

Hierarchical and Double-Network Hydrogels in Vat Photopolymerisation: Microgel Reinforcement, Interpenetration and Energy Dissipation

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Statement of Significance

Hydrogel toughness is not established by water content, crosslink density or elongation at break alone. Vat-printed double and hierarchical hydrogels use distinct network levels to fix geometry, redistribute load, dissipate energy and recover after deformation. This review separates homogeneous, double-network, microgel-reinforced, fibre-assisted and supramolecular architectures and defines hydration-, cycle- and fracture-aware reporting requirements for printed hydrogel mechanics.

Keywords: vat photopolymerisation; digital light processing; hydrogel; double network; hierarchical network; microgel reinforcement; interpenetrating polymer network; energy dissipation; toughness; swelling; hysteresis

Abstract

Hydrogels combine high water content with a polymer network, but the same hydrated state that enables transport and compliance commonly limits strength, crack resistance and dimensional stability. Vat photopolymerisation adds a further constraint: the material must form a geometrically stable network on the optical timescale of printing, whereas many toughening mechanisms rely on slow physical association, secondary crosslinking, microstructural rearrangement or post-print equilibration. Hierarchical and double-network strategies separate structural continuity from energy dissipation. Demonstrated VPP routes include covalent networks reinforced by hydrophobic association, metal-carboxyl coordination, thermoreversible polysaccharide helices, preformed microgels and post-print dynamic networks; fibre-assisted bulk UV photocuring provides an adjacent architecture boundary rather than direct VPP evidence. Some systems form both networks during exposure; others print a primary network and create the secondary network by cooling, immersion, coagulation, dark polymerisation or another controlled step. Primary studies show that tough hydrogel architectures can be shaped by DLP, projection stereolithography and LCD-VPP into lattices, optical elements and other complex geometries. Microgel-reinforced VPP has demonstrated up to four-fold increases in stress at failure and work of fracture at a 30% microgel volume fraction, while temperature-controlled projection stereolithography has produced highly stretchable and compression-resistant acrylamide/ κ -carrageenan double networks. These values remain formulation-specific and do not define universal hydrogel targets. This review develops a network-architecture and qualification framework for printed hydrogels. It separates double networks from semi-interpenetrating networks, particle-reinforced hydrogels, supramolecular single networks and self-healing systems; links sacrificial-bond dissipation to hysteresis, recovery and fatigue; and requires mechanical testing to be tied to hydration, swelling, cycle number and specimen geometry. The central conclusion is that printed hydrogel toughness is not a single material constant but the outcome of how multiple network levels share load, dissipate energy and recover in the hydrated state.

1. Introduction

A hydrogel is mechanically unusual because a large fraction of its volume is liquid while a sparse polymer structure carries load. Increasing covalent crosslink density can raise stiffness and improve shape retention, but commonly reduces extensibility, transport and swelling capacity. Reducing crosslink density improves compliance but can produce low green strength, crack sensitivity and dimensional drift.

Double-network and hierarchical architectures address this conflict by assigning different functions to different structural levels. A load-bearing network maintains continuity, while a second network, sacrificial association, microgel population or reinforcing fibre system dissipates energy, redistributes stress or limits swelling. The two contributions can be chemically distinct even when they are formed from one vat.

Vat photopolymerisation imposes three linked questions:

- Can the first network form rapidly enough to reproduce the projected geometry?

- Can the secondary toughening structure be created without destroying optical printability or dimensions?
- Do the final hydrated mechanics remain stable after swelling, cyclic loading, dehydration and rehydration?

The central engineering problem is to separate the network required for printing from the mechanisms required for hydrated damage tolerance, then prove that they remain coupled in the final object.

2. Network terminology

Table 1. Hydrogel architectures that should not be treated as synonyms

Architecture	Defining structure	Typical toughening route	Qualification consequence
Single covalent network	One continuous chemically crosslinked network.	Chain extensibility, network uniformity or architecture alone.	Do not call double network merely because two monomers are present.
Double network	Two interpenetrating networks with distinct mechanical roles; at least one is usually highly connected or sacrificial.	Sacrificial scission, physical association, chain entanglement or load redistribution.	Identify both networks and their formation sequence.
Semi-interpenetrating network	One crosslinked network containing a non-crosslinked linear or branched polymer.	Entanglement, friction, crystallisation or physical association.	Demonstrate which component is not permanently networked.
Microgel-reinforced network	Preformed crosslinked particles embedded in and connected by a continuous secondary network.	Particle deformation, interface friction, local damage and percolating-matrix reinforcement.	Report microgel fraction, distribution, interface and continuous-network formation.
Supramolecular hydrogel	Network continuity depends partly or predominantly on reversible noncovalent bonds.	Coordination, host-guest, ionic, hydrophobic or hydrogen-bond exchange.	May be tough without being a formal double network.
Fibre-reinforced hydrogel	A polymer network contains nanofibres or another connected reinforcing phase.	Load transfer, crack bridging, hydrogen bonding and swelling constraint.	A fibre phase is not automatically a second polymer network.

