Toughening of bio-ceramics scaffolds by polymer infiltration

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General abstract

The life expectancy improvement and the research of a constantly better quality of life make prosthesis more and more necessary. Hip-joint replacement is one of the most mature fields of bone substitution and the clinical success associated to the use of ceramics led to the implantation of more than 4 millions ceramic components worldwide since 1990, with a strongly growing market. Current synthetic bone substitutes market is about 40 million € in Europe, with an expected 12% yearly increase (www.frost.com).

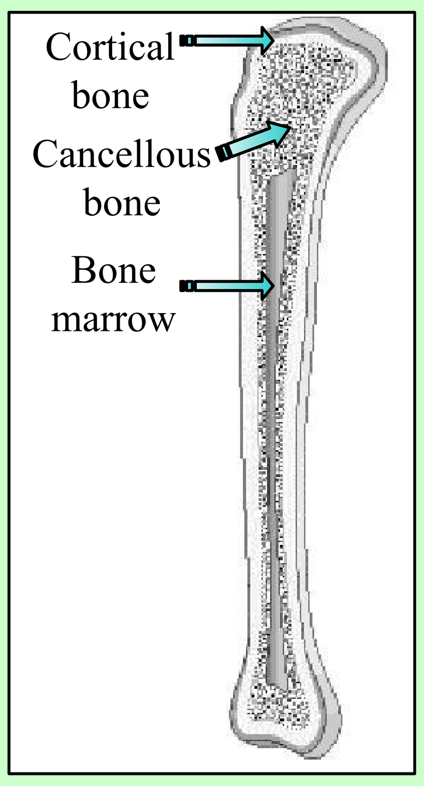
Highly porous scaffolds with open structure are today the best candidates for cancellous bone substitution. As compared to autografts, synthetic bone substitutes involve less invasive surgery and are available in large quantities. As compared to xenografts, the risk of rejection is much less important and the transmission of diseases is avoided. Current synthetic scaffolds are processed from ceramic or polymer, but a better combination of mechanical and biological properties may be achieved with a composite structure.

In this work, polycaprolactone – coated alumina scaffolds were produced and characterized to validate the concept of polymer-ceramic composites with increased fracture resistance. It was found that the elastic behaviour of the composites is controlled on the first order by the ceramic scaffold, while the fracture energy mainly depends on the polymer phase. A 10 to 20 vol.% addition of polycaprolactone to alumina scaffolds led to a 7 to 13-fold increase of the fracture energy. SEM observations showed that toughening is due to crack bridging by polymer fibrils.

Technical abstract

Alumina scaffolds were sintered using a foam-replication technique. An open porous structure was achieved with ~ 70% porosity and 150 µm mean pore size. The polymer coating was obtained by infiltrating the scaffold with either a polycaprolactone (PCL) solution in chloroform or a polycaprolactone nanodispersion in water. The latter was obtained by an emulsion-diffusion technique. Dynamical Young modulus measurements and four-point bending tests were conducted to evaluate the composites mechanical properties.

Purpose: cancellous bone substitution



Bone: a porous composite material

- inorganic ⟹ ceramic
- organic ⟹ polymer

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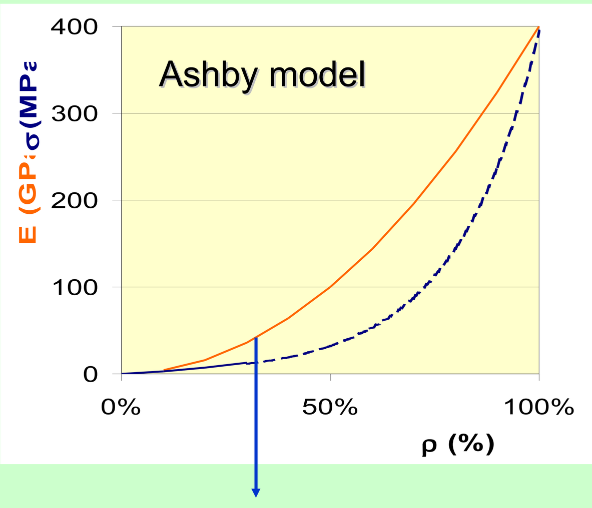
Ceramic scaffolds infiltrated with polymer

