

Hydrogen-Bonded and Multiple-Supramolecular Photopolymer Networks: Association Strength, Rate Dependence and Fatigue Recovery

Reversible non-covalent association, viscoelastic timescales, toughness and environmental qualification

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Abstract

Hydrogen-bonded and other supramolecular photopolymer networks use reversible non-covalent association to dissipate energy, recover interfaces and create stimuli-responsive printed materials. Unlike dynamic covalent networks, the load-bearing state can change without bond-breaking chemistry, so association strength, lifetime, density and environmental sensitivity become primary state variables. This review examines single and multiple hydrogen-bond motifs, deep-eutectic and ionogel-like photocurable systems, dual covalent/supramolecular networks and other reversible associations relevant to vat photopolymerisation. Published DLP-compatible systems demonstrate improved toughness, self-healing, assembly welding, reprocessability and stimuli response, while also showing strong sensitivity to humidity, solvent, temperature, pH and strain rate. The main qualification challenge is therefore rate dependence: a network may appear strong in a rapid tensile test yet creep under sustained load, or may heal in a solvent environment while losing dimensional stability. A framework is proposed that separates association kinetics from permanent crosslink density and couples mechanical testing across strain rate and frequency with humidity conditioning, damage recovery, fatigue, creep and dimensional metrology. Keywords: hydrogen bonding; supramolecular network; vat photopolymerisation; DLP; self-healing; toughness; fatigue; rate dependence; deep eutectic solvent

1. Significance and scope

Supramolecular networks obtain part of their mechanical integrity from reversible associations rather than permanent covalent crosslinks alone. Hydrogen bonds are especially attractive because their strength and density can be tuned through donor and acceptor chemistry, and multiple interactions can act cooperatively. This review owns hydrogen-bonded and multiple-supramolecular photopolymer networks: association strength, rate dependence and fatigue recovery. It includes dual networks where a permanent covalent scaffold stabilises a reversible supramolecular phase. It does not treat every polar photocurable resin as supramolecular; reversible association must contribute measurably to function.

1.1 Corpus boundary

ER-13 retains the umbrella scope for self-healing and interlayer repair. ER-318 is limited to hydrogen-bonded and multiple supramolecular photopolymer networks, including association strength, rate dependence, environmental sensitivity and fatigue or recovery. Evidence transferred from non-vat processes is used only for mechanism context and is not treated as direct VPP performance evidence.

2. Association strength, lifetime and cooperativity

A hydrogen bond is not a fixed crosslink. Its lifetime depends on temperature, solvent, local polarity, mechanical load and the identity of donor and acceptor groups. Multiple hydrogen bonds can increase effective association strength through cooperativity, but they can also slow molecular rearrangement and reduce healing rate. The useful engineering descriptors are therefore not simply bond energy and concentration. Association lifetime, cluster size, connectivity, segmental mobility and the distribution of permanent versus reversible constraints govern the macroscopic response. When several supramolecular motifs coexist, assigning a mechanical effect to one interaction requires controls. Ionic association, microphase separation, crystallisation and hydrogen bonding can all contribute to toughness or self-recovery in the same material. [3-6]

3. Vat-photopolymerised supramolecular systems

Recent vat-photopolymerisation studies demonstrate several implementation routes. Multiple hydrogen bonds in poly(urethane-urea) elastomers can improve energy dissipation and interlayer cohesion while a covalent network preserves overall stability. Deep-eutectic and ionogel-like resins use dense hydrogen-bonding environments to combine printability with self-healing or recovery. Polymerisable deep eutectic solvent systems have also been used for DLP printing, assembly welding and reprinting. In these materials, reversible physical interactions can facilitate reassembly, but their behaviour is strongly linked to solvent content and composition. Supramolecular PVA-methacrylate/acrylic-acid systems illustrate another design route in which reversible interactions modify transport and pH response after DLP printing. Such application-specific functions should be separated from generic claims of self-healing or high toughness. [1-5]

4. Rate dependence and viscoelasticity

Because supramolecular bonds continuously dissociate and reform, measured modulus, strength and toughness depend strongly on loading rate and temperature. A network can look stiff when the test is faster than bond exchange and soft when the test is slow enough for associations to rearrange. Qualification should therefore include more than one strain rate or frequency. Dynamic mechanical analysis, stress relaxation and creep provide complementary information. Time-temperature superposition may be useful only when morphology and association mechanism remain unchanged across the tested range. Reporting a single tensile curve is insufficient for a supramolecular network intended for long-term load bearing. The relevant service question is whether the association lifetime is long enough to support the load yet short enough to permit recovery after damage. [3-5]

5. Humidity, solvent, pH and thermal environment

Hydrogen bonds compete directly with water and other protic or polar solvents. Humidity can weaken associations, increase segmental mobility and change ionic conductivity or phase morphology. In some deep-eutectic systems, environmental water can also alter the solvent network itself. Environmental conditioning should therefore be treated as a mechanistic test. Mass uptake, dimensions, modulus, relaxation and recovery should be measured together. A healing event observed only in a swelling solvent should be reported as solvent-assisted healing, not as autonomous recovery. pH-responsive systems require additional controls because ionisation changes both hydrogen bonding and electrostatic interactions. The printed object's response can therefore reflect multiple coupled mechanisms rather than one reversible bond family. [1-5]

6. Toughness, fatigue and self-recovery

Reversible associations can dissipate crack-tip energy by sacrificial bond breaking, which improves toughness when rebonding occurs behind the process zone. This mechanism can also reduce hysteresis recovery if reassociation is slow relative to the loading cycle. Fatigue qualification should include cyclic loading at more than one amplitude and recovery interval. Immediate recovery, delayed recovery and recovery after thermal or solvent treatment are distinct behaviours. Residual strain and stiffness should be tracked alongside peak strength. For printed parts, interlayer interfaces deserve separate attention. Supramolecular interactions may enhance interfacial interlocking or welding, but bulk self-recovery does not automatically establish recovery of layer adhesion after repeated fatigue. [1,3-6]

7. Minimum qualification matrix

A defensible qualification set separates permanent crosslink contribution from reversible association and explicitly maps rate, environment and damage history.

