

## 1<sup>st</sup> PhD Symposium—Gembloux Agro Bio-Tech



## Evaluation of Rheology and Printability of Starch-Chitosan-Gluten hydrogel: First Approach and Perspectives

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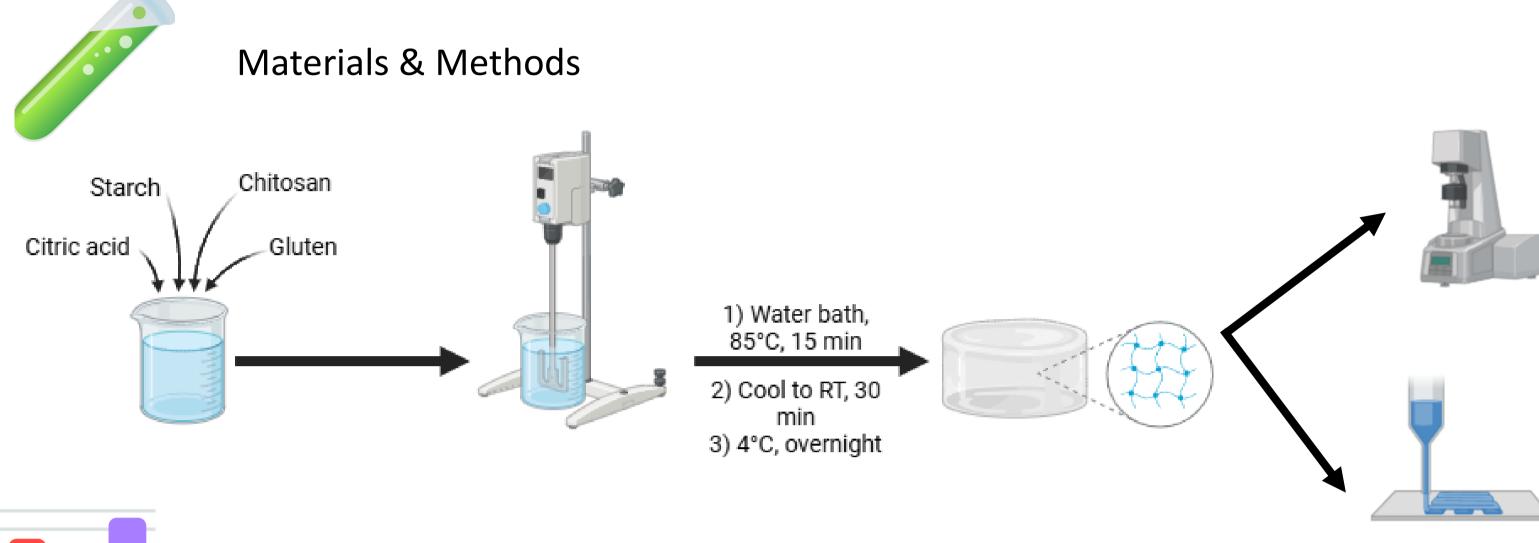
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- Additives manufacturing (3DP) enables the fabrication of complex and customized structures.
- Biopolymer like starch and gluten offer eco-friendly, biodegradable and functional material option.
- **Starch-based hydrogels** exhibits high water retention, flexibility and responsiveness to stimuli<sup>1</sup>.
- Application include **biomedical and wearable sensor**<sup>2</sup>.
- Limited research exists on starch-gluten hydrogels for 3DP.



