

Methacrylated Kappa-Carrageenan Photoresins: Algal Source, Sulfation, Methacrylation, Thermo-Ionic-Photo Networks, Extrusion and DLP, Hydration and Qualification

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Statement of Significance

Kappa-carrageenan is not defined by its polymer name alone. Algal species and harvest, extraction and alkali history, sulfate and 3,6-anhydrogalactose content, molar-mass distribution, counterions, moisture and ash define the feedstock. Methacrylation adds a second identity; cooling, ion exposure and light then create distinct network states.

Keywords: kappa-carrageenan; methacrylated carrageenan; sulfate; ionic gelation; photocrosslinking; extrusion bioprinting; DLP; qualification

Abstract

Photocurable kappa-carrageenan systems span methacrylated kappa-carrageenan (MA-kappa-CA) that retains thermoreversible and cation-responsive assembly, dual ionic-photo bioinks, DLP formulations and composites with gelatin methacrylate or hydroxyapatite. Mihaila et al. established the chemically and physically crosslinked derivative; Lim et al. resolved the KCl/UV sequence for extrusion; Kumari et al. transferred the chemistry to DLP; and Kansiz et al. varied methacrylation and mineral loading. This review separates parent identity, substitution, thermal and ionic history, photoconversion, process, hydration, network attribution and biological evidence.

1. Scope and boundaries

ER-130 owns material-specific identity and qualification of chemically photocurable kappa-carrageenan derivatives. It covers algal source and extraction, sulfate and 3,6-anhydrogalactose state, molar mass and counterions, methacrylation, thermal and ionic pre-gelation, photochemistry, extrusion or DLP, washing, hydration, mechanics and biology.

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-123 chitosan; ER-125 alginate; and ER-127 to ER-129 other plant-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].

Kappa-, iota- and lambda-carrageenan are not interchangeable. Methacrylic-anhydride feed is not measured substitution. Cooling-induced helix aggregation is not KCl or Ca²⁺ crosslinking, and neither is covalent conversion. Unmodified kappa-carrageenan blended into GelMA is not a photocurable carrageenan derivative, even if the composite photocures.

2. Controlled carrageenan-photoresin state chain

State	Minimum identity	Failure if omitted
Incoming kappa-carrageenan	Algal species/part, harvest, extraction and alkali history, lot, sulfate, 3,6-anhydrogalactose, molar mass, counterions, ash, moisture and storage	Carrageenan name replaces feedstock identity
Photoactive derivative	MA feed basis, reaction, purification, measured substitution, sulfate/counterion retention, residuals and storage	Feed ratio or acronym is treated as identity
Ink or precursor	Solids, ions, co-macromers/minerals/cells, pH, thermal history, initiator, optical state, temperature and age	Thermal, ionic and formulation states disappear
Article	Extrusion/DLP process, ion/light sequence, post-cure, wash, conversion, soluble fraction, residuals, hydrated dimensions and mechanics	Pre-gelled, covalent, washed and hydrated states are conflated

Table 1. Minimum state chain for photocurable kappa-carrageenan 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 Carrageenan type, sulfate state and counterions are upstream coordinates

Kappa-carrageenan is an algae-derived sulfated galactan whose gelation depends on coil-to-helix association, temperature and cations. Commercial grade, species and extraction are not sufficient identity: sulfate and 3,6-anhydrogalactose content, molar-mass distribution, potassium, sodium and calcium state, moisture, ash and thermal history govern viscosity, gel temperature and ionic response before methacrylation or exposure.

The parent-polymer and methacrylation coordinates discussed here follow the evidence base in reference [1].

3.2 Methacrylation creates chemical cure without deleting physical gelation

Mihaila et al. introduced methacrylate groups onto kappa-carrageenan and varied the degree of methacrylation to tune hydration, dissolution, morphology, compressive and rheological properties [1]. Their micromolded hydrogels combined physical and chemical crosslinking and supported encapsulated fibroblasts. The evidence establishes a dual-capable derivative, not a universal modulus or swelling value, because polymer identity, substitution, ion state, initiator, light dose and conditioning remain formulation-specific.