The literature is not completely consistent in its terminology. ER-67 therefore reports the architecture used by each source and avoids assigning a double-network label solely from a performance increase.

3. Why toughening and VPP are in tension

Many tough hydrogel mechanisms require a network to reorganise after deformation. VPP, in contrast, benefits from rapid gelation and immediate spatial confinement. A formulation that gels too slowly can blur, collapse or lose particle uniformity; a formulation that becomes rigid too quickly may suppress the rearrangement required for energy dissipation.

The competition can be written qualitatively as:

printing rate and geometric fixation versus network rearrangement, dissipation and recovery

The solution is often sequential or hierarchical. The primary network fixes geometry during exposure. The secondary network or reversible association is then created during the same exposure, in the dark after exposure, during cooling, or through an immersion or conditioning step.

4. Demonstrated VPP architectures and adjacent photocure boundaries

4.1 Covalent network plus hydrophobic association

Xiang and co-workers developed a DLP-printable formulation based mainly on acrylamide and stearyl methacrylate. The resulting hydrogel combined a covalent network with hydrophobic association and was reported by the authors as a double network with improved strength and toughness [1]. The dissipative level is a reversible physical association rather than a brittle sacrificial covalent network, consistent with the self-recovery reported by the authors. The architecture shows that reversible hydrophobic domains can be generated within a directly photocured system rather than added only after printing.

4.2 Covalent network plus metal-carboxyl coordination

Dong and co-workers printed acrylic-acid hydrogels containing Zr^{4+} under digital light. Carboxyl- Zr^{4+} coordination complexes formed as physical crosslinks and provided rapid toughening, antishwelling behaviour and high-fidelity printing [2]. Water incubation subsequently changed local chemistry and coordination, increasing stiffness and enabling shape fixation after manual deformation.

This route is better described as a physically crosslinked metal-coordination supramolecular network than automatically as a classical brittle-first-network double network. The reversible coordination state, ion content and incubation history belong in the material definition.

4.3 Photochemical primary network plus thermoreversible secondary network

Temperature-controlled projection stereolithography (TOPS) prints an acrylamide network above the sol-gel transition of κ -carrageenan and forms the secondary physical network during cooling. Kunwar and co-workers reported 37 μm lateral and 180 μm vertical resolution. For the investigated formulation, they reported ultimate tensile stress of approximately 200 kPa at 2400% strain as the headline optimised result, with averaged values in the results section nearer 175 ± 37 kPa, and compression stress of 15 MPa at 95% strain [3].

The key engineering point is not the numerical performance alone. Printing occurs in a state where the polysaccharide remains processable, while the final double network is completed by a controlled temperature transition. Temperature is therefore both a rheological and network-formation variable.

4.4 Microgel assembly created during DLP

Wang and co-workers used a ternary aqueous two-phase emulsion to create GelMA microgels and assemble them during DLP bioprinting. A methacrylated galactoglucomannan component stabilised the emulsion and covalently connected the converted microgels, while removal of the dextran-rich phase produced interconnected void space [4].

This is a bottom-up microgel-assembly route rather than a conventional homogeneous double network. The local microgel surfaces, connecting phase and removable continuous phase jointly determine the final hierarchy.

4.5 Preformed microgels plus a percolating continuous network

Crosby and co-workers formulated NorHA microgels swollen with acrylamide monomer and used DLP with combined light and dark polymerisation to create a secondary continuous polyacrylamide network through the microgel population. At 30% v/v microgels, the reported stress at failure and work of fracture increased by as much as four-fold and swelling decreased [5].

The work directly demonstrates the ER-67 hierarchy: a preformed crosslinked particle phase and a later percolating network share load. Uniformity through the build, particle settling, scattering and interface connectivity are therefore as important as bulk composition.

