

Covalent Adaptable Networks and Vitrimer Topology in Vat Photopolymerisation: Exchange Kinetics, Reprocessing and Dimensional Stability

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3Dresyns Engineering Review ER-63 · Version 1.1 · No proprietary formulation composition disclosed

Statement of Significance

Covalent adaptable networks must exchange rapidly enough for intended repair or reprocessing while remaining dimensionally and mechanically stable during service. This review separates associative and dissociative exchange, stress relaxation, creep, welding, reshaping, reprocessing and recycling, and proposes a qualification architecture based on exchange kinetics, service-to-activation separation, dimensional retention and property recovery.

Keywords: vat photopolymerisation; covalent adaptable network; vitrimer; dynamic covalent bond; stress relaxation; creep; topology exchange; reprocessing; transesterification; boronate ester; vinylogous urethane

Abstract

Vat photopolymerisation normally converts a low-viscosity reactive formulation into a permanently crosslinked thermoset whose network topology is effectively fixed after cure. Covalent adaptable networks introduce exchangeable covalent bonds that permit the cured topology to rearrange under a defined stimulus while retaining, or temporarily modifying, network connectivity. This creates routes to stress relaxation, welding, reshaping, repair, hot-press reprocessing, chemical transformation and, in selected systems, preparation of a second-generation printable resin. The engineering opportunity is accompanied by a fundamental conflict. Bond exchange must be sufficiently slow under storage, printing and service conditions to preserve dimensions and load-bearing performance, yet sufficiently rapid under an intended activation condition to enable useful topology rearrangement. The relevant property is therefore not simply the presence of a dynamic bond, but a temperature-time-stress window connecting exchange kinetics, segmental mobility, creep resistance and the geometry of the printed part. Published VPP systems include catalyst-free boronate-ester networks with room-temperature exchange, thermally activated thioester-anhydride systems, transesterification-based acrylate vitrimers, vinylogous-urethane methacrylic networks and bio-based vitrimer formulations. They demonstrate reconfiguration, interfacial welding, reduced mechanical anisotropy, hot-press reprocessing and second-generation resin preparation. The numerical outcomes remain chemistry-, formulation-, geometry- and protocol-specific. This review develops a process-resolved framework for qualifying VPP covalent adaptable networks. It distinguishes associative and dissociative exchange, separates stress relaxation from creep, defines the service-to-reprocessing window, and requires retained dimensions and properties to be reported together with exchange rate. It also separates repair, welding, reshaping, reprocessing, chemical recycling and reprinting, which are frequently conflated in circularity claims.

1. Introduction

Conventional radical VPP produces a crosslinked network whose shape and topology are established during photopolymerisation and post-cure. Heating may soften the network, but it does not normally permit permanent topology rearrangement without bond scission or degradation.

Covalent adaptable networks (CANs) contain reversible or exchangeable covalent linkages. Under an appropriate stimulus, these bonds permit the network to reorganise, relax stress or form new interfacial connections. A recent perspective identifies repair, reprocessing and reprinting as distinct routes toward closed-loop vat photopolymerisation [1].

photocurable liquid -> crosslinked printed network -> activated covalent exchange -> rearranged or reprocessed network

The central engineering question is not whether a dynamic group is present. It is:

Can the printed network remain dimensionally and mechanically stable throughout storage and service, while exchanging rapidly and reproducibly under a deliberately selected activation condition?

2. Definitions and network classes

Term	Operational meaning in ER-63	What it does not prove
Covalent adaptable network	Crosslinked network containing reversible or exchangeable covalent bonds that permit topology change under defined conditions.	Vitrimer behaviour, useful reprocessing or negligible service creep.
Associative exchange	A new bond is formed as the previous network bond is displaced; idealised connectivity is maintained during exchange.	Constant modulus or shape at every temperature.
Dissociative exchange	A bond cleaves before the replacement bond forms, temporarily reducing connectivity.	Complete depolymerisation or solubility.
Vitrimer	Associative CAN used here as a network that can rearrange through bond exchange while retaining overall network connectivity [1].	A universally sharp topology-freezing temperature.
Dynamic thermoset	Broad descriptive category including associative, dissociative or hybrid networks.	A specific exchange mechanism.

These definitions describe mechanisms, not commercial performance classes. A formulation can contain dynamic bonds and still exchange too slowly for practical reprocessing, too rapidly for service stability, or too heterogeneously for reproducible dimensional recovery.