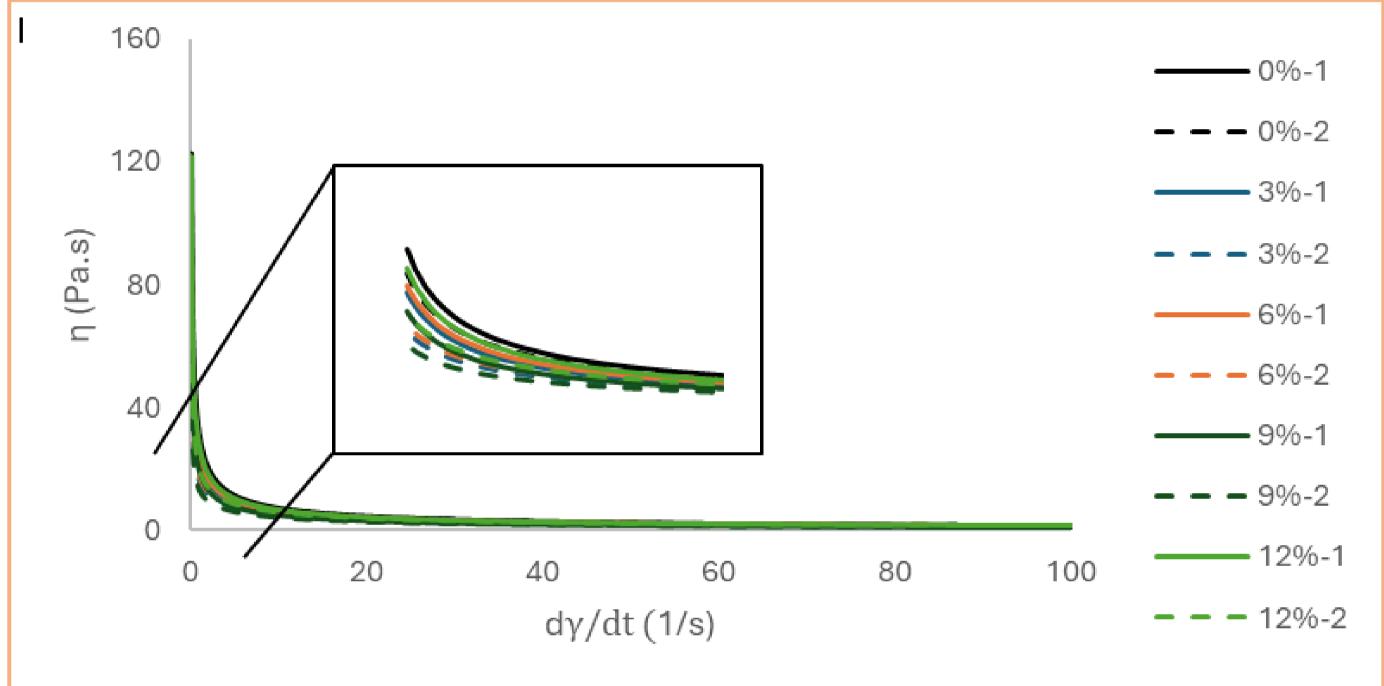
- Formulation of starch-gluten hydrogels for Direct Ink Writing (DIW).
- Evaluation of the rheological properties to ensure printability.



- Hydrogel was produced using unmodified wheat starch (9.5% w/v), gluten (0-12% w/  $w_{\text{starch}}$ ), citric acid (2.5% w/w) and chitosan (0.5% w/w)<sup>3</sup>
- Rheology characterization was carried out with an Anton Parr MCR302: viscosity/ hysteresis, amplitude and frequency sweep tests were done. Printing test with DIW was carried out.

