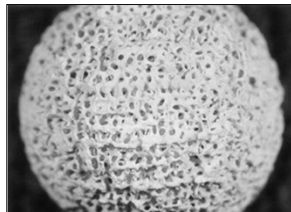


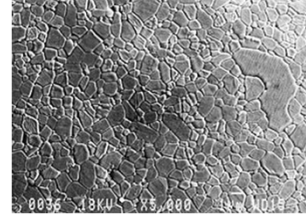
TYPES OF BIOMATERIALS

- **Metals**
- **Ceramics**
- **Polymers**
- **Natural Biomaterials**
- **Composites**

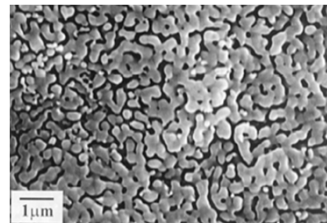


Classes of Bioceramics

- Bioinert Ceramics
- Bioactive Ceramics
- Bioresorbable Ceramics



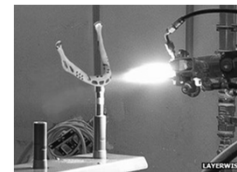
Alumina, SEM, www.cermtec.com



Ca-P Thin Film, SEM, Langstaff et al, 1999

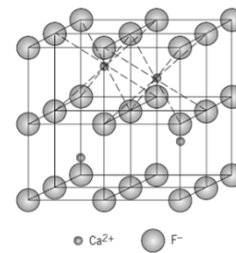
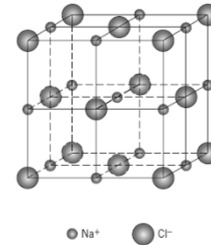
Biomaterial: Ceramics

- Metallic+Non-Metallic elements
- Types of Ceramics used clinically
 - Al_2O_3
 - Calcium phosphate ceramics
 - Glass and Glass ceramics
- Fabrication
 - Casting
 - Solid state sintering-hot isostatic pressing
 - Plasma spraying as coatings on implants



Ceramic Crystal Structure

- **More complex than those of metals**
 - Two elements or more, ions instead of atoms
 - Depends on the magnitude of charge
 - Depends on relative size of cation vs. anion
- **Bioceramics: A_mX_p -type crystal structure**
 - Cation and Anion not of the same charge mag.
 - ZrO_2 and Al_2O_3



Ceramic Mechanical Properties

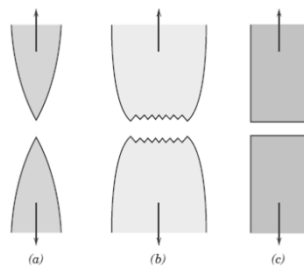


Figure 8.1 (a) Highly ductile fracture in which the specimen necks down to a point. (b) Moderately ductile fracture after some necking. (c) Brittle fracture without any plastic deformation.

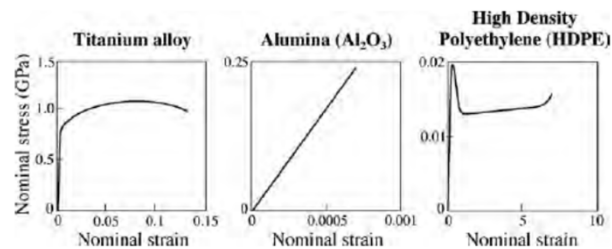


FIGURE 1.1.3.2 Representative nominal stress versus nominal strain plots for three different classes of implantable material: ductile metal (titanium alloy; 6 wt% Al, 4 wt% V); ceramic (alumina); and crystalline polymer (high density polyethylene).

Ceramic Mechanical Properties

Critical stress for crack propagation

$$\sigma_c = \left(\frac{2E\gamma_s}{\pi a} \right)^{1/2} \quad (8.3)$$

E = modulus of elasticity

γ_s = specific surface energy

a = one half the length of an internal crack

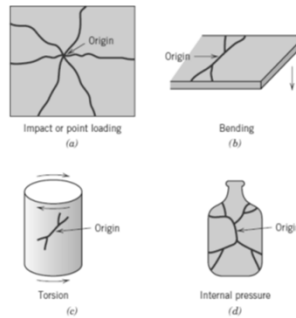


Figure 12.29 For brittle ceramic materials, schematic representations of crack origins and configurations that result from (a) impact (point contact) loading, (b) bending, (c) torsional loading, and (d) internal pressure. (From D. W. Richerson, *Modern Ceramic Engineering*, 2nd edition, Marcel Dekker, Inc., New York, 1992. Reprinted from *Modern Ceramic Engineering*, 2nd edition, p. 681, by courtesy of Marcel Dekker, Inc.)

Ceramic Mechanical Properties

Figure 8.1 (a) Highly ductile fracture in which the specimen necks down to a point. (b) Moderately ductile fracture after some necking. (c) Brittle fracture without any plastic deformation.

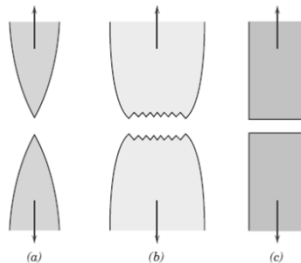


Figure 8.5 (a) Photograph showing V-shaped "chevron" markings characteristic of brittle fracture. Arrows indicate origin of crack. Approximately actual size. (b) Photograph of a brittle fracture surface showing radial fan-shaped ridges. Arrow indicates origin of crack. Approximately 2 \times . [(a) From R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc. Photograph courtesy of Roger Slutter, Lehigh University. (b) Reproduced with permission from D. J. Wulpi, *Understanding How Components Fail*, American Society for Metals, Materials Park, OH, 1985.]

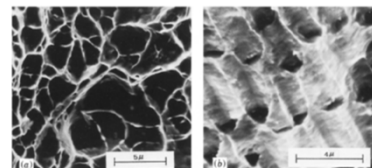
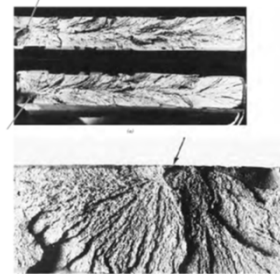


Figure 8.4 (a) Scanning electron fractograph showing spherical dimples characteristic of ductile fracture resulting from uniaxial tensile loads, 3300 \times . (b) Scanning electron fractograph showing parabolic-shaped dimples characteristic of ductile fracture resulting from shear loading, 5000 \times . (From R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

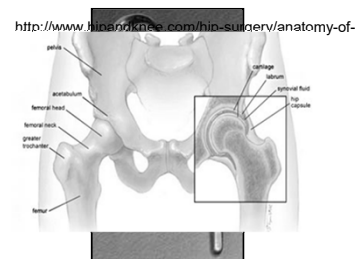


Classes of Bioceramics

- **Bioinert Ceramics**
 - Exhibit morphological fixation without biochemical bonding
 - Ceramic bearing surfaces
 - Alumina
 - Zirconia
- **Bioactive Ceramics**
- **Bioresorbable Ceramics**

Ceramics for Hip: Cartilage or Bone

- **Most Common**
 - **Alumina and Zirconia**
 - Cartilage
 - **Calcium Phosphate Coating**
 - Bone bonding
 - **Bioactive Glass Coating**
 - Bone bonding
- Readings (Ratner: Sec.I.2.4, 1.2.6, Sec. II.5.6; Callister: Chaps. 12, 13 and 22.10-hip)

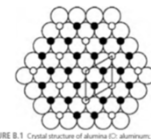


**Stryker Trident®
Ceramic System**

Alumina

• Structure

- Hexagonal organization with Al ions at octahedral interstitial sites
- 99.5% Al_2O_3 , 0.5% MgO (aids sintering)



• Properties

- High strength and high abrasion resistance
- Density of 3.97 g/cm^3 , $E = 300 \text{ GPa}$
- $K_{Ic} = 3\text{-}5 \text{ MPa}\sqrt{\text{m}}$ – low fracture toughness
- Low coefficient of friction
 - Surface roughness $<0.02 \text{ microns}$
- Biocompatible

