Topics

- biomaterials versus biological materials
- materials properties
- types of materials
- body response to implanted materials and blood clotting

Biomaterials versus Biological Materials

First, we need to make a distinction between *biomaterials* and *biological materials*. A biomaterial is an engineered material designed to replace part of a living system or to function in intimate contact with tissues or physiological fluids. A biological material is a material produced by a living system, such as bone or cartilage. We will focus on biomaterials, although biomedical engineers do study the chemical and mechanical properties of biological materials as well.

Ideally, a biomaterial should be inert, in the sense that it triggers no adverse reactions when in contact with tissues. We do not consider materials that contact the skin, such as hearing aids or artificial limbs, as biomaterials, since the skin acts as a protective barrier against the external world. So, even though hearing aids and artificial limbs fall within the domain of biomedical engineering, we will not consider such systems here either. This is because the unique challenge that underlies the design of biomaterials is to make a material that successfully carries out its function (e.g., an artificial heart valve) without causing an adverse reaction (e.g. blood clotting).

When employing biomaterials, we need to be concerned not only with the effect of the material on the body as noted above, but also with the effect that the body will have on the material (e.g. degradation or abrasion).

A new area of relevance to biomaterials is tissue engineering. Biomaterials are used as scaffolds to control the growth of tissues starting from cell cultures.

Problem Area	Example
Replacement of diseased or damaged part	Artifical hip joint, kidney dialysis machine
Assist in healing	Sutures, bone plates and screws
Improve function	Cardiac pacemaker, contact lens
Correct functional abnormality	Spinal rod
Cosmetic alteration	Mammoplasty, chin augmentation
Aid to diagnosis	Probes and catheters
Aid to treatment	Catheters, drains

Examples of Biomaterial Uses (Park and Lakes, *Biomaterials, an Introduction* 2nd Edition)

Materials for Use in the Body

Material	Advantages	Disadvantages	Examples
Polymers	Resilient	Not strong	Sutures, blood
Nylon	Easy to fabricate	Deform with time	vessels, hip socket,
Silicone		May degrade	ear, nose, other soft
Teflon			tissues
Dacron			
Polylactides/Glycolides	biodegradable	Variability	Sustained drug release device
Metals	Strong	May corrode	Joint replacement,
Titanium	Ductile	Dense	bone plates and
Stainless steel			screws, dental root
Co-Cr alloys			implant
Gold			
Coromias	Often biogemnetible	Drittla	Dontal hin goaleat
Aluminum oxide	Strong in	Difficult to fabricate	Dental, hip socket
Carbon	compression	Not resilient	
Hydroxyapatite	compression	Not resilient	
Composites	Strong	Difficult to make	Joint implants, heart
Carbon-carbon			valves

Performance of Biomaterials

The successful application of a biomaterial in the body depends on many factors, including the material properties, the mechanical design of the object, the biocompatibility of the material, and other factors not always under the control of the engineer, such as the technique of the surgeon.

If we assign a value *f* for the probability that a device will fail, then we can refer to the reliability, *r*, as

r = 1 - f

It is usually the case that there are multiple possible failure modes. Then, the total reliability r_t is the product of the individual reliabilities $r_i = (1 - f_i)$

$$r_t = \prod_i r_i$$

This captures the important idea that if all but one failure mode is controlled very well, the material's reliability is still no better than that associated with the uncontrolled failure mode. This is analogous to the cliché about a chain being no stronger than its weakest link.

We have referred to biocompatible as an important issue. This is the one issue not faced by conventional materials engineers. Biocompatibility refers to the acceptance of a material by the living system. It is easier to define a biocompatible material by what it does *not* do.

A biocompatible material does not Irritate or inflame surrounding tissues Promote infection Incite allergic reactions Cause cancer Cause scarring or restenosis (vessel clogging by ingrowing cells) Cause blood clotting (thrombosis)

The likely failure modes depend very much on the application. Fatigue refers to the weakening of a material after excessive strain. This is important for a heart valve, but not so important for a contact lens. Blood clotting is important for a vascular implant, but not so important for a dental implant.

Failure modes likely depend on the passage of time after the material is implanted. For example, in total hip replacement, infection is most likely immediately after surgery. Loosening and fracture become more important as time passes as sketched below (not to scale. After Park and Lakes).



Example

Consider the probabilities of failure of a knee replacement in the first year are 5% for infection, 3% for wear, 2% for loosening, 1% for surgical complications, and 4% for fracture. Calculate the reliability for the first year.

$$r_t = \sum_i r_i$$

$$r_t = (1 - 0.05)(1 - 0.03)(1 - 0.02)(1 - 0.01) = 0.89$$

So, 89% of replacements will be reliable for one year (11% will fail.)

If there is a 10% chance that a patient complains of excessive pain, the reliability is now

$$r_t = (1 - 0.05)(1 - 0.03)(1 - 0.02)(1 - 0.01)(1 - 0.10) = 0.80$$

Now there is a 20% chance of failure within the first year. Pain may result from loosening, or it may not have a readily identifiable cause. This illustrates another challenge for biomaterials design – individual patient variability. We are not all alike either in terms of our immune system, mechanical properties, or pain tolerance.

Materials Properties

Stress, Strain and Moduli

Deformations are caused by stresses (applied forces)... http://www.polial.polito.it/cdc/Mercurio/Polymer/mercurio_mechpro/05MP_Concepts.htm

Deformations can be produced by forces which cause a body to be stretched, compressed, twisted or sheared. These forces can also be combined to produce more complex types of deformation (for example, flexure).



Extension by stretching in one direction is the simplest type of deformation:



Rectangular specimens subjected to different loads in tensile mode

To take into account the influence of the cross-sectional area on the response of the material we define stress as the force exerted on a body per unit cross sectional area. By stretching a body using a force (in the above case the force is weight), the tensile stress (in the direction of elongation), becomes

 $Stress = \frac{Force}{Cross - sectional area}$

If the same weights were placed on the rectangular specimens to cause a contraction in the longitudinal direction, the resulting stress would be called compressive stress.

Apart from tensile and compressive stress, the other common type of stress encountered in mechanics is shear stress. This relates to the force which distorts rather than extends a body.



Cylindrical specimen subjected to simple shear, e.g. during cutting.

In the above example where a solid section is sheared,

 $Shear stress = \frac{Shearing force}{Cross - sectional area}$

Deformations are quantified in terms of strains... http://www.polial.polito.it/cdc/Mercurio/Polymer/mercurio_mechpro/05MP_Concepts.htm

Strain is the change in one dimension produced as a result of an applied force and it is expressed as the ratio of the amount of deformation to the sample's original dimension. In the case of tension,

 $Strain = rac{Extension}{Original \ length}$

Strain is often expressed as % – i.e. the strain multiplied by 100.



Stretching a circular bar (extension exaggerated)

Assuming the force applied causes the original length of 0.5 m (metres) to extent to a new length of 0.9 m, then the strain experienced by the body along its length becomes

$$\frac{1.01 - 1.0}{1.0} \times 100 = 1\%$$

If the change in dimension occurs in the opposite direction, the resulting strain is compressive.

