

Cyanate-Ester, Maleimide/Bismaleimide and Benzoxazine Photopolymers for Vat Photopolymerisation: Photo-Triggered Networks, Thermal Post-Cure and Qualification

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Statement of Significance

High-temperature labels can conceal different network-forming reactions. Cyanate esters form polycyanurate triazine networks by catalytic cyclotrimerisation; maleimide or bismaleimide building blocks can be methacrylate-functionalised, blended or reacted through ene/Michael chemistry; benzoxazine systems may use a photoreactive handle to fix shape before thermally opening oxazine rings. ER-106 separates the light-defined green body from the final thermoset and requires chemistry-specific evidence at every stage.

Keywords: vat photopolymerisation; cyanate ester; polycyanurate; maleimide; bismaleimide; benzoxazine; projection micro-stereolithography; Hot Lithography; thermal post-cure; high-temperature thermoset; conversion; qualification.

Abstract

Cyanate-ester, maleimide/bismaleimide and benzoxazine formulations extend vat photopolymerisation toward high-temperature thermosets, but they do not share one cure mechanism. Primary demonstrations include Hot Lithography of an unfilled cyanate-ester formulation through photo-induced catalytic polytrimerisation, stereolithography of a methacrylate-functionalised bismaleimide oligomer, and projection micro-stereolithography of photocurable benzoxazine precursors followed by thermal ring-opening polymerisation. In these routes, light may create the final network, activate a latent catalyst or only establish a shape-retaining intermediate. Post-cure temperature can increase conversion and properties while also causing diffusion, overgrowth, oxidation, warpage, cracking or volatile loss. Reported high glass-transition and decomposition temperatures remain formulation-, conversion-, method- and specimen-specific. This review defines an identity gate, stage-resolved conversion controls, vat-stability requirements and a qualification chain for geometry, residuals, mechanical performance, thermal service, dielectric claims and ageing.

1. Scope and boundaries

ER-106 owns cyanate-ester/polycyanurate, maleimide/bismaleimide and benzoxazine routes when used as photoprintable high-temperature thermosets or as thermally advanced printed intermediates. It covers chemical identity, catalyst or photoreactive handle, vat state, light-defined conversion, thermal post-cure, residual functionality, dimensional retention and final qualification.

ER-27 retains generic conversion metrology; ER-31 shrinkage and stress; ER-59 sequential dual cure; ER-61 gelation and vitrification; ER-72 environmental ageing; ER-80 in-can stability; ER-91 evidence density; ER-92 residual-reactant hazard; ER-100 corpus architecture; ER-103 polyurethane/polyurea; ER-104 fluorinated and fluoropolymer-derived systems; ER-105 polyimide and polyimide-precursor routes; and ER-107 phenolic, lignin-derived and bio-aromatic systems [C1-C13].

The review does not treat all imide-containing materials as bismaleimides, does not call every photo-fixed benzoxazine a fully polymerised polybenzoxazine, and does not infer service temperature from one DSC, DMA or TGA number. A printed green body and a thermally post-cured article are different controlled states.

2. Chemical-identity and reaction-state gate

Family	Geometry-fixing event	Final-network evidence
Cyanate ester	Photo-generated or photo-activated catalytic centre plus elevated-temperature reaction	Loss of OCN bands, triazine formation, residual catalyst/co-catalyst and post-cure conversion
Functionalised bismaleimide	Radical polymerisation of grafted methacrylate or other added photoreactive groups	Identity of the photoreactive network and evidence for any later maleimide participation
Maleimide hybrid	Radical, thiol-Michael/ene or interpenetrating-network route, depending on formulation	Stoichiometry, competing reactions, residual maleimide and network topology
Photocurable benzoxazine	Photoreactive substituent forms a shape-retaining network	Thermal ring opening, phenolic network formation and residual oxazine or photoreactive groups

Table 1. Minimum identity gate for the three high-temperature thermoset families.

Names must follow the load-bearing final network. A bismaleimide-derived methacrylate resin can retain imide rings yet be fixed principally through methacrylate chain growth. A benzoxazine bearing photocurable groups can yield an interpenetrating or sequential network rather than a native polybenzoxazine alone. The formulation ledger should therefore state monomers, oligomers, reactive diluents, catalyst, co-catalyst, initiator, inhibitor and every post-cure step.

3. Demonstrated cyanate-ester routes

Wolff et al. demonstrated photo-induced catalytic polytrimerisation of a novolac-based cyanate ester and printed pure polycyanurate structures by Hot Lithography [1]. Their formulation combined a photolabile iron-arene complex with nonylphenol as an active-hydrogen co-catalyst. Irradiation at elevated temperature generated a solid network, and subsequent thermal treatment raised conversion. The exact catalyst and co-catalyst remain part of the cured composition and must not be omitted from chemical, dielectric or extraction claims.

