

Network-State Metrology in Photopolymers: Gel Fraction, Effective Crosslink Density and the Non-Equivalence of Conversion, Insolubility and Modulus

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Statement of Significance

Photopolymer networks are routinely described with a single convenient scalar: degree of conversion, gel fraction, swelling ratio, modulus or an inferred crosslink density. These quantities are related, but they are not interchangeable. A material can reach high double-bond conversion while retaining soluble species, can possess a high gel fraction while remaining weakly crosslinked, or can show a high modulus because it is glassy rather than because its elastically active network density is high.

ER-182 defines a metrology architecture for resolving those distinctions. It treats each network-state measurement as a method-dependent observation with a defined specimen state, solvent or temperature history, constitutive assumptions and uncertainty. The objective is not to prescribe one universal crosslink-density equation. It is to prevent a measurement on one axis from being silently promoted into a claim on another.

Keywords: photopolymer; network metrology; gel fraction; sol fraction; swelling; crosslink density; degree of conversion; modulus; Flory-Rehner; rubber elasticity; qualification

Abstract

Photopolymerisation transforms a reactive liquid into a heterogeneous network whose state cannot be represented completely by degree of conversion alone. Sarkar et al. combined conversion, polymerisation stress, temperature and shrinkage measurements with viscoelastic modelling and showed that different curing conditions can produce different inferred network structures from the same initial resin [1]. Martens and Anseth related swelling and compressive response of photocrosslinked acrylated poly(vinyl alcohol) networks to network structure [2]. Steindl et al. measured double-bond conversion, gelation, swelling, gel fraction and mechanical response in related photopolymer networks, and their results indicate that high conversion and high gel fraction do not by themselves define one unique network architecture [3].

ER-182 therefore separates five metrology axes: chemical conversion, soluble/insoluble fraction, equilibrium or time-dependent swelling, mechanically inferred effective network density, and final mechanical response. It defines the assumptions behind extraction and swelling methods, distinguishes topological crosslinks from elastically active network chains, and requires temperature and physical state to accompany modulus-based inference. It also addresses specimen preparation, residual species, solvent selection, extraction completeness, drying, heterogeneity and uncertainty. No conversion value, gel fraction, swelling ratio or inferred crosslink density is treated as a universal acceptance limit.

1. Scope, terminology and ownership

ER-182 owns measurement and inference of photopolymer network state after or during cure. Its central question is not how polymerisation proceeds, but what can defensibly be concluded from the available measurements about the resulting network.

Degree of conversion is the fraction of a specified reactive group transformed according to a stated analytical method and reference state. **Gel fraction** is the mass fraction that remains insoluble after a defined extraction and drying procedure. **Sol fraction** is the complementary extractable fraction only when the mass balance and method justify that interpretation. **Swelling ratio** describes solvent uptake under a declared basis and state. **Effective crosslink density** is an inferred measure of elastically active network constraints under the assumptions of the chosen model. **Modulus** is a mechanical response measured at a stated temperature, frequency or strain/time regime and is not itself a direct count of chemical crosslinks.

ER-027 retains ownership of conversion metrology as a primary subject. ER-061 retains gelation and vitrification mechanisms. ER-090 retains viscoelastic response. ER-182 uses those quantities only to establish network-state inference and the limits of equivalence among them.

Measurand	Direct observation	Inference commonly attempted	Principal limitation
Degree of conversion	Loss of specified reactive functionality	Extent of network formation	Does not uniquely define topology, extractables or elastic activity
Gel fraction	Insoluble dry mass after extraction	Fraction incorporated into an infinite network	Depends on solvent, time, diffusion, drying and degradation
Swelling	Solvent uptake / polymer volume fraction	Network constraint or mesh scale	Requires solvent interaction and network-model assumptions

Measurand	Direct observation	Inference commonly attempted	Principal limitation
Rubber-region modulus	Stress response in a defined regime	Effective elastic-chain density	Requires appropriate frequency and network temperature, elasticity assumptions
Glassy modulus / hardness	Mechanical resistance in a glassy state	Sometimes misused as crosslink-density proxy	Strongly affected by T _g , free volume, morphology and test method

2. Network state is multidimensional

A photopolymer network contains more information than the fraction of reacted double bonds. The same conversion can be distributed among intramolecular loops, pendant reacted groups, elastically active junctions, dangling chains and densely connected regions. Conversely, two networks with different conversion can show similar bulk modulus if one is measured deeper in the glassy regime or contains reinforcing physical interactions.

Sarkar et al. demonstrated this problem directly by measuring several quantities during photopolymerisation rather than inferring structure from conversion alone [1]. Their analysis linked cure protocol to different network structures and spatial heterogeneity in crosslink density. The transferable conclusion is methodological: network structure requires more than one observable and the inference depends on the model used to connect those observables.

