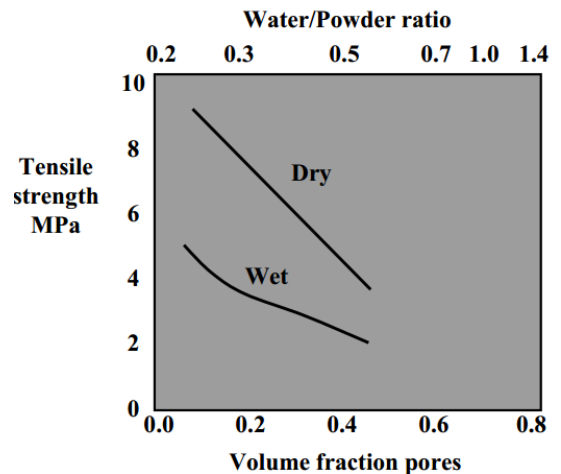
- Y axis = strength of gypsum yielded
- X axis = how much excess water is added on top of the stoichiometric ratio
- **Dry powder**
 - Has -0.5 excess water → indicates not enough water
 - No mechanical properties
- **Stoichiometric point**
 - The exact ratio of water is added according to the gypsum setting reaction
 - $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 - The maximum strength (top of Y axis at 0.0 excess water) is a theoretical value. It can never be reached because it is impossible to make each water molecule contact each CaSO_4 in a perfect ratio and not form porosities
 - Hence, you realistically need more water than the ideal stoichiometric ratio
- **Minimum mixing liquid requirement**
 - In a realistic setting, this is the highest achievable strength for set gypsum
 - This is because water particles have to coat the gypsum in addition to reacting with it. Without coating, it will be too dry and impossible to work with
 - Slightly more water than stoichiometric ratio
 - Due to excess water, its evaporation will form small porosities, but it is minimized
 - This excess water (to fill the pores) is called the gauging volume
- **Critical porosity**
 - 0.6 volume fraction excess water
 - Too many porosities in the set gypsum
 - There is no mechanical strength
 - Useless

- Gypsum strength when **drying**

- The gypsum setting reaction is exothermic
- Can reach temperatures of 60°C



- As stated before, having excess water will form porosities in the gypsum
 - If these porosities are filled with water, the gypsum is weak (left side of X axis)
 - If water evaporates, the porosities are still there but the strength of the gypsum increases drastically (right side of X axis)



- X axis = amount of excess water is proportional to volume fraction of pores in the gypsum (hence the 2 X axes)
- Y axis = strength of gypsum when set
- When dried, gypsum strength increases by about 2x
- Dry = useful in ortho
- Wet = useful when working on wax-ups
 - Water occupies the porosities and prevents infiltration of wax
 - Has to be handled differently as it is weaker

Metals

- Types of bonds

- Primary
 - Ionic – strong and non directional
 - Covalent – strong and directional
 - Metallic – strong and non directional
- Secondary
 - Electrostatic – weak and non directional

- Ionic bonds**

- Ions
 - Forms when atoms want to give up or accept an electron
 - Goal of the atom is to achieve stable noble gas configuration by filling its valence electron shell
- Ionic bonds form between 2 atoms with greatly differing electronegativities ($X_a \ll X_b$)
- Structure
 - Tends to order itself in an orderly lattice
 - This is to maintain neutrality of charge
 - Very few defects in crystal
- Properties
 - Strong and stiff (resists compression/tension well)
 - If tension is too great, the crystal will crack
 - No elastic deformation
 - Brittle
 - Electrically conductive only if melted/dissolved
 - Non directional bonds

- Covalent bonds**

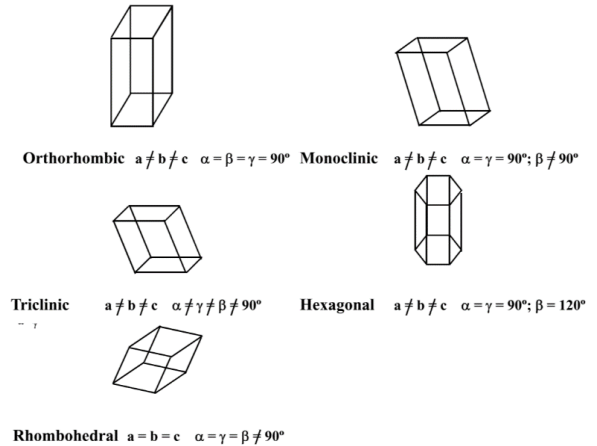
- Electronegativities of the atoms are similar
- Electrons are shared
- Properties
 - Generally stiff
 - Brittle
 - Directional bonds

- Metallic bonds**

- Positive metal ions surrounded by a sea of electrons
- Each unit electrically neutral and there is no electric attraction like there is in ionic bonds
- Many defects in the crystalline structure because it doesn't need to neutralize charges like ionic bonds
- Not as resistant to change as ionic bonds because atoms can simply slide past each other
- Properties
 - Not brittle
 - It is TOUGH → can undergo a lot of deformation
 - Shear is possible
 - Is ductile → can be drawn out due to atoms sliding past each other
 - Electrically conductive without melting
- Exceptions to brittleness
 - Metals can be brittle if it is very high quality (has very little defects in its crystal organization)
 - Cold working the metal

- Crystalline lattice possible organizations

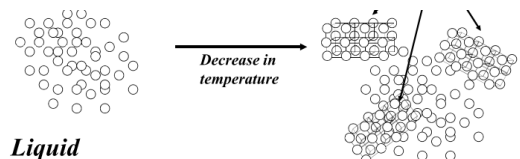
- Classified based on dimension size (a, b, c) and angles between each dimension (α, β, γ)



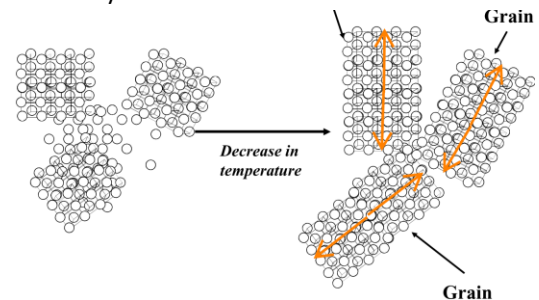
- Don't need to know the shapes above, just realize that crystals can be classified on length and angle of the dimensions
- In the shapes above, atoms can be placed in various corners or surfaces
 - If the atom is in the corner = each atom fills $1/8^{\text{th}}$ of a crystal unit
 - If the atom is on an edge = each atom fills $1/4^{\text{th}}$ of a crystal unit
 - If the atom is on a face = each atom fills $1/2$ of a crystal unit
 - Significance = describes how densely packed the atoms are. The denser the crystal, the stronger

- Solidification of metals

- In a liquid bath of melted metal atoms, bring the temperature down
- The decreased energy in the system will bring the atoms closer together

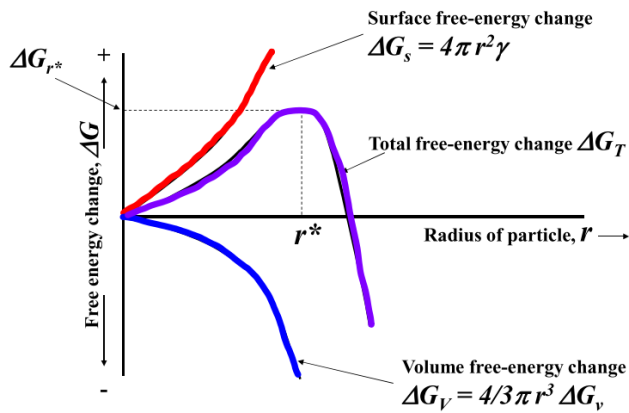


- Metal atoms start solidifying by forming "nucleation sites" of crystallization



- As temperature continues to drop, the nuclei grow into 'grains' in their original orientation
- Each grain has the same properties as the metal
- Slow cooling = grains can orient together slowly = more uniform metal = weaker (explained later)

- Energy changes during crystallization



- Red line

- In a liquid bath, metal atoms are constantly colliding with each other and forming small particles
- However, the nucleation particles break apart because of the increase in surface free energy change
- Forming a surface means electrons must act in an unfavourable way

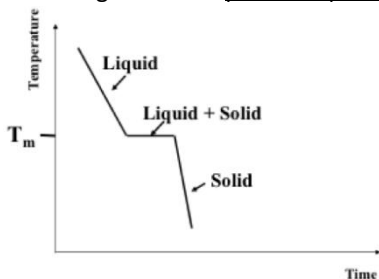
- Blue line

- When particles form, a volume is established
- Atoms in the center of the volume do not interact with the system, so they are basically “removed” → this leaves more energy to the melted atoms
- Therefore, forming nucleation particles is somewhat favourable

