

Toughening Mechanisms in Vat-Photopolymerised Thermosets: Network Topology, Phase Morphology, Reinforcement and Process Trade-Offs

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Statement of Significance

Vat-photopolymerised parts are often labelled tough when only one tensile, flexural or impact result has improved. Such a result does not identify why the material absorbed more energy, whether the mechanism survives post-cure and ageing, or whether the gain is retained across orientations and feature scales. This review separates toughening mechanism from measured outcome and defines the evidence required to attribute improved performance to network topology, reversible interactions, crystallinity, phase morphology, particulate reinforcement, chain transfer or molecular orientation.

Keywords: vat photopolymerisation; toughening mechanisms; network topology; crosslink density; bimodal networks; sacrificial bonds; semicrystallinity; rubber toughening; core-shell nanoparticles; phase morphology; chain transfer; molecular orientation; SLA; DLP

Abstract

Vat photopolymerisation requires rapid spatial fixation of a liquid resin, a condition that commonly favours multifunctional precursors, early gelation and highly crosslinked glassy networks. These features support print fidelity but can suppress chain extensibility and concentrate deformation. The resulting stiffness-toughness conflict has generated multiple toughening routes that are frequently grouped together despite operating through different physical mechanisms. This review organises dry VPP thermoset toughening into homogeneous co-reactive blending, bimodal long-chain/short-crosslinker networks, elastomeric click networks, sacrificial non-covalent interactions, semicrystallinity combined with dynamic bonds, core-shell particles, covalently incorporated hyperbranched rubbers, controlled phase morphology, nanofiller crack bridging, thiol-acrylate chain transfer and light-directed molecular orientation. Representative studies show that similar improvements in tensile work, elongation, impact response or cracked-specimen resistance can arise from fundamentally different structures. The same additive can also increase viscosity, attenuation, shrinkage, anisotropy or post-cure sensitivity. A mechanism claim therefore requires more than a property increase: it requires direct evidence of the proposed topology or morphology, a matched formulation control, process-state data and a response that is consistent with the claimed dissipation route. Fracture-test validity remains outside this paper and is treated in ER-70. The central conclusion is that toughening is a causal architecture, not a marketing label or a single number. A defensible VPP material claim must link precursor structure, resin optics and rheology, gelation and conversion, final network or phase state, conditioning, deformation mechanism and failure mode.

1. Scope and evidence-selection method

ER-68 addresses mechanisms used to increase deformation capacity and energy absorption in final, predominantly dry polymeric thermosets produced by SLA, DLP, LCD/MSLA, hot lithography and closely related vat-photopolymerisation routes. It does not pool values across formulations and does not define a universal target for toughness.

Shared measurement conventions, reporting rules and disclosure boundaries for this series are defined in [RP-02](#); this review states only the topic-specific content.

The evidence set prioritises studies that connect a formulation or processing change to at least one structural observation and one mechanical response. Numerical values are retained only as source-specific examples. The scope excludes hydrated hydrogel networks, which are treated in ER-67; fracture-method validity and damage tolerance, which are treated in ER-70; fatigue, creep and stress relaxation, which are treated in ER-39; and healing or repair after damage, which are treated in ER-13.

2. Toughness is an outcome, not a mechanism

Toughening describes a causal change that allows a material to absorb more energy before unstable failure. The observed outcome can appear as increased strain at break, a larger area under a stress-strain curve, higher impact energy, delayed notch failure, greater cracked-specimen resistance or a transition from brittle rupture to yielding. These measurements are not interchangeable.

