

Amphiphilic Copolymers at the Air-Water Interface for the Preparation of Calcium Phosphate Thin Films

O. Casse¹, A. Taubert²

¹ University of Basel, Basel, Switzerland. ² University of Potsdam, Golm, Germany.

INTRODUCTION: A series of poly(n-butyl acrylate)-block-poly(acrylic acid) in a Langmuir monolayer system is presented as a good template to generate calcium phosphate (CaP) thin films. Those hybrid flexible (later on you say that they are not flexible, see purple text below) films offer controlled thickness and organic-inorganic ratio. As fixed horizontal surfaces offer simpler conditions for study and modeling of processes such as charge interaction, complexation, and crystal nucleation when compared to colloids, those films can be considered as a step towards the coating of organic particles and surfaces.

METHODS: A KSV Langmuir-Blodgett system with moving barriers assigned to surface pressure control and automatic dipping for solid substrates was used to create the films. Subphases consisted of buffered calcium solutions in a Teflon trough. After the polymer was cast on the water surface from a small volume of a chloroform solution, time was left for the calcium to complex with the acrylic acid moieties. The phosphate counter-ion was then added with a syringe at the bottom of the trough through the polymer monolayer.

Optical, transmission/scanning electron and atomic force microscopies were used to characterize the films.

RESULTS: Films were obtained only at basic pH, whereas at low pH the polymer monolayer would keep most of its original elasticity. Organic/inorganic ratio within the films were controlled by 3 parameters: the polymer monolayer stress ("solid" or "liquid" phase of the Langmuir isotherm), the supersaturation of the subphase and the mineralization time. In all cases at basic pH the elastic polymer monolayer was rendered stable over time and compact (unable to extend upon decompression) and brittle when transferred to solid substrates.

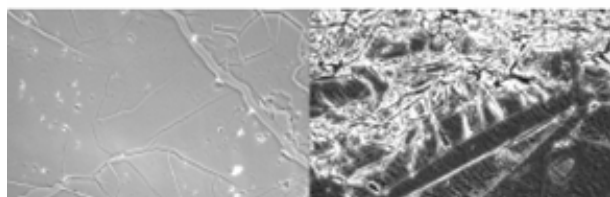


Fig. 1: optical microscopy images of a dried

hybrid CaP-polymer film transferred on glass (left: bright field, right: dark field, wrapped film after collapse), width 300µm.

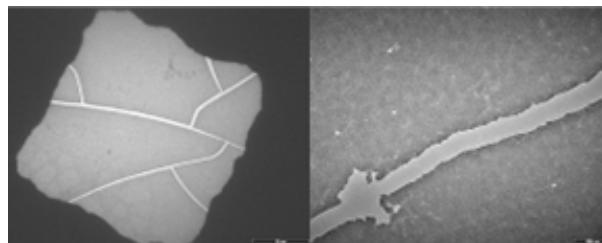


Fig. 2: Transmission electron microscopy images (left width: 60µm, right width: 2µm)

DISCUSSION & CONCLUSIONS: The wide-scale monolayer homogeneity of the films shown above speak in favour of a mechanism of mineralization where the CaP was nucleated by the polymer carboxylic acid moieties (fast with respect to the further growth of CaP). Other mechanisms including nucleation of CaP in solution before aggregation under the polymer monolayer would result in very inhomogeneous mineral layers in terms of thickness and density, non of which has been observed in TEM or optical microscopy.

REFERENCES: ¹ E. DiMassi (2002), *Langmuir, Polymer-Controlled Growth Rate of an Amorphous Mineral Film Nucleated at a Fatty Acid Monolayer*, **18**, pp 8902-8909. ² E. Eghbali, O. Colombani (2006), *Langmuir, Rheology and Phase Behaviour of poly(n-butyl-acrylate)-block-poly(acrylic acid) in aqueous solution*, **22**(10), pp 4766-4776.

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