Qualification should therefore define the network state as a vector of measurements rather than a scalar. Which components are required depends on the claim. A dimensional-stability claim may need conversion, residual species and mechanical state. An extractables claim may require a validated extraction method and chemical analysis. A swelling-sensitive application may require solvent uptake and post-equilibration mechanics. No single test is promoted to universal status.

3. Degree of conversion is chemical, not topological

Spectroscopic conversion measurements follow the disappearance of a selected reactive band or another chemical marker. They answer how much of that functionality reacted under the measurement definition. They do not identify whether each reaction created an elastically useful connection between network strands.

A difunctional or multifunctional monomer can react in ways that create cycles or pendant structures. Chain transfer can change the length distribution between junctions. Phase separation can produce regions with different local conversion and stiffness. Vitrification can arrest motion while leaving residual unsaturation. Post-cure can advance conversion without reproducing the network topology that would have formed under a different cure path.

Steindl et al. provide a concrete example in which network-forming chemistry changed the conversion at gelation, final conversion, swelling and mechanical properties together [3]. Their data support the principle that conversion belongs in a multiparametric description, not as a synonym for crosslink density.

4. Gel fraction measures insolubility under a method

Gel-fraction testing appears simple: extract the specimen, dry the retained network and compare masses. The apparent simplicity conceals several method dependencies. Solvent identity, specimen dimensions, extraction time, temperature, agitation, solvent replacement, diffusion path, chemical compatibility and drying endpoint can all alter the result.

A high retained mass can mean that most polymeric material is incorporated into an insoluble network. It can also include trapped soluble species, poorly extracted oligomers, fillers, pigments or other insoluble constituents. A low retained mass can reflect true soluble material, network degradation during extraction or loss of a component that was never intended to be covalently bound.

Gel fraction is therefore a method-defined quantity. The report must state the initial mass basis, non-polymeric insoluble fraction where relevant, solvent, extraction conditions, drying conditions and mass-constancy rule. If extraction completeness has not been demonstrated for the specimen geometry, the result is a lower-bound statement about what was removed, not proof that all sol was removed.

5. Sol fraction is not automatically residual monomer

The material removed during extraction can contain unreacted monomer, oligomer, linear or branched polymer, photoinitiator fragments, additives, inhibitors, plasticisers or degradation products. Reporting sol fraction = residual monomer is therefore generally unjustified without composition analysis.

When chemical identity matters, gravimetric sol fraction should be paired with an analytical method appropriate to the extracted species, such as chromatography or spectroscopy. A mass balance can then distinguish total extractable mass from selected chemical constituents.

This distinction is particularly important for regulated, optical, electronic or long-term-contact applications because a small extractable fraction can still contain a functionally important species, while a large extractable fraction can be dominated by a benign soluble component deliberately present in the formulation.

6. Swelling probes network constraint and solvent interaction

Crosslinked networks resist unlimited dissolution but can take up solvent. Equilibrium swelling therefore carries information about the balance between polymer-solvent mixing and elastic retraction of the network. Classical Flory-Rehner approaches exploit that balance to estimate a network parameter from the swollen state.

Martens and Anseth used equilibrium swelling and compressive response to relate photocrosslinked PVA hydrogel properties to network structure [2]. Later work has shown why the model assumptions must remain visible. Borges, Papavasiliou and Teymour explicitly analyse limitations of classical Flory-Rehner treatment for complex hydrogel architectures and show that crosslinker architecture and branching can make a single classical molecular-weight-between-crosslinks interpretation incomplete [6,7].

The engineering conclusion is not that swelling is unreliable. It is that swelling becomes quantitative network metrology only when the solvent interaction model, composition, temperature, equilibrium criterion, polymer density and network architecture are appropriate to the specimen.

7. Equilibrium must be demonstrated, not assumed

A swelling measurement at a chosen time is not necessarily an equilibrium swelling measurement. Thick specimens, glassy networks, strong solvent interactions and constrained geometries can produce long diffusion times. Simultaneous extraction and swelling can further change the network composition while dimensions evolve.

Time-series mass or dimension measurements should be used when the equilibration time is not already validated. A plateau should be defined by a pre-established criterion and not selected visually after the desired value appears. If the network continues to hydrolyse, oxidise or otherwise react in the solvent, equilibrium swelling and chemical ageing are confounded.

The specimen history also matters. Drying a network before swelling can create a different morphology or residual stress from measuring it in an as-cured state. Repeated swelling/drying cycles may not be non-destructive. The state used for the measurement must therefore be part of the result.

8. Flory-Rehner output is model-dependent

An equation can return a precise number even when its assumptions are weak. Classical swelling models typically require a polymer-solvent interaction parameter, polymer density and assumptions about network elasticity and homogeneity. The inferred molecular weight between crosslinks or crosslink density inherits uncertainty from every one of these quantities.

