Sustainable Reinforcement of 3D Printable Material via Bio-Inspired Mineralization

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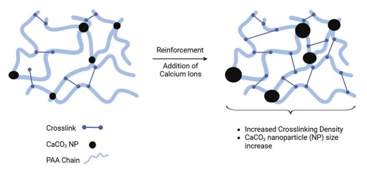
DAVID AND LORRAINE FREED UGRS UNDERGRADUATE RESEARCH SYMPOSIUM

Introduction

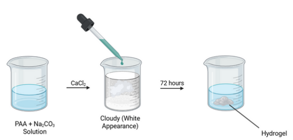
Hydrogels inspired by natural systems are gaining interest for their self-healing and tunable mechanical properties. However, many current formulations are not compatible with 3D printing or require complex crosslinking methods to do so. This study investigates a simple, bioinspired hydrogel system composed of poly(acrylic acid), calcium ions, and carbonate ions, which undergoes spontaneous reinforcement via crosslinking and mineralization. Our objective is to evaluate the printability and mechanical reinforcement of this hydrogel when exposed to additional calcium ions.

Current Understanding of Ion-Induced Reinforcement



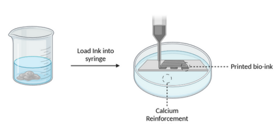
Materials & Methods

Hydrogel Synthesis Procedure



1) 1.25% (w/v) sodium carbonate, Na2CO3, is mixed with 3.75% (w/v) polyacrylic acid, PAA.
2) The above solution is added to 2.5% (w/v) calcium chloride dihydrate, CaCl2•2H2O, where calcium carbonate particles are formed and cross-link with the PAA over a period of 72 hours.

Standard 3D Printing Procedure



The raw hydrogel, 72 hours after synthesis, is washed in DI water to remove all unbound ion and particle impurities through simple diffusion. After the washed ink is placed into the bioprinter and a CAD file with the desired printing path is uploaded, the ink is printed into a petri dish containing a shallow calcium ion bath. When the ink comes in contact with the calcium bath, diffusion causes calcium ions to enter the ink, reinforcing it and allowing it to retain its shape.

Results and Discussion

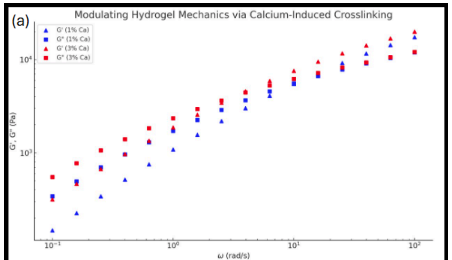


Fig 1a. Storage (G′) and loss (G″) moduli of PAA-based hydrogels measured across a range of angular frequencies (0.1–100 rad/s) at 1% strain using a 20 mm parallel plate geometry. Samples were exposed to either 1 wt% or 3 wt% $CaCl_2$ solutions prior to testing.

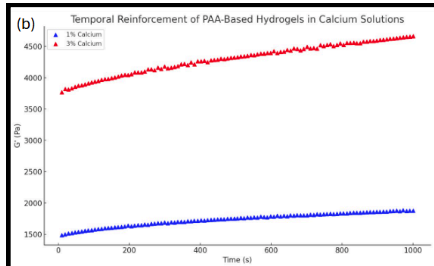


Fig 1b. Temporal reinforcement of hydrogels during a 15-minute time sweep at 1% strain using a 20 mm parallel plate geometry. Gels were exposed to either 1 wt.% or 3 wt.% $CaCl_2$ solutions prior to testing.

The increase in both storage and loss moduli with an increase in calcium bath concentration, from 1% to 3%, is depicted in **Figure 1 (a)**. Rheological experimentation determined that increasing calcium bath concentration improves the reinforcement of the hydrogel material, suggesting that printing into a calcium bath with a higher concentration will generate a more structurally supported scaffold. **Figure 1 (b)** reveals that even after being removed from the calcium bath, a reinforcement in moduli continually occurs for at least 15 minutes, alluding that some portion of the reinforcement mechanics are due to a slower mineralization process.

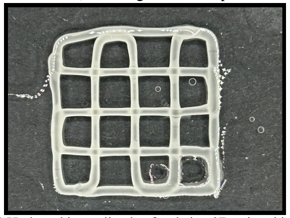


Figure 2 Hydrogel immediately after being 3D printed into 3% (w/v) calcium bath. The print retained its shape, and the was prevented from flowing into itself through the reinforcement process

Using the knowledge gained from rheology, and the confirmation that higher calcium bath concentrations are more ideal for 3D printing conditions, the ink was printed into a calcium bath with concentration of 3% (w/v) (**Figure 2**). As hypothesized, the reinforcement mechanism which occurred on contact and in soaking with the calcium ions allowed the scaffold to retain its shape, and remained unchanged even weeks after the experiment concluded. Under the guide of the rheology results, 3D printing and reinforcing of the ink was successful.

Conclusion and Future Work

Our findings show that the bio-inspired hydrogel undergoes quantifiable stiffening upon exposure to excess calcium ions, which is confirmed by an increase in storage modulus (G′) over time during rheological testing. This supports our hypothesis that calcium ions contribute to mechanical reinforcement through enhanced ionic crosslinking and potential mineralization within the gel network. These results highlight the potential of this system for applications requiring tunable mechanical properties, such as 3D printing, tissue scaffolds, or load-adaptive biomaterials. Future work will involve assessing the printability of the hydrogel across varying calcium concentrations and conditions and conducting further analyses to confirm the presence of inorganic mineral phases.

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References