

Ionomeric and Ionic-Cluster Photopolymer Networks: Morphology, Conductivity, Self-Recovery and Environmental Sensitivity

Ionic association, cluster morphology, transport, recovery and coupled environmental state

Juan Segurola

3Dresyns by Resyner Technologies S.L.

© 2026 Juan Segurola. All Rights Reserved.

Correspondence: info@3Dresyns.com · www.3Dresyns.com

ER-320 · Engineering Review · Version 0.4 · 27 September 2026

Abstract

Ionomeric and ionic-cluster photopolymer networks contain reversible electrostatic associations that act as physical crosslinks, conduction pathways or microphase-organising motifs. Their behaviour is governed not only by ionic-group concentration but also by counterion identity, cluster morphology, water content, dielectric environment and temperature. These variables couple mechanics and transport: conditions that increase ion mobility and self-recovery can also reduce modulus, increase creep or change dimensional stability. Photopolymerisable ionic gels, deep-eutectic systems and dynamically crosslinked DLP resins demonstrate that ionic and hydrogen-bond interactions can support self-healing, assembly, recyclability and sensing. This review focuses on ionomeric and ionic-cluster networks as material-state systems, separating reversible ionic association from permanent covalent crosslinking and from liquid electrolyte effects. A qualification framework is proposed around ionic morphology, conductivity, humidity response, stress relaxation, creep, self-recovery, leaching and dimensional retention.

Keywords: ionomer; ionic cluster; photopolymer; DLP; ionic gel; conductivity; self-recovery; humidity; creep

1. Significance and scope

Ionic groups in polymer networks can aggregate into clusters or multiplets whose association provides reversible physical crosslinking. In solvent-rich systems the same ions can also support conductivity and sensing, creating a direct coupling between mechanical and electrical function. This review owns ionomeric and ionic-cluster photopolymer networks: morphology, conductivity, self-recovery and environmental sensitivity. Hydrogen bonding is considered only where it couples to ionic association; ER-318 remains the primary location for multiple hydrogen-bond networks.

1.1 Corpus boundary

ER-13 retains the umbrella scope for self-healing and interlayer repair. ER-318 retains hydrogen-bonded and multiple-supramolecular photopolymer networks. ER-320 is limited to ionomeric and ionic-cluster photopolymer networks, especially morphology, coupled ionic transport, self-recovery and environmental sensitivity; electrical recovery is treated separately from mechanical recovery.

2. Ionic association and morphology

An ionomer is not defined by ions alone but by how ionic groups are distributed within the polymer. Counterion valence, ionic-group spacing, backbone polarity and phase segregation determine whether ionic groups remain isolated or form clusters with a distinct relaxation response. Cluster morphology can act as a reversible physical network superimposed on a permanent covalent scaffold. Mechanical behaviour therefore depends on both networks. Swelling or temperature can disrupt ionic clusters without breaking the covalent structure. Direct structural methods such as scattering or spectroscopic probes are valuable where available. Mechanical signatures alone cannot uniquely identify ionic clustering because microphase separation and hydrogen bonding can produce similar relaxation behaviour. Equivalent ionic-group concentration can produce different morphologies when counterion size, valence or backbone polarity changes. Qualification should therefore report counterion identity and conditioning history, not only nominal ionic content. Cluster formation can also be kinetically trapped during photopolymerisation. Post-cure annealing or solvent removal may continue to reorganise ionic domains after geometric printing is complete, so the final material state should be defined after a controlled conditioning step. [1,2]

3. Photopolymerisable ionic gels and dynamic DLP networks

Photopolymerised ionic gels based on polymeric deep-eutectic systems demonstrate that dynamic noncovalent interactions can coexist with 3D printing, large strain and electrical self-healing. Such systems are useful examples of coupling transport and recovery. Other DLP-printed healable and recyclable polymers combine hydrogen bonding and ionic bonding to enable assembly and post-print repair. These studies show that reversible ionic interactions can be functional, but they also highlight that liquid content and mobile species may contribute strongly to the response. The distinction between a dry ionomer and an ionogel is therefore essential. A solvent-rich ionic network can recover rapidly because ions and chains are highly mobile, while a dry ionomer may show much slower exchange and greater service stiffness. For vat printing, ionic groups and salts can alter resin viscosity, refractive index and photoinitiator environment. Cure-depth calibration and feature fidelity should therefore be repeated when ionic composition or water content changes. Residual mobile electrolyte can also influence washing and drying. A printed part may change conductivity and dimensions during post-processing even without further photochemical conversion, making post-print conditioning part of the material specification. [1-4]

4. Conductivity as a state variable

Electrical conductivity depends on ion concentration, mobility and connectivity of transport pathways. Humidity, temperature and deformation can change all three. Conductivity should therefore be measured with the same conditioning history used for mechanical testing. A rise in conductivity after damage does not prove mechanical healing, and recovery of mechanical continuity does not prove restoration of the original ionic pathway. Multifunctional qualification should track both quantities independently. For sensing applications, hysteresis, drift and cycle-to-cycle repeatability are as important as peak sensitivity. Reversible cluster rearrangement can create memory effects that alter the baseline signal after repeated strain. Electrical measurements should distinguish bulk ionic conductivity from electrode contact effects. Apparent signal recovery after damage may reflect reconnection at the electrode or surface rather than restoration of the internal transport network. Frequency-dependent impedance can help separate ionic transport, interfacial polarisation and electrode contributions, especially in humid or solvent-rich materials where a single DC conductivity value is insufficient. [1,2]

