

Methacrylated Silk-Fibroin Photoresins: Protein Source, GMA Functionalisation, Aqueous DLP, Hydration, Mechanics, Biological State and Qualification

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Statement of Significance

Methacrylated silk fibroin is not one material. Silkworm species, cocoon history, degumming severity, dissolution, regenerated-protein molecular distribution, glycidyl-methacrylate reaction, purification and storage define the incoming macromer. Concentration, initiator, optical dose, washing, hydration and secondary beta-sheet formation then define different network and article states. Qualification must preserve that chain rather than treating the label Sil-MA as a transferable specification.

Keywords: silk fibroin; Sil-MA; glycidyl methacrylate; DLP; vat photopolymerisation; hydrogel; hydration; beta sheet; degradation; bioprinting; qualification

Abstract

Primary studies demonstrate aqueous DLP printing of glycidyl-methacrylate-functionalised Bombyx mori silk fibroin, with properties altered by GMA feed, measured lysine modification, macromer concentration, photoinitiator and exposure. The founding study reported 141-705 mM GMA feeds, 22-42% lysine modification, 10-30% Sil-MA, 3.5 mW/cm² and 3 s per layer, but those values describe one controlled route rather than a universal resin. Subsequent cartilage, sealant, protocol and graphene-oxide studies add distinct formulations, article states and biological models. This review defines a traceable chain from protein source through functionalisation, printing, washing, hydration, secondary-structure evolution, mechanics, degradation and biological state, and proposes minimum release gates for silk-derived photocurable constructs.

1. Scope and boundaries

ER-121 owns material-specific identity and qualification of methacrylated silk-fibroin photoresins, especially GMA-functionalised regenerated Bombyx mori fibroin used in aqueous DLP. It covers protein-source and degumming history, dissolution, functionalisation, purification, formulation, light processing, washing, hydration, mechanical state and degradation attribution.

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 double-network architecture; ER-86 extractables; ER-100 corpus architecture; and ER-122 to ER-126 the neighbouring collagen, chitosan, hyaluronic-acid, alginate and dextran 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].

Silkworm source is not degumming history. GMA feed is not measured substitution. A regenerated-fibroin solution is not Sil-MA. A photocured green object is not the washed or hydrated article. Beta-sheet-rich physical reinforcement is not automatically a second covalent network. Cell viability in one construct and model is not regulatory approval.

2. Controlled silk-photoresin state chain

State	Minimum identity	Failure if omitted
Incoming fibroin	Silkworm species/source, cocoon lot, degumming, dissolution, molecular distribution, purity and storage	The word silk replaces protein identity
Photoactive derivative	GMA feed and reaction, purification, drying, measured incorporation and calculation basis	Feed or Sil-MA acronym is treated as chemistry
Vat or bioink	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 silk-fibroin 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 GMA functionalisation and aqueous DLP

Kim et al. produced Sil-MA by reacting regenerated Bombyx mori fibroin with 141-705 mM GMA during dissolution, followed by dialysis and freeze-drying [1]. Proton NMR associated increasing GMA feed with 22-42% modification of lysine residues. With LAP, 10-30% Sil-MA was DLP printed; 3.5 mW/cm² for 3 s per layer was reported for that equipment and formulation. These are route-specific parameters, not transferable defaults.

3.2 Concentration, hydration and mechanics are coupled

In the same study, higher Sil-MA concentration increased stiffness and strength while reducing water uptake and pore size [1]. The reported 30% formulation reached 910 kPa compressive stress at break and supported suturing demonstrations, whereas 10%, 20% and 30% hydrogels displayed markedly different water uptake. Comparisons therefore require matched dry, green, washed and equilibrated states, specimen geometry and test method.

3.3 Printed cartilage constructs are an exact formulation-model pair

Hong et al. applied DLP-printed Sil-MA hydrogels to cartilage tissue engineering [2]. The printing route, cell source, construct geometry, culture history and in-vivo model are inseparable from the outcome. The study supports feasibility for its tested construct; it does not establish that every silk source, modification level, initiator or exposure produces an equivalent biological article.

