Next-generation Edible Inks for 3D Printing: Protein Colloidal Hydrogels via pH-Temperature Route

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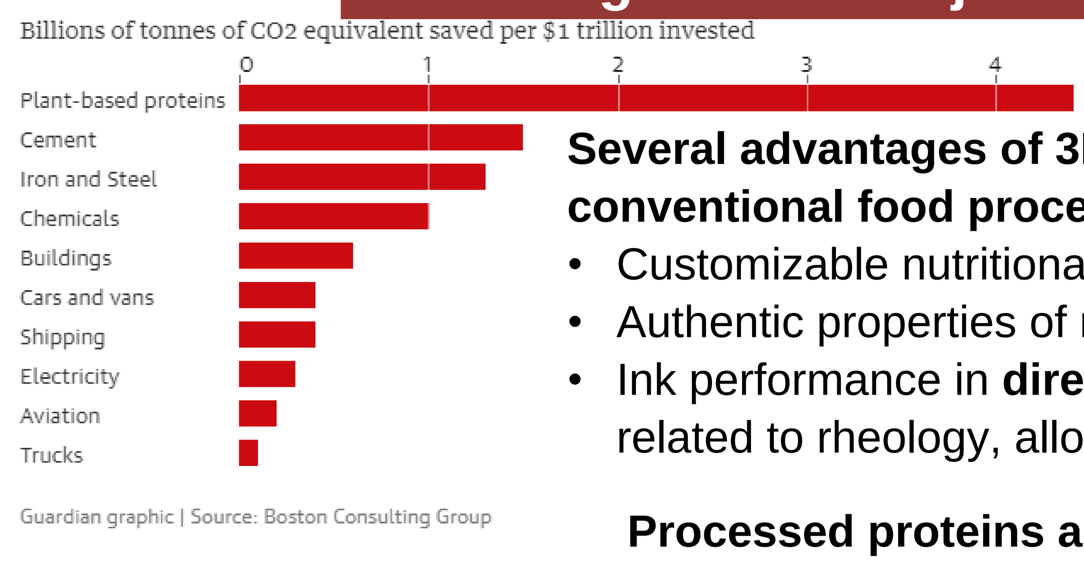
Background & Objectives



Several advantages of 3D printing over conventional food processings [2]:

- Customizable nutritional and sensorial attributes
- Authentic properties of meat & seafood analogs
- Ink performance in **direct-write approach** related to rheology, allow *higher design control.*

Plant proteins can deliver higher *emission reductions* than materials in other sectors per capital invested[1].

Processed proteins as functional building blocks with applications as *fat replacements* [3], *interfacial stabilizers, structuring agents* [4], and *fiber formers* [5], with most previous studies focusing on dairy proteins.

However, there is a need for **robust, clean-label** protein inks & **understanding of microstructure-rheology relations** to optimize 3D printing performance.

Objectives: To investigate the ability to process native potato proteins into colloidal hydrogels as edible inks via pH-temperature route for extrusion-based 3D-printing.

Methodologies

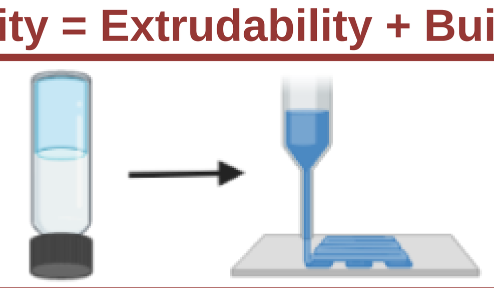
Characterization of native protein suspensions across pH

- Particle size distribution
- Zeta potential
- DSC
- Rheology

Ink Preparation & Screening

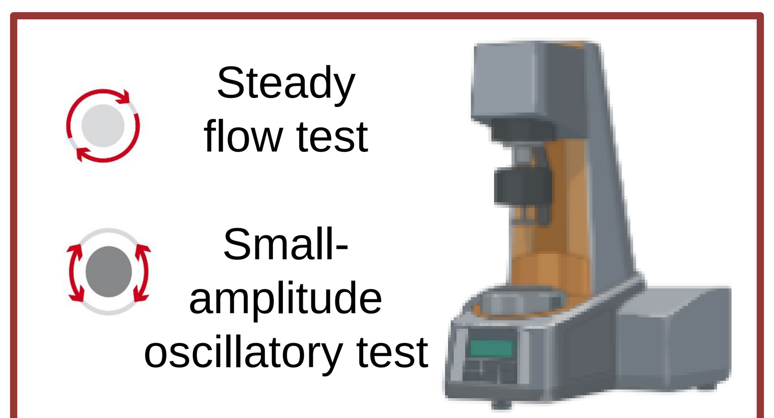
Potato Protein → **Colloidal Hydrogels**

