Towards fully biobased porous polymer materials obtained from 3D-printed biomass-derived hydrogels

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1. INTRODUCTION AND AIM

Environmental concerns over fossil-based superabsorbent polymers have driven the search for bio-based alternatives[1,2]. Bio-based hydrogels derived from proteins and polysaccharides offer sustainable options, combining biodegradability with functional gelation and absorption properties[3,4]. This work explores the tailoring of porous structures derived from biomass-based hydrogels by dispersing a protein (BSA) into an alginate matrix, followed by calcium crosslinking and processing through 3D gel extrusion printing and freeze-drying. The study reveals critical formulation and crosslinking relationships influencing final properties, aiming to assess these systems' potential to rival synthetic absorbents in single-use applications.

2. METHODOLOGY

Bio-based ink preparation

Bioink was prepared by dissolving BSA in water, followed by sodium alginate dispersion. The resulting solution was crosslinked with calcium chloride to form a stable hydrogel encapsulating the protein.

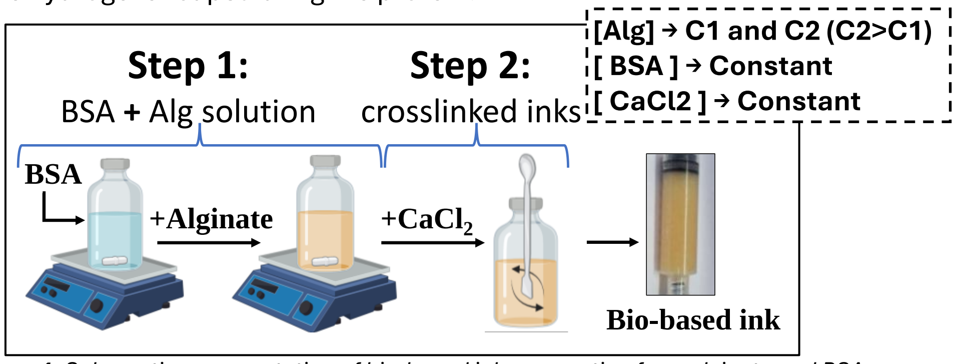

Figure 1. *Schematic representation of bio-based ink preparation from alginate and BSA.*

Porous Hydrogel Structures via 3D Printing

Scaffolds were fabricated using bio-based inks via 3D printing, followed by freezing at two rates: slow freezing at –20 °C and rapid freezing in liquid nitrogen (–195 °C). Porous structures were obtained through subsequent freeze-drying.

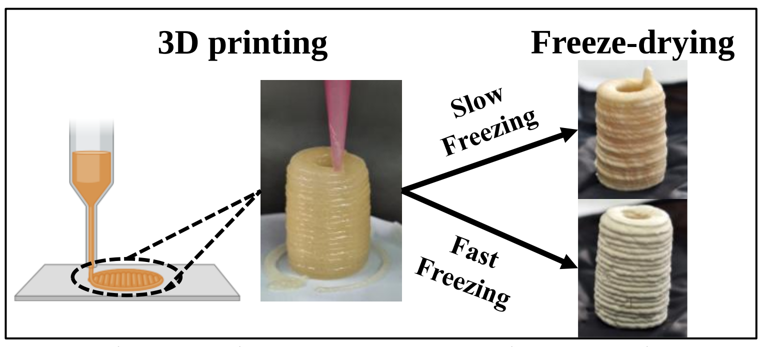

Figure 2. *Formation of 3D-printed porous structures using gel extrusion and freeze-drying.*