If the deformation manifests itself as a distortion of geometry, then strain is defined as shear strain:



Twisting a circular bar

In both cases the angle of distortion is θ . The shear strain is defined as the tangent of the angle θ , i.e. tan θ .

Stress-Strain relationships for solids...

http://www.polial.polito.it/cdc/Mercurio/Polymer/mercurio_mechpro/05MP_Concepts.htm

Materials deform *elastically* or *inelastically*. During elastic deformation, the stress in a body is directly related to the strain, and vice-versa. Therefore, when the force is removed (i.e. when stress becomes zero) then strain returns to zero. The plot of stress against strain produces a straight line; the stress can be increased or decreased, and stress and strain are always proportional to each other.



Linear elastic stress-strain relationship

This behavior is like that of a spring...

If the stress is a compressive or tensile stress, the slope of the linear elastic portion of the stressstrain curve is the Modulus of Elasticity (or Young's Modulus).

If the stress is a shear stress, the slope of elastic portion of the stress-strain curve is the Modulus of Rigidity (or Shear Modulus)

Consider a tensile stress, denoted by the Greek letter $\boldsymbol{\sigma}$ (sigma), as the force (F) normalized by the cross-sectional area (A) of the material:

$\sigma = F/A$

Now attach an extensioneter to the sample. The extension extension the change in length of the sample as it is being pulled.



Denote strain by the Greek letter $\boldsymbol{\mathcal{E}}$ (epsilon), as the change in length of the fiber normalized by the initial length.

$$\boldsymbol{\varepsilon} = (\mathbf{l}_1 - \mathbf{l}_0) / \mathbf{l}_0$$

Now, plot stress versus strain. The slope of this line will give you the elastic modulus ${\bf E}$ of the material.

$\sigma = E \varepsilon$

This technique applies for small forces which do not irreversibly stretch the material. The material is in the **elastic regime**.

Note that E [=] σ [=] pressure since ε is dimensionless.

The shear modulus, G, may similarly be defined by

$\sigma_s = F_s / A = Gtan\theta$

Note also that G [=] σ_s [=] pressure since tan θ is dimensionless.

- *Stiff* materials have a high modulus. This means that the deformation (strain) resulting from the applied force (stress) is low.
- *Flexible* materials have a low modulus. They undergo large deformations with relatively low applied forces.

Young's Modulus for Typical Materials http://www.mse.cornell.edu/courses/engri111/modulus.htm

Material	Modulus (GPa)
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Ceramics, glasses, and semiconductors:	
Diamond (C)	1000
Tungsten Carbide (WC)	450 -650
Silicon Carbide (SiC)	450
Aluminum Oxide (Al_2O_3)	390
Berylium Oxide (BeO)	380
Magnesium Oxide (MgO)	250
Zirconium Oxide (ZrO)	160 - 241
Mullite $(Al_6Si_2O_{13})$	145
Silicon (Si)	107
Silica glass (SiO ₂)	94
Soda-lime glass (Na ₂ O - SiO ₂)	69
Metals:	
Tungsten (W)	406
Chromium (Cr)	289
Berylium (Be)	200 - 289
Nickel (Ni)	214
Iron (Fe)	196
Low Alloy Steels	200 - 207
Stainless Steels	190 - 200
Cast Irons	170 - 190
Copper (Cu)	124
Titanium (Ti)	116
Brasses and Bronzes	103 - 124
Aluminum (Al)	69
Polymers:	
Polyimides	3 - 5
Polyesters	1 - 5
Nylon	2 - 4
Polystryene	3 - 3.4
Polyethylene	0.2 -0.7
Rubbers	0.01-0.1

Biological Tissues (from Enderle, Blanchard, Bronzino)	
Hydroxyapatite (HA) mineral	114-130
Bone (cortical)	18-20
Collagen	1.2
Elastin	1

Poisson Ratio, Bulk Modulus and relationships among Young's Modulus and Shear Modulus

Poisson's Ratio, $v = -\varepsilon_{\parallel}/\varepsilon_{\perp}$; accounts for strains in orthogonal (perpendicular) directions

Most common materials have $v \sim 0.33$ Rubbery materials have $v \sim 0.5$

Bulk Modulus, $K = -V(\partial P/\partial V) = \rho(\partial P/\partial \rho)$; relation between 3D stress (P) and 3D strain (ΔV)

For isotropic materials in the linear elastic regime,

K = E/[3(1-2v)] = 2G(1+v)/[3(1-2v)]

For ductile materials, increasing the stress above a certain limit will give rise to inelastic deformations, known as yielding. In other words, when the stress is removed, the strain does not return to zero (and the original shape is not fully restored) since some deformation has permanently set in. The stress level at which this occurs is referred to as the yield stress or yield point.



The applied force takes the material beyond the linear elastic region. Continued loading causes permanent deformation, and ultimately, failure of the material. Concepts of ultimate tensile strength and toughness...



The amount of permanent deformation is evident after the force applied is removed.

Example. Bone properties (after Enderle, Blanchard, Bronzino)

A 7 mm cube of bone is compressed in increments of 0.05 mm. The force required for each incremental deformation was measured and is tabulated below. Plot stress-strain behavior and determine E and UTS for the bone.

Force (N)	Strain (%)	Stress (MPa)
0		
67.9		
267.6		
640.2		
990.2		
1265.1		
1259.9		
1190.9		
1080.8		
968.6		
814.2		
	Force (N) 0 67.9 267.6 640.2 990.2 1265.1 1259.9 1190.9 1080.8 968.6 814.2	Force Strain (N) (%) 0 67.9 267.6 640.2 990.2 1265.1 1259.9 1190.9 1080.8 968.6 814.2

Crystalline versus Rubbery Elasticity Behavior after <u>http://www.ece.mcmaster.ca/~ibruce/courses/EE3BA3_lecture4.pdf</u>

Crystalline Materials

Rubbery Materials



Elastic behavior of biological materials

Collagen

- key structural component in vertebrates, found in bone, skin, ligaments, tendons
- protein with some cross-links between chains
- fairly crystalline
- $E \sim 1$ GPa

Elastin

- A protein, less abundant than collagen
- Mixed with collagen in skin, vascular walls, lung tissue and other places
- Rubbery elasticity
- $E \sim 1 \text{ MPa}$
- Some cross-linking, but different from that of collagen

Keratin

- Protein found in har (horns, hooves, beaks, feathers)
- Similar to collagen but with more cross-links, making it much stiffer

Apatite (hydroxyapatite)

- Mineral in bone and calcified cartilage
- A hydrated calcium phosphate
- E ~ 100 GPa
- Density~ $3,000 \text{ kg/m}^3$

Bone

- Roughly 43% Hydroxyapatite, 36% collagen, 14% water
- Cortical or compact bone is ~90% solid
 - \circ E ~ 20 GPa
 - $\circ \quad UTS \sim 200 \text{ MPa}$
 - Failure strain 1.5%
- Trabecular or spongy bone is ~80-80% cavities filled with marrow
- Synthesis and repair
 - Synthesized by osteoblasts
 - Resorbed by osteoclasts
 - Continuous repair (remodeling)

