

Itaconic-Acid-Derived Photoresins for Vat Photopolymerisation: Unsaturated Polyesters, Poly(ester amide)s, Itaconamides, Reactive Diluents and Qualification

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Statement of Significance

Itaconic acid carries an exomethylene group that can be retained in unsaturated polyesters or transformed into itaconate and itaconamide monomers, but neither the renewable feedstock nor the word unsaturated proves efficient vat cure. ER-110 separates the itaconate curing group from auxiliary (meth)acrylate diluents, distinguishes direct VPP evidence from adjacent polymer chemistry, and closes identity, vat state, conversion, extraction, properties and renewable-carbon accounting on the exact formulation.

Keywords: vat photopolymerisation; itaconic acid; itaconate; itaconamide; unsaturated polyester; poly(ester amide); reactive diluent; SLA; DLP; conversion; biobased carbon; qualification.

Abstract

Itaconic-acid-derived photoresins offer several chemically distinct routes to VPP. The pendant exomethylene can remain along an unsaturated polyester or poly(ester amide), be installed in low-molar-mass itaconate reactive diluents, or be incorporated into amino-acid-derived itaconamides. Direct SLA and DLP studies show that viscosity, wavelength-specific cure, conversion, crosslink density, glass transition, strength and elongation depend strongly on polyester architecture, diluent identity and concentration, and post-cure. Acrylate-free itaconate diluents and high renewable-content formulations are feasible, but these labels do not establish low hazard, complete cure, biodegradability or life-cycle benefit. Recent itaconamide systems expand the design space toward monomers derived from alanine, valine, isoleucine and phenylalanine; their reported elongation and study-specific sustainability score remain formulation-specific. ER-110 provides a reaction- and state-resolved qualification architecture spanning chemical identity, complete-resin optics and rheology, spatial conversion, extractables, thermal and mechanical function, ageing and auditable biobased-content claims.

1. Scope and boundaries

ER-110 owns VPP resins in which itaconic-acid-derived functionality materially contributes to the printable liquid or the cured network: unsaturated polyesters, poly(ester amide)s, itaconate reactive diluents and itaconamides. It covers feedstock and derivative identity, cure-bearing double bonds, comonomers, optical-rheological state, working curves, conversion, extraction, thermal-mechanical response, ageing and renewable-carbon accounting.

ER-11 retains generic bio-based design; ER-27 conversion metrology; ER-41 liquid resistance; ER-59 dual cure; ER-61 gelation and vitrification; ER-63 adaptable networks; ER-72 ageing; ER-80 in-can stability; ER-92 residual-reactant hazard; ER-100 corpus architecture; ER-107 phenolic/lignin systems; ER-108 furan/FDCA systems; and ER-109 isosorbide systems [C1-C13].

Itaconic acid is not succinic acid. Succinic acid may be a polyester comonomer, but it does not supply the cure-bearing itaconate exomethylene. The review does not transfer bulk UV-cure results to printed parts, pool acrylate-free itaconates with (meth)acrylate-diluted polyesters, or infer sustainability, biodegradability, low toxicity or service fitness from renewable origin.

2. Chemical-identity and reaction gate

The exomethylene of itaconic acid is conjugated to two electron-withdrawing carboxyl groups. Its reactivity depends on substitution, ester or amide formation, local mobility and the competing chemistry of any diluent. In an unsaturated polyester the itaconate group is distributed along an oligomer; a low-molar-mass diitaconate or itaconamide presents a different functionality, viscosity and defect landscape. Methacrylate or acrylate diluents introduce a second vinyl family and must not be reported merely as viscosity modifiers.

Declared system	Geometry-fixing chemistry	Minimum identity evidence	Claim withheld
Itaconate polyester	Radical cure of pendant itaconate unsaturation	Composition, Mn/dispersity, unsaturation retention, isomerisation and inhibitor	All double bonds equally reactive
Poly(ester amide)	Itaconate cure in an ester/amide backbone	Amide fraction, architecture, reactive-group density and hydrolysis state	Amide automatically improves durability
Itaconate reactive diluent	Low-molar-mass itaconate co-network	Exact ester, functionality, purity, volatility and conversion	Acrylate-free means low hazard
Itaconamide monomer	Radical cure of amino-acid-derived itaconamide	Amino-acid precursor, stereochemistry, substitution and residual synthesis species	Natural precursor proves biocompatibility
Itaconate plus (meth)acrylate	Mixed vinyl network	Each vinyl family, ratio and mechanism-resolved conversion	Properties belong to itaconate alone

Table 1. Identity and reaction gate for itaconic-acid-derived photoresins.

3. Direct evidence chain

3.1 Poly(ester amide) stereolithography

Vetri Buratti et al. synthesised an itaconic-acid-based poly(ester amide), formulated it as a photocurable resin and demonstrated stereolithography [1]. This is direct VPP evidence rather than only bulk-film cure. The amide-bearing architecture, reactive-diluent package, initiator, exposure and post-cure form one controlled system; the study does not establish a universal advantage for every itaconate polyester or every amide fraction.

