

# Non-Covalent Glassy Networks for Photocurable Materials: Physical Crosslinks, Relaxation, Reprocessability and Service Limits

*Using slow supramolecular bond dynamics to obtain glass-like response without confusing recoverability with permanent stability*

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## Abstract

Non-covalent networks are often associated with soft, rapidly relaxing materials, yet sufficiently strong and slow supramolecular associations can produce glass-like response with high modulus or compressive strength while retaining recoverability. Published supramolecular polymer glasses and slow-dissociative crosslink networks demonstrate that bond lifetime can shift the balance between stiffness, damage recovery and flow. [1-3] Translating these principles into photocurable materials creates a hybrid design problem: covalent photopolymerisation may fix geometry while non-covalent interactions control secondary stiffness, relaxation or reprocessability. ER-420 separates physical crosslink density from covalent conversion, defines time-temperature dependent qualification, and warns against equating short-time modulus with service stability. A material may behave as a glass on a tensile-test timescale yet creep, heal or flow over longer periods. Qualification therefore requires relaxation spectra, creep, recovery, thermal history and repeated reprocessing evidence at the intended use timescale.

**Keywords:** supramolecular glass; non-covalent network; physical crosslink; hydrogen bonding; relaxation; self-recovery; reprocessability; photocurable materials

## 1. Scope: glass-like does not mean permanently crosslinked

Supramolecular glassy polymers can exhibit high stiffness because their non-covalent bonds dissociate slowly relative to the test timescale. Huang et al. demonstrated glass-like supramolecular networks with slow, tunable dissociation kinetics and high compressive strength combined with rapid recovery. [1] The important engineering variable is therefore bond lifetime relative to loading time, not a binary classification of solid versus dynamic material.

## 2. Physical crosslinks and bond lifetime

Hydrogen bonds, host-guest complexes, ionic clusters and metal-ligand interactions can act as physical crosslinks. Their equilibrium strength and dissociation kinetics both matter. Two networks with similar instantaneous modulus can have different stress relaxation if one bond population exchanges faster. Characterisation should therefore include time-dependent tests and, when possible, temperature dependence from which relaxation mechanisms can be compared.

## 3. Supramolecular polymer glasses

Optically responsive supramolecular polymer glasses based on strong UPy association demonstrate that non-covalent networks can combine stiffness with stimuli-responsive healing or debonding. [2] Such systems illustrate a useful principle for photocurable materials: a rigid state can arise from reversible interactions, but optical or thermal stimulation may deliberately lower viscosity. This is function only if the trigger window is separated from storage and service conditions.

**Table 1. Non-covalent network functions and risks**

| Function                  | Desired mechanism             | Principal risk                                |
|---------------------------|-------------------------------|-----------------------------------------------|
| High short-time stiffness | Slow bond dissociation        | Long-time creep                               |
| Self-recovery             | Reversible reassociation      | Incomplete recovery under service constraints |
| Healing                   | Interfacial bond reformation  | Weak interface or environmental sensitivity   |
| Reprocessing              | Sufficient bond exchange/flow | Loss of geometry or cumulative degradation    |

## 4. Coupling to photocurable covalent networks

A photocurable material can use covalent crosslinks to establish permanent shape while non-covalent associations tune modulus, toughness or self-recovery. Alternatively, the network may rely primarily on physical crosslinks after a photochemical synthesis step. These architectures must be distinguished because reprocessability and creep differ. Gel fraction and solvent resistance can help identify the covalent contribution.

## 5. Time-temperature equivalence and service window

A physical network that is glassy at room temperature can soften as temperature accelerates bond exchange. Short mechanical tests therefore provide only one point on a relaxation map. Creep, stress relaxation and dynamic mechanical analysis should be used to define the service window. Time-temperature shifting can be informative only if the same mechanism persists over the range.

## 6. Recovery, healing and reprocessing

Recovery after compression or cutting is not equivalent to reprocessing into a new shape. Healing concerns restoration across damage interfaces, while reprocessing requires macroscopic flow or exchange sufficient to erase prior geometry. Each function should be tested separately with retained mechanical properties and dimensional fidelity after the operation. Repeated cycles are needed to expose cumulative damage or loss of associating groups.

