

Photocurable Cellulose-Derived Photoresins: Cellulose and CMC Identity, Carboxymethyl and Methacrylate Substitution, Nanocrystal Functionalisation, Aqueous DLP/TPP, Hydration and Qualification

Juan Segurola

3Dresyns by Resyner Technologies S.L.

Registered tax address: General Etxague 15B, 20003 Donostia / San Sebastian, Gipuzkoa, Spain

VAT number: ESB24827511

Correspondence: info@3Dresyns.com | Website: www.3Dr

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Statement of Significance

Cellulose, sodium carboxymethylcellulose and cellulose nanocrystals are not one resin family. Plant source, pulping and purification, molecular distribution, crystallinity, particle dimensions, surface charge, carboxymethyl substitution, methacrylate substitution and salt form define the feedstock before formulation, exposure, washing, hydration or drying defines the article.

Keywords: cellulose; carboxymethylcellulose; methacrylated CMC; cellulose nanocrystals; DLP; two-photon polymerisation; hydrogel; qualification

Abstract

Photocurable cellulose-derived systems span dissolved methacrylated carboxymethylcellulose (mCMC), mCMC reinforced with native or methacrylated cellulose nanocrystals (CNCs), and CNCs bearing a covalently attached photoinitiator. Melilli et al. demonstrated aqueous DLP of mCMC, Soullard et al. separated DLP and two-photon polymerisation formulations and their different resolution limits, Soullard et al. also quantified the effect of CNC and mCNC fillers, and Wang et al. used photoactive CNCs as initiator, crosslinker and nanofiller in a methacrylate composite. This review separates parent-cellulose identity, two independent substitution coordinates, nanoparticle functionalisation, optical process, network attribution and article state.

1. Scope and boundaries

ER-128 owns material-specific identity and qualification of photocurable cellulose-derived formulations for vat photopolymerisation. It covers cellulose or CMC source, molecular and supramolecular state, parent carboxymethyl degree of substitution, methacrylation, CNC dimensions and surface chemistry, aqueous formulation, DLP or TPP exposure, post-cure, washing, hydration, mechanics and biological evidence.

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 to ER-127 neighbouring natural-polymer derivative families. [C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,C11,C12,C13,C14,C15].

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

Cellulose is not CMC, and dissolved CMC is not a CNC dispersion. Parent CMC degree of carboxymethyl substitution is not degree of methacrylation. A methacrylated CNC filler is not equivalent to a dissolved mCMC macromer, and a photoactive-CNC/methacrylate nanocomposite is not neat cellulose resin. DLP and TPP settings are not transferable.

2. Controlled cellulose-photoresin state chain

State	Minimum identity	Failure if omitted
Incoming cellulose/CMC	Source and lot, isolation/purification, salt form, molar-mass distribution, parent DS, crystallinity, moisture and storage	Cellulose or CMC name replaces feedstock identity
Photoactive derivative	Reaction feed, pH/time/temperature, purification, measured methacrylation and, for CNCs, dimensions and surface chemistry	Feed ratio or derivative acronym is treated as identity
Vat/nanocomposite ink	mCMC and CNC solids, dispersion, medium, pH/ions, initiator, absorber, temperature, age and optical state	Colloid, formulation and network ownership disappear

State	Minimum identity	Failure if omitted
Article	DLP/TPP exposure, post-cure, wash, green/hydrated dimensions, conversion, soluble fraction, residuals and mechanics	Green, washed, hydrated and dried objects are conflated

Table 1. Minimum state chain for photocurable cellulose-derived 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 CMC identity contains two independent substitution coordinates

Soullard et al. used sodium CMC with weight-average molar mass 90.5 kg/mol and parent carboxymethyl degree of substitution 0.7 [2]. Methacrylic-anhydride/OH feed ratios of 1.24 and 2.48, aqueous reaction at pH 8, 14 days of dialysis and freeze-drying yielded NMR methacrylation degrees of 34 plus or minus 4% and 50 plus or minus 5%. The parent carboxymethyl DS, reaction feed and measured methacrylation degree are separate quantities.