TABLE B.1 Mechanical Properties of 99.5% Alumina	
Density	3.97 gm/cm^3
Flexural strength	345 MPa
Elastic modulus	300 GPa
Shear modulus	124 GPa
Bulk modulus	172 GPa
Poisson's ratio	0.21
Compressive strength	2100 MPa
Hardness	1000 kg/mm^2
Fracture toughness	$3.5 \text{ MPa}\cdot\text{m}^{1/2}$

Alumina

• Fabrication

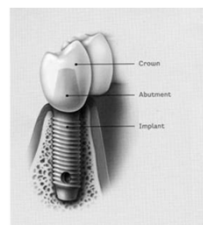
- Hot isostatic pressing (1600-1700°C)
- Small grain size ($<4 \text{ mm}$)
 - If increased size to 17 mm, reduces yield stress by 20%

• Applications

- Used as artificial eye, in dental and orthopedics



Source: medgadget.com



Source: premieroralsurgery.com

Ceramic Mechanical Properties

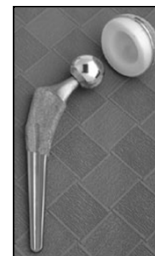
Table 8.1 Room-Temperature Yield Strength and Plane Strain Fracture Toughness Data for Selected Engineering Materials

Material	Yield Strength		K_{Ic}	
	MPa	ksi	MPa \sqrt{m}	ksi $\sqrt{in.}$
Metals				
Aluminum Alloy ^a (7075-T651)	495	72	24	22
Aluminum Alloy ^a (2024-T3)	345	50	44	40
Titanium Alloy ^a (Ti-6Al-4V)	910	132	55	50
Alloy Steel ^a (4340 tempered @ 260°C)	1640	238	50.0	45.8
Alloy Steel ^a (4340 tempered @ 425°C)	1420	206	87.4	80.0
Ceramics				
Concrete	—	—	0.2–1.4	0.18–1.27
Soda-Lime Glass	—	—	0.7–0.8	0.64–0.73
Aluminum Oxide	—	—	2.7–5.0	2.5–4.6
Polymers				
Polystyrene (PS)	—	—	0.7–1.1	0.64–1.0
Poly(methyl methacrylate) (PMMA)	53.8–73.1	7.8–10.6	0.7–1.6	0.64–1.5
Polycarbonate (PC)	62.1	9.0	2.2	2.0

^a Source: Reprinted with permission, *Advanced Materials and Processes*, ASM International, © 1990.

Alumina

- **Advantages**
 - Relatively chemically inert
 - Used for over 20 years in orthopedic applications
 - Biocompatible
 - Thin fibrous capsule formed which allows cementless fixation of prosthesis
 - Good wear resistance and high strength
 - Provides lubrication
- **Disadvantages**
 - Poor shear strength
 - Less useful as screws or plates
 - Stress shielding
 - 380-420 GPa vs. 0.05-5GPa for cancellous or 7-25 for cortical bone



**Stryker
Trident®
Ceramic
System**

Zirconia

- ZrO_2
 - Tetragonal structure stabilized by yttrium oxide, Y_2O_3
- Articulating ball in total hip prostheses
- Low surface roughness (Ra) vs. Co-Cr
- Advantages over alumina
 - Hardness
 - Higher strength
- Composites

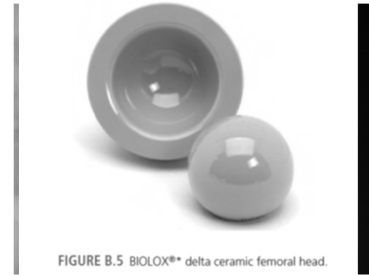


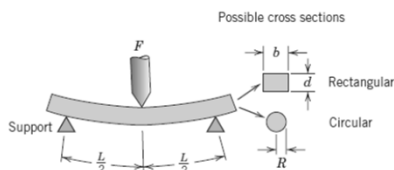
FIGURE B.5 BIOLOX** delta ceramic femoral head.

BIOLOX** Delta Ceramic Femoral Head

The new alumina matrix composite, BIOLOX® delta developed by CeramTec AG, is used by Zimmer Inc. to fabricate femoral heads. This composite has excellent biocompatibility, low wear rates, high hardness, and is very stable *in vivo*-like environments. The implant made from this composite meets the increasing demands of development of a durable implant for young and active patients. The heads fabricated from this ceramic have improved mechanical properties compared to standard alumina heads. The composite consists of about 75% alumina, 24% zirconia, and 1% chromium oxide. Alumina provides the hardness and the wear resistance, while zirconia along with chromium oxide provides improved mechanical properties. The pink color of the implant is also derived from chromium oxide (Figure B.5).

So

Ceramic Mechanical Properties



$$\sigma = \text{stress} = \frac{Mc}{I}$$

where M = maximum bending moment
 c = distance from center of specimen to outer fibers
 I = moment of inertia of cross section
 F = applied load

	$\frac{M}{I}$	$\frac{c}{I}$	$\frac{I}{I}$	$\frac{\sigma}{I}$
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

where F_f is the load at fracture, L is the distance between support points, and the other parameters are as indicated in Figure 12.32. When the cross section is circular, then

$$\sigma_{fs} = \frac{3F_f L}{2bd^2} \quad \sigma_{fs} = \frac{F_f L}{\pi R^3} \quad (12.7b)$$

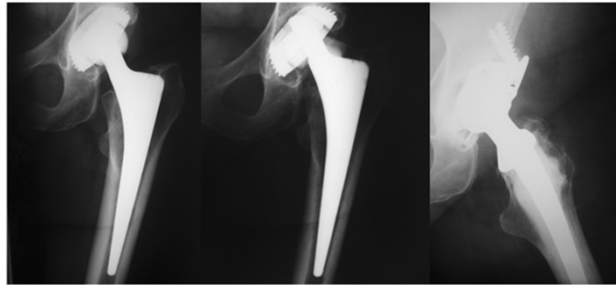
where R is the specimen radius.

Material	Flexural Strength		Modulus of Elasticity	
	MPa	ksi	GPa	10^6 psi
Silicon nitride (Si_3N_4)	250–1000	35–145	304	44
Zirconia ^a (ZrO_2)	800–1500	115–215	205	30
Silicon carbide (SiC)	100–820	15–120	345	50
Aluminum oxide (Al_2O_3)	275–700	40–100	393	57
Glass-ceramic (Pyroceram)	247	36	120	17
Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)	185	27	145	21
Spinel (MgAl_2O_4)	110–245	16–35.5	260	38
Magnesium oxide (MgO)	105 ^b	15 ^b	225	33
Fused silica (SiO_2)	110	16	73	11
Soda-lime glass	69	10	69	10

^a Partially stabilized with 3 mol% Y_2O_3 .

^b Sintered and containing approximately 5% porosity.

Durability of Biolox Al₂O₃ Ceramic on Polyethylene (coP) bearings in THA 0.29% in 22 years



Radiographs of the hip with the fractured ceramic head.
Left: directly post-OP; Middle: Fracture of ceramic head at 6.25 years postop; Right: After revision arthroplasty

Beckmann et al., BMC Muscul. Disord. 2015, 16:249

Ceramic-on-Ceramic (C-on-C) Bearings

- **Used largely in Europe (~50%)**
 - 1970: introduced in France by Pierre Boutin
 - <10% in UK and USA
 - Good for young, active patients
- **Advantages**
 - High level of Hardness and Scratch resistance
 - Superior lubrication and wear
 - Inert degradation products
- **Disadvantages**
 - Poor shear strength
 - fracture often occurs at the OR
 - Stress shielding
 - Costly



Stryker
Trident®
Ceramic
System

Comparison of THA Articulation

Orthopedic Reviews 2011; volume 3:e16

Total Hip Arthroplasty - over 100 years of operative history

Stephen Richard Knight,¹ Randeep Aujla,² Satya Prasad Biswas³

¹University of Leicester; ²University Hospitals of Leicester, Medical School, Leicester; ³Kettering General Hospital, Kettering, UK

Table 1. Comparison of materials used in total hip arthroplasty.