3.4 Sealant evidence is not a generic vat-resin claim

Kim et al. prepared a 25% w/v Sil-MAS formulation with 0.3% w/v LAP, using a defined Bombyx mori degumming, LiBr dissolution, 424 mM GMA reaction, seven-day dialysis and freeze-drying route [3]. Spot curing at 365 nm used 6 mW/cm² for 10-30 s, while DLP specimens used 50 micrometre layers and shorter layer exposures. Adhesion and animal results belong to the sealant formulation, exposure and models, not to Sil-MA as a universal class.

3.5 Protocol and hybridisation expose additional coordinates

The published protocol makes explicit that synthesis, DLP processing and characterisation are a controlled workflow and that methacrylation, light intensity, initiator and bioink concentration tune performance [4]. Ajiteru et al. covalently combined glycidyl-methacrylated silk fibroin with graphene oxide for a DLP-printable electroconductive biocomposite [5]. That hybrid is a new material identity and must not be used as evidence for neat Sil-MA.

4. Photochemistry, protein structure and process state

Sil-MA concentration, protein molecular distribution, solution age, temperature, salts and additives influence viscosity and light transport. GMA incorporation supplies vinyl functionality, while LAP concentration, wavelength, irradiance, exposure, oxygen, layer thickness and optical attenuation control polymerisation. Degumming and dissolution can change chain length; drying, solvent history, strain and incubation can change beta-sheet content. These covalent and physical coordinates require separate measurements.

A claim of dual reinforcement requires evidence that distinguishes photocrosslinked methacrylate connectivity from fibroin physical association or beta-sheet crystallisation. Minimum controls include uncured fibroin, photocured Sil-MA, post-treated Sil-MA and, where relevant, hybrid-only controls. Conversion, secondary structure, swelling and mechanics must be measured on matched states rather than inferred from one another.

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
Secondary structure	Method- and state-specific beta-sheet 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 silk-fibroin 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
Protein identity	Species/source, cocoon lot, degumming, dissolution, molecular distribution, purity and storage	Generic silk-fibroin equivalence
Functionalisation	Reaction conditions, purification, measured incorporation method/result and storage	GMA feed or Sil-MA 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 silk-fibroin photocurable constructs.

7. Failure-mode interpretation

- A nominally identical Sil-MA becomes much less viscous: verify silkworm and cocoon source, degumming, dissolution, chain degradation, concentration, temperature, storage and freeze-thaw history before changing exposure.
- A higher GMA feed does not increase modulus: measure incorporated functionality and conversion; feed, lysine loss 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 graphene-oxide hybrid prints better than neat Sil-MA: retain hybrid identity, filler state and optical absorption; do not transfer the result to unfilled silk resin.
- Cells remain viable after printing: retain the exact protein route, formulation, light, wash, construct and model; do not infer approval or universal biocompatibility.

8. Minimum workflow and research priorities

- Freeze species and cocoon source, sericin-removal conditions, dissolution chemistry, molecular distribution, purity, bioburden and storage.
- Report GMA 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 protein 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

Methacrylated silk-fibroin photoresins are a family of controlled protein, derivative, formulation, network and article states. Source, degumming and dissolution define the regenerated fibroin; GMA route and measured incorporation define the photoactive derivative; formulation and exposure define the green network; washing, hydration and secondary-structure history define the tested article.

Primary evidence supports precise aqueous DLP printing, concentration-dependent mechanics and hydration, cartilage constructs, rapidly photocurable sealants, reproducible protocols and electroconductive hybrids. Each result remains bounded to its exact chemistry, formulation, exposure, article state and model.

Release therefore requires traceability from cocoon to measured derivative, vat state, optical process, wash, hydrated geometry, conversion, secondary structure, residuals, mechanics, degradation and biological model. The name Sil-MA alone is not a material specification.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use related but non-identical protein 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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