Cartilage (articular – joint surfaces)

- Roughly 3% proteoglycan, 15% collagen, 75% water
- E ~ 30 GPa
- Synthesized by chondrocytes

Tendons

- Roughly 1% proteoglycan, 3% elastin, 20% collagen, 60-70% water
- $E \sim 1$ GPa
- Synthesized by tenocytes

Ligaments

- Roughly 1% proteoglycan, 3% elastin, 20% collagen, 60-70% water
- E ~ 400 MPa

Arteries

- Roughly 15-20% elastin, 10% collagen, 60-70% water
- $E \sim 0.3$ MPa, rubbery

Skin

- Roughly 3% elastin, 10% collagen, 60% water
- Random orientation of collagen fibers gives very rubbery elasticity

Dentin

- Roughly 80% hydroxyapatite, 10% collagen; enamel 85% hydroxyapatite
- Very crystalline elasticity



Fig. 8.6 Typical stress-strain behaviors of tendon (T), ligament (L), cartilage (C), aorta (A), skin (S), and mitral valve tissue (M) are compared. The X's at the ends of the curves indicate tailure; tendon tailure is beyond the boundary of the graph.

Example: materials applications

Why would the following NOT be a good idea?

- a. metal tube used as an endovascular graft to repair an aneurysm
- b. silicone rubber used to repair as ligament or tendon
- c. silicone rubber pin used to fix a bone fracture
- d. a ceramic used as a skin graft

Surface Roughness

Surface texture is the combination of fairly short wavelength deviations of a surface from the nominal surface. Texture includes roughness, waviness, and lay, that is, all of the deviations that are shorter in wavelength than form error deviations.



Roughness. Roughness includes the finest (shortest wavelength) irregularities of a surface. Roughness generally results from a particular production process or material condition.

Waviness. Waviness includes the more widely spaced (longer wavelength) deviations of a surface from its nominal shape. Waviness errors are intermediate in wavelength between roughness and form error. Note that the distinction between waviness and form error is not always made in practice, and it is not always clear how to make it. New standards are emerging that define this distinction more rigorously as developed in later sections.

Lay. Lay refers to the predominant direction of the surface texture. Ordinarily lay is determined by the particular production method and geometry used.

Turning, milling, drilling, grinding, and other cutting tool machining processes usually produce a surface that has lay: striations or peaks and valleys in the direction that the tool was drawn across the surface. The shape of the lay can take one of several forms. Other processes produce surfaces with no characteristic direction: sand casting, peening, and grit blasting. Sometimes these surfaces are said to have a non-directional, particulate, or protuberant lay.

Profile

A profile is, mathematically, the line of intersection of a surface with a sectioning plane which is (ordinarily) perpendicular to the surface. It is a two-dimensional slice of the three-dimensional surface. Almost always profiles are measured across the surface in a direction perpendicular to the lay of the surface.



A profile is a two-dimensional picture of a three dimensional surface that may be thought of as the result of a sectioning place cutting the surface. Profiles are ordinarily taken perpendicular to the lay.



An important concept in surface finish is the breaking of a surface profile into different components by wavelength. There is a hierarchy of components, as shown.

SURFACE ROUGNESSES PRODUCED BY COMMON PRODUCTION PROCESSES





Higher or lower values may be obtained under special conditions

http://icrank.com/cgi-bin/pageman/pageout.cgi?path=/data/surface_finish.htm&t=2

Measuring surface roughness

Profilometers

www.microphotonics.com

The TR100 Portable Surface Roughness Tester is a pocket-size economically priced instrument for mesuring surface texture. All results are traceable to standards. The instrument can be used in any measuring positions even in the vertical.

The large LCD display can switch the data from Ra values to Rz values at the touch of a botton. A special CAL botton allows a quick external calibration which increase the reliability of the technique. A beep signal informs the user when a measurement is finished.

The TR100 can operate on various surfaces including outer cylinder, outer cones, grooves and recesses greater than 80x30mm. The instruments is ideal for a wide range of applications.

The piezo-electric operated diamond stylus

insures very reliable measurementa that are conformed to ISO Class 3. Ra is computed conform to ISO and Rz is conform to DIN standard.



Atomic Force Microscopes – elaborate, nano-sized profilometers (can be used in many other modes as well

www.spmtips.com



Fig.1 SEM image of silicon cantilever of the 17^{th} series.



Fig.2 Silicon chip of the 17th series has 1 rectangular cantilever.

www.spmtips.com



Fig.1 SEM image of uncoated silicon SPM tip



Fig.2 SEM image of uncoated tip end

Case study: RMS roughness on silicon wafer. In this study a HI'RES probe was used to measure roughness of a silicon wafer. The RMS roughness obtained when scanning by HI'RES probe is twice as large as the result obtained by conventional silicon etched probe. Images are made by Dimension 5000 AFM.



AFM images of silicon wafer surface made by HI'RES probe (left) and conventional silicon etched probe (right). Images courtesy of Dr. S. Magonov (Veeco Instruments).

http://www.pacificnanotech.com/nano-roughness single.html

The atomic force microscope is ideal for quantitatively measuring the nanometer scale surface roughness and for visualizing the surface nano-texture on many types of material surfaces. Advantages of the AFM for such applications are derived from the fact that the AFM is nondestructive and it has a very high three dimensional spatial resolution.



X: 1.79 um Y: 1.79 um Z: 29.16 nm

This contact mode AFM image shows the grains at the surface of a metal bonding pad. The image size is 1.79×1.79 microns and the maximum height of a feature in the image is 29.2 nanometers.

Measuring the surface texture of samples with horizontal length scale of less than 10 microns and a vertical length scale of 100 nanometers is critical for many areas of science and technology. For example, surface texture can alter the optical properties of materials, control adhesive properties of polymers, affect the yield of processed silicon wafers, and control the density of stored magnetic materials.

Line Roughness:

After acquiring an AFM image it is possible to measure the 1-D surface roughness on a line in the horizontal or vertical direction in the image. After identifying the line for the measurement, a computer calculates all of the relevant parameters. Below is an illustration of the 1-D surface roughness measured on a polymer film.



Figure 3: Line surface roughness of a polymer film showing a value for Ra of about .71 nanometers. There are larger features on the image, as large as 18.39 nanometers, but they are not included in the calculations of these line roughness parameters.

Area Roughness:

Optimal characterization of surface texture is often expressed with area roughness calculations that are made on the entire surface. Surface roughness calculations are similar to line roughness calculations but they include data in the x and y plane of the surface.



Figure 4: This is a 1 μm X 1 μm image of a bare silicon wafer image with the Nano-RTM AFM system. The area roughness values shown are for the entire image.

Surface/Area Roughness Calculations

Surface and area roughness parameters are meant to help quantify the surface texture of a material. Initially such parameters were used for characterizing machined surfaces; now they are used for characterizing all types of high technology and nanomaterials.

