

Boronic-Ester Dynamic Photopolymer Networks: Humidity, Diol Exchange, Self-Healing and Service Stability

Dynamic B-O exchange, environmental sensitivity, recovery and dimensional qualification

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Abstract

Boronic-esters are dynamic covalent linkages formed by reversible condensation and exchange between boronic-acid-derived groups and diols. Their rapid metathesis, chemical tunability and sensitivity to water make them attractive for adaptive photopolymer networks, but those same features complicate service-state qualification. This review separates four engineering questions that are often conflated: whether the printed network can rearrange, whether damage can recover, whether dimensional anisotropy can be reduced, and whether the material remains stable under realistic humidity, solvent and thermal histories. Evidence across vat-photopolymerised boronic-ester systems and the broader dynamic B-O literature supports stress redistribution and shows that related boronic-ester networks can enable welding, self-healing or reprocessing under system-specific conditions, while water content, diol structure, boron speciation, static-crosslink fraction and activation temperature can shift the balance between useful rearrangement and creep or hydrolysis. A qualification framework is proposed that combines chemical-state measurements, moisture conditioning, stress relaxation, damage-recovery testing, dimensional metrology and repeated-cycle controls. The central conclusion is that boronic-esters should be treated as service-state variables rather than as a generic self-healing label: network exchange is valuable only when its rate, trigger and reversibility remain separated from the load-bearing and environmental requirements of the printed part. Keywords: boronic ester; dynamic covalent network; vat photopolymerisation; self-healing; stress relaxation; humidity; hydrolysis; anisotropy; reprocessing

1. Significance and scope

Dynamic boronic-esters are among the most accessible reversible covalent motifs for polymer networks because boronic acids and diols can form exchangeable B-O-C linkages without requiring permanent chain scission. In photopolymer additive manufacturing, this creates a route to retain the geometric precision of a permanently crosslinked object while introducing post-print network rearrangement. This review owns the qualification problem for boronic-ester dynamic photopolymer networks: humidity and water response, diol exchange, self-healing, service stability and the distinction between useful relaxation and unacceptable dimensional drift. It does not replace the broader self-healing framework of ER-13, nor reviews dedicated to other dynamic chemistries such as transesterification, disulfide exchange, imine chemistry or Diels-Alder networks.

1.1 Corpus boundary

ER-13 retains the umbrella scope for self-healing and interlayer repair across photopolymer additive manufacturing. ER-113 retains acid-triggered de-crosslinking, reprocessing and polymer recovery. ER-311, ER-312, ER-313 and ER-314 retain transesterification, non-cyclic disulfide, imine/hydrazone and Diels-Alder dynamic-network families, respectively. ER-315 is limited to boronic-ester network chemistry, humidity and water response, diol exchange, service-state stability and qualification of boronic-ester-enabled recovery.

2. Chemical basis of boronic-ester exchange

Boronic-esters form through reversible reactions between boronic-acid-derived species and diols. Exchange can proceed through associative or dissociative pathways depending on molecular structure, solvent, water activity and pH. The relevant engineering variable is therefore not simply whether a boronic-ester is present, but the exchange rate under the actual service condition. Reviews of dynamic B-O networks consistently identify water sensitivity as a defining feature. Water can shift equilibria toward hydrolysis, alter boron speciation and plasticise polar networks. Diol geometry and neighbouring substituents also affect stability and exchange kinetics. A formulation that relaxes rapidly in a dry thermal test may therefore behave differently after humid storage, immersion or repeated cleaning. The boronic-acid pKa, local polarity and the presence of neighbouring amines or other coordinating groups can shift the balance between neutral boronic ester and boronate-like states. These changes affect both exchange kinetics and susceptibility to hydrolysis. For engineering comparison, chemical identity should therefore include the boron-containing motif and diol family rather than the generic label boronic ester. [1,2]

Exchange-rate measurements should distinguish equilibrium redistribution from irreversible loss of functionality. If the network relaxes because B-O bonds hydrolyse without re-forming, the observed stress decay is not equivalent to vitrimer-like topology rearrangement. Spectroscopic or chemical-state evidence after the test is needed whenever hydrolysis is plausible. [1,2]