3.3 Reported substitution levels must retain their analytical basis

Lim et al. prepared 3% (w/v) kappa-carrageenan at 80 degrees C, added methacrylic anhydride under pH 8 control, dialysed for four days and freeze-dried the derivative [2]. The authors labelled low, medium and high MA-kappa-CA by the methacrylic-anhydride feed concentration added during synthesis (4, 8 and 12% w/v) and reported those same figures as MA substitution ratios; proton NMR demonstrated the vinyl and methyl signals but did not quantify substitution. Feed concentration and analytically measured degree of methacrylation must not be compared as the same quantity. Reaction feed, NMR integration basis, polymer repeat-unit basis and retained sulfate/counterion state must remain visible so those labels are not treated as interchangeable degrees of substitution across studies.

A published 2025 correction to reference [1] [1c] must be reviewed before any Mihaila-derived numerical comparison is released.

3.4 Extrusion uses an ordered ionic-photo sequence

Lim et al. formulated 3% (w/v) MA-kappa-CA with 0.25% (w/v) Irgacure 2959 and used a coaxial nozzle to contact the extrudate with KCl (500 mM) before UV exposure [2]. Their lattices were exposed at 250-450 nm and 7.3 mW/cm² for 15 s; cell-encapsulation specimens used 360-380 nm for 10 s. KCl concentration, diffusion time, nozzle geometry and temperature own the first network, while wavelength, irradiance, time and substitution own the second. Neither step alone qualifies the dual-crosslinked article.

3.5 DLP, minerals and hybrid macromers change process and network ownership

Kumari et al. reported DLP bioprinting of kappa-carrageenan hydrogels for cell-loaded scaffolds [3], so projector spectrum, layer exposure, resin depth and absorber state require a separate working curve from extrusion. Kansiz et al. found that both methacrylation level and hydroxyapatite addition affected printability and mechanics in extrusion bioinks [4]. Menaga and Kumari combined kappa-CA-MA with GelMA, 0.4% LAP and 420 nm exposure for 20 s [5]; its mechanics, release and biological results belong to a two-macromer hybrid.

4. Thermal, ionic and optical process control

Algal lot, molar mass, sulfate and anhydrogalactose composition, counterions, concentration, pH, ionic strength, temperature, heating/cooling rate and ageing control the precursor. Methacrylation, initiator, absorber, wavelength, irradiance, exposure, oxygen and layer or filament geometry control photoconversion. These variables must be monitored on the production ink over its full use-life, not inferred from the polymer label.

Native kappa-carrageenan, thermal-only, ion-only, photo-only and combined controls are required to assign yield stress, shape retention, conversion, swelling and mechanics. In composites, matched MA-kappa-CA, hydroxyapatite, GelMA and full-formulation controls are needed to distinguish mineral reinforcement, carrageenan junctions and co-macromer cure.

5. Hydration, ion exchange and biological boundaries

Evidence block	What it can show	What it cannot establish alone
Parent identity	Method-specific type, composition, molar mass, sulfate, counterions and thermal response	Methacrylation, conversion or article performance
Process window	Formulation-, ion-, temperature-, printer- and geometry-specific deposition and cure	Transferable extrusion/DLP settings or bulk conversion
Hydration/ion exchange	Medium-, counterion-, temperature- and time-specific mass, dimensions and mechanics	Universal degradation mechanism or service life

Evidence block	What it can show	What it cannot establish alone
Biological model	Response of the exact construct, extract or antimicrobial dose in the stated model	General safety, clinical efficacy or regulatory approval

Table 2. Evidence blocks that must remain separate for carrageenan 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]. Cell viability, antibacterial activity or one scratch assay does not establish universal biocompatibility, wound-healing efficacy or approval.

