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UV-Curable Methacrylated Zein Inks: Tailoring Biopolymer-Based Materials for 3D Printing

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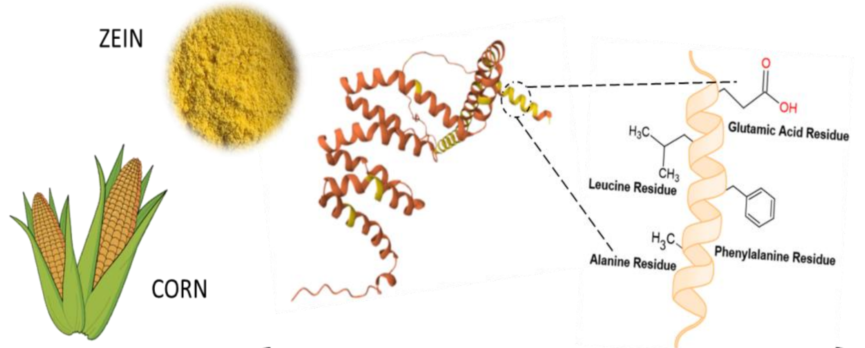
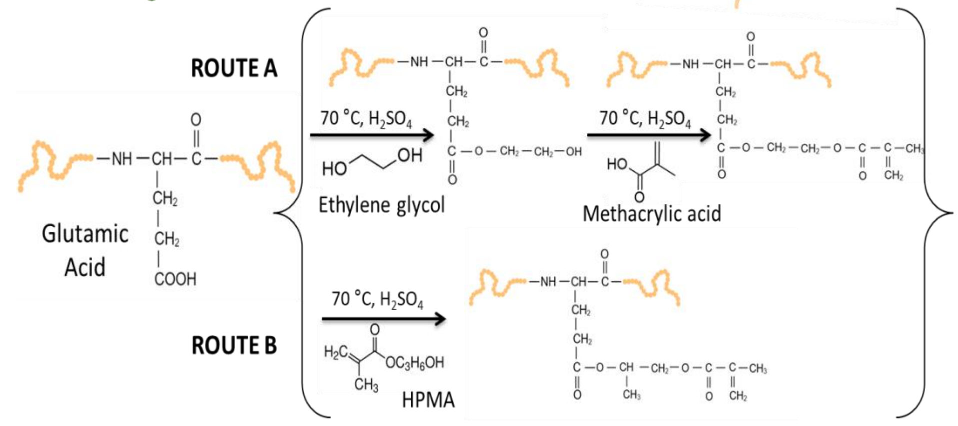
Background

As 3D printing continues to evolve, the development of new printable materials is crucial for advancing a wide range of applications in this field. Zein, a by-product of corn processing, is a biodegradable biopolymer and sustainable alternative to synthetic polymers. It has gained attention for its biocompatibility and versatility in various applications, including 3D printing. However, the use of zein in extrusion-based 3D printing remains underexplored, especially in the context of UV-crosslinkable systems. This research study explores the development of a zein-based ink for pneumatically driven extrusion 3D printing. It investigates two approaches to modifying zein through methacrylation to achieve a UV-crosslinkable ink formulation, aiming to expand its potential in areas such as soft tissue engineering and environmentally conscious manufacturing.