Ceramic ⟹ ↑ E, bioactivity

Polymer ⟹ ↘ brittleness



At 30% density :
E = 30 GPa
σ_R = 12 MPa

MODEL MATERIALS:

- Ceramic: ALUMINA
- ρ = 3.98 g/cm³
- E = 400 GPa
- σ_R = 400 MPa
- K_{Ic} = 3.5 MPa·m$^{1/2}$

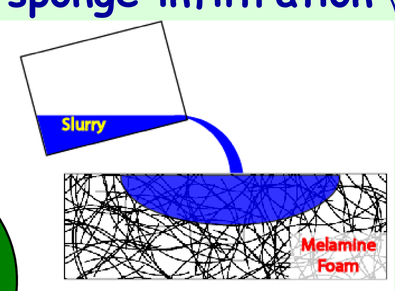
- Polymer: POLYCAPROLACTONE
- ρ = 1.145 g/cm³
- M_w = 80000 g/mol
- σ_R = 33 MPa
- ε_R = 800%
- KV = 350 J/m

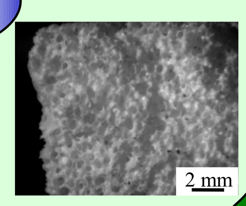
Methods

Processing of porous alumina: foam-replication technique

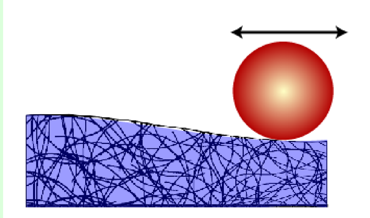
Slurry: Al_2O_3 powder + Solvent (H2O) + Dispersant (Darvan C) → Dispersion

Polymer sponge infiltration





Homogenization



Sintering: 50°C/h → 600°C 5h (Debinding) → 300°C/h → 1600°C 2h30 → 300°C/h

PCL Solution in chloroform — or — → Infiltration → Drying → **Composite**

Processing of polycaprolactone nanoparticles: emulsion-diffusion technique

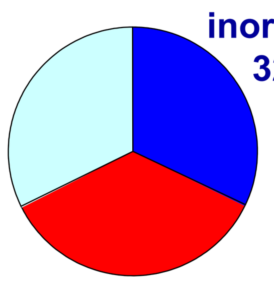
PCL in ethyl acetate (EtAc) + Pluronic (surfactant) in water

- Sonication → Nanoparticles (PCL+EtAc stabilized by Pluronic) in suspension in water
- Dilution → Removal of the EtAc from the nanoparticles
- Evaporation → Concentration of the suspension