Prosthesis	Advantages	Disadvantages
Metal-on-polyethylene	Large volume of evidence to support use Predictable lifespan Cost effective	Polyethylene debris leading to aseptic loosening
Metal-on-metal	Potentially longer lifespan than polyethylene due to reduced wear Larger femoral head - therefore lower dislocation rate	Metallosis Potential carcinogenic effect of metal ions
Ceramic-on-ceramic	Low friction Low debris particles Inert substance	Expensive Require expert insertion to prevent early damage Can produce noise on movement

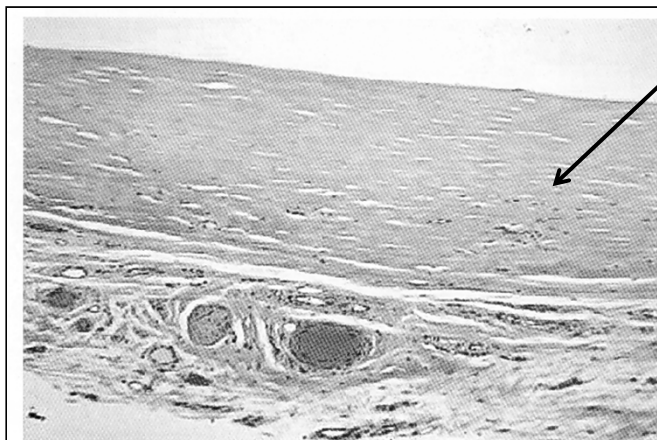
Classes of Bioceramics

- **Bioinert Ceramics**
- **Bioactive Ceramics**
 - Elicit a specific biological response which results in biological bonding
 - Formation of carbonated hydroxyapatite layer at tissue-material interface
 - Bioactive glasses
- **Bioresorbable Ceramics**

Tissue-Material Fixation

Type of bioceramic	Type of attachment	Example
1	Dense, nonporous, nearly inert ceramics attach by bone growth into surface irregularities by cementing the device into the tissues, or by press fitting into a defect (termed morphological fixation).	Al_2O_3 (single crystal and polycrystalline)
2	For porous inert implants bone ingrowth occurs, which mechanically attaches the bone to the material (termed biological fixation).	Al_2O_3 (porous polycrystalline) Hydroxyapatite-coated porous metals
3	Dense, nonporous, surface-reactive ceramics, glasses, and glass-ceramics attach directly by chemical bonding with the bone (termed bioactive fixation).	Bioactive glasses Bioactive glass-ceramics Hydroxyapatite
4	Dense, nonporous (or porous), resorbable ceramics are designed to be slowly replaced by bone.	Calcium sulfate (plaster of Paris) Tricalcium phosphate Calcium phosphate salts

Inert vs. Bioactive: Fibrous Capsule



Chapter 4.2, Fig. 9 Fibrous capsule composed of dense, compacted collagen. This fibrous capsule had formed around a Mediport catheter reservoir. Loose connective tissue with small arteries, veins, and a nerve is identified below the acellular fibrous capsule.

Bioactive Materials

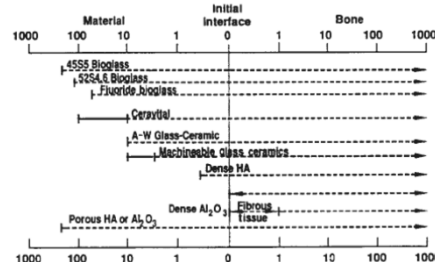


FIGURE I.2.4.2 Comparison of interfacial thickness (μm) of reaction layer of bioactive implants of fibrous tissue of inactive bioceramics in bone.

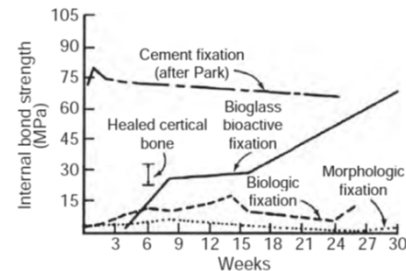
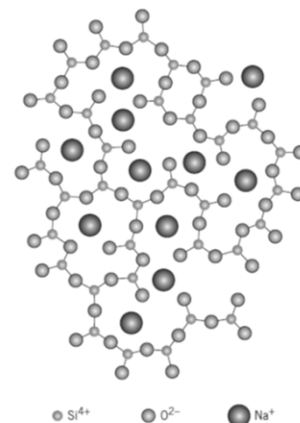


FIGURE I.2.4.7 Time dependence of interfacial bond strength of various fixation systems in bone. (After Hench, 1987.)

- Light micrograph of a 45S5 Bioglass® implant (BG) bonded to rat bone (B) after 1 year
- Bone cells (O) in conjunction with the hydroxylcarbonate apatite layer (Ca-P) formed on top of the silica gel (S). (Hench et al, 1982)

Bioactive Glasses

- **Composition and Structure**
 - SiO_2 , Na_2O , CaO , P_2O_5
 - Less than 60% SiO_2
 - High network former content
 - Na_2O , CaO
 - High $\text{CaO}/\text{P}_2\text{O}_5$ ratio
 - Example: 45S5 bioactive glass ($\text{CaO}/\text{P}_2\text{O}_5 = 5$)
 - 45% SiO_2 , 24.5% Na_2O , 24.5% CaO , 6% P_2O_5



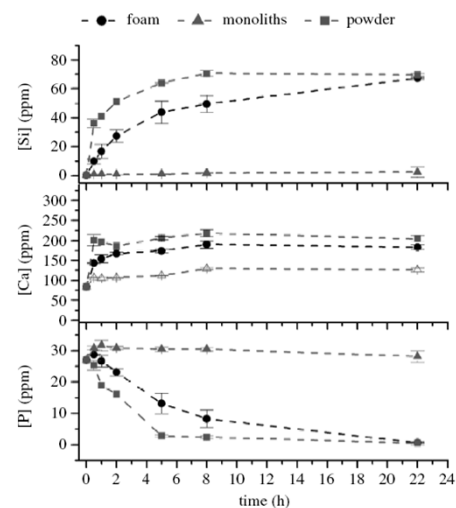
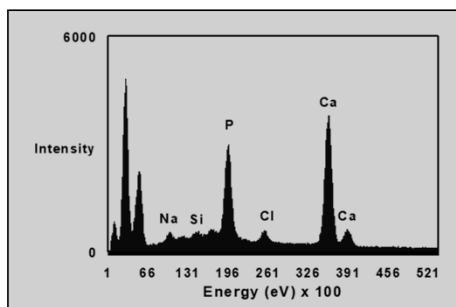
Silica Structure, Callister, 5th Ed, 2000

Bioactivity

- **Osteointegration**
 - Chemical integration between bone and implant
 - Example: bioactive glass
- **Osteoconduction**
 - Materials that provide a scaffold for bone-forming cells and subsequent bone formation
 - Interconnecting porosity for cell and vascular ingrowth
 - Example: hydroxyapatite
- **Osteoinduction**
 - Materials that have a capacity to induce bone
 - Recruit stem cells
 - Induce proliferation and differentiation
 - Example: demineralized bone matrix

Bioactive Glasses

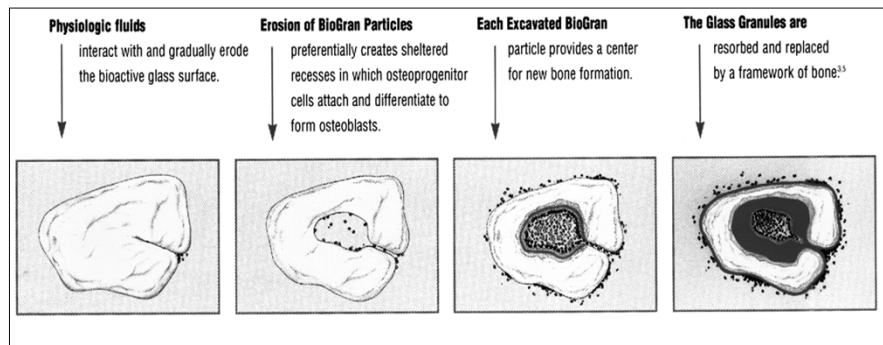
- **Properties**
 - Osteoinductive, osteoconductive, osteointegrative



In Vivo Bioactivity

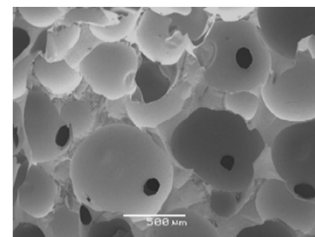
Applications

BIOGRAN® - bone/dental filler, 300-355 μm , Orthovita, Melvern, PA
Dental and orthopedic applications



Bioactive Glasses

- **Advantages**
 - Can elicit targeted cell response (bioactivity)
 - Tissue-material interface formation (biomimetic)
- **Disadvantages**
 - Dissolution products
 - Poor mechanical properties



BG Foam, SEM, Jones et al, 2006

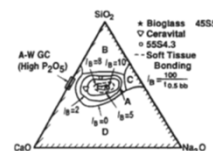


FIGURE 1.2.4.5 Compositional dependence (in wt.%) of bone bonding and soft tissue bonding of bioactive glasses and glass-ceramics. All compositions in region A have a constant 6 wt. % of P_2O_5 . A-W glass ceramic has higher P_2O_5 content (see Table 1.2.4.5 for details). I_b , Index of bioactivity.