3.2 Acrylate-free itaconate diluents

Pérocheau Arnaud et al. developed itaconic-acid-based reactive diluents for renewable, acrylate-free UV-curing additive-manufacturing materials [2]. The work establishes that viscosity reduction and network participation can be obtained without an acrylate group, but acrylate-free is a compositional statement. Cure rate, residual itaconate, sensitisation, extractables and printed-part performance still require direct measurement.

3.3 Polyester architecture and diluent concentration

Papadopoulos et al. compared UV-curing polyesters from itaconic acid and developed structure-property relationships for additive manufacturing [3]. A companion study varied diluent concentration and measured printing and material properties [4]. Together they show that polyester composition and dilution cannot be collapsed into an itaconic-acid content axis: viscosity, double-bond density, conversion, network spacing and thermal-mechanical state move together.

A later DLP study varied ACOMO and IBOA composition in itaconate-polyester resins [5]. The authors reported printed Tg values up to 98 °C, 5% mass-loss temperatures of approximately 250 °C or higher and biobased content up to about 85%. The maximum Tg and maximum biobased content occur in different formulations; the mass-loss threshold is a study-wide observation rather than a co-located maximum. ACOMO and IBOA remain named reactive components, not inert processing aids.

3.4 Renewable (meth)acrylate diluents and itaconamides

Bösche et al. combined an itaconic-acid polyester with renewable-resource-derived (meth)acrylates from furfuryl alcohol, tetrahydrofurfuryl alcohol, solketal and diacetone glucose [6]. Rigid cyclic diluents produced the strongest reported property response, including Tg above 70 °C and tensile modulus up to 0.4 GPa. The curing network is nevertheless mixed itaconate/(meth)acrylate; the diluent's carbon origin and chemistry must remain explicit [C12].

Carmenini et al. prepared itaconamide monomers from alanine, valine, isoleucine and phenylalanine and tested sixteen VPP formulations [7]. Monomers were incorporated up to 40 mol%. The most ductile formulation, based on n-octylamine as the study's non-amino-acid comparator, increased elongation at break by 385% relative to the blank, from 3.5% to 17%; the best amino-acid-derived aliphatic monomer, based on isoleucine, reached a 300% increase, or 14%. The phenylalanine derivative was interpreted as reinforcing through π - π interactions at low loading, but at 40 mol% it fell below the blank. Their Sustainable Formulation Score reached 51.8 for Phe-MEIA40. These are study-specific values; the score is not an LCA, universal sustainability scale or hazard qualification.

4. Vat state, cure and storage

Itaconate oligomers can be too viscous for reliable recoating, motivating reactive dilution. Yet diluent addition changes absorber concentration, radical kinetics, functionality and shrinkage as well as viscosity. Working curves must therefore be measured on the complete resin at the actual wavelength, temperature, layer thickness and waiting time. The 405 nm LCD conditions reported for one itaconamide series cannot be transferred to another initiator or optical package [7].

State variable	Failure risk	Minimum control
Unsaturation inventory	Itaconate loss, isomerisation or mixed-vinyl misassignment	NMR/FTIR, functionality and separate conversion signals
Complete-resin optics	Under-cure, overgrowth or composition-dependent depth	Spectrum, Dp, Ec and spatial conversion
Vat rheology	Slow recoating, sedimentation or ageing drift	Viscosity versus shear, temperature, time and storage
Diluent state	Volatility, extraction or disproportionate homopolymerisation	Identity, fraction, vapour/mass loss and residual analysis
Post-cure	Green-part differences hidden by additional conversion	Dose, spectrum, temperature, time and final conversion

Table 2. Minimum state controls for itaconate and itaconamide vats.

5. Conversion, extraction and network architecture

Total C=C conversion can conceal preferential methacrylate or acrylate consumption while itaconate groups remain. Mechanism-resolved spectroscopy, depth-resolved sampling and green/washed/post-cured states are required. Gel fraction does not identify soluble residual monomer; chromatography or another compound-specific method is needed. A high post-cure conversion does not erase a weak or contaminated green-part interface.

Crosslink density is governed by oligomer architecture, reactive-group density, diluent functionality, conversion and defects. Raising diluent concentration may improve flow and light penetration while increasing shrinkage, lowering renewable fraction or changing extraction. Amide hydrogen bonding and aromatic interactions can alter strength and elongation, but their contribution must be separated from conversion and network density.

6. Thermal, mechanical and liquid-state qualification

Tg, 5% mass-loss temperature, tensile modulus, strength, elongation and toughness are not interchangeable. ISO 527-1:2019, ISO 527-2:2025 and ISO 178:2019 provide tensile and flexural anchors [S1-S3]; ISO 11357-2:2020, ISO 11358-1:2022 and ISO 6721-11:2019 support glass-transition, thermogravimetric and dynamic-mechanical measurements [S4-S6]. Printed orientation, conditioning, strain rate and post-cure remain part of every result.

