

Isosorbide-Derived Photoresins for Vat Photopolymerisation: Methacrylate and Thiol-Yne Routes, Rigidity, Toughening, Thermal State and Qualification

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Statement of Significance

Isosorbide is a rigid bicyclic diol, not a photoreactive resin by itself. Vat use requires installed methacrylate, alkyne or another light-reactive functionality, and the bond that fixes geometry must be named independently from the renewable scaffold. ER-109 separates methacrylate-chain-growth and thiol-yne-step-growth routes, prevents high glass-transition temperature from being confused with thermal-service qualification, and links composition, optical state, conversion, toughness, extraction and retained function to the exact printed network.

Keywords: *vat photopolymerisation; isosorbide; isomannide; isoidide; isosorbide methacrylate; thiol-yne; DLP; fracture toughness; glass transition; thermal degradation; extractables; qualification.*

Abstract

Isosorbide-derived photoresins combine a renewable rigid bicyclic core with separately installed photoreactivity. Direct VPP evidence includes DLP processing of isosorbide dimethacrylate blends, isosorbide/vanillin ester and ester-imine thermosets, and thiol-yne networks prepared from dipropargyl derivatives of isosorbide and its epimers. These routes cannot be pooled: methacrylate chain growth and thiol-yne step growth differ in stoichiometry, gelation, oxygen response, residual groups and network defects. In one methacrylate study, neat isosorbide methacrylate was brittle, while furan-derived comonomers reduced viscosity and raised measured fracture energy; the same comonomers changed optical attenuation, conversion and thermal response. Dynamic ester or imine chemistry may permit reprocessing or chemical recycling, but recovery, soluble products and retained quality must be closed separately. Renewable origin does not establish renewable-carbon fraction, low hazard, hydrolytic stability, biodegradability or circularity. ER-109 provides an identity-first qualification architecture for printability, conversion, thermal state, fracture, liquid exposure and repeated processing without transferring results across formulations or cure mechanisms.

1. Scope and boundaries

ER-109 owns isosorbide-derived photoresins proposed for VPP, including isosorbide dimethacrylate, methacrylated isosorbide/vanillin blends, ester-imine dynamic networks, and dialkyne isosorbide-family monomers cured with multifunctional thiols. It covers chemical identity, functionality, vat state, working curves, conversion, network architecture, thermal and fracture response, extraction, dynamic processing and qualification.

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; ER-72 environmental ageing; ER-80 in-can stability; ER-92 residual-reactant hazard; ER-100 corpus architecture; ER-107 phenolic/lignin-derived systems; and ER-108 furan/FDCA materials [C1-C12].

This paper does not treat isosorbide, isomannide and isoidide as interchangeable stereochemical labels; infer VPP behaviour from a thermoset cast outside a vat; call every isosorbide derivative a dimethacrylate; transfer methacrylate kinetics to thiol-yne formulations; or equate high T_g, successful reprocessing or one recycling cycle with safe high-temperature service or closed-loop circularity.

2. Chemical-identity and reaction gate

Isosorbide, isomannide and isoidide are dianhydrohexitol stereoisomers whose hydroxyl orientation and derivative reactivity can differ. Methacrylation installs vinyl groups that cure by radical chain growth. Diallyl-carbonate substitution, dipropargyl carbonate formation and vanillin-derived methacrylation install different reactive handles. In thiol-yne systems, each alkyne can undergo sequential thiol additions; stoichiometric accounting must therefore use reactive equivalents rather than monomer names alone.

