You just learned about the rules-of-mixtures (ROM) and modified-rule-of-mixtures (MROM). This module will focus in more detail on MROM structure factors (bonding, arrangement, defects) that are important to explain the properties. Remember that the composition structure factor for a composite includes the VOLUME percentages of the continuous (matrix) and dispersed (filler) phases.
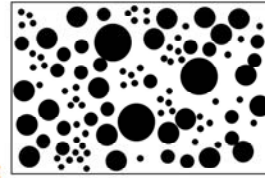
You will learn to identify the phases, interfaces, and defects in a composite. You will practice using examples of the ROM to predict real composite properties.
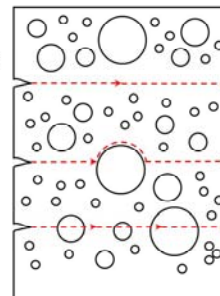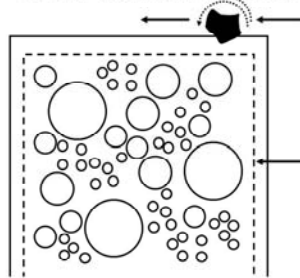
Look at the schematic of the composite to the right. **[CLICK]** The particles that are dispersed can have **[CLICK]** different shapes (here they are round), **[CLICK]** different sizes (here they differ by a factor of about 10), and **[CLICK]** different distribution patterns (where regions have more or less than the average filler). These are ARRANGEMENT FACTORS.

Now lets look at the anisotropy caused by these effects. **[CLICK]** ANISOTROPY is a new word for you. ISOTROPIC means that the properties are the same in all directions. Variations in structure cause most materials to be anisotropic. **[CLICK]** In most composites, the external surface tends to be matrix phase only at first. So, if an abrasive particle were moving across the first surface it would see matrix-only until some of the filler particles are exposed during abrasion. The smaller the region you focus on, the more will be the tendency to have different local properties. You could pick a region that was almost all filler and another that was almost all matrix. Properties vary locally.

[CLICK] One of the most important considerations for us is the path that a crack might take. It is possible that a crack could propagate through the material and never encounter a filler particle. Since the matrix is normally weak and the filler is strong, the material would behave as though it was weak. If the crack did encounter a filler particle, but the interface were weakly bonded or unbonded, the crack would simply circumvent the particle. It would have to take a longer path but the material would still fail. We would like the filler interface to be well-bonded (coherent) and force the crack through the strong filler particle. In this last case, the crack would either take much longer and require more energy to cross the filler particle – or it might actually be stopped by the filler particle.
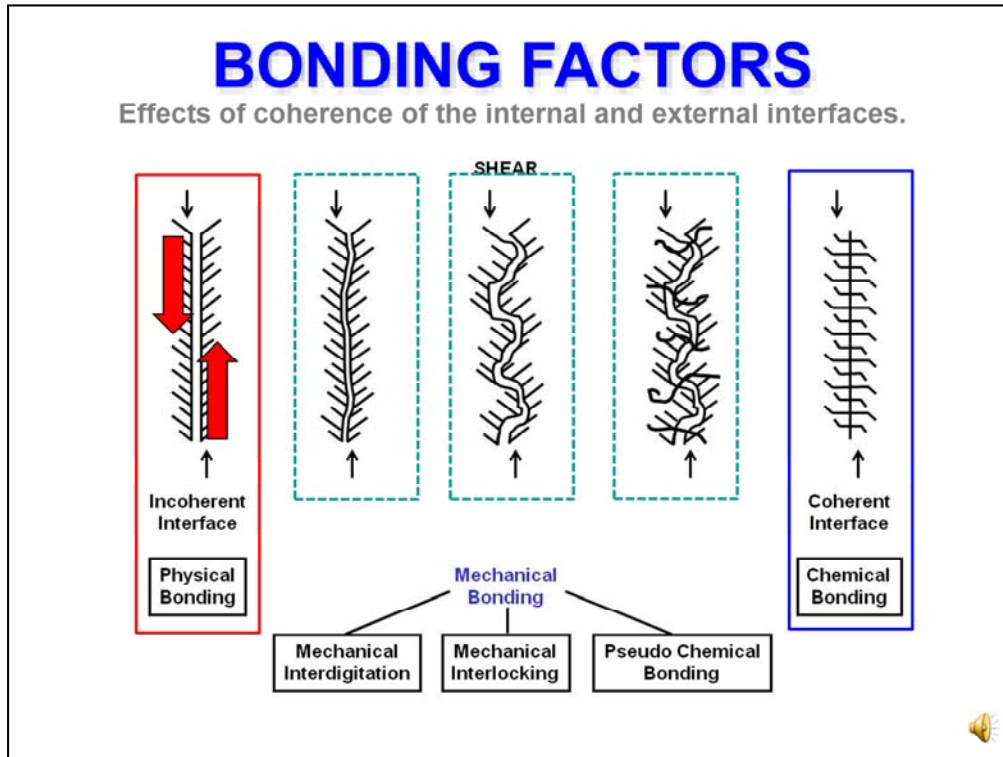
Now let's examine the full range of interfaces from the **[CLICK]** weakest (INCOHERENT, Physically bonded interface) to the **[CLICK]** strongest (COHERENT, Chemical bonded interface). Imagine that going from LEFT to RIGHT you are going from weak to strong interfaces. We will consider the situation for shear stresses **[CLICK]** acting to slide open or pull open the interface.

