

Methacrylated-Starch Photoresins: Botanical Source, Amylose/Amylopectin Composition, Gelatinisation, Substitution, Aqueous DLP, Hybrid Bioinks and Qualification

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Statement of Significance

Methacrylated starch is not one material. Botanical source, amylose/amylopectin composition, granule and molecular state, gelatinisation or dissolution, derivatisation, purification and storage define the macromer. Concentration, initiator, optical control, exposure, post-cure, washing and hydration define distinct resin and article states.

Keywords: starch; methacrylated starch; amylose; amylopectin; gelatinisation; degree of substitution; DLP; hydrogel; bioink; qualification

Abstract

Photocurable starch systems span methacrylic-anhydride starch, glycidyl-methacrylate starch, pentenoate-thiol networks and hybrid bioinks. These are not interchangeable. Noe et al. demonstrated aqueous DLP of methacrylated high-amylose maize starch with LAP, while Hedin et al. established UV crosslinking of GMA-modified cornstarch. Van Nieuwenhove et al. showed that starch-pentenoate/gelatin networks can phase-separate, and Zhou et al. reported that low-substitution methacrylated starch alone printed poorly but improved in a methacrylated-chitosan hybrid. This review separates parent-starch identity, chain processing, substitution, formulation, optical exposure, network attribution, hydration, enzymatic degradation and biological evidence.

1. Scope and boundaries

ER-127 owns material-specific identity and qualification of photocurable starch derivatives for vat photopolymerisation and related light-assisted biofabrication. It covers botanical source, amylose/amylopectin composition, molecular distribution, granule disruption, gelatinisation or dissolution, derivatisation, purification, aqueous formulation, exposure, post-cure, washing, hydration, mechanics and enzyme-sensitive change.

ER-06 retains biological-response methodology; ER-10 geometric metrology; ER-15 degradation and mechanical evolution; ER-27 conversion; ER-33 washing and drying; ER-67 generic hybrid-network architecture; ER-86 extractables; ER-100 corpus architecture; and ER-121 to ER-126 neighbouring natural-polymer derivative families. [C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13,C14].

General AM characteristics, geometric test artefacts and geometrical tolerancing should follow the declared standards [S1,S3,S4].

Botanical source is not amylose fraction. Gelatinisation is not molecular dissolution, and derivatisation feed is not measured substitution. Methacrylic-anhydride starch, GMA-starch and starch-pentenoate are distinct chemistries. Neat starch networks are not starch/chitosan or starch/gelatin hybrids, and in-vitro amylase loss is not a universal in-vivo resorption rate.

2. Controlled starch-photoresin state chain

State	Minimum identity	Failure if omitted
Incoming starch	Botanical species/grade and lot, amylose/amylopectin method/result, molecular distribution, moisture, purity and storage	The word starch replaces polymer identity
Photoactive derivative	Granule disruption or dissolution, reagent/feed, catalyst, solvent, purification, drying, measured substitution and calculation basis	Feed or derivative acronym is treated as chemistry
Vat or bioink	Derivative concentration, water/buffer, initiator, absorber, hybrid components, cells/additives, temperature and age	Formulation and biological state disappear
Article	Exposure/layer strategy, post-cure, green geometry, wash, hydration, conversion, soluble fraction, residuals and mechanics	Green, post-cured, washed and hydrated objects are conflated

Table 1. Minimum state chain for photocurable starch networks.

This material and article chain is separate from process and production-site qualification under ISO/ASTM 52920:2023 [S2].

3. Primary evidence and controlled interpretation

3.1 Methacrylic-anhydride starch enables aqueous DLP under an exact protocol

Noe et al. gelatinised high-amylose maize starch in DMSO and reacted it with methacrylic anhydride, reporting a degree of substitution of 0.08 by ¹H NMR [1]. A 10 wt% aqueous formulation with LAP was printed at 385 nm, 10 mW/cm², 5 s per 50 micrometre layer. Those settings belong to that starch lot, substitution, concentration, initiator, printer and post-cure, not to a generic starch resin.

