Peculiarities of alginate gellation triggered by calcium ions in the presence of hydroxyapatite particles

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INTRODUCTION: Hydroxyapatite (HAP), a crucial constituent of natural bone mineral, significantly enhances the osteoconductivity of alginate hydrogels (AH) in biodegradable composites mimicking the mineral composition, porosity, and mechanical properties of bone tissue. Ionic crosslinking of sodium alginate hydrogels with Ca^{+} ions result in the rapid formation of egg-box structures, leading to enthalpy-driven hydration and dehydration mechanisms observable through swelling and subsequent shrinkage of the crosslinked aerogel. The fast shrinkage induces non-linear sizing of water-containing pockets, impacting the unilinear pore size distribution of freeze-dried aerogels, thereby influencing the porosity and mechanical properties of the final scaffolds.

EXPERIMENTAL: Kinetics of gel-sol phase transformations of 2 % AH gel with fixed amount of mixture of hydroxyapatite (HAP) in 2 % $CaCl_2$ water bath with mass ratios of HAP to $CaCl_2$ (100:0, 35:75, 50:50, 75:35 and 0:100 respectively) was observed on a plate-plate Anton Paar 302 rheometer. Viscoelastic measurements were conducted in linear viscoelastic region (LVE) with constant strain (γ = 0.1 %) and varying angular frequencies (ω= 0.1, 0.5 and 1 rad. s^{-1} that simulated different mixing rates. Once that viscoelastic parameters (Transient complex viscosity (η^{*+}), Storage modulus (G') and Loss modulus (G'')) reached their plateau values, samples were removed from rheometer were freeze dried for morphological observation with Scanning electron microscope (SEM) Hitachi S-4700, (Chiyoda City, Tokyo, Japan).

RESULTS AND DISCUSSION: Kinetic of Ca+ ions induced crosslinking of alginate hydrogels is a complex, non-linear process governed by colloidal forces and change in system enthalpy, dependent on ions concentration and mixing frequency. Stepwise process of adsorption of Ca^{2+} ions onto HAP particles and their release into sodium alginate hydrogel results in nonlinear time-dependent crosslinking kinetic dependent on suspension ions concentration and mixing rate followed by reversable hydration and dehydration. Formation of smaller egg-box structures that contain interlocked water is observable through change in rheological parameters and in structure of freeze-dried aerogels.

CONCULSIONS: Step-wise adsoption of Ca^{+} ions ono HAP particles in $CaCl_2$ suspension, enables their controlled release once the suspension is poured into sodium alginate hydrogel and formation of uniform pores size distribution.

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