

Optimization of Alginate Templated Polypyrrole Composites for Tissue Engineering Scaffolds

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Statement of Purpose: Alginic acid and its salts (alginates) are linear carbohydrates that are typically extracted from seaweed. The material is a block copolymer of β -D-mannuronate (M) and α -L-guluronate (G)¹, with the latter residue playing an important role in the presence of certain metal ions having a charge of two or greater. Ca^{2+} , for example, acts as an efficient cross-linker, which results in a gel with variable viscoelasticity. The rigidity of the material is largely a function of the ion density and distribution in the host polymer. We are interested in alginate templated composites of containing polycationic intrinsically conducting polymers (ICPs), particularly polypyrrole PPy, that do not need additional dopants such as polystyrene sulfonate (PSS). These composites are being developed as 3D printable intrinsically conducting polymer scaffolds for tissue engineering.

Methods: Sodium alginate (ALG) dissolved in 50mL of deionized water to a concentration of 2% (w/v) was used as the base for these constructs. Pyrrole and sodium persulfate (NaPS) were added and stirred at for an optimized time of 6h in an ice bath to allow the alginate templated polymerization of polypyrrole (PPy). This was followed by 48h of dialysis for purification. To ensure full polymerization of pyrrole, a slight excess (2.5X instead of the stoichiometric 2.33X molar equivalents) of sodium persulfate was used. Variables investigated included concentration of pyrrole, concentration of sodium bicarbonate, and reaction temperature. Resultant materials were analyzed using FTIR with an ATR attachment, rheometer for viscosity, 4-point probe for conductivity, compression testing, SEM, and a pH meter.

Results: Early polymerized materials exhibited decreased solution viscosity, fragile hydrogels upon crosslinking, and poor, powdery cast films. IR spectroscopy revealed the presence of a carbonyl peak (ca. 1725 cm^{-1}), indicating the oxidative degradation of alginate, which explained the degraded material properties. Acid produced during the pyrrole polymerization was found to decompose the NaPS to other, more kinetically aggressive oxidants that attacked the alginate. Therefore, a sodium bicarbonate buffer was optimized to allow the formation of robust, flexible films upon drying. As expected, increasing the polypyrrole content did have a significant impact on the viscosity of ALG-PPy solutions ($p=0.02$ and 0.03 for 2eq and 5eq PPy, respectively). Both 3 and 5 eq. of polypyrrole had higher conductivities compared to the 1 eq. PPy; however, the increase in polypyrrole concentration from 3 to 5 equivalents did not exhibit a significant increase. Compression testing indicated that the stiffness as well as the ultimate compressive strength

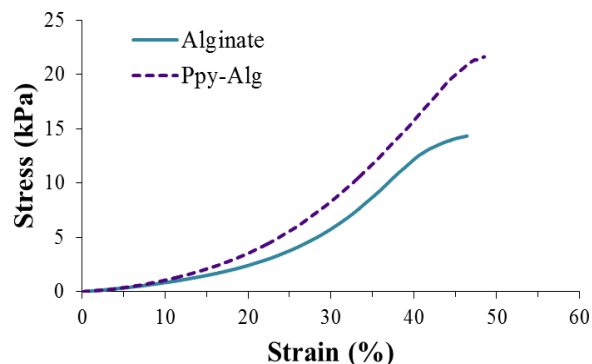


Figure 1: Compression Testing of ALG and 1eq ALG-PPy Hydrogels using Shimadzu EZ-L (1mm/min; RT; 10N load cell)

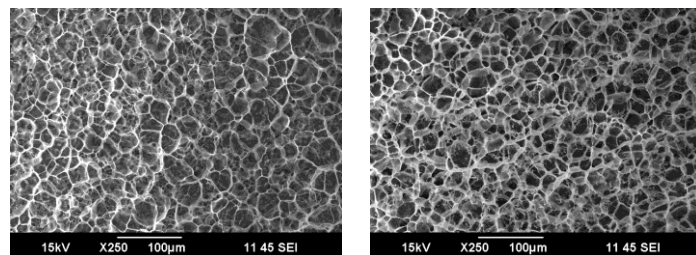


Figure 2: SEM (250X Mag) of calcium crosslinked ALG (L) and ALG-PPy(R) hydrogels.

increases with incorporation of PPy into the ALG matrix (Fig 1). SEM images corroborate the ALG templating of the PPy as no distinctive aggregates of the PPy are evident (Fig 2).

Conclusions: Control of pH is key for protecting alginate from oxidation during the template-guided polymerization of pyrrole. By controlling the reaction environment, higher quality constructs (increased conductivity and hydrogel formation) can be achieved. Additional investigation into further increasing conductivity and generating 3D printed free-standing hydrogel structures using this material are underway.

References:

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