Printability = Extrudability + Buildability

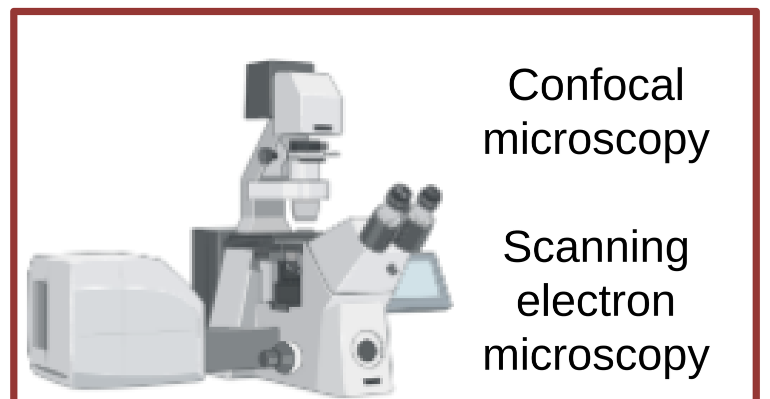


Sol-gel testing → ***3D-printing extrudability* testing**

Structure-Function of Extrudable Inks



- Steady flow test
- Small-amplitude oscillatory test



- Confocal microscopy
- Scanning electron microscopy

Acknowledgements

This work was made possible thanks to Massachusetts State Grange, Commonwealth Honors College, and USDA-NIFA & Hatch Grant funds, and generous potato protein donation from Avebe.

Physiochemical & Rheological Properties of Native Suspensions

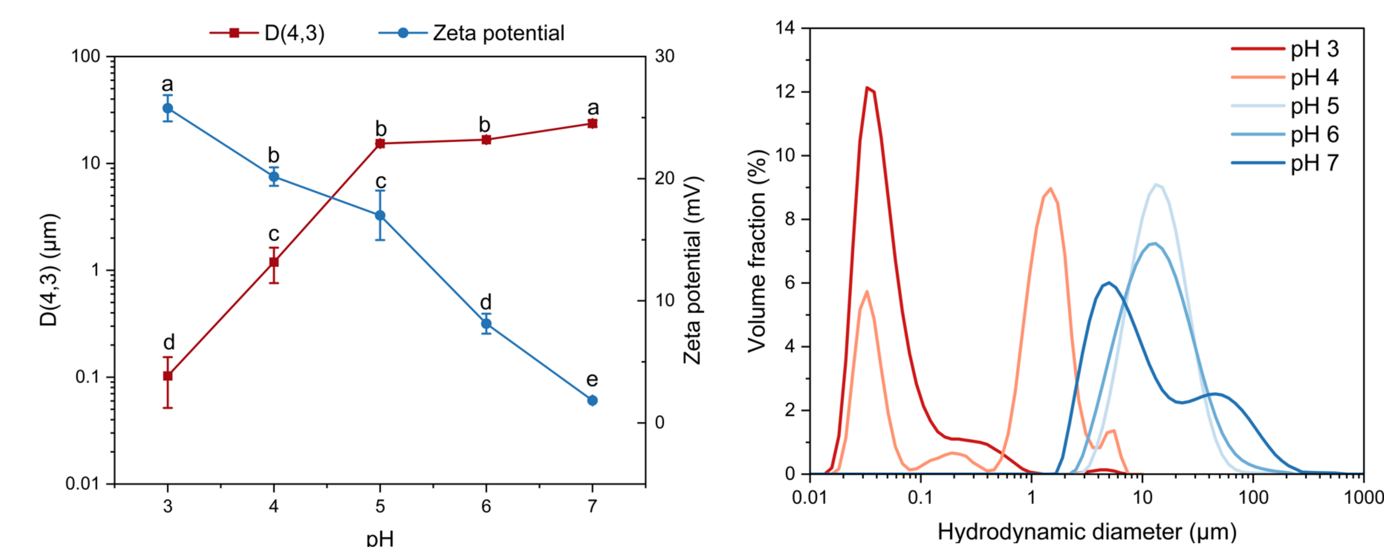


Figure 1. Impact of pH on mean particle diameter, zeta potential, and particle size distribution of 30% potato protein suspensions.