Declared system	Geometry-fixing chemistry	Minimum identity evidence	Claim withheld
Isosorbide dimethacrylate	Radical methacrylate chain growth	Substitution, purity, inhibitor, initiator and vinyl conversion	Native isosorbide polymerisation
IM with mono-/dimethacrylate diluent	Copolymerised methacrylate network	Functionality, composition, optical absorption and spatial conversion	Toughening or T _g as intrinsic to isosorbide
Isosorbide/vanillin ester-imine resin	Methacrylate cure plus later ester/imine dynamics	Bond inventory, catalyst or treatment, soluble fraction and retained network	Automatic recyclability from imine presence
Dipropargyl isosorbide-family resin	Thiol-yne radical step growth	Stereoisomer, alkyne/thiol equivalents, conversion and residual groups	Methacrylate kinetics or oxygen response
Unfunctionalised isosorbide polyester	No VPP cure unless photoreactivity is separately installed	Architecture and explicit photoreactive group	Transfer from thermal processing

Table 1. Identity and reaction gate for isosorbide-derived photoresins.

3. Evidence chain

3.1 Isosorbide methacrylate as a rigid thermoset precursor

Sadler et al. reported isosorbide methacrylate as a low-viscosity crosslinking resin cured by free radicals [1]. Their exact system had viscosity 157 cP, extent of cure 85%, T_g above 240 °C, modulus about 4 GPa and strength 85 MPa. This is primary chemistry and thermoset evidence, but it is adjacent to VPP unless working curves, recoating and printed-object uniformity are demonstrated. The values are not class properties of isosorbide.

3.2 Photopolymerisable isosorbide resins

Lastovickova et al. evaluated photopolymerisable resins containing bio-derived isosorbide and reported strong formulation dependence in resin, cure and polymer properties [2]. Most characterisation was performed on photocured cast specimens; the study additionally printed one optimised urethane-(meth)acrylate resin by SLA and reported similar modulus but reduced strength relative to both the photocured specimens and a commercial high-temperature SLA resin. Printer, exposure parameters and post-cure are not visible in the openly available record, so printed-part properties remain method-specific and are not transferred here.

3.3 DLP methacrylate systems

Chu et al. printed isosorbide-methacrylate blends with furfuryl methacrylate or bis(hydroxymethyl)furan dimethacrylate by 405 nm DLP [3]. Blend viscosities were at most 107 cP (0.107 Pa·s) at 21 °C, against the study's own stated threshold of 1000 cP; neat IM is 157 cP. The reported working-curve parameters changed with composition; BHMF-M absorbed at the printing wavelength and reduced as-printed conversion as its content rose (predicted through-thickness conversion 0.42 at 20% BHMF-M versus 0.31 at 80%), while post-curing brought all systems to 80-86% and made the differences negligible. Neat IM was brittle, with G_{Ic} reported at 37 J/m²; low BHMF-M additions raised G_{Ic} to at least about 100 J/m². BHMF-M/IM systems retained T_g above 200 °C by the study's storage-modulus criterion, whereas monofunctional FM reduced crosslink density and T_g. These are formulation-, wavelength-, post-cure- and method-specific results.

3.4 Ester, ester-imine and thiol-yne routes

Liguori et al. designed four methacrylated isosorbide/vanillin resins for DLP and separated ester-only from ester-imine network behaviour [4]. More methacrylated vanillin improved printing quality but lowered thermal stability; the flexible Schiff-base derivative reduced rigidity while improving solvent resistance. Reprocessing or chemical-recycling results were strongest for the ester-imine network, but retained modulus alone does not close recovered mass, chemical identity, losses or repeated-cycle performance.

Moraru et al. reported thiol-yne photoresins from dipropargyl derivatives of isosorbide, isomannide and isodide with a trifunctional thiol, and DLP-printed the optimised isosorbide formulation [5]. Real-time FTIR and DSC supported reaction analysis, while residual thiols enabled a later PEG-methacrylate surface modification. This route is not a methacrylate analogue: stereoisomer, functional-equivalent balance, residual thiol/alkyne, surface grafting and extraction state must be reported explicitly.

