

Photocurable Guar-Gum-Derived Hydrogels: Botanical Identity, Hydroxypropylation, Methacrylation, Dual Networks, Extrusion, Hydration and Qualification

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Statement of Significance

Guar gum is not one invariant photocurable feedstock. Botanical source, endosperm recovery, galactose-to-mannose ratio, molar-mass distribution, hydroxypropylation, purification and moisture precede methacrylation. Native GG, HPG, GG-MA and HPG-MA have distinct hydration, rheology and network functions. Dynamic borate or boronate junctions must also be separated from irreversible radical crosslinks.

Keywords: guar gum; hydroxypropyl guar; methacrylated guar; photocrosslinking; dual network; boronate; extrusion bioprinting; hydration; qualification

Abstract

Photocurable guar-derived hydrogels span GG-MA macromonomers, HPG-MA networks, hybrid permanent-reversible networks and cell-laden extrusion inks. Tiwari et al. linked GG-MA molar mass and methacrylation to swelling, enzymatic degradation and endothelial-cell response. Ospennikov et al. combined HPG-MA photochemistry with reversible phenylboronate-diol links. Shang et al. reported a monophasic GG-MA extrusion bioink. Non-photo HPG/borate systems provide essential controls for reversible-network attribution. This review keeps those material and article states separate.

1. Scope and boundaries

ER-135 owns identity and qualification of native, hydroxypropylated and methacrylated guar in photocurable hydrogels. It covers botanical and recovery state, molar mass, substitution, purification, ink rheology, photoconversion, permanent and reversible network attribution, extrusion, washing, swelling, degradation, mechanics and biological boundaries.

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 network architecture; ER-86 extractables; ER-100 corpus architecture; and ER-121 to ER-134 neighbouring photocurable biopolymer systems. [C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13,C14,C15,C16,C17,C18,C19,C20,C21,C22].

General AM characteristics and geometric test artefacts should follow the declared ISO/ASTM standards [S1,S3].

Native GG, HPG, GG-MA, HPG-MA and carboxymethyl-hydroxypropyl guar are not interchangeable. A derivative name or reagent feed is not measured substitution. Gelation by borate, boronate, nanoparticle association or entanglement is not photoconversion. Print fidelity is not bulk cure, and a cell response in one formulation is not a general safety conclusion.

2. Controlled guar-derived photocurable state chain

State	Minimum identity	Failure if omitted
Incoming guar	Botanical/recovery source, grade/lot, molar mass, galactose:mannose ratio, protein, ash, moisture, microbial state and storage	Guar name replaces feedstock identity
HPG or methacrylated derivative	Derivative class, reagent/feed, reaction/purification, measured substitution, molar-state change, residuals and storage	Trade name or reagent feed replaces derivative identity
Precursor	Polymer solids, reversible linker, pH, salts, cells, initiator, hydration, rheology, optical state, shear history and age	Network roles and working life disappear
Article	Extrusion/light process, post-cure, wash, conversion, soluble fraction, residuals, hydrated dimensions, mechanics and biology	Deposited, cured, washed and hydrated states are conflated

Table 1. Minimum state chain for guar-derived photocurable constructs.

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 Botanical, recovery and molecular state precede derivatisation

Guar is a seed-endosperm galactomannan. Species and cultivar, growing and storage history, split or flour recovery, protein and ash, galactose-to-mannose ratio, molar-mass distribution, moisture, microbial burden and solution preparation influence hydration, association and shear response. Hydroxypropylation weakens intermolecular association and improves ambient hydration, but its degree of substitution and molecular-state consequences must be measured rather than inferred from a trade name.

3.2 GG-MA establishes molar-mass and methacrylation dependence

Tiwari et al. modified guar with glycidyl methacrylate and evaluated GG-MA macromonomers over reported molar-mass and methacrylation ranges [1]. Pore structure, swelling, enzymatic mass loss and EA.hy926 response depended on macromonomer identity and concentration. These data establish a controlled dependency, not universal design values. Parent GG molar mass, purified GG-MA molar mass, measured methacrylation, solids and irradiation conditions must remain attached to each result.