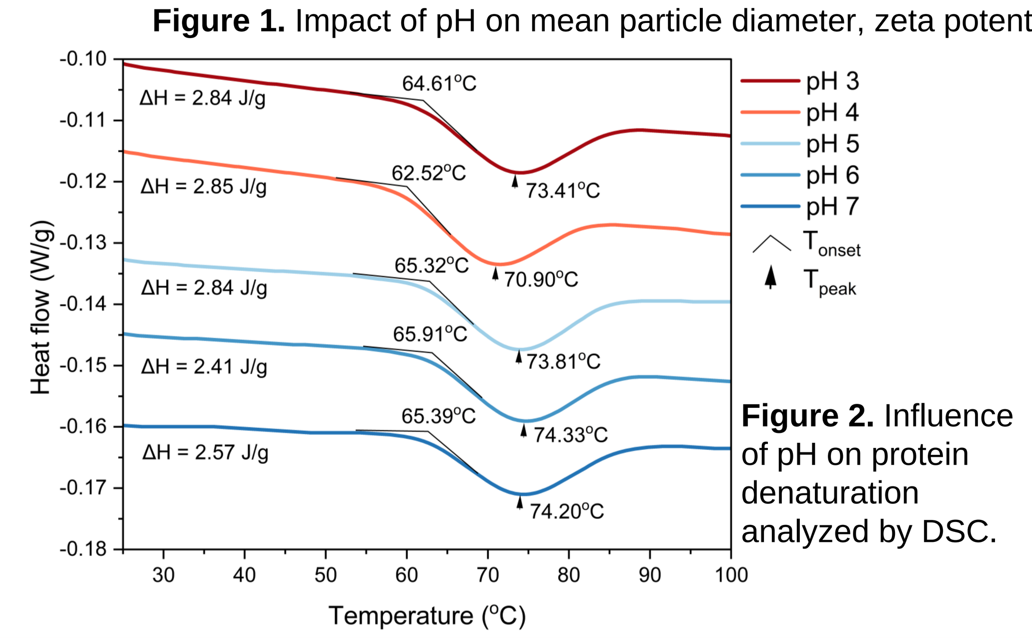


Figure 2. Influence of pH on protein denaturation analyzed by DSC.

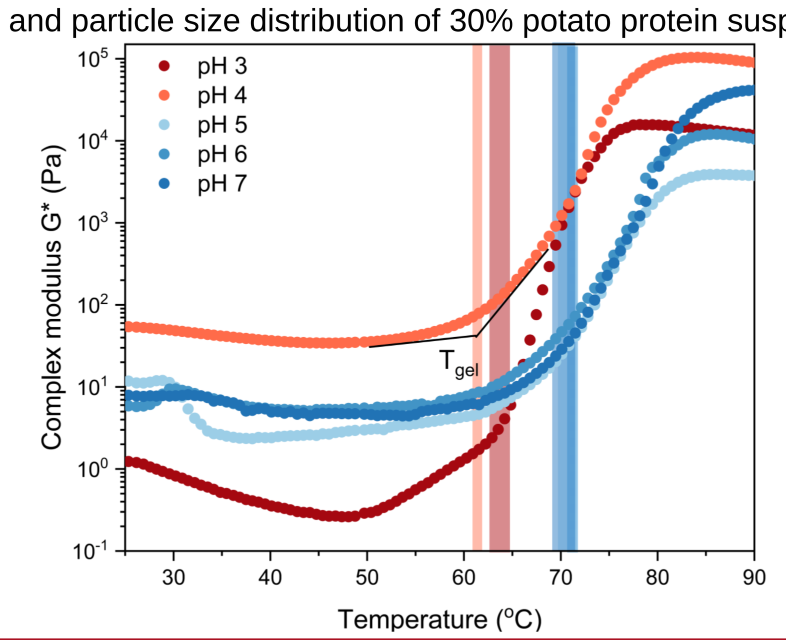


Figure 3. Influence of pH on thermal gelation of proteins: T_{gel} is the gelation temperature.