3. Implementation in vat photopolymerisation

Recent vat-photopolymerisation work has demonstrated hybrid networks that combine dynamic boronic-ester crosslinks with non-dynamic acrylate crosslinks. This architecture is useful because the permanent fraction can preserve shape while the exchangeable fraction redistributes

stress. It also makes interpretation harder: improved isotropy or recovery cannot be attributed to complete network reshuffling when a static network remains. Bonacini and co-workers reported a photocurable boronate-ester-containing network for vat printing in which post-print thermal treatment promoted exchange and reduced mechanical anisotropy. The result demonstrates that bond exchange can erase part of the process history, but it does not establish zero anisotropy or universal healing. The degree of improvement depends on network composition, thermal history and the fraction of constraints that are actually dynamic. For VPP, the dynamic motif must coexist with optical and rheological requirements of the uncured resin. Strongly absorbing additives, phase separation or moisture-driven aggregation can change cure depth and lateral feature growth before any post-print exchange is considered. Printability and adaptability are therefore coupled but distinct qualification requirements. The static-crosslink fraction is particularly important in hybrid networks. Increasing permanent connectivity can suppress creep and preserve shape, yet it also reduces the fraction of network constraints that can relax. A useful formulation window is therefore expected to be application-specific rather than monotonic with dynamic-bond content. [3-5]

4. Humidity, water and chemical environment

Humidity must be treated as a first-class state variable. At minimum, qualification should distinguish dry-as-prepared, laboratory ambient, controlled high-humidity and immersion states. Because water participates directly in boronic-acid/boronic-ester equilibria, conditioning history can change both chemistry and mechanics rather than acting only as an external plasticiser. A defensible study therefore records mass uptake, dimensional change, modulus or strength after conditioning, recovery after redrying and the corresponding chemical-state evidence. pH-sensitive applications require additional caution because boronate formation and exchange can be strongly altered by ionisation state. Apparent recovery after wetting is not sufficient evidence of durable self-healing if the network has simultaneously softened or partially hydrolysed. Conditioning should also include realistic solvent exposure when the printed part is cleaned, sterilised or used in contact with aqueous media. Solvent uptake can accelerate segmental mobility and exchange, creating an apparent healing benefit that disappears after drying. Conversely, drying can lock in stresses or dimensions that differ from the as-printed state. For long-term applications, equilibrium conditioning alone is insufficient. Repeated humidity cycling can generate hysteresis in mass, dimensions and mechanical response. Cycling data are therefore more informative than a single dry-versus-wet comparison when service includes daily or seasonal environmental variation. [1,2]

5. Self-healing, welding and reprocessing are different tests

Self-healing should be defined against a specific damage mode and recovered property. Surface closure, recovery of tensile strength, fracture resistance, fatigue life and leak tightness are different observables. Interfacial welding between two prepared surfaces is likewise not equivalent to autonomous crack repair inside a bulk part. Reprocessing is a more demanding claim because the network must undergo sufficiently large-scale topology change to reshape or remould while retaining useful properties afterward. Boronic-ester exchange can enable this in suitable systems, but the activation conditions may be incompatible with a given service envelope. The appropriate question is therefore whether the healing or reprocessing window is sufficiently separated from normal use. A recovery ratio should always name the property in the numerator and denominator. Tensile-strength recovery, elongation recovery, fracture-energy recovery and dimensional recovery are not interchangeable. The location of failure after healing is also informative: failure away from the healed interface supports stronger evidence of interfacial restoration than failure repeatedly at the repaired plane. [1,2,4,5]

Autonomous healing and stimulus-assisted healing should likewise be reported separately. If heat, pressure, solvent or water is required, those conditions are part of the repair process and may limit where the material can be used. [1,2,4,5]

6. Stress relaxation, creep and dimensional retention

The same exchange process that enables healing can cause time-dependent deformation under sustained load. Stress-relaxation experiments are therefore necessary but not sufficient. They should be paired with creep or dimensional-retention measurements under representative load, temperature and humidity. For printed parts, orientation adds another layer. If dynamic exchange reduces layerwise anisotropy during thermal conditioning, the same treatment may also alter dimensions, residual stress or surface finish. A qualification plan should measure both mechanical homogenisation and geometric change rather than treating one as proof of the other. Stress relaxation should be measured in the linear viscoelastic regime where possible, with strain-independence verified. Creep should extend long enough to reveal whether deformation approaches a plateau or continues to accumulate. Short tests can overstate service stability in networks whose exchange time is hours rather than minutes. Dimensional retention should include features that are sensitive to internal stress and free-surface motion, such as thin beams, unsupported walls and holes. Bulk coupons alone may miss local shape changes caused by exchange-assisted stress release. [3-5]

7. Minimum qualification matrix

A useful qualification matrix separates chemistry, mechanics, environment and geometry. Exchange kinetics should be measured at more than one temperature and humidity. Mechanical recovery should include an undamaged control exposed to the same conditioning. Dimensional measurements should include build-direction and in-plane axes. Repeated cycles are necessary because boronic species, catalysts, water content or static network damage can accumulate.