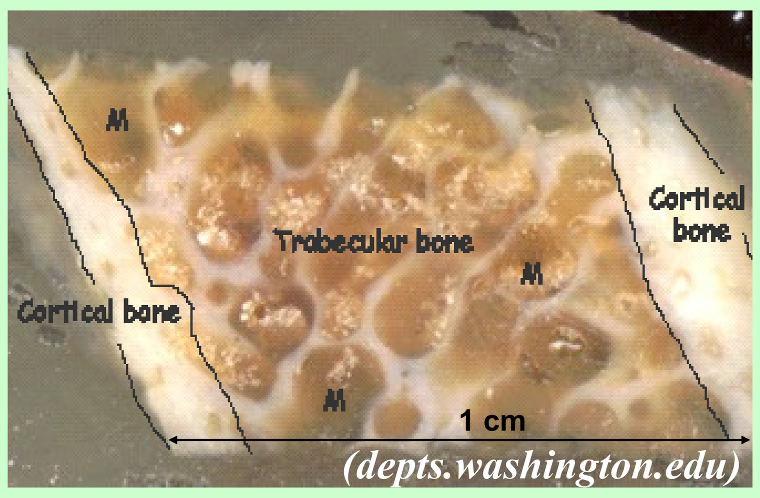
Size of PCL nanoparticles: 150 nm

Microstructure: a porous composite material

BONE

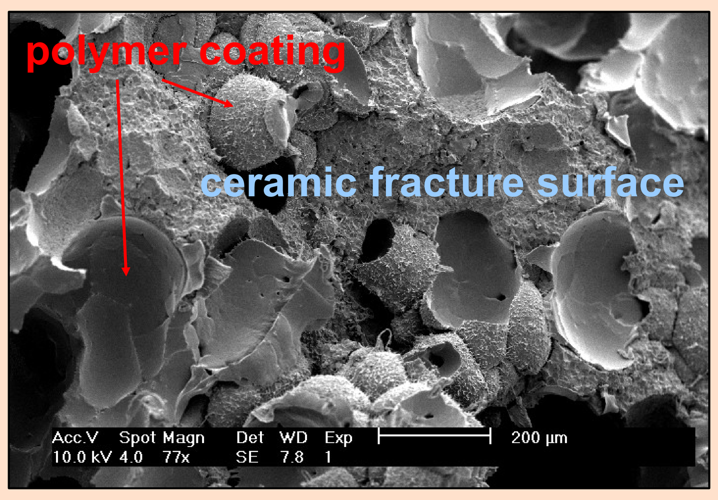


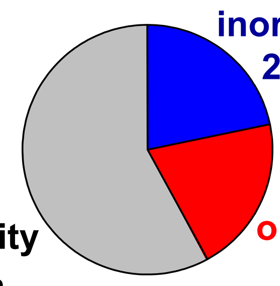
Inorganic/organic ratio = 1:1



(depts.washington.edu)