Note: An excellent resource for the definitions of surface roughness parameters can be found on the web at the URL: <u>www.predev.com/smg/parameters.htm</u>

Sources of Error in Area/Surface Roughness Measurements

There are two primary potential sources of error in using an AFM for measuring surface textures. The first is the probe geometry and the second is the length scale of the measurement.

Probe Geometry:

The surface texture that is measured with an AFM depends on the geometry of the probe tip. If the probe tip is larger than the features causing the surface texture, then the surface roughness measurements will appear smaller than they should be. This possible source of error is avoided by using the sharpest possible probe.

Length Scale:

Within the image used for the surface/area roughness calculation there must be an adequate sampling of the features giving rise to the surface texture. As a result, it is possible to get a different surface texture when the scan size is changed. This problem is avoided by using the same size scan range when surface roughness on several samples is being compared.

From www.predev.com/smg/parameters.htm

Ra - Average Roughness

Also known as Arithmetic Average (AA), Center Line Average (CLA), Arithmetical Mean Deviation of the Profile.

The average roughness is the area between the roughness profile and its mean line, or the integral of the absolute value of the roughness profile height over the evaluation length:

$$R_a = \frac{1}{L} \int_0^L |r(x)| \mathrm{d} x$$

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When evaluated from digital data, the integral is normally approximated by a trapezoidal rule:

$$R_a = \frac{1}{N} \sum_{n=1}^{N} \left| r_n \right|$$

Graphically, the average roughness is the area (shown below) between the roughness profile and its center line divided by the evaluation length (normally five sample lengths with each sample length equal to one cutoff):



The average roughness, Ra, is an integral of the absolute value of the roughness profile. It is the shaded area divided by the evaluation length, L. Ra is the most commonly used roughness parameter.

The average roughness is by far the most commonly used parameter in surface finish measurement. The earliest analog roughness measuring instruments measured only Ra by drawing a stylus continuously back and forth over a surface and integrating (finding the average) electronically. It is fairly easy to take the absolute value of a signal and to integrate a signal using only analog electronics. That is the main reason Ra has such a long history

Ra does not tell the whole story about a surface. For example, here are three surfaces that all have the same Ra, but you need no more than your eyes to know that they are quite different surfaces. In some applications they will perform very differently as well.



These three surfaces all have the same Ra, even though the eye immediately distinguishes their different general shapes.

These three surfaces differ in the shape of the profile - the first has sharp peaks, the second deep valleys, and the third has neither. Even if two profiles have similar shapes, they may have a different spacing between features. The following three surfaces also all have the same Ra.



If we want to distinguish between surfaces that differ in shape or spacing, we need to calculate other parameters for a surface that measure peaks and valleys and profile shape and spacing. The more complicated the shape of the surface we want and the

more critical the function of the surface, the more sophisticated we need to be in measuring parameters beyond Ra.

Rq (σ_s in MMD text) - Root-Mean-Square Roughness

The root-mean-square (rms) average roughness of a surface is calculated from another integral of the roughness profile:

$$R_q = \sqrt{\frac{1}{L}\int_0^L r^2(x) \mathrm{d}x}$$

The digital equivalent normally used is:

$$R_q = \sqrt{\frac{1}{N} \sum_{n=1}^{N} r_n^2}$$

For a pure sine wave of any wavelength and amplitude Rq is proportional to Ra; it's about 1.11 times larger. Older instruments made use of this approximation by calculating Rq with analog electronics (which is easier than calculating with analog electronics) and then multiplying by 1.11 to report Rq. However, real profiles are not simple sine waves, and the approximation often fails miserably. Modern instruments either digitize the profile or do not report Rq. There is never any reason to make the approximation that is proportional to Ra.

Rq has now been almost completely superseded by Ra in metal machining specifications. Rq still has value in optical applications where it is more directly related to the optical quality of a surface.

Rt, Rp, and Rv

The peak roughness Rp is the height of the highest peak in the roughness profile over the evaluation length (p1 below). Similarly, Rv is the depth of the deepest valley in the roughness profile over the evaluation length (v1). The total roughness, Rt, is the sum of these two, or the vertical distance from the deepest valley to the highest peak.



$$R_{v} = \left|\min\left[r(x)\right], \quad 0 < x < L$$

$$R_p = |\max[r(x)], \quad 0 < x < L$$

$$R_{r} = R_{p} + R_{v}$$

These three extreme parameters will succeed in finding unusual conditions: a sharp spike or burr on the surface that would be detrimental to a seal for example, or a crack or scratch that might be indicative of poor material or poor processing.

Rtm, Rpm and Rvm

These three parameters are mean parameters, meaning they are averages of the sample lengths. For example, define the maximum height for the i-th sample length as Rpi. Then Rpm is:

$$R_{pm} = \frac{1}{M} \sum_{i=1}^{M} R_{pi}$$

Similarly,

$$R_{\nu m} = \frac{1}{M} \sum_{i=1}^{M} R_{\nu i}$$

and

$$R_{rm} = \frac{1}{M} \sum_{i=1}^{M} R_{n} = R_{pm} + R_{vm}$$

where Rvi is the depth of the deepest valley in the i-th sample length and Rti is the sum of Rvi and Rpi:

$$R_{vi} = \left|\min[r(x)]\right| \quad il < x < (i+1)l$$
$$R_{vi} = \left|\max[r(x)]\right| \quad il < x < (i+1)l$$
$$R_{ii} = R_{pi} + R_{vi}$$

These three parameters have some of the same advantages as Rt, Rp, and Rv for finding extremes in the roughness, but they are not so sensitive to single unusual features.

Rz(DIN)

Rz(DIN), i.e. Rz according to the German DIN standard, is just another name for Rtm in the American nomenclature. (over five cutoffs)

$$R_{z}[\text{DIN}] = R_{tm}$$

Rz(ISO) = Rt



There are also roughness spacing parameters, hybrid parameters and statistical representations of surfaces....

Note, as the roughness increases, so does the surface area.

Lo - Actual Profile Length

One way to describe how a real profile differs from a flat line is to determine how long the real profile is compared to the horizontal evaluation length. Imagine the profile as a loose string that can be stretched out to its full length.

The 2-D length of a profile comes from the following equation:

$$L_o = \int_0^L \sqrt{1 + \left(\frac{\mathrm{d} r(x)}{\mathrm{d} x}\right)^2} \,\mathrm{d} x$$

For a digital evaluation, Lo depends on the spacing of the points we choose to approximate dr/dx:

$$L_{o} = \sum_{n=1}^{N} \sqrt{\left(\frac{L}{N}\right)^{2} + \left(r_{n+1} - r_{n}\right)^{2}}$$

Lr - Profile Length Ratio

The profile length ratio, Lr, is the profile length normalized by the evaluation length:

$$L_{r} = \frac{L_{o}}{L}$$

The profile length ratio is a more useful measure of surface shape than Lo since it does not depend on the measurement length.

