

Material Operating Windows in Tomographic Volumetric Additive Manufacturing: Gelation Criteria, Inhibition Reserve, Optical Transport and Exposure Drift

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Statement of Significance

Tomographic volumetric additive manufacturing does not operate at one transferable resin threshold. It operates inside a system-specific separation window between the least-exposed target location and the most-exposed background location, while inhibition, optical transport, rheology and resin history influence the conversion and gelation response. This review defines a qualification architecture for that material operating window and separates dose-field reconstruction from evidence that the resin has gelled, developed recoverable green strength and remained stable across batches and reuse states.

Keywords: tomographic volumetric additive manufacturing; volumetric photopolymerisation; material operating window; gelation criterion; oxygen inhibition; dose margin; optical transport; scattering; resin history; exposure drift; qualification.

Abstract

Tomographic volumetric additive manufacturing forms a three-dimensional object by accumulating projected exposure throughout a resin volume. The geometry is reconstructed optically, but the decision to remain liquid, gel or become a recoverable green body is made by the material. This review treats tomographic VAM as a material-window problem rather than as a single threshold-dose problem. It distinguishes conversion onset, operational gelation and green-part recovery; defines the minimum target exposure, maximum background exposure and criterion-specific gel exposure needed to describe dose separation; and introduces normalised target margin, background reserve and combined exposure-window descriptors as reporting aids rather than standards. The framework then links these quantities to inhibitor and oxygen state, intensity-time history, absorption, scattering, refraction, rheology, sedimentation, thermal state, resin reuse and adaptive exposure control. Algorithmic correction and closed-loop feedback can reshape the delivered dose field or compensate for drift, but they do not replace formulation qualification or establish that a nominally identical resin state is stable. A minimum qualification matrix is proposed for resin identity, photochemical response, optical transport, reconstructed field, motion stability, green recovery, final conditioned properties, batch variation and uncertainty. Existing 3Dresyns volumetric-manufacturing documentation is treated only as implementation context. No current product label or successful print is interpreted as evidence of a universal gel threshold or transferable tomographic operating window.

1. Scope and evidence boundary

This review is restricted to integrated-dose tomographic volumetric additive manufacturing. In this architecture, a sequence of angular projections deposits a three-dimensional exposure field and the resin discriminates target from non-target regions through its response to the accumulated local optical history [1,2]. The paper does not review machine architectures, projection algorithms or reconstruction mathematics as independent subjects. It considers them only to the extent that they determine the exposure field presented to the resin.

Dual-wavelength xolography and two-photon polymerisation are excluded from the technical core because their spatial selectivity is generated by different mechanisms. The separate Perspective, Spatial Selectivity Mechanisms in Volumetric Photopolymerisation, compares those mechanisms. ER-75 instead asks a narrower qualification question: under a declared tomographic system and resin state, what evidence demonstrates a positive and reproducible separation window between target gelation and background cure?

Scientific statements derive from the cited peer-reviewed literature. ISO/ASTM documents are used only for terminology and geometric-capability context. RP-02 supplies the shared evidence-to-decision conventions for the Engineering Review series. Manufacturer documentation is segregated and is not treated as independent scientific validation.

2. Threshold language must identify the measured event

The word threshold is often used as though one scalar dose separated liquid from solid. Photopolymerisation does not provide one method-independent event. Detectable conversion can precede network percolation; gelation can precede sufficient green strength for recovery; and a recoverable part can still possess spatially heterogeneous conversion, residual monomer or inadequate final properties. The result depends on the observable, criterion, irradiance, temperature, oxygen and inhibitor state, optical path and resin history [6-8].

ER-75 therefore requires every threshold claim to identify the event that was measured. A fluorescence or scattering onset is not automatically a gel point. A rheological crossover is an operational criterion whose frequency and acquisition conditions must be reported. Visual recovery of an object is a handling result, not a conversion measurement. Final mechanical performance belongs to the conditioned part and cannot be inferred from any of these earlier events.

Table 1. Distinct events that are often compressed into one threshold claim

Event	Minimum declared criterion	What it establishes	What it does not establish
Photochemical induction end	Signal departs from the dark or inhibited baseline under a stated intensity-time history.	The formulation has begun a measurable reaction or optical change.	Network connectivity, green strength or final conversion.
Conversion onset	Spectroscopic or calorimetric signal exceeds a defined detection and uncertainty limit.	A monitored functional group is reacting.	Gelation or spatially uniform mechanics.
Operational gelation, H _{g,c}	Declared rheological, mechanical or extraction criterion c under stated conditions.	A continuous network is assigned by that criterion.	Recoverability, final modulus or low extractables.
Green recovery, H _{green}	Object survives a defined removal, drainage and handling sequence.	The printed geometry has usable early integrity.	A valid gel point, final dimensional stability or service performance.
Final conditioned state	Declared wash, post-cure, ageing and conditioning followed by a specified test.	The property of the delivered state under the stated method.	A transferable VAM operating window for another process or resin state.

