

Chitosan-Derived Photocurable Hydrogels: Molecular Weight, Degree of Deacetylation, Methacrylation, Acid-Neutral State, Hybrid PEG Networks, SLA/4D Printing and Qualification

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Statement of Significance

Methacrylated chitosan is not one material. Biological source, molecular-weight distribution, degree and pattern of deacetylation, acid dissolution, neutralisation, derivatisation, purification and storage define the macromer. PEGDA hybridisation and hydroxybutyl substitution create distinct chemistries, while exposure, washing, hydration and thermal programming define distinct article states.

Keywords: *chitosan; methacrylated chitosan; CsMA; deacetylation; molecular weight; PEGDA; SLA; 4D printing; hydrogel; qualification*

Abstract

Chitosan-derived photocurable hydrogels cannot be specified by the word chitosan alone. Molecular-weight distribution, degree and pattern of deacetylation, acid dissolution, neutralisation, derivatisation and purification determine the incoming macromer. Morris et al. demonstrated SLA manufacture of chitosan:PEGDA hybrid gels, while Seo et al. used hydroxybutyl-methacrylated chitosan for temperature-reversible SLA 4D printing. Bucciarelli et al. showed that CsMA concentration, temperature and shear rate govern solution viscosity, while CsMA concentration, photoinitiator concentration and UV exposure jointly alter compression modulus, morphology, degradation and solubilisation. This review separates neat derivatives from PEG hybrids and distinguishes pH/ionic history, temporary shape change and permanent network state.

1. Scope and boundaries

ER-123 owns material-specific identity and qualification of chitosan-derived photocurable hydrogels, including methacrylated and hydroxybutyl-methacrylated routes, PEGDA hybrids and SLA/4D constructs. It covers source, molecular-weight distribution, degree and pattern of deacetylation, acid dissolution, neutralisation, derivatisation, formulation, exposure, washing, hydration and programmed thermal response.

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, ER-122 and ER-124 to ER-126 neighbouring natural-polymer derivative families. [C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13].

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

Molecular weight is not degree of deacetylation. Acid dissolution is not neutralisation. Methacrylation feed is not measured substitution. CsMA, HBC-MA and chitosan:PEGDA are different chemistries. Temporary thermoresponsive movement is not permanent covalent shape change, and one biological model is not general approval.

2. Controlled chitosan-photoresin state chain

State	Minimum identity	Failure if omitted
Incoming chitosan	Chitosan source, molecular weight, degree of deacetylation, dissolution and neutralisation, molecular distribution, purity and storage	The word chitosan replaces polymer identity
Photoactive derivative	methacrylation reagent, feed and reaction, purification, drying, measured incorporation and calculation basis	Feed or CsMA acronym is treated as chemistry
Vat or biotink	Derivative concentration, water/buffer, initiator, absorber, cells or additives, temperature and age	Formulation and biological state disappear
Article	Exposure and layer strategy, green geometry, wash, hydration, secondary structure, conversion, residuals and mechanics	Green, washed, hydrated and tested objects are conflated

Table 1. Minimum state chain for methacrylated chitosan photocurable 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 Chitosan:PEGDA hybrids are not neat CsMA

Morris et al. manufactured chitosan:PEGDA hybrid-gel scaffolds by stereolithography and evaluated mechanical properties, cytocompatibility and manufacturability [1]. The evidence belongs to a hybrid network: PEGDA contribution, chitosan fraction, acid state and neutralisation cannot be omitted or transferred to a neat CsMA claim.

3.2 Concentration, hydration and mechanics are coupled

Chitosan molecular weight and degree and pattern of deacetylation affect solubility, charge density, viscosity and chain association. Acid identity and concentration, pH, salt, temperature and neutralisation history are therefore formulation coordinates. Methacrylation feed is not measured substitution, and measured substitution does not erase the parent-polymer distribution.