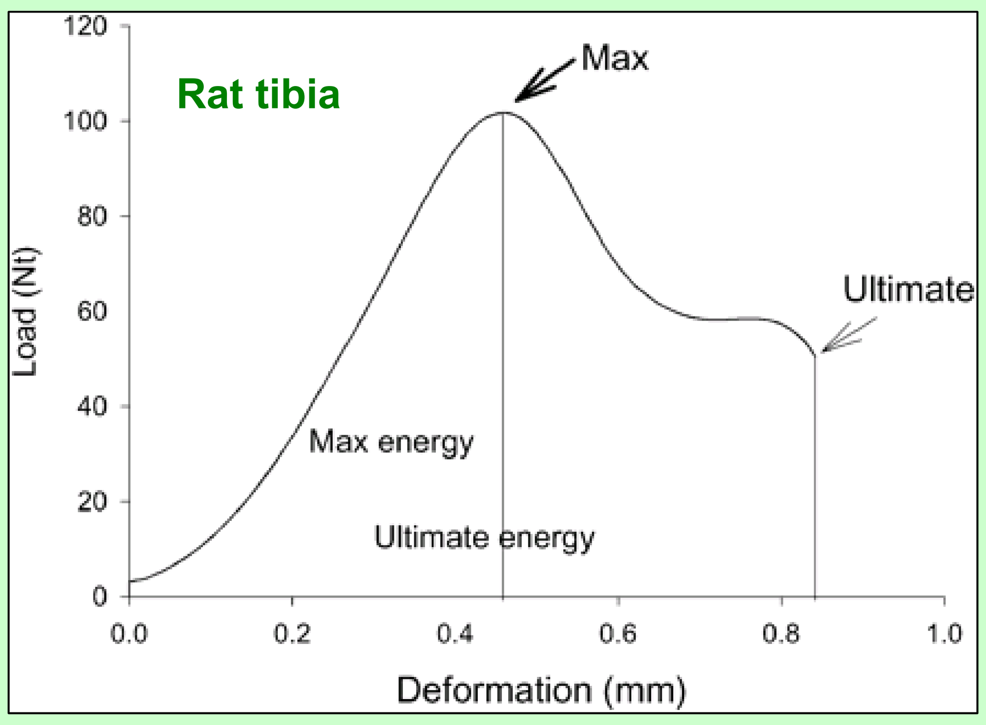
COMPOSITE



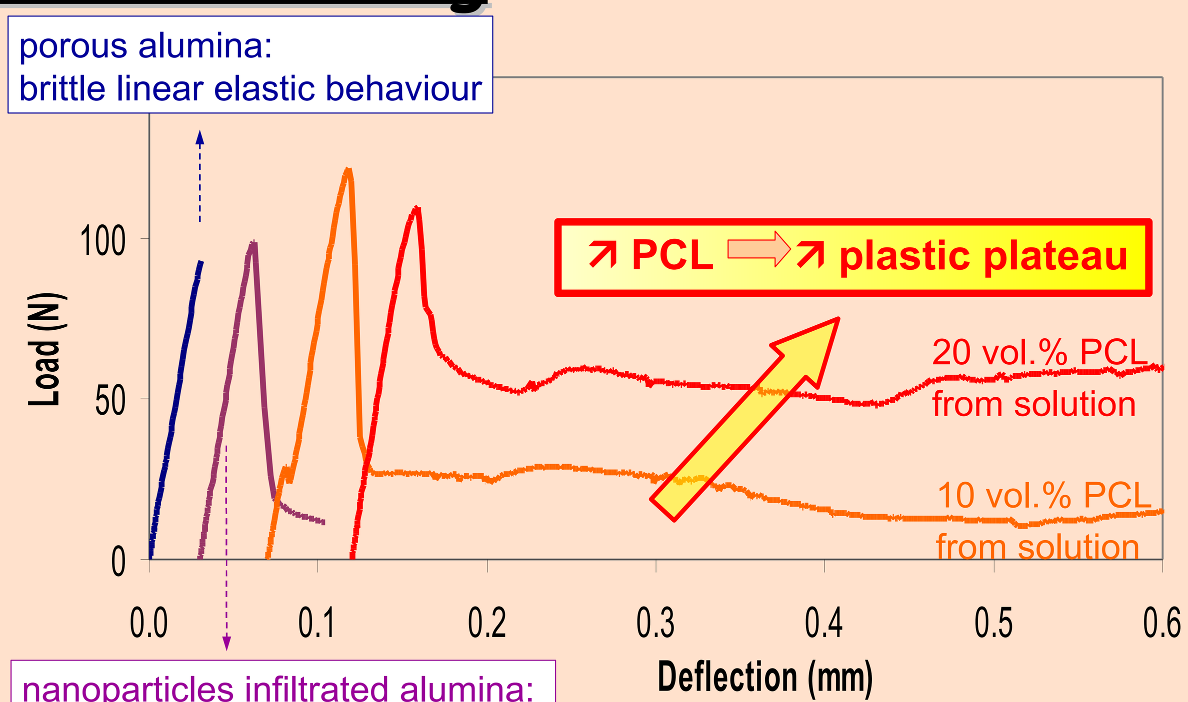


Inorganic/organic ratio = 1:1

Mechanical properties: bending

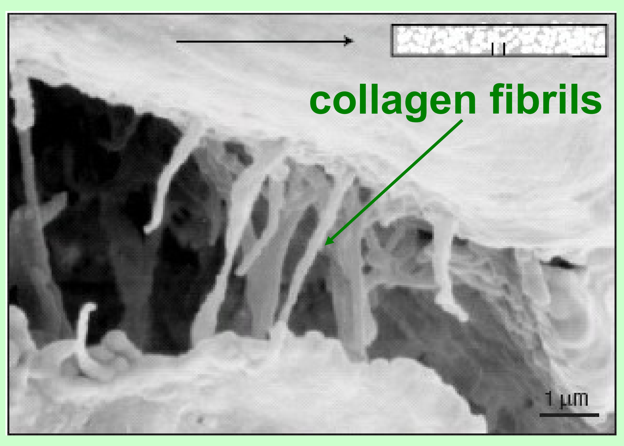


Huang TH, Lin SC, Chang FL, Hsieh SS, Liu SH, Yang RS. Effects of different exercise modes on mineralization, structure, and biomechanical properties of growing bone. J Appl Physiol 2003; 95: 300-307.