3. Reconstructed exposure field and material separation window

Tomographic reconstruction predicts or estimates a local actinic exposure field. The field may be expressed as incident exposure, absorbed exposure or a model-derived dose-like quantity. These are not interchangeable. ER-75 uses H only after the report states how it was obtained, including wavelength band, irradiance calibration, optical model, vessel geometry, refraction treatment and whether absorption or scattering was incorporated [1,2,4].

For a selected gelation criterion c and a frozen resin state, define H_{g,c} as the local exposure assigned to that gelation event under the same intensity-time and environmental conditions used for printing. Define H_{t,min} as the lowest reconstructed local exposure within the target volume and H_{b,max} as the highest reconstructed local exposure outside the target volume after the complete projection sequence.

$$m_t = H_{t,min} / H_{g,c} - 1$$

$$r_b = 1 - H_{b,max} / H_{g,c}$$

$$W_H = \min(m_t, r_b)$$

The normalised target margin m_t is positive when the least-exposed target location exceeds the declared gel exposure. The background reserve r_b is positive when the most-exposed non-target location remains below it. W_H is the smaller of the two margins. These quantities are proposed reporting aids, not standardised material constants. They are valid only for the declared criterion, intensity-time history, temperature, atmosphere, optical model, resin batch and history state. A positive W_H does not prove adequate green strength, dimensional fidelity or final properties.

The separation problem is stricter than maximising a target-to-background ratio. Both sides must be referenced to a measured material event. A high ratio can still fail if the target remains below gelation; a low background can coexist with insufficient target network development; and an apparently positive static window can close during the print if optical or chemical state changes.

4. Inhibition reserve and intensity-time history

Oxygen and added inhibitors consume initiating or propagating radicals and can delay the rise in polymerisation rate. This delay can contribute to a nonlinear response that assists target-background discrimination, but it is not a free or invariant threshold. Oxygen concentration, headspace, vessel permeability, waiting time, mixing, fill level, temperature and irradiance all influence the induction period and subsequent conversion [7].

A dose value alone is therefore insufficient whenever reciprocity has not been established. Two exposure histories with equal integrated H can generate different radical concentrations, oxygen depletion histories, thermal excursions and network states. Reports should preserve irradiance and time separately, record the full projection duration, and state whether the resin was pre-equilibrated in air, inerted, degassed or deliberately oxygenated.

For a declared signal and intensity, H_{ind} may be reported as the integrated exposure at the end of the operational induction period. The ratio $H_{ind}/H_{g,c}$ can describe how much of the criterion-specific gel exposure occurs before the monitored response leaves the inhibited regime. It must not be treated as a universal inhibitor-content measurement, because the same formulation can produce a different ratio when intensity, geometry or oxygen transport changes.

5. Gelation, post-gel conversion and green-part recovery

Gelation establishes network continuity, but it does not guarantee that an object can be removed from the surrounding liquid. Post-gel conversion develops stiffness while mobility progressively decreases. A tomographic projection sequence must therefore provide enough target exposure not only to cross an assigned gel criterion but also to create a spatially continuous green body that survives the defined recovery operation [1,2,8].

The distinction is particularly important near thin features and internal channels. A local voxel may satisfy a spectroscopic or rheological gel criterion while the connected geometry remains too weak to resist drainage, buoyancy, handling or capillary forces. ER-75 therefore requires a separate H_{green} or equivalent process-specific recovery endpoint. The recovery test should declare waiting time, drainage orientation, removal method, temperature, cleaning contact and the minimum feature set used to judge survival.

Additional target exposure can improve green strength but also reduces background reserve. The optimisation objective is not maximum conversion during projection. It is a positive material window that gives sufficient target network development while maintaining non-target removability and the required geometry. Final post-cure can complete conversion after recovery, but it cannot restore geometry already lost through background gelation or inadequate green strength.

6. Optical transport is part of the material state

The computed projection sequence reaches the resin through a vessel and a wavelength-dependent optical path. Refraction at the container, absorption by the formulation, scattering from particles or phase heterogeneity, and changes in refractive index during cure alter the relation between commanded intensity and local actinic exposure [2,4,9]. The material window must therefore be tied to an optical state rather than to nominal projector settings.