Ink Screening

Prototype Observations

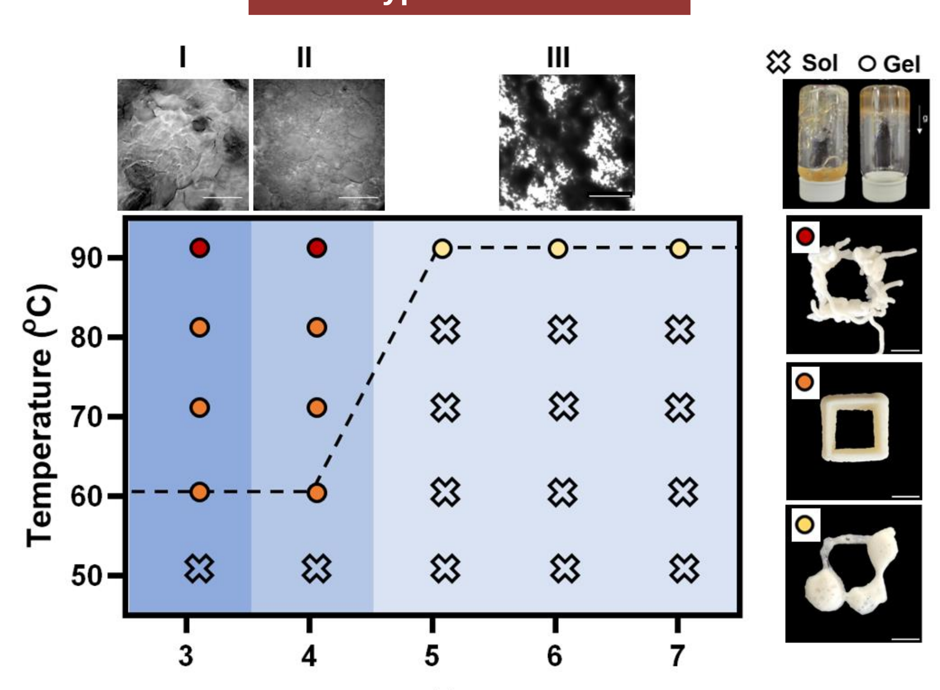


Figure 4. State diagram, photographs and micrographs of heated protein dispersions across pH 3-7, with different extrusion behaviors.

