

Furan, Furfuryl, Tetrahydrofurfuryl and FDCA-Derived Materials for Vat Photopolymerisation: Chemical Identity, Radical and Diels-Alder Routes, Dynamic Networks and Qualification

Juan Segurola

3Dresyns by Resyner Technologies S.L.

© 2026 Juan Segurola. All Rights Reserved.

Correspondence: info@3Dresyns.com · www.3Dresyns.com

ER-108 · Engineering Review · Version 0.2 · 31 August 2026

Statement of Significance

A furan ring, a furfuryl substituent, a hydrogenated tetrahydrofurfuryl group and an FDCA-derived polyester are chemically different states. In many printable systems the bond that photopolymerises is a methacrylate or acrylate, while the furan-derived unit acts as a pendant group, precursor or reversible Diels-Alder partner. ER-108 establishes an identity gate that prevents renewable-feedstock language from replacing network chemistry, separates direct VPP demonstrations from adjacent solid-state or thermoplastic 3D-printing evidence, and defines the conversion, optical, thermal, extraction and dynamic-network evidence required for qualification.

Keywords: vat photopolymerisation; furan; furfuryl methacrylate; tetrahydrofurfuryl methacrylate; 5-hydroxymethylfurfural; FDCA; Diels-Alder; retro-Diels-Alder; vitrimer; dynamic network; qualification.

Abstract

Furan-derived materials enter additive manufacturing through distinct routes that cannot be pooled as one resin family. Primary VPP studies include stereolithography of a 5-hydroxymethylfurfural-derived imine-bearing methacrylate oligomer, DLP printing of a glycerol-diacrylate/tetrahydrofurfuryl-methacrylate vitrimer, and furfuryl-methacrylate photoresins assembled with maleimide partners through Diels-Alder chemistry. These systems fix geometry primarily by radical polymerisation of acrylate or methacrylate groups; the furan-derived structure may alter polarity, rigidity, optical response or later dynamic chemistry but is not automatically the photoreactive bond. Tetrahydrofurfuryl groups no longer contain an aromatic furan ring, and FDCA polyesters reported for thermoplastic 3D printing are adjacent evidence rather than VPP validation. Diels-Alder and transesterification claims require direct proof of the active exchange reaction, temperature window, topology and retained properties. Renewable origin does not establish renewable-carbon fraction, low toxicity, biodegradability, circularity or favourable life-cycle performance. ER-108 therefore links exact chemical identity to resin state, working curve, conversion, leaching, thermal transitions, exchange kinetics and application-representative retained function.

1. Scope and boundaries

ER-108 owns the identity and qualification of furan-, furfuryl-, tetrahydrofurfuryl- and FDCA-derived materials when proposed for VPP. It covers 5-HMF-derived methacrylate oligomers, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, furan/maleimide Diels-Alder adducts, dynamic transesterification in furan-adjacent formulations, FDCA boundaries, optical and rheological state, conversion, extraction and retained properties.

ER-11 retains the generic bio-based-design framework; ER-27 conversion metrology; ER-41 liquid resistance; ER-59 sequential dual cure; ER-61 gelation and vitrification; ER-63 covalent adaptable networks and vitrimer topology; ER-72 environmental ageing; ER-80 in-can stability; ER-92 residual-reactant hazard; ER-100 corpus architecture; and ER-107 phenolic/lignin-derived photopolymers [C1-C11].

The paper does not treat every material containing a five-membered oxygen heterocycle as equivalent, call tetrahydrofurfuryl methacrylate an aromatic furan monomer, transfer thermoplastic FDCA-polyester 3D-printing results to VPP, infer cationic polyfurfuryl-alcohol curing from methacrylate evidence, or call any thermally repairable network a vitrimer without exchange-topology evidence.

2. Chemical-identity gate

Furan is an unsaturated aromatic heterocycle. Furfuryl alcohol contains a furan ring connected to a hydroxymethyl group, while furfuryl methacrylate places a methacrylate ester on that alcohol. Tetrahydrofurfuryl methacrylate contains a saturated tetrahydrofuran ring and therefore differs in aromaticity, oxidation pathways and Diels-Alder capability. FDCA contains a furan ring bearing two carboxyl groups and commonly forms polyesters by condensation. The name of the renewable precursor does not reveal which bond forms the printed network.

