An introduction to bioceramics

Antonio Licciulli
Definition of biomaterials

Biomaterial is defined as a material designed to interface with biological systems to evaluate, to support or replace any tissue, organ or body function


The performance of materials used in the medical field are evaluated on their biofunctionality and biocompatibility.

The biofunctionality refers to the property that a device must have to play a certain function from the standpoint of physical and mechanical.

The biocompatibility refers to the ability of the device to continue to perform that particular function throughout the useful life of the plant and is closely related to interaction between the biomaterials and the tissues with which they come in contact.

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Classification of bioceramics

- Ceramic for biological use, are divided into the following categories:

1) **Bioinert** (Al$_2$O$_3$, glassy carbon) do not provoke or undergo reactions with the medium in contact with physiological

2) **Absorbable** (hydroxyapatite) filling materials which make it possible during and after their dissolution, reformation of the tissues

3) **Bioactive** (eg bioglass) increased phenomenon of adhesion, through stimulation of bone regrowth
Overview of the uses of ceramics in medicine

<table>
<thead>
<tr>
<th>Application</th>
<th>Material(s) used</th>
<th>Application</th>
<th>Material(s) used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthopedic load-bearing applications</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>Temporary bone space fillers</td>
<td>Trisodium phosphate, calcium and phosphate salts</td>
</tr>
<tr>
<td>Coatings for chemical bonding (orthopedic, dental and maxillary prosthetics)</td>
<td>HA, surface-active glasses and glass-ceramics</td>
<td>Periodontal pocket obliteration</td>
<td>HA, HA-PLA composites, trisodium phosphate, calcium and phosphate salts, surface-active glasses</td>
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<tr>
<td>Dental implants</td>
<td>$\text{Al}_2\text{O}_3$, HA, surface-active glasses</td>
<td>Maxillofacial reconstruction</td>
<td>$\text{Al}_2\text{O}_3$, HA, HA-PLA composites, surface-active glasses</td>
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<tr>
<td>Alveolar ridge augmentations</td>
<td>$\text{Al}_2\text{O}_3$, HA, HA-autogenous bone composite, HA-PLA composite, surface-active glasses</td>
<td>Percutaneous access devices</td>
<td>Bioactive glass-ceramics</td>
</tr>
<tr>
<td>Otolaryngological applications</td>
<td>$\text{Al}_2\text{O}_3$, HA, surface-active glasses and glass-ceramics</td>
<td>Orthopedic fixation devices</td>
<td>PLA-carbon fibers, PLA-calcium/phosphorus-base glass fibers</td>
</tr>
<tr>
<td>Artificial tendons and ligaments</td>
<td>PLA-carbon fiber composites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coatings for tissue ingrowth (cardiovascular, orthopedic, dental, and maxillofacial prosthetics)</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Type of tissue response

<table>
<thead>
<tr>
<th>Biological Behavior</th>
<th>Type of response</th>
<th>Tissue reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>toxic</td>
<td>toxicity</td>
<td>The surrounding tissue dies</td>
</tr>
<tr>
<td>unsuitable</td>
<td>rejection</td>
<td>Forms a cyst insulating the object inserted into the fabric with the presence or absence of pus</td>
</tr>
<tr>
<td>almost inert</td>
<td>acceptance</td>
<td>Develops a fibrous tissue of variable thickness</td>
</tr>
<tr>
<td></td>
<td>biological</td>
<td></td>
</tr>
<tr>
<td>active</td>
<td>biological</td>
<td>They form an interfacial bond between the fabric and material</td>
</tr>
<tr>
<td></td>
<td>acceptance</td>
<td></td>
</tr>
<tr>
<td>resorbable</td>
<td>biological</td>
<td>The material is replaced in time from the surrounding tissue</td>
</tr>
<tr>
<td></td>
<td>acceptance</td>
<td></td>
</tr>
</tbody>
</table>

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The living factories of Bioceramics

- Living organisms construct mineralized skeletons from 550 million years, biominerals are known so far about 80 and belonging to three groups
  - Calcium phosphates
  - Calcium carbonates
  - Silica (opal)
Natural Bioceramics: Mollusk Shell

- **Shell Composition is**
  - Calcium carbonate
  - Organic layer (Conchiolin, perlucin)

- **Outer CaCO$_3$ layer Crystalized in Aragonite form**
  - A hard and high strength form of CaCO$_3$ to protect it from surroundings.