Rheological Insights

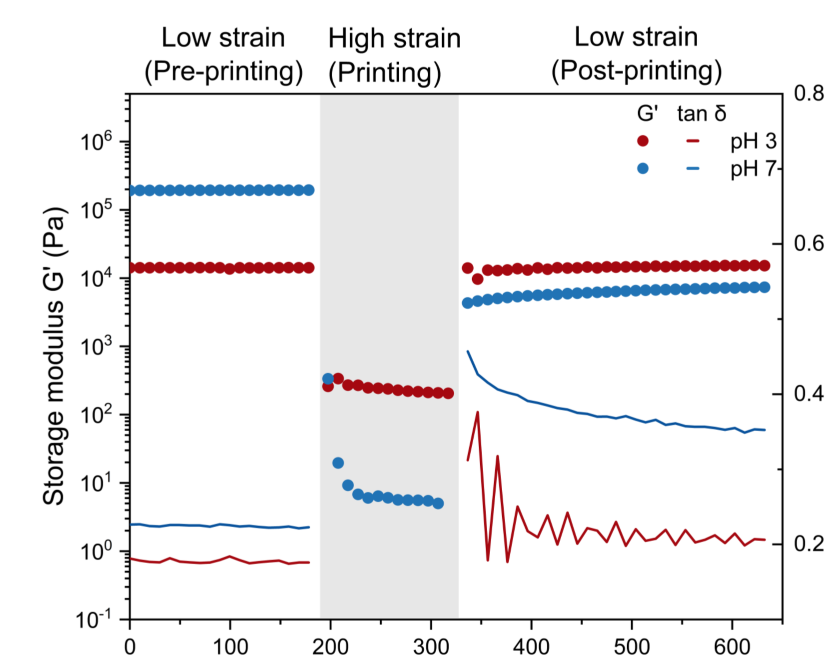
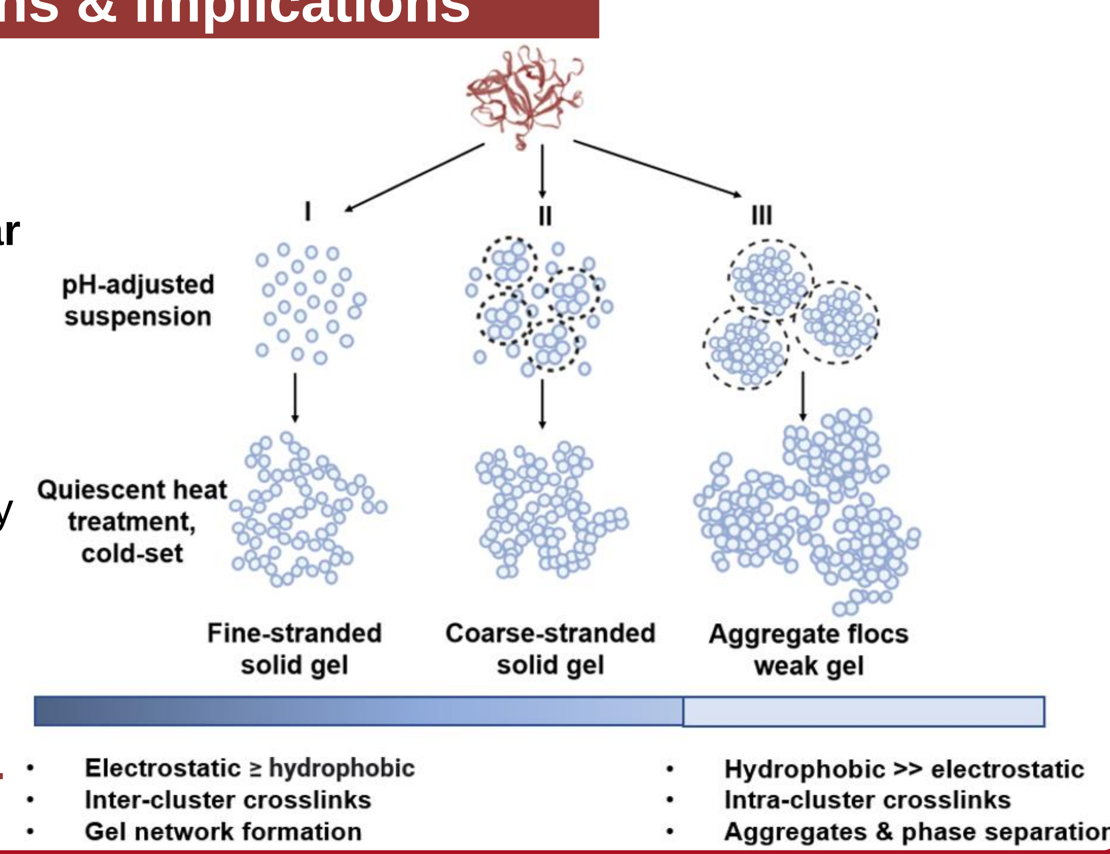


Figure 5. Three-step oscillatory recovery test of recoverable (pH 3) and non-recoverable (pH 7) 90°C protein gels.

Conclusions & Implications

- State diagram was established to relate protein printability to pH-temperature treatments.
- **Colloidal hydrogels at pH 3 and 4 were extrudable,** which were either **jammed granular microgels** or **dense particulate aggregates.**
- Thermal treatments could **enhance structural strength** of printed inks.
- Heating proteins to temperature that promotes **partial unfolding and aggregation**, but not fully unfolding, generated **higher printing fidelity.**

Controlling the pH and temperature of protein dispersions alters the molecular & mesoscopic interactions between protein "building blocks".



Extrudable Inks (pH 3 & 4) Properties

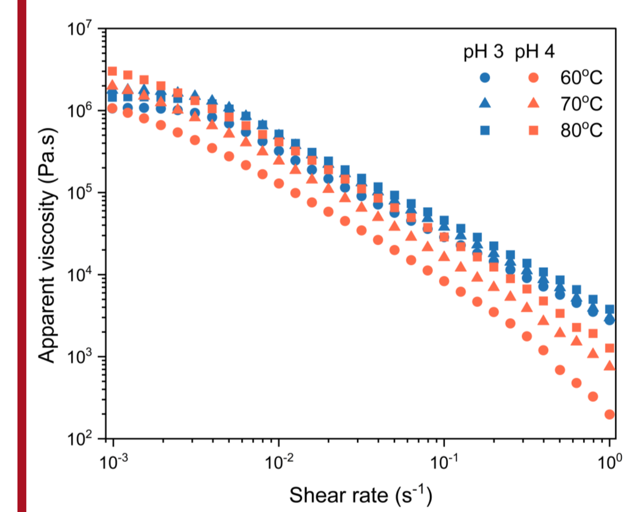


Figure 6. Steady-flow shear viscosity of pH 3 & pH 4 inks show **shear-thinning** behaviors.