4.6 Fibre-assisted double networks

Roig-Sanchez and co-workers combined photocured poly(acrylic acid) with bacterial-cellulose nanofibres in a one-step UV process. A low nanofibre fraction increased stiffness and produced lower, non-pH-dependent swelling compared with the corresponding PAA hydrogel or with PAA containing cellulose nanocrystals [6].

ER-67 reads this as indicating that reinforcement depends on connectivity, aspect ratio, interface and hydrogen-bonding architecture rather than on cellulose content alone. This study is a bulk UV photocuring demonstration rather than a printed one; it is included as a fibre-reinforcement architecture boundary, and its process window is not transferred to VPP.

4.7 Dynamic post-print network for repair and reinforcement

Guida and co-workers reported an LCD-VPP GelMA-PVA system in which the photocrosslinked GelMA network provided printability and a post-print PVA-borate network introduced self-healing and reinforcement. Hydroxyapatite-containing formulations retained repair capability and reached swollen-state compression moduli above 60 kPa under the reported conditions [10].

The study sits on the boundary with ER-13. ER-67 uses it to illustrate sequential network formation and load sharing; the autonomous repair mechanism and healing qualification remain ER-13 territory.

4.8 Photochemical double network plus post-treatment for wet adhesion

Mu and Xing used green-LED photopolymerisation of acrylic acid and acrylamide in the presence of sodium alginate to form a double-network hydrogel, followed by tannic-acid treatment to enhance wet adhesion. The reported formulation reached approximately 862% tensile strain and 0.77 MPa tensile stress under its stated conditions [8].

This study is included as a chemistry and post-treatment boundary rather than as direct VPP evidence. It demonstrates that a secondary immersion step can change both the network state and the surface function, so adhesion measurements must be tied to the complete post-treatment history.

5. Microgel-reinforced and particle-based double networks

Microgels can be understood as pre-crosslinked network domains. When dispersed in a second precursor and connected by a continuous matrix, they create a particulate hierarchy with several potential dissipation mechanisms:

- microgel deformation and local damage;
- sliding or friction at particle-particle and particle-matrix contacts;
- crack deflection around domains;
- load transfer through the continuous secondary network;
- reversible bond rupture within or between microgels;
- swelling mismatch that prestresses or constrains the matrix.

The particle-based double-network concept predates its direct VPP implementation. Zhao and co-workers printed tough particle-based DN hydrogels by using highly crosslinked microgels as a rheology-controlling first network and curing a sparsely crosslinked continuous network after deposition [7]. Crosby et al. later translated the same general architecture to vat photopolymerisation [5].

The two routes should not be conflated. Extrusion requires a yield-stress ink; VPP requires optical penetration, low settling and sufficient projection-defined conversion. The network concept transfers, but the process qualification does not.

6. Energy-dissipation mechanisms

Toughness emerges when the material absorbs energy over a substantial volume around a crack or defect rather than concentrating deformation at one covalent bond population. In hierarchical hydrogels, dissipation can result from:

- irreversible scission of a brittle sacrificial network;
- reversible rupture and reformation of ionic, coordination or hydrophobic associations;
- uncoiling or disentanglement of physical polymer chains;
- microgel deformation, interface friction and particle rearrangement;
- fibre pull-out, crack bridging or hydrogen-bond rupture;
- solvent redistribution and poroelastic flow during loading.

A high area under one tensile curve does not identify which mechanism is active. Hysteresis, recovery after rest, cyclic softening, fracture tests, time dependence and structural observation are needed to distinguish reversible from irreversible dissipation.

7. One-pot versus sequential network formation

Table 2. Network-formation sequences used in printed tough hydrogels, with bulk-photocure routes included as architecture boundaries

Sequence	Representative route	Primary advantage	Principal risk
Simultaneous during exposure	Covalent polymerisation plus hydrophobic or coordination association [1,2].	No separate process step; geometry and toughening evolve together.	Toughening chemistry may alter optical cure and gelation.
Print hot, form second network on cooling	Acrylamide/k-carrageenan TOPS [3].	Secondary physical network does not block high-temperature printing.	Thermal distortion, nonuniform cooling and geometry-dependent kinetics.
DLP plus dark polymerisation	Microgel-reinforced acrylamide network [5].	Extends conversion beyond illuminated interval and connects particles.	Spatial confinement can change after exposure; oxygen and timing matter.
DLP microgel formation and assembly	Aqueous two-phase emulsion bioresin [4].	Creates porous hierarchy from one processable emulsion.	Emulsion stability, phase removal and cell/process constraints.
Post-print ionic or dynamic crosslinking	GelMA-PVA-borate [10]; alginate or tannic-acid routes [8].	Separates printability from secondary function.	Diffusion gradients, swelling and dimensional drift.
One-step fibre-assisted network	PAA/bacterial-cellulose nanofibres [6].	Fast preparation with reduced swelling.	Optical scattering and uncertain network connectivity at different fibre states.