- **The inner CaCO$_3$ layer is crystalized in calcite form**
  - A soft and less strength form of CaCO$_3$, and also with high %age of binding material (Conchiolin & perlucin) to comfort the animal
Biogenic silica

- Biogenic silica (BSi), also referred to as opal, biogenic opal, or amorphous opaline silica, forms one of the most widespread biogenic minerals.

- BSi is an amorphous metal oxide formed by complex inorganic polymerization processes.
Natural Bioceramics: Natural Pearls

Nacre
- Also known as mother-of-pearl, is a naturally-occurring organic/inorganic composite, composed of crystalline and organic substances forming the iridescent inner lining of the shell.

Pearl
- It forms by the foreign nuisance that entered in the shell creating discomfort for the Animal and to get himself relaxed, it coat this with nacre and thus later it becomes a pearl with time.

Mikimoto pearls
- Artificially these pearls are made by growing mollusks and adding each animal some little stone which with time appears to be a pearl.
Natural Bioceramics: Teeth

- **Tooth enamel**
  - Hardest and most mineralized substance of body, crystalline calcium phosphate is major mineral and high strength is because of large number of minerals
Bone: a natural composite material

- **The bone** tissue is a dense organic matrix, consisting mainly of collagen, which presents inorganic deposits of hydroxyapatite \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\) and calcium carbonate \(\text{CaCO}_3\).

- The bone is present in the skeleton of bony fishes and land vertebrates.

- And produced by cells called osteoblasts become osteocytes that maturing (bone cells).

- The cells are separated, but preserving minutes cytoplasmic connections between themselves and with the blood vessels.

- The bone grows and is remodeled by the action of osteoblasts and osteoclasts, which are cells responsible for the construction and bone resorption, and everything is under hormonal control.
Natural Bioceramics: Bones Composition

- Hydroxyapatite (A natural Bioceramic inorganic)
- Collagen Fibers (Organic)
- Living Cells and blood vessels
The different types of bone cells

- **Osteoblast** - found within the bone, its function is to form the tissue and minerals that give bone its strength.

- **Osteoclast** - a very large cell (20-100 μm) formed in bone marrow that can have till 10 nuclei; its function is to absorb and remove unwanted tissue.

- **Osteocyte** - found within the bone, its function is to help maintain bone as living tissue.

- **Fat cells** and **hematopoietic cells** are found within the bone marrow.

- **Ematopoietic cells** are those that produce blood cells.
**Anatomy and function of bone**

Beneath the hard outer shell of the periosteum there are tunnels and canals through which blood and lymphatic vessels run to carry nourishment for the bone.

What are the functions of bone?

- Bone provides shape and support for the body, as well as protection for some organs.
- Bone also serves as a storage site for minerals and provides the medium (marrow) for the development and storage of blood cells.
Bioglass

- Bioglass is a commercially available family of bioactive glasses, composed of SiO2, Na2O, CaO and P2O5 in specific proportions.
- The proportions differ from the traditional soda-lime glasses in low amount of silica (less than 60 mol.%), high amount of sodium and calcium, and high calcium/phosphorus ratio.
- High ratio of calcium to phosphorus promotes formation of apatite crystals; calcium and silica ions can act as crystallization nuclei.

- Professor Larry Hench developed Bioglass at the University of Florida in the late 1960s. He was challenged by a MASH army officer to develop a material to help regenerate bone, as many Vietnam war veterans suffered badly from bone damage.
Bioglass 45S5

- Bioglass 45S5, one of the most important formulations, is composed of SiO2, Na2O, CaO and P2O5.

- The 45S5 name signifies glass with 45 wt.% of SiO2 and 5:1 ratio of CaO to P2O5. Lower Ca/P ratios do not bond to bone.

- The key composition features of Bioglass is that it contains less than 60 wt% SiO2, high Na2O and CaO contents, high CaO/P2O5 ratio, which makes Bioglass highly reactive to aqueous medium and bioactive.
Mechanical properties of bioglass

- High bioactivity is the main advantage of Bioglass, while its disadvantages includes mechanical weakness,

- Low fracture resistance due to amorphous 2-dimensional glass network.

- The bending strength of most Bioglass is in the range of 40–60 MPa, which is not enough for load-bearing application.