The larger the value of L_r , the sharper or crisper the surface profile appears and the larger the true surface area of the surface is. In some applications, particularly in coating, where good adhesion is needed, it may be desirable to have a large value of L_r , i.e. a large contact surface area.

If the Euclidean length is L and actual length is Lo, the surface, the Euclidean surface area will be $A = L^2$ and the actual surface area will be $Ao = Lo^2$. So, the fractional increase in surface area over the Euclidean area due to roughness is given by $Ao/A = Lr^2$

Surface Wetting and Contact Angle

web.mit.edu/agrawala/www/NIRT/ca.html

Wetting is the term used to describe all phenomena which involve contacts between three phases, of which at least two are fluid. At that line of contact, three interfaces meet, each with its own interfacial tension (or interfacial energy/ unit energy).

One of the important parameters which is used to characterize the extent of wetting is the **Contact Angle**. It is defined as the angle formed at the interface between the liquid and the substrate when we place a liquid droplet on a specimen surface. By definition, a fluid which 'beads up' on a surface droplet is non-wetting and a contact angle higher than 90 degrees is displayed. When the droplet 'wets out' across the surface, wetting is obtained and the contact angle is less than 90 degrees.

The Contact Angle is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect as shown below



It can be seen from this figure that low values of contact angle indicate that the liquid spreads well, while high values indicate less complete wetting. If the angle is less than 90 degrees the liquid is said to wet the solid. If it is greater than 90 degrees it is said to be non-wetting. A zero contact angle represents *complete wetting*.

The contact angle is a function of the liquid's surface tension and the surface 'free' energy of the substrate.

Surface Tension after http://www.ksvinc.com/surface_tension1.htm

Surface tension is a measurement of the cohesive energy present at an interface. The molecules of a liquid attract each other. The interactions of a molecule in the bulk of a liquid are balanced by an equal attractive force in all directions. Molecules on the surface of a liquid experience an imbalance of forces as indicated below.



The net effect of this situation is the presence of free energy at the surface. The excess energy is called surface free energy and can be quantified as a measurement of energy/area. It is also possible to describe this situation as having a line tension or surface tension which is quantified as a force/length measurement. The common units for surface tension are dynes/cm or mN/m. These units are equivalent. This excess energy exists at the interface of two fluids. If one of the fluids is the vapor phase of a liquid being tested the measurement is referred to as surface tension. If the surface investigated is the interface of two liquids the measurement is referred to as <u>interfacial tension</u>. In either case the more dense fluid is referred to herein as the 'heavy phase' and the less dense fluid is referred to as the 'light phase'. Solids also may be described to have a surface free energy at their interfaces but direct measurement of its value is not possible through techniques used for liquids. (see Contact Angle Theory section for advise on calculating solid surface free energies)

Polar liquids, such as water, have strong intermolecular interactions and thus high surface tensions. Any factor which decreases the strength of this interaction will lower surface tension. Thus an increase in the temperature of this system will lower surface tension. Any contamination, especially by surfactants, will lower surface tension. Therefore researchers should be very cautious about the issue of contamination.

Liquid on a solid:

At the heart of theory of Contact Angles, lies the Young equation where, γ represents the surface tension values between the corresponding interfaces.

The Young Equation arises form a force balance about the three phase contact line.

However, this equation is only valid for finite contact angles in case of mechanical equilibrium, so it does not apply when spreading takes place.



Young Equation:

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$$

To encourage wetting, γ_{sl} , γ_{lv} should be made as small as possible. This is done in practice by adding a surfactant (see Figure 1 below) to the liquid phase. The surfactant adsorbs to both the liquid-solid and liquid-vapor interfaces, lowering those interfacial tensions.



Representative Contact Angles of different solids with water

Polypropylene	95°-105°	TFE	120° -125 °
Polyethylene	95°-104°	Polystyrene	84 °-91 °
PMMA	~75 °	Nylon	~70 °
PET	~87 °	Polycarbonate	66 °

Teflon	112°	Graphite	80 ° -86 °
HOPG	85°-90°	Silicon	45-50°

The wettability has important implications for how proteins interact with surfaces.

Lysozyme adsorption on ultrafiltration membranes.... Sethuraman A, Vedantham G, <u>Przybycien TM</u>, <u>Belfort G</u> (2004) "Protein Unfolding at Interfaces: Slow Dynamics of α -Helix to β -Sheet Transition," *Proteins: Structure, Function and Bioinformatics* **56**, 669-678.

Description and properties of the nanoporous substrates (membranes).

Nanoporous Substrates			Contact	Wettability
(membrane)	Symbol	MWCO ^a (kDa)	angle $(\theta)^{b}$	$\cos(\theta)$
Poly(tetrafluoroethylene)	PTFE	unknown	120 ± 3	-0.499 ± 0.045
Poly(vinylidine difluoride)	PVDF	20	76 ± 2	0.243 ± 0.033
Poly(sulfone)	PS	20	70 ± 2	0.343 ± 0.033
Poly(ether sulfone)	PES	10	55 ± 2	0.574 ± 0.028
Poly(vinyl pyrolidinone)-				
poly(ether sulfone)	pvp-PES	10	48 ± 2	0.669 ± 0.026
Regenerated cellulose	RC	10	27 ± 2	0.891 ± 0.016



Fraction of secondary structure components, f_i , of adsorbed native (full symbols) and mutant (W62G, open symbols) lysozyme versus wettability ($\cos \theta$) of the nanoporous substrates. Ordered helix (α -helix, \bullet , \bigcirc), sheet (β -sheet, \blacksquare , \Box) and random/turns (unordered, unordered helix and turns, \blacktriangle , Δ) for lysozyme adsorbed onto six nanoporous substrates in PBS buffer at pH 7.4 and 25 °C for 300 min. The six horizontal full and dashed arrows identify the fractional structural components in free solution for the native and W62G mutant, respectively.



Fraction of secondary structure components of adsorbed native lysozyme versus initial concentration of native lysozyme in free solution. Ordered helix (α -helix, \bullet), sheet (β -sheet, \blacksquare) and random/turns (unordered, unordered helix and turns, \blacktriangle) for lysozyme adsorbed onto Teflon substrate in PBS buffer at pH 7.4 and 25 °C for 300 min. The three horizontal full arrows identify the fractional structural components in free solution for the native lysozyme, respectively. **Insert:** Adsorption isotherm.



Fraction of secondary structure components of adsorbed native lysozyme versus time. Ordered helix (α -helix, \bigcirc), sheet (β -sheet, \square) and random/turns (unordered, unordered helix and turns, Δ) for lysozyme adsorbed onto Teflon substrate in PBS buffer at pH 7.4 and 25 °C for 300 min. The three horizontal full arrows identify the fractional structural components in free solution for the native lysozyme. The three solid lines are the model fits and use the initial time points of each period as a starting point. The rate constants for the best fit were: $k_1 = 1.22 \times 10^{-3} t + 0.42$; $k_{-1} = 9.95 \times 10^{-5} t + 0.13$;

 $k_2 = -2.95 \times 10^{-7} t + 3.06 \times 10^{-4}$; and $R^2 = 0.988$. Insert: Adsorption kinetics.