Table 1. Mechanical outcomes that should not be treated as mechanism names

Observed outcome	Typical measurement	Possible causes	What remains unproven
Higher elongation at break	Unnotched tensile test	Lower effective crosslink density, extensible chains, yielding, plasticisation	Energy dissipation at a crack or notch
Higher tensile toughness	Area under stress-strain curve	Higher stress, higher strain, or both	Fracture toughness or damage tolerance
Higher impact value	Izod, Charpy or drop impact	Crack deflection, yielding, inertia and specimen geometry	A valid KIC, GIC or mechanism
Higher conditional crack resistance	Notched or cracked specimen	Bridging, phase deformation, residual stress, crack-path change	Method validity or transfer to other orientations
Thermoplastic-like yielding	Yield point, necking and strain hardening	Heterogeneous rubber domains or topology-controlled network	Reprocessability or true thermoplastic structure
Self-recovery after deformation	Unload-rest-reload or shape recovery	Reversible bonds, crystallinity, viscoelastic relaxation	Healing of a severed crack or interface

A mechanism statement should explain where deformation occurs, what dissipates energy, whether that event is reversible, and which structural level remains load-bearing. A performance label alone cannot supply that explanation.

3. Why VPP networks tend to become brittle

Print fidelity and green strength often favour high reactive functionality, rapid network formation and limited molecular mobility. The same features can produce a narrow distribution of short network strands, early vitrification, high local stress and little opportunity for yielding. Reactive diluents may improve processing while raising crosslink density; post-cure may improve conversion while reducing extensibility; and a cure gradient can create local weak or over-crosslinked regions even when average conversion is high.

The engineering objective is therefore not simply to lower crosslink density. A useful formulation must preserve a connected load-bearing network while introducing one or more deformation mechanisms that activate before catastrophic crack growth. Those mechanisms must remain compatible with the resin state, the optical field and the complete washing and post-curing workflow.

4. Homogeneous network-topology routes

4.1 Co-reactive blending without an observed second phase

Idrees and co-workers blended a brittle methacrylated vinyl-ester system with a commercial urethane-acrylate resin. A substantial urethane-acrylate fraction, approximately 60 wt% in the tested system, was required before the combined property balance improved, and higher additions reduced other mechanical properties [1]. The authors did not observe nanoscale phase separation and interpreted the response as toughening of a single-network blend through chemistry and network structure. This route is important because it shows that improved energy absorption does not require a discrete rubber phase.

The qualification burden is to demonstrate that the blend is chemically incorporated, that the response is not caused by residual uncured species or simple plasticisation, and that the selected composition does not sacrifice conversion, modulus, dimensional stability or solvent resistance beyond the application limit.

4.2 Bimodal long-chain and short-crosslinker networks

Samson and co-workers combined a long 10 kg/mol polycaprolactone dimethacrylate with a small multifunctional crosslinker to create a bimodal network [2]. The long chains provided extensibility while the short crosslinker increased reactivity and green-body stiffness. One selected formulation reached 11 MPa tensile strength at 116% elongation and was printed at 8 s per 50 micrometre layer on a low-cost DLP system under the authors' stated conditions. The route also produced approximately 25% linear shrinkage in both thickness and diameter after extraction of predominantly non-reactive diluent and drying, showing that mechanical success and dimensional qualification are separate questions.

A bimodal claim requires evidence for both strand populations and their incorporation. Molecular-weight labels alone are insufficient if the low-molecular-weight fraction acts mainly as an extractable diluent or if the long chains fail to join the network.

4.3 Elastomeric backbones and thiol-ene click networks

Moore and co-workers used thiol-ene chemistry to crosslink unmodified commercial liquid polybutadiene through pendent olefinic groups [3]. Increasing crosslink density increased tensile stress and reduced strain at break, while formulations were downselected for printability and demonstrated on commercial DLP printers. The study provides a direct reminder that an elastomeric backbone is not itself a toughness guarantee: network density and reaction stoichiometry still control the final balance.

The reported dark-cure behaviour also creates a process boundary. Continued reaction after exposure can improve interlayer continuity or conversion, but it can alter feature dimensions and must be included in the temporal definition of the printed state.

5. Reversible interactions, crystallinity and sacrificial dissipation

5.1 Sacrificial hydrogen bonding in a glassy network

Fang and co-workers introduced non-covalent hydrogen bonding into a glassy, shape-memory VPP network [4]. Under the stated tensile conditions, the selected material combined a toughness of 38.3 ± 4.3 MJ/m³, a Young modulus of 1.1 ± 0.1 GPa, a breaking stress of 46.2 ± 1.9 MPa and a strain at break of $99 \pm 14\%$. The authors attributed the energy absorption to sacrificial hydrogen bonding between urethane and carboxyl groups.