Classes of Bioceramics

- **Bioinert Ceramics**
- **Bioactive Ceramics**
- **Bioresorbable Ceramics**
 - **Degrade gradually and allow for replacement by host tissue**
 - **Calcium phosphate ceramics**
 - Tricalcium phosphate
 - Hydroxyapatite

Calcium Phosphates

- **Calcium sulfate: Plaster of Paris**
- **Hydroxyapatite: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$**
 - **Ca/P=1.67, E = 40-116 GPa**
 - **Carbonate, fluorine, and chlorine ions incorporated into structure**
- **Tricalcium Phosphate: $\text{Ca}_3(\text{PO}_4)_2$**
 - **Ca/P=1.50**
 - **Alpha and beta crystal form**
 - **Ionic substitution with carbonate**

Apatites and other phosphates

- **Hydroxyapatite**
 - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
 - Hexagonal symmetry
 - $a=0.95 \text{ nm}$, $c=0.68 \text{ nm}$
 - Most similar to bone mineral
 - Bioactive, osteoconductive
- **Ca/P ratio, acidity, and solubility are closely related**
 - $\text{Ca/P} < 1$, high acidity and solubility
 - $\text{Ca/P} = 1.67$ for stoichiometric HA

TABLE I.2.4.10 Typical Mechanical Properties of Dense Hydroxyapatite Ceramics	
Theoretical density	3.156 g cm ³
Hardness	500–800 HV, 2000–3500 Knoop
Tensile strength	40–100 MPa
Bend strength	20–80 MPa
Compressive strength	100–900 MPa
Fracture toughness	approx. 1 Mpa m ^{0.5}
Young's modulus	70–120 GPa

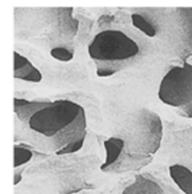
(Vallet-Regi M et al., 2004)

Sex	Bone site (rabbits)			
	Rear tibia	Femur	Front tibia	Rib
Male	2.07 ± 0.12	2.08 ± 0.13	2.06 ± 0.09	1.97 ± 0.05
Female	2.07 ± 0.09	2.08 ± 0.08	2.11 ± 0.08	1.95 ± 0.05

(Kourkouvelis N et al., 2011)

Calcium Phosphates

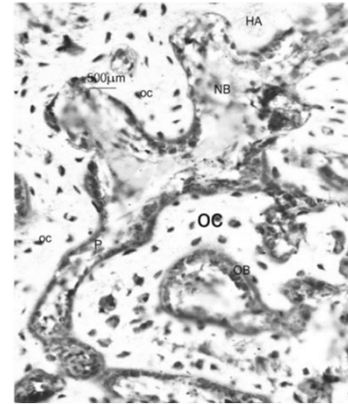
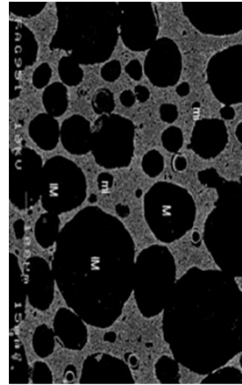
- **Biological or synthetic**
 - Porous, derived from coral, pore > 100 μm
- **Bioactive**
 - Osteointegration, osteoconduction, osteoinduction
- **Biodegradable**
 - β -TCP > HA



news.bbc.co.uk

Degradation and Osteointegration of HA

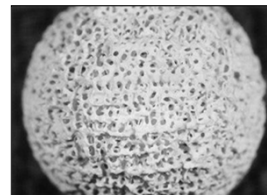
- **Physical properties**
 - Form (particulate or bulk)
 - Porosity (interconnectivity, size)
 - Crystallinity (grain size, crystal size)
- **Chemical properties**
 - Ionic substitutions
 - Other elemental impurities
- **Biological properties**
 - pH
 - Age, species, sex



Damien et al, 2002

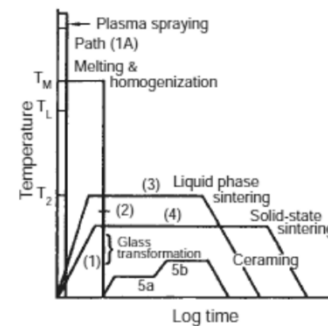
Porosity vs. Mechanical Properties

- **Material Porosity**
 - Total void volume
 - Average Pore diameter
 - Total surface area
 - Interconnectivity between pores
- **Compressive & Tensile strength**
 - Compressive strength (σ_c) vs. total pore volume (V_p)
 - $\sigma_c = 700e^{-5V_p}$
 - Tensile strength (σ_t) vs. volume fraction of microporosity (V_m)
 - $\sigma_t = 200e^{-20V_m}$



Ceramics

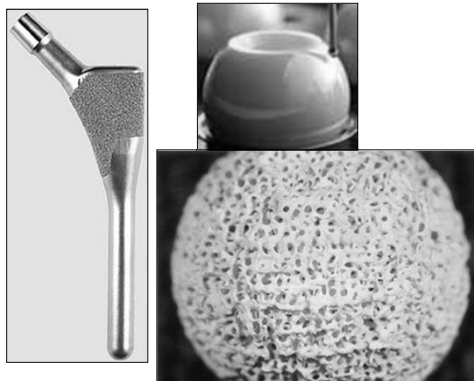
- **Bioactive**
 - Bioactive surface functionalization
 - **Biomimetic**
 - **Degradation products well tolerated**
 - **Poor Mechanical Properties**
 - Low shear strength
 - Low ductility
 - Low viscoelastic response
 - Low fracture toughness
 - Brittle fracture
- Not used in high load-bearing condition



BIOMATERIALS: Ceramics

Applications

Load bearing conditions
Joint replacement
Orthopedic/Dental



Advantages

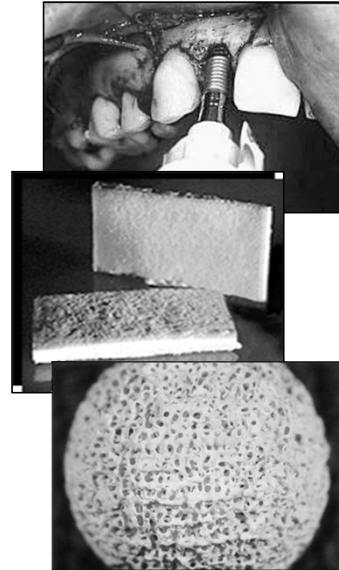
Controllable design
Biocompatible/Inert
Lubrication
Biomimetic
Bioactive

Limitations

Stress Shielding
Low fracture toughness

TYPES OF BIOMATERIALS

- **Metals**
- **Ceramics**
- **Glasses Ceramics**
- **Polymers**
- **Natural Biomaterials**
- **Composites**



Biomaterials: Polymers

- **Readings: Ratner - Sec.I.2.2, II.5.6**
Callister – Chap. 14, 15, 8.12
- **Two Classes**
 - **Homopolymer**
 - Listed in Figure 5, p.71 Ratner
 - **Co-Polymer**
 - Listed in Figure 6, p.72 Ratner
- **Application**
 - **Wound healing (skin)**
 - **Cardiovascular and Orthopedic**