Sequential processing is not automatically a disadvantage. It can protect the printing window from a secondary chemistry that would otherwise raise viscosity, scatter light or interfere with radical conversion. The cost is a second material-state transition that must be controlled and documented.

8. Swelling, dehydration and rehydration

Hydrogel mechanics are inseparable from water content. A secondary network can reduce equilibrium swelling by constraining chain expansion, but the same constraint can raise residual stress or reduce transport. Dehydration can temporarily increase apparent stiffness and create gradients; rehydration can alter dimensions, hysteresis and network recovery.

Kunwar et al. explicitly examined swelling, dehydration and rehydration of TOPS-printed networks [3]. Dong et al. observed property changes during water incubation as coordination complexes rearranged [2]. Anindita and co-workers used the opposite sequence: dry PEG macromonomer networks were printed first and only then converted into hydrogels by swelling, producing compressive toughness up to 1.3 MJ m⁻³ [9].

The all-PEG route is important as a boundary: a printed hydrogel can be tough without a classical double network. ER-67 therefore treats network hierarchy as one powerful design strategy, not as the only path to tough VPP hydrogels.

9. Optical and rheological constraints

Hydrogel toughening components can change the optical and rheological state of the resin before any mechanical benefit is realised. Microgels, nanofibres, phase-separated droplets, hydroxyapatite and coordination complexes can increase scattering or absorption. Polysaccharides and particle populations can raise viscosity, yield stress or sedimentation resistance.

A useful VPP qualification should therefore link:

resin microstructure -> optical transport and flow -> first-network conversion -> second-network formation -> hydrated mechanics

Microgel concentration should not be selected only from final tensile performance. Crosby et al. also evaluated viscosity, settling and scattering of the microgel-containing resins [5]. This is the correct process-material linkage for a particle-reinforced vat formulation.

10. Mechanical qualification in the hydrated state

Double-network hydrogel claims should not rely on one unnotched monotonic tensile result. At minimum, the measurement set should be selected from:

- tensile modulus, strength and strain at break;
- compression stress-strain response and unloading recovery;
- work of extension or compression under a stated integration convention;
- fracture energy, tearing or notched response where damage tolerance is claimed;
- loading-unloading hysteresis at stated strain levels;
- cyclic softening, recovery time and retained response;
- swelling ratio, water content and dimensional state;
- rate and temperature dependence;
- orientation and print-location dependence.

The test state must identify whether the sample is as-printed, washed, swollen to equilibrium, dehydrated, rehydrated, healed or mechanically preconditioned. Numerical comparison across different hydration states is not valid without an explicit conversion or conditioning model. No published ISO, ASTM or DIN standard directly governs tensile or compression testing of hydrated hydrogels, hysteresis and recovery reporting for soft hydrated networks, fracture or tearing of printed hydrogels, swelling-state conditioning, or qualification of vat-photopolymerised hierarchical hydrogels. Relevant ISO/TC 276 work remains at working-draft stage (ISO/WD TS 25812; ISO/WD 26013); protocols adopted today must therefore be fully documented as in-house methods.

11. Proposed reporting descriptors

The following descriptors are proposed as reporting aids. They are not standardised quantities and do not replace full curves.

11.1 Dissipated-energy fraction

$$\eta_{\text{diss}} = W_{\text{dissipated}} / W_{\text{loading}}$$

W_{loading} is the area under the loading curve from zero to the declared maximum strain, and $W_{\text{dissipated}}$ is the area enclosed by the loading-unloading loop over the same interval. Both energies must be calculated from

the same loading-unloading cycle, strain limit, rate and hydration state. η_{diss} describes hysteresis, not fracture toughness, and the symbol D is reserved for damage in this series.

11.2 Cycle-retention profile

$$R_{\text{cyc}}(n) = P_n / P_1$$

P can be peak stress, loading energy, unloading energy or another declared response. The complete sequence should be reported because rapid first-cycle softening can be hidden by comparing only the first and last cycles. R_{cyc} is normalised to the first loading cycle and therefore describes progressive softening under repeated loading; it is a different quantity from the reprocessing property-retention ratio $R_{P,n}$ used in ER-63 and ER-66, which is normalised to the pristine or original conditioned material.