A reversible-interaction claim should be tested with matched chemistry, temperature and moisture controls. Hydrogen bonding can also change resin association, glass transition, water uptake and rate dependence. Increased tensile area does not by itself prove bond rupture and reformation.

5.2 Semicrystallinity combined with dynamic thioester chemistry

Kuenstler and co-workers combined a thiol-ene network with semicrystallinity and dynamic thioester bonds [5]. The crystallisable phase contributed a physical switching and reinforcement level, while thiol-thioester exchange enabled chemical degradation to functional oligomers and subsequent repolymerisation. The study also demonstrated stiff and soft printed lattices, shape memory and self-healing functions. ER-68 includes it only as a network-toughening boundary: recycling, exchange kinetics and healing require the separate evidence defined in ER-63 and ER-13.

Crystallinity must be measured rather than inferred from opacity or a product label. DSC, diffraction and temperature-dependent mechanical response are needed to separate crystalline reinforcement from glass-transition effects or simple phase separation.

6. Heterogeneous phase and particulate routes

6.1 Polysiloxane core-shell nanoparticles

Li and co-workers incorporated approximately 132 nm polysiloxane core-shell nanoparticles into an epoxy-based stereolithography resin [6]. At 5 wt% loading, the source reported large increases in tensile and flexural strain at break and a 166.3% increase in fracture toughness while retaining useful transparency, thermal stability and print accuracy. Shell thickness and interfacial design controlled the outcome. This is a classic particulate route in which a soft core can deform and promote matrix shear yielding while a compatible shell transfers load and limits aggregation.

The mechanism cannot be assigned from particle presence alone. The particle-size distribution, shell chemistry, dispersion, interface, cured morphology and fracture surface must be linked to the mechanical change. Aggregates can become critical flaws rather than tougheners.

6.2 Covalently incorporated hyperbranched rubber domains

Musil and co-workers synthesised methacrylate-functionalised hyperbranched polyethylene rubbers and used them as macromonomer tougheners in a brittle styrene-maleimide photopolymer [7]. Rubber molar mass, functionality and loading changed miscibility, phase separation and thermomechanical response. At 20 wt% loading, selected systems developed yield, necking and strain hardening while maintaining glass-

transition temperatures around 100 °C. AFM documented morphology changes with rubber molar mass and methacrylate functionalisation; tensile testing directly showed yield, necking and strain hardening in the selected 20 wt% 2PE formulation.

The study also shows why resin processability belongs inside a mechanism review. Hot lithography at 80 °C was used to manage viscosity and miscibility. A formulation that toughens well after bulk cure may be unusable in an unheated vat or may phase-separate during residence.

6.3 Reactive aromatic-polyester modification

Lin and co-workers synthesised an aromatic polyester for stereolithography resin toughening and reported simultaneous improvements in fracture resistance, elongation, modulus and hardness together with favourable liquid miscibility and room-temperature processability [8]. The accessible publisher record supports rigid aromatic content and favourable compatibility as design features; it does not by itself establish covalent incorporation or a controlled heterogeneous morphology.

For this class, the critical evidence is whether the modifier is covalently connected, remains as a separate phase, or does both. Microscopy, spectroscopy, extraction and thermal analysis should be interpreted together; otherwise the same mechanical result can be assigned to incompatible mechanisms.

6.4 Graphene and other rigid nanofillers

Feng and co-workers added 0.5 wt% graphene nanoplatelets to a DLP resin and reported a 28% increase in fracture toughness and a 14% increase in flexural modulus, with crack bridging, pull-out and deflection features [9]. The same filler increased viscosity and reduced cure depth from 0.48 ± 0.02 mm to 0.14 ± 0.02 mm in the reported formulation. The case demonstrates the central VPP trade-off: a reinforcing phase can improve the solid while degrading optical penetration and process latitude.