- Its Young's modulus is 30–35 GPa, very close to that of cortical bone, which can be an advantage. Bioglass implants can be used in non-load-bearing applications, for buried implants loaded slightly or compressively.
Bond formation from bioglass

1) Replacement of the alkali ions between the glass and the hydrogen of the solution

2) Rupture of the siloxane bonds with the formation of a large surface concentration of silane groups

3) It forms a glass surface with a double protective film of calcium phosphate gel and rich in silicon

4) the film amorphous calcium phosphate to form hydroxyapatite crystals crystallizes

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Time dependence of bone bonding
Interfacial bond strength over time

![Graph showing the time dependence of interfacial bond strength for various fixation systems in bone.]
1. When PerioGlas is exposed to organic fluids, one realizes an ion exchange at the surface of the material.

2. The exchange of ions causes the release of sodium ions and calcium, with the formation in a few minutes dil a layer of silica gel on the surface of PerioGals.

3. Rapidly forms a layer of calcium phosphate on silica gel, which crystallizes in idrosi-carbonate-apatite replaced, indistinguishable dall'apatite natural bone tissue and dental.

4. The cells produce collagen, which is incorporated into the newly formed surface layer, establishing a membership with the interface speed yields PerioGlas. The osteoblast bone deposited on this layer.

"Clear" The difference in bone regeneration.
Bone growth through the Bioglass

- Surgical site of a periodontal defect of 8 mm
- Note how PerioGlas easily adapts to the bone defect
- Return after 6 months, filling is evident on bone mesiobuccal and messa surfaces
CaP materials

- Calcium phosphate materials have been widely used as implant materials since significant research in the early 1970’s demonstrated the biocompatibility and utility of these materials as implants.

- Within this class of calcium phosphates known as orthophosphates, there exists a tremendous diversity of chemical and structural variations. A high degree of biocompatibility, minimal if any inflammatory response or foreign body response and no evidence of local or systemic toxicity.

- This is because the calcium and phosphate ions are the most common ions in the body and these compounds allow direct bonding of soft tissue or bone cells.
CaP in detail

- **Calcium Hydroxyapatite** [Ca10(OH)2(PO4)6]
  - CaHA is generally used in applications where a more durable form of material is required. HA must meet the requirements of ASTM F1185 and ISO 13779. Stoichiometric hydroxylapatite has a Ca/P ratio of 1.67.

- **β Tricalcium Phosphate** [Ca3(PO4)6]
  - β TCP has a higher solubility than HA and is generally selected for applications where dissolution of the implant is desired. Our β TCP meets the requirements of ASTM F1088. Stoichiometric tricalcium phosphate has Ca/P ratio of 1.5.

- **Biphasic Calcium Phosphate**
  - Biphasic CaP is a HA/β TCP combination. The most commonly used forms are 60% HA/40% β TCP and 85% HA/15% β TCP. Biphasic CaPs has to meet the requirements of the combined ASTM F1185 and ISO 13779 and the STM F1088. Biphasic CaPs have Ca/P ratios of 1.5 to 1.67.

- **Fluorapatite**
  - Fluorapatite is very similar to hydroxylapatite but some of the hydroxyl groups that define the HA are replace with fluorine ions.
Order of solubility

Fluoroapatite

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$

Beta-Tricalcium Phosphate $\text{Ca}_3(\text{PO}_4)_2$

Alpha-Tricalcium Phosphate $\text{Ca}_3(\text{PO}_4)_2$

Amorphous Calcium Phosphate

Tetracalcium Phosphate $\text{Ca}_4\text{P}_2\text{O}_9$
Select the right CaP material

- The only calcium phosphate that is stable in contact with water is hydroxylapatite (HA)\(_2\), and this is the form found naturally as bone mineral.
- In applications where a stable, but biocompatible material is desired, HA is the material of choice.
- If the goal is remodeling, then more soluble forms might be of interest.
- Regardless of the composition, all calcium phosphates are osteoconductive.
- Osteoconduction helps to increase the activity of bone forming cells (osteoclasts).
- Bone cells preferentially grow inside of porous materials. An ideal scaffold consists of interconnected pores in the size range of 50 to 400 microns\(_6,7,8\).
- In contrast, for applications where inertness is required such as soft tissue augmentation, dense, nonporous, nearly insoluble HA particles with a minimal surface area are ideal.
HA Powder: Precipitation method

1 L of 0.3M H₃PO₄ in double-distilled water - Ammonia was added till a constant pH 10 was obtained.

1 L of 0.5M Ca(NO₃)₂.4H₂O prepared in double-distilled water, was slowly added maintaining a Ca/P ratio of 1.67.

The solution was maintained at a constant pH 10 by adding small amount of ammonia.