An incoherent interface that is flat has only weak physical bonding along the surface (like van der Waals attractions). It provides no opportunity for properties to be effectively shared from the matrix phase with the filler phase.

[CLICK] By making the interface irregular rather than smooth, it is possible to increase the resistance to sliding. Now the INTERDIGITATED surfaces have to be pulled slightly apart to allow sliding.

[CLICK] By creating surfaces that have undercuts and can become INTERLOCKED, we create a much strong interface. To pull apart the interface you need to break off pieces of material. Even though there is no chemical bonding from one side to the other, chemical bonds must be broken to destroy the interlocked interface. This is the major type of bonding used in situations in dentistry.

[CLICK] A molecular version of the same thing can occur when polymer molecules become entangled and interlocked across an interface. Generally, monomer in the matrix soaks into the edges of polymer or dispersed composite particles and during matrix polymerization these new and old molecules become interlocked. We call this PSEUDO-CHEMICAL bonding -- because it is strong and approximates true chemical bonding.

True CHEMICAL bonding would be ideal to bond the surfaces. However, it is rare and often does not form a very high density of bonds -- limiting its effectiveness.

KNOW THESE TERMS. These will be used often in dentistry to describe both internal and external interfaces.
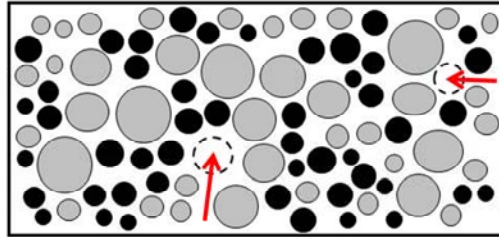
Examine the composite in the figure. Do you see the pores? **[CLICK]** In this case the pores represent about 4% of the volume and would cause about 15% reduction in ultimate strength. Internal pores and external scratches are sites that stress is concentrated during tension – leading to crack formation.

[CLICK] Now let's follow this problematic event for a single pore.

[CLICK] When tensile stress is applied to a pore, **[CLICK]** cracks form that are perpendicular to the stress. This is called CRACK INITIATION.

[CLICK] Continued stress from mechanical fatigue, thermal cycling, or hydration-dehydration stresses will PROPAGATE the crack. If the crack runs into a reinforcing filler phase and the interface is strong, the crack might be driven into the particle and stopped. Otherwise, it will continue to grow around the particle.