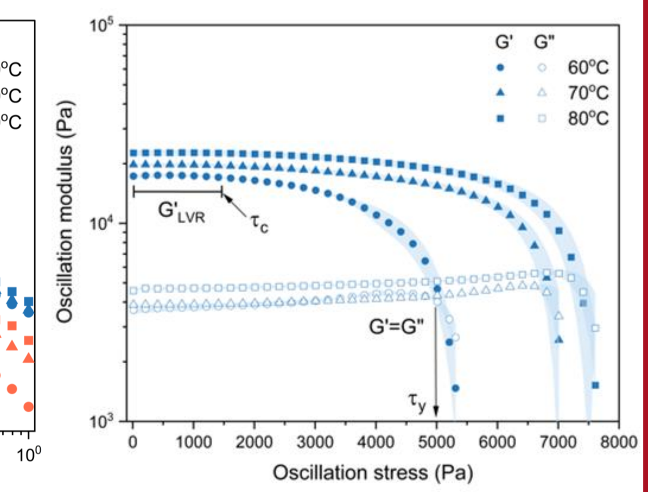
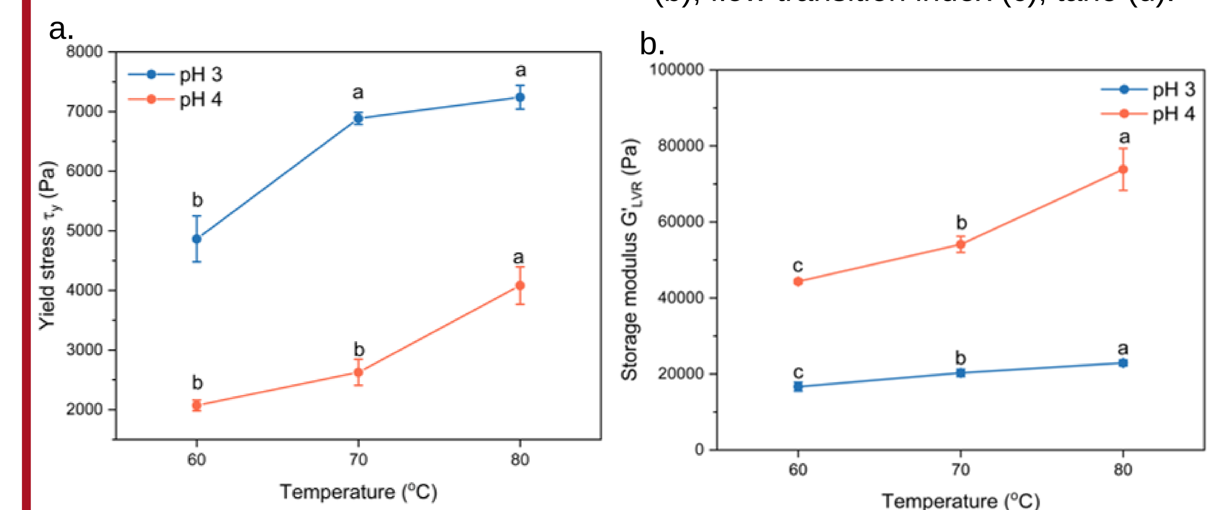
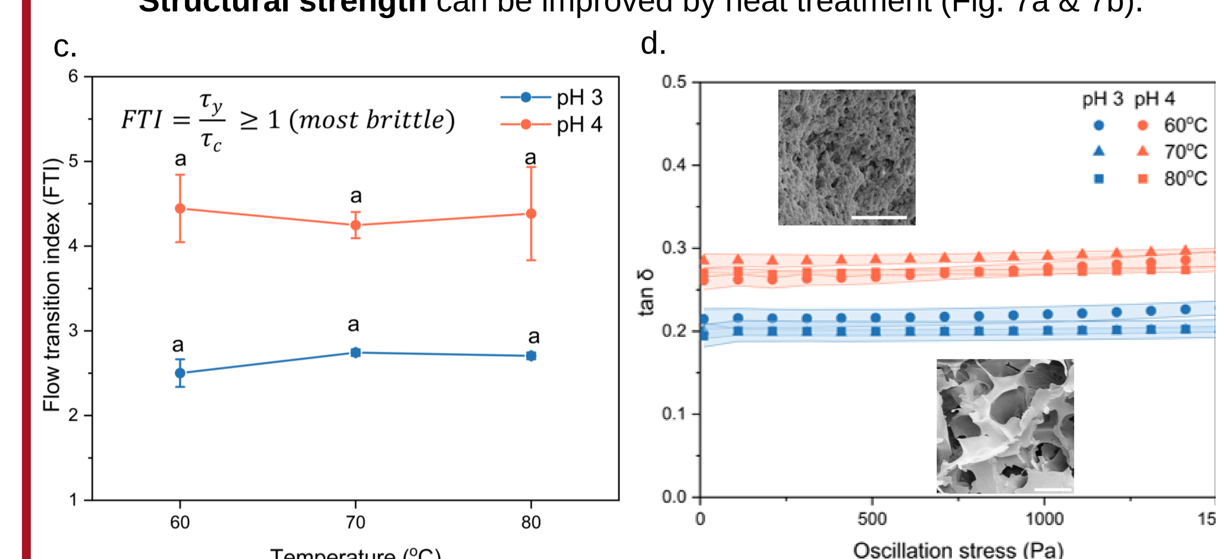