Declared material	Geometry-fixing chemistry	Evidence required	Claim withheld
5-HMF-derived methacrylate oligomer	Radical methacrylate polymerisation	Precursor, imine/oligomer structure, functionality, conversion and network state	Native furan polymerisation or FDCA identity
Furfuryl methacrylate formulation	Radical methacrylate cure; optional furan/maleimide DA adducts	FMA identity, DA conversion, free furan/maleimide, vinyl conversion and extractables	Automatic reversibility or closed-loop circularity
Tetrahydrofurfuryl methacrylate formulation	Radical methacrylate cure; other exchange chemistry may be separate	Saturated-ring identity, co-monomer, catalyst, conversion and exchange mechanism	Aromatic furan reactivity or DA behaviour
FDCA-derived polyester	Usually condensation polyester; VPP needs separately installed photoreactivity	FDCA incorporation, molecular architecture and explicit VPP-reactive functionality	Transfer from thermoplastic 3D-printing evidence to VPP
Poly(furfuryl alcohol)	Acid-catalysed furan chemistry, not methacrylate radical cure	Catalyst, condensation mechanism, volatiles and actual AM process	Evidence from FMA or THFMA systems

Table 1. Identity and reaction gate for furan-related additive-manufacturing materials.

3. Direct VPP evidence

3.1 5-HMF-derived imine-bearing methacrylate oligomer

Risangud et al. synthesised a furan-based methacrylate oligomer through imination of 5-HMF with aminoethanol and formulated it with PEGDMA or TEGDMA for stereolithography [1]. Across FBMO:diluent ratios from 50:50 to 90:10, the authors reported viscosities of 0.04-0.28 Pa·s at 10 s⁻¹ and compressive moduli from 0.53 ± 0.04 to 144 ± 6.70 MPa depending on formulation and printed internal structure. These ranges demonstrate tunability within that study; they are not intrinsic properties of 5-HMF or furan chemistry.

3.2 Tetrahydrofurfuryl-methacrylate vitrimer formulation

Grauzeliene et al. combined glycerol 1,3-diglycerolate diacrylate with tetrahydrofurfuryl methacrylate and printed the formulation by DLP [2]. The reported 60:40 composition showed 100% shape recovery and, after welding, a seven-fold tensile-strength improvement relative to the original as-printed specimen; the study reports welding and repair as separate operations with separate figures. The dynamic process was assigned to high-temperature transesterification, not to aromatic furan chemistry. The exact catalyst, hydroxyl/ester balance, temperature, time and network state are therefore part of the claim.

3.3 Furfuryl methacrylate and Diels-Alder preassembly

Zhang et al. used furfuryl methacrylate and 4,4'-bismaleimidodiphenylmethane in methacrylate photoresins assembled through Diels-Alder chemistry, with HEMA enabling 93% conversion under the optimised conditions [3]. UV post-curing increased tensile strength, whereas excessive UV or solvent exposure caused oligomer leaching. Thermal post-curing activated retro-Diels-Alder behaviour and altered mechanical robustness and shape-memory response. These results require stage-resolved accounting of DA adducts, vinyl conversion, soluble species and thermal history.

4. Adjacent evidence and non-transfer boundaries

Wang et al. studied highly photosensitive furan acrylate derivatives and solid-state photopolymerisation [4]. That work can inform molecular photosensitivity but does not establish vat rheology, working curves, recoating, oxygen exposure, washing or three-dimensional conversion. Geng et al. reported FDCA-based polyesters as 3D-printing materials [5], but the cited work is adjacent thermoplastic-polyester evidence rather than vat photopolymerisation; the cited record does not establish the printing process, and no process-specific result is transferred here. ER-108 includes it only to establish the FDCA material class and prevent cross-process transfer.

Likewise, poly(furfuryl alcohol)/cellulose materials reported for extrusion do not prove a photoacid-cured PFA vat. A future native furfuryl-alcohol VPP claim would require direct evidence for resin stability, acid generation, spatial cure, volatile balance, washing and final network identity. Patent or supplier formulation suggestions cannot substitute for primary VPP evidence.

5. Optical, rheological and storage state

Furan-derived chromophores, imines, maleimides, photoinitiators and coloured reaction products can change absorption at the exposure wavelength. Cure depth must be measured on the complete formulation rather than inferred from one constituent. DA preassembly can change molecular mass and viscosity before printing; storage time and temperature can alter the equilibrium and therefore the vat state. Tetrahydrofurfuryl groups have different absorption and chemical stability from aromatic furans.