3. RESULTS

Rheological properties towards printability of bio-based inks

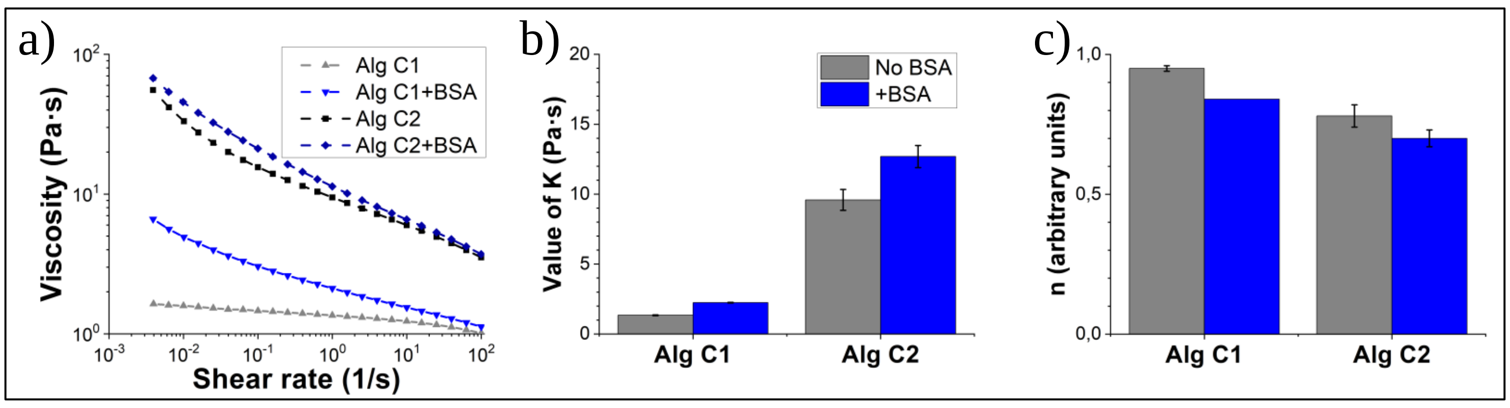

Figure 3. *Rheological characterization of alginate-BSA mixtures: (a) viscosity vs. shear rate, (b) consistency index (K), (c) flow index (n).*

Viscosity flow curves (viscosity vs. shear rate) were fitted using the Power Law model.

$$\eta = K\dot{\gamma}^{n-1}$$

Higher alginate content and BSA addition increase viscosity and enhance shear-thinning behavior. At high shear rates, two viscosity plateaus appear, varying with alginate concentration.

+ CaCl$_2$

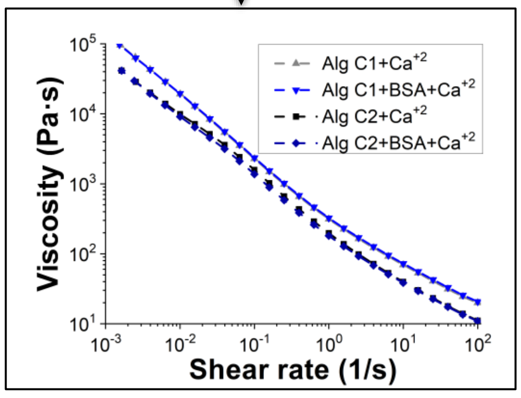

Figure 4. *Viscosity curves after calcium crosslinking of alginate-BSA inks.*

BSA *has no impact* into viscosity flow curves post-calcium crosslinking!

Table 1. *Consistency index (K) and flow index (n) as function of Alginate*

Samples	K (Pa·s)	n
...using Alg C1	≈250	≈0,22
...using Alg C2	≈460	≈0,20

All samples exhibit a strong shear-thinning behavior. Higher alginate concentration leads to increased viscosity.

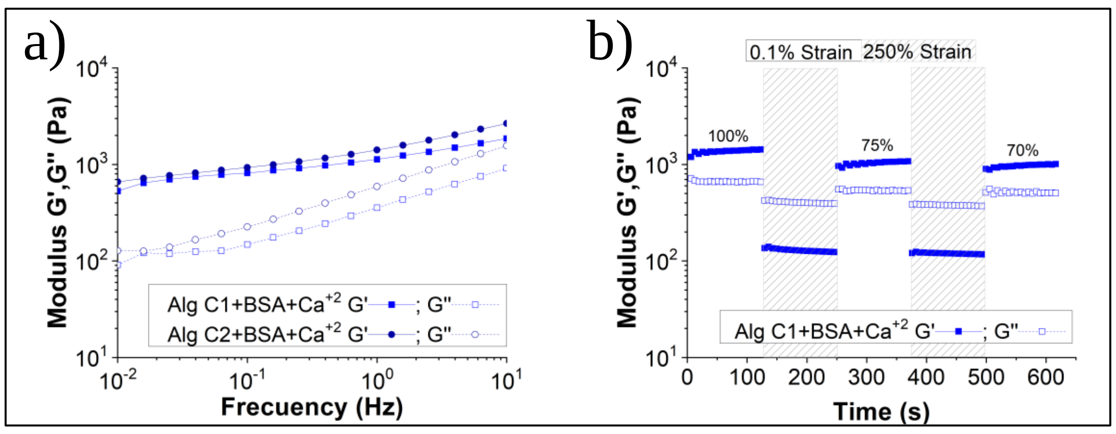

Figure 5. *Viscoelastic properties of BSA containing inks: a) moduli vs. frequency, (b) recovery after high-strain deformation.*

The viscoelastic moduli show clear frequency dependence, reflecting the dynamic nature of ionic crosslinking. Similar G′ values across samples suggest that calcium concentration plays a dominant role over alginate content. Recovery tests indicate ~75% modulus recovery, pointing to partial structural restoration after shear.