4. Optical, rheological and storage state

A low monomer viscosity does not prove stable recoating of the complete resin. Isosorbide functionality, furan or vanillin chromophores, imines, thiols, alkynes, inhibitors and photoinitiator products alter viscosity and absorption. Working curves must be measured on the final formulation at the actual wavelength and temperature. A diluent that improves flow can lower crosslink density; a chromophore that controls cure depth can also create conversion gradients.

State variable	Failure risk	Minimum control
Derivative identity	Wrong cure route or functionality assigned	NMR/FTIR, substitution distribution, purity and inhibitor
Complete-resin optics	Under-cure, excessive depth or lateral broadening	Spectrum, D _p , E _c and geometry-resolved conversion
Vat rheology	Slow recoating or composition drift	Viscosity versus shear rate, temperature, time and ageing
Reactive equivalents	Thiol-yne off-stoichiometry or residual functionality	Alkyne and thiol equivalents plus stage-resolved conversion
Post-cure/dynamic treatment	Additional cure confused with annealing or bond exchange	Dose, temperature, time, mass change and soluble fraction

Table 2. Minimum state controls for isosorbide-derived VPP formulations.

5. Conversion and network architecture

Methacrylate conversion, alkyne conversion, thiol conversion, imine exchange and ester cleavage answer different questions. A green-part conversion can differ from the post-cured state, and a high surface conversion can conceal a through-thickness gradient. Gel fraction and compound-specific extractables are needed alongside spectroscopy. For thiol-yne systems, residual thiol used intentionally for grafting must be distinguished from uncontrolled stoichiometric excess and from mobile extractables.

The rigid isosorbide core can raise glassy modulus and restrict mobility, but the network response also depends on functionality, comonomer structure, conversion, defects and thermal history. Monofunctional FM can act as a chain extender and reduce effective crosslink density; BHMF-M carries different functionality and optical absorption. No single isosorbide-content axis predicts cure, toughness or T_g.

6. Thermal-state and fracture gate

High T_g does not by itself define a safe service temperature. DMA criterion, DSC transition, storage-modulus retention, creep, thermal expansion, oxidation and decomposition must be reported separately. In the Chu et al. systems, T_g and 5% mass-loss temperature changed differently with comonomer fraction [3]. Service claims require retained stiffness and fracture performance after representative temperature/time exposure, not an isolated onset value.

Fracture energy, tensile strength, modulus and flexural strength are not interchangeable. The G_{Ic} increase reported for BHMf-M/IM compact-tension specimens must retain specimen geometry, notch preparation, loading rate, orientation and post-cure. A printed open structure showing geometrical fidelity does not validate component-level damage tolerance.

ISO 527-1:2019, ISO 527-2:2025 and ISO 178:2019 provide tensile and flexural anchors [S1-S3], while ISO 13586:2018 addresses linear-elastic fracture toughness [S4]. ISO 11357-2:2020, ISO 11358-1:2022 and ISO 6721-11:2019 support glass-transition, thermogravimetric and dynamic-mechanical measurements [S5-S7]. None replaces reporting of the complete specimen and thermal history.

7. Liquid, extraction and dynamic-network qualification

Water or solvent exposure can plasticise a network, hydrolyse ester bonds, shift imine equilibria, extract residual monomer or photoinitiator products, and change mass through competing uptake and loss. ISO 62:2008, ISO 6427:2025 and ISO 175:2010 provide general anchors [S8-S10], but compound-specific analysis is still required. Dental composite evidence for isosorbide derivatives remains adjacent to VPP and cannot establish printed-part biocompatibility [6].

Reprocessing, chemical recycling and surface grafting are distinct operations. A dynamic bond must be identified, activated under a declared condition and followed through products, losses and retained properties. Nearly preserved elastic modulus after one cycle does not prove unchanged chemistry, zero mass loss, indefinite cycling or environmental benefit. ER-63 retains the generic covalent-adaptable-network framework [C6]; ER-109 applies it to isosorbide ester and ester-imine systems.