Ester and amide groups can interact with water, and residual diluent can be extracted or plasticise the network. ISO 62:2008, ISO 6427:2025 and ISO 175:2010 provide general water-uptake, extractable-matter and liquid-immersion anchors [S7-S9]. Qualification still requires application-specific media, time, temperature, mass balance, dimensional change and retained properties. No renewable or amino-acid precursor removes this obligation.

7. Renewable-content and sustainability gate

A molecule may be synthesised from a renewable precursor while a formulation contains fossil-derived comonomers, initiator, absorber or additives. ISO 16620-2:2019 determines biobased carbon content, while ISO 16620-4:2024 addresses biobased mass content [S10-S11]. Feedstock attribution, carbon fraction, mass fraction, manufacturing energy, yield, solvents, service life and end-of-life are separate quantities.

Acrylate-free does not mean non-sensitising; amino-acid-derived does not mean biocompatible; high biobased content does not mean biodegradable; and a formulation score does not replace life-cycle assessment. Sustainability claims must state the system boundary, weighting choices and measured inventory. ER-110 does not rank formulations across incompatible boundaries.

8. Qualification architecture

Gate	Minimum evidence	Release question
Feedstock and derivative	Itaconic precursor, derivative identity, purity, unsaturation retention and renewable accounting	Is the cure-bearing material named correctly?
Printable vat	Complete-resin optics, rheology, working curve, stability and recoating	Does the exact formulation print reproducibly?
Network formation	Vinyl-family-resolved conversion, depth uniformity and gel fraction	Which groups fix geometry and which remain?
Workflow closure	Wash/post-cure mass balance, extractables and residual analytics	What mobile or reactive species remain?
Property duty	Conditioned tensile/flexural, thermal state, liquids and ageing	Does performance persist in the declared use?
Sustainability	Biobased carbon/mass, inventory boundary, process inputs and end-of-life	Is the environmental claim auditable?

Table 3. Qualification chain for itaconic-acid-derived photoresins.

9. Failure-mode interpretation

- The polyester contains itaconic units but cures poorly: verify retained exomethylene, isomerisation, inhibitor, mobility and wavelength-specific initiation.
- Reactive diluent lowers viscosity: remeasure optics, conversion partition, shrinkage, extraction and renewable fraction.
- A formulation is acrylate-free: identify the itaconate cure chemistry and withhold low-hazard claims until residual and toxicological evidence closes them.
- The maximum Tg and maximum biobased content occur in different formulations: never merge them into a synthetic best case.
- Elongation rises with an itaconamide: retain monomer fraction, conversion, post-cure, test geometry and conditioning.
- An amino-acid-derived monomer is used: do not infer biocompatibility, biodegradation or food-contact suitability.
- A sustainability score improves: disclose its weights and boundary and do not relabel it as LCA.
- Thermal decomposition exceeds 250 °C: withhold a high-temperature service rating until Tg, creep, oxidation and retained mechanics are qualified.

10. Minimum workflow and research priorities

- Freeze precursor, derivative, polyester composition, molar mass, unsaturation retention, inhibitor and impurity profile.
- Name every reactive diluent and quantify it by functionality, mass fraction and carbon origin.
- Measure spectrum, working curve, viscosity, ageing and recoating on the complete resin at print conditions.
- Resolve itaconate and auxiliary-vinyl conversion through depth and across green, washed and post-cured stages.
- Close gel fraction, compound-specific extractables, mass loss and residual photochemistry.
- Separate tensile, flexural, fracture, thermal transition, decomposition, creep and liquid-retention claims.
- Report biobased carbon, biobased mass and process inventory under declared boundaries.
- Test storage stability, print reproducibility and property retention across independently prepared batches.

11. Conclusions

Itaconic acid supplies a versatile renewable scaffold and a potentially cure-bearing exomethylene, but VPP performance belongs to a defined derivative, polyester architecture, diluent package and workflow. Poly(ester amide), unsaturated-polyester, itaconate-diluent and itaconamide evidence must remain chemically separated.

Direct studies establish printable SLA, DLP and LCD systems and show large formulation-dependent shifts in viscosity, conversion, Tg, modulus and elongation. Mixed itaconate/(meth)acrylate networks, acrylate-free systems and amino-acid-derived monomers answer different design questions; none alone proves low hazard, biodegradability or circularity.

Qualification therefore requires identity, complete-resin state, reaction-resolved conversion, extraction closure, conditioned properties, ageing and auditable biobased-content accounting. ER-110 provides this chain without authorising a formulation or intended use.

Limitations

This qualitative engineering review is not a systematic meta-analysis. Direct VPP studies use heterogeneous chemistries, printers, wavelengths, specimens and post-cures. Numerical maxima are not pooled. No proprietary formulation, exposure schedule, toxicological qualification, life-cycle assessment, regulatory approval or universal service limit is supplied.

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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