State variable	Failure risk	Minimum control
Furan/THF identity	Wrong photochemical or dynamic mechanism assigned	Structure and saturation state confirmed
DA preassembly	Time-dependent viscosity, free maleimide/furan or stoichiometric drift	Conversion, ratio, temperature, age and soluble fraction
Optical package	Under-cure, excessive cure depth or composition gradient	Complete-resin spectrum, working curve and through-thickness conversion
Inhibitor/initiator	Premature dark cure or incomplete radical conversion	Identity, concentration, temperature and aged-resin comparison
Wash/post-cure	Leaching, additional conversion or network rearrangement	Solvent, time, dose, temperature, mass change and extract analysis

Table 2. Minimum state controls for furan-related VPP formulations.

6. Conversion, Diels-Alder state and extractables

A single FTIR conversion number can conceal several reactions. In FMA/BSM formulations, DA conversion and methacrylate conversion answer different questions. The DA adduct changes precursor architecture, while radical conversion creates the permanent printed network. Retro-DA heating can release lower-molar-mass species without necessarily depolymerising the radical network. State-resolved spectroscopy, gel fraction and compound-specific extraction are required.

ISO 6427:2025 supplies a conventional anchor for organic-solvent-extractable matter, and ISO 175:2010 remains a general immersion framework [S8,S9]. Neither identifies imines, residual maleimides, furfuryl methacrylate, HEMA, photoinitiator products or catalysts. The leaching observed by Zhang et al. after excessive UV or solvent exposure makes workflow-specific mass and chemical closure a release requirement [3].

7. Dynamic-network and circularity gate

Reversibility must be assigned to the active chemistry. DA/retro-DA exchange involves furan and maleimide partners and may be dissociative over the relevant temperature range. Transesterification requires ester and hydroxyl functionality plus a kinetic pathway, commonly catalyst- and temperature-dependent. A saturated tetrahydrofuran ring is not itself a DA diene. Repair, welding, shape recovery, reprocessing and chemical recycling are distinct outcomes and need separate mass, geometry and property accounting.

ER-63 retains the generic vitrimer and covalent-adaptable-network framework [C6]. ER-108 adds the furan-specific identity questions: which furan remains available after initial DA assembly, whether retro-DA changes soluble fraction or topology, whether side reactions occur on repeated cycles, and whether the final radical network permits macroscopic flow. One successful repair does not establish indefinite recyclability or closed-loop material recovery.

8. Mechanical, thermal and liquid qualification

ISO 527-1:2019, ISO 527-2:2025 and ISO 178:2019 provide tensile and flexural anchors [S1-S3]. Report geometry, internal architecture, build orientation, post-cure, conditioning and full curves. The compressive-modulus range in [1], the repair-strength change in [2] and tensile changes in [3] answer different questions and must not be ranked as one furan material property.

ISO 11357-2:2020, ISO 11358-1:2022 and ISO 6721-11:2019 anchor thermal transitions, mass loss and dynamic-mechanical response [S4-S6]. Exchange activation, glass transition, softening, degradation and retro-DA onset must be separated. ISO 62:2008 and ISO 175:2010 support water and liquid conditioning [S7,S9]. Imine hydrolysis, ester cleavage, plasticisation, extraction and reversible association require mechanism-specific interpretation.

9. Qualification architecture

Gate	Minimum evidence	Release question
Feedstock and derivative	5-HMF/FMA/THFMA/FDCA identity, synthesis route, impurities and renewable-carbon accounting	Is the material named and sourced correctly?
Printable vat	Viscosity, temperature, optical state, working curve, stability and recoating	Does the complete resin remain printable?
Network formation	Vinyl conversion, DA state, gel fraction and spatial uniformity	Which reaction fixes geometry and which remains dynamic?
Workflow closure	Wash/post-cure mass change, extractables and residual analytics	What soluble or reactive species remain?
Dynamic function	Exchange chemistry, temperature/time, topology and repeated-cycle retention	Is repair or reprocessing mechanistically supported?
Final duty	Mechanical, thermal, liquid, ageing and component-level retention	Does the exact object meet its declared duty?
Circularity	Recovery yield, energy/reagents, quality retention and fate of losses	Is the circular claim auditable rather than rhetorical?

Table 3. Qualification chain for furan-related VPP materials.