- Purple line

- Combine the energies of the red and blue lines
- Initially, it is not favourable for particles to grow because the surface free energy counteracts the volume free energy
- Surface free energy is a r^2 function whereas volume free energy is a r^3 function. Eventually, volume free energy will catch up and make it more favourable to nucleate
- If the small particles can clump enough and reach the critical radius (r^*), then nucleation is more favourable rather than breaking apart again
- This happens when you decrease temperature

- Phase transition diagrams for a pure component



- During phase transition (liquid → solid or vv), there is no change in temperature because the heat is being used for the phase change

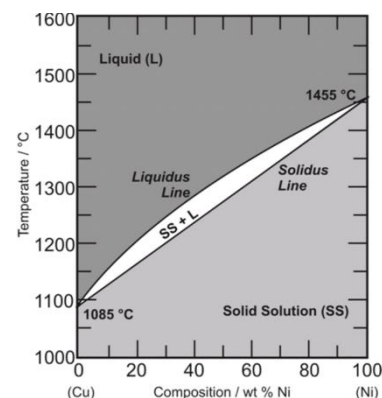
- Alloys come in 2 configurations

- Alloy: metallic compound containing 2 or more metallic elements
 - More abundant metal = principle metal
- Substituted alloy: principle metal forms a lattice. The alloy metal atoms substitute certain positions on the lattice. For example, some copper atoms replacing gold atoms in a gold lattice
 - Diameters of atoms must be within 15%
 - Each metal needs to have the same crystal structure (like FCC, BCC)
 - Similar electronegativities
 - Same valence
 - Due to these requirements, the resulting alloy will look identical to the principle metal
- Interstitial alloy: the alloy does not substitute the main lattice. It squeezes into random spaces inside the lattice
 - This type of alloy will not be studied

- Some definitions

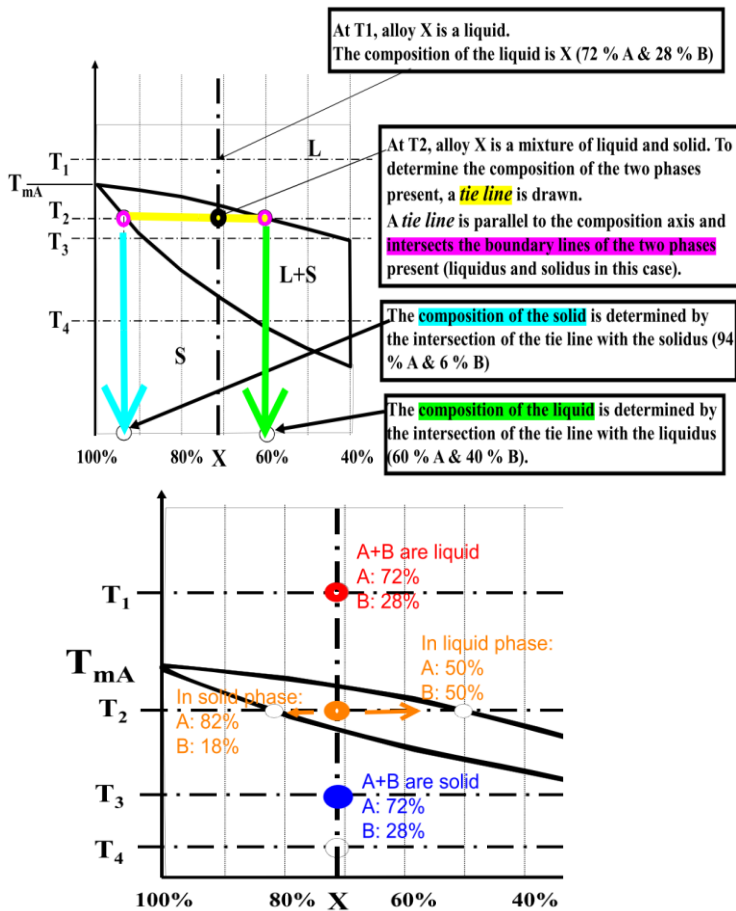
- Phase: chemically homogenous portion of a microstructure (in an alloy of A and B, a phase is an area where A and B are equally abundant)
- Component: distinct chemical substance from which the phase is formed

- Phase transition diagrams for an alloy



- On the left, it is pure Cu. Therefore, there is a sharp distinction between liquid and solid phases (just like the pure component transition diagram)
- On the right, it is pure Ni. Same story as the left
- In the middle, there are varying ratios of Cu/Ni. It is not pure therefore it is an alloy
 - With an alloy, the transition temperatures are not perfectly clear
 - At a given temperature, one metal may be melting whereas the other metal is still solid
 - There is an “in-between” phase
- 3 questions answered by a phase diagram
 - What phases are present for any given composition and temperature?
 - What is the composition of the phases present for any given composition and temperature?
 - What is the proportion of the identified phases?

- Examples of using the phase diagram



- Lever rule (not on exam)

$$I_{\text{solid}} * W_{\text{solid}} = I_{\text{liquid}} * W_{\text{liquid}}$$

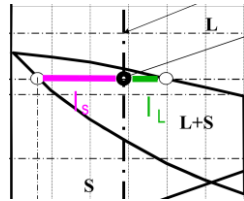
- I = lever arm

- W = weight

$$I_S = A_S - A_X$$

$$I_L = A_X - A_L$$

- By plugging in the values, it is possible to get the proportion of the identified phases



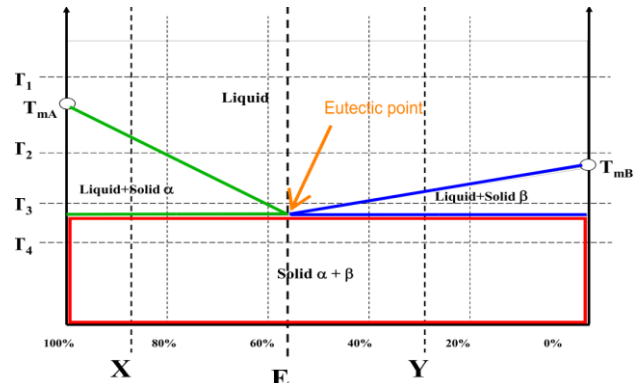
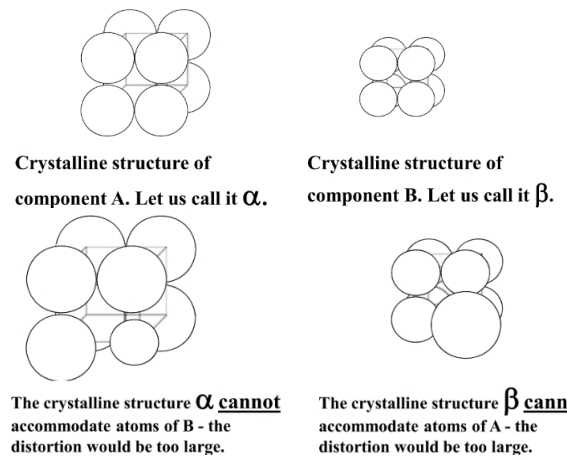
- At a given temperature, is the solution more liquid or more solid? (on exam)

- Looking at the tie line, see which intersection is closer. That is the more dominant phase
- In the image above, $I_L \ll I_S$. Therefore, the liquid phase is much more dominant

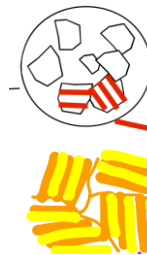
- Special type of alloys: eutectic alloys

- Like a normal alloy, it is a 2+ component system (we will deal with just 2)
- They can have no solid solutions or only a limited solid solution
 - Note: a solid solution is a solid mixture containing a minor component uniformly distributed within the crystal lattice of the major component
- Unlike the alloys covered before, eutectic alloys have metals with different properties/sizes

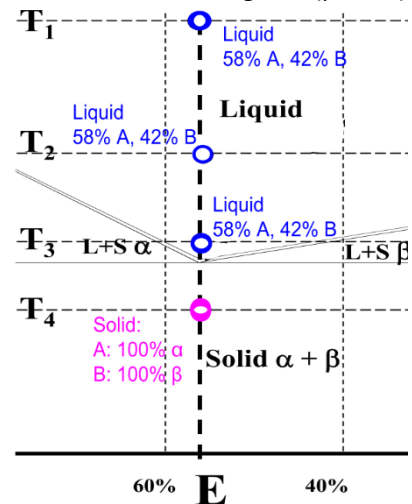
- Eutectic alloy with no solid solution



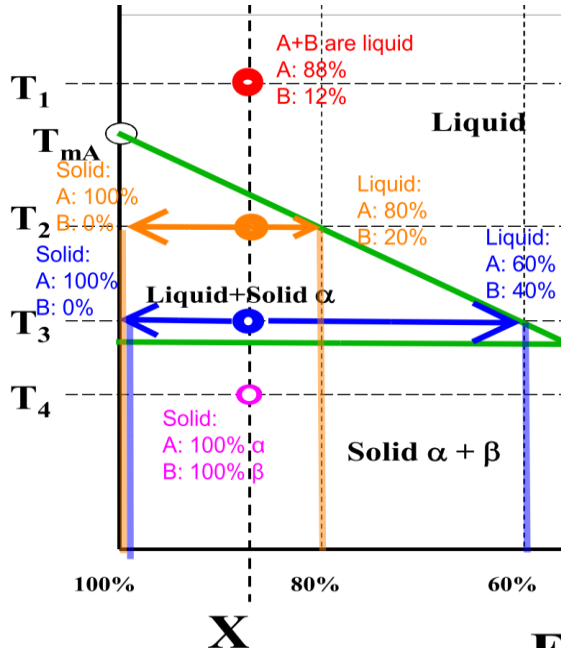
- 3 alloys will be studied, (X, E, and Y) to see what phase the metals are in with each configuration
- In the liquid/solid phase, use tie lines (just like before). Since the solidus line is flat, the solid will always be 100%. Only the liquidus line is relevant
- Analyzing the E alloy**
 - Also known as the "eutectic composition"
 - At this ratio of A:B, solidification happens immediately, much like a pure metal
 - However, alloy cannot solidify into a uniform crystal because A and B are too different