Fraction of secondary structure components of adsorbed native lysozyme versus amount of lysozyme adsorbed for (i) six different surfaces and hence wettabilities (on each substrate after 300 min) (\bigcirc , \square , \triangle), and (ii) nine different lysozyme bulk concentrations, C_i, (on Teflon for 300 min) (\bigcirc , \blacksquare , \blacktriangle), and (iii) 17 different time points (on Teflon at 16 mg/ml) (\boxtimes , $\oslash \triangle$). Ordered helix (α -helix, \bigcirc , \bigcirc , \bigotimes), sheet (β -sheet, \square , \blacksquare , \boxtimes) and random/turns (unordered, unordered helix and turns, \triangle , \bigstar , \bigstar). Three horizontal full arrows identify the fractional structural components in free solution for the native lysozyme.

Types of Materials

Polymers

Polymers are macromolecules built up from individual small molecules called monomers. Polymers can be made quite rigid or quite soft. Some are relatively inter, and some are quite reactive. Biodegradable polymers exist that are designed to fall apart at a controlled rate in the body. This is how absorbable sutures are made (stitches that don't need to be removed). There are two major categories of polymerization reactions: condensation reactions and addition reactions.

Example condensation reaction: Polyamides (such as Nylon)

NH ₂ RNH ₂	+	HOOCR'COOH	→ HCOOR'CONHRNH ₂ + H ₂ O
di-amine		dicarboxylic acid	amide

To make a polymer via condensation reactions, each monomer has to have two reactive groups. R refers to a non-reactive functional group (e.g. CH_2)

Nylon was the first polymer produced commercially. It was invented at DuPont by Wallace Carothers and ushered in the polymers revolution (think of life before polymers). At the end of his life, he apparently considered himself a professional failure.

Example Condensation Polymers



Addition Polymerization (e.g. polyethylene)



Example of monomers that are polymerized by addition polymerization

Styrene	$CH_2=CH-C_6H_5$
Propylene	$CH_2=CH-CH_3$
Vinyl chloride	CH ₂ =CHCl

The key variable that can be controlled for a polymer is the molecular weight. This controls the rigidity of the polymer because this influences the entanglement of chains. Increasing molecular weight yields more rigid materials. Molecular weights can be varied from a few thousand to several million g/mole.



Polymer properties are highly dependent on temperature. Polymers can be either amorphous (non-crystalline) or semi-crystalline. Crystallinity refers to the existence of high degrees of order in the chain folding. The polymer above is amorphous. The polymer below has crystallinity



Semi-crystallin polymers are usually more rigid than amorphous polymers. Amorphous polymers can be glassy (relatively stiff but still non-crystalline) or rubbery. The transition between glassy and rubbery behavior occurs at the *glass transition temperature* (T_g). Rubbery behavior starts above T_g . Below T_g , the polymer is glassy. T_g depends very much on the type of side groups the polymer has.

Often, biomaterials have to combine both strength and flexibility. In these cases, block copolymers are made that include stretches of one type of monomer followed by stretches of another type of monomer. One block may be glassy and the other rubbery.



The ability to prepare copolymers of different monomers with different properties provides a high level of control over the final properties of the material.

Ceramics

Ceramics are rigid, polycrystalline materials, usually inorganic, including for example silicates and metal oxides. Ceramic materials are sometimes made by fusing colloidal particles together. Colloids are solid particles with sizes on the order of several nanometers to about 1 micrometer.

Ceramic materials are held together by ionic bonds between positively and negatively charged atoms, such as the bond between Na^+ and Cl^- to make NaCl.

Ceramics exhibit high inertness to body fluids and high compressive strength. They have been used for dental implants for years. Whereas metals and plastics (polymeric materials) can deform under shear, ceramics do not. This is because the ionic attractions between the atoms making up the ceramic do not easily slide past one another. This makes them rigid, but brittle. Ceramic materials can be sensitive to small cracks. Under stress, the cracks can propagate and the material will fracture. An interesting result of this is that ceramics often are very strong under compression but weak under tension (pull apart). To be strong under tension, it is critical to prepare a ceramic with few defects (microcracks). Carefully made glass fibers can be made that have tensile strengths twice that of steel.

Response to Shear



While some polymers also are brittle, ones with rubbery character are not brittle. Rubbery polymers and metals are ductile, meaning they are deformed under stress and can be sheared.

Natural bone is contains a type of ceramic material called hydroxyapatite (a calcium phosphate compound). When synthetic hydroxyapatite is used as an implant, natural bone can grow around it. This is a very biocompatible material when used for bone applications.

The manufacture of a ceramic is illustrated by the process to make hydroxyapatite. An aqueous solution of $Ca(NO_3)_2$ and NaH_2PO_4 is precipitated and dried to form a fine powder. The powder is dried and heated ("calcined") for several hours at 900°C to promote crystallization. Then, the powder is pressed into a final form at high pressure and sintered at 1050° to 1200°C for several hours. Sintering causes the individual particles to fuse.



Metals and metal alloys

Atoms held together by metallic bonds and surrounded by a mobile sea of valence electrons Structure: grains comprising crystalline lattices

The three main crystalline structures of metals: www.ndted.org/EducationResources/CommunityCollege/Materials/Structure/metallic structures.htm

Body-Centered Cubic (BCC) Structure

The body-centered cubic unit cell has atoms at each of the eight corners of a cube (like the cubic unit cell) plus one atom in the center of the cube (left image below). Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. It is said to have a coordination number of 8. The bcc unit cell consists of a net total of two atoms; one in the center and eight eighths from corners atoms as shown in the middle image below (middle image below). The image below highlights a unit cell in a larger section of the lattice.



The bcc arrangement does not allow the atoms to pack together as closely as the fcc or hcp arrangements. The bcc structure is often the high temperature form of metals that are close-packed at lower temperatures. The volume of atoms in a cell per the total volume of a cell is called the **packing factor**. The bcc unit cell has a packing factor of 0.68.

Some of the materials that have a bcc structure include lithium, sodium, potassium, chromium, barium, vanadium, alpha-iron and tungsten. Metals which have a bcc structure are usually harder and less malleable than close-packed metals such as gold. When the metal is deformed, the planes of atoms must slip over each other, and this is more difficult in the bcc structure. It should be noted that there are other important mechanisms for hardening materials, such as introducing impurities or defects which make slipping more difficult. These hardening mechanisms will be discussed latter.

Face Centered Cubic (FCC) Structure

The face centered cubic structure has atoms located at each of the corners and the centers of all the cubic faces (left image below). Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. Additionally, each of its six face centered atoms is shared with an adjacent atom. Since 12 of its atoms are shared, it is said to have a coordination number of 12. The fcc unit cell consists of a net total of four atoms; eight eighths from corners

atoms and six halves of the face atoms as shown in the middle image above. The image below highlights a unit cell in a larger section of the lattice.