Figure 7. Oscillatory stress sweep of representative pH 3. Secondary properties include yield stress (a), storage modulus (b), flow transition index (c), tanδ (d).



Structural strength can be improved by heat treatment (Fig. 7a & 7b).



Heat treatment didn't affect **inherent pH-influenced gel types** shown in SEM (Fig. 7c & 7d).

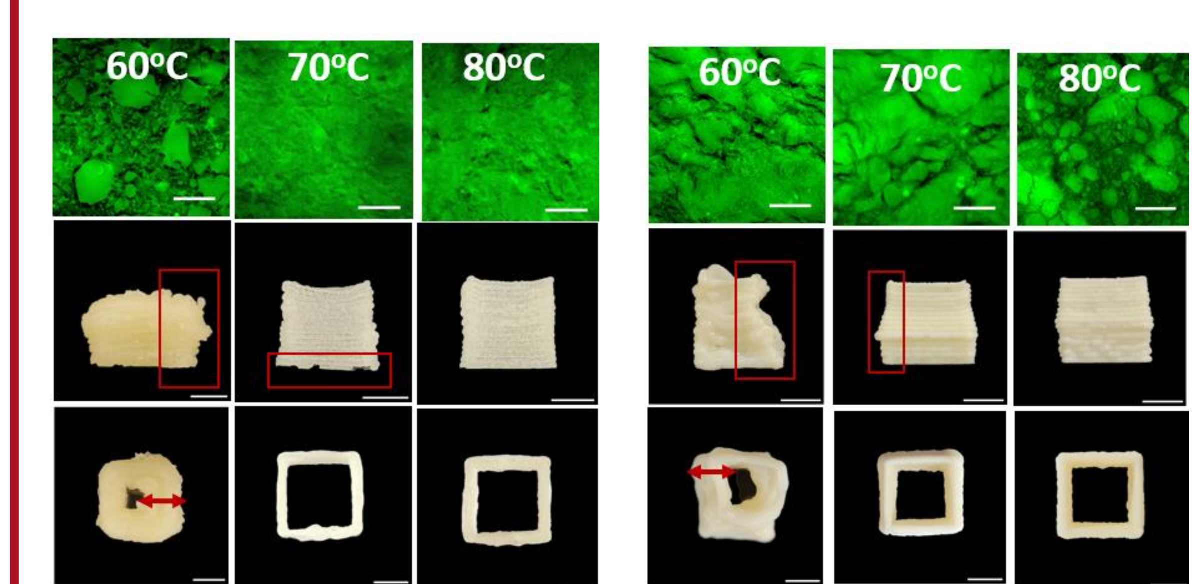


Figure 7. Confocal images, and 3D-construct photographs of printed inks at **pH 3 (left) & pH 4 (right)** processed across heat treatments.

References

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