Inverse-rendering and differentiable optical models can account for vessel refraction and scattering and can improve the delivered field [4]. Adaptive projection can update the exposure sequence as the print evolves [5]. These are powerful system controls, but they do not convert unknown optical properties into a validated material. The input spectra, refractive index, attenuation coefficients or empirical transmission maps and their uncertainty still need to be measured for the actual resin state.

Filled, pigmented, phase-separating or high-refractive-index formulations require additional controls. Scattering can redistribute exposure into non-target regions; absorption can starve deep target locations; and sedimentation can change both effects during the projection sequence. Silica-glass VAM illustrates that highly loaded formulations can be processed, but only through a formulation and optical workflow designed for that material system rather than by transferring a neat-resin threshold [9].

Table 2. Variables that couple the reconstructed field to the material response

Domain	Required record	Risk if omitted
Actinic source	Spectrum, irradiance calibration, temporal sequence, polarisation if relevant, and measurement plane.	Nominal power is mistaken for local exposure.
Vessel and immersion path	Material, wall thickness, curvature, refractive index, fill height and external medium.	Refraction and interface losses are assigned to resin chemistry.

Domain	Required record	Risk if omitted
Resin optical state	Absorption, transmission, scattering or empirical field map at the print temperature and history state.	Target and background doses are reconstructed from the wrong medium.
Dynamic optical change	Evidence for photobleaching, darkening, phase change, index change or cure-induced scattering during the print.	A static calibration is applied after the optical state has moved.
Spatial model	Algorithm version, voxel grid, interpolation, refraction/scattering assumptions and uncertainty.	Software output is treated as measured absorbed dose.
Validation geometry	Through-volume features, internal voids, thin walls and positions spanning the build volume.	A central bulk object masks edge and depth failure.

7. Rheology, motion and residence-time stability

Tomographic VAM exposes a volume over a finite interval while the container rotates or the projected field changes. Density gradients, sedimentation, buoyancy, convection, surface motion and viscoelastic relaxation can therefore alter the composition or position of the material during exposure. Rheology is not only a recoating variable, because there is no layer-by-layer recoating step; it is a stability variable over the full exposure and recovery interval.

Loterie and co-workers reported no significant sedimentation for resins above 10 Pa s during a 20 s manufacturing interval in their specific system [2]. That result must not be converted into a universal minimum viscosity. Required viscosity or yield behaviour depends on particle size and density, temperature, rotation, exposure time, geometry and the allowable displacement. A low-viscosity neat resin may remain stable, whereas a filled formulation with the same viscosity may segregate.

The report should therefore state viscosity or a relevant flow curve at print temperature, thixotropic history where applicable, density, particle or dispersed-phase information, dwell before exposure, total exposure time and any evidence of spatial composition drift. Stability should be assessed over the maximum intended vat-residence period, not only over one fast demonstration print.

8. Resin history and exposure drift

Nominal formulation identity does not guarantee an unchanged operating window. Reuse can change oxygen content, inhibitor state, dissolved photoproducts, temperature, contamination, water content and optical transmission. Automatic-exposure work reported approximately forty percent variation in the exposure time required between operating sessions, with resin history and reuse identified as important contributors [3]. This is evidence that the state variable is the prepared resin system, not only the recipe name.

Each qualification run should carry a resin-state identifier that includes batch, age, storage, opening history, prior illumination, reuse count or cumulative exposure, filtration, replenishment, temperature, atmosphere and time in the vessel. A threshold curve measured on fresh resin should not be applied automatically to a reused volume. If material is blended or topped up, the mass fractions and mixing history should be recorded.

A simple history-retention descriptor may be reported as $R_H(k) = H_{g,c}(k)/H_{g,c}(0)$, where k identifies a declared reuse or ageing state. Values above or below one indicate movement of the criterion-specific gel exposure relative to the fresh baseline. R_H is not a stability conclusion by itself; the optical state, green recovery and final properties must also remain within their release criteria.

9. Adaptive exposure and closed-loop control boundary

Sensor-based exposure control can detect evolving scattering or other process signatures and adapt the projected sequence [3,5]. Closed-loop control can enlarge the practical operating region by compensating for measurable drift. It must nevertheless be reported as part of the process definition: sensor type, observable, calibration, sampling rate, control law, permitted correction range and final applied exposure history.

A controller can also mask an unstable resin by repeatedly correcting for changing response. Successful adaptation therefore does not demonstrate material stability. Qualification should report both the uncontrolled material drift and the corrected outcome, or otherwise provide a bounded baseline showing that the controller operates within a validated

compensation range. ER-71 addresses in-situ monitoring and closed-loop process control; ER-75 treats feedback only as one input to the realised material window.