In the fcc structure (and the hcp structure) the atoms can pack closer together than they can in the bcc structure. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer. To picture packing arrangement, imagine a box filled with a layer of balls that are aligned in columns and rows. When a few additional balls are tossed in the box, they will not balance directly on top of the balls in the first layer but instead will come to rest in the pocket created between four balls of the bottom layer. As more balls are added they will pack together to fill up all the pockets. The packing factor (the volume of atoms in a cell per the total volume of a cell) is 0.74 for fcc crystals. Some of the metals that have the fcc structure include aluminum, copper, gold, iridium, lead, nickel, platinum and silver.

Hexagonal Close Packed (HPC) Structure

Another common close packed structure is the hexagonal close pack. The hexagonal structure of alternating layers is shifted so its atoms are aligned to the gaps of the preceding layer. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer just like in the fcc structure. However, instead of being a cubic structure, the pattern is hexagonal. (See image below.) The difference between the HPC and FCC structure is discussed later in this section.



The hcp structure has three layers of atoms. In each the top and bottom layer, there are six atoms that arrange themselves in the shape of a hexagon and a seventh atom that sits in the middle of

the hexagon. The middle layer has three atoms nestle in the triangular "grooves" of the top and bottom plane. Note that there are six of these "grooves" surrounding each atom in the hexagonal plane, but only three of them can be filled by atoms.

As shown in the middle image above, there are six atoms in the hcp unit cell. Each of the 12 atoms in the corners of the top and bottom layers contribute 1/6 atom to the unit cell, the two atoms in the center of the hexagon of both the top and bottom layers each contribute $\frac{1}{2}$ atom and each of the three atom in the middle layer contribute 1 atom. The image on the right above attempts to show several hcp unit cells in a larger lattice.

The coordination number of the atoms in this structure is 12. There are six nearest neighbors in the same close packed layer, three in the layer above and three in the layer below. The packing factor is 0.74, which is the same as the fcc unit cell. The hcp structure is very common for elemental metals and some examples include beryllium, cadmium, magnesium, titanium, zinc and zirconium.

Structure of Metals www.science.uwaterloo.ca/~cchieh/cact/applychem/metals.html

Periodic Table of Metal Structures Be Li Na Mg AI) Са Fe κ Sc Т Y Cr Mn Co Ni Cu Zn Ga Rb Sr Ϋ́ Zr Nb Мо Tc Ru (Rh) (Pd) (Ag) Cd In (Sn Cs Ва [Lu] HF Та W Re Os r Pt П Au Hg Pb Eu Ce [Nd] (Pm) (Sm) Gd Tb Dy [Ho] Fr Tm [La] hc (4 H) other CCP HCP BCC

Since the periodic table is a useful tool for representing information, the structure types of metals can be displayed using a period table.

In the above diagram, the ccp (fcc) structures are represented by a red circle, whereas the hcp structures are represented by black hexagon. Some examples of these structures are also given on page 77 in Inorganic Chemistry by T.W. Swaddle, Academic Press.

Copper is the most common mentioned metal that has the fcc structure. This element is one of the noble metals. It has been widely used for door knobs and other tools, and has been widely recognized. Yet, most nobel metals, Cu, Ag, Au, Ni, Pd, Pt, Rh, and Ir have fcc type structures. Among the group 2 elements, only Ca and Sr have the fcc structure, whereas Be and Mg have hcp structures. So do Zn, Cd, Sc, Y, Lu, Ti, Zr, Hf, Tc, Re, Ru, Os and most rare earth elements.

Amazingly, the hcp and fcc structures are very similar in many aspects, but nature knows best. The structures adopted by various metals occur by their design. When crystallization takes place, the atoms arrange themselves according to their structure types.

Alkali metals, Li, Na, K, Rb, and Cs all have the body centered cubic (bcc) structure. In addition, the vanadium and chromium groups also have the bcc structure. Furthermore, at room temperature, iron has a bcc structure. This type of structure has two atoms per unit cell, and it is slightly less densely packed as the fcc or hcp types.

Polonium (Po) has been reported to have a simple cubic crystal structure. From packing point of view, this type of arrangement is not stable, and this structure type is not common. The cubic unit cell contains only one sphere, and the edge length is exactly equal to the diameter of the sphere. We usually choose the origin to be the center of an atom, but if you choose the origin to be the center among 8 spheres, your cube will enclose a whole atom. You can work out the fraction of space occupied by spheres in such an arrangement to be $\pi/6$ (0.52), much less than the bcc structure type.

If you go back to the periodic table of structure types, you will see that the rare earth elements have fcc (ccp), hcp, bcc, and another type marked by hc(4 H). In other words, these 14 elements exemplify many types of structures. The hc (4 H) type has a complicated packing sequence such as ABAC, ABCB, etc. That is why they are designated as (4 H). The structure of Sm (samarium) for example has a very complicated sequence of ACACBCBAB ACACBCBAB (see page 309 of The Crystal Chemistry and Physics of Metals and Alloys by W.B. Pearson, Wiley Interscience, 1972)

Crystalline Grains



Photomicrograph of a steel. You can see the grains in which the crystals have grown in different directions. www.schoolscience.co.uk



Dislocations

www.ndt-ed.org/EducationResources/CommunityCollege/Materials/Structure/linear_defects.htm

There are two basic types of dislocations, the edge dislocation and the screw dislocation. Actually, edge and screw dislocations are just extreme forms of the possible dislocation structures that can occur. Most dislocations are probably a hybrid of the edge and screw forms but this discussion will be limited to these two types.

Edge Dislocations

The edge defect can be easily visualized as an extra half-plane of atoms in a lattice. The dislocation is called a line defect because the locus of defective points produced in the lattice by the dislocation lie along a line. This line runs along the top of the extra half-plane. The interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line.



Understanding the movement of a dislocation is key to understanding why dislocations allow deformation to occur at much lower stress than in a perfect crystal. Dislocation motion is analogous to movement of a caterpillar. The caterpillar would have to exert a large force to move its entire body at once. Instead it moves the rear portion of its body forward a small amount and creates a hump. The hump then moves forward and eventual moves all of the body forward by a small amount.





As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half. However, only a small fraction of the bonds are broken at any given time. Movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

Screw Dislocations

There is a second basic type of dislocation, called screw dislocation. The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end

so that the metal begins to rip. This is shown in the upper right image. The lower right image shows the plane of atoms just above the rip. The atoms represented by the blue circles have not yet moved from their original position. The atoms represented by the red circles have moved to their new position in the lattice and have reestablished metallic bonds. The atoms represented by the green circles are in the process of moving. It can be seen that only a portion of the bonds are broke at any given time. As was the case with the edge dislocation, movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

If the shear force is increased, the atoms will continue to slip to the right. A row of the green atoms will find there way back into a proper spot in the lattice (and become red) and a row of the blue atoms will slip out of position (and become green). In this way, the screw dislocation will move upward in the image, which is perpendicular to direction of the stress. Recall that the edge dislocation moves parallel to the direction of stress. As shown in the image below, the net plastic deformation of both edge and screw dislocations is the same, however.