Rigid fillers should therefore be qualified as a coupled dispersion-optics-mechanics problem. The lowest loading that is printable and the loading that maximises a mechanical result are not necessarily the same.

7. Chain-transfer control of network topology

Bian and co-workers used an in situ thiol-acrylate chain-transfer strategy in a triazine-based DLP resin containing polysulfide rubber [10]. The low-viscosity ink remained below 150 cP and supported 50 micrometre printing. Relative to the reference triazine network, the optimised system increased elongation at break by 462.4% and tensile toughness by 640.5% while retaining a tensile strength of 45.7 MPa. These results support a formulation-specific chain-transfer toughening route; exact thiol identity, conversion and post-cure attribution remain tied to the source methods.

Chain transfer changes strand length, branching, effective crosslink density and free volume. It should not be described merely as adding a soft rubber. A mechanism claim should include stoichiometry, evidence for thiol consumption, conversion before and after post-cure, gel fraction or extraction, and thermal consequences. The cited study also reported thermotolerance as an open limitation, illustrating that topology optimisation moves rather than eliminates trade-offs.

8. Light-directed molecular orientation

Sun and co-workers blended 3 wt% of the nematic liquid crystal 5CB into an acrylic photosensitive resin and used SLA exposure to orient both the liquid crystal and surrounding polymer chains [11]. At 25 micrometre layers and the selected orientation, the source reported 122.2 MPa tensile strength, 23.4% elongation, 222.1 MPa flexural strength and 11.09 kJ/m² impact strength. The improvement diminished when liquid-crystal content or layer thickness prevented effective orientation.

This mechanism is intentionally anisotropic. The printed direction, light field, layer thickness and test direction are part of the material definition. A high result in the aligned direction cannot be released as an isotropic resin property.

Table 2. Representative VPP toughening architectures and their evidence boundaries

Route	Structural level	Representative evidence	Primary qualification risk
Co-reactive blend [1]	Single network with composition-dependent topology	Composition sweep, conversion, thermal and mechanical tests; no observed nanoscale phase separation	Plasticisation or incomplete cure mistaken for topology control
Bimodal network [2]	Long macromer strands plus short multifunctional crosslinker	Molecular identity, gel content, rheology, tensile and printed structures	Solvent-removal shrinkage and extractables
Elastomeric thiol-ene [3]	Polybutadiene backbone crosslinked through pendent olefins	Reaction selectivity, working curves and crosslink-density trend	Dark cure and stoichiometric sensitivity
Sacrificial H bonds [4]	Covalent glassy network plus reversible association	Matched formulation and high tensile energy absorption	Moisture, rate and temperature dependence
Semicrystalline dynamic network [5]	Covalent network plus crystals and exchangeable thioesters	Thermomechanics, exchange/reprocessing and printed lattices	Multiple mechanisms conflated into one toughness claim
Core-shell particles [6]	Soft nanoscale cores with compatible shells in rigid matrix	Particle size, shell design, dispersion and fracture response	Aggregation, opacity and flaw creation
Hyperbranched rubber [7]	Covalently incorporated rubber-rich domains	AFM/SEM morphology, yielding and hot-lithography process data	Vat instability and temperature-specific miscibility
Aromatic polyester modifier [8]	Rigid aromatic modifier with favourable compatibility	Chemical identity, liquid miscibility and multi-property response	Covalent incorporation and controlled morphology require direct evidence
Graphene [9]	Rigid platelet reinforcement and crack-path interaction	Fractography, mechanical response, viscosity and cure depth	Optical attenuation and agglomeration
Thiol-acrylate chain transfer [10]	Topology and free-volume control with rubber incorporation	Spectroscopy, solvent retention, post-cure and mechanical response	Lower thermal performance or incomplete final cure
Light-oriented LC [11]	Anisotropic molecular orientation fixed by layerwise cure	POM, XRD, layer-thickness study and directional mechanics	Directional overclaim and aggregation at excess loading