- Therefore, it undergoes eutectic reaction where A and B crystallize in layers
- In real life, appears as lamellar structures seen on the solidified grains (picture)



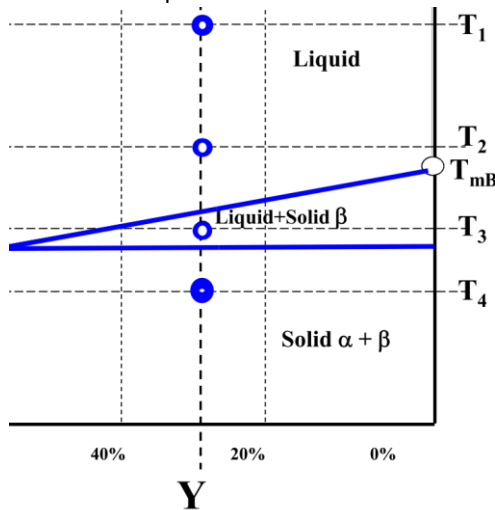
Analyzing the X alloy



- T_1 = A and B are liquidized
- T_2 = Some A atoms solidify into crystal α . Other A and B atoms are randomly dispersed as liquid
- T_3 = More A atoms solidify into crystal α
- T_4 = alloy cannot solidify into a uniform crystal because A and B are too different
 - Therefore, it undergoes eutectic reaction where previously formed α crystals are "entrapped" into "islands"
 - Because the solidification process is slower than the E alloy, islands will form instead of having a lamellar structure

Analyzing the Y alloy

- Unlabelled for practice

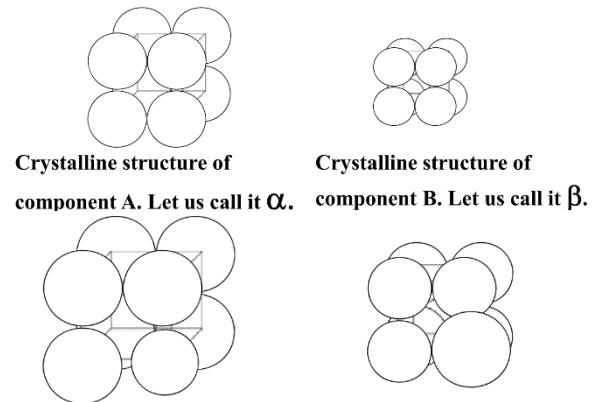


- T_1 : A+B are liquid. 28% A, 72% B
- T_2 : A+B are liquid. 28% A, 72% B
- T_3 : Solid is 100% B. Liquid is 40% A, 60% B
- T_4 : A+B are solid. A is 100% in α , B is 100% in β

Islands or no islands?

- Solidifying E alloy = no islands
 - Lamellar structure means that any cracks will propagate straight through the alloy
 - Higher ductility
 - Used for soldering because mechanical properties are not necessary and it is nice to have an alloy that liquefies quickly
- Solidifying X or Y alloy = islands
 - Islands means that cracks will be impeded
 - Fracture toughness increased
 - Lower ductility
 - However, reduced overall toughness due to lower ductility
 - For load bearing uses, use the X or Y alloy, and avoid E alloy
 - For fracture resistance uses (and don't need ductility), use the purest alloy possible (100% metal A or 100% metal B)

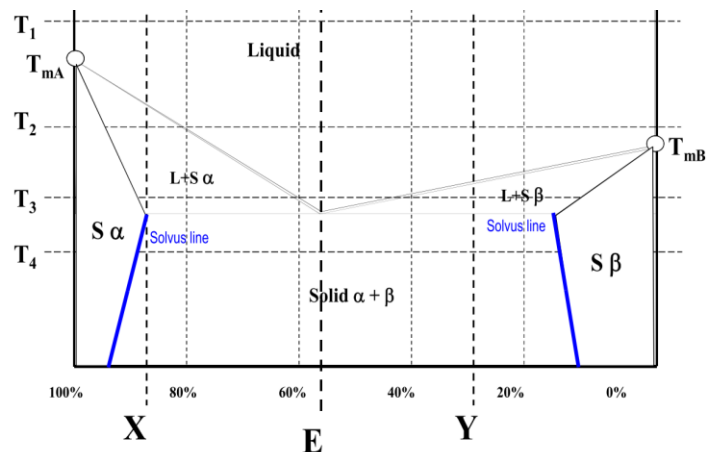
Eutectic alloy with some solubility



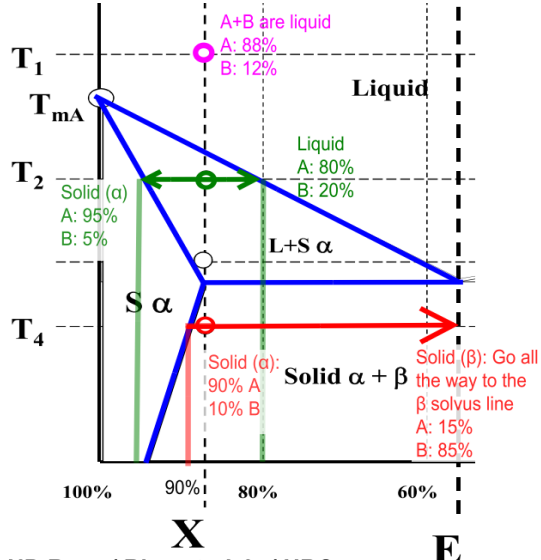
The crystalline structure α can accommodate atom(s) of B.

The crystalline structure β can accommodate atom(s) of A.

- Because the 2 metals are now able to incorporate each other in their crystals, the phase diagram changes slightly
 - Addition of a solvus line
 - Solvus line: describes the solubility of B in A and A in B

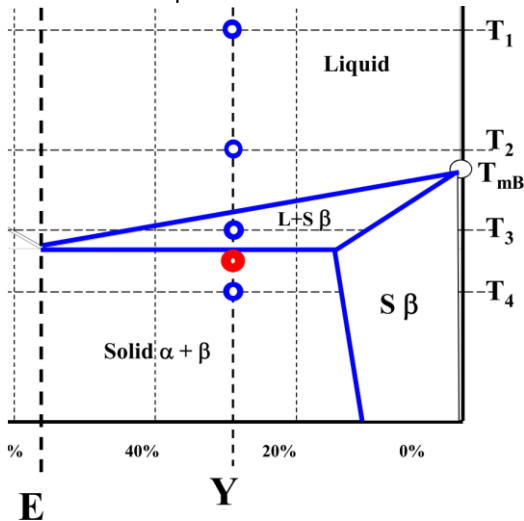


Analyzing the X alloy



Analyzing the Y alloy

- Unlabelled for practice

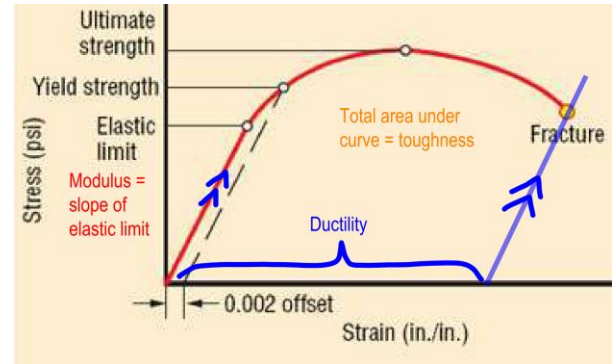


- T₁: A+B are liquid. 28% A, 72% B
- T₂: A+B are liquid. 28% A, 72% B
- T₃
 - Liquid: 40% A, 60% B
 - Solid (β crystal): 10% A, 90% B
- T₄
 - Solid (α crystal): 90% A, 10% B
 - Go all the way to solvus line on α side
 - Solid (β crystal): 15% A, 85% B
- Note: the red dot
 - At the red dot, the β crystal can accommodate metal A by about 17%
 - At T₄ (lower temp), the β crystal can only accommodate metal A by 15%
 - At higher temperatures, crystal lattice is flexible and can be distorted to fit metal A, which is not the right size
 - At lower temperatures, the ability to distort and incorporate misfitted atoms diminishes