3.2 Concentration couples cure kinetics, stiffness and swelling

In the same study, 5, 10 and 15 wt% formulations differed in photorheology, handling and swelling, and compression was measured on the 10 and 15 wt% articles only [1]. Reported compressive moduli of about 12.7 and 20.3 kPa for the 10 and 15 wt% articles and equilibrium water contents of 78% and 73% are study-specific. The 5 wt% specimen fractured during swelling, which is a censored mechanical event rather than a complete equilibrium value.

3.3 GMA-starch is a separate derivative and initiation route

Hedin et al. modified cornstarch with glycidyl methacrylate in DMSO, obtained a reported degree of substitution of 0.08, and UV-crosslinked aqueous material with potassium persulfate [2]. The GMA substitution route and its reported degree of substitution, KPS initiation and the QCM-D surface-adsorption observations cannot be merged with methacrylic-anhydride/LAP DLP evidence; the mechanism by which GMA attaches to the starch hydroxyls - epoxide ring-opening versus transesterification - is not resolved by that report and is not asserted here.

3.4 Pentenoate and hybrid networks require component-specific attribution

Van Nieuwenhove et al. combined starch-pentenoate with methacrylamide-modified gelatin through an interpenetrating-network (IPN) strategy and observed separated starch domains in a surrounding gelatin matrix [3]. The measured 14-63 kPa storage-modulus range belongs to those film compositions and substitution levels. It is evidence for a hybrid architecture, not neat methacrylated starch or vat-printing performance.

3.5 Hybrid bioink printability does not transfer to the starch component alone

Zhou et al. reported insufficient printing accuracy for methacrylated starch alone at a substitution degree of 0.013, then improved extrusion/UV printing with a 10:1 starch-to-methacrylated-chitosan blend plus glycerol [4]. The reported 150-200 kPa compressive strength, 50-60% deformation, cell viability and alpha-amylase/lysozyme degradation belong to that exact hybrid, formulation, process and test model.

4. Photochemistry, starch structure and process state

Amylose/amylopectin composition, molecular degradation, residual granules, gelatinisation, solvent history, concentration, temperature and ageing control viscosity and association. Derivatisation supplies unsaturation, while initiator, wavelength, irradiance, exposure, oxygen, layer thickness and absorber control radical conversion and cure depth. Optical and rheological working windows must be measured on the production formulation.

Retrogradation and hydration can evolve after printing independently of covalent conversion. GMA, methacrylic-anhydride and pentenoate-thiol routes require separate chemical controls. Starch/chitosan and starch/gelatin systems require neat-component and hybrid controls so that network formation, print support, swelling, mechanics and degradation are not assigned to the wrong component.

5. Hydration, degradation and biological boundaries

Evidence block	What it can show	What it cannot establish alone
Parent-starch analysis	Method-specific source, composition, granule and molecular-state evidence	Derivative substitution, network conversion or article performance
Hydration/equilibration	Medium- and time-specific mass, dimensions, swelling and mechanics	Conversion, in-use lifetime or degradation mechanism
Enzymatic incubation	Enzyme-, activity-, medium-, geometry- and time-specific mass/property evolution	Universal in-vivo resorption
Biological model	Response of the exact construct or extract in the stated cell, tissue or animal model	General safety, clinical efficacy or regulatory approval

Table 2. Evidence blocks that must remain separate for photocurable starch systems.

ISO 10993-12:2021/Amd 1:2025 and ISO 10993-18:2020/Amd 1:2022 anchor sample preparation and chemical characterisation [S5,S6]. ISO 10993-1:2025 frames biological-safety evaluation within risk management [S7]. None

converts extract viability or one cell, enzyme or animal model into general biocompatibility, clinical efficacy or regulatory approval.

Reference [5] provides the paired in-vitro mesenchymal-stem-cell study for the gelatin/starch hydrogel family described in reference [3].