Table 1. Minimum qualification matrix for hydrogen-bonded and supramolecular photopolymer networks.

Domain	Minimum measurement	Primary failure interpretation
Association	Evidence for reversible donor-acceptor or supramolecular interactions and their environmental dependence	Polarity alone does not prove a load-bearing supramolecular network
Rate dependence	Tensile or compression response at multiple rates plus DMA or relaxation	Single-rate strength can hide service creep or rapid softening
Environment	Humidity, solvent and pH conditioning with mass and dimensional tracking	Water or solvent can change both association and morphology
Recovery	Defined damage and recovery interval with matched controls	Visual closure is not equivalent to mechanical recovery
Fatigue	Cyclic loading with hysteresis, residual strain and recovery tracking	Reversible bonds may dissipate energy but fail to re-form fast enough
Geometry	Feature-level dimensions after conditioning and recovery	Swelling or relaxation can erase intended printed tolerances

8. Interpretation matrix

The same macroscopic observation can arise from different supramolecular mechanisms. Matched controls, conditioning history and time-dependent testing are needed to distinguish useful reversible association from plasticisation or phase rearrangement.

Table 2. Interpretation matrix for common supramolecular-network observations.

Observation	Plausible interpretation	Discriminating control
High toughness at rapid loading	Sacrificial bonds may dissipate energy before they can reform	Repeat at slower rates and measure hysteresis recovery
Self-healing improves in solvent	Solvent-assisted mobility or swelling may dominate	Dry healing control and post-dry mechanical retest
Humidity lowers modulus but increases recovery	Water may weaken associations while accelerating rebonding	Mass uptake and DMA across humidity
Interlayer strength improves after annealing	Association or chain diffusion may weld interfaces	Non-associating control and fracture-location mapping
Fatigue life improves after rest periods	Time-dependent reassociation is active	Vary rest time systematically and track stiffness recovery

9. Limitations and evidence gaps

Supramolecular materials are especially sensitive to test protocol, yet many studies report only one loading rate and one conditioning state. This limits transfer of headline toughness or healing values to long-duration engineering service. Deep-eutectic and ionogel-like systems can contain substantial mobile liquid fractions. Their recovery mechanisms may include solvent redistribution and phase reorganisation in addition to hydrogen-bond reassociation, so controls are required before assigning causality. Fatigue data for printed supramolecular networks remain less mature than monotonic tensile data. Recovery between cycles, environmental ageing and interlayer-specific fracture therefore remain priority evidence gaps. [1-6]

10. Conclusions

Hydrogen-bonded and multiple-supramolecular networks expand the design space of vat-photopolymerised materials by adding reversible energy dissipation, recovery, welding and stimuli response. Published systems show that these functions can coexist with high-resolution printing and permanent covalent stabilisation. Their qualification differs fundamentally from that of purely permanent thermosets. Association lifetime, strain rate, humidity, solvent content, temperature and fatigue history are part of the material state. The correct target is not maximum hydrogen-bond density but a balance between service stiffness, damage tolerance and recovery on the relevant timescale. Claims of toughness or self-healing should therefore be attached to explicit loading rates, conditioning states and recovery protocols. [1-6]

References

1. Liu M, Zhang G, Hu Y, Bo C, Dai Y, Hu L, Zhu G, Zhou Y. High-biobased polymerizable deep eutectic solvents for sustainable DLP printing: assembly welding and reprintable printing. *Green Chemistry*. 2024;26:10441-10455. doi:10.1039/D3GC02662K.
2. Satpute H, Suryavanshi P, Banerjee S. Supramolecular Chemistry Empowers Vat Photopolymerization Mediated DLP-3D Printing of PVA-MA-AA Resin for pH-Responsive Drug Delivery Applications. *Chemistry of Materials*. 2025;37(6):2155-2165. doi:10.1021/acs.chemmater.4c02802.
3. Li Y, Kankala RK, Wu L, Chen AZ, Wang SB. 3D-Printed Photocurable Resin with Synergistic Hydrogen Bonding Based on Deep Eutectic Solvent. *ACS Applied Polymer Materials*. 2023;5(1):991-1001. doi:10.1021/acsapm.2c01916.
4. Yang X, Bai C, Zhu B, Wu J, Wang M, Wang Y, Wu T, Liu D, Jiang P, Wang X. Multiple H-bonds induced mechanically robust vat photopolymerization 3D printing poly(urethane-urea) elastomers. *Materials Horizons*. 2025;12:833-844. doi:10.1039/D4MH01191K.
5. Huang CW, Wen SC, Hsiao CH, Zhang CZ, Lin KC, Yu SS. Digital Light Processing of Soft Robotic Gripper with High Toughness and Self-Healing Capability Achieved by Deep Eutectic Solvents. *Advanced Functional Materials*. 2024;34:2314101. doi:10.1002/adfm.202314101.
6. Roppolo I, Caprioli M, Pirri CF, Magdassi S. 3D Printing of Self-Healing Materials. *Advanced Materials*. 2024;36(9):2305537. doi:10.1002/adma.202305537.

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.