Altering metal/alloy characteristics

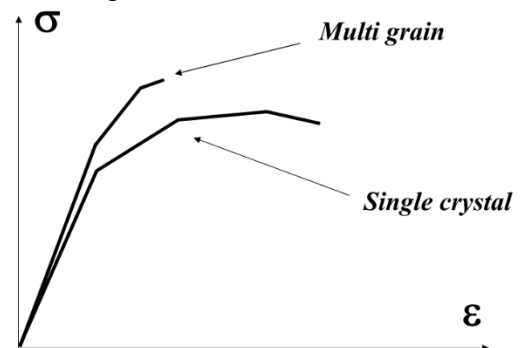
- Grain size and boundary area
 - Recall: solidification of metals starts with nucleation sites which turn into "grains"

	Small grain	Large grain
Boundary area (area between grains)	Large	Small
Modulus	Same	Same
Ductility	↓	↑
Toughness	↓	↑
Yield strength	↑	↓
Strength	↑	↓
Fracture toughness	↑	↓



- Modulus is about the same because under low stress, metals A + B behave the same. The difference is seen when you get closer to the fracture or higher stress/strain areas
- Small grains are crack resistant as a crack in one grain will not propagate easily into the next grain
- If the metal was 1 big grain, one fracture would propagate through the whole thing

Number of grains



Avoiding or inducing grains

- Avoid grains**: keep the metal near the solidus line for a long time. The grains will orient and form large crystals (unwanted if fracture resistance is desired)
- Form grains**: add nucleating agents like metal particles (above the critical radius) to make grain formation favourable

Controlling mechanical properties during metal casting

- Quenching (controlling grain size)
 - When the metal finishes transitioning from metal to solid, quench it in water/oil to rapidly bring down the temperature
 - Freeze the metal in its small-grain form without letting the grains re-orient and become large

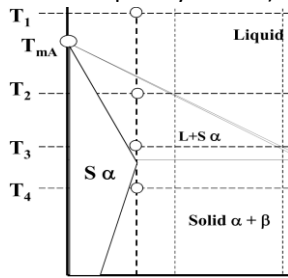
Coring

- Happens when the metal is rapidly cooled down while still in the liquid/solid phase
- Forms inhomogeneity within the crystals
- This is unwanted. Cool the L+S phase slowly
- Alloys with a large L+S phase are at higher risks of coring
- In real life, it will appear as separation of the metal layers. A nucleus of metal alloy will be blanketed in another metal, and another, and another, etc. This is prone to erosion



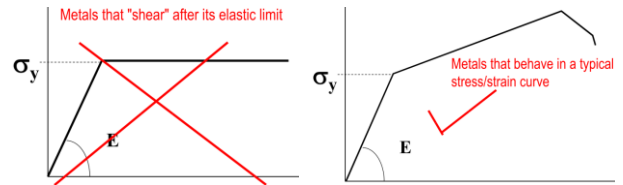
Precipitation hardening

- Requirements
 - You need to have a eutectic alloy
 - The alloy should have a variable solvus line (i.e. not vertical, but sloped)
 - The alloy needs to cross the solvus line
- It is a solid state reaction, meaning it works when the alloy is solidified (but not completely cooled)
- Steps
 - Liquefy the alloy (like T_1)
 - Bring it down to about the solidus line (T_2)
 - Now, there will be liquid A+B and solid A+B in the α form
 - Quickly quench it so α grains don't grow into large crystals
 - Now, you're left with solid α grains. This is "metastable" because there's no β crystals
 - Bring the temperature back up, but not too high to melt anything. Somewhere like T_4
 - Remember, this is a solid state reaction
 - This allows β crystals precipitate within the already-present α crystals
 - It is better to have the solvus line as high as possible so that a lot of solid state reactions can happen without liquefying
- Advantages
 - Large grain boundary area
 - Precipitating β forms "islands" \rightarrow acts as obstacles for fracture propagation
 - Significant changes to mechanical properties

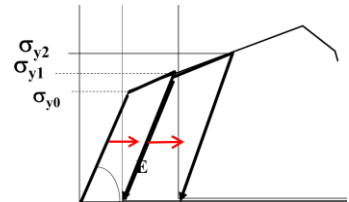


Controlling mechanical properties after casting

Cold work



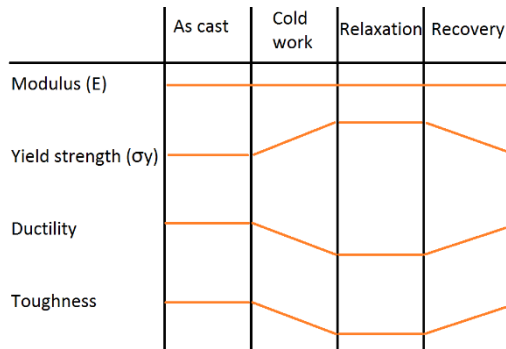
- Only works on metals that display non-shear and traditional stress/strain relationships
 - It can be done to metals on the left, but there's no point because you'll never increase yield strength (σ_y) which is the goal
- Up to the metal's yield strength, you can stress it over and over again, but it will return to its original shape



- If you stress the metal past the yield strength (σ_{y0}), it will undergo permanent deformation. If you unload after permanent deformation, it will not return to its original strain of 0
- Since the metal is deformed, it now has a new yield strength (σ_{y1}) which is greater than the original yield strength
- By cold working it again, YS goes higher (σ_{y2})
- Now, the metal can withstand much greater stresses without deforming. More elastic
- Modulus stays about the same
- Ultimate strength is the same
- Resilience (AUC for the elastic region) is increased
- Ductility (ϵ until fracture) is decreased
- Toughness (AUC until fracture) is decreased
- In general, you can say the metal is more brittle
- If these properties are desired, stop here. If you cold worked the metal to make it into the desired shape but you want its original mechanical properties back (like ductility), then you need to heat treat it

Heat treatment

- Relaxation
 - Slight heat to relieve stresses from cold working the metal
 - Does nothing to mechanical properties
- Annealing/recovery
 - Heat the metal under its solvus line
 - The cold worked metal will keep its physical shape, but it will recover its original stress/strain curve
- Don't heat too long or else it'll cause grain growth which is bad + irreversible (unless you melt)



- Applications to dental tools

- Perio probes: cold worked, not annealed (bending would make it harder to use)
- Cast clasps: low elastic limit, low resilience
- Wrought wire clasp: high resilience and high elastic limit, but brittle

- Dental alloys classification

- Background
 - Noble metals – does not easily lose electrons
 - Mostly gold and platinum
 - Low melting temp and does not oxidize → melting it is easy, and does not require special inert gases to melt
 - Heavy → centrifuged and shaped easily
 - Good biocompatibility
 - Base metals – readily loses electrons (oxidizes)
 - Better mechanical properties
 - Higher melting temp and oxidizes → more rigorous and complex melting procedure
 - Not as biocompatible
- Classification based on noble content
 - High noble alloy: $\geq 60\%$ noble or $>40\%$ if gold
 - Noble alloy: $\geq 25\%$ noble
 - Base alloy: $<25\%$ noble
- Classification based on mechanical properties
 - Assume all alloys were annealed
 - Base metals are inherently type IV

Type	$\sigma_{Y0.001}$ (in MPa)	ϵ_{max} (in %)
I	140	18
II	140~200	18
III	200~340	12
IV	≥ 340 (500 if hardened)	10 (2 if hardened)