The precipitates were filtered out, washed repeatedly and dried at 65°C for 24 h.

The calcined powder was grinded using a planetary ball mill using zirconia balls for 30 min and sieved through 80 mm mesh.

Calcination in air at 900°C for 60 min - heating rate 5°C/min.

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\[ \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \]

\[ \text{Ca(NO}_3\text{)}_2\cdot 4\text{H}_2\text{O in water} \]

Add \( \text{NH}_3 \) till pH-10 stir

\[ \text{Mix} \]

Add \( \text{NH}_3 \) till pH-10

Keep for ageing 1 day

Drying and sintering

\[ \text{H}_3\text{PO}_4 + 3\text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_3\text{PO}_4 + 3\text{H}_2\text{O} \]

\[ 6(\text{NH}_4)_3\text{PO}_4 + 10\text{Ca(NO}_3\text{)}_2\cdot 4\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{OH} \quad \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \]
HA particle features

DLS: particle size ~ 500 nm

TEM: particle size ~ 150 nm

The BET specific surfaces was equal to 12 m$^2$/g that corresponds to an estimated equivalent spherical diameter ($d_{\text{BET}}$) of 159 nm.

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Hydrothermal synthesis of hydroxyapatite

\[5 \text{Ca(OH)}_2 + 3 \text{H}_3\text{PO}_4 \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH} + 9 \text{H}_2\text{O}\]
Wollastonite /HA composite

HA
d=150nm

Acicular wollastonite
d=20-50μm
SBF test results

bioactivity after one week

Formazione di nuovi e più densi strati di apatite

Superficie del dispositivo, dopo di 7 giorni in SBF a 37°C, composta di Ca e P, mentre non vi è alcuna traccia di Si
Risultati: Caratterizzazione polveri

Analisi XRD

Elevato grado di purezza
Elevato grado di cristallinità

Marina Carrozzo, SIB 2012
Prosthesis for Hip and knee

- The replacement of a head joint with artificial components back to the beginning of 1900.

- The first hearing was made by Smith-Petersen with: glass, metal derivatives of celluloid
Prosthesis for Hip and knee: ceramic and titanium

Nelle protesi d’anca la palla femorale di $\text{Al}_2\text{O}_3$ è legata al tronco metallico.
Prosthesis for Hip and knee

- Improvements in durability and compatibility of materials for hip replacements
- New designs to help patients of any age
- Choices of hip joint materials:
  - Metal-on-polyethylene
  - Metal-on-metal
  - Ceramic-on-ceramic
  - Ceramic-on-polyethylene
Prosthesis for Hip and knee: Hip Replacement Components

- Acetabular component - consists of two components
  - Cup - usually made of titanium
  - Liner - can be medical grade plastic, metal or ceramic

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Prosthesis for Hip and knee: Ceramic-on-Poly Overview

- Cup made of Marathon cross-linked poly
- Ball made of Biolox Delta Ceramic
  - Composite zirconia aluminum ceramic

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Prosthesis for Hip and knee: Ceramic-on-Ceramic Overview

- Ball and cup made of alumina ceramic
- Shorter clinical history
- Not toxic to the body

*Not currently available from DePuy Orthopaedics.*

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Ceramic femoral heads offer:

- Excellent compatibility within the body
- Good mechanical performance
- Very hard and scratch-resistant
- Chemical and temperature stability
Prosthesis for Hip and knee: Ceramic-on-Ceramic Wear

- 100-200 times less wear rate than other materials in mechanical tests
- Resistance to deformation and surface scratching
- Less particle debris around joint available to get into the body
Friction and wear in total hip replacement

- The wear of $\text{Al}_2\text{O}_3$ to $\text{Al}_2\text{O}_3$ is 10 times lower than the metal-polyethylene;
Bioceramic coatings by plasma spray
Hydroxyapatite composite structures obtained by sol gel process

- HA/TiO$_2$ coating
Lower jaw prosthesis with plasma spraied coating

- A high-temperature plasma spray was used to cover the jaw part with a bioceramic.
Natural foams

Bone tissue

Marine (porifera)

Bread

Vegetable

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Macroporous foams
Classification of ceramic foams