[CLICK] Ultimately, cracks intersect the external surfaces or become interconnected within the material and create a new external interface across the material which we define as failure. This is crack TERMINATION. The material is breaking into pieces.

IDENTIFICATION OF PHASES
Recognition of continuous and dispersed phases and defects.
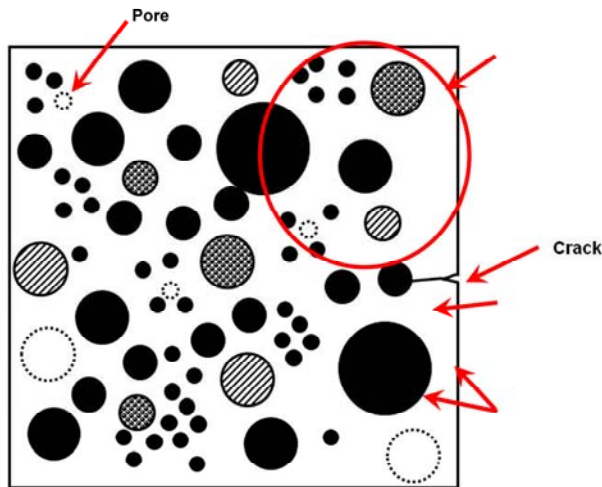
$$X_c = (X_1)(V_1)(I_1) + (X_2)(V_2)(I_2) + (X_3)(V_3)(I_3) + (X_4)(V_4)(I_4) + (\sigma)(10^{-nv})$$

Continuous   Dispersed1   Dispersed2   Dispersed3   Defects

Study the complex composite in the figure for a few moments -- and see if you can recognize all the structures that are involved. The circles with the dotted lines represent pores. The slit along the right hand side is meant to represent a crack. Circles with the same internal texture are the same dispersed phase. [PAUSE for 5 seconds] Now let's go through the identification steps. The normal order is to ID the continuous phase, dispersed phase, and interfaces – in that order.

Where is the continuous phase? **[CLICK]** Is there more than one continuous phases? **[CLICK]** NO - - There is only one. That is typical.

How many dispersed phases are there? **[CLICK]** There are both solid dispersed phases and pores. **[CLICK]**

How many internal and external interfaces are there? **[CLICK]** There is 1 external interface and 5 internal interfaces **[CLICK]** between the 3 dispersed types of particles and matrix – and between the surface on the pore and surfaces on the crack.

Can you write the MROM expression for this composite? **[CLICK]** You are not expected to generate the expression, but you should know what the parts of the expression represent. The property of the composite (Xc) such as strength is equal to the property of each phase times its volume percent times its interfacial correction factor and the adjustment for the pore (and crack) effects with the exponential at the end.

COMPOSITE PREDICTIONS

Using the ROM and MROM for properties.

ROM EXPRESSION:

Physical Properties: (most follow rules)
Density (ρ) .... $\rho_c = (\rho_1)(V_1)+(\rho_2)(V_2)$
Thermal Properties ....
    Melting Point (exception)   **XXXX**
    Heat Capacity ......
    Coefficient of Thermal Expansion ......
Electrical ....
Optical ....
Surface ....
Chemical Properties: (all follow rules)
Solubility ....
Absorption ....
....
Mechanical Properties: (all follow rules)
Modulus .... $E_c = (E_1)(V_1)+(E_2)(V_2)$
Elastic Limit ....
Compressive Strength ....
.....
Biological Properties: (most follow rules)
Biocompatibility ....
Toxicity ....

All properties -- except for a couple of exceptions -- can be predicted using the ROM as a first-order approximation. As more the details of the interfaces and defects are known for the MROM expression, the more closely the approximation will match the actual properties.

The major exception to this the ROM involves temperature properties -- such as melting point. The melting point is NOT an average of the components. Since the materials are only physically mixed, the lowest melting phase melts first -- followed by the others – and affected by any chemical reactions or solutions are occurring at the same time.

ROM EXAMPLE

Application of rules to typical dental composite restorative material.