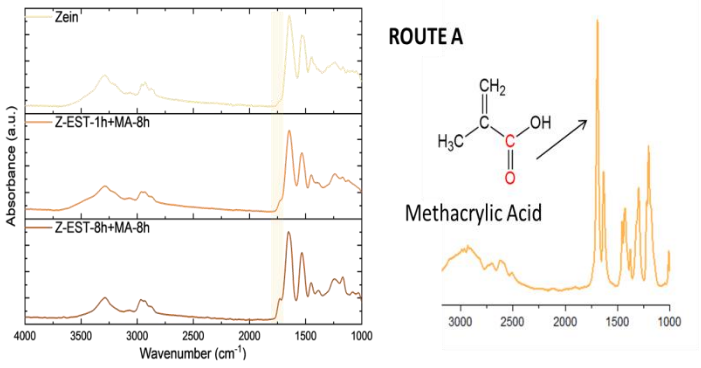
Experimental



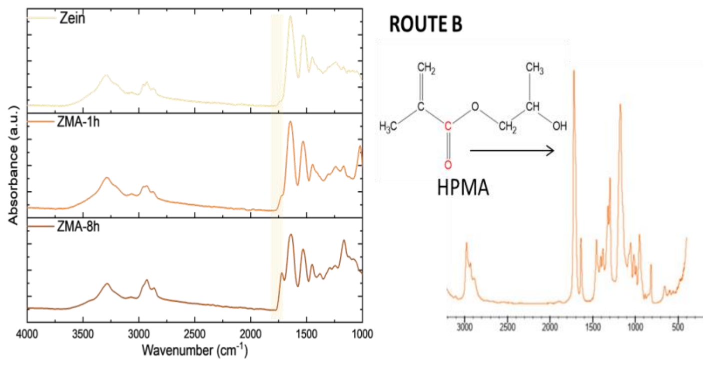


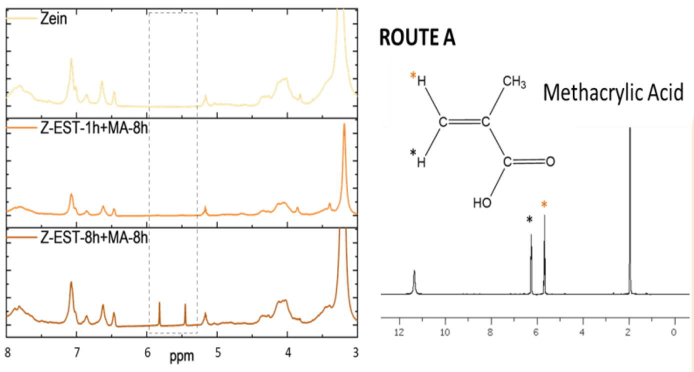
Results

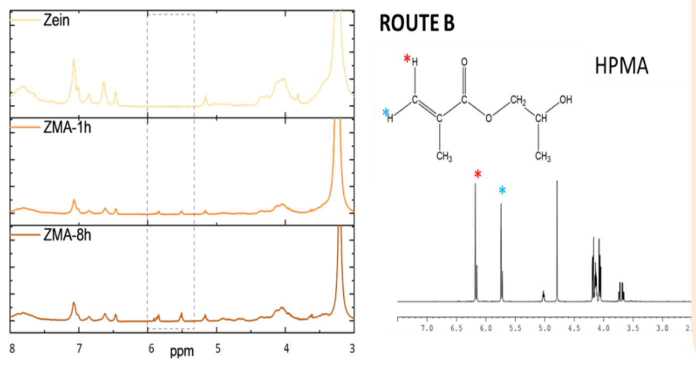
Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR)



Proton Nuclear Magnetic Resonance (^{1}H-NMR)







FTIR and ^{1}H-NMR analyses confirm methacrylation via both modification routes, as evidenced by the C=O stretching vibration and C=C proton signals (5.6–6.0 ppm) within the methacrylate moieties of methacrylic acid (MA) and hydroxypropyl methacrylate (HPMA).

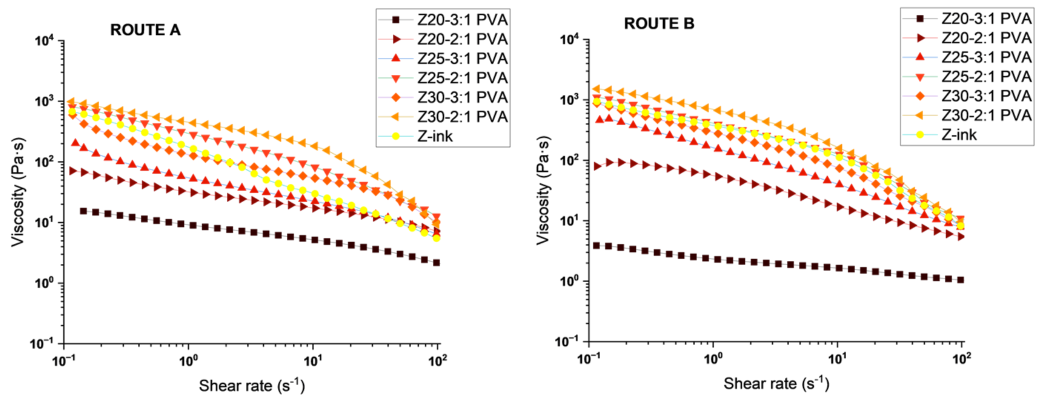
The degree of substitution depends on the reaction time:
Route A: Substitution increases up to ~5% after 8 h esterification and 8 h methacrylation; no change when esterified for only 1 h.
Route B: Substitution increases from ~5% (1 h) to ~15% (8 h) reaction time.