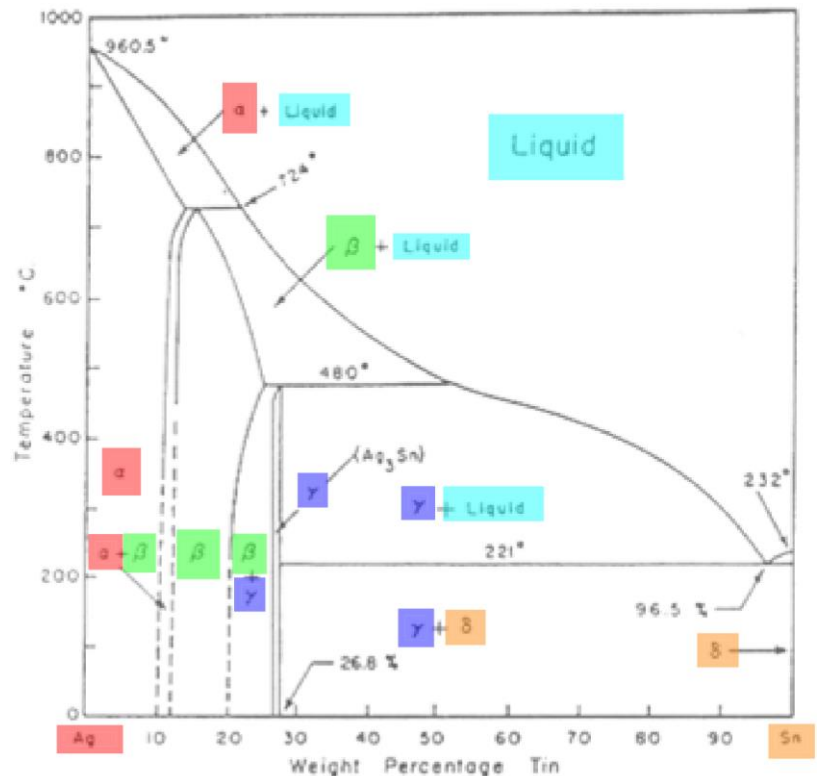
- Dental relevance

- Inlay
 - Noble type 1, type 2 for bigger inlays
 - Softer alloys are desired for small preparations because you can burnish and cold work it into the preparation and get tight margins
 - Do not over-burnish, too much cold working will make the alloy turn brittle
- Crown and bridge
 - Noble type 3, type 4
 - Base Cr-Co, Ni-Cr, Ti
 - Deformation is not wanted due to higher stresses
- Removable partial
 - Noble type 4
 - Base Cr-Co, Ni-Cr, Ti
- Metallo-ceramic crowns
 - Noble type 4 (Au-Pd-Pt, Au-Pd-Ag, Au-Pd, high Pd)
 - Base Cr-Co, Ni-Cr, Ti
 - ANY deformation will put stress on the brittle ceramic and cause fracture. A very strong alloy is needed
 - Downside is, it cannot be burnished because it is so stiff
 - Metal and ceramics bond to each other through an oxide layer. To accomplish this, noble metals have impurities added which will oxidize. Base metals don't have a problem as they oxidize on their own
- Gold and amalgam
 - When they come in contact, can trigger a galvanic reaction in the mouth
 - Surface area of the noble metal dictates how fast the base metal will corrode
 - In amalgams, will cause release of Hg, Sn, and eventually restoration failure
 - Don't do them in the same quadrant

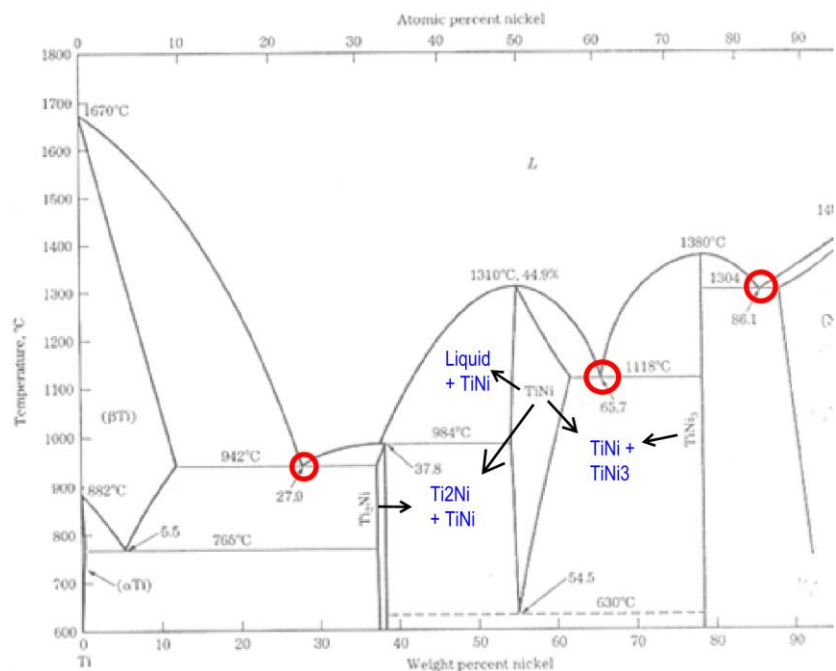
Metal	Atomic radius	Electro-negativity	Crystalline lattice	Valence	Young's modulus	Yield strength	Tensile strength	T_m
Ti	0.147	1.5	HCP	2, 3, 4	117	170-900	340-1200	1668
V	0.136	1.6	BCC	2, 3, 4, 5				1890
Al	0.143	1.6	FCC	3	70			660
Au	0.144	2.5	FCC	1, 3	77			1064
Cu	0.128	2.0	FCC	1, 2	130		170-1000	1083
Pd	0.137	2.2	FCC	2, 3, 4	112			1552
Pt	0.139	2.2	FCC	2, 3, 4	147			1772
Ag	0.144	1.9	FCC	1, 2	71			962
Cr	0.129	1.7	BCC	2, 3, 6				1903
Co	0.125	1.9	HCP	2, 3	211		230-1000	1495
Ni	0.125	1.9	FCC	1, 2, 3	210		340-1400	1455

Phase diagrams

- Tin-Silver alloy
 - So many letters → each greek letter represents a crystalline structure
 - α (red) = pure crystal of Ag
 - δ (orange) = pure crystal of Sn
 - Displays “peritectic” properties
 - Rather than separation or lamellar formation of crystals, whole different crystals form instead
 - Incongruous melting
 - Forms multiple types of crystals
 - α , β , γ , δ
 - Looks complicated, but straightforward
 - Pick a certain ratio (X axis)
 - Vary the temperature (Y axis)
 - See which crystals will be formed
 - For instance, let's say I wanted an alloy in purely the γ form. I don't want any other crystal because it will be prone to corrosion. Then, I can interpret that the ratio needs to be 26.8% Sn and temp can be 0~480C. This is where Ag_3Sn is formed (seen in amalgam)



- Titanium-Nickel alloy
 - Some spaces are left blank
 - Use the surrounding labelled areas to fill in the blank ones
 - Blank ones were filled in with blue text
 - V notches = possible eutectic points
 - Superior curvy lines = liquidus line
 - How to interpret this graph
 - Pick a composition (X axis)
 - Draw a vertical line at that composition
 - Select several points along that vertical line, which varies the temperature
 - If a point falls in a single phase, it is whatever you melted
 - If a point falls in 2 phases, draw a tie line, drop at the intersection, then determine the compositions



Ceramics

Definition

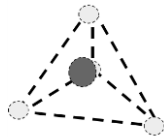
- Ceramic:** crystalline, inorganic, non-metallic materials which consist of metallic and non metallic elements bonded primarily by ionic and/or covalent bonds
 - Hand made
 - Crucial step is the firing step
 - Note: they are “non-metallic” in the sense that their mechanical properties are not like metals. It actually does contain some metal
 - Ionic/covalent bonds → make the material strong, stiff, and brittle. Very little elastic deformation
- Glasses:** ceramic materials in which the constituents are heated to fusion and then cooled to a rigid condition without crystallization
- Dental ceramics are glasses which are filled with ceramic component

Types of ceramics

- Traditional:
 - From naturally occurring materials
 - Clay, feldspar, silica
 - In dentistry, we use traditional ceramics
- Industrial/engineered:
 - Al_2O_3 , SiC, B_4C , TiO_2 , SiN
 - More pure and better mechanical properties

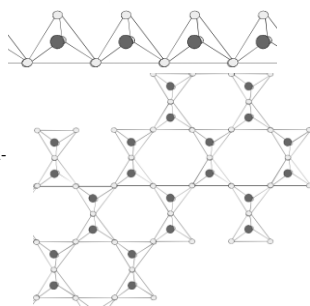
Ceramics are based on chemistry of SiO_4^{4-}

- Electronegativity of Si is 1.9, and O is 3.4
- This difference in electronegativity is not enough to be an ionic bond, but too polar to be covalent
- Using math, it is about 50/50 ionic/covalent
- Structurally, SiO_4 is a tetrahedron



Polymerization of SiO_4

- Si tetrahedron shares 2 oxygens: forms a chain or ring. Each subunit is SiO_3^{2-}
- Si tetrahedron shares 3 oxygens: forms a sheet. Each subunit is now $\text{Si}_2\text{O}_5^{2-}$
- Si tetrahedron shares 4 oxygens: forms a 3D network called **silica**



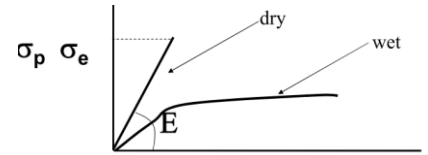
Kaolinite or clay

- Sheet of $\text{Si}_2\text{O}_5^{2-}$
- It is negatively charged
- Not stable in nature
- Will need to be neutralized with a positive sheet like $\text{Al}_2(\text{OH})_4^{2+}$ → this is kaolinite or clay
- Kaolinite is given the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$



