Bioinspired Approach to 3D-Printed Auxetic Polymer-Hydrogel Composite via Frontal Polymerisation for Robust Scaffolds

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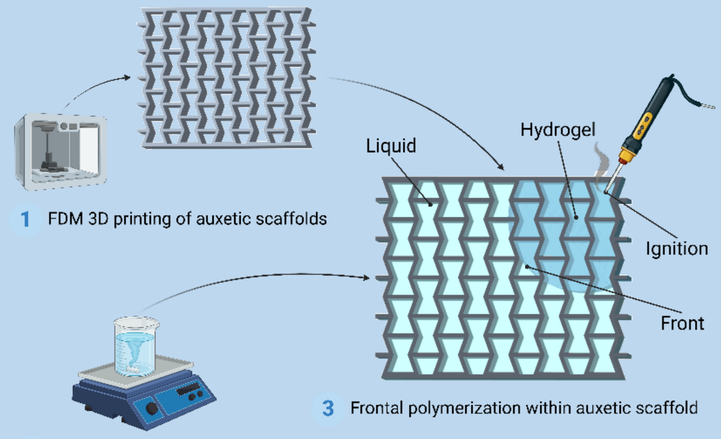
Introduction

This research presents an innovative bioinspired 3D-printed auxetic polymer-polymer composite synthesized via frontal polymerisation (FP), a self-sustained and energy-efficient polymerisation technique [1]. Frontal polymerisation uniquely enables the seamless filling of voids within complex 3D structures, addressing challenges that are otherwise difficult to overcome. The integration of frontally polymerised gel into mechanically robust 3D-printed auxetic structure benefits from a synergistic enhancement of structural integrity and functional performance. This composite overcomes the limitations inherent to each material, such as the low toughness of the printed auxetic structure or the brittleness of frontally polymerised polymer. Its promising application in tissue engineering and regenerative medicine lies in the ability to create 3D-printed auxetic scaffolds seamlessly filled with FP hydrogel, which is the core motivation behind this research.



Results and discussion

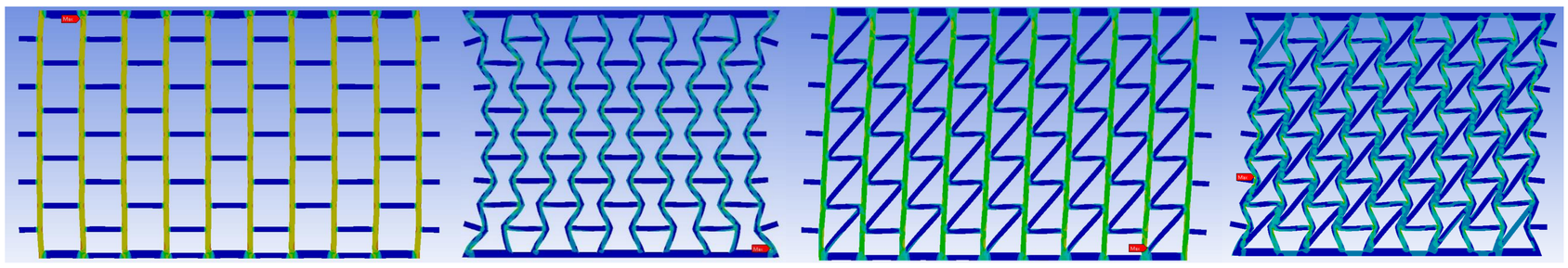


Figure 1: Finite element analysis prediction of stress concentration and deformation in non-auxetic and auxetic structures

- **Biomimetic patterns**, inspired by Hexactinellid sponges [2], were successfully implemented in the auxetic structures (Fig.1).

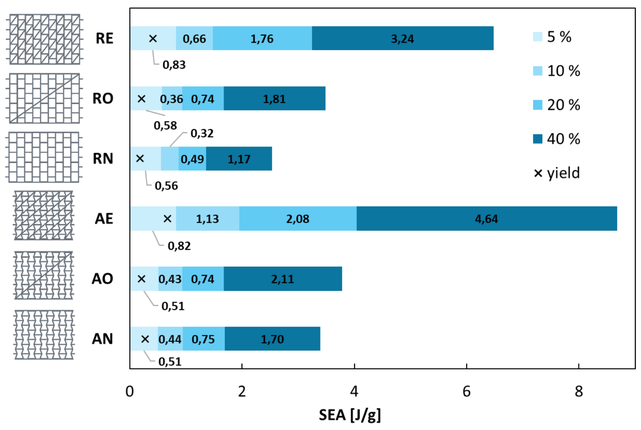


Figure 2: Increment of normalized specific energy absorption (SEA) of 3D-printed structures (PETG) at selected strain values

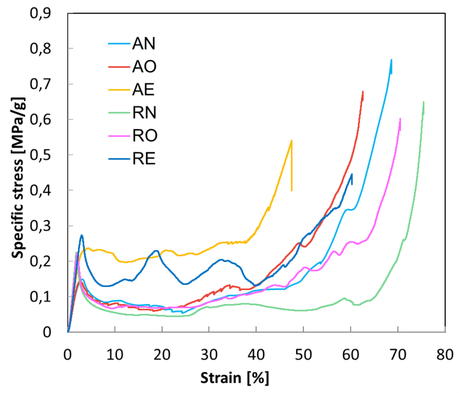


Figure 3: Compression test curves of unfilled 3D-printed structures (PETG)

- **Specific energy absorption** was significantly improved by the bioinspired reinforcement and was notably **higher in auxetic structures** compared to non-auxetic (Fig. 2).

