

Conversion Metrology and Spatial Cure Heterogeneity in Vat Photopolymerisation: From Exposure to Network State

Juan Seguro

3Dresyns by Resyner Technologies S.L.

© 2026 Juan Seguro. All Rights Reserved.

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

ER-027 · Engineering Review · Version 1.1 · 2026

Statement of Significance

Cure depth and degree of conversion are not interchangeable measurements. A working curve can describe the geometric response of a resin to exposure while leaving the local chemical conversion, network heterogeneity and post-cure evolution unresolved. This review defines a conversion-metrology framework for VPP that separates exposure, gelation/solidification, chemical conversion, refractive-index evolution and final properties. The central objective is to make claims about curing state traceable to an actual measurand rather than to exposure time or printed thickness alone.

Keywords: vat photopolymerisation; degree of conversion; Raman spectroscopy; FTIR; interferometry; cure heterogeneity; photopolymerisation kinetics; DLP; post-cure; conversion mapping

Abstract

Vat photopolymerisation converts a spatially patterned light field into a crosslinked network, but the resulting network state is not described completely by cure depth or a pass/fail print. Chemical conversion can vary through thickness, across projected features and during post-cure; different analytical methods also interrogate different volumes and functional groups. Recent DLP research has demonstrated full-field in-situ interferometric monitoring of curing dynamics and has combined interferometry with Raman spectroscopy to relate optical evolution to chemical conversion. This Engineering Review separates five quantities: delivered exposure, geometric solidification, degree of conversion, network/property evolution and residual/leachable chemistry. It proposes a minimum reporting architecture for spectroscopic conversion measurements, spatial mapping, in-situ monitoring, post-cure history and conversion-property interpretation. Residual-species toxicology is deliberately excluded because it is addressed elsewhere; 3Dresyns Fine Tuners and CRT tools are included only as implementation context and not as substitutes for conversion measurement.

1. Introduction

VPP studies frequently use exposure time, cure depth, hardness or successful printing as shorthand for curing. These quantities are related, but they answer different questions. Exposure is an input; cure depth is a geometric response; degree of conversion is a chemical measurement; modulus and shrinkage are network-level outputs. Conflating them can make a material appear fully cured because a self-supporting layer formed even though reactive groups continue to convert during later exposure or post-cure.

The distinction is now experimentally accessible. Zhang, Zhang and Zhao developed in-situ interferometric curing monitoring for DLP-VPP to resolve spatiotemporal curing dynamics and link refractive-index evolution to degree of curing, with validation against FTIR [1]. In 2026, Zhang and co-workers combined the same interferometric concept with Raman spectroscopy in wavelength-selective VPP, showing that conversion and reaction pathways depend on wavelength and exposure duration [2]. These studies support a metrology-centred view in which curing claims are tied to specific observables.

2. Five quantities that should not be collapsed

Quantity	Typical measurement	What it establishes	What it does not establish
Exposure	Irradiance × time; spectral dose	Delivered optical input	Chemical conversion
Geometric solidification	Cure depth, thickness, feature formation	Macroscopic solidification boundary	Uniform network state
Chemical conversion	FTIR/Raman/NMR functional-group change	Consumption of selected reactive groups	Residual-species identity or mechanics by itself
Network/property evolution	Modulus, shrinkage, stress, Tg, RI	Consequences of network formation	Unique conversion value without calibration
Residual/leachable chemistry	Chromatography/extraction	Mobile chemical species under stated extraction	Spatial conversion map

Table 1. Distinct quantities in VPP curing.

3. Degree of conversion is a method-defined measurand

Spectroscopic conversion is normally derived from the change of a reactive-band signal relative to an internal reference or baseline. The result depends on spectral assignment, sampling depth, optical geometry, normalisation, specimen thickness and whether the method probes one surface, a bulk path or a local voxel. A reported conversion percentage is therefore incomplete without the analytical method and calculation. Raman and FTIR can both be useful, but they should not be assumed numerically interchangeable without method-specific validation.