3.3 HPG-MA separates irreversible cure from reversible boronate links

Ospennikov et al. methacrylated a characterised HPG and photocrosslinked HPG-MA with TPO-Li [2]. A second architecture copolymerised 3-acrylamidophenylboronic acid, adding reversible PBA-diol junctions to the irreversible methacrylate network. The two link classes affected modulus, swelling and pH-regulated release differently. HPG substitution, HPG-MA modification, AAPBA content, pH, polymer concentration and light exposure are therefore independent control coordinates.

3.4 Monophasic GG-MA extrusion couples rheology, dose and article state

Shang et al. reported GG-MA hydrogels at two methacrylation levels and screened concentration for extrusion, mechanical response, swelling, degradation and rabbit BMSC culture [3]. The reported Young's moduli and 60-day mass-loss values belong to the tested formulations, cure and conditioning. Shang et al. name conflicting derivatisation reagents: the Materials list specifies "Methacrylic anhydride (Sigma Aldrich, USA)" while the synthesis paragraph states "Methyl acrylate (MAA) was then slowly added at molar ratios of 1:0.5 and 1:2". These are different compounds and methyl acrylate cannot yield a methacrylate ester; the reagent is taken to be methacrylic anhydride, consistent with the Materials list, the GG-MA designation and the ¹H-NMR methacrylate substitution determination. The inconsistency is a defect in the source text and is recorded here rather than normalised.

3.5 Dynamic guar networks are mechanistic comparators, not photo evidence

Shibaev et al. formed CMHPG/borate gels with cobalt-ferrite nanoparticles at pH 10.7 and assigned reshaping and self-healing to labile cross-links contributed both by borate-diol junctions and by polymer-nanoparticle association [4]. Berlangieri et al. resolved HPG/borax/glycerol formulation effects by NMR, rheology and SAXS [5]. These studies support dynamic-network controls and conditioning sensitivity. They do not establish methacrylate conversion, photocure depth, printed-article fidelity or biological suitability.

4. Formulation, rheology and optical-process control

Parent lot and derivative state, GG or HPG concentration, methacrylation, reversible-linker content, pH, salts, cells and initiator define the precursor. Hydration time, temperature, ageing, shear history, cartridge residence, nozzle and pressure define extrusion. Spectrum, irradiance, exposure, oxygen, depth and geometry define photoconversion. Each coordinate requires monitoring on the complete formulation.

Parent-polymer, GG-MA or HPG-MA, dark, initiator-light, no-methacrylate, no-reversible-linker and complete-formulation controls are required. Matched pH and ionic conditions separate entanglement, borate or boronate exchange, nanoparticle association and irreversible radical crosslinking. Without those controls, rheology, recovery, self-healing and mechanics cannot be assigned to a network owner.

5. Washing, hydration, degradation and biological boundaries

Evidence block	What it can show	What it cannot establish alone
Feedstock/derivative identity	Method-specific molar mass, substitution, purity, residual and solution state	Photoconversion or article performance
Rheology/extrusion	Formulation-, hydration-, temperature-, shear-, nozzle- and geometry-specific deposition	Network ownership or transferable settings

Evidence block	What it can show	What it cannot establish alone
Network/article state	Permanent/reversible contributions, conversion, soluble fraction, hydration, dimensions and mechanics	Universal degradation or service life
Biological model	Response of the exact extract, hydrogel or cell-loaded print in the stated model	General safety, clinical efficacy or regulatory approval

Table 2. Evidence blocks that must remain separate for guar-derived photoresins.

ISO 10993-12:2021/Amd 1:2025 and ISO 10993-18:2020/Amd 1:2022 anchor sample preparation and chemical characterisation [S4,S5]. ISO 10993-1:2025 frames biological safety within risk management [S6]. Endothelial-cell or BMSC viability, proliferation, migration or differentiation in a stated model does not establish universal biocompatibility, therapeutic efficacy or regulatory approval.