3.3 HBC-MA thermoreversibility is chemistry- and programming-specific

Seo et al. used hydroxybutyl methacrylated chitosan as a photo-crosslinkable and temperature-reversible polymer in SLA 4D printing [2]. Thermal response and shape change belong to that HBC-MA chemistry and programmed state. They are not generic properties of methacrylated chitosan.

3.4 Modelled CsMA property ranges are design-space-specific

Bucciarelli et al. modelled CsMA solution viscosity against concentration, temperature and shear rate and linked hydrogel properties to CsMA concentration, photoinitiator and UV exposure [3]. Their reported 12-64 kPa stiffness range and stability up to 60 days are formulation- and protocol-specific, not universal chitosan values.

3.5 Acid, neutral, cured, washed and degraded states must stay separate

Acid-solubilised, neutralised, photocured, washed, hydrated and degraded articles must remain separate. Degradation or solubilisation requires medium, pH, enzyme if used, temperature, replenishment, geometry and time; ionic decomplexation must not be relabelled covalent chain scission.

4. Photochemistry, polymer structure and process state

Chitosan molecular weight, deacetylation, pH, acid and salt state, concentration, temperature and age control viscosity and association. Derivatisation supplies photoreactivity, while initiator, wavelength, irradiance, exposure, oxygen, layer thickness and absorption control polymerisation. Neutralisation and washing can change dimensions and properties independently of conversion.

PEGDA hybrids require component-specific controls, and HBC-MA thermal reversibility requires a defined programming and recovery history. Conversion, ionic state, hydration and physical association must be measured independently on matched article states.

5. Hydration, degradation and biological boundaries

Evidence block	What it can show	What it cannot establish alone
Hydration/equilibration	Medium- and time-specific mass, dimensions, swelling and mechanics	Conversion, in-use lifetime or degradation mechanism
Polymer association	Method- and state-specific acid-neutral and physical association or other conformational content	Covalent conversion or a verified second network
Enzymatic incubation	Enzyme-, activity-, medium-, temperature-, geometry- and time-specific mass/property evolution	Universal in-vivo resorption
Biological model	Response of the exact construct in the stated cell, tissue or animal model	General safety, clinical efficacy or regulatory approval

Table 2. Evidence blocks that must remain separate for chitosan photo-networks.

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], while ISO 22442-1:2020 is relevant when animal-derived starting materials enter a medical-device claim [S8]. None of these standards converts a favourable cell or animal observation into general clinical suitability.

6. Release matrix

Gate	Minimum evidence	Claim withheld
Chitosan identity	Species/source, raw polymer lot, deacetylation, dissolution, molecular distribution, purity and storage	Generic chitosan equivalence

Gate	Minimum evidence	Claim withheld
Functionalisation	Reaction conditions, purification, measured incorporation method/result and storage	methacrylation feed or CsMA acronym as identity
Vat process	Concentration, initiator, wavelength, irradiance, exposure, layer thickness, temperature and ageing	Transferable print settings
Network attribution	Conversion plus independent secondary-structure and physical-state evidence with controls	Unverified dual network
Article state	Green, washed and hydrated x/y/z, mass, residuals and conditioning history	Unqualified dimensions or mechanics
Biological boundary	Exact formulation, construct, dose, wash, model, endpoint and statistics	Universal biocompatibility or clinical suitability

Table 3. Minimum release architecture for methacrylated chitosan photocurable constructs.

7. Failure-mode interpretation

- A nominally identical CsMA becomes much less viscous: verify source, molecular weight, deacetylation, acid dissolution and neutralisation, chain degradation, concentration, temperature, storage and freeze-thaw history before changing exposure.
- A higher methacrylation feed does not increase modulus: measure incorporated functionality and conversion; feed, measured degree of substitution and network density are different quantities.
- The green object is accurate but expands after washing: report x/y/z, mass and medium history after a defined wash and equilibration; do not publish green dimensions as in-use dimensions.
- Mechanical strength rises during incubation: measure water content and secondary structure before assigning further covalent cure or degradation.
- A PEGDA hybrid prints better than neat CsMA: retain hybrid identity, filler state and optical absorption; do not transfer the result to neat chitosan resin.
- Cells remain viable after printing: retain the exact chitosan route, formulation, light, wash, construct and model; do not infer approval or universal biocompatibility.