Rheological evaluation

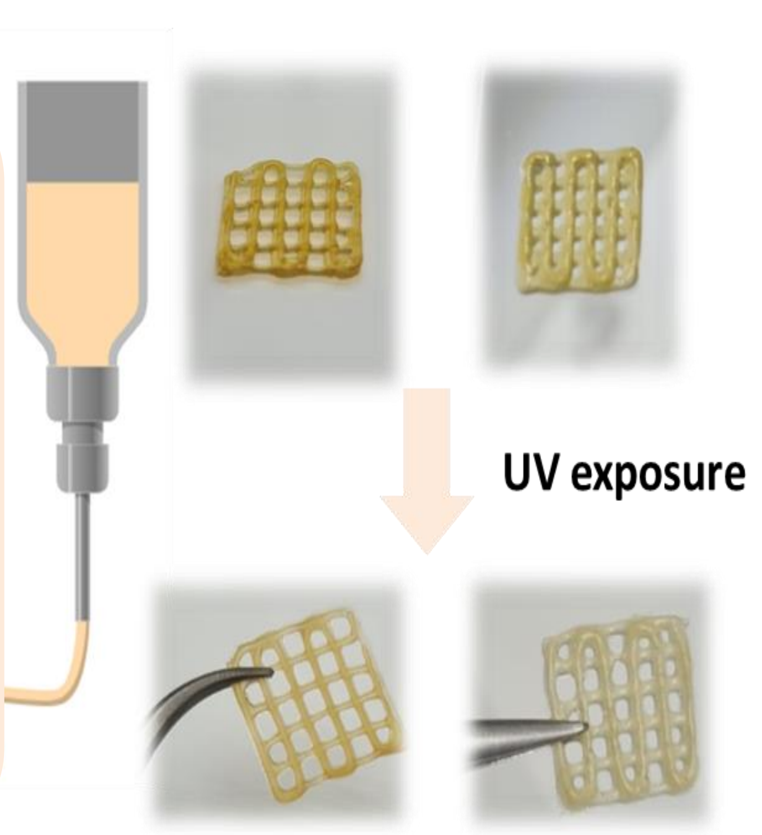
Hydrogel precursor solutions were prepared by dissolving two types of methacrylated zein in DMSO at varying concentrations, with polyvinyl alcohol (PVA) added as a thickener. The final ink formulation included triethylene glycol dimethacrylate (TEGDMA) as a crosslinker and a photoinitiator system (camphorquinone and ethyl 4-dimethylaminobenzoate). All samples exhibit shear-thinning behavior, with viscosity decreasing as shear rate increases. PVA acts as a thickener, increasing zero-shear viscosity for shape fidelity while allowing easy extrusion under stress. The addition of TEGDMA and the photoinitiator system has minimal effect on the ink's rheology before UV curing.

Sample ID	Zein:DMSO (% w/v)	Zein:PVA (w/w)	Crosslinker (% w/w*)	Photoinitiator (% w/w*)	Co-photoinitiator (% w/w*)
Z20-3:1 PVA	20	3:1	–	–	–
Z20-2:1 PVA	20	2:1	–	–	–
Z25-3:1 PVA	25	3:1	–	–	–
Z25-2:1 PVA	25	2:1	–	–	–
Z30-3:1 PVA	30	3:1	–	–	–
Z30-2:1 PVA	30	2:1	–	–	–
Z-ink	30	3:1	10	0.2	0.4

* Percentages reported to the total mass of the ink formulation



3D Printability



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