For the reported PT-30 formulation, initial irradiation between 80 and 100 °C produced chemistry- and method-specific conversion values, while post-curing increased the maximum reported IR conversion to $86 \pm 2\%$ [1]. Hot Lithography was demonstrated at 90 °C with 50 μm layers. The printed DMA specimens reached a reported glass-transition temperature of 336 ± 5 °C and degradation onset of 426 °C after the study's post-cure. These figures are not generic cyanate-ester specifications.

The same study observed slight overpolymerisation attributed to diffusion of the catalytic system [1]. Consequently, cure-depth calibration alone is insufficient: lateral growth, catalyst diffusion, thermal history and post-cure geometry must be measured together.

4. Demonstrated maleimide/bismaleimide routes

Hua et al. synthesised an amino-containing bismaleimide backbone and grafted glycidyl methacrylate to obtain a photocurable oligomer for SLA [2]. The tested resin also contained reactive diluents and photoinitiator. The reported maximum tensile strength of 72.6 MPa, glass-transition temperature of 155 °C and storage modulus of 3625 MPa at 35 °C belong to the stated formulation, printing and test procedures [2]. They do not establish the performance of unmodified bismaleimide or all bismaleimide-containing photoresins.

The source characterised curing as free-radical polymerisation with a minor cationic contribution and used a staged thermal post-cure of 160 °C for 1 h, 180 °C for 1 h, 200 °C for 1 h and 220 °C for 2 h [2]. Maleimide groups can participate in several reactions, including radical homopolymerisation, copolymerisation and nucleophile addition. Which route dominates depends on substituents, partners, stoichiometry and temperature. When a methacrylate group supplies most of the light reactivity, the manuscript and qualification record should say so explicitly rather than attributing the entire printed network to maleimide chemistry.

5. Demonstrated benzoxazine routes

Lu et al. designed low-viscosity photocurable benzoxazines for high-resolution projection micro-stereolithography [3]. Complex objects were obtained after thermal treatment of the as-printed structures. The reported thermally polymerised material reached a glass-transition temperature of 264 °C; the 4.91 ± 0.21 GPa flexural modulus belongs to the higher-performing PBZ-C2 design cured to 240 °C, while the C5 analogue reached 3.00 ± 0.21 GPa [3]. These are property coordinates for those molecular designs and test states, not universal benzoxazine values.

As adjacent non-VPP evidence, Jehl et al. reported a UV-curable polybenzoxazine vitrimer processed by UV-assisted material extrusion and designed for reshaping and recycling [4]. It must not be cited as a vat-photopolymerisation demonstration. The source demonstrates one closed loop through each of two routes, not repeated cycling. Dynamic-network functionality does not by itself prove repeated closed-loop performance for every geometry, contamination state or thermal history. Each cycle must retain mass balance, network chemistry, geometry and application properties within declared limits.

6. Vat temperature, viscosity and storage stability

Elevated temperature can lower viscosity and activate latent chemistry, broadening the formulation window beyond room-temperature vats. It also accelerates dark reaction, catalyst migration, inhibitor depletion and component loss. Record vat, recoater, platform and resin temperatures separately, together with warm-up time, residence time, shear history and viscosity drift.

Wolff et al. reported an initial formulation viscosity of about 0.1 Pa·s at the evaluated elevated-temperature condition and growth to 3.5 Pa·s during 72 h at 100 °C [1]. That result supports a bounded proof of stability, not indefinite pot life. A production release requires build-duration and reuse studies on the exact formulation and hardware.

7. Light cure, thermal post-cure and dimensional closure

These systems are often sequential. Light establishes a green body, while thermal treatment advances cyclotrimerisation, ring opening or secondary network formation. Measure mass and x/y/z dimensions after printing, washing, drying and every post-cure plateau. A higher final conversion can coexist with warpage, cracking or feature loss.

Stage	Minimum measurements	Release failure
Liquid vat	Composition, viscosity, spectra, latency and thermal history	Premature reaction or non-uniform exposure response
As printed	Feature transfer, green strength, insoluble fraction and residual functionality	Shape is present but chemistry is not yet service-ready
Intermediate post-cure	Temperature, time, atmosphere, mass, conversion and dimensions	Exotherm, diffusion, oxidation, warpage or cracking
Final conditioned article	Network identity, residuals, morphology, mechanics, thermal and dielectric response	Headline property lacks final-state traceability

Table 2. State-resolved controls for sequentially cured high-temperature photoresins.

8. Conversion, residuals and catalyst closure

Cyanate conversion should use the disappearance of OCN bands and formation of triazine markers with an explicit internal reference and sampling position. Benzoxazine conversion requires evidence for oxazine-ring opening and the final phenolic network. Functionalised bismaleimide systems require separate tracking of methacrylate and maleimide functionalities where both may react.

