

Methacrylated Gellan-Gum Photoresins: Microbial Identity, Acyl State, Methacrylation, Thermo-Ionic-Photo Networks, Extrusion, Hydration and Qualification

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Statement of Significance

Gellan gum is not defined by its trade name alone. Producing microorganism, fermentation and recovery, high- or low-acyl state, molar-mass distribution, counterions, moisture and ash define the parent polymer. Methacrylation adds a second identity; temperature, ions and light then create separable physical, ionic and covalent network states.

Keywords: gellan gum; gellan gum methacrylate; acyl state; ionic gelation; photocrosslinking; extrusion printing; hydration; qualification

Abstract

Photocurable gellan-gum systems span gellan gum methacrylate (GGMA), injectable GGMA/PEG-dimethacrylate formulations, ionically or photo-crosslinked cell carriers, and extrusion-printed composites. Pacelli et al. linked functionalisation to solubility, mechanics, swelling and release; Tsaryk et al. compared ionic and photo-crosslinked cell constructs; D'Amora et al. resolved synthesis, printing and post-crosslinking; and Annurakshita et al. added ionic pre-crosslinking and gallol functionality. This review separates parent identity, substitution, thermo-ionic history, photoconversion, process, hydration, network attribution and biological evidence.

1. Scope and boundaries

ER-131 owns material-specific identity and qualification of chemically photocurable gellan-gum derivatives. It covers microbial source and recovery, acyl state, molar mass and counterions, methacrylation, thermal and ionic pre-gelation, photochemistry, extrusion, washing, hydration, mechanics, release 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 generic dual-network architecture; ER-86 extractables; ER-100 corpus architecture; ER-125 alginate; ER-130 kappa-carrageenan; and ER-127 to ER-129 other polysaccharide derivatives. [C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13].

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

High-acyl and low-acyl gellan gum are not interchangeable. Methacrylic-anhydride feed is not measured substitution. Cooling-induced association is not cation crosslinking, and neither is covalent conversion. Unmodified gellan gum blended into a photocurable partner is not a photocurable gellan derivative, even when the composite solidifies under light.

2. Controlled gellan-photoresin state chain

State	Minimum identity	Failure if omitted
Incoming gellan gum	Producing strain/process, recovery and deacylation, grade/lot, high- or low-acyl state, molar mass, counterions, ash, moisture and storage	Trade name replaces feedstock identity
Photoactive derivative	MA feed basis, reaction, purification, measured substitution, acyl/counterion state, residuals and storage	Feed ratio or GGMA acronym is treated as identity
Ink or precursor	Solids, ions, co-crosslinker/additives/cells, pH, thermal history, initiator, optical state, temperature and age	Thermal, ionic and formulation states disappear
Article	Extrusion, photo/ion sequence, post-cure, wash, conversion, soluble fraction, residuals, hydrated dimensions and mechanics	Deposited, covalent, ionic, washed and hydrated states are conflated

Table 1. Minimum state chain for photocurable gellan-gum networks.

3. Primary evidence and controlled interpretation

3.1 Microbial origin, acyl state and counterions are upstream coordinates

Gellan gum is an anionic microbial exopolysaccharide built from a repeating tetrasaccharide containing glucose, glucuronic acid and rhamnose. Producing strain and fermentation, recovery and deacylation, high- or low-acyl state, molar-mass distribution, sodium, potassium, calcium and magnesium state, moisture, ash and thermal history govern dissolution, viscosity, gel temperature and ionic response before derivatisation or light exposure.

3.2 Methacrylation creates chemical cure without deleting thermo-ionic gelation

Pacelli et al. modified gellan gum with methacrylic groups and varied functionalisation, then combined GGMA with PEG dimethacrylate to reduce fragility [1]. Solubility, mechanics, swelling, diffusion of sulindac and vitamin B12, and fibroblast cytotoxicity were evaluated. The work establishes derivative- and formulation-specific relationships, not a universal modulus or release law, because parent identity, substitution, co-crosslinker, initiator, light dose and conditioning remain formulation coordinates.