10. Minimum qualification architecture

A material operating window should be released only after the resin, optical system, reconstructed field and recovered object have been linked by a common state record. The following matrix is a minimum architecture, not a universal test standard.

Table 3. Minimum evidence architecture for a tomographic VAM material window

Domain	Minimum record or measurement	Required conclusion
Resin identity	Controlled formulation/version, batch, storage, age, water content where relevant, inhibitor and photoinitiator identity at the permitted disclosure level.	The material state can be reproduced and distinguished from adjacent versions.
Actinic response	Intensity-resolved induction, conversion and criterion-specific gel response at print temperature and atmosphere.	$H_{g,c}$ and H_{ind} belong to the declared intensity-time regime.
Green recovery	Defined object-removal test and H_{green} or equivalent endpoint.	Target exposure creates connected recoverable geometry, not only local reaction.
Optical state	Spectrum, transmission/absorption, scattering or empirical field map, refractive index and vessel path.	Commanded projections can be related to a bounded local exposure field.
Field separation	$H_{t,min}$, $H_{b,max}$, $H_{g,c}$, m_t , r_b and W_H with model and uncertainty.	Target and background are separated relative to a measured material event.
Motion stability	Rheology, density, temperature, exposure time and spatial-composition check.	The material does not move or segregate beyond the allowed limit.
History stability	Fresh and declared reuse/ageing states, including R_H and optical change.	The released window remains valid over the intended material-history range.
Geometric verification	Through-volume artefact with internal and external features, registered to CAD.	The window produces spatial fidelity throughout the intended build region.
Final state	Wash, post-cure and conditioning followed by dimensional and application-relevant property tests.	Green success is not substituted for delivered-part qualification.
Reproducibility	Replicates, batches, sessions, uncertainty and failed-build accounting.	The release decision is not based on one successful demonstration.

11. Reporting descriptors and their limits

The descriptors below are proposed as compact reporting aids. They do not replace response curves, spatial maps or uncertainty and are not asserted as standards.

- $H_{g,c}(I,T,O_2,S)$: criterion-specific gel exposure at irradiance I , temperature T , oxygen/atmosphere state O_2 and resin-history state S .
- H_{green} : minimum local or system exposure associated with survival of a declared recovery operation. The mapping from local field to object recovery must be stated.
- m_t and r_b : normalised target margin and background reserve relative to $H_{g,c}$.
- $W_H = \min(m_t, r_b)$: the limiting exposure-separation margin for the declared field and criterion. Positive W_H is necessary but not sufficient for release.
- $R_H(k)$: ratio of criterion-specific gel exposure in a declared history state k to the fresh baseline. It describes drift, not overall material retention.

All descriptors should be accompanied by the complete field distribution or appropriate percentiles. Extreme minima and maxima can be sensitive to numerical noise, segmentation and isolated voxels; the method used to define the target and background sets must therefore be stated. For production decisions, local feature classes and critical regions may need separate margins rather than one whole-volume scalar.

12. Failure modes and interpretation errors

Table 4. Common failures in tomographic VAM material-window claims

Observation	Interpretation error	Required response
One cuvette cure threshold is repeatable	A universal resin threshold is declared.	State the criterion, intensity, geometry, atmosphere and optical path; validate in the tomographic system.
Spectroscopic conversion begins	Gelation is claimed.	Measure or justify a network-connectivity criterion.
A shape is visible in the vat	Green recovery is assumed.	Apply a defined removal and handling test.
Target/background dose ratio is high	A positive material window is assumed.	Reference $H_{t,min}$ and $H_{b,max}$ to $H_{g,c}$ and report both margins.
Equal integrated dose gives different results	Measurement error is assumed.	Test intensity-time reciprocity, oxygen depletion and thermal history.
Static optical calibration fits the first print	Optical state is treated as invariant.	Measure or monitor cure-induced and history-induced optical change.
Adaptive control produces a good object	The resin is called stable.	Report controller action and independently bound material drift.
High viscosity prevents one sedimentation event	A universal viscosity requirement is claimed.	Relate stability to particles, density, temperature, motion and exposure time.
Fresh and reused resin share a product code	The same threshold is applied.	Assign history states and remeasure the operating window.
Final part passes one property test	The VAM window is transferred to another machine or geometry.	Requalify the optical field, criterion, recovery and critical feature set.