- Open cells
- Closed cells
Classification of ceramic foams

- ceramic strut

- Strut detail showing cavity left by templating material
Mechanical properties of strut based foams

- Relative density
  \[ \frac{\rho}{\rho_s} = C_1 \left( \frac{t}{L} \right)^2 \]

- Relative modulus
  \[ \frac{E}{E_s} = C_2 \left( \frac{t}{L} \right)^4 = C_3 \left( \frac{\rho}{\rho_s} \right)^2 \]
Foam materials

Strength - Density

Inaccessible region

Potentially accessible region

Potentially accessible region


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Porosity Vs. pore size

Mechanical properties


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Foams manufacturing


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# Ceramic Foam Filters for Metal Casting

<table>
<thead>
<tr>
<th>Type</th>
<th>Foam-Zr</th>
<th>Foam-SiC</th>
<th>Foam-AL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>70%~85%</td>
<td>85%~90%</td>
<td>85%~90%</td>
</tr>
<tr>
<td>Pore Size</td>
<td>10PPI~60PPI</td>
<td>10PPI~60PPI</td>
<td>10PPI~60PPI</td>
</tr>
<tr>
<td>Density</td>
<td>1.3~1.5 g/cm³</td>
<td>0.45~0.7 g/cm³</td>
<td>0.4~0.7 g/cm³</td>
</tr>
<tr>
<td>Surface area</td>
<td>&gt;1.0X10⁴ cm²/g</td>
<td>&gt;2.0X10⁴ cm²/g</td>
<td>&gt;5.0X10⁴ cm²/g</td>
</tr>
<tr>
<td>Compression Strength</td>
<td>≥1.5MPa</td>
<td>≥1MPa</td>
<td>≥1MPa</td>
</tr>
<tr>
<td>Operation Temperature</td>
<td>1720°C</td>
<td>1500°C</td>
<td>1200°C</td>
</tr>
<tr>
<td>Thermal Stability</td>
<td>Not break after 5 times thermal shock testing</td>
<td>Not break after 5 times thermal shock testing</td>
<td>Not break after 3 times thermal shock testing</td>
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<tr>
<td>1100°C~Room Temperature</td>
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<tr>
<td>Application</td>
<td>Stainless Steel, Alloy</td>
<td>Iron</td>
<td>Cuprum, Aluminum</td>
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<tr>
<td>Material</td>
<td>Zirconia</td>
<td>Silicon Carbide</td>
<td>Aluminium Oxide</td>
</tr>
</tbody>
</table>

![Images of ceramic foam filters](www.ceramic-foam.com)
Porous burners

Heat transport for stabilization of the reaction zone

Heat removal out of the reaction zone by radiation and conduction of the solid body as well as by convective heat transfer and dispersion

Heat transport in axial direction by radiation, conduction, dispersion, and convection

Combustion region

Ignition temperature

Preheating region

Fresh gas mixture


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Polymer replica Si-SiC foams

- Foam coating with a slurry
- 1st pyrolysis
- Corners smoothing with a ceramic polymer and 2nd pyrolysis
- Si infiltration

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ROLE OF BIOMATERIAL SCAFFOLD

- before being resorbed, it acts as a matrix for cell adhesion in order to adjust some processes / cellular functions (e.g., mitosis, synthesis, migration, contraction) of the cells in vivo or of seeded cells in vitro

- reinforces the defect, while maintaining its shape and prevents the distortion of the surrounding tissue

- acts as a barrier to prevent the entry of surrounding tissue in the defect
Bone

Bone is living tissue that makes up the body's skeleton. There are three types of bone tissue, including the following:

- **compact tissue** - the harder, outer tissue of bones.
- **cancellous tissue** - the sponge-like tissue inside bones.
- **subchondral tissue** - the smooth tissue at the ends of bones, which is covered with another type of tissue called cartilage. Cartilage is the specialized, gristly connective tissue that is present in adults, and the tissue from which most bones develop in children.