Figure 7: Composite model system (PETG-epoxy resin) on the left and polymer-hydrogel composite (PLA-acrylate) on the right

Figure 6: Compression test setup

- By combining 3D-manufacturing with frontal polymerisation, a complex-shaped structure was obtained from a hydrogel that is otherwise shapeless and hardly processable (Figure 7).

Table 1: Swelling test results

Solvent	Crosslinker conc.	Swelling ratio
H_2O	4,7 %	253 %
DMSO	4,7 %	137 %

- Using optimized hydrogel formulation, the effect of solvent on hydrogel swelling ratio was studied (Table 1).

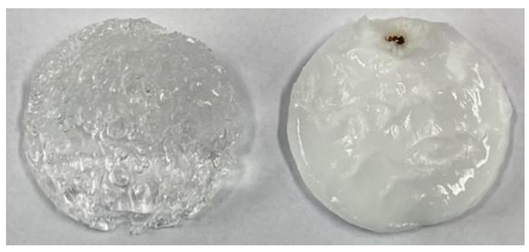


Figure 4: Swelled FP acrylamide hydrogels

- **The frontal polymerisation (FP)** was initiated using a heated tip, producing a reaction front peaking at approximately **160 °C** (Figure 5). Post-polymerization, samples were thoroughly washed in water for 24 hours to remove residual DMSO.

- For mechanical testing, three formulations were chosen with varying ratios of **water** and **DMSO** concentration (Table 2).

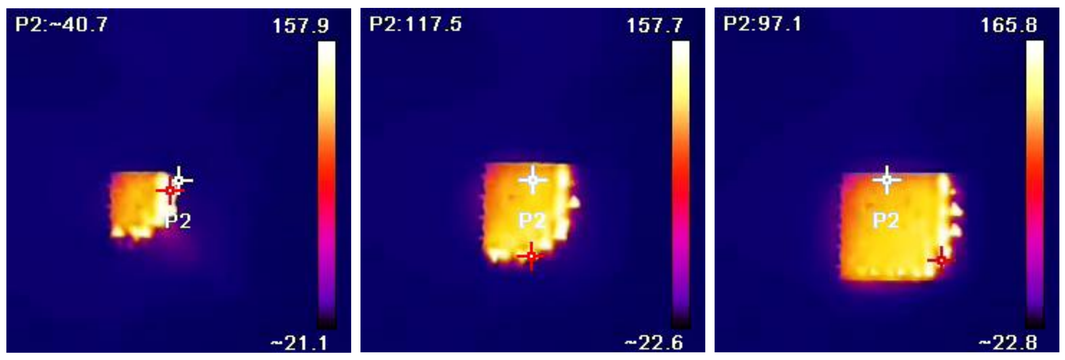


Figure 5: Front propagation during frontal polymerisation of acrylic-based mixture within 3D-printed scaffold (polylactic acid), resulting in polymer-hydrogel composite

- The compression test (Figure 6) were conducted in order to determine strength, stiffness, and deformation characteristics.

Table 2: Solvent concentration

	H_2O	DMSO
A	75 %	25 %
B	50 %	50 %
C	25 %	75 %

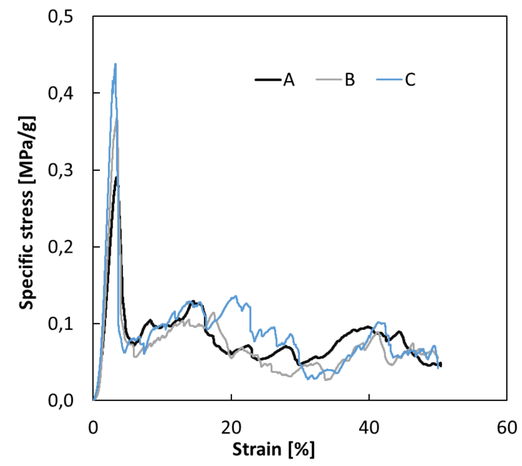


Figure 8: Compression test curves of polymer-hydrogel formulations

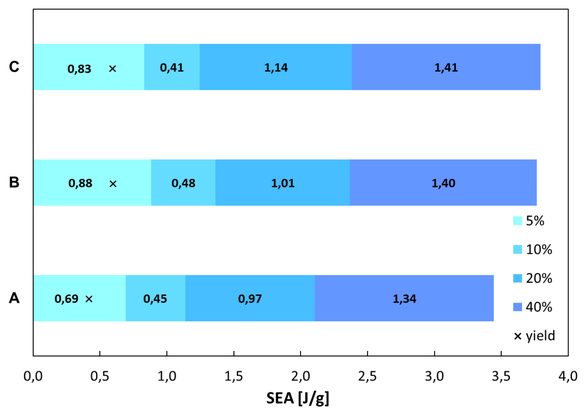


Figure 9: Increment of SEA for polymer-hydrogel composite

- The compression test curves exhibit distinct deformation regions (Figure 8): an **elastic region**, followed by a **collapse region** (progressive buckling and folding). At higher strains, the curve would gradually transition into the **densification stage** (as seen in Figure 3), where pore collapse leads to a steep increase in stress values.
- As can be seen in Figure 9, specific energy absorption values were highest for higher DMSO concentration

Conclusion

This study presents a novel 3D-printed auxetic polymer-polymer composite synthesized via frontal polymerisation, offering significant advantages in mechanical strength, energy absorption and process efficiency. The ability to use a hydrogel as the filling material and fabricate the scaffold from biocompatible or biodegradable materials makes this approach particularly promising for biomedical engineering, paving the way for advanced biomaterial applications in tissue engineering and regenerative medicine.

Acknowledgments

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References:

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