Polymers in Medicine

• Homopolymers

- Polymethylmethacrylate (PMMA)
- Polyethylene (PE)
- Polytetrafluoroethylene (PTFE)
- Polyvinyl Chloride (PVC)
- Polydimethylsiloxane (PDMS)
- Polyacrylamides (PAGE)
- Polyamides (Nylon)
- Polycaprolactone (PCL)

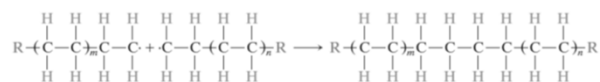
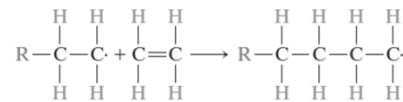
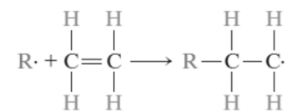
• Co-Polymers

- Polyurethanes
- Polyhydroxethylmethacrylate (pHEMA)
- Polyesters (PGA, PLA, PLGA)

Polymers Synthesis

• Addition Polymerization

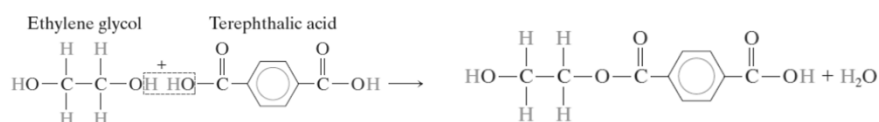
- Unsaturated monomers are attached one at a time to form a chain
- Reactive species (R) disrupts the double bond
- Initiation: R can be free radical
- Propagation
- Termination



- MW depends on rate and duration of each step of the reaction, especially the propagation

Polymers Synthesis

- **Condensation Polymerization**
 - Two monomers react via condensation reaction
 - Monomer has at least two reactive sites, functional groups instead of double bonds
 - Small molecule (water or methanol) is condensed or released
 - Reaction time is longer than Addition Polymerization
 - More expensive
- **Production of Poly(ethylene-terephthalate)**



Polymer Structure

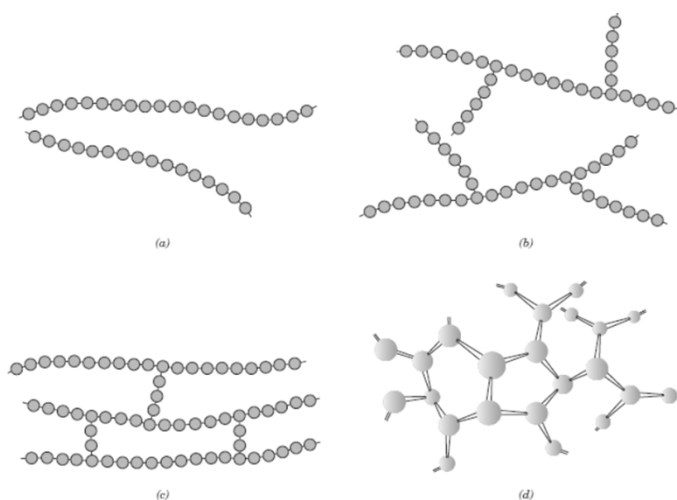


Figure 14.7 Schematic representations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures. Circles designate individual repeat units.

Mechanical Properties of Polymers

Polymer	σ_{UTS} (MPa)	E (GPa)	Ductility ϵ_f (%)	Poisson's Ratio
Polyethylene	7-40	0.1-1.4	1000-15	0.46
Polypropylene	20-35	0.7-1.2	500-10	-
Polystyrene	14-83	1.4-4	60-1	0.35
Polyester	55	2	300-5	0.38
Polyamide (nylon)	55-83	1.4-2.8	200-60	0.32-0.40

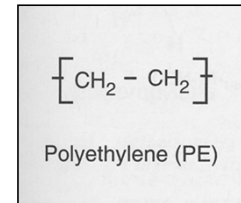
Polymer in THA: Replace Cartilage



FIGURE II.5.6.10 Examples of the three types of bearing couples used in modern THA. From top to bottom: metal-on-polymer, ceramic-on-ceramic, and metal-on-metal (Linge™ line from Wright Medical Technology, Inc. Arlington, TN, USA).

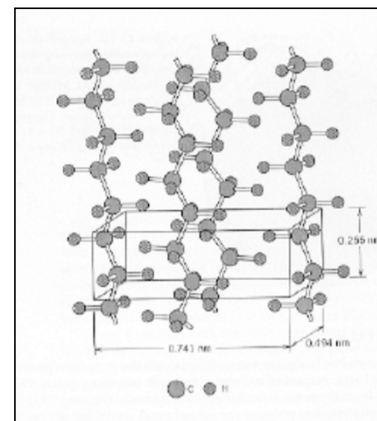
Polymers in Medicine

- **Polyethylene (PE, HDPE, UHMWPE)**
 - HDPE and UHMWPE are used clinically
 - Linear polymer chain
 - Synthesized via addition polymerization
 - Crosslinked via Gamma radiation (2.5-5.0 Mrad)
 - heat treated to reduce residual free radicals
 - $T_m = 130-136^\circ\text{C}$
 - Applications
 - Acetabular component of hip and knee prostheses
 - Artificial Cartilage



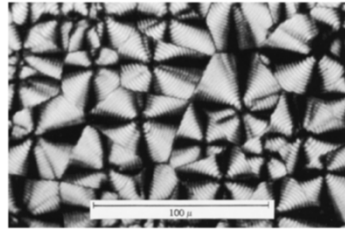
Polymer: Crystal Structure

- **Polyethylene**
 - orthorhombic crystal structure
 - Bi-functional monomer unit, with two reactive bonds through which the chain is propagated
 - Ribbon like chains folded in lamellae of about 10nm in thickness
 - Lattice parameters:
 - $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$, $a = 0.494 \text{ nm}$, $b = 0.741 \text{ nm}$, $c = 0.255 \text{ nm}$,
 - $\angle \text{C-C} = 109.5^\circ$, conserved thorough out the backbone



Polyethylene: Crystal Structure

Figure 14.14 A transmission photomicrograph using cross-polarized light showing the spherulite structure of polyethylene. Linear boundaries form between adjacent spherulites, and within each spherulite appears a Maltese cross. 525 \times . (Courtesy F. P. Price, General Electric Company.)



Doremus, B. W., Roberts, and D. Turnbull (Editors), *Growth and Perfection of Crystals*, General Electric Company and John Wiley & Sons, Inc., 1958, p. 498.]

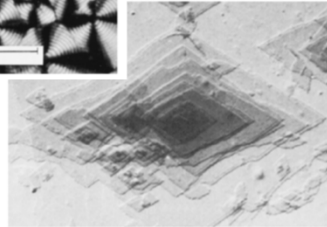
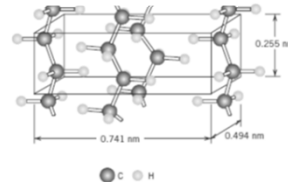


Figure 14.10 Arrangement of molecular chains in a unit cell for polyethylene. (Adapted from C. W. Bunn, *Chemical Crystallography*, Oxford University Press, Oxford, 1945, p. 233.)

Orthorhombic



Polymers in THA: Acetabular Cup

- Charnley: PTFE (1950) to UHMWPE (1962)
- UHMWPE (100-250k mers, MW~4M g/mol)
 - Structurally long chains of PE
 - Aligned chains joined by VW forces
 - Low coefficient of friction, self lubrication
 - Susceptible to oxidation
 - Leading to increased wear and reduced fatigue resistance
 - Wear products ($>10^9$ /yr, 1-10microns)
- 1998: highly crosslinked UHMWPE – Gamma or e-beam along with heat treatment
- 2007: Anti-oxidant doped UHMWPE –Vitamin E
- Vitamin E neutralized free radicals in polymer formed or left over from sterilization by radiation



00208 0.5 & 10 Examples of the new type of bearing cup (acetabular cup) for total hip replacement. The cup is made of UHMWPE. © 2000 Wright Medical Technology, Inc. All rights reserved.

