
Investigating Biomimetic Calcium Phosphate and Carbonate Mineral Formation within Multilayered Biopolymer Films using Small Angle Neutron Scattering.

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We have produced a multilayered template using chitosan and iota-carrageenan as a substrate for mineralised calcium phosphate or calcium carbonate through exposure to a simulated body fluid (SBF) or simulated sea-water (SSW), respectively. A film consisting of 120-bilayers of these alternating charged biopolymers was successfully dip-coated onto microscope slides and mineralised. The films produced showed striking iridescence due to the periodically alternating nanoscale structure, a golden sheen was observed when the unmineralised film was swollen and transitioned to a blue colour upon mineralisation. Cryo-SEM and TEM images showed the nanoscale structure responsible for the observed iridescence can be attributed to the dense interfaces between the chitosan and iota-carrageenan bilayers.

Small angle neutron scattering measurements were conducted using QUOKKA at the Australian Nuclear Science and Technology Organisation (ANSTO). These measurements revealed a scattering feature, between 0.002-0.006 Å⁻¹, exclusively for mineralised samples. The large structure (150 nm) responsible for this feature was modelled as lamellar objects attributed to the interfaces between the chitosan and iota-carrageenan layers. This feature becomes more prominent as the nSLD contrast against D₂O increases with more mineralised samples. The power law slope of low-q scattering is also shown to increase from 2.2 to 3.8, from an unmineralised to the most mineralised film. This result shows that increase in the overall smoothness and rigidity of the biopolymer film is achieved with mineralisation. A high-q scattering feature was observed between 0.01-0.05 Å⁻¹, arising from spacing between the polymer mesh within the swollen multilayered film. However, this feature was shown to have no significant changes upon mineralisation. These parameters were compared with films mineralised with different heavy metal ion treatments (Cu²⁺, Zn²⁺, Pb²⁺ and Cd²⁺) to observe the effect on mineral nucleation, which is of concern for shell-fish growth near industrial areas. Additionally the effect of acidic molecules (L-Glutamic acid, Citric acid and poly-acrylic acid) was also measured, to access the mineralisation influence of calcium ion adsorption on carboxylic acid groups.