8. Minimum workflow and research priorities

- Freeze chitosan source, molecular-weight distribution, degree and pattern of deacetylation, purity, bioburden and storage.
- Report methacrylation feed, pH, temperature, time, mixing, purification, dialysis cutoff and duration, drying, measured incorporation and calculation basis.
- Map viscosity, absorbance and working curves over temperature, ageing and the complete build-duration window.
- Measure conversion, gel fraction, residuals and retained chitosan on matched green, washed and hydrated states.
- Quantify secondary structure independently from covalent conversion and distinguish physical reinforcement from a verified second network.
- Track mass and x/y/z dimensions through washing, equilibration, drying, rehydration and degradation.
- Report enzyme or medium identity, activity, pH, temperature, replenishment, geometry and time rather than one generic degradation rate.
- Separate model-specific viability, differentiation, adhesion or healing observations from safety, efficacy and regulatory conclusions.

9. Conclusions

Chitosan photocurable hydrogels are controlled parent-polymer, derivative, formulation, network and article states. Source, molecular weight and deacetylation define the incoming chitosan; acid/neutral state and derivatisation define the macromer; formulation and exposure define the green network; washing and hydration define the tested article.

Primary evidence supports SLA manufacture of chitosan:PEGDA hybrids, thermoresponsive HBC-MA 4D constructs and tunable CsMA hydrogels. These results do not make the chemistries interchangeable.

Release requires traceability through molecular distribution, deacetylation, acid and neutralisation history, substitution, formulation, exposure, wash, hydration, residuals, mechanics, degradation and programmed response. CsMA alone is not a specification.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use related but non-identical chitosan routes, formulations, printers, exposures, 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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References - independent scientific evidence

- [1] Morris, V.B., Nimbalkar, S., Younesi, M., McClellan, P. and Akkus, O. Mechanical Properties, Cytocompatibility and Manufacturability of Chitosan:PEGDA Hybrid-Gel Scaffolds by Stereolithography. *Annals of Biomedical Engineering* 45 (2017) 286-296. DOI: [10.1007/s10439-016-1643-1](https://doi.org/10.1007/s10439-016-1643-1).
- [2] Seo, J.W., Shin, S.R., Park, Y.J. et al. Hydrogel Production Platform with Dynamic Movement Using Photo-Crosslinkable/Temperature Reversible Chitosan Polymer and Stereolithography 4D Printing Technology. *Tissue Engineering and Regenerative Medicine* 17 (2020) 423-431. DOI: [10.1007/s13770-020-00264-6](https://doi.org/10.1007/s13770-020-00264-6).
- [3] Bucciarelli, A., Selicato, N., Coricciati, C., Rainer, A., Capodilupo, A.L., Gigli, G., Moroni, L., Polini, A. and Gervaso, F. Modelling Methacrylated Chitosan Hydrogel Properties through an Experimental Design Approach: From Composition to Material Properties. *Journal of Materials Chemistry B* 12(40) (2024) 10221-10240. DOI: [10.1039/d4tb00670d](https://doi.org/10.1039/d4tb00670d).