10. Failure-mode interpretation

- The formulation is called furan-based but cures through methacrylate groups: report both precursor origin and geometry-fixing network rather than implying native furan polymerisation.
- A THFMA resin is assigned Diels-Alder reversibility: reject the inference unless a separate unsaturated furan partner is present and directly evidenced.
- Viscosity changes during storage: measure DA state, oligomer distribution and temperature history before changing exposure settings.
- More UV increases initial strength but also leaching: close mass and chemical extraction rather than optimising mechanics alone.
- Thermal treatment improves repair: distinguish exchange, additional radical cure, physical annealing and degradation.
- An FDCA polyester reported as a 3D-printing material is adjacent thermoplastic evidence: do not transfer its processability or properties to a vat formulation without installed photoreactivity and direct VPP data. The cited title does not establish the printing process, so no extrusion-specific claim is made here.
- A cytotoxicity assay passes: retain cell type, extraction protocol and endpoint; do not infer biocompatibility, implantation safety or low residuals.
- A renewable precursor is used: calculate renewable-carbon fraction and withhold biodegradability and life-cycle benefit until separately demonstrated.

11. Minimum workflow and research priorities

- Name the exact furan-related structure and identify the bond that photopolymerises.
- Freeze precursor synthesis, functionality distribution, DA stoichiometry, inhibitor, initiator, catalyst, impurities and storage state.
- Measure complete-resin spectrum, working curve, viscosity and stability at the actual wavelength and vat temperature.
- Quantify vinyl conversion separately from DA conversion or transesterification state.
- Close gel fraction, extractables and compound-specific residuals after washing and every post-cure stage.
- Separate Tg, exchange activation, retro-DA, softening and decomposition using complementary thermal and mechanical methods.
- Test repair, welding, reprocessing and shape memory as distinct functions over repeated controlled cycles.
- Qualify water, solvent, humidity, heat and light exposure through retained application-relevant properties.
- Report renewable feedstock, renewable carbon, recovered mass and retained quality as separate circularity quantities.
- Develop direct VPP studies for genuinely FDCA-derived photocurable oligomers and native furfuryl-alcohol photoacid systems before class-wide claims.

12. Conclusions

Furan-related feedstocks do not create one photopolymer family. The direct VPP evidence examined here fixes geometry mainly through acrylate or methacrylate radical polymerisation, while furan-derived groups provide precursor identity, tunable structure or a separate Diels-Alder handle. Tetrahydrofurfuryl methacrylate is a saturated-ring monomer and cannot inherit aromatic furan reactivity. FDCA polyester printing outside VPP remains adjacent evidence only.

Primary studies support stereolithographic 5-HMF-derived methacrylate oligomers, a DLP-printed THFMA-containing transesterification network, and FMA/maleimide DA-derived photoresins with workflow-sensitive leaching and thermal response. Their numerical results remain composition-, process-, geometry- and method-specific.

Qualification requires identity, complete-resin optical and rheological state, reaction-separated conversion, extractables, thermal transitions, exchange kinetics, retained properties and auditable circularity. ER-108 supplies that chain without authorising a formulation or intended use.

Limitations

This qualitative engineering review is not a systematic meta-analysis. Direct VPP evidence remains limited and chemically heterogeneous; several FDCA and poly(furfuryl alcohol) examples are deliberately treated as adjacent non-VPP evidence. Numerical values are not pooled or ranked. No proprietary formulation, universal exposure, toxicological qualification, life-cycle assessment or regulatory approval is provided.

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 cited primary literature and official standards.

Company information

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

References - independent scientific evidence

- [1] Risangud, N., Mama, J., Sungkhaphan, P., Pananusorn, P., Termkunanon, O., Arkana, M.S., Sripraphot, S., Lertwimol, T. and Thongkham, S. Synthesis and Characterization of Furan-Based Methacrylate Oligomers Containing the Imine Functional Group for Stereolithography. *ACS Omega* 9(28) (2024) 30771-30781. DOI: 10.1021/acsomega.4c03274. <https://doi.org/10.1021/acsomega.4c03274>
- [2] Grauzeliene, S., Schuller, A.-S., Delaite, C. and Ostrauskaite, J. Development and Digital Light Processing 3D Printing of a Vitrimer Composed of Glycerol 1,3-Diglycerolate Diacrylate and Tetrahydrofurfuryl Methacrylate. *ACS Applied Polymer Materials* 5(9) (2023) 6958-6965. DOI: 10.1021/acsapm.3c01018. <https://doi.org/10.1021/acsapm.3c01018>
- [3] Zhang, T., Voet, V.S.D., Folkersma, R. and Loos, K. In Situ Photoresin Synthesis via Reactive Diluents for Vat Photopolymerization. *Biomacromolecules* 26(11) (2025) 8017-8026. DOI: 10.1021/acs.biomac.5c01471. <https://doi.org/10.1021/acs.biomac.5c01471>
- [4] Wang, J., Wang, Y., Liu, B. and Fu, T. Highly Photosensitive Furan Acrylate Derivatives and Their Solid-State Photopolymerization. *New Journal of Chemistry* (2022). DOI: 10.1039/D2NJ03138H. <https://doi.org/10.1039/D2NJ03138H>
- [5] Geng, Y., Wang, Z., Hu, X., Li, Y., Zhang, Q., Li, Y., Wang, R. and Zhang, L. Bio-Based Polyesters Based on 2,5-Furandicarboxylic Acid as 3D-Printing Materials: Design, Preparation and Performances. *European Polymer Journal* 114 (2019) 476-484. DOI: 10.1016/j.eurpolymj.2018.10.041. <https://doi.org/10.1016/j.eurpolymj.2018.10.041>