Fritschen et al. used Raman spectroscopy to quantify post-treatment-dependent crosslinking/conversion in DLP-printed resin systems, illustrating how solvent extraction and extended UV treatment alter the final printed state [3]. More broadly, simultaneous in-situ photopolymer measurements show that conversion, shrinkage, stress and viscoelastic evolution can develop on different trajectories even within one formulation [4]. Inline NMR monitoring provides another route for observing reaction progress under controlled light-intensity variation, but its sampling geometry and conversion definition remain method-specific [5].

4. Spatial heterogeneity is intrinsic to light-based curing

Light intensity changes with depth because of absorption, scattering and optical boundary conditions. Laterally, projected intensity, pixel spread, feature adjacency and oxygen access can produce different histories. Consequently, one surface spectrum or one bulk average can conceal gradients. The relevant spatial dimension depends on the question: through-thickness conversion for layer bonding, lateral conversion near a microfeature boundary, or full-field evolution during an exposure.

In-situ interferometric curing monitoring provides a complementary route because refractive-index evolution can be mapped over the projected field without repeatedly extracting the specimen [1]. The method is indirect and therefore requires calibration/validation against chemical conversion, but it demonstrates the feasibility of resolving curing dynamics spatially and temporally rather than treating a layer as one scalar state.

5. Post-cure creates a second material state

The as-printed green part and the final post-cured part should be treated as separate material states. Additional irradiation can raise conversion, alter network mobility, reduce or redistribute residual reactive groups and change mechanical/thermal properties. A conversion study should therefore state whether the measurement is in-resin, immediately after printing, after washing, after post-cure or after conditioning. Comparing samples at different states without naming them can create false formulation effects.

6. Conversion-property coupling is real but not one-to-one

Conversion influences network formation, but equal conversion values do not guarantee equal crosslink topology, modulus, shrinkage or residual stress. Sarkar et al. demonstrated simultaneous changes in conversion, polymerisation stress, temperature and shrinkage and used them to infer evolving relaxation behaviour and crosslink heterogeneity [4]. The engineering implication is that conversion is an essential state variable, not a universal predictor of every final property.

Block	Minimum information	Reason	Claim boundary
Light field	Wavelength/spectrum, irradiance method, exposure, geometry	Defines optical input	Time alone is insufficient
Resin state	Composition class, age, temperature, oxygen condition	Controls kinetics	No cross-formulation inference
Sampling	Location, depth, thickness, orientation, spatial resolution	Defines sampled volume	One point is not a full-field map
Spectroscopy	Method, bands, reference, baseline, calculation	Makes conversion reproducible	Percent conversion is method-dependent
Process state	As-printed, washed, post-cured, conditioned	Separates manufacturing states	No mixing of states
Replicates/uncertainty	n, variability, calibration or validation	Quantifies confidence	Single trace is feasibility only
Property link	Matched mechanical/thermal/optical test where claimed	Tests conversion-property coupling	Correlation is not universal causation

Table 2. Minimum reporting framework for conversion studies.

7. 3Dresyns implementation examples

Fine Tuner FT1 Bio is a current manufacturer-documented photoaccelerant for increasing cure speed over a defined UV/visible wavelength range. It illustrates how a formulation variable can change photoreactivity, but product positioning does not establish a degree-of-conversion value, conversion gradient or final-property gain without measurement on the complete resin-process state [M1].

Fine Tuner LB1 Bio is a manufacturer-documented light-blocking and resolution modifier. It illustrates the distinction between optical confinement and chemical conversion: reducing cure depth or light spread does not by itself quantify conversion inside the retained solid [M2].

The 3Dresyns Curing Rate Table (CRT) system provides empirical cure-depth versus exposure information for process calibration. CRT data are geometric/process-control data and should not be relabelled as spectroscopic degree-of-conversion measurements. Conversion metrology can complement CRT when the scientific question concerns network state rather than printability alone. [M3]

Source basis: current 3Dresyns controlled product and process documentation, August 2026. The examples are included to connect the metrology framework to implementation and are not independent scientific evidence.