11.3 Recovery after rest

$$R_{\text{rec}}(t) = P_{\text{after rest}}(t) / P_{\text{initial}}$$

The rest time, temperature, hydration and strain history must be specified. Recovery of one property does not establish restoration of fracture resistance or network topology, and $R_{\text{rec}}(t)$ is distinct from the healing-efficiency conventions used in ER-13, which require matched damage and healing controls.

11.4 Hierarchical phase fraction

For microgel systems, report $\phi_{\text{mg, resin}}$, the microgel volume fraction in the starting resin, and, where possible, $\phi_{\text{mg, hyd}}$, the corresponding volume fraction in the final hydrated material. State how each value was measured or calculated and do not treat them as interchangeable because microgels and the continuous phase may swell differently. For fibres or particulate phases, report mass or volume fraction, geometry, distribution and the method used to determine them.

12. Qualification matrix

Table 3. Minimum evidence architecture for hierarchical and double-network VPP hydrogels

Domain	Minimum record or measurement	Required conclusion
Starting resin	Component functions, water content, pH/ions, viscosity, stability and spectrum.	Defines the printable state.
Primary photochemical network	Wavelength, irradiance, exposure, conversion, gelation and green mechanics.	Shows how geometry is established.
Secondary network	Chemistry, trigger, timing, diffusion path and direct structural evidence.	Shows that a second load-sharing or dissipative level formed.
Hierarchy distribution	Microgel/fibre/phase fraction, spatial distribution and settling/scattering.	Establishes uniformity through the printed object.
Hydration state	Medium, temperature, swelling time, equilibrium criterion and water content.	Defines the material state tested.
Mechanical response	Tension, compression, hysteresis, cyclic recovery and fracture-relevant test.	Separates stiffness, strength, dissipation and damage tolerance.
Dimensional response	CAD, as-printed, post-network and equilibrium-swollen dimensions.	Separates printing error from swelling or secondary-network change.
Ageing and cycling	Repeated loading, dehydration/rehydration and relevant environmental exposure.	Tests durability of the hierarchy.
Application layer	Device-specific function and biological evidence, where relevant.	Prevents material-level data from becoming device claims.

13. Failure modes and interpretation errors

Table 4. Common failure modes in printed hierarchical hydrogels

Observation	Possible cause	Required control
High initial toughness, severe second-cycle softening	Irreversible sacrificial-network damage.	Cycle-resolved hysteresis and recovery after controlled rest.
Good dry mechanics, weak swollen material	Dehydration-induced reinforcement or incomplete equilibration.	Equilibrium-swollen testing and water-content record.
Secondary network forms only near the surface	Diffusion-limited ions, polymer or crosslinker.	Sectioned spatial mapping and geometry-dependent kinetics.
Microgel-rich top or bottom region	Settling, flotation or recoating-induced segregation.	Through-build imaging and concentration mapping.
Poor VPP resolution after reinforcement	Scattering, absorption or viscosity increase.	Resin optics, working curve and feature-specific calibration.

Observation	Possible cause	Required control
Large post-print dimensional drift	Swelling, cooling, immersion or secondary crosslinking.	Multi-state dimensional record.
Double-network claim without direct architecture evidence	Two ingredients assumed to equal two networks.	Chemistry, extraction/swelling and control formulations.
Self-healing inferred from physical contact	Adhesion or swelling instead of network repair.	Matched damage, healing and fracture-location controls.
Biocompatible or tissue-ready claim from hydrogel identity	Application inference without finished-device evidence.	Separate biological and intended-use qualification.

14. Scope boundaries within the Engineering Review series

ER-67 is restricted to hydrated network hierarchy, load sharing and energy dissipation.

- ER-13 addresses self-healing and interlayer repair. ER-67 includes dynamic bonds only as contributors to a multi-network architecture and does not replace healing qualification.
- ER-15 addresses transport, degradation and mechanical evolution in tissue-engineering scaffolds. ER-67 does not infer tissue suitability from hydrogel mechanics.
- ER-24 addresses soft-robotics materials and device actuation. ER-67 treats hydrogel mechanics before device-level actuation.
- ER-43 addresses intentionally different printed material regions and graded interfaces. ER-67 concerns multiple network levels inside one hydrogel material.
- ER-59 addresses dual-cure sequence as a general network-forming architecture. ER-67 addresses the final hydrated hierarchy and its damage-dissipation behaviour.
- ER-60 addresses polymerisation-induced phase separation. Microgel or fibre hierarchies in ER-67 may be heterogeneous without being PIPS-generated.
- ER-61 addresses gelation, vitrification and mobility arrest. ER-67 uses gelation as one stage but focuses on hydrated post-gel mechanics.
- Fracture toughness and damage tolerance across vat-printed thermosets are treated separately, in preparation as ER-70. ER-67 defines hydrogel-specific network mechanisms and hydration controls that precede a fracture claim.