6. Release matrix

Gate	Minimum evidence	Claim withheld
Parent identity	Algal source, extraction, lot, sulfate/anhydrogalactose, molar mass, counterions, ash, moisture and storage	Generic kappa-carrageenan 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 or DLP hardware, spectrum, irradiance, exposure and geometry	Transferable deposition or cure settings
Network attribution	Conversion plus native, thermal-only, ion-only, photo-only, combined and matched composite controls	Unverified physical, ionic, covalent or filler ownership
Article state	Green, post-cured, washed, hydrated and dried x/y/z, mass, ions, 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 kappa-carrageenan constructs.

7. Failure-mode interpretation

- The nominally same ink gels in the syringe: check carrageenan type and lot, sulfate, molar mass, counterions, solids, pH, temperature history, cooling rate and age before changing pressure or exposure.
- Higher methacrylic-anhydride feed lowers viscosity but does not give the expected cured modulus: measure incorporated substitution, sulfate/counterion state and conversion; feed, helix disruption, ionic junctions and covalent density are different quantities.
- Filaments hold shape in KCl but relax in culture medium: quantify ion exchange, soluble fraction, mass and x/y/z dimensions before and after photoconversion, washing and equilibration in the intended medium.
- An extrusion formulation fails in DLP: build a projector-specific cure-depth and lateral-fidelity window using the complete resin. Nozzle flow, KCl delivery and filament cooling do not qualify vat exposure or through-layer cure.
- Hydroxyapatite or GelMA improves mechanics: retain matched component controls and report particle size/loading or GelMA substitution and concentration; the response cannot be assigned to MA-kappa-CA alone.
- A cell-loaded or antimicrobial construct passes: retain exact derivative, ions, co-materials, initiator, light dose, wash, dose, model, duration and endpoint; do not infer clinical safety, efficacy or regulatory approval.

8. Minimum workflow and research priorities

- Freeze algal species and fraction, harvest and extraction, lot, sulfate and anhydrogalactose content, molar-mass distribution, counterions, ash, moisture and storage before derivatisation.
- Report methacrylation reagent and feed basis, pH, time, temperature, purification, drying, measured substitution method/result, residual reagents, salt form and storage.
- Map concentration, pH, ionic strength, K/Na/Ca content, thermal cycles, viscosity, yield stress, gel temperature, optical attenuation and working curves over ink age and build duration.
- Record extrusion nozzle/flow/temperature and ion-delivery sequence or DLP projector, spectrum, irradiance, exposure, layer, resin depth and geometry, plus post-cure and wash.
- Measure conversion, insoluble and soluble fractions, residual initiator and methacrylation reagents, counterion exchange and x/y/z dimensions in green, washed, hydrated and dried states.
- Use native, thermal-only, ion-only, photo-only and combined controls, plus matched mineral or GelMA controls, to assign deposition, cure, mechanics and hydrated stability.
- Test swelling, mass loss and mechanical retention in defined media over time and temperature; distinguish ion exchange and dissolution from chemical or enzymatic backbone degradation.
- Separate extract cytotoxicity, direct contact, cell-laden printing, antibacterial tests, scratch assays, tissue models and animal observations from safety, efficacy and regulatory conclusions.

9. Conclusions

Photocurable kappa-carrageenan materials are controlled algal-feedstock, derivative, thermal, ionic, formulation, optical-process and article states. Sulfation, counterions and methacrylation are independent identity coordinates.

Primary evidence supports physically and chemically crosslinked MA-kappa-CA, ordered KCI/UV extrusion, DLP bioprinting and mineral or GelMA composites. These architectures, exposures and network owners are not interchangeable.

Release requires traceability through source, composition, counterions, methacrylation, thermal/ionic history, formulation, process, conversion, 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 carrageenan grades, substitution definitions, counterions, thermal histories, formulations, 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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