Properties of kaolinite/clay

- When it is moist, the sheets slide past each other and the material is highly deformable
- When it is dry, there are strong electrostatic interactions holding the sheets where they are. The material becomes brittle



Talc

- Like clay, it is a sheet of $\text{Si}_2\text{O}_5^{2-}$
- However, the positive sheets are $\text{Mg}_3(\text{OH})_2^{4+}$
- Talc is given the formula $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$

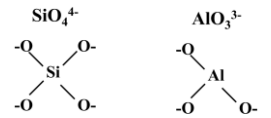


Silica (SiO_2)

- Melts at very high temps (1710 C)
- Used as a filler in ceramics and composites
- Can come in 3 types of crystals, depending on the temperature they were made in
 - <573C, 573~867 C: Quartz
 - 867~1470 C: Tridymite
 - 1710~1470 C: Cristobalite
- Each crystal has a different coefficient of thermal expansion
- Will not melt during the firing process of a dental ceramic. Will remain crystallized

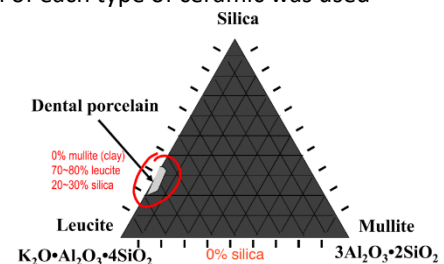
Feldspars

- Replaces Si^{4+} with Al^{3+}
- Since Al only binds 3 O's, the network is **negatively charged** in a network
- Cationic ions like Na, Ca, Mg, and Ba are added
- Low melting point
- Most types of feldspar form an amorphous glass matrix and poor mechanical properties
- If only some of the Si's are replaced with Al (called feldspathic), you get better mechanical properties (analogous to β grains forming within α grains in alloys). However, feldspathic is still pretty weak



In dentistry, ceramics involves a mixture of all 3 traditional ceramics (clay, feldspar, silica)

- Normally, dental ceramics uses very little or no clay (3~5% max), 20~25% silica as a filler, and the major component is feldspar
- A composition diagram is used to easily portray how much of each type of ceramic was used



- Types of casts in dentistry

	Pros	Cons
Pure Metal	-Strongest -Most conservative	-Ugly
Pure Ceramic	-Esthetic -Biocompatible -High compressive strength -Insulation for pulp	-Brittle (easy crack propagation) -Low fracture toughness -Less conservative -Wears opposing tooth
Metallo-ceramic	-Best of both worlds	

- How metalloceramic casts are made:

- Paint ceramic on to a metal coping
 - Note: an opaque ceramic is applied first to hide the esthetics of the oxidized metal. Then, the dentin/enamel mimicking porcelains can be applied for optimal esthetics
- Fire it at 700~1300 C
 - Sinter the cast in a vacuum to squeeze any pores (formed by H₂O evap) out of the ceramic
 - Vacuuming ↑ transverse strength
 - Note: this may cause significant cast shrinkage, so always make the cast way bigger before firing
- Feldspar in the ceramic fuses to the metal oxide layer
- The cast is now cooled

- Fusing temperature

- What do you need to melt anyway?
 - You want to melt the feldspar
 - You don't want to melt the metal, because the coping will sag. You want to preserve the structure of the coping
 - You don't need to melt the silica or alumina crystals because you don't need them to bond to anything – just provide structural rigidity
- So what temperature is needed?
 - A dental ceramic contains silica, feldspar, and clay
 - Structurally, it looks like Si and Al crystals dispersed in an amorphous matrix of feldspar
 - It is amorphous because the Na in the feldspar disrupts complete crystallization
 - Since it is amorphous instead of crystalline, the melting temperature of feldspar is low
- Classification of fusing temperature
 - High fusing: >1300 C (only used in Pt alloys)
 - Medium fusing: 1100~1300 C
 - Low fusing: 850~1100 C
 - Very low fusing: <850 C

- In dentistry, the feldspar of choice is leucite (K₂O*Al₂O₃*4SiO₂)

- Note: since leucite incorporates Si as well, it is more accurate to call it a feldspathic
- Leucite is special because it can crystallize → better mechanical properties
- Also, leucite has a high coefficient of thermal expansion (CTE). This is good because it makes the ceramic compatible with metal alloys

- Why is leucite used over other feldspars when coating metal copings? (know this!)

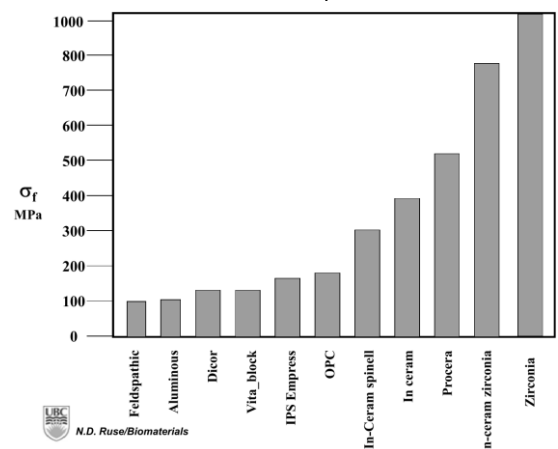
- Has to do with the cooling phase
- Leucite has high coefficient of thermal expansion (α)
- This is desirable as it enhances the metal – ceramic bond
- Metal α = ceramic α
 - Theoretically ideal
- Metal α < ceramic α
 - Ceramic will shrink a lot, whereas metal won't shrink as much
 - Ceramic is held in tension as the metal does not allow it to shrink much
 - Ceramic cannot handle tensile stress very well, and will likely fracture
- Metal α > ceramic α
 - Metal shrinks a lot, whereas ceramic won't shrink as much
 - Metal cannot shrink too much, so it starts to bend instead. This causes ceramic to crack
- In real life, it is ideal to have metal α slightly higher than ceramic α . This way, the ceramic is under slight compressive stress, which it can handle 1000x better than tension

- Review: 3 criteria for metal-ceramic compatibility

- Oxide layer needs to form on the metal
 - Titanium → oxide layer too thick → fractures
 - Magnesium → good thickness of oxide layer
- T_{melting} ceramic << T_{melting} metal
 - Make sure the metal coping does not sag when it reaches the temperature to melt the ceramic
- $\alpha_{\text{metal}} \geq \alpha_{\text{ceramic}}$

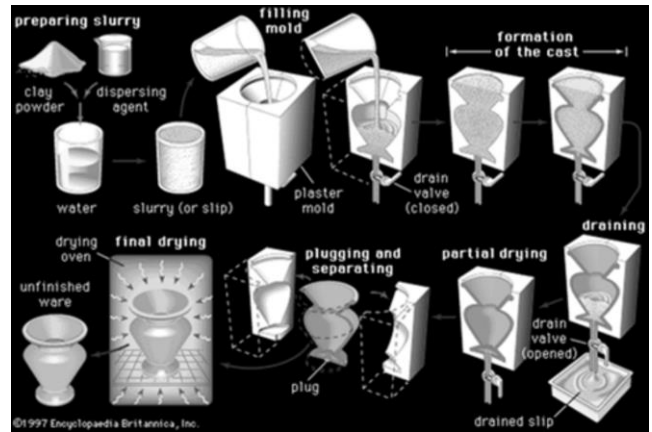
- All-ceramic casts

- Becoming more popular nowadays
- Many types:
 - Feldspathic based
 - Glass-ceramic
 - Glass-ceramic leucite reinforced
 - Glass-ceramic other reinforcements
 - Injection molded glass ceramic
 - Glass infiltrated alumina/spinell/zirconia core