3. Exchange chemistries demonstrated in light-based additive manufacturing

3.1 Thioester-anhydride exchange

Podgórski, Huang and Bowman developed an MSLA-compatible dynamic thiol-ene resin based on thermally reversible thioester-anhydride links. The reported formulation exceeded 90% thiol-ene conversion within 12 s

under the stated conditions. Exchange ranged from minutes to seconds at 80-140 °C, while little to no exchange was observed below 60 °C. Printed objects were reconfigurable above 80 °C. Depolymerisation at 120 °C was demonstrated by reacting the dynamic network with a fresh excess-monomer mixture; heating alone activated exchange, stress relaxation and reshaping but was not established as a standalone complete-depolymerisation route [2].

This study illustrates a useful separation between service and activation conditions, but its numerical thresholds are specific to the resin, catalyst, specimen and measurement protocol.

3.2 Boronate-ester exchange

Boronate esters can undergo rapid catalyst-free metathesis. Robinson and co-workers incorporated dynamic boronate-ester crosslinks into oxygen-tolerant thiol-ene printing resins and modulated network stability by adding static crosslinks. Their selected hybrid network combined a reported characteristic relaxation time of 7 s with residual stress of 18%, while supporting interfacial welding and post-print functionalisation [3].

The same fast exchange that enables room-temperature adaptation can create creep or loss of form. Static crosslinks, entanglements, glassy mobility restriction or another structural constraint may therefore be needed to preserve geometry.

3.3 Transesterification-based acrylate vitrimers

Rossegger and co-workers introduced a methacrylate-phosphate transesterification catalyst compatible with acrylate VPP. The catalyst was selected to improve solubility in photocurable resin, preserve storage stability and avoid a strong penalty to cure kinetics. The resulting networks were printed at high resolution and underwent thermally activated topology rearrangement [4].

Hydroxyl-ester exchange has also been combined with hydrogen-bonded sacrificial interactions to strengthen printed acrylate vitrimers while retaining thermally activated reprocessability [5]. These systems demonstrate that the permanent or quasi-permanent load-bearing network and the exchange pathway can be engineered separately but remain mechanically coupled.

3.4 Vinylogous-urethane networks

Ballester-Bayarri and co-workers reported methacrylic vinylogous-urethane CAN resins for VPP. Resin viscosity and optical response were adjusted for printing, and the cured material exhibited stress relaxation at elevated temperature, pressure-assisted reshaping and amine-mediated solubilisation. The solubilised material was methacrylate-functionalised and combined with fresh reactive components to prepare a second-generation printable resin. The authors noted that only a very low concentration of the original crosslinked material remained and that the recovered material was “not chemically similar to the initial one”; this supports a transformed-feedstock route rather than an ideal closed loop [6].

This distinction is important: reprintability after chemical transformation and addition of fresh reactive material is a different claim from direct recovery of the original resin.

4. Exchange rate is not a material constant

Stress relaxation is frequently interpreted using a characteristic time at which the relaxation modulus falls to a selected fraction, commonly 1/e, of its initial value. The measured time depends on temperature, strain amplitude, linearity of the experiment, specimen state and the chosen criterion.

$$G(t = \cdot) / G(0) = 1/e \text{ (declared operational criterion)}$$

An Arrhenius relation is often fitted over a limited temperature range:

$$\ln(\tau^*) = \ln(A) + Ea / (R T)$$

This fit should not be treated as universally valid across phase transitions, catalyst changes, moisture uptake, degradation or a shift in exchange mechanism. The activation energy obtained from stress relaxation is an apparent network parameter under the tested conditions, not automatically the elementary chemical activation energy.

5. Stress relaxation and creep are complementary

Stress relaxation measures the decrease in stress required to hold a fixed deformation. Creep measures deformation accumulated under a fixed load. A network can relax stress rapidly and still require sufficient elastic or static connectivity to resist unacceptable long-term deformation.

Test	Boundary condition	Primary question	Required report
Stress relaxation	Fixed strain	How rapidly can the network redistribute imposed stress?	Temperature, strain, $G(t)$, criterion for τ^* , linearity and specimen state.
Creep	Fixed stress	Does the part retain dimensions under sustained service load?	Stress, temperature, duration, compliance/strain and recovery.
Creep recovery	Load removed after creep	How much deformation is reversible and how much is permanent?	Loading and recovery times plus residual strain.
Thermal reshaping	Applied deformation during activation	Can topology exchange fix a new shape?	Pressure/strain, temperature, time, dimensions before and after.

