Dynamic Mineralization: Multidirectional, Low-Temperature, and Rapid Process to Deposit Hydroxyapatite Microfilms on Polyether-Ether-Ketone for Osseointegration

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Statement of purpose

- Chronic lower back pain is the leading cause of disability in the world[1].
- Spinal fusion is a common procedure to treat the disease[2].
- Hydroxyapatite coatings are used to enhance the osseointegration of intervertebral spacers used in spinal fusion.
  - Coating strategies are typically unidirectional, high-temperature, or require extended incubation.
- Additively manufactured intervertebral spacers with complex structural features represent a paradigm shift (**Fig.1**) in the field and the functionality of coatings could be greatly enhanced by the incorporation of biologics.

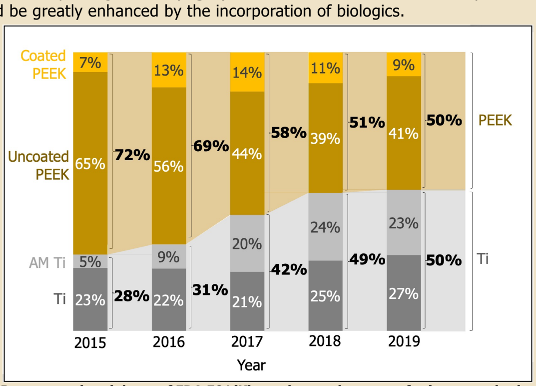

Fig. 1: Percentage breakdown of FDA 501(K) regulatory clearances for intervertebral spacers[3]

Objective

To develop a coating method that is simultaneously multidirectional, low-temperature, and rapid.

Methods

Fabrication

- **Precursor $CaCO_3$ layer (Fig. 2):**
  - A base layer of $CaCO_3$-NP is deposited on polyether-ether-ketone substrates with and without embedded hydroxyapatite particles (PEEK-OPTIMA™ HA and PEEK-OPTIMA™) by convective self-assembly (CSA) at 130°C.
  - The base layer is then cold-sintered by immersion in supersaturated $Ca(HCO_3)_2$[4] at 130°C for 10 min to induce heterogeneous nucleation and growth of $CaCO_3$ on the coated substrate.
- **Final hydroxyapatite coating (Fig. 2):**
  - The precursor $CaCO_3$ layer is converted to carbonate apatite by dissolution-recrystallization processes in phosphate buffered saline (PBS)[5].

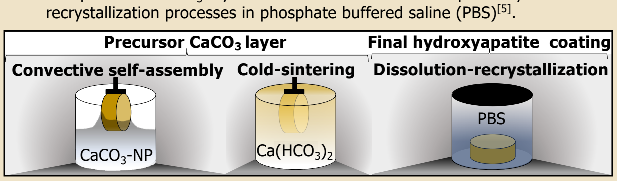

Fig. 2: Coating process

Characterization

- Scanning electron microscopy (**SEM**) was performed to assess the morphology and thickness of the coating.
- X-ray diffraction (**XRD**) was used to determine the phase composition.
- X-ray photoelectron spectroscopy (**XPS**) and Fourier Transform Infrared Spectroscopy (**FTIR**) was used to determine the calcium-to-phosphorus (Ca/P) ratio and chemical composition.
- Scratch test was used to determine the tribological properties of the coating.

Acknowledgements

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References

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Results

Morphology

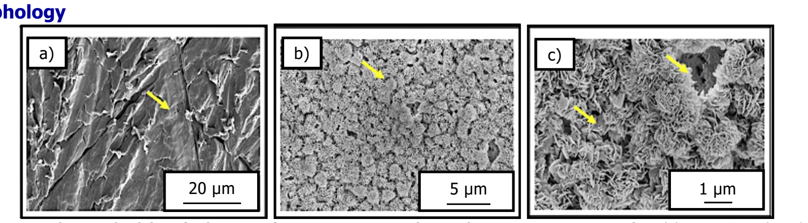

Fig. 3: SEM micrographs (planar) of uncoated PEEK-OPTIMA™ and coated PEEK-OPTIMA™ HA. a) Undulations on roughened surface; **b)** Coating comprised of rosette clusters; **c)** Rosette clusters comprised of nanoplatelets and adjacent voids .

Conformal coating

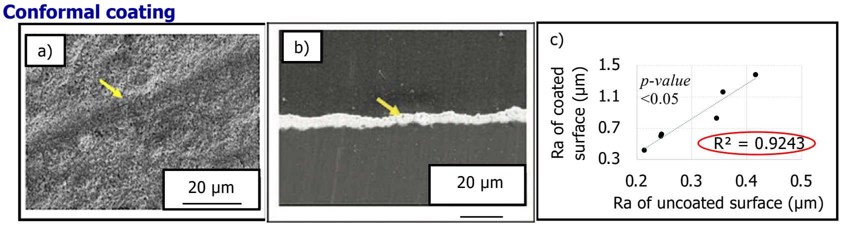

Fig. 4: a) SEM micrographs of the coating on PEEK-OPTIMA™ in planar view showing undulations that mirror the roughened substrate; **b)** Cross section view of the coating on PEEK-OPTIMA™; **c)** Strong correlation between R_a of uncoated and coated surface of samples (PEEK-OPTIMA™ HA and PEEK-OPTIMA™).

Chemical composition

- XRD patterns indicated that the coating is comprised of carbonate apatite[3].
- XPS spectra indicated that the calcium-to-phosphorus (Ca/P) ratio of coated PEEK-OPTIMA™ HA and PEEK-OPTIMA™ were 1.6[3].

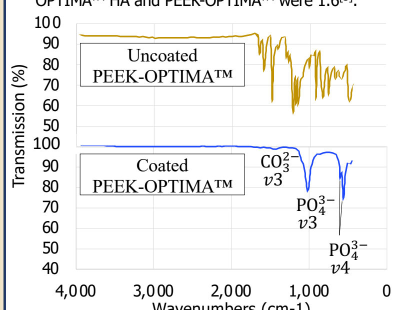

Fig. 5: FTIR spectra of uncoated and coated PEEK-OPTIMA™. Only peaks characteristic of carbonate apatite were detected on the coated sample.

Adhesion strength

Deposition method	Immersion in SBF		Dynamic mineralisation
CaP phase	Amorphous apatite	Hydroxyapatite*	Bone-like apatite
Substrate	Polyurethane	PEEK	PEEK-OPTIMA™ HA, PEEK-OPTIMA™

*No XRD phase identification provided

Fig. 6: Comparison of analogues of adhesion strength / coating performance for biomimetic and dynamic mineralization coatings on soft substrates[6][7]

Conclusions

- A contiguous and conformal coating of carbonate apatite was formed by a process that is simultaneously multidirectional, low-temperature, and rapid.
- The coating is comprised of nanoplatelets of carbonate apatite comparable to bone mineral. The nanocrystalline coating also encapsulates the substrate.
- The coating's nanostructure exhibits outstanding tribological performance to withstand frictional stresses characteristic of the spacer implantation process (an order of magnitude higher than comparable wet chemical and low-temperature techniques).

Significance

- The low-temperature technique enables the incorporation of antimicrobial and osteo-inductive biologics to address key causes of implant failure: prosthetic infection and non-union.
- Versatile technique suitable for different substrate types
- Flexibility to form hydroxyapatite or carbonate apatite by tailoring PBS concentration.
  - Hydroxyapatite clinically relevant, whereas carbonate-rich hydroxyapatite is bioresorbable by osteoclasts