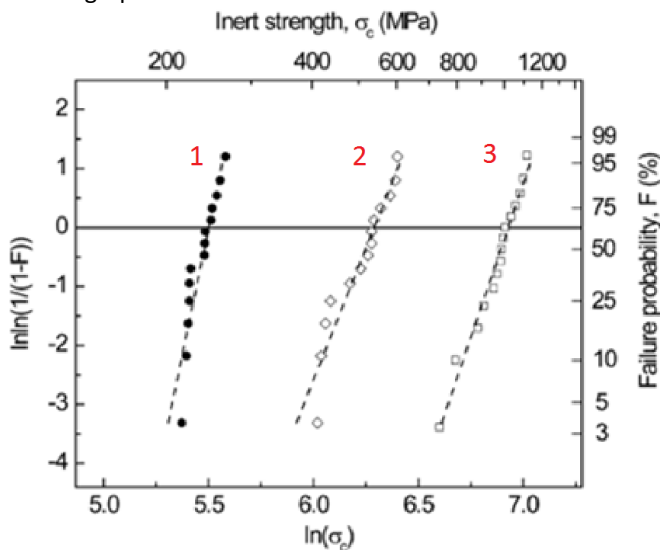
- All ceramic casts
 - Feldspathic based
 - Glass ceramic
 - SiO_2 crystals
 - Feldspar amorphous material
 - K1C (fracture toughness) is low
 - Glass ceramic with leucite reinforcement
 - Remember, leucite is a unique feldspar because it is crystalline instead of amorphous
 - When this material is fired, there will be silica crystals but also **leucite crystals**
 - K1C is increased, but not by much
 - This is also more compatible if you wanted to bond a ceramic to a metal
 - **Empress** – glass ceramic with leucite
 - **Mica** – still has feldspathic glass and refractory silica, **but it forms in flakes, which gives reinforcement. No longer used**
 - Glass ceramic with other reinforcements
 - **Empress II** – modifies feldspar with lithium disilicate → will crystallize while allowing higher V_f → better mechanical properties
 - **Emax** – also lithium disilicate. However, manages to push V_f to 70~80% (very high)
 - Used in CAD/CAM or presses
 - Good for anteriors, not for posteriors
 - Crystalline ceramics with glass reinforcement
 - Uses **industrial/engineered** ceramics
 - Much better mechanical properties
 - Used for large restorations, long span bridges, etc
 - Made by slip casting
 - Ceramic is poured into a mold
 - When the ceramic dries, remove from mold
 - Then, the ceramic is fired
 - The ceramic acts as a scaffold. It can be controlled to have a certain number of pores in the scaffold
 - Pores are then infiltrated with feldspathic
 - Makes V_f controllable
 - Also, feldspathics are translucent which gives a natural tooth-like appearance
 - **Vita in-ceram**
 - Uses a ceramic scaffold/core of Al_2O_3
 - **Spinell in-ceram**
 - Instead of Al_2O_3 , uses MgAlO_4
 - This is a mixed oxide of 2 metals
 - Better than Al_2O_3 (alumina)
 - **Zirconia in-ceram**
 - Al_2O_3 reinforced with ZnO_2
 - Not pure zirconia
 - **Procera**
 - Uses alumina and zirconia core
 - Rather than slip casting, uses sintering

- Visual for “slip casting”



- Properties of zirconia (ZnO_2)
 - Zirconia liquefies at ~2750 C
 - When it cools, it undergoes different crystal structures
 - 2750C → 2370C: cubic crystal
 - 2370C → 1170C: tetragonal crystal
 - <1170: monoclinic crystal
 - Turning into the monoclinic form is associated with 4% increase in volume
 - This shatters the zirconia during cooling
 - To prevent shattering, you use 2 strategies:
 - Add an impurity like MgO , Y_2O_3 , CeO_2 , CaO
 - Quench zirconia in the tetragonal form
 - Result:
 - Zirconia is locked in a tetragonal form
 - The impurities keep it stable in tetragonal form
 - This state is called partially stabilized zirconia (PSZ)
 - PSZ is pretty cool
 - When a material cracks, there is a lot of stress at the tip of the crack which causes elongation
 - The crack tip has a lot of stress energy
 - In partially stabilized zirconia, this stress causes the tetragonal crystal to pop into the monoclinic form
 - When it switches to monoclinic, it expands by 4%
 - The monoclinic crystal at the crack tip now “rounds off” the crack
 - Crack can no longer propagate
 - Concerns with low temperature degradation
 - When zirconia is loaded cyclically in a wet environment, some crystals can turn into monoclinic form and shatter the ceramic
 - Also, adjusting the zirconia with a bur may cause crystals to go monoclinic
 - Sandblasting, a treatment done before bonding metals, may not be applicable to zirconia
 - However, not enough evidence that this happens in real life

- Applications of zirconia in real life
 - Zirconia reinforced alumina has the greatest fracture strength, despite being brittle
 - K1C of 8~12
 - Zirconia reinforced resin composite
 - Resin composites have a K1C of 1
 - This is not enough energy at the crack tip to turn the tetragonal zirconia into monoclinic
 - No benefits – useless
 - Zirconia reinforced feldspathic
 - Like composite, no benefit for the same reason
- Ceramics – bottom line
 - Core can be made of industrial type ceramics
 - However, the veneer (surface of the ceramic) must be a feldspathic ceramic due to esthetic constraints
- Visualizing the mechanical properties of ceramics
 - Normal distribution patterns
 - Mean and standard deviation is all you need to understand the whole distribution pattern
 - “Mean” is at 50%
 - Easy to work with
 - Does not apply to ceramics, because ceramics behave erratically and have more variation
 - Weibull distribution patterns
 - More fitting for ceramics
 - Wider distribution → more variation
 - Instead of a “mean” or “SD”, Weibull graphs are characterized by a characteristic value and Weibull modulus (i.e. reliability)
 - The characteristic value is at 63.2%
- Weibull graph



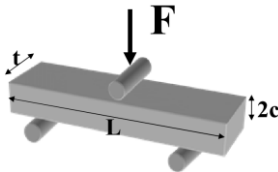
- Axes
 - X axis = stress (in exponential scale)
 - Y axis = probability of failure
- Important points
 - When the plot crosses the 63% F line, this corresponding X value is its **flexural strength**
 - The slope is its **reliability**

- Interpretation of the graph
 - 3 has the highest flexural strength because it crosses the characteristic value line at ~1000 MPa
 - 1 is the most reliable since it's the steepest slope
 - Steeper slope = smaller range of possible forces that fracture that material
 - Shallow slope = a wide range of forces can possibly fracture that material
 - Slope >10 → considered reliable
- For dentistry purposes, is reliability or flexural strength more important?
 - Both are important
 - Look at flexural strength first. Make sure that it can withstand forces in the mouth
 - If all your choices are not limited by their flexural strength, then look at reliability
- Ceramics in bridges
 - Looked at the 20 year survival of 3 materials
 - A = zirconia with Al
 - 3 unit bridge → needs 3+mm connectors
 - 4 unit bridge → needs 5+mm connectors
 - 5 unit bridge → needs 6+mm connectors
 - B = zirconia with Yttrium
 - 3 unit bridge → needs 2.5+mm connectors
 - 4 unit bridge → needs 4.1+mm connectors
 - 5 unit bridge → needs 4.9+mm connectors
 - C = lithium disilicate
 - 3 unit bridge → needs 3.7+mm connectors
 - 4 unit bridge → needs 6+mm connectors
 - 5 unit bridge → not possible under 6mm
 - Note: 6mm is the limit of practicality in dentistry
 - Only zirconia cores can survive 5 unit bridges
 - But remember, **the veneer is just as important as the core, because the veneer is the esthetic part**
 - Veneers are made of feldspathic
 - Feldspathic veneers work well in metal ceramic crowns, since the metal exerts a compressive force on it, preventing it from fracture
 - However, when the same ratio of core:veneer is used in a zirconia core, there is more fracture
 - Possible reason: zirconia insulates heat while feldspathic does not. During cooling after drinking something hot, the feldspathic will shrink a lot while the zirconia cools slowly. This exerts tensile stresses
 - Slow cooling is used to minimize tensile stress on the feldspathic, so the zirconia and feldspathic cool at the same rate
 - However, this means the zirconia isn't “quenched” in tetragonal form
 - Some zirconia will turn monoclinic → expands → tensile stress on feldspathic
 - Not a complete solution to the problem
- Although chipping rates are higher in zirconia core ceramics, it is not as visible

- Computer aided design and machinery (CAD/CAM)
 - Computer can mill out a block of material into a tooth structure to be used as crowns/onlays/inlays
 - The block material can be ceramic or composite

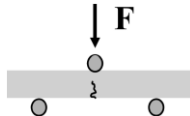
Composite	Ceramic
-Easy to mill	-Hard to mill
-Moderate esthetics	-Excellent esthetics
-Cheaper	-More expensive
-Fixed with resin, but ↓ strength by 50%	-Also needs to be fixed with resin

- How ceramics are made with in CAD/CAM
 - Normally, just the “core” part of the ceramic comes in a block
 - For example, Emax will come in a green block of uncrystallised lithium disilicate
 - Stick it into the machine to mill it
 - Fire it to crystallize it
 - Will look ugly, once finished, so apply a veneer coating of feldspathic on top
- 3 point bending tests



- Can be used to determine the flexural strength and the flexural modulus of the ceramic
- Determining flexural modulus (E_f)

$$E_f = \frac{L^3}{48I} \left(\frac{dF}{dv} \right) = \frac{L^3}{32tc^3} \left(\frac{dF}{dv} \right)$$



- Determining flexural strength (σ_f)
 - Formulas differ depending on the cross section of the object being bent. We'll use rectangular cross section with dimensions $t \times 2c \times L$

$$\sigma_f = 3LF/8tc^2$$

- This formula can be manipulated to isolate C. By isolating C, it tells you the **minimum thickness of the ceramic needed to withstand force F**

$$c = (3LF/8t\sigma_f)^{1/2}$$

- Assume $F = 700N$, $L = 20 \text{ mm}$, $t = 5\text{mm}$. It is evident that as the flexural strength (σ) increases, the thickness needed to withstand 700N force decreases. Since this is a $^{1/2}$ function, increasing σ yields diminishing returns