Together, **compact** and **cancellous** tissues are called the **periosteum**.
Bone composition

- *Cellular* (osteoblast, osteoclast, osteocyte)
- ECM mineralized

**Organic**
- (collagen and proteoglycans)

**Inorganic**
- (crystals HA-like)

<table>
<thead>
<tr>
<th>Componenti</th>
<th>Quantità in peso %</th>
</tr>
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<tbody>
<tr>
<td>Matrice inorganica</td>
<td>69</td>
</tr>
<tr>
<td>Matrice organica di cui:</td>
<td></td>
</tr>
<tr>
<td>collagene</td>
<td>90-96</td>
</tr>
<tr>
<td>altro</td>
<td>4-10</td>
</tr>
<tr>
<td>Acqua</td>
<td>9</td>
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</tbody>
</table>

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Construction of bone substitutes

The field of TISSUE ENGINEERING has emerged with the goal to bridge the gap between the need and the lack of ideal bone graft


- CELLS
- SCAFFOLD
- GROWTH FACTORS
- POROSITY
- DEGRADATION RATE
- MECHANICAL PROPERTIES

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Design criteria of the scaffold

**MORPHOLOGY**

- High degree of porosity (> 80%)
- Highly interconnected pore
- Control pore size

**Large pores:**
for adhesion and cell proliferation (e.g., osteoblast):
- 150-300 µm
- 100-400 µm

**Small pores:**
For the transport of nutrients and removal of waste substances and release of growth factors
- 0.1-10 µm

**MECHANICAL PROPERTY**

Mechanical response adequate to support the hydrostatic pressure and to preserve the geometry of the pores required for cell growth during the phases of in vitro culture (or the efforts in vivo).

**BIOLOGICAL REQUIREMENTS**
*(Chemical Composition)*

- Biocompatibility
- Osteoconductive
- Osteoinductive
- Degradation rate comparable with the rate of formation of new tissue.

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Design criteria of the scaffold

MORPHOLOGY

POROSITY

MECHANICAL PROPERTY

BIOLOGICAL RESPONSE

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Manufacturing Process

“Green” coated foams ready for sintering
Manufacturing Process

Sintered foam parts
Bioceramic Scaffolds

Advantages

✓ Biological compatibility and activity
✓ Less stress shielding
✓ No disease transmission
✓ Unlimited material supply

Disadvantage

✓ Brittleness – not for load bearing applications

Materials commonly used

✓ Hydroxyapatite
✓ Tricalcium phosphate
✓ Glass ceramics (Ca-P-Si system)

• Ca_{10}(PO_4)_6(OH)_2
• Main component of bone and tooth minerals
• Ca/P ratio : 1.67
• Excellent biocompatibility
• Chemically similar to bone

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Fabrication Processes for Porous Scaffolds

- **PARTICULATE LEACHING**
  - (agenti porogeni)

- **PHASE SEPARATION**
  - (freeze drying, phase inversion, cocontinuous blends)
  - MA - J BIOMED MATER RES. (2001)

- **EMULSION (MICROSFERE) SINTERING**

- **GAS FOAMING**
  - NAM - J BIOMED MATER RES. (2000)

- **SPONGE REPLICATION**

- **MODULATION OF MICROSTRUCTURE**

- **RAPID PROTOTYPING**
  - (Fused Deposition Modeling FDM
    Selective Laser Sintering SLS
    Three-dimensional Printing Stereolithography SL)
  - HUTMACHER - J BIOMED MATER RES. (2000)

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HA Scaffold: Sponge replica method

- Slurry preparation (70% solid load)
- PU Sponge (density of 30 Kg/m³, 25 ppi) impregnation and squeezing
- Sintering of the infiltrated sponge at three sintering temperature (1200, 1250, 1300°C)

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Replication Method
Raw Material-Reticulated Foam

Poliurethan sponge

SEM micrograph
Manufacturing with sponge replica method

- Green” coated foams ready for sintering

- Sintered foam parts
HA microstructure of starting powders

**Composition**

* Hydroxyapatite

**In-house powder**

**Commercial**

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XRD analysis
HA morphology at SEM

Scaffold

Sponge

In-house powder

Commercial

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HA morphology vs temperature

a) and d) \( T_{\text{sint}} = 1200^\circ\text{C} \)

b) and e) \( T_{\text{sint}} = 1250^\circ\text{C} \)

c) and f) \( T_{\text{sint}} = 1300^\circ\text{C} \)

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Microstructure of hydroxyapatite before and after the onset of sintering

Microstructural evolution of hydroxyapatite as a function of sintering temperature, below 1000 °C there is a substantial modification of the size of the powders
Sintering, grain growth and coarsening

Microstructural evolution of hydroxyapatite obtained from a green of nanopowders (University of Salento) varying the sintering temperature, evidence of abnormal growth of the grains from 1300 °C
HA Scaffold compressive strength

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