The 2025 boronate-ester VPP study is instructive: dynamic specimens relaxed stress and showed reduced orientation dependence. Under the reported creep protocol at 65 °C and 0.025 MPa, the tested dynamic network showed minimal but measurable creep. Full isotropy was not achieved; the remaining orientation dependence was attributed to the retained static crosslink fraction limiting complete topological rearrangement [7].

6. The service-to-reprocessing window

A useful CAN requires two different kinetic regimes.

service: $\tau_{\text{exchange}} \gg \text{service time of interest}$

reprocessing: $\tau_{\text{exchange}} \ll \text{allowed processing time}$

The transition between these regimes is not a universal temperature. It depends on time, stress, geometry, thermal gradients and the property that must remain stable. A part can appear dimensionally stable during a short screening test while creeping during months of service.

The appropriate output is therefore a temperature-time-stress map rather than one topology-freezing number. Where a topology-freezing temperature is reported, the viscosity, relaxation-time or experimental criterion used to define it must be stated.

7. Catalyst, latency and photopolymerisation compatibility

A catalyst can accelerate exchange but may also alter the liquid resin and primary photocure. Relevant interactions include:

- solubility and storage stability in the uncured resin;
- absorption or quenching at the print wavelength;
- acid-base interaction with initiators, inhibitors, pigments or fillers;
- change in photopolymerisation rate or limiting conversion;
- migration, extraction or volatility after cure;
- catalyst deactivation or loss during repeated processing.

Rossegger et al. selected an organic phosphate specifically because conventional transesterification catalysts can be poorly soluble in photocurable acrylates and can compromise cure or pot life [4]. Podgórski et al. further demonstrated that catalyst deactivation could erase the dynamic response and shift the activation threshold [2].

Catalyst loading should therefore be qualified simultaneously against printability, exchange kinetics, service creep and extractability. Faster exchange is not unconditionally better.

8. Repair, welding, reshaping, reprocessing, recycling and reprinting

Claim	Minimum demonstrated operation	Evidence boundary
Repair	Damaged article regains a defined property after controlled treatment.	Report damage geometry and retained property; visual closure is insufficient.
Welding	Two interfaces develop covalent continuity through exchange.	Test interface strength/fracture and include non-dynamic control.
Reshaping	Article is fixed into a new geometry without fragmentation.	Report permanent dimensions and recovery after unloading/conditioning.
Reprocessing	Fragments or ground material are reconsolidated.	Report mass balance, pressure, temperature and retained properties over cycles.
Chemical recycling	Network is converted into defined reusable chemical feedstock.	Identify products, yield, purification and reuse.
Reprinting	Recovered material contributes to a new printable feedstock.	State fresh-resin fraction and whether chemistry matches the original material.

Voet emphasised that direct reprinting of VPP CANs commonly requires addition of fresh resin because the original (meth)acrylate network formation is irreversible [1]. The vinylogous-urethane work similarly produced a second-generation resin after chemical solubilisation and methacrylate functionalisation, not direct restoration of the initial liquid resin [6].

9. Dimensional stability and mechanical anisotropy

Dynamic exchange can relax residual stress and improve bonding across layer interfaces, but it cannot be assumed to remove every source of print anisotropy. Optical exposure gradients, layer geometry, incomplete conversion, static crosslinks and physical defects remain.

Bonacini and co-workers reported 5-8% shrinkage for the tested formulations, stress relaxation and creep recovery, and reduced mechanical anisotropy relative to a static reference. Tensile specimens were compared at 0° and 90° orientations. The reported reduction in anisotropy remained incomplete and was linked to the static crosslink fraction constraining full topological rearrangement [7].

A dimensional qualification must therefore measure the same object at defined stages:

as printed -> post-cured -> exchange-activated -> unloaded/conditioned -> aged

Improved isotropy should be supported by matched orientation testing and uncertainty, not by one surface-smoothing image or one tensile direction.

10. Bio-based vitrimer routes

Renewable feedstock and dynamic exchange address different sustainability variables. Bio-based content does not establish reprocessability, and reprocessability does not establish low environmental impact.

Greivule and co-workers reported acrylated epoxidized rapeseed-oil vitrimers with catalyst-free and Zn(acac)2-assisted transesterification. Catalyst-containing systems reached reported relaxation times as low as 10 min. Ground material was hot-pressed at 200 °C for 2 h under a 1-ton load. The AERO30 formulation recovered 98% of its pristine tensile strength after a first reprocessing cycle, whereas a different formulation, AERO20, retained about 50% after a second cycle. These values are formulation- and cycle-specific and must not be represented as one two-cycle trajectory for a single formulation [8].