Standards and measurement references

- [S1] ISO 527-1:2019. Plastics - Determination of tensile properties - Part 1: General principles. Edition 3; confirmed 2025; stage 90.92 (to be revised); revision ISO/AWI 527-1, catalogue ID 93712, under development. <https://www.iso.org/standard/75824.html>
- [S2] ISO 527-2:2025. Plastics - Determination of tensile properties - Part 2: Test conditions for moulding and extrusion plastics. Edition 3. <https://www.iso.org/standard/527-2>
- [S3] ISO 178:2019. Plastics - Determination of flexural properties. Edition 6; published standard under revision in 2026. <https://www.iso.org/standard/70513.html>
- [S4] ISO 11357-2:2020. Plastics - Differential scanning calorimetry (DSC) - Part 2: Determination of glass transition temperature and step height. Edition 3; confirmed current in 2025. <https://www.iso.org/standard/77310.html>
- [S5] ISO 11358-1:2022. Plastics - Thermogravimetry (TG) of polymers - Part 1: General principles. Edition 2. <https://www.iso.org/standard/79999.html>
- [S6] ISO 6721-11:2019. Plastics - Determination of dynamic mechanical properties - Part 11: Glass transition temperature. Edition 2; confirmed current in 2024. <https://www.iso.org/standard/74988.html>
- [S7] ISO 62:2008. Plastics - Determination of water absorption. Edition 3; confirmed in 2021; stage 90.60, systematic review closed in 2026 with outcome pending. <https://www.iso.org/standard/41672.html>
- [S8] ISO 6427:2025. Plastics - Determination of matter extractable by organic solvents (conventional methods). Edition 4. <https://www.iso.org/standard/88109.html>
- [S9] ISO 175:2010. Plastics - Methods of test for the determination of the effects of immersion in liquid chemicals. Edition 3; confirmed current in 2026. <https://www.iso.org/standard/55483.html>

Related Engineering Review boundaries

- [C1] Segurola, J. Molecular Design of Bio-Based Photoresins for Vat Photopolymerisation. ER-11. Zenodo or controlled version (2026).
- [C2] Segurola, J. Conversion Metrology and Spatial Cure Heterogeneity in Vat Photopolymerisation. ER-27. Zenodo or controlled version (2026).
- [C3] Segurola, J. Chemical Resistance and Solvent Uptake of Vat-Printed Photopolymers. ER-41. Zenodo or controlled version (2026).
- [C4] Segurola, J. Sequential Dual-Cure Networks in Vat Photopolymerisation. ER-59. Zenodo or controlled version (2026).
- [C5] Segurola, J. Gelation, Vitrification and Mobility Arrest in Vat Photopolymerisation. ER-61. Zenodo or controlled version (2026).

- [C6] Segurola, J. Covalent Adaptable Networks and Vitrimers Topology in Vat Photopolymerisation. ER-63. Zenodo or controlled version (2026).
- [C7] Segurola, J. Environmental Ageing and Property Retention in Vat Photopolymerisation. ER-72. Zenodo or controlled version (2026).
- [C8] Segurola, J. In-Can Stability and Premature Polymerisation in Radiation-Curable Formulations. ER-80. Zenodo or controlled version (2026).
- [C9] Segurola, J. Residual Reactants, Impurities and Manufacturing Conversion as Hidden Drivers of Photopolymer Hazard. ER-92. Zenodo or controlled version (2026).
- [C10] Segurola, J. From Individual Reviews to a Qualification Corpus. ER-100. Zenodo or controlled version (2026).
- [C11] Segurola, J. Phenolic, Lignin-Derived and Bio-Aromatic Photopolymers for Vat Photopolymerisation. ER-107. Zenodo or controlled version (2026).