For copolymers and mixed solvents the interaction description becomes more complex. Godbole et al. developed a multicomponent Flory-Rehner treatment and demonstrated that solvent composition and effective interaction parameters matter to the predicted swelling of random copolymer networks [5]. Borges et al. further show that branch and crosslinker architecture can require information beyond the classical result [6,7].

For qualification, an inferred value should therefore be labelled by method, model and parameter set. Crosslink density = X is incomplete. A defensible form is effective network density inferred from equilibrium swelling using model M , solvent S , temperature T and stated interaction parameters.

9. Effective crosslink density is not chemical crosslink count

Elastic network theories often relate modulus in an appropriate rubbery regime to the density of elastically active chains. This is an effective mechanical quantity. Loops, dangling ends, trapped entanglements, physical associations and heterogeneous domains can cause it to differ from a chemical count of crosslink reactions.

The distinction matters because photopolymer networks are rarely ideal phantom or affine networks. A formulation with more multifunctional monomer can increase nominal functionality while also increasing cyclisation or heterogeneity. A chain-transfer agent can delay gelation and alter strand lengths. A nanofiller can raise measured modulus without creating additional covalent network junctions.

ER-182 therefore uses **effective crosslink density** for mechanical or swelling-based inference unless a method truly identifies chemical junctions. The qualifier is not editorial caution; it is part of the measurand definition.

10. Modulus requires temperature, frequency and physical state

Rubber-elasticity inference requires a mechanical regime in which network entropy meaningfully controls the response. A modulus measured far below glass transition is dominated by glassy segmental constraints and cannot be inserted uncritically into a rubber-elasticity relation.

Dynamic mechanical analysis is particularly useful because it reveals storage and loss response over temperature or frequency. But the selected plateau, transition region and frequency must be stated. A network with a broad transition or multiple phases may not provide one unambiguous rubbery plateau.

Static compression or tension can also support network characterisation when strain range, rate, geometry and constitutive assumptions are appropriate. Martens and Anseth used compressive modulus alongside swelling rather than treating one measurement as sufficient [2]. The general rule is convergence of independent observables, not mechanical-number substitution.

11. Gel fraction and modulus can move in different directions

High gel fraction states that most measured mass resisted the extraction method. It does not state how densely the insoluble network is connected. A lightly crosslinked but percolated network may be almost entirely insoluble and still swell strongly. Conversely, a more tightly constrained network may have similar gel fraction but much lower swelling.

Steindl et al. measured high gel fractions together with different swelling and mechanical behaviour across related network chemistries [3]. Billiet et al. likewise reported substantial gel formation at relatively low double-bond conversion in photocrosslinked gelatin systems [4]. These examples directly reject a one-to-one mapping between conversion and gel fraction.

A useful network-state matrix therefore reports conversion, gel/sol fraction and a network-constraint metric separately. Agreement strengthens interpretation; disagreement is information that requires explanation rather than a reason to discard one test.

12. Spatial heterogeneity defeats bulk-only interpretation

Photocuring is spatial. Optical attenuation, oxygen access, temperature, local composition and geometry can create gradients. A bulk gel fraction averages those regions. A bulk swelling ratio does the same. A specimen can therefore meet an average value while containing a weak surface, under-cured core or highly crosslinked skin.

Sarkar et al. explicitly address heterogeneity in inferred crosslink density under different curing conditions [1]. For printed or thick photopolymer parts, ER-182 therefore requires the sampling strategy to match the failure mode. Sectioning, micro-spectroscopy, micro-mechanical testing, solvent uptake by region or another spatially resolved method may be needed when local state controls performance.

A homogeneous coupon is not evidence that a complex geometry has homogeneous network state. The transfer must be demonstrated or bounded.

13. Extraction can change the object being measured

Gel-fraction and swelling procedures are not always passive observations. Solvent can plasticise the network, extract unreacted species, relax residual stress, promote post-reaction, hydrolyse susceptible bonds or alter morphology. Drying after extraction can create collapse or additional physical association.

The measurement protocol must therefore distinguish **as-cured state**, **solvent-equilibrated state**, **post-extraction dry state** and **reconditioned state**. Mechanical tests made after extraction describe the extracted network, not necessarily the delivered product before extraction.

Where the purpose is to quantify extractables, this state change is intentional. Where the purpose is to infer in-service mechanics, it may make the specimen non-representative. The protocol should state which question is being answered.

14. Measurement uncertainty and mass-balance closure

Network-state metrology often combines several measured quantities into one inferred parameter. Uncertainty can therefore amplify. Small errors in dry mass, swollen mass, density or polymer volume fraction can materially change a swelling-derived result, especially when the model is nonlinear.