Bergia and co-workers used methacrylated cellulose extracted from aloe-vera waste as a crosslinker in a DLP-printable vitrimer. The system underwent thermally activated rearrangement. In the reported repair test, a controlled hole was produced, the corresponding insert was reintroduced and the specimen was treated at 160 °C for 4 h; the repaired specimen recovered 95.4% of the elastic modulus of the pristine heat-treated baseline. Hot-press recycling was evaluated separately at 160 °C under a 5-ton load for 1 h [9].

These values are formulation-specific demonstrations. Circularity claims still require energy, solvent, catalyst, recovered-mass and repeated-cycle accounting.

11. Proposed qualification architecture

Domain	Minimum measurement	Decision enabled
Liquid resin	Viscosity, storage stability, catalyst/dynamic-component identity, optical response.	Can the formulation be printed reproducibly?
Primary cure	Conversion, gel content, working curve, dimensions and post-cure state.	Was a defined initial network produced?
Exchange kinetics	Stress relaxation at multiple temperatures with declared τ^* criterion.	How rapidly does topology rearrange?
Service stability	Creep and recovery across relevant time-temperature-stress conditions.	Will dimensions and load-bearing response persist?
Activation process	Actual specimen temperature, pressure/strain, dwell and gradients.	Can the exchange treatment be reproduced?

Domain	Minimum measurement	Decision enabled
Reprocessing	Mass balance, cycles, retained mechanics, dimensions and chemistry.	Does reuse preserve useful material performance?
Interface repair/welding	Matched fracture or mechanical test and failure location.	Did dynamic covalent continuity form?
Ageing	Humidity, solvent, oxidation and catalyst-retention controls.	Does exchange capability and service stability persist?

12. Proposed engineering descriptors

The following quantities are proposed as reporting aids and are not standardised performance indices.

12.1 Characteristic relaxation time

$$\tau^*(T) = \text{time at the declared } G(t)/G(0) \text{ criterion}$$

The criterion, temperature, strain and specimen state must accompany every value.

12.2 Reprocessing property retention

$$R_{P,n} = P_{\text{after cycle } n} / P_{\text{pristine}}$$

P must be one explicitly defined property measured using the same method and conditioning. Strength retention and elongation retention should not be collapsed into one value.

12.3 Dimensional retention after exchange activation

$$R_D = 1 - |D_{\text{conditioned}} - D_{\text{reference}}| / D_{\text{reference}}$$

The dimension, datum, conditioning period and registration method must be declared. The expression is a proposed bookkeeping descriptor, not a universal dimensional-accuracy metric.

12.4 Service/activation separation ratio

$$S_E = \tau^*(T_{\text{service}}) / \tau^*(T_{\text{activation}})$$

A large value indicates kinetic separation under the chosen test conditions. It does not replace creep testing or establish a universal acceptance limit.

13. Failure modes and interpretation errors

Observation	Possible failure	Required control
Fast stress relaxation	Unacceptable service creep or shape drift.	Long-duration creep at service conditions.
Successful hot pressing	Void-rich reconsolidation or lower toughness.	Microscopy, density and matched mechanics.
Closed crack after heating	Contact without restored load transfer.	Fracture or interface test.
Lower anisotropy	Post-cure conversion rather than bond exchange.	Static-network control with matched cure history.
Repeated print from recovered feedstock	Large fraction of fresh resin or changed chemistry.	Mass balance and feedstock identity.

Observation	Possible failure	Required control
Apparent Arrhenius linearity	Fit across a transition or mechanism change.	Inspect residuals and limit fitted range.
Dynamic additive present	Host network lacks exchangeable bonds.	Chemical mechanism and relaxation evidence.
Good initial reprocessing	Catalyst loss or degradation over cycles.	Repeat-cycle kinetics and chemical analysis.

14. Scope boundaries

ER-63 is restricted to covalent topology exchange and its qualification.

- ER-13 addresses whether damage or an interlayer interface recovers function. ER-63 addresses the covalent-exchange mechanism and service/reprocessing kinetics.
- ER-59 addresses creation of the initial final network through two programmed cure stages. A dual-cure material is not automatically a CAN.
- ER-62 addresses renewed chain growth from dormant RAFT, photoiniferter or nitroxide-derived sites. CAN exchange rearranges existing network topology rather than restarting chain propagation.
- ER-31 addresses shrinkage, residual stress and warpage. ER-63 asks whether later exchange can relax stress without sacrificing dimensional stability.
- ER-74 addresses programmed bond scission, depolymerisation, recovered-product identity and material-loop evidence. Associative exchange and reshaping remain under ER-63 unless actual lower-molecular-weight recovery is demonstrated.