8. Conclusions

- Exposure, cure depth, degree of conversion and final properties are related but non-equivalent quantities.
- Conversion values require a defined spectroscopic or otherwise validated measurement procedure.
- Spatial and temporal heterogeneity can be hidden by single-point or bulk-average measurements.
- As-printed and post-cured parts are different material states and should be reported separately.
- Working-curve/CRT calibration and conversion metrology are complementary rather than interchangeable.
- Conversion-property claims should be tested with matched specimens under the same process and conditioning state.

Limitations

This review is a focused engineering synthesis, not a systematic review. Conversion methods differ in sampling volume, spectral assignment and calibration, so numerical conversion values are not pooled across studies. The review excludes biological interpretation of residual/leachable species and does not disclose proprietary 3Dresyns formulations or dosage guidance.

Author contributions

Juan Segurola: conceptualisation, literature synthesis, engineering framework, writing and critical review.

Competing interests

The author is affiliated with 3Dresyns by Resyner Technologies S.L. Commercial 3Dresyns materials are identified only as implementation examples supported by controlled product documentation. They are not treated as independent peer-reviewed evidence and no proprietary formulation composition is disclosed.

Data availability

No new experimental dataset was generated for this review. Scientific statements are attributed to the cited literature; commercial examples are separated from the independent evidence base.

Company information

Legal company name: 3Dresyns by Resyner Technologies S.L. Registered tax address: General Etxague 15B, 20003 Donostia / San Sebastián, Gipuzkoa, Spain VAT number: ESB24827511 Contact email: info@3Dresyns.com Company website: www.3Dresyns.com

References

- [1] Y. Zhang, H. Zhang, X. Zhao, In-situ interferometric curing monitoring for digital light processing based vat photopolymerization additive manufacturing, *Additive Manufacturing* 81 (2024) 104001. DOI: 10.1016/j.addma.2024.104001.
- [2] Y. Zhang, A. Nooner, S. Velankar, D. Hershner, S. Li, J.J. Schwartz, X. Zhao, Toward wavelength-selective vat photopolymerization: combined in situ interferometry and Raman characterization of a candidate single-monomer resin system, *Polymer Chemistry* (2026). DOI: 10.1039/D6PY00410E.
- [3] A. Fritschen, A.K. Bell, I. Königstein, L. Stühn, R.W. Stark, A. Blaeser, Investigation and comparison of resin materials in transparent DLP-printing for application in cell culture and organs-on-a-chip, *Biomaterials Science* 10 (2022) 1981-1994. DOI: 10.1039/D1BM01794B.
- [4] S. Sarkar, P.J. Baker, E.P. Chan, S. Lin-Gibson, M.Y.M. Chiang, Quantifying the sensitivity of the network structure and properties from simultaneous measurements during photopolymerization, *Soft Matter* 13 (2017) 3975-3983. DOI: 10.1039/C7SM00419B.
- [5] G.D. Ammini, J.P. Hooker, J. Van Herck, A. Kumar, T. Junkers, Comprehensive high-throughput screening of photopolymerization under light intensity variation using inline NMR monitoring, *Polymer Chemistry* 14 (2023) 2708-2716. DOI: 10.1039/D3PY00190C.

Manufacturer documentation

- [M1] 3Dresyns, Fine Tuner FT1 Bio, TDS-FT1-BIO-EN v1.0, manufacturer product documentation, accessed 20 August 2026. <https://www.3dresyns.com/products/fine-tuner-ft1-bio-biocompatible-photo-accelerant-up-to-410-nm>
- [M2] 3Dresyns, Fine Tuner LB1 Bio, manufacturer product documentation, accessed 20 August 2026. <https://www.3dresyns.com/products/fine-tuner-lb1-bio-biocompatible-resolution-increaser-for-improving-resolution>
- [M3] 3Dresyns, Curing Rate Tables (CRT) — Calibration Data System, manufacturer process documentation, accessed 20 August 2026. <https://www.3dresyns.com/products/curing-rate-tables-crt-calibration-data-system>

Copyright

© 2026 Juan Seguro. All Rights Reserved.