Polymers in Medicine

- **Polyethylene (PE)**

- **Advantages**

- Low coefficient of friction (.15-0.20 dry on SSL)
 - Resistance to lipid adsorption
 - Relatively strong at high density
 - Highest abrasion resistance
 - Highest impact strength
 - Lightweight (0.94 g/cm³)
 - Economical



BIOMET

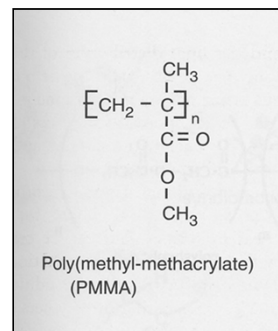
- **Disadvantages**

- Wear products nonbiocompatible
 - Non-biodegradable

Polymers in Medicine

- **Polymethylmethacrylate (PMMA)**

- Oldest polymer in service
 - Hydrophobic linear chain polymer
 - Synthesized via free radical polymerization



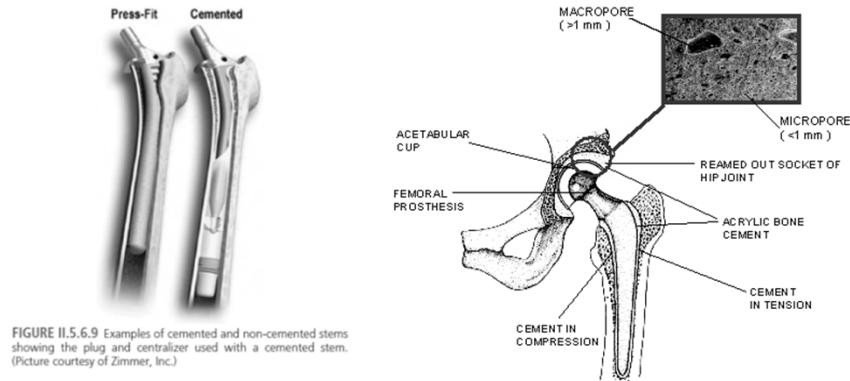
- **Applications**

- Intraocular Lens
 - Hard contact lenses
 - Bone cement



Stryker SIMPLEX® PMMA Cement

Polymers in THA: PMMA Cement



To Cement or not to Cement?

Polymers in Medicine

• Polymethylmethacrylate (PMMA)

– Advantages

- Good optical properties
- Relatively biocompatible

– Disadvantages

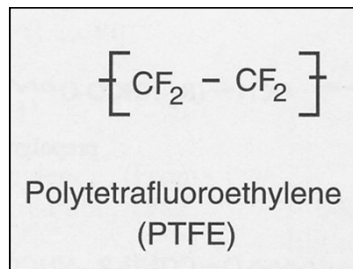
- Exothermic reaction during polymerization
- Toxic monomer if degraded



BIOMET
COBALT™ HV BONE CEMENT
Radiopaque Bone Cement

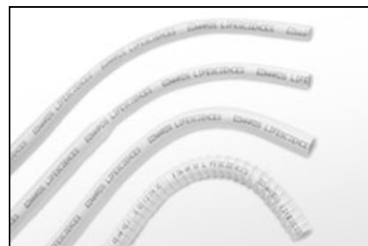
Polymers in Medicine

- **Polytetrafluoroethylene (PTFE, Teflon)**
- **Similar to PE, except H is replaced by F**
 - Synthesized via condensation polymerization
 - $T_m = 327^\circ\text{C}$



Polymers in Medicine

- **PTFE: Applications**
 - **Cardiovascular grafts**
 - Artificial blood vessel
 - Coatings for metallic devices
 - **Orthopedic soft tissue replacements**
 - Ligaments
 - Tendons



Edwards Lifespan ePTFE

Polymers in Medicine

- **PTFE**

- **Advantages**

- Low coefficient of friction - lubrication
 - Chemically stable
 - Anti-adhesion surface (hydrophobic)

- **Disadvantages**

- Poor fatigue strength - Wear products
 - Difficult to process
 - Non-reactive thermally and chemically
 - Expensive

Polymers in Medicine

- **PTFE + hexafluoropropylene (FEP-Teflon)**

- **hexafluoropropylene**

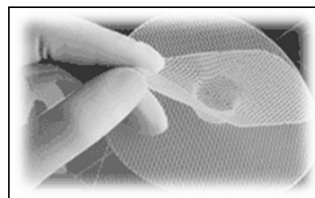
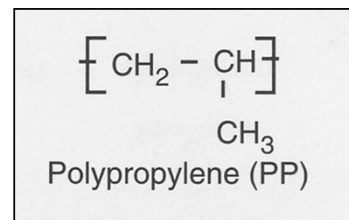
- Added to increase processability
 - Melting pt at 265°C vs. 327°C for PTFE
 - Still Chemically stable
 - Maintains low friction coefficient

Polymers in Medicine

- **Polyethylene Glycol (PEG)**
 - Water soluble, waxy polymer
 - Photopolymerizable hydrogel
 - Used in cosmetic industry
 - Used in drug delivery
 - Used to graft onto material surface and form non-fouling surfaces

Biomaterial: Polymers

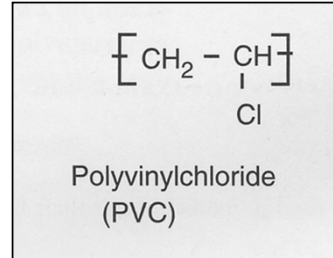
- **Polypropylene (PP)**
 - High rigidity and good chemical resistance
 - Relatively high tensile strength
 - Improved resistance to stress cracking when compared to PE
 - Used as surgical mesh, onlays in hernia repair



Ethicon PROLENE®
Hernia System

Biomaterial: Polymers

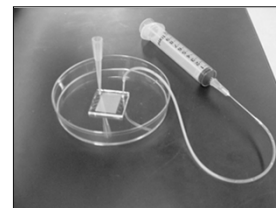
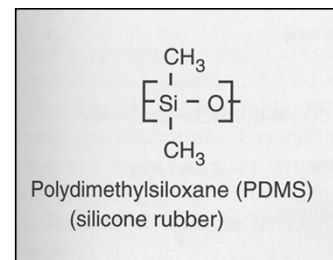
- **Polyvinyl Chloride (PVC)**
 - Derived from mineral oil, natural gas
 - 25% of all medical plastics (Baxter)
 - Used as tubing in biomedical application
 - Blood transfusion
 - Dialyses
 - Brittle
 - only used as a non-permanent biomaterials



Baxter

Biomaterial: Polymers

- **Polymethylsiloxane (PDMS)**
 - Silicone oxygen backbone
 - Properties are relatively insensitive to temperature
 - Highly flexible material
 - Used as insulator coating for pacemakers, catheters
 - Used in micropatterning & microfluidics (BIOMEMS)

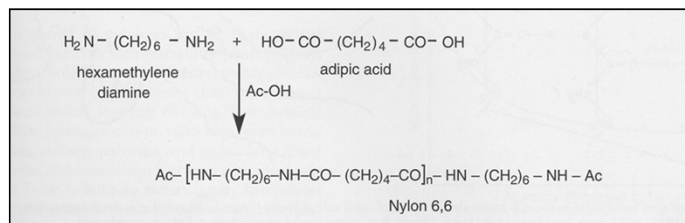


Biomaterial: Polymers

- **Polyamides (Nylon)**
 - Highly elastic material
 - Flexible and durable
 - More hydrophobic than PU
 - Used as sutures, catheters and soft tissue replacement grafts

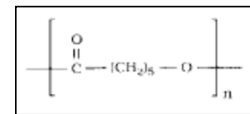


Fostalon 5000



Biomaterial: Polymers

- **Poly-ε-Caprolactone (PCL)**
 - Aliphatic polyester synthesized in the 1930s
 - Semicrystalline Polymer ($T_m = 60^\circ\text{C}$)
 - Degraded by hydrolysis and micro-organisms
 - Autocatalyzed by the carboxylic acid end groups
 - Forms carbon dioxide and water as products
 - Lower degradation rate than poly-α-hydroxyesters
 - Used as Capronor™
 - Transdermal contraceptive device
 - Implanted for up to 1 year