Table 1. Minimum qualification matrix for boronic-ester dynamic photopolymer networks.

Domain	Minimum measurement	Primary failure interpretation
Chemical state	Boron/diol state before and after conditioning; evidence of hydrolysis or exchange	Uncontrolled chemistry can mimic mechanical healing or cause irreversible network loss
Environment	Dry, ambient, high-humidity and immersion conditioning with mass and dimensional tracking	Water may alter equilibrium, swelling and mechanical state
Dynamics	Stress relaxation across temperature and humidity; activation energy only where model fit is justified	Relaxation rate defines the mobility window but does not establish service stability
Damage recovery	Defined cut/fracture/weld geometry with matched undamaged controls	Recovery must be attached to a property, not visual closure alone
Creep and shape	Sustained-load deformation and post-conditioning dimensional metrology	Useful exchange can become unacceptable service creep
Cycling	Multiple heal/reprocess/condition cycles with retained-property metrics	Dynamic groups or network architecture may degrade across cycles

8. Interpretation and decision rules

The most defensible engineering interpretation is to treat boronic-ester exchange as a controllable mobility mechanism. A material is not qualified merely because it contains dynamic B-O bonds. It is qualified only when the exchange window produces the intended repair or homogenisation while creep, hydrolysis, swelling and irreversible chemical change remain within application-specific limits. This distinction is especially important for additive manufacturing, where the printed object contains process history. Dynamic exchange can partly erase that history, but it can also erase intended dimensional information. The qualification target is therefore not maximum exchange rate. It is the minimum exchange required to obtain the desired functional recovery without loss of shape, stiffness, chemical resistance or long-term stability.

Table 2. Interpretation matrix for common boronic-ester network observations.

Observation	Plausible interpretation	Discriminating control
Fast stress relaxation in dry heat	Exchange is active, but service stability is not established	Pair with creep and dimensional retention at lower temperature and humid states
Strength recovers after wet conditioning	Healing, plasticisation or reversible hydrolysis may contribute	Dry-back control plus chemical-state and fracture-location analysis
Anisotropy decreases after annealing	Exchange may redistribute interlayer constraints	Track absolute modulus, dimensions and static-crosslink contribution
Repeated healing becomes faster	Residual solvent, water or accumulated network damage may increase mobility	Mass balance, dry conditioning and cycle-resolved spectroscopy
Reprocessed part retains shape but loses stiffness	Topology rearranged while permanent damage or dilution reduced network integrity	Compare crosslink density, swelling and thermal state before and after reprocessing

9. Limitations and evidence gaps

Direct vat-photopolymerisation evidence for boronic-ester networks remains narrower than the broader self-healing and hydrogel literature. Results from soft, solvent-rich or biologically oriented systems should not be transferred directly to dry structural photopolymers without confirming network state and loading conditions. Published studies also use different definitions of healing efficiency, anisotropy and reprocessability. Cross-study comparisons should therefore be based on reported test geometry, conditioning, temperature and recovery metric rather than headline percentages. Long-duration creep, outdoor humidity cycling and repeated cleaning remain underreported relative to short thermal-relaxation experiments. These gaps matter because service stability can fail on a much longer timescale than laboratory healing. [3-5]

10. Conclusions

Boronic-ester dynamic networks provide a credible route to adaptive vat-photopolymerised materials. Published evidence supports stress redistribution, welding, self-healing, reprocessing and reduction of mechanical anisotropy in selected systems. None of these outcomes is universal. Humidity, water activity, diol structure, boron speciation, static-crosslink fraction, temperature and load history jointly determine whether exchange is beneficial. Qualification should therefore couple chemical-state measurements with environmental conditioning, relaxation, creep, damage recovery and dimensional metrology. Boronic-esters are best treated as service-state variables whose kinetics must be engineered relative to the intended duty cycle. [1-5]

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated for this review. The analysis is based on the cited literature and the stated engineering scope.