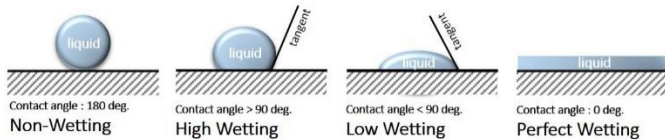
σ_f (MPa)	C (mm)
100	3.24
150	2.65
400	1.62
1000	1.02

- You want to minimize C because that means the least amount of tooth structure can be removed

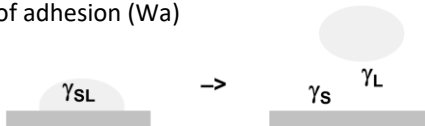
Adhesives

Definitions

- **Adhesion:** intermolecular interactions binding 2 surfaces
 - With solids it is nearly impossible because it would require atomic smoothness to bring the solid atoms towards each other. Also, smooth surfaces are prone to contamination
 - Instead, liquids are used which can adapt to the surface to allow intermolecular interaction. Also has the benefit of **chemical bonding** and **mechanical interlocking** once the liquid is solidified
 - Therefore, adhesives are liquids
- **Wetting:** adhesion between liquid and solid

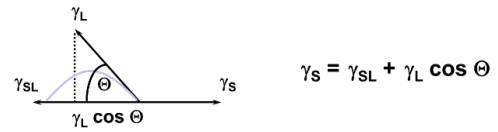


Work of adhesion (W_a)



- Energy required to separate the droplet from the solid surface
- When the droplet is bound to the surface, the energy holding them together is γ_{SL}
- When separated, each surface has an energy γ_S , γ_L
- In a dry environment
 - $W_a = (\gamma_S + \gamma_L) - \gamma_{SL}$
 - $W_a > 0$ (it takes energy to separate surfaces)
 - Any liquid will interact, even if it's a little bit, with the surface
 - This gives slight adhesion
 - Makes W_a always > 0
 - Increasing γ_S will increase adhesion
- In a wet environment
 - $W_a = 2\gamma_L + 2[E_{\gamma_1\gamma_2} - E_{\gamma_1\gamma_L} - E_{\gamma_2\gamma_L}]$
 - The liquid in the environment will compete to bind to the droplet or the surface
 - If the liquid has higher affinity for one, it will separate the layers
 - So, W_a can be $+$ or $-$
 - If W_a is $-$, then there will be spontaneous separation
 - In dentistry, adhesives need to be tested in a wet environment to make sure that it will not separate due to water in saliva
 - Manufacturers will test for 24 hours, but this is not enough for proper evaluation
 - 30~90 days in water is more suitable

Young's equation for adhesion



- Don't need to memorize it, just know the key point
- γ = face surface energy
- For good adhesion, you want θ to be 0°
- If θ is 0° , then $\cos\theta = 1$
- **Substituting it into the equation, we find that $\uparrow \gamma_{Solid}$ and $\downarrow \gamma_{Liquid}$ will maximize our wetting**
- Separation patterns of adhesive and its surface
 - Adhesive between 2 surfaces
 - Adhesive failure
 - Cohesive failure
 - Mixed failure
- Work of maximum adhesion ($W_{a\max}$)
 - Combines W_a formula and Young's formula
 - Don't need to know the math, but by combining both formulas, we get:
 - $W_{a\max} = 2\gamma_L$
 - Describes how much "cohesive strength" there is, AKA how much is needed for cohesive failure
- Conclusions/summary
 - Molecular contact must be achieved
 - Substrata/solid should have high surface energy
 - Adhesives/liquid should have low surface energy
 - Low contact angle
 - High spreading coefficient
 - High work of adhesion = good adhesion
 - Cohesive strength of the adhesive is the limiting factor in how well 2 surfaces adhere
 - Dry vs wet environments play a role
- Steps to achieve adhesion in dentistry
 - **Pre conditioning** – optimizes the surface characteristics of the substratum
 - **Priming** – ensures substratum compatibility with the adhesive
 - **Adhesion** – application and curing of the adhesive layer
- Possible substrata
 - Enamel
 - Dentin
 - Metals/alloys
 - Ceramics
 - Polymers
 - Composites
- Hybrid layer – resin impregnated layer

- Preconditioning for tooth structure

	Enamel	Dentin
Properties	-95~98% HA -2~5% organics + H ₂ O -Scalloped	-55% HA, 30% collagen -15% H ₂ O -Tubular
What happens when it is etched with acid?	-A layer of HA dissolves, no demineralization -Increases surface area -Creates micro-porosities (50 um) -Exposes high surface energy substratum	-Demineralization of the collagen fibers -Removal of the smear layer (if total etch is used) -5 um demineralized dentin surface -Enlarged tubules -Surface is moist, porous, and low surface energy
Etchants used	-Phosphoric acid (5, 10, 32, 34, 35, 37%) -Maleic acid (10%)	
In practice	-Rinse completely -Dry as much as possible	-Don't etch as long -Rinse completely -Keep it slightly wet so collagen fibers don't collapse

- Preconditioning for dental biomaterials

Metals /alloys	-Acid etch → only decontaminates, does not condition -Sandblasted with Al ₂ O ₃ particles -Considered to “cold work” the metal, so metal properties can change -Rocatec 3M – sandblasting and silica coating -COEJET – sandblasting material
Composites	-Sandblasting, like metals -However, material is being removed rather than dimpled like in metals -Make sure not to lose too much material
Traditional ceramics (feldspathic)	-Hydrofluoric acid 4.5~9% -Dissolves glass -Need to protect the patient
Industrial ceramics	-Acid etch → only decontaminates -Sandblasting is an option, but not recommended due to monoclinic phase transition of the zirconia

- Priming

- Goal: make the substratum compatible with methacrylate (a hydrophobic substance) because it is the key functional group in any adhesive
- Does not need to be applied on enamel because enamel already has a high surface energy from etching
- Dentin primers: HEMA, glutaraldehyde
 - Dentin is hydrophilic, methacrylate is phobic
 - HEMA is amphiphilic – allows compatibility
 - HEMA contains water to “re-fluff” collagen
- Metal primers: tin plating, silicoater
- Ceramic primers: silane
- Time must be given for primer to penetrate layers
- Keep it thin, it does not contribute to strength
- Evaporate the solvent afterwards

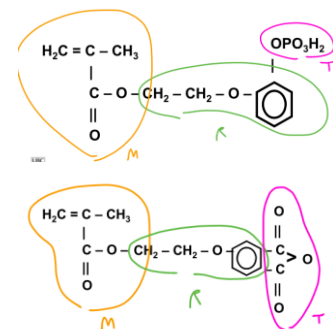
- Adhesive

- Smooths out the rough surface by filling in porosities
- Too thin = disappears into dentin tubules
- Too thick = like primer, does not contribute to strength. Has a low γ_L , so don't make it thick otherwise cohesive failure is possible
- Many types: 4-META, PMDM, Phenyl-P, PENTA, MDP, GPDM, PAMM
- All have a similar structure, where M = methacrylate, R = spacer, and T = tooth binding group (see below)

- Bonding systems

Preconditioner	Primer	Adhesive
-Called “total etch multistep” or “etch and rinse multistep” - <u>Gold standard</u> , outperforms all other systems		
Preconditioner	Primer + Adhesive	
-Called “total etch 2 step” or “etch and rinse 2 step” -Most technique sensitive, have to get right amount of H ₂ O		
Preconditioner + Primer	Adhesive	
-Called “self etching” or “etch and no rinse” -Has acidic monomer. Not acidic enough to properly etch enamel, but can cause unwanted continued etching -Does not remove the smear layer, it's incorporated		
Preconditioner + Primer + Adhesive		
-Called “self etching one step system or “all in one” -If adhesive is hydrophobic, then primer can't contain water to “re-luff” the collagen (if there was water, it would separate from the adhesive and the product would be useless) -Since no water, can't penetrate deep into dentin		

System	Steps (estimated time in seconds)	Total time (estimate)
Total-etch multistep system (or “total-etch multi-bottle” or “etch-and-rinse multi-bottle” or “smear removal multi-bottle”)	Etch (20), rinse (10), dry (5) Apply primer (5), dry (5) Apply adhesive (5), dry (5) Cure (10)	65 seconds
Total-etch 2-step system (or “total-etch, 1 bottle” or “etch-and-rinse 1 bottle” or “smear removal, 1 bottle”)	Etch (20), rinse (10), dry (5) Apply primer and adhesive (5), dry (5) Cure (10)	55 seconds
Self-etching 2-step system (or “smear dissolving, 1 bottle”)	Apply self-etching primer (20), dry (5) Apply adhesive (5), dry (5) Cure (10)	45 seconds
Self-etching 1-step system (or “smear dissolving, all-in-1”)	Apply (20), dry (5) Cure (10)	35 seconds



Dental cements

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