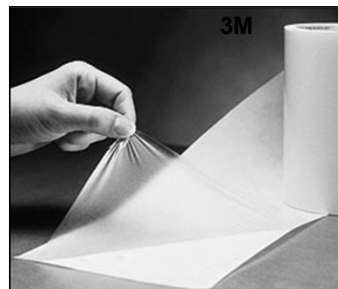


Polymers in Medicine

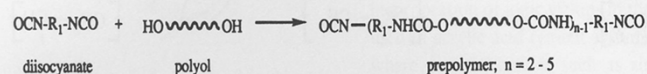
- **Co-Polymers**
 - Polyurethanes
 - Polyhydroxethylmethacrylate (pHEMA)
 - Polyesters (PGA, PLA, PLGA)

Biomaterial: Polymers

- **Polyurethanes (PU)**
 - Block copolymers (hard and soft blocks)
 - Blood biocompatible
 - Good fatigue properties
 - Used as tape, insulator coating in pacemaker leads



Polyurethane



Implantable cardioverter defibrillators (ICDs)

- ICDS for treating tachyarrhythmia
- Polyurethane-coated ICD leads
- Medtronic Sprint Quattro™ 6944
 - Steroid eluting for reduced inflammation at the tissue-electrode interface
 - Silicone insulation with PU overlay for smooth lead passage
 - Electrode composition
 - Platinum/Iridium with porous Titanium Nitride coating

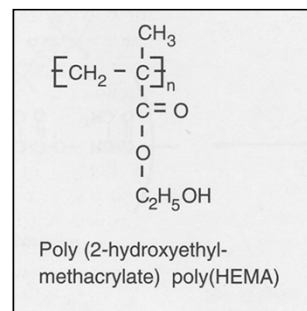


Medtronic

Biomaterial: Polymers

- Polyhydroxyethylmethacrylate (PHEMA)
 - Hydrogel material: permeable
 - Water content similar to living tissue (58% in ACUVUE®)
 - Relatively Inert and non-degradable
 - Used as contact lenses

HEMA/
MA UV
blocker



Biodegradable: Definitions

- Bioerodible: Degrade by hydrolysis
- Bioresorbable: Degrade by cellular activity
- Biodegradable: Degrade by enzymatic activity

Terms usually used interchangeably now

Bioerosion: the most general term

- Physical erosion: dissociation, dissolution
- Chemical erosion: hydrolysis (backbone & side chain)
- Enzymatic erosion: enzymatic hydrolysis and conversion
- Bacterial erosion: specific bacterial degradation

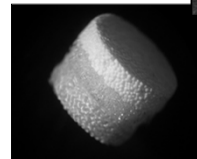
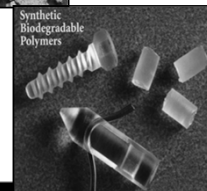
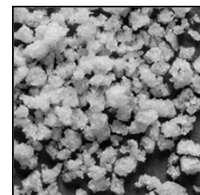
From K Leong Lecture Notes

Polymers in Medicine

• Poly- α -hydroxyesters

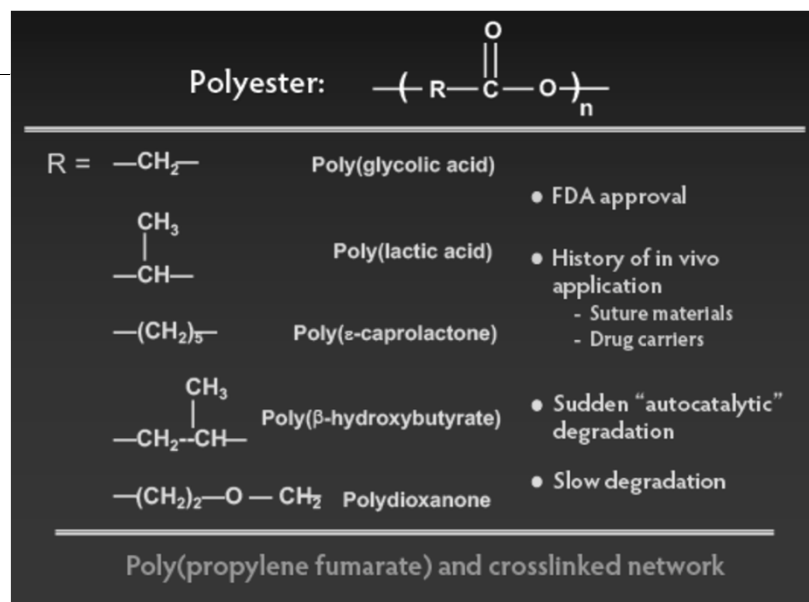
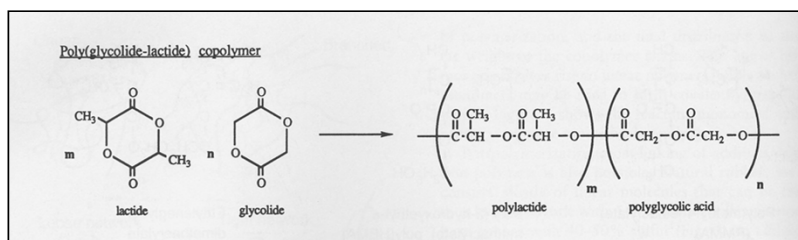
– Applications

- Cardiovascular grafts – heart valve
- Orthopedic – fixation devices, sutures
- Drug Delivery
- Tissue Engineering applications



Polymers in Medicine

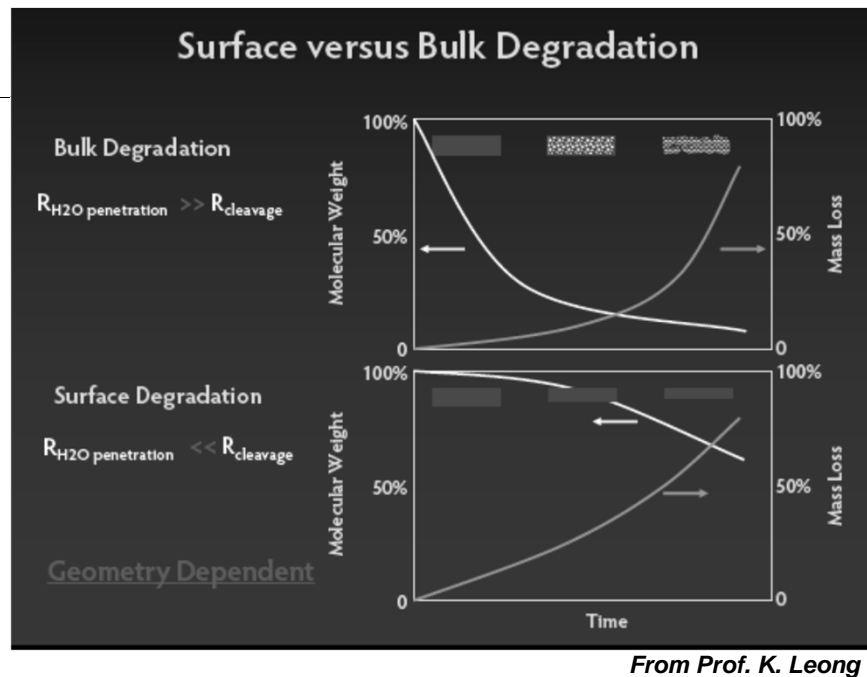
- **Poly- α -hydroxyesters**
 - Polyglycolic acid (PGA)
 - Polylactic acid (PLA, D or L or D,L)
 - Polylactic-co-glycolic acid (PLGA)
 - Synthesized via condensation polymerization



From Prof. K. Leong

Polymers in Medicine

- **Poly- α -hydroxyesters (PGA, PLA, PLGA)**
 - Random or block co-polymer
 - Surface energy depend on LA:GA ratio
 - PLA – hydrophobic
 - PGA – hydrophilic
 - Degradation products
 - Lactic acid and/or glycolic acid
 - Acidic degradation products pH <4.0
 - Process via the normal metabolic cycles