9. Process-mechanism coupling

A toughening component changes the starting resin before it changes the solid. The complete path is:

precursor architecture -> resin compatibility and stability -> optical transport and flow -> gelation and conversion -> phase or topology development -> washing and post-cure -> final deformation and failure

Each arrow can reverse an expected benefit. A soft modifier can lower viscosity yet reduce green strength. A nanoparticle can increase crack deflection yet reduce cure depth. Faster gelation can freeze a useful morphology or arrest it too early. Post-cure can strengthen a network while consuming the mobility required for yielding. Solvent extraction can reveal a robust network but introduce large dimensional change.

The selected mechanism must therefore be qualified on the actual printer, wavelength, irradiance, exposure strategy, layer thickness, temperature, geometry and post-processing route. Bulk-cured plaques are useful formulation controls, but they do not replace printed-state evidence.

10. Evidence required to assign a mechanism

A causal mechanism should satisfy four levels of evidence. First, the proposed structural feature must exist. Second, its amount or state must vary in a controlled way. Third, the mechanical response must change consistently with that variation. Fourth, competing explanations must be excluded with matched controls.

Table 3. Minimum evidence architecture for a VPP toughening-mechanism claim

Domain	Minimum record or measurement	Decision supported
Starting chemistry	Reactive functions, molecular-weight class, additive identity, stoichiometry and concentration	Defines the proposed architecture and matched control
Resin state	Viscosity versus relevant shear/temperature, stability, dispersion and optical spectrum	Shows that the mechanism-bearing formulation is processable
Cure state	Working curve, conversion, gelation, dark cure and post-cure history	Separates network development from nominal exposure
Topology or morphology	Gel fraction/extraction, DMA/DSC, spectroscopy, microscopy, scattering or diffraction as appropriate	Demonstrates the structural feature instead of inferring it
Mechanical response	Full tensile/flexural curves, impact or cracked test where relevant, replicate scatter and orientation	Defines the actual improved outcome
Mechanism-specific observation	Fractography, particle deformation, pull-out, yielding, hysteresis, recovery or directional texture	Connects structure to energy dissipation
Trade-off controls	Modulus, Tg, shrinkage, absorption, resolution, chemical resistance and ageing	Prevents selective reporting of one improved metric
Representative article	Feature-scale and geometry-specific validation under the complete workflow	Bounds the claim to the intended manufacturing state

No single method proves all routes. AFM may be decisive for nanoscale rubber domains, XRD or POM for orientation, DSC for crystallinity, extraction for network connectivity and fractography for crack-path interaction. Method selection should follow the proposed mechanism rather than a fixed checklist.

11. Trade-offs and optimisation logic

The optimal formulation is not necessarily the one with the largest tensile area or elongation. It is the formulation that meets the defined application criteria while preserving a controllable manufacturing window. Common trade-offs include:

- toughness versus modulus, hardness or heat resistance;
- particle or domain content versus viscosity, stability and optical penetration;
- lower crosslink density versus green strength, solvent resistance and creep;
- reversible interactions versus moisture, temperature and loading-rate sensitivity;
- crystallinity versus optical clarity and dimensional evolution;
- directional reinforcement versus isotropy and build-orientation robustness;
- post-cure conversion versus residual mobility and ductility;
- solvent-enabled printability versus extraction time and shrinkage.

Optimisation should use a constrained decision rather than a single maximum. RP-02 supplies the shared evidence-to-decision logic; the topic-specific requirement here is that the selected formulation preserve both the mechanism and the process state that created it.

12. Conditioning, ageing and persistence

A toughening mechanism can be transient. Residual solvent may inflate elongation. Physical associations may rearrange during storage. Crystals may anneal. Rubber domains may oxidise or debond. Post-cure can continue after the nominal process, and humidity can alter hydrogen-bonded systems. Testing should therefore declare the interval after print and post-cure, temperature, humidity, solvent history and any mechanical preconditioning.