3.3 Ionic and photo-crosslinked articles are distinct biological test objects

Tsaryk et al. evaluated ionically crosslinked and photo-crosslinked GGMA with human mesenchymal stem cells and nasal chondrocytes [2]. Both materials were non-cytotoxic in extraction assays and did not induce the reported pro-inflammatory endothelial response; encapsulated cells remained viable for at least two weeks, while apoptosis was observed in the photo-crosslinked condition. Those results require retention of network route, cell type, construct state and duration and cannot be collapsed into a generic biocompatibility claim.

3.4 Extrusion requires an ordered thermal-photo-ionic process record

D'Amora et al. dissolved low-acyl gellan gum at 1% w/v and 90 degrees C, reacted it with methacrylic anhydride at 50 degrees C and pH 8-8.4 for 6 h, precipitated, dialysed for 72 h and lyophilised [3]. They printed 2 or 4% w/v GGMA at formulation-specific temperatures, used 365 nm UV for 10 min at a reported 10 J/cm² setting, then immersed scaffolds for 10 min in 0.05% w/v calcium chloride. Chemistry, thermal deposition, photoconversion and ionic post-treatment are four controlled stages, not one generic cure.

3.5 Composite functionality changes network and claim ownership

D'Amora et al. incorporated black-soldier-fly eumelanin or hydroxyapatite and printed lattices at 35% and 45% infill [3]. Four-percent GGMA constructs retained structural integrity in the reported 28-day study; 30% HAp relative to GGMA produced a 32.5 kPa storage modulus, 3.5-fold above neat GGMA, and osteoblast responses depended on additive. Annurakshita et al. used mild ionic pre-crosslinking before photocure and added gallol groups for adhesion and antioxidant function [4]. These effects belong to complete composite architectures.

4. Thermal, ionic and optical process control

Polymer lot, acyl state, molar mass, counterions, concentration, pH, ionic strength, temperature, heating/cooling rate and ageing control the precursor. Methacrylation, initiator, co-crosslinker or additive, wavelength, irradiance, exposure, oxygen and filament geometry control covalent cure. These variables require monitoring on the production ink over its use-life rather than inference from the GGMA acronym.

Parent gellan gum, thermal-only, ion-only, photo-only and combined controls are required to assign yield stress, shape retention, conversion, swelling and mechanics. Composite studies additionally require matched GGMA, PEG-DMA, HAp, pigment or gallol controls to distinguish junction-zone, covalent, filler and functional-additive contributions.

5. Hydration, ion exchange, release and biological boundaries

Evidence block	What it can show	What it cannot establish alone
Parent identity	Method-specific acyl state, molar mass, counterions and thermo-ionic response	Methacrylation, conversion or article performance
Process window	Formulation-, temperature-, ion-, printer- and geometry-specific deposition and cure	Transferable settings or bulk conversion
Hydration/release	Medium-, counterion-, solute-, temperature- and time-specific mass, dimensions, mechanics and diffusion	Universal degradation or release mechanism
Biological model	Response of the exact construct, extract or cell-loaded formulation in the stated model	General safety, clinical efficacy or regulatory approval

Table 2. Evidence blocks that must remain separate for gellan-gum 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]. One extraction assay, cell-loading study, release experiment or osteoblast endpoint does not establish universal safety, efficacy or approval.

Reference [5] provides the tribological bridge between methacrylated kappa-carrageenan and gellan-gum hydrogels and is retained as targeted supporting evidence.