Biodegradable Polymers: Thermal

Polymer ^a	M_w	T_g (°C)	T_m (°C)	T_d (°C)	H_f (Jg ⁻¹)	X_c (%) ^b
Poly(ortho esters)						
t-CDM:1,6-HD = 35:65 [1a]	99 700	55	-	358	Amorphous	
t-CDM:1,6-HD = 70:30 [1b]	101 000	84	-	362	Amorphous	
t-CDM:1,6-HD = 90:10 [1c]	131 000	95	-	338	Amorphous	
Poly(glycolic acid) [2]	50 000	35	210	254	71	52
Poly(lactic acids) [3]						
L-PLA	50 000	54	170	242	41	30
L-PLA	100 000	58	159	235	20	15
L-PLA	300 000	59	178	255	39	29
D,L-PLA	21 000	50	-	255	Amorphous	
D,L-PLA	107 000	51	-	254	Amorphous	
D,L-PLA	550 000	53	-	255	Amorphous	
Poly(β -hydroxybutyrate) [4]						
Homopolymer (0 mol% HV) [4a]	370 000	1	171	252	51	-
Copolymer (7 mol% HV) [4b]	450 000	-1	160	243	32	-
Copolymer (11 mol% HV) [4c]	529 000	2	145	235	12	-
Copolymer (22 mol% HV) [4d]	227 000	-5	137	251	7	-
Poly(ϵ -caprolactone) [5]	44 000	-62	57	350	34	-
Polyanhydrides						
Poly(CPP-SA-ISO anhydride) [6]	31 000	-	46	297	1.2	-
Poly(SA-HDA anhydride) [7]	142 000	-	49	292	2.5	-
Poly(trimethylene carbonate) [8]	48 000	-15	-	261	Amorphous	
Polyiminocarbonates						
Poly(BPA-iminocarbonate) [10]	105 000	69	-	135	Amorphous	
Poly(DTH-iminocarbonate) [11] ^c	101 000	55	-	138	Amorphous	

^aNumbers in square brackets refer to the structures provided in the text.

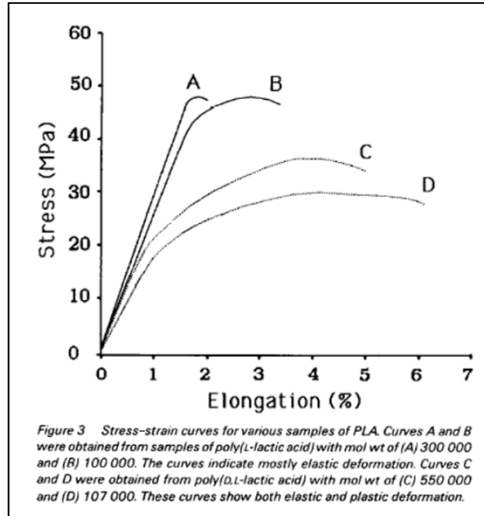
^b X_c was calculated from H_f , based on a calibration value of 72.3 J/g determined for PGA with a crystallinity of 52% (Reference 55).

^cDTH: Dat-Tyr-Hex.

Polymer Mechanical Properties

Polymer ^a	M_w	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural modulus ^b (MPa)	Yield (%)	Elongation Break (%)
Poly(ortho esters)						
t-CDM:1,6-HD = 35:65 [1a]	99 700	20	820	950	4.1	220
t-CDM:1,6-HD = 70:30 [1b]	101 000	19	800	1000	4.1	180
t-CDM:1,6-HD = 90:10 [1c]	131 700	27	1150	1250	3.4	7.0
Poly(glycolic acid) [2]	50 000	N/A	N/A	N/A	N/A	N/A
Poly(lactic acids) [3]						
L-PLA	50 000	28	1200	1400	3.7	6.0
L-PLA	100 000	50	2700	3000	2.6	3.3
L-PLA	300 000	48	3000	3250	1.8	2.0
D,L-PLA	21 000	N/A	N/A	N/A	N/A	N/A
D,L-PLA	107 000	29	1900	1950	4.0	6.0
D,L-PLA	550 000	35	2400	2350	3.5	5.0
Poly(β -hydroxybutyrate) [4]						
Homopolymer (0 mol% HV) [4a]	370 000	36	2500	2850	2.2	2.5
Copolymer (7 mol% HV) [4b]	450 000	24	1400	1600	2.3	2.8
Copolymer (11 mol% HV) [4c]	529 000	20	1100	1300	5.5	1.7
Copolymer (22 mol% HV) [4d]	227 000	16	620	750	8.5	36
Poly(ϵ -caprolactone) [5]	44 000	16	400	500	7.0	80
Polyanhydrides						
Poly(CPP-SA-ISO anhydride) [6]	31 000	N/A	N/A	N/A	N/A	N/A
Poly(SA-HDA anhydride) [7]	142 000	4	45	N/A	14	85
Poly(trimethylene carbonate) [8]	48 000	0.5	3	N/A	20	160
Polyiminocarbonates						
Poly(BPA-iminocarbonate) [10]	105 000	50	2150	2400	3.5	4.0
Poly(DTH-iminocarbonate) [11] ^c	101 000	40	1630	N/A	3.5	7.0

Mechanical Properties of PLA



Polymers in Medicine

• PLA, PGA, PLGA

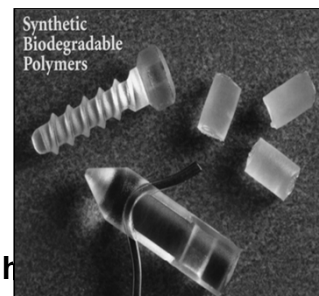
– Sutures: PGA (Dexon™), PLLGA 10/90 (Vicryl®),

– Advantages

- Biodegradable
- Biocompatible
- Found in FDA – approved devices

– Disadvantages

- Acidic degradation products may be toxic at high concentrations
 - Implantation site (vasculature, transport)
- Relatively weak mechanical properties



Polymer in THA: Replace Cartilage and Improve Fixation

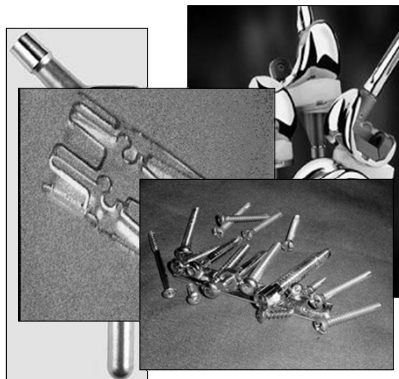


FIGURE II.5.6.9 Examples of cemented and non-cemented stems showing the plug and centralizer used with a cemented stem. (Picture courtesy of Zimmer, Inc.)

Biomaterials: Metals

Applications

Load bearing conditions
Joint replacement
Fixation device, cardiovascular



Advantages

Controllable design
Biocompatible
Blood-compatible

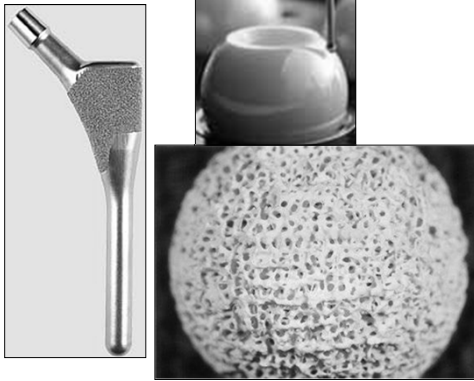
Limitations

Stress Shielding
Corrosion
Fatigue and wear
Lifetime

BIOMATERIALS: Ceramics

Applications

Load bearing conditions
Joint replacement
Orthopedic/Dental



Advantages

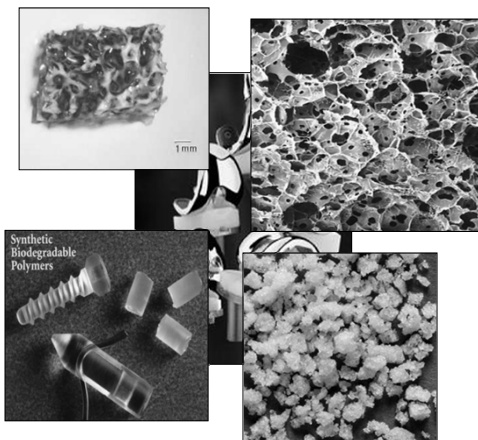
Controllable design
Biocompatible/Inert
Lubrication
Biomimetic
Bioactive

Limitations

Stress Shielding
Low fracture toughness

BIOMATERIALS: Polymers

Polyesters - sutures
Polyanhydrides-drug delivery
Polycaprolactone – drug delivery



Advantages

Controllable design
Biocompatible
Biodegradable

Limitations

Mismatch in properties
Degradation products