Mass measurements should include balance capability, specimen handling and evaporation control. Density values should be measured or justified for the actual network state rather than copied automatically from liquid resin. Solvent temperature and composition should be controlled when they affect density or interaction parameters.

A useful extraction mass balance distinguishes initial specimen mass, known insoluble inorganic content, retained dry polymer-containing mass and recovered extractable mass where collection is quantitative. Failure of the balance is itself a finding and should not be hidden by reporting only the final percentage.

15. Qualification architecture

A practical qualification programme begins with the claim and chooses complementary measurements:

1. define the network-dependent property or risk to be controlled;
2. specify the incoming material, cure and conditioning state;
3. measure chemical conversion when residual reactivity matters;
4. measure gel/sol fraction when incorporation or extractables matter;
5. use swelling when solvent-responsive network constraint is relevant;
6. use appropriately conditioned mechanical or DMA measurements when effective elasticity matters;
7. add chemical analysis when extractable identity matters;
8. map spatial variation when geometry or optical access can create gradients;
9. quantify repeatability and method uncertainty;
10. establish acceptance criteria against the intended function rather than against literature values.

Qualification question	Minimum useful evidence	Invalid shortcut
Is reactive functionality substantially consumed?	State-matched conversion method	Treating high hardness as high conversion
Is most polymer mass in an insoluble network?	Validated extraction + dry mass basis	Treating low swelling as high gel fraction
Is network constraint sufficiently high?	Swelling/model or rubber-region mechanics with assumptions	Treating gel fraction as crosslink density
Are extractables controlled?	Extraction mass + identity-sensitive analysis where needed	Treating sol fraction as residual monomer
Is state uniform through the part?	Spatially representative sampling	One bulk coupon or surface measurement

16. Change control and transfer

Changes that alter network formation or measurement validity require impact assessment. These include resin formulation, monomer functionality, chain-transfer chemistry, photoinitiator, absorber or pigment, filler, cure spectrum, irradiance, dose profile, temperature, oxygen environment, layer or section thickness, post-cure and conditioning.

Measurement-method changes matter as well: solvent identity, extraction time, specimen dimensions, drying method, DMA frequency, test temperature, density assumption or interaction parameter can shift the reported network metric without any material change.

Method transfer between laboratories therefore requires more than agreeing on a formula. It requires matched specimen preparation, environmental control, equipment capability, calculation conventions and reference materials or bridging specimens.

17. Reporting rules and decision boundaries

Every network-state number should carry enough metadata to reproduce its meaning. At minimum:

- material and formulation identity;
- specimen geometry and sampling location;
- print/cure/post-cure history;
- conditioning history;
- measurement method and instrument;
- temperature and time/frequency state;
- solvent, extraction and drying details where applicable;
- density and interaction parameters used in modelling;
- equation/model and assumptions;
- uncertainty or repeatability;
- whether the result is direct or inferred;
- acceptance criterion and functional rationale.

Terms such as fully cured, 100% crosslinked, complete network or no residual monomer should not be inferred from a single bulk metric. They require a definition and evidence appropriate to that definition.

18. Limitations and conclusions

The literature used here spans acrylate and methacrylate networks, hydrogels and other photopolymer systems. Their numerical results are not pooled into universal photopolymer limits. Solvent interaction, network architecture, glass transition, morphology and chemical functionality differ substantially across these materials.

The central conclusion is metrological: conversion, gel fraction, swelling, effective crosslink density and modulus are distinct observables or inferences. They can correlate within a controlled material family, but correlation does not make them equivalent. Gel fraction measures insolubility under a defined extraction. Swelling measures solvent uptake under a defined thermodynamic and kinetic state. Effective network density is model-dependent. Modulus depends on test regime and physical state. Conversion measures reacted chemical functionality.

A qualified network-state claim therefore requires a chain from the intended function to the selected measurements, their assumptions and their uncertainty. The strongest defensible statement is not that one scalar proves a network is fully cured, but that a defined material and process state satisfies specified chemical, extractable, structural and mechanical criteria under controlled measurement methods.

Related Engineering Review boundaries

ER-027 owns degree-of-conversion metrology as a primary subject.

ER-061 owns gelation and vitrification mechanisms.

ER-090 owns viscoelastic response and rheological/mechanical interpretation as a primary subject.

ER-181 owns post-cure process delivery rather than network-state metrology.

ER-182 owns the inference architecture linking conversion, gel/sol fraction, swelling and effective network density while preserving their non-equivalence.

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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 and AI-assistance statement

No new experimental dataset was generated. Scientific statements derive from the cited primary literature and the controlled Engineering Review corpus. Generative AI assisted drafting, literature synthesis and document QA but is not an author. Juan Segurola retains responsibility for the final article.