8. Qualification architecture

Gate	Minimum evidence	Release question
Feedstock and derivative	Stereoisomer, substitution, purity, impurities and renewable-carbon accounting	Is the material named and sourced correctly?
Printable vat	Complete-resin optics, viscosity, working curve, stability and recoating	Does the exact formulation print reproducibly?
Network formation	Mechanism-specific conversion, gel fraction and spatial uniformity	Which reaction fixes geometry?
Workflow closure	Wash/post-cure mass balance, extractables and residual analytics	What mobile or reactive species remain?
Thermal/fracture duty	T _g criterion, decomposition, creep, fracture method and retained performance	Is the declared service window supported?
Dynamic or surface function	Bond inventory, treatment, products and repeated-cycle or graft verification	Is the added function mechanistically closed?
Circularity	Recovered mass, energy/reagents, quality retention and fate of losses	Is the circular claim auditable?

Table 3. Qualification chain for isosorbide-derived photoresins.

9. Failure-mode interpretation

- The precursor is called isosorbide-based, but the curing bond is methacrylate or thiol-yne: report both renewable scaffold and geometry-fixing chemistry.
- Viscosity falls after adding a reactive diluent: remeasure optical attenuation, functionality, shrinkage, conversion and network density.
- T_g exceeds 200 °C: withhold a 200 °C service rating until creep, oxidation, dimensional stability and retained fracture are qualified.
- G_{Ic} rises after comonomer addition: retain the compact-tension method and do not infer universal impact strength or fatigue resistance.
- A thiol-yne resin leaves residual thiol for grafting: quantify whether the group is covalently bound, accessible and stable after washing.
- A dynamic network is reprocessed once: close mass recovery, chemical identity, soluble products and repeated-cycle retained quality.
- A dental composite assay is favourable: do not transfer it to a printed VPP object, another extraction protocol or an implantation claim.
- Renewable origin is declared: report renewable-carbon fraction and withhold biodegradability and life-cycle benefit until measured.

10. Minimum workflow and research priorities

- Name the dianhydrohexitol stereoisomer, derivative, substitution distribution and reactive-function equivalents.
- Freeze synthesis, purification, inhibitor, initiator, thiol/alkyne ratio, catalyst and storage state.
- Measure complete-resin spectrum, working curve, viscosity, ageing and recoating at the actual print conditions.
- Quantify green, washed and post-cured conversion with mechanism-specific signals and through-thickness locators.
- Close gel fraction, extractables and compound-specific residuals after each workflow stage.
- Separate T_g criterion, storage-modulus retention, creep, oxidation and decomposition before assigning a service window.
- Measure fracture, fatigue or impact with application-relevant geometry rather than transferring a single toughness metric.
- Track reprocessing, recycling and grafting through mass balance, chemistry and repeated-cycle property retention.
- Report renewable feedstock, renewable carbon, recovered mass and environmental performance as separate quantities.

11. Conclusions

Isosorbide is a renewable rigid scaffold, not a cure mechanism. Direct VPP studies now support methacrylate and thiol-yne routes, but their stoichiometry, kinetics, residual groups and network defects are different. The strongest engineering comparisons therefore occur within a controlled formulation and workflow, not across the entire isosorbide family.

Methacrylate DLP evidence shows that comonomers can reduce viscosity and improve measured fracture energy while changing absorption, green conversion, crosslink density and thermal response. Ester-imine and thiol-yne studies extend the design space toward dynamic processing and surface modification, yet neither establishes universal recyclability, low extractables or safe high-temperature duty.

Qualification requires exact identity, complete-resin optical and rheological state, mechanism-resolved conversion, extraction closure, thermal and fracture methods, retained properties and auditable recovery. ER-109 supplies that chain without authorising a formulation or intended use.

Limitations

This qualitative engineering review is not a systematic meta-analysis. The direct VPP evidence is chemically heterogeneous and several thermoset or dental studies are deliberately treated as adjacent 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

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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).
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