6. Release matrix

Gate	Minimum evidence	Claim withheld
Parent identity	Botanical/recovery source, lot, molar mass, galactose:mannose ratio, protein, ash, moisture and storage	Generic guar equivalence
Derivatisation	Reaction/purification, measured HPG and methacrylate substitution, residuals, stability and molecular-state record	Acronym or reagent feed as derivative identity
Network attribution	Parent, derivative, dark, no-methacrylate, no-reversible-linker and complete controls plus conversion	Unverified permanent or reversible ownership
Process	Complete formulation, hydration/rheology/age, extrusion hardware, spectrum, irradiance, exposure and geometry	Transferable deposition or cure settings
Article state	Green, post-cured, washed, hydrated and dried x/y/z, mass, soluble fraction, residuals, mechanics and conditioning	Unqualified dimensions, mechanics or stability
Biological boundary	Exact derivative, formulation, print/light stress, wash/extract, model, dose, endpoint, duration and statistics	Universal biocompatibility or clinical suitability

Table 3. Minimum release architecture for guar-derived photocurable constructs.

7. Failure-mode interpretation

- The nominally same guar ink hydrates or extrudes differently: verify botanical/recovery lot, molar mass, galactose-to-mannose ratio, derivative substitution, moisture, salts, hydration protocol, temperature, shear history and cartridge age before changing exposure.
- A GG-MA or HPG-MA hydrogel is stiffer: separate polymer concentration, measured substitution, conversion, soluble fraction and hydration state before assigning the change to methacrylation alone.
- A dual network self-heals or responds to pH: use no-PBA or no-borate and no-methacrylate controls, then measure exchange and permanent-network retention independently.
- Extruded filaments retain shape but soften after washing: quantify conversion, leachable fraction, equilibrium swelling and x/y/z dimensions in green, washed and hydrated states.
- Degradation differs between formulations: retain enzyme or medium identity, activity, temperature, sample geometry, network state, mass basis and mechanical retention; dissolution is not necessarily cleavage.
- A cell-laden GG-MA construct shows proliferation or chondrogenic markers: retain cell source, passage, printing stress, light dose, wash, culture duration, controls and endpoint; withhold clinical claims.

8. Minimum workflow and research priorities

- Freeze species/cultivar where available, seed-endosperm recovery, grade and lot, molar-mass distribution, galactose-to-mannose ratio, protein, ash, moisture, microbial state, storage and hydration protocol.
- For HPG, GG-MA and HPG-MA, report reagent identity and feed basis, reaction, purification and drying, measured substitution method/result, residual reagents, molecular-state change and storage.
- Map polymer concentration, reversible linker, pH, salts, cells and initiator, plus viscosity, yield stress, recovery, ageing, optical attenuation and conversion over the working interval.
- Record printer, nozzle, pressure or flow, speed, layer, temperature and geometry, plus spectrum, irradiance, exposure, oxygen, post-cure and wash.
- Measure methacrylate conversion, permanent and reversible network contributions, insoluble and soluble fractions, residual initiator and derivatisation reagents, and x/y/z dimensions through article states.
- Use parent-polymer, derivative, dark, initiator-light, no-methacrylate, no-reversible-linker and complete controls to assign hydration, rheology, deposition, photoconversion and mechanics.

- Test swelling, dissolution, enzymatic and non-enzymatic mass loss, and mechanical retention in defined media over time; distinguish soluble release, reversible-link disruption and backbone or network cleavage.
- Separate extrusion injury, curing injury, extract cytotoxicity, proliferation, migration, differentiation and tissue models from safety, efficacy and regulatory conclusions.

9. Conclusions

Photocurable guar-derived materials are controlled botanical-feedstock, recovery, molecular, derivative, formulation, reversible-network, optical-process, washing and article states.

Primary evidence supports photopolymerisable GG-MA, HPG-MA permanent-reversible networks and GG-MA extrusion bioinks. Dynamic HPG or CMHPG networks define useful comparators but do not prove photocure.

Release requires traceability through source, molar mass, substitution, purification, formulation, rheology, process, conversion, network attribution, washing, soluble fraction, residuals, hydration, dimensions, mechanics and biological model.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use different guar identities, derivatives, substitution definitions, formulations, light conditions, article states and biological models. Numerical values are study-specific evidence, not 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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