13. Scope boundaries within the Engineering Review series

- Spatial Selectivity Mechanisms in Volumetric Photopolymerisation compares integrated-dose, dual-wavelength and nonlinear selectivity mechanisms. ER-75 does not repeat that architecture comparison and is restricted to qualification of the tomographic integrated-dose material window.
- ER-27 addresses conversion metrology and spatial cure heterogeneity. ER-75 uses conversion only as one state variable and requires separate gelation and recovery endpoints.
- ER-30 addresses oxygen inhibition at free and interfacial surfaces. ER-75 treats inhibition only as one contributor to whole-volume tomographic dose discrimination.
- ER-32 addresses vat ageing, reuse and state drift across VPP. ER-75 applies those controls to movement of a tomographic gel and exposure window.
- ER-36 addresses rheology, recoating and dispersion control of filled suspensions. ER-75 uses rheology only to qualify motion and composition stability during volumetric exposure.
- ER-61 addresses gelation, vitrification and mobility arrest. ER-75 imports a declared gel criterion but does not redefine network-state metrology.
- ER-71 addresses in-situ monitoring and closed-loop process control. ER-75 records controller action only to distinguish corrected performance from intrinsic material stability.
- Xolography and two-photon polymerisation are excluded because their selectivity is not generated by the same integrated-dose field.

14. 3Dresyns implementation boundary

The current 3Dresyns public page on volumetric additive manufacturing presents volumetric materials and system matching as formulation- and process-specific engineering work [M1]. That positioning is implementation context. It is not independent evidence of a universal tomographic gel threshold, exposure window or compatibility with every volumetric printer.

No current standard 3Dresyns product is identified in this review as independently qualified across machines by a published $H_{g,c}$, $H_{t,min}$, $H_{b,max}$ and W_H programme. Product labels, wavelength labels, cure-speed descriptions, viscosity values or successful example prints must not be converted into a transferable tomographic operating-window claim.

A future product-specific claim would require, at minimum:

- a controlled resin identity and version;
- the exact tomographic machine, vessel, wavelength distribution and irradiance calibration;
- temperature, atmosphere, fill level and resin-history state;
- criterion-specific induction, conversion, gelation and green-recovery data;
- optical transport and reconstructed-field validation through the intended build volume;
- target margin, background reserve and uncertainty for representative critical geometries;
- reuse, batch and session stability;
- post-processing, dimensions and final-property qualification.

A made-to-order or customised formulation would remain system-specific until those controls were completed for the selected printer and workflow. Manufacturer development data should be labelled as such until independently published or externally validated.

15. Design rules

- Define the measured event before using the word threshold.
- Preserve irradiance and time separately until reciprocity is demonstrated.
- Reference target and background exposures to the same criterion-specific gel state.
- Measure green recovery separately from gelation and final properties.
- Treat the vessel, optical path and resin as one optical system.
- Record cure-induced and history-induced optical change.
- Qualify motion and composition stability over the complete exposure and vat-residence interval.
- Assign an explicit resin-history state to every threshold and print.
- Report adaptive-control action rather than presenting the corrected result as intrinsic material stability.
- Use through-volume validation geometries and include internal voids and thin features.
- Report uncertainty and failed builds, not only the best object.
- Rebuild the window after any formulation, vessel, machine, wavelength, temperature or recovery change.

16. Research priorities

The first priority is a reproducible, intensity-resolved assignment of gelation and green-recovery criteria under tomographic illumination rather than a transferred layer-wise working curve. The second is dynamic optical characterisation that links evolving transmission, scattering and refractive index to the actual projection sequence. The third is interlaboratory comparison of target and background margins using shared geometries and declared uncertainty.

Further work is needed on history-dependent chemistry, especially oxygen and inhibitor re-equilibration, photoproduct accumulation, water uptake, temperature and reuse. For filled or phase-structured formulations, motion, sedimentation and optical-state evolution should be measured together. Closed-loop control studies should report the correction authority consumed by the material drift so that robust control is not confused with a stable resin.

17. Conclusions

Tomographic volumetric additive manufacturing is governed by a coupled optical and material separation problem. Projection algorithms define a candidate exposure field; the resin determines whether each location remains liquid, crosses a declared gel criterion or develops recoverable green strength.

A single threshold-dose value cannot represent this system. The minimum target exposure, maximum background exposure and criterion-specific gel exposure must be reported together, with intensity-time history, atmosphere, optical state, rheology and resin history. The proposed target margin, background reserve and W_H descriptors make the limiting side of the window visible but do not replace full maps, response curves or uncertainty.

The central engineering principle is: a tomographic reconstruction is qualified only when the realised exposure field and the measured material-state transitions remain separated across the intended volume, geometry, history and recovery workflow.

Limitations

This review is a literature-based engineering synthesis and does not report a new experimental dataset or a quantitative meta-analysis. Source studies