## 7. Moisture and competitive interactions

Hydrogen-bonded networks can be sensitive to water or polar solvents that compete for association sites. Ionic or host-guest systems have their own environmental sensitivities. Humidity can therefore reduce modulus or change relaxation rate without changing covalent conversion. Environmental conditioning belongs in the qualification state definition.

## 8. Optical and dimensional stability

For photocurable optical or precision parts, local rearrangement of physical crosslinks can create stress relaxation and dimensional drift. A material can retain mass and apparent shape while its residual stress, birefringence or microgeometry changes. Dimensional metrology should therefore accompany relaxation measurements when tolerances are tight.

**Table 2. Minimum time-dependent qualification**

| Test                           | What it resolves                 | Why needed                                      |
|--------------------------------|----------------------------------|-------------------------------------------------|
| Stress relaxation              | Bond/network relaxation times    | Instantaneous modulus can hide rapid relaxation |
| Creep                          | Dimensional stability under load | Service failure can occur without fracture      |
| DMA versus temperature         | Transition and kinetic windows   | Defines trigger/service separation              |
| Repeated recovery/reprocessing | Cycle durability                 | One successful cycle is insufficient            |

## 9. Failure modes

Relevant failures include excessive creep, stress relaxation under preload, thermal softening, humidity-induced loss of association, incomplete recovery and irreversible damage after repeated reprocessing. The diagnostic experiment should vary time or temperature to distinguish bond-exchange kinetics from covalent degradation.

## 10. Qualification decision boundary

A non-covalent glassy network is qualified only for a declared time-temperature-humidity window. High instantaneous modulus cannot compensate for unacceptable creep, and successful single-cycle healing cannot establish durable reprocessability. If the application depends on reversibility, the trigger must remain separated from service conditions with a demonstrated safety margin.

## 11. Evidence gaps

The strongest supramolecular-glass literature is not specific to VPP. Direct evidence integrating photopolymer cure, printed geometry and long-duration relaxation remains limited. Another gap is consistent reporting of bond lifetime or relaxation spectrum alongside claimed self-healing and reprocessing.

## 12. Research priorities

Photocurable studies should combine conversion, gel fraction, DMA, creep and recovery across temperature and humidity. Reprocessing should be evaluated over multiple cycles with dimensional and mechanical retention. Architectures that separate permanent covalent shape-fixing from reversible secondary interactions are particularly suitable for mechanistic comparison.

## 13. Measurement architecture for supramolecular glasses

A short-time modulus should be treated as one point on a relaxation spectrum. A stronger evidence package combines DMA over frequency and temperature, stress relaxation, creep and recovery after unloading. Thermal analysis identifies transitions that may move the system from glass-like to rapidly exchanging behaviour. When a covalent photopolymer scaffold is present, gel fraction and solvent resistance help separate the permanent network from the reversible secondary associations.

## 14. Fatigue and repeated recovery

Repeated association and dissociation can dissipate energy, but cyclic loading may also create irreversible chain scission or loss of supramolecular motifs. Recovery should therefore be measured after controlled rest times across multiple cycles. A material that returns to its original shape but loses stiffness is not fully recovered. Likewise, apparent healing caused by viscoelastic closure should be distinguished from restoration of interfacial strength.

## 15. Discriminating experiment set

A useful design compares the same covalent backbone with and without the supramolecular motif, then tests both across temperature and loading time. Creep, relaxation, fracture or compression recovery and dimensional drift are measured. A second branch introduces humidity or a competitive solvent to challenge the non-covalent interaction specifically. The resulting difference between controls isolates the contribution and vulnerability of the physical crosslinks.

## 16. Engineering conclusion

Non-covalent glassy networks show that reversible interactions can generate unexpectedly stiff materials, but their engineering identity is inseparable from timescale and environment. For photocurable systems, the most defensible architecture often combines a permanent shape-fixing network with a deliberately chosen reversible interaction. Qualification must show both the useful dynamic function and the absence of unacceptable creep or trigger activation during ordinary service.

## References

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## Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-420 contains no comparative product recommendation.

## Data availability

ER-420 is a literature-based engineering review; no new experimental dataset was generated.