3.2 Early aqueous mCMC DLP establishes a formulation-specific process window

Melilli et al. methacrylated medium-viscosity sodium CMC with methacrylic anhydride under pH control, purified the product by precipitation, dialysis and freeze-drying, and printed a 20 mg/mL aqueous mCMC formulation with LAP [1]. Their Asiga UV-MAX process used 385 nm, 30 mW/cm² and 50 micrometre layers followed by a 6 min post-cure. The reported sub-2 s gelation, 87 wt% insoluble fraction, swelling and extract-viability results belong to that exact formulation, medium and article-conditioning sequence.

3.3 DLP resolution is coupled to transmission, exposure and post-cure

Soullard et al. printed 2 wt% mCMC with methacrylation degree 34% and 0.15 wt% LAP at 385 nm and 18 mW/cm², using 5 s for the first layer and 4 s thereafter [2]. They reported 85 micrometre X/Y resolution but a 250-500 micrometre minimum printable thickness for successive identical layers because light transmission promoted peripheral cure. A 3 min 365/405 nm post-cure at 6 mW/cm² converged the measured shear moduli across layer counts.

3.4 TPP is a separate formulation and process state

The same study used 4 wt% mCMC with methacrylation degree 50% and I2959 for TPP, not the DLP formulation [2]. At 532 nm with femtosecond pulses, 4 mW laser power, 187.5 micrometre/s scan speed and 2 s exposure, the authors printed 30 micrometre cavities and reported 10 micrometre resolution. Those voxel-scale results cannot qualify a projector DLP working curve, layer thickness or build-scale post-cure.

3.5 CNC functionalisation changes network ownership

Soullard et al. functionalised cotton CNCs with methacrylic anhydride and compared native CNC and mCNC fillers in 2 wt% mCMC [3]. The 0.5 wt% mCNC condition improved cure speed, resolution and hydrated stability relative to mCMC alone, but remains a filled mCMC network. Wang et al. instead attached more than 2000 BAPO-derived photoactive groups per CNC so the particles acted as initiator, crosslinker and nanofiller with a monofunctional methacrylate [4]. That article is a covalent nanocomposite, not neat CNC or neat cellulose.

4. Photochemistry, colloidal state and process control

CMC salt form, molecular distribution, parent DS, methacrylation, concentration, pH, ionic strength, temperature and ageing control solution state and viscosity. CNC source, dimensions, crystallinity, sulfate or other surface groups, aggregation and optical scattering additionally alter a filled formulation. Initiator, wavelength, irradiance, absorber, exposure and layer or voxel strategy must be measured on the production ink.

Methacrylation can lower CNC dispersibility even when it enables covalent participation. Native CNCs may be physical reinforcements; mCNCs may also become network junctions; photoinitiator-bearing CNCs add initiation ownership. Neat-mCMC, native-CNC-filled, mCNC-filled and photoactive-CNC formulations therefore require separate controls, conversion measurements and soluble-fraction accounting.

5. Hydration, washing and biological boundaries

Evidence block	What it can show	What it cannot establish alone
Parent identity	Method-specific molar mass, parent DS, crystallinity, CNC dimensions and surface chemistry	Methacrylation, conversion or article performance
Optical/process window	Formulation-, printer- and geometry-specific cure, resolution and build behaviour	Transferable DLP/TPP settings or bulk conversion
Hydration/soluble fraction	Medium- and time-specific mass, dimensions, retention and mechanics	Covalent conversion, degradation mechanism or service life

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

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

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 within risk management [S7]. An extract assay or one fibroblast model does not establish universal biocompatibility, clinical efficacy or regulatory approval.