Liquid absorption of 3D printed bio-based porous structures

Porous structure morphology

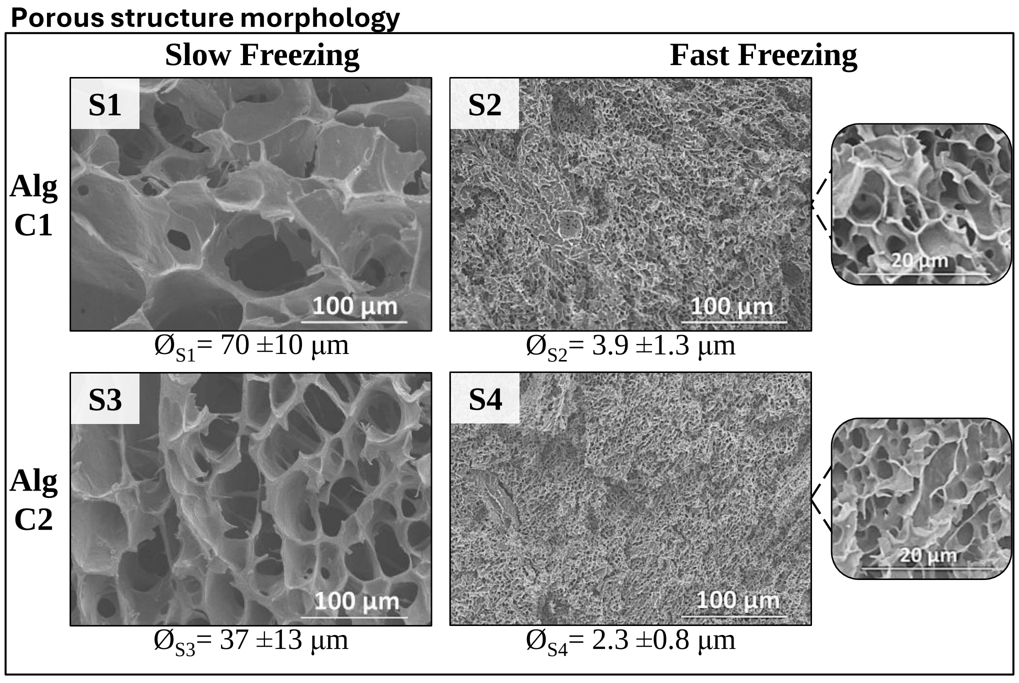

Figure 6. *SEM images of BSA containing freeze-dried scaffolds*

Higher solid content slightly reduces pore size due to increased sample density. Rapid freezing results in smaller pores by promoting greater ice nucleation.

Liquid absorption

The free swelling capacity (FSC) was ensured as the liquid uptake after 30 min, calculated from the sample's dry (W_d) and wet (W_f) weights.

$$FSC = \frac{W_f - W_d}{W_d} \; [g/g]$$

Absorption was tested using two model liquids: a polar solution (0.9 wt% saline) and a non-polar liquid (rapeseed oil).

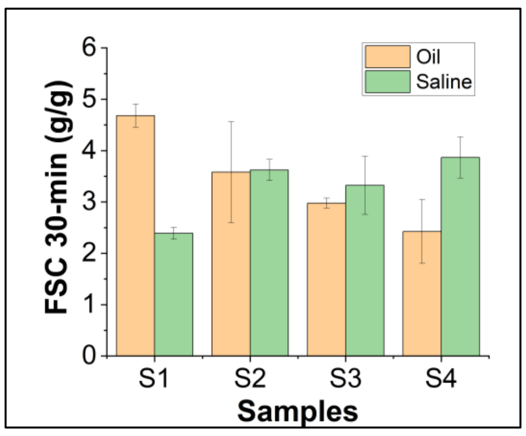

Figure 7. *Absorption capacity of scaffolds in rapeseed oil and saline solution*

Oil absorption increases with larger pores in low solid, slow-frozen samples (S1), reaching 4.7 g/g.
For saline, no clear correlation to morphology is seen, but higher solid content (S3, S4) appears to improve absorption

4. CONCLUSIONS

- 3D-printed porous bio-based scaffolds were successfully fabricated using alginate and BSA bio-based compounds.
- BSA addition increases viscosity and enhances shear-thinning in uncross-linked inks, but shows minimal impact after calcium crosslinking
- Frequency-dependent moduli and ~75% recovery after shear suggest dynamic, partially reversible ionic crosslinking dominated by calcium content
- Higher solid content and rapid freezing reduce pore size. Oil absorption benefits from larger pores, while saline uptake improves with higher solid content

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