

Non-Cyclic Disulfide-Exchange Photopolymer Networks: Radical and Metathesis Routes, Light and Thermal Activation, Repair and Recycling

Controlling S-S exchange without conflating reversible metathesis, photolysis and irreversible network degradation

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Abstract

Disulfide bonds provide a dynamic covalent motif that can exchange thermally, photochemically or through radical pathways. In photocured networks this creates routes to stress relaxation, welding, repair and recycling, but the same S-S chemistry can also cause chain scission or irreversible oxidation. This review separates exchange from degradation, examines wavelength dependence and network mobility, and defines qualification tests for reversible mechanical recovery rather than one-time softening.

Keywords: disulfide exchange; dynamic covalent network; photopolymerisation; self-healing; recycling; stress relaxation

1. Significance and scope

Non-cyclic disulfide-exchange photopolymer networks are significant because S-S bond exchange can provide repair or recycling through radical or metathesis routes without requiring complete network depolymerisation. Qualification must identify the operative activation route and separate productive exchange from oxidation, reduction or irreversible chain scission. Proprietary formulations and machine-specific tuning rules are outside scope.

1.1 Corpus boundary

ER-312 owns non-cyclic disulfide exchange networks formed or processed as photocurable materials. ER-311 owns transesterification-vitrimer exchange and creep/reprocessing behaviour; ER-111 retains dithiolane/lipoate ring-opening networks; ER-313 owns imine/hydrazone exchange; ER-315 owns boronic-esters.

2. Mechanistic basis

Disulfide exchange can proceed through radical homolysis/recombination or other metathesis pathways depending on substituents and activation. Light used for curing can itself cleave selected disulfides, so cure wavelength may determine whether the final network retains dynamic S-S bonds [1].

3. State variables and process control

Exchange requires both reactive bonds and segmental mobility. A high disulfide concentration in a rigid, highly crosslinked network may relax more slowly than a lower concentration in a mobile network. Temperature, wavelength, oxygen and crosslink density should therefore be recorded together. [1,2]

4. Principal failure modes

Uncontrolled photolysis can convert intended disulfides into less dynamic monosulfidic structures or radicals that trigger side reactions. Oxidation state drift and chain scission can mimic stress relaxation while reducing strength. Repeated healing cycles are needed to distinguish reversible exchange from consumptive chemistry. [2]

5. Measurement architecture

Raman or another sulfur-sensitive method, DMA/stress relaxation, tensile recovery after controlled damage and cycling under light or heat are useful. Wavelength-dependent controls should confirm whether the cure step preserves or destroys the intended S-S population [1].

6. Evidence hierarchy and transfer

Wavelength-dependent thiol-ene networks show that curing colour can program later disulfide dynamics. Broader 3D-printed dynamic-covalent literature documents repair and reprocessing concepts, while reprogrammable printed networks demonstrate the importance of separating exchange pathway from macroscopic recovery [1-3].

7. Qualification architecture

A disulfide-network qualification package should retain disulfide identity, activation mode, redox environment, exchange kinetics, mechanical recovery and chemical state before and after repair or recycling. Light and thermal activation should be challenged separately, with controls that suppress radical or metathesis pathways as appropriate. Transfer is justified only when the same exchange mechanism and damage-recovery relation are demonstrated in the new geometry.

8. Interpretation and decision logic

Decision logic should distinguish reversible disulfide exchange from irreversible scission or side chemistry. Repair or recycling claims require a repeatable chemical-state signature together with recovery of mechanical performance over multiple activation cycles.

Table 1. Qualification matrix for non-cyclic disulfide-exchange photopolymer networks.

State variable	Minimum evidence	Qualification purpose
S-S bond state	Raman/spectroscopy	Confirms dynamic motif survives cure
Mobility	DMA and Tg	Bounds exchange accessibility
Relaxation	Stress relaxation versus stimulus	Measures exchange
Healing	Strength recovery cycles	Tests repair

9. Diagnostic interpretation matrix

The diagnostic matrix should distinguish radical exchange, non-radical metathesis, irreversible cleavage, oxidation-state drift and apparent healing caused by viscous flow. Chemical-state evidence is needed alongside mechanical recovery to assign the repair pathway.

Table 2. Diagnostic interpretation matrix for non-cyclic disulfide exchange.

Observed deviation	Competing mechanism	Discriminating check
No healing	Network too rigid	DMA/mobility comparison
Permanent softening	Scission not exchange	Bond-state analysis
Wavelength effect	Photolysis during cure	365/450 nm control
Cycle decay	Consumptive side reaction	Repeated chemistry/mechanics

Repair and recycling claims should be separated. Repair asks whether a damaged interface regains mechanical continuity while the bulk network remains substantially intact; recycling asks whether the material can be reshaped or reprocessed with controlled retention of chemistry and properties. Repeated cycling should therefore record strength recovery, dimensional retention, bond-state evidence and any drift in glass transition or modulus. Non-cyclic disulfides are treated here separately from dithiolane/lipoate ring-opening systems so that the exchange mechanism and its evidence remain attributable [1-3].

10.1 Repair, recycling and service retention

Disulfide networks can respond through radical, metathesis and photochemical pathways whose relative importance depends on bond environment, mobility, wavelength and temperature. A repair experiment alone cannot identify which pathway operated. Wavelength-dependent controls, dark thermal controls and bond-state spectroscopy are needed to distinguish direct photolysis from thermally accelerated exchange and from nonspecific softening. This distinction matters because a stimulus that enables rapid repair may also consume network functionality or change crosslink density during repeated exposure [1-3].

9. Stimulus selectivity and exchange pathway

10. Limitations and evidence gaps

Disulfide chemistry varies with substitution and network environment. Results from elastomers or solution polymers do not directly define kinetics in glassy printed thermosets. The review therefore emphasises measured bond state and mobility rather than nominal disulfide content.

11. Conclusions

A disulfide photopolymer is repairable only when the intended S-S population survives cure, exchange proceeds under bounded conditions and mechanical function recovers reproducibly. Stress relaxation without chemical-state evidence is not enough to establish reversible network repair.

References

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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.