Persistence should be evaluated with the stressor relevant to the intended claim. A room-temperature tensile result does not establish retention after thermal ageing, chemical exposure, repeated impact or cyclic loading. Fatigue and time-dependent behaviour remain within ER-39, but ER-68 requires enough ageing evidence to show that the proposed mechanism is still present when the mechanical claim is released.

13. Failure modes and interpretation errors

Table 4. Common failure modes in VPP toughening studies

Observation or claim	Possible error	Required control
Higher elongation after adding modifier	Residual modifier or solvent acts as plasticiser	Extraction, mass balance, conversion and conditioned retest
Rubber added, therefore rubber toughening	Rubber is dissolved, aggregated or poorly bonded	Morphology and interface evidence
Two components, therefore double network	Co-reactive blend forms one network	Connectivity and phase-specific evidence
Rough fracture surface proves higher toughness	Surface roughness follows crack path but not critical energy	Matched mechanical result and crack preparation
Nanofiller increases one coupon value	Aggregation or attenuation creates feature-scale defects	Dispersion, optics, cure depth and geometry study
Thermoplastic-like tensile curve	Yielding is treated as proof of thermoplasticity	Network classification and reprocessing/rheology if claimed
Post-cure improves strength	Additional conversion is called a toughening mechanism	Before/after conversion, modulus, strain and fracture comparison
Aligned specimen gives high strength	Directional response released as isotropic property	Full build/test orientation matrix
High tensile toughness equals fracture toughness	Unnotched work is converted into KIC or GIC language	Apply ER-70 cracked-specimen and validity framework
Best formulation selected from many without full reporting	Unsuccessful or censored results removed	Preserve all formulations, failures and selection criteria

14. Scope boundaries within the Engineering Review series

ER-68 is restricted to the causal architectures used to increase energy absorption and ductility in final dry VPP thermosets.

- ER-13 addresses self-healing and interlayer repair. ER-68 includes reversible bonds only as deformation and dissipation mechanisms before failure.
- ER-20 addresses T_g, HDT and service-temperature qualification. ER-68 records thermal trade-offs but does not define temperature allowables.
- ER-31 addresses shrinkage, residual stress and warpage. ER-68 records these only when a toughening route changes the final material state.
- ER-36 addresses rheology, recoating and dispersion control. ER-68 requires those controls but focuses on the mechanical mechanism in the cured polymer.
- ER-39 addresses fatigue, creep and stress relaxation. ER-68 does not convert monotonic toughness into service lifetime.
- ER-60 addresses polymerisation-induced phase separation as a morphology-forming process. ER-68 uses phase morphology only where it acts as a toughening architecture.
- ER-61 addresses gelation, vitrification and mobility arrest. ER-68 treats them as process variables that can enable or suppress toughening.
- ER-63 addresses covalent adaptable networks and vitrimers. ER-68 does not infer exchange, reprocessability or recyclability from improved ductility.
- ER-64 addresses thiol-ene and thiol-yne photopolymerisation as reaction classes. ER-68 includes thiol chemistry only where it controls a demonstrated toughening architecture.
- ER-65 addresses cationic ring-opening photopolymerisation. ER-68 does not treat epoxy or hybrid chemistry as a toughness mechanism without structure-property evidence.
- ER-66 addresses high-molecular-weight polymer latexes and coalescence. Pre-existing latex particles are not classified here as in-situ rubber domains unless their final network role is demonstrated.
- ER-67 addresses hierarchical and double-network hydrogels in the hydrated state. Dry thermoset mechanisms are not transferred to soft hydrated networks.
- ER-70 addresses fracture-test validity, KIC, GIC, J-R behaviour and damage tolerance. ER-68 does not validate those quantities.

15. 3Dresyns implementation boundary

3Dresyns currently markets multiple photopolymers using labels such as ABS-like, PEEK-like, Clear & Tough and ENG2 Tough, together with conventional tensile, flexural, hardness, elongation and impact data [M1-M4]. Those labels and values describe intended performance classes under stated conditions; they do not identify a specific toughening mechanism.