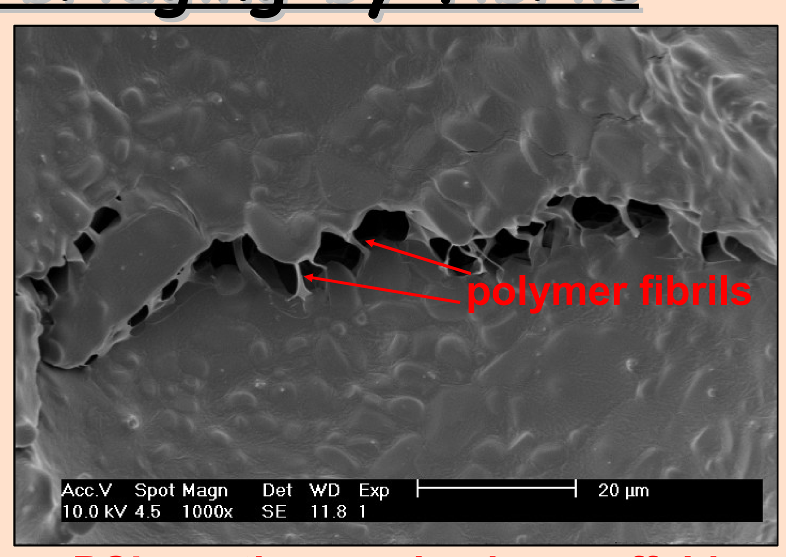


Reinforcement mechanism: crack bridging by fibrils

Human bone



Nalla RK, Kinney JH, Ritchie RO. Mechanical fracture criteria for the failure of human cortical bone. Nat Mater 2003; 2: 64-168.



PCL coating on alumina scaffold

Glossary

Autograft: tissue transplanted from one part of the body to another in the same individual (www.medterms.com).

Xenograft: surgical graft of tissue from one species to an unlike species (www.medterms.com).

Bone substitute: synthetic material with optimized structure, biocompatibility and mechanical characteristics to match those of natural bone.

Alumina (Al_2O_3): bioinert and biocompatible ceramic.

Cellular solid: material presenting an open and interconnected porosity (synonyms: sponge, scaffold, foam with open porosity).

Macropore: pore of >100 µm diameter, suitable for bone ingrowth.

Slurry: dispersion of a powder (i.e. ceramic) in a solvent.

Foam-replication: technique used to obtain ceramic scaffolds by infiltrating a polymer foam with a ceramic slurry; the final structure will correspond to a replica of the initial polymer structure.

Polycaprolactone ($C_6H_{10}O_2$): biocompatible polyester.

Pluronic: non-ionic surfactant; triblock copolymer poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide).

Fibril: fibre-like material; collagen (organic part of bone) is a typical fibrillar structure.

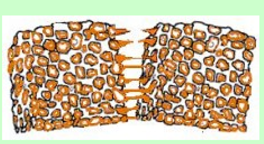
Emulsion-diffusion: technique used in polymer nanospheres processing; a surfactant enables an emulsion first, then the diffusion of the solvent leads to a dispersion of particles in water so that solvent-free particles are obtained.

Conclusions

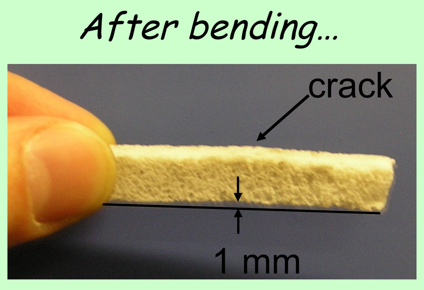
Good similarities with cancellous bone for:

- **macrostructure**: interconnected open macroporous composite structure;
- **mechanical properties**: presence of a ductile plateau and similar force-deflection curve;
- **reinforcement mechanims**: crack bridging by organic fibrils (collagen in bone, polycaprolactone in alumina scaffolds).

Bridging PCL fibrils during bending



After bending...



Prospects

MECHANICS
- Better understanding of the key parameters of toughness (porosity, quantity of polymer, interface, …);
- Better understanding of the interface role.

BIOLOGY
- Choice of a biodegradable polymer;
- Optimisation of the biodegradation kinetics of the composite;
- Optimisation of the mechanical and biological properties for specific bones substitution.