6. Release matrix

Gate	Minimum evidence	Claim withheld
Parent identity	Cellulose/CMC source and lot, molar-mass/crystalline state, salt form, parent DS and storage	Generic cellulose or CMC equivalence
Derivatisation	Reaction and purification record, measured methacrylation method/result, CNC surface identity and storage	Feed or acronym as photoactive identity
Vat process	Complete formulation, optical properties, DLP/TPP hardware, wavelength, power, exposure and geometry	Transferable cure or resolution settings
Network attribution	Conversion plus neat-mCMC, native-CNC, mCNC and photoactive-CNC controls and soluble fraction	Unverified filler, junction or initiator ownership
Article state	Green, post-cured, washed, hydrated and dried x/y/z, mass, residuals and conditioning history	Unqualified dimensions or mechanics
Biological boundary	Exact formulation, wash, construct/extract dose, model, endpoint and statistics	Universal biocompatibility or clinical suitability

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

7. Failure-mode interpretation

- The nominally same mCMC ink becomes more viscous: check CMC lot, molar-mass distribution, parent DS, methacrylation, salt form, concentration, pH, ionic strength, temperature and age before changing exposure.
- A higher methacrylic-anhydride feed gives no expected modulus gain: measure incorporated methacrylation and conversion; parent DS, reaction feed, incorporated functionality and network density are different quantities.
- CNC addition accelerates cure but reduces reproducibility: verify CNC source, dimensions, surface charge, methacrylation, dispersion and optical attenuation, then retain neat-mCMC and matched native-CNC controls.
- X/Y features print but channels close through Z: build a formulation-specific optical working window and test feature direction, thickness and exposure; nominal pixel size is not three-dimensional article resolution.
- The washed hydrogel changes dimensions or modulus: report wash medium, exchanges, time, temperature and equilibration, and compare green, post-cured, washed and hydrated states.
- A fibroblast extract test passes: retain the exact formulation, post-cure, wash, extraction ratio, duration, cell line and endpoint; do not infer clinical suitability or regulatory approval.

8. Minimum workflow and research priorities

- Freeze cellulose botanical or microbial source, pulping/purification route, lot, molar-mass distribution, crystallinity, moisture, ash and storage.
- For CMC report salt form, parent carboxymethyl DS and method, reaction feed, pH, time, temperature, purification, drying and measured methacrylation with calculation basis.
- For CNCs report source, hydrolysis or isolation route, dimensions, crystallinity, surface charge chemistry, solids, aggregation, functionalisation and incorporated-group method.
- Map concentration, pH, ionic strength, viscosity, absorbance or scattering, gel time and working curves over temperature, ageing and the full build-duration window.
- Record DLP projector or TPP laser, wavelength, irradiance or power, exposure, layer or voxel strategy, optics, platform treatment, post-cure and wash sequence.
- Measure conversion, insoluble and soluble fractions, residual initiator/reagents, CNC retention and x/y/z dimensions on matched green, washed and hydrated articles.
- Use neat-mCMC, native-CNC, mCNC and photoactive-CNC controls to assign physical reinforcement, covalent junctions, initiation and optical effects.
- Separate extract cytotoxicity, direct-contact response, cell-laden printing and tissue or animal observations from safety, efficacy and regulatory conclusions.

9. Conclusions

Photocurable cellulose-derived materials are controlled feedstock, derivative, colloid, formulation, process and article states. Parent CMC DS and methacrylation are independent; CNC identity and surface functionalisation add particle-specific coordinates.

Primary evidence supports aqueous mCMC DLP, formulation-specific DLP and TPP resolution windows, mCNC-reinforced mCMC hydrogels and multifunctional photoactive-CNC composites. These architectures and exposure regimes are not interchangeable.

Release requires traceability through cellulose source, molecular or nanocrystal state, both substitution coordinates, formulation, optical process, post-cure, washing, hydration, conversion, soluble fraction, residuals, dimensions, mechanics and biological model.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use non-identical cellulose sources, CMC grades, substitution definitions, CNC preparations, formulations, optical processes and test states. Numerical values are study-specific evidence and are 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

3Dresyns by Resyner Technologies S.L. | General Etxague 15B, 20003 Donostia / San Sebastian, Gipuzkoa, Spain | VAT ESB24827511 | info@3Dresyns.com | www.3Dresyns.com

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