ISO 6427:2025 provides a conventional anchor for solvent-extractable matter, while ISO 175:2010 addresses effects of immersion in liquid chemicals [S7,S8]. Neither substitutes for compound-specific analysis of monomers, catalysts, co-catalysts, initiator fragments, reactive diluents or thermolysis products. ER-92 retains generic residual-reactant hazard [C8].

9. Mechanical, thermal and dielectric qualification

ISO 527-1:2019, ISO 527-2:2025 and ISO 178:2019 provide tensile and flexural anchors [S1-S3]. Report specimen geometry, build orientation, surface, post-cure, conditioning and failure mode. A single room-temperature strength value cannot establish retention at service temperature.

ISO 11357-2:2020, ISO 11358-1:2022 and ISO 6721-11:2019 anchor glass-transition, mass-loss and dynamic-mechanical measurements [S4-S6]. DSC, DMA and TGA answer different questions; a degradation onset cannot be used as a continuous-use temperature. Dielectric

claims require frequency, temperature, humidity, specimen thickness, electrodes and residual catalyst state. Iron-containing catalytic systems especially require explicit bounding where electromagnetic or dielectric performance matters.

10. Qualification architecture

Block	Evidence	Decision
Identity	Precursors, photoreactive handles, catalyst, co-catalyst and diluent	What actually forms the network?
Vat state	Temperature-resolved rheology, spectra, dark stability and reuse	Can a full build be completed reproducibly?
Light-defined state	Working curve, conversion, green strength and lateral growth	Is geometry fixed without uncontrolled diffusion?
Thermal advancement	Conversion, exotherm, atmosphere, mass and dimensional trajectory	Does post-cure improve chemistry without losing geometry?
Final residual state	Extractables and compound-specific analytics	Are monomers and catalyst-derived species controlled?
Duty evidence	Mechanical, thermal, dielectric, chemical and ageing retention	Does the final article meet its declared environment?

Table 3. Release architecture for cyanate-ester, maleimide/bismaleimide and benzoxazine VPP.

11. Failure-mode interpretation

- The vat thickens during a long heated build: examine dark catalytic reaction, inhibitor depletion and residence time before increasing temperature.
- The part prints but distorts during thermal treatment: map stage-resolved conversion, exotherm, mass and anisotropic dimensions.
- The cyanate-ester feature grows laterally: separate optical penetration from catalyst diffusion and thermally driven reaction.
- A bismaleimide-derived resin meets strength targets: preserve the exact grafting, diluent, cure and test state; do not generalise to neat BMI.
- A benzoxazine green body is dimensionally accurate: withhold final polybenzoxazine identity until ring-opening and residual oxazine are verified.
- TGA onset is high: do not equate it with glass transition, creep resistance, oxidation stability or continuous-use temperature.
- A dynamic network is reprocessable: quantify material recovery and property retention over defined cycles before claiming closed-loop reuse.

12. Minimum workflow and research priorities

- Freeze precursor identity, functionalisation, catalyst, co-catalyst, initiator, inhibitor, diluent, water and storage history.
- Measure viscosity, spectra and dark reactivity at actual vat temperature over a full production-duration envelope.
- Use chemistry-specific conversion markers for OCN/triazine, maleimide/(meth)acrylate and oxazine/phenolic states.
- Record feature transfer and mass/dimensional trajectories across printing, cleaning and every thermal plateau.
- Quantify gel fraction, extractables and compound-specific residuals in the final conditioned article.
- Separate Tg, storage modulus, degradation, oxidation, creep and continuous-duty claims.
- Develop reference specimens that expose catalyst diffusion, thermal gradients and post-cure cracking.
- Report dielectric data with frequency, temperature, humidity, geometry and catalyst state.
- Test ageing and property retention at declared service temperature rather than extrapolating from aromatic structure.

13. Conclusions

Cyanate esters, maleimide/bismaleimide derivatives and benzoxazines offer credible routes to thermally capable vat-photopolymerised parts, but their light and heat histories cannot be collapsed into one cure label. Light may form a final network, activate a catalyst or create only a green body for later thermal advancement.

Primary evidence demonstrates pure-polycyanurate Hot Lithography, SLA of a methacrylate-functionalised bismaleimide oligomer and projection micro-stereolithography of photocurable benzoxazines followed by thermal treatment. Their high-property coordinates remain bounded to exact formulations, conversion states and tests.

Release therefore requires identity, heated-vat stability, spatial conversion, post-cure mass and geometry, residual chemistry and application-specific retention. No single Tg, TGA onset, tensile value or aromatic label can replace that chain.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use different precursors, functionalisation routes, catalysts, initiators, diluents, wavelengths, printers, temperatures, post-cures and tests. Numerical values are not pooled or ranked. No proprietary formulation assay, universal printing window, continuous-use rating, dielectric certification, toxicological qualification 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 the cited primary literature and official standards.

Company information

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