6. Release matrix

Gate	Minimum evidence	Claim withheld
Starch identity	Botanical source/grade and lot, composition method/result, molecular/granule state, moisture, purity and storage	Generic starch equivalence
Functionalisation	Chain-processing and reaction conditions, purification, measured substitution method/result and storage	Derivatisation feed or acronym as identity
Vat process	Concentration, initiator, absorber, wavelength, irradiance, exposure, layer thickness, temperature and ageing	Transferable print settings
Network attribution	Conversion plus neat-component and hybrid controls, phase-state and soluble-fraction evidence	Unverified IPN or dual network
Article state	Green, post-cured, washed and hydrated x/y/z, mass, residuals and conditioning history	Unqualified dimensions or mechanics
Biological boundary	Exact formulation, construct/extract dose, wash, model, endpoint and statistics	Universal biocompatibility or clinical suitability

Table 3. Minimum release architecture for photocurable starch constructs.

7. Failure-mode interpretation

- A nominally identical starch resin becomes much more viscous: verify botanical source, amylose/amylopectin composition, granule disruption, molecular degradation, concentration, temperature, ageing and retrogradation before changing exposure.
- A higher derivatisation feed does not increase modulus: measure incorporated functionality and conversion; feed, substitution, chain degradation and network density are different quantities.
- The green object is accurate but changes after washing: report x/y/z, mass, medium and time after defined washing and equilibration; do not publish green dimensions as hydrated dimensions.
- Stiffness rises during storage or incubation: test water content, amylose association and retrogradation before assigning further covalent cure.
- A starch/chitosan or starch/gelatin hybrid prints better than neat starch: retain component ratios, substitution, additives and phase state; do not transfer the result to neat starch resin.
- Cells remain viable in an extract or printed construct: retain the exact starch route, formulation, exposure, wash, extract ratio, cell model and endpoint; do not infer approval or universal biocompatibility.

8. Minimum workflow and research priorities

- Freeze botanical species, cultivar or commercial grade, source lot, amylose/amylopectin method and result, molecular distribution, moisture, purity and storage.
- Report granule disruption, gelatinisation or dissolution, solvent, temperature, time, derivatisation reagent and feed, catalyst, purification, drying, measured substitution and basis.
- Map concentration, viscosity, gel or retrogradation history, absorbance and working curves over temperature, ageing and the complete build-duration window.
- Measure conversion, gel fraction, soluble fraction, residual initiator/reagents and starch retention on matched green, washed and hydrated states.
- Use neat-component and hybrid controls to separate covalent conversion, physical association, phase separation and support from a verified interpenetrating or dual network.
- Track mass and x/y/z dimensions through printing, post-cure, washing, equilibration, drying, rehydration and storage.
- Report alpha-amylase or other enzyme source and activity, co-enzyme conditions, medium, pH, temperature, replenishment, geometry and time; separate solubilisation from backbone cleavage.
- Separate extract cytotoxicity, direct-contact response, cell-laden printing and tissue-model observations from safety, efficacy and regulatory conclusions.

9. Conclusions

Photocurable starch materials are controlled parent-polymer, derivative, formulation, network and article states. Botanical source and amylose/amylopectin composition define the incoming starch; chain processing and measured

substitution define the macromer; formulation and exposure define the green network; post-cure, washing and hydration define the tested article.

Primary evidence supports aqueous DLP of one methacrylated high-amylose maize-starch system, UV curing of GMA-starch, starch-pentenoate hybrid films and high-precision starch/chitosan hybrid printing. These chemistries and process windows are not interchangeable.

Release requires traceability through botanical source, composition, molecular and granule state, derivatisation, formulation, exposure, post-cure, wash, hydration, conversion, residuals, mechanics, enzyme testing and biological model. Methacrylated starch alone is not a specification.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use non-identical starch sources, molecular states, derivative chemistries, formulations, light processes, specimens and biological models. Numerical values are retained as study-specific evidence and must not be treated as universal design values.

Author contributions

Juan Segurola: conceptualisation, evidence synthesis, boundary definition, engineering interpretation, manuscript preparation and final author verification.

Competing interests

The author is founder and CEO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated. Scientific statements derive from the cited primary literature and official standards. The review package includes QA and source-boundary controls.

Company information

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