BIS-GMA, TEGDMA, HQ, CQ
25 w/o (50 v/o)
ρ = density = 1.2 gms/cm^3
α = LCTE = 44 ppm/°C
S = solubility in water = 4%
ΔV = polymerization shrinkage = 6%
CS = compressive strength = 150 MPa
E = modulus = 3,500 MPa

Li-Al-Silicate Glass Filler
75 w/o (50 v/o)
ρ = 3.0 gms/cm^3
α = 10 ppm/°C
S = 0%
ΔV = 0%
CS = 1500 MPa
E = 35,000 MPa

Physical Property Calculations:
Density: $\rho_c = \rho_1 V_1 + \rho_2 V_2 = (1.2)(50\%) + (3.0)(0.50\%) = $ 2.1 gms/cm^3
LCTE: $\alpha_c = \alpha_1 V_1 + \alpha_2 V_2 = (44)(50\%) + (10)(50\%) = $ 27 ppm/°C

Chemical Property Calculations:
Solubility: $S_c = S_1 V_1 + S_2 V_2 = (4\%)(50\%) + (0\%)(50\%) = $ 2%
Shrinkage: $\Delta V_c = \Delta V_1 V_1 + \Delta V_2 V_2 = (6\%)(50\%) + (0\%)(50\%) = $ 3%

Mechanical Property Calculations:
Comp Str: $CS_c = CS_1 V_1 + CS_2 V_2 = (150)(50\%) + (1500)(50\%) = $ 825 MPa*
Modulus: $E_c = E_1 V_1 + E_2 V_2 = (3500)(50\%) + (35,000)(50\%) = $ 19,250 MPa*

Now let's take a look at an example of a real composite. This is a very simple example – made from 2 monomers (BIS-GMA, TEGDMA), an inhibitor (HQ), and an initiator (CQ) – to which Li-Al-Silicate Glass reinforcing particles have been added. Shown in the Table are the properties of the individual phases – density, LCTE, solubility, polymerization shrinkage, compressive strength, and modulus.

[CLICK] Now let's try to calculate 6 different properties using the ROM approach. Remember – use the volume percent for the calculations.

>What is the composite's density? **[CLICK]** [PAUSE for 3 seconds.] This is very close to the real value.

>What is the composite's LCTE? **[CLICK]** [PAUSE for 3 seconds.] This is very close to the real value.

>What is the composite's solubility? **[CLICK]** [PAUSE for 3 seconds.] This is very close to the real value.

>What is the composite's polymerization shrinkage? **[CLICK]** [PAUSE for 3 seconds.] This is very close to the real value.

>What is the composite's compressive strength? **[CLICK]** [PAUSE for 3 seconds.] This is way too high. It does not include the impact of defects which will make the value more like 200 MPa.

>What is the composite's modulus? **[CLICK]** This is slightly high.

QUICK REVIEW
Review of composite structure, properties, and calculations.

- **What 3 major structure FACTORS are considered by the MROM?**
  ARRANGEMENT, BONDING, and DEFECTS.

- **What INTERFACIAL BONDING type is most common in dentistry?**
  MECHANICAL INTERLOCKING

- **What are the steps in ANALYZING composite microstructure?**
  ID CONTINUOUS PHASES, DISPERSED PHASES, and DEFECTS.

- **How do PORES weaken a composite structure?**
  CRACK FORMATION.

- **Which property is NOT predicted by the ROM?**
  MELTING TEMPERATURE

Here is a quick review of the concepts from this module.

[CLICK] (1) What 3 major structure FACTORS are considered by the MROM?
[CLICK]

[CLICK] (2) What INTERFACIAL BONDING type is most common in dentistry?
[CLICK]

[CLICK] (3) What are the steps in ANALYZING composite microstructure?
[CLICK]

[CLICK] (4) How do PORES weaken a composite structure?
[CLICK]

[CLICK] (5) What property is NOT predicted by the ROM?
[CLICK]

THANK YOU.