No current standard 3Dresyns product is identified in this review as an independently validated core-shell-particle, hyperbranched-rubber, chain-transfer-toughened, semicrystalline-dynamic or light-oriented VPP platform. A mechanism statement would require formulation-specific structural evidence rather than inference from a product name or mechanical profile.

A future mechanism-qualified development programme would require, at minimum:

- a controlled baseline and matched modifier series;
- resin compatibility, stability, viscosity and optical qualification;
- conversion, gelation and post-cure state;
- direct topology, morphology or interaction evidence appropriate to the proposed route;
- full mechanical curves and fracture-relevant testing where a crack claim is made;
- orientation, feature-scale, conditioning and ageing controls;
- documented trade-offs in thermal, chemical and dimensional performance.

16. Design rules

- Name the mechanism, the structural level on which it acts and the evidence that proves it exists.
- Keep tensile toughness, impact resistance, fracture toughness and damage tolerance as separate claims.
- Use a matched formulation control; do not compare only with an unrelated commercial resin.
- Measure resin optics, flow and stability after adding the toughening component.
- Report green, washed and post-cured states separately where the network continues to develop.
- Use microscopy, spectroscopy, extraction, thermal analysis or diffraction according to the proposed mechanism.
- Preserve unsuccessful formulations and censored specimens in the evidence record.
- Release directional or temperature-dependent performance only within the tested coordinates.
- Treat thermoplastic-like yielding as a mechanical response, not proof of thermoplastic chemistry or recyclability.
- Apply ER-70 before using KIC, GIC, J-R or damage-tolerant language.

17. Research priorities

- in-situ mapping of phase formation during projected exposure and dark cure;
- quantitative links between domain size, interface strength and feature-scale failure;
- low-scattering core-shell and rubber architectures for high-resolution VPP;
- topology-controlled formulations that retain toughness after complete post-cure and ageing;
- mechanism-resolved tests that combine spectroscopy, thermal analysis, local mechanics and fractography;
- orientation-aware optimisation of liquid-crystal and fibrous reinforcement;
- open datasets containing failed formulations, resin stability and complete stress-strain curves;
- interlaboratory studies separating formulation effects from printer and post-processing effects.

18. Conclusions

Vat-photopolymerised thermosets can be toughened through several distinct architectures: redistribution of network strand length, incorporation of extensible backbones, reversible sacrificial interactions, crystallinity, particulate domains, controlled phase morphology, chain transfer, crack-path modifiers and directed molecular orientation. These routes do not support the same claim and do not impose the same processing risks.

The minimum defensible sequence is:

controlled chemistry -> qualified resin state -> defined cure history -> proven topology or morphology -> mechanism-consistent deformation -> bounded mechanical claim

A larger mechanical number establishes an outcome. A toughening-mechanism claim requires a causal chain and matched controls. Fracture toughness and damage tolerance require the additional cracked-specimen validity framework in ER-70.

Limitations

The evidence base spans different chemistries, printers, wavelengths, temperatures, post-cures, specimen geometries and mechanical methods. Values are not pooled and no mechanism ranking is proposed. Several sources use the word toughness for tensile work or another study-specific metric; this review retains the source meaning while separating it from fracture-mechanics terminology.

Commercial formulations are incompletely disclosed, and direct comparison can be confounded by conversion, residual solvent, geometry, orientation and ageing. The review does not establish design allowables, universal optimum concentrations or application-specific acceptance thresholds. Standards and live manufacturer pages were checked to the status available on 22 August 2026 and should be rechecked before release if publication is delayed.

Author contributions

Juan Segurola: conceptualisation, evidence selection, engineering framework, manuscript preparation and final author review.

Competing interests

The author is founder, Chief Executive Officer and Chief Technology Officer of 3Dresyns by Resyner Technologies S.L. Commercial products are discussed only within the explicitly labelled manufacturer implementation boundary.

Data availability

No new experimental dataset was generated. The review is based on the cited publications, standards records and publicly accessible manufacturer documentation.

Company information

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