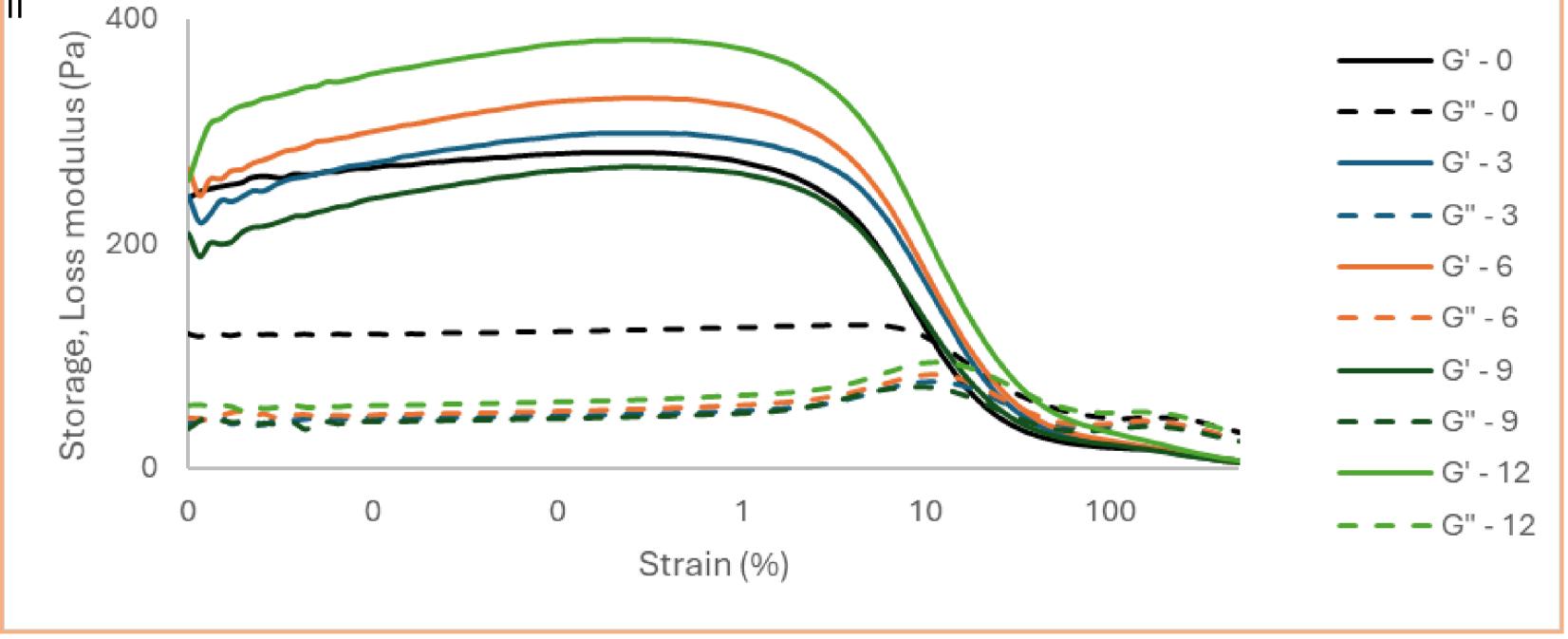


## Results & Discussion



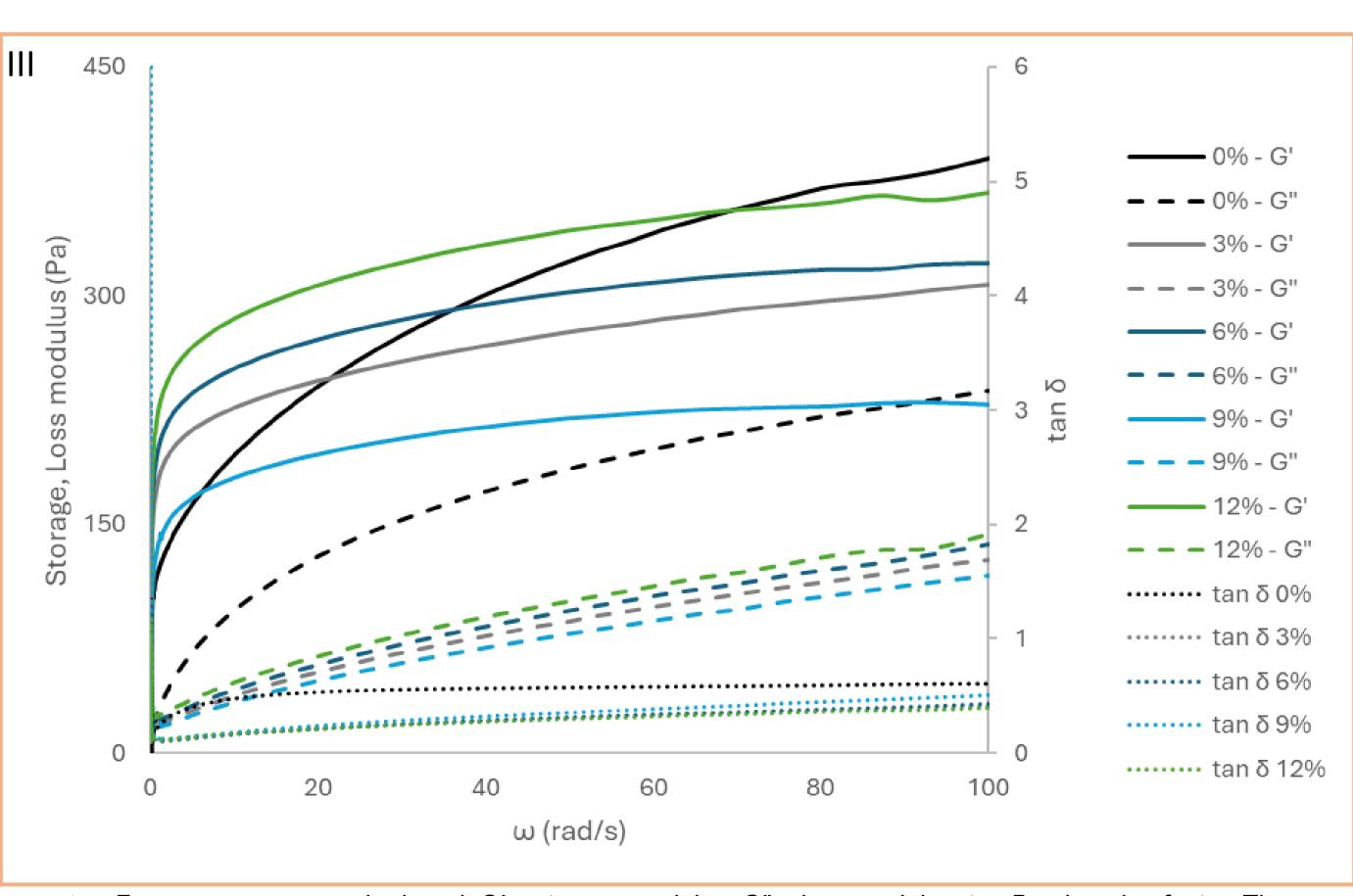
Graph 1. Hysteresis curve of different hydrogels. The percentage is relative to gluten content. Solid lines show the viscosity as shear rate increases. Dash lines show the viscosity as shear rate decreases.