The dislocations move along the densest planes of atoms in a material, because the stress needed to move the dislocation increases with the spacing between the planes. FCC and BCC metals have many dense planes, so dislocations move relatively easy and these materials have high ductility. Metals are strengthened by making it more difficult for dislocations to move. This may involve the introduction of obstacles, such as interstitial atoms or grain boundaries, to "pin" the dislocations. Also, as a material plastically deforms, more dislocations are produced and they will get into each others way and impede movement. This is why strain or work hardening occurs.

In ionically bonded materials, the ion must move past an area with a repulsive charge in order to get to the next location of the same charge. Therefore, slip is difficult and the materials are brittle. Likewise, the low density packing of covalent materials makes them generally more brittle than metals.

Stainless steels, cobalt chrome alloys, titanium, www.orthoteers.co.uk

Stainless steel-

- Iron based alloy containing chromium, nickel, molybdenum. Usually annealed, cold worked or cold forged for increased strength. A range of strength and ductilities can be produced.
- Strong
- Cheap
- Relatively *ductile* therefore easy to alter shape. Useful in contouring of plates and wires during operative procedures.
- Relatively biocompatible
- The chromium forms an oxide layer when dipped in nitric acid to reduce corrosion and the molybdenum increases this protection when compared to other steels.
- Can still undergo corrosion if carbon gets to the surface.
- *High Young's modulus* 200 GPascals (10× that of bone) so can lead to stress shielding of surrounding bone which can cause bone resorption.
- Used in plates, screws, external fixators, I.M. nails.
- Composition of 316L Stainless Steel: Iron- 60%, Chromium- 20% (major corrosion protection), Nickel- 14% (corrosion resistance), Molybdenum- 3% (protects against pitting corrosion), Carbon- 0.03% (incr. strength), Manganese, Silicon, P, S, 3% (control manufacturing problems).

Titanium and its alloys

- Excellent resistance to corrosion
- Young's modulus approximately half that of stainless steel, therefore less risk of stress protection of bone, stress riser at end of plate or nail.
- More expensive than stainless steels.
- *Poorer wear* characteristics than others, therefore not considered suitable as a load bearing surface these days.
- Can be brittle i.e. less ductile than stainless steel, but more ductile titanium alloys being produced
- Can be as strong as stainless steels
- Used in plates, screws, I.M. nails, external fixators. Useful in halos as more MR scan compatible than other metals.

Biocompatibility, Thrombosis and the Blood Clotting Cascade

Biocompatibility is ultimately a matter of controlling the surface chemistry of a material. This becomes apparent if you consider that only the surface of a material is exposed to the surrounding tissue environment.

For some applications, smoothness is essential. This pertains to joint replacements. If a surface is rough, it causes greater friction. This is bad for function. Furthermore, asperities (bumps) on a surface that is sheared against another surface (e.g. a ball in socket hip joint) can be sheared off. These fine particles sometimes are inflammatory.

Friction is a physical process. The biological response to a material is often based on how proteins in solution (in the blood or in interstitial fluid) respond to the implanted surface. If proteins in blood adsorb (stick) to the surface, they can trigger the blood clotting cascade. The resulting thrombus (clot) can obstruct blood flow (bad for a vascular implant) or it can be sheared off the surface of the implant and be carried by the blood through the circulatory system until it eventually reaches a vessel that is too narrow to pass. Then it becomes lodged. If this happens in the brain or lungs, it can be very dangerous. A thrombus that shears off is called an embolus.

There are two diametrically opposed strategies to control the biological response to a surface. One is to try to keep the surface pristine – absolutely free of adsorbing proteins. This is very difficult to achieve. The other approach is to make the surface so attractive to more inert proteins that they rapidly adsorb and prevent the clotting proteins from adsorbing. A variant on this is to recruit cells to grow over the surface – trying to mask the surface with a natural cellular surface. This can go too far, though, as in the case of vascular graft restenosis where cells keep growing until they eventually clog the vessel.

As we discussed, one of the challenges for engineering biomaterials is to make them biocompatible. The image below shows a thrombus (blood clot) that has traveled to a point where it clogs a small diameter blood vessel. This particular image comes from a patient with a blood disorder, not from an implant case, but it illustrates the problem.



This fibrin and platelet thrombus in a small peripheral artery in the heart is characteristic for thrombotic thrombocytopenic purpura. For this reason, patients with TTP may die from heart failure. From http://wwwmedlib.med.utah.edu/WebPath/CVHTML/CV071.html

The Blood Clotting Cascade

When blood contacts a wound, proteins in blood respond by adsorbing to the wound site and initiating a multi-enzyme pathway called the blood clotting cascade. The final product is a clot. This is essential to stop bleeding. When blood contacts a foreign surface, such as an implant, a similar response occurs. This is how biomaterials can cause thrombosis. The biomaterial-induced thrombosis follows the *intrinsic pathway* (foreign surface) shown below. When blood vessels are damaged, the extrinsic pathway is followed.



Figure 10.37. Blood-Clotting Cascade. A fibrin clot is formed by the interplay of the intrinsic, extrinsic, and final common pathways. The intrinsic pathway begins with the activation of factor XII (Hageman factor) by contact with abnormal surfaces produced by injury. The extrinsic pathway is triggered by trauma, which activates factor VII and releases a lipoprotein, called tissue factor, from blood vessels. Inactive forms of clotting factors are shown in red; their activated counterparts (indicated by the subscript "a") are in yellow. Stimulatory proteins that are not themselves enzymes are shown in blue. A striking feature of this process is that the activated form of one clotting factor catalyzes the activation of the next factor. from http://www.ncbi.nlm.nih.gov/books/bv.fcgi?rid=stryer.figgrp.1401

Platelets in the blood are stimulated to adhere and become activated by thrombin. Fibrinogen helps platelets bind together to form a "plug" held together by a fibrin gel.

Surface modification to improve biocompatibility.

There are many approaches being taken to improve biocompatibility. Here is an example of an approach that is taken to minimize platelet binding:

Grafting poly(sulfobetaine) polymers to poly(urethane) decreases platelet binding. Reproduced from Jiang et al, Blood compatibility of polyurethane surface grafted copolymerization with sulfobetaine monomer, *Colloids and Surfaces B: Biointerfaces* **36**, 27-33 (2004).

The experiment involves soaking the material in platelet-rich blood plasma and observing the adhered platelets by scanning electron microscopy.



PU-g-sulfobetaine-1h

PU-g-sulfobetaine-3h

Structure of poly(sulfobetaine) (from Kitano et al. Hydrogen-Bonded Network Structure of Water in Aqueous Solution of Sulfobetaine Polymers, *J. Phys. Chem. B.* **106**, 11391 -11396 (2002).



Other approaches involve binding *heparin* to surfaces. Heparin is an anticoagulant that disrupts the clotting cascade. Another approach is to coat surfaces with poly(ethylene oxide) (PEO), also known as poly(ethyleneglycol) (PEG). PEO-coated surfaces are highly resistant to protein adsorption, through an as-yet incompletely understood mechanism.