5. Humidity, solvent and counterion effects

Water strongly changes the dielectric environment and can dissociate ionic pairs or plasticise the polymer. Counterions can also migrate, exchange with external ions or leach into contacting media. Qualification should include controlled humidity, immersion where relevant, and dry-back measurements. Mass change, conductivity, modulus and dimensions should be recorded together so that improved mobility is not mistaken for stable self-recovery. Applications involving skin, biological tissue or outdoor use should consider ion exchange with salts and pH variation. The resulting changes may be reversible, partially reversible or permanent depending on the chemistry and network architecture. Leaching measurements should be tied to both performance and safety where relevant. Loss of a mobile ionic component can reduce conductivity or cluster density even when the part appears dimensionally unchanged. Repeated humidity cycles are especially informative because they reveal hysteresis between wetting and drying. A reversible first cycle does not guarantee stable transport or mechanics after many cycles. [1,3,4]

6. Self-recovery, creep and fatigue

Dynamic ionic clusters can break under load and re-form after unloading, dissipating energy and supporting recovery. The benefit is strongly rate dependent. At slow loading or sustained stress, the same mobility can produce creep. Fatigue testing should record stiffness, residual strain, conductivity where applicable and recovery after defined rest periods. A network that recovers electrically but accumulates mechanical deformation is not fully self-recovering for structural use [1,2,5].

Printed geometry adds an additional constraint: swelling or cluster redistribution can change feature dimensions and interlayer stress. Dimensional metrology should therefore accompany recovery claims. [1,2,5]

7. Minimum qualification matrix

A minimum qualification set should link ionic morphology and transport to mechanics and environment, with dry and humid states treated as distinct material conditions.

Table 1. Minimum qualification matrix for ionomeric and ionic-cluster photopolymer networks.

Domain	Minimum measurement	Primary failure interpretation
Ionic state	Ionic-group and counterion identity; evidence of clustering or phase organisation where feasible	Ions may be present without forming a functional physical network
Transport	Conductivity versus humidity, temperature and strain	Electrical recovery can diverge from mechanical recovery
Environment	Water/solvent uptake, dry-back response and ion release where relevant	Humidity can dominate mobility and modulus
Mechanics	Rate-dependent strength, relaxation and creep	Dynamic clusters can dissipate energy but also create drift
Recovery	Mechanical and electrical recovery after defined damage and rest	One recovered function does not prove full restoration
Geometry	Dimensional retention during conditioning and cycling	Swelling or cluster redistribution may alter printed tolerances

8. Interpretation matrix

Ionic networks often show coupled electrical and mechanical changes. Interpretation should therefore avoid assuming that improvement in one domain implies restoration in the other.

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

Observation	Plausible interpretation	Discriminating control
Conductivity rises with humidity	Water increases ion dissociation and mobility	Track mass uptake and modulus simultaneously
Cut interface restores electrical signal rapidly	Ionic pathway reconnects before bulk mechanics recover	Independent tensile or fracture recovery test
Material becomes softer after repeated sensing cycles	Cluster rearrangement or solvent redistribution may accumulate	Rest-time study plus water-content control
Healing improves at high temperature	Ion mobility rises, but creep risk also increases	Long-duration creep at the same temperature
Dry-back restores stiffness but not conductivity	Counterion redistribution or leaching may be irreversible	Ion analysis and repeated conditioning cycle

9. Limitations and evidence gaps

Many photopolymerisable ionic systems are ionogels or deep-eutectic networks rather than dry engineering ionomers. Their high mobility is valuable for sensors but limits direct transfer to structural applications. Long-term counterion migration, leaching, electrode-interface stability and dimensional drift remain incompletely characterised across many printed systems. Standardised reporting of ionic content, water content and conditioning history is essential because these variables can dominate both conductivity and mechanics. [1-5]

10. Conclusions

Ionomeric and ionic-cluster photopolymer networks provide a versatile route to reversible physical crosslinking, electrical transport and self-recovery. Printed ionic gels and dynamically crosslinked DLP systems demonstrate that these functions can be integrated into complex geometries. [1-5]

Their qualification must treat morphology, counterion state, water content and temperature as coupled variables. Conductivity, stiffness, creep and dimensional stability should be measured under the same environmental history. The useful design target is not maximum ion mobility but controlled mobility that supports the intended recovery or sensing function without unacceptable drift, leaching or loss of geometry. [1-5]

References

1. Hu J, Yao X, Li T, Li X, Wei W, Liu J. Supramolecular Ionic Gels with High Elasticity and Self-Healing Based on Polymeric Deep Eutectic Solvent for 3D-Printable Soft Sensors. ACS Applied Polymer Materials. 2023;5(11):9650-9658. doi:10.1021/acsapm.3c02114.

2. Zhu G, Hou Y, Xiang J, Xu J, Zhao N. Digital Light Processing 3D Printing of Healable and Recyclable Polymers with Tailorable Mechanical Properties. ACS Applied Materials & Interfaces. 2021;13(29):34954-34961. doi:10.1021/acsami.1c08872.

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. 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.

5. 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.