15. 3Dresyns implementation boundary

3Dresyns currently presents 3Dresyn Vitrimer 3R-D70 as a complete printable vitrimer resin and 3D-ADD AA3 as an additive with latent vitrimeric catalytic functionality and support for thermally activated dynamic network exchange [M1-M2]. Circular RePrint Bio DP80/DP150 and the corresponding DP80 and DP150 additives are separately positioned as made-to-order or custom-developed depolymerisable and reprint systems [M3-M5]. Their bond-scission and recovery claims are adjacent implementation context governed scientifically by ER-74 rather than evidence of CAN exchange under ER-63.

These are first-party manufacturer descriptions. They cannot by themselves establish:

- universal exchange kinetics or a useful stress-relaxation rate;
- negligible creep, dimensional drift or catalyst migration during service;
- repair efficiency, welding strength or repeated-cycle property retention;
- recovered-feedstock identity, mass balance or closed-loop recovery;
- compatibility with every resin, printer, geometry or application.

Every complete resin and host formulation requires direct photopolymerisation, stress-relaxation, creep, dimensional, repair/reprocessing and repeated-cycle validation. The AA3 page states that final performance depends on formulation composition, photoinitiator system, exposure conditions, printer type and post-processing [M1]. The 3R-D70 and Circular RePrint pages likewise require workflow- and application-specific validation [M2-M5].

16. Design rules

- Name the dynamic bond and exchange mechanism; do not use vitrimer as an unexplained product adjective.

- Measure stress relaxation and creep. One cannot substitute for the other.
- Define the service and activation conditions as time-temperature-stress states.
- Use a static-network control with matched primary cure and thermal history.
- Report pressure, geometry and actual specimen temperature during welding or reprocessing.
- Separate repair, reshaping, reprocessing, chemical recycling and reprinting claims.
- Quantify property retention over repeated cycles and include mass balance.
- Revalidate photokinetics and storage stability whenever catalyst or dynamic crosslinker loading changes.

17. Research priorities

The most valuable next steps are not simply faster exchange reactions. They are wider and better controlled service-to-activation windows. Priorities include:

- long-duration creep datasets at realistic service temperatures and loads;
- spatial mapping of exchange and thermal gradients in complex printed geometries;
- catalysts that are soluble, nonmigrating and minimally disruptive to photocure;
- repeated-cycle mass balances and property-retention trajectories;
- methods that separate dynamic-bond exchange from residual photopolymerisation during thermal treatment;
- recovered-feedstock identity and fresh-resin fraction reporting for reprinting claims;
- standardised or interlaboratory stress-relaxation and creep protocols for VPP CANs.

18. Conclusions

Covalent adaptable networks add a topology-exchange pathway to the cured photopolymer. That pathway can enable stress relaxation, welding, reshaping, reprocessing and selected chemical recovery routes, but it also creates risks of creep, dimensional drift, catalyst instability and overbroad circularity claims.

The defining engineering problem is kinetic separation:

stable during storage and service -> rapidly exchangeable during controlled activation -> stable again after conditioning

A defensible VPP CAN qualification therefore requires primary-cure state, exchange kinetics, service creep, actual activation conditions, dimensional retention, repeated-cycle properties and mass balance. The presence of a dynamic bond or catalyst is only the beginning of that evidence chain.

A vitrimeric VPP material is useful only when topology exchange is fast enough to process and slow enough to serve.

Limitations

The reviewed studies use different dynamic chemistries, catalyst systems, print wavelengths, specimen states, relaxation criteria and thermal histories. Their exchange times, temperatures, shrinkage, mechanical recovery and resolution values are not transferable material constants.

The literature also uses vitrimer, dynamic thermoset, CAN, recyclable and reprocessable with variable precision. ER-63 adopts explicit operational definitions but does not claim that one terminology convention is legally or universally standardised. No universal acceptance limit is proposed for τ^* , S_E , creep, dimensional retention or reprocessing efficiency.

Author contributions

Juan Seguro: conceptualisation, literature synthesis, engineering framework, writing and critical review.

Competing interests

The author is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L., which commercialises or develops 3Dresyn Vitrimer 3R-D70, 3D-ADD AA3 and Circular RePrint DP80/DP150 materials discussed in this review. Manufacturer-controlled descriptions are segregated from peer-reviewed evidence and are not treated as independent validation of universal exchange kinetics, repair efficiency, repeated-cycle retention, recovered-feedstock identity or closed-loop recovery.

Data availability

No new experimental dataset was generated for this review.

Company information

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