15. 3Dresyns implementation boundary

3Dresyns currently offers a hydrogel product family — including swellable, absorbent, non-swellable and stimuli-responsive photopolymer systems — which the company positions by hydrated behaviour and does not describe in network-architecture terms. No current standard 3Dresyns product is identified in this review as an independently validated double-network, microgel-reinforced or hierarchical hydrogel VPP platform, and no product is described by the company in double-network, interpenetrating-network or microgel terms.

A future custom hydrogel platform would require, at minimum:

- controlled identity and function of each network-forming component;
- resin optical and rheological qualification at the intended wavelength and temperature;
- proof of primary and secondary network formation;
- hydration-, swelling- and cycle-resolved mechanical data;
- spatial uniformity data for microgels, fibres, particles or ions;
- dimensional measurements after every secondary-network and conditioning step;
- application-specific biological or device qualification where applicable.

Product and marketing labels such as hydrogel, swellable, super absorbent, soft, flexible, self-healing, scaffold, cell adhesion, cell infiltration, tissue engineering or biocompatible must not be converted into a network-architecture claim without direct structural and mechanical evidence. A large stiffness change between the dry printed state and the swollen state is a solvent-plasticisation effect and is not, by itself, evidence of a second network or of sacrificial-bond energy dissipation.

16. Design rules

- Name both network levels and the mechanism that creates each one.
- Separate the network required for printing from the network required for toughness.
- Test the final material at a declared hydration and conditioning state.
- Report hysteresis, recovery and cycle history, not only the first loading curve.

- Use fracture-relevant methods before claiming damage tolerance.
- Map microgel, fibre or ionic-network distribution through the printed object.
- Rebuild optical calibration after adding any hierarchical phase.
- Measure dimensions after cooling, immersion, swelling or secondary crosslinking.
- Do not use double network as a generic synonym for multicomponent hydrogel.
- Keep material mechanics separate from biomedical or device-level suitability.

17. Research priorities

- VPP chemistries that generate high green strength without suppressing secondary-network mobility;
- microgel populations with reduced scattering and programmable particle-matrix interfaces;
- in-situ monitoring of dark polymerisation, cooling-induced networks and immersion-driven crosslinking;
- spatially patterned secondary networks within one printed hydrogel;
- fracture and fatigue methods adapted to small, hydrated, additively manufactured specimens;
- network-recovery studies extending beyond a few cycles and short rest times;
- multiscale models coupling projected dose, diffusion, swelling and energy dissipation;
- standardised reporting of hydration state, hysteresis and dimensional change.

18. Conclusions

Hierarchical and double-network hydrogels provide a way to separate geometric fixation from hydrated damage tolerance. The first network can establish the printed shape, while a second network, microgel population, fibre phase or supramolecular association redistributes load and dissipates energy.

The useful engineering sequence is:

printable precursor -> primary network and geometry -> secondary hierarchy -> hydrated conditioning -> dissipation, recovery and fracture response

A tough hydrogel is not established by a high strain at break alone. The architecture must be identified, the hydration state fixed, the dissipated energy and recovery measured, and the result retained under cycles and dimensional changes relevant to the intended use.

In vat-printed hydrogels, toughness is a property of the complete network hierarchy and its hydration history, not of one crosslink density or one tensile curve.

Limitations

The evidence set spans DLP, projection stereolithography, LCD-VPP, extrusion printing and non-print photopolymerisation. Extrusion and bulk-photocure studies are used only for architecture or mechanism boundaries; their process windows are not transferred to VPP. Numerical mechanical results are formulation-, geometry-, rate- and hydration-specific and are not pooled.

The terms double network, hierarchical network and supramolecular network remain inconsistently applied across the literature. This review therefore does not impose a universal taxonomy where the source evidence is insufficient. No universal standards-based acceptance values for VPP hydrogel toughness, hysteresis or healing are proposed.

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. No current commercial 3Dresyns product is presented as an independently validated double-network, microgel-reinforced or hierarchical hydrogel VPP platform.

Data availability

No new experimental dataset was generated for this review.

Company information

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