Standards and measurement references

- [S1] ISO/ASTM 52927:2024. Additive manufacturing - General principles - Main characteristics and corresponding test methods. Edition 1. <https://www.iso.org/standard/81802.html>
- [S2] ISO/ASTM 52920:2023. Additive manufacturing - Qualification principles - Requirements for industrial additive manufacturing processes and production sites. Edition 1. <https://www.iso.org/standard/76911.html>
- [S3] ISO/ASTM 52902:2023. Additive manufacturing - Test artefacts - Geometric capability assessment of additive manufacturing systems. Edition 2. <https://www.iso.org/standard/79683.html>
- [S4] ISO 1101:2017. Geometrical product specifications (GPS) - Geometrical tolerancing - Tolerances of form, orientation, location and run-out. Edition 4. <https://www.iso.org/standard/66777.html>
- [S5] ISO 10993-12:2021 with Amendment 1:2025. Biological evaluation of medical devices - Part 12: Sample preparation and reference materials. Edition 5. <https://www.iso.org/standard/88205.html>
- [S6] ISO 10993-18:2020 with Amendment 1:2022. Biological evaluation of medical devices - Part 18: Chemical characterization of medical device materials within a risk management process. Edition 2. <https://www.iso.org/standard/64750.html>
- [S7] ISO 10993-1:2025. Biological evaluation of medical devices - Part 1: Requirements and general principles for the evaluation of biological safety within a risk management process. Edition 6. <https://www.iso.org/standard/10993-1>
- [S8] ISO 22442-1:2020. Medical devices utilizing animal tissues and their derivatives - Part 1: Application of risk management. Edition 3. <https://www.iso.org/standard/74280.html>

Related Engineering Review boundaries

- [C1] Segurola, J. Biological Response in Photopolymer Additive Manufacturing: A Review of Formulation Chemistry, Workflow Variables and Qualification Constraints in Dental and Biomedical Applications. ER-06. Zenodo (2026).
- [C2] Segurola, J. Metrology of Vat Photopolymerisation: Resolution, Trueness, Precision and Geometric Fidelity Across Scales. ER-10. Zenodo (2026).
- [C3] Segurola, J. Transport, Degradation and Mechanical Evolution in Vat-Printed Tissue-Engineering Scaffolds: Coupled Design and Qualification. ER-15. Zenodo (2026).
- [C4] Segurola, J. Conversion Metrology and Spatial Cure Heterogeneity in Vat Photopolymerisation: From Exposure to Network State. ER-27. Zenodo (2026).
- [C5] Segurola, J. Washing- and Drying-Induced Extraction, Property Change and Dimensional Response in Vat-Printed Photopolymers. ER-33. Zenodo (2026).

- [C6] Segurola, J. Hierarchical and Double-Network Hydrogels in Vat Photopolymerisation: Microgel Reinforcement, Interpenetration and Energy Dissipation. ER-67. Zenodo (2026).
- [C7] Segurola, J. Analytical Extractables and Leachables from Vat-Printed Photopolymers: Specimen State, Extraction Design, Analytical Coverage and Cross-Study Comparability. ER-86. Zenodo (2026).
- [C8] Segurola, J. From Individual Reviews to a Qualification Corpus: Evidence Architecture Across Engineering Reviews ER-01 to ER-99. ER-100. Zenodo (2026).
- [C9] Segurola, J. Methacrylated Silk-Fibroin Photoresins: Protein Source, GMA Functionalisation, Aqueous DLP, Hydration, Mechanics, Biological State and Qualification. ER-121. Zenodo (2026).
- [C10] Segurola, J. Collagen Methacryloyl Photoresins: Collagen Source, Methacrylation, Triple-Helix State, Low-Temperature DLP, Hydration, Enzymatic Degradation and Qualification. ER-122. Zenodo (2026).
- [C11] Segurola, J. Hyaluronic-Acid Methacrylate/Methacryloyl Photoresins: Source, Molecular Weight, Substitution, DLP Hybrid Networks, Hydration, Hyaluronidase Degradation and Qualification. ER-124. Zenodo (2026).
- [C12] Segurola, J. Alginate-Methacrylate Photoresins: Source, M/G Composition, Methacrylation Route, Covalent-Ionic Dual Networks, Hydration, Degradation and Qualification. ER-125. Zenodo (2026).
- [C13] Segurola, J. Dextran-Methacrylate Photoresins: Molecular Weight, Degree of Substitution, Solvent State, DLP Hybrid Networks, Washing, Degradation and Qualification. ER-126. Zenodo (2026).