6. Release matrix

Gate	Minimum evidence	Claim withheld
Parent identity	Microbial process, recovery/deacylation, lot, acyl state, molar mass, counterions, ash, moisture and storage	Generic gellan-gum equivalence
Derivatisation	Reaction/purification record, measured substitution, retained ionic identity, residuals and stability	Feed or acronym as derivative identity
Process	Complete formulation, thermal/ion sequence, extrusion hardware, spectrum, irradiance, exposure and geometry	Transferable deposition or cure settings
Network attribution	Conversion plus parent, thermal-only, ion-only, photo-only, combined and matched composite controls	Unverified physical, ionic, covalent or additive ownership
Article state	Green, post-cured, ion-treated, washed, hydrated and dried x/y/z, mass, residuals, mechanics and conditioning	Unqualified dimensions, mechanics or stability
Biological boundary	Exact derivative, ions, formulation, wash/extract, model, dose, endpoint, duration and statistics	Universal biocompatibility or clinical suitability

Table 3. Minimum release architecture for photocurable gellan-gum constructs.

7. Failure-mode interpretation

- The nominally same ink gels in the syringe: check acyl state and lot, molar mass, counterions, solids, pH, temperature history, cooling rate and age before changing pressure or exposure.
- Higher methacrylic-anhydride feed does not give the expected cured modulus: measure incorporated substitution and conversion; feed, chain modification, thermo-ionic junctions and covalent density are different quantities.
- Filaments print cleanly but change in culture medium: quantify counterion exchange, soluble fraction, mass and x/y/z dimensions before and after photocure, calcium treatment, washing and equilibration in the intended medium.
- A PEG-DMA, HAP, eumelanin or gallol formulation improves performance: retain matched component controls and report molecular mass, loading, particle distribution or substitution. The response cannot be assigned to GGMA alone.
- Drug diffusion, swelling or mass change is reported: retain solute identity and size, loading, medium, pH, temperature, sink conditions, specimen geometry and sampling corrections; do not infer a universal release mechanism.
- A cell or tissue model passes: retain exact derivative, ions, additives, initiator, light dose, wash or extract, dose, model, duration and endpoint; do not infer clinical safety, efficacy or regulatory approval.

8. Minimum workflow and research priorities

- Freeze producing strain and fermentation/recovery, deacylation, commercial grade and lot, high- or low-acyl state, molar-mass distribution, counterions, ash, moisture and storage.
- Report methacrylation reagent and feed basis, pH, time, temperature, purification, drying, measured substitution method/result, residual reagents, salt form and storage.
- Map solids, pH, ionic strength and composition, thermal cycles, viscosity, yield stress, gel temperature, optical attenuation and cure response over ink age and build duration.
- Record printer, nozzle, pressure or flow, deposition temperature, speed and geometry, plus spectrum, irradiance, exposure, photo/ion sequence, post-cure and wash.
- Measure conversion, insoluble and soluble fractions, residual initiator and derivatisation reagents, counterion exchange and x/y/z dimensions in green, washed, hydrated and dried states.
- Use parent, thermal-only, ion-only, photo-only and combined controls, plus matched co-crosslinker, mineral, pigment or gallol controls, to assign deposition, cure and mechanics.
- Test swelling, diffusion, mass loss and mechanical retention in defined media over time and temperature; distinguish ion exchange and dissolution from backbone degradation.
- Separate extract cytotoxicity, direct contact, cell encapsulation, release, differentiation, tissue models and animal observations from safety, efficacy and regulatory conclusions.

9. Conclusions

Photocurable gellan-gum materials are controlled microbial-feedstock, acyl-state, derivative, thermal, ionic, formulation, optical-process and article states. Counterions and measured methacrylation are independent identity coordinates.

Primary evidence supports injectable GGMA/PEG-DMA, ionically or photo-crosslinked cell carriers, extrusion-printed GGMA composites and ionic-pre-gel/photo-cure architectures. Their formulations, network owners and biological models are not interchangeable.

Release requires traceability through source, acyl state, counterions, methacrylation, thermo-ionic history, formulation, process, conversion, washing, soluble fraction, residuals, hydration, dimensions, mechanics, release and biological model.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use different gellan grades, substitution definitions, co-crosslinkers, counterions, thermal histories, printing processes, article states and biological models. Numerical values are study-specific evidence, not universal design values.

Author contributions

Juan Seguro: 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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