- In 3DP, gels have to recover structure/viscosity when shear rate  $(d\gamma/dt)$  return to zero ≡ hysteresis.
- . The curves when  $(d\gamma/dt) \nearrow does not fit totally when <math>(d\gamma/dt) \searrow \longrightarrow a loss of$ structure/viscosity of approx. 12% is observed.
- Probable cause:  $\alpha(1-6)$  bonds present in amylopectin were broken during high  $(d\gamma/dt)$ .



Graph 2. Amplitude sweep on hydrogels. G' = storage modulus, G" = loss modulus. The numbers are relative to gluten content.

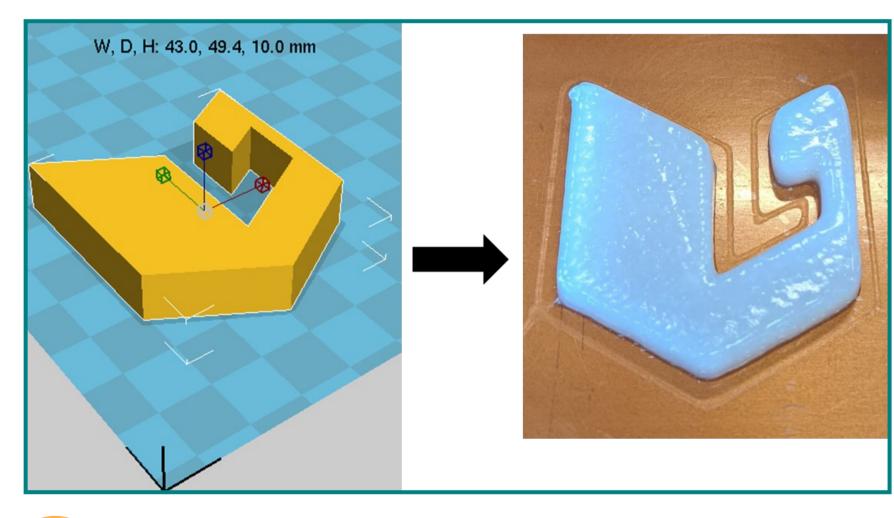
- Amplitude sweep: determination of linear viscoelasticity region (LVE-R)  $\Longrightarrow$  LVE-R >> = OK for 3DP.
- In LVE-R: the stress and strain is proportional and therefore no structural deformation is present.
- . Gluten  $\nearrow$  LVE-R  $\nearrow$  = positive correlation.



Graph 3. Frequency sweep on hydrogel. G' = storage modulus, G" = loss modulus, tan  $\delta$  = damping factor. The percentage is relative to gluten content.

Yang, Z. et al. (2021), International Journal of Biological Macromolecules <sup>2</sup> Ma, C. et al. (2022), ACS Sustainable Chemistry and Engineering <sup>3</sup> Ji, S. et al. (2022), Carbohydrate Polymers

- Frequency sweep: determination of G', G'' and tan  $\delta \longrightarrow$  Indication on solid/liquid-like behavior.
- G'>>G'' & tan  $\delta$ <1 for all gels  $\Longrightarrow$  solid-like behavior  $\Longrightarrow$  OK for 3DP.
- Gluten  $\nearrow$  tan  $\delta \supseteq$  = positive correlation



- Printing parameters based on lit.<sup>3</sup>
- Printable but presence of air bubbles, not all layers was deposited and not "handleable".



- Rheological properties of the formulation are desirable.
- Hydrogels are printable but some issues was pointed out.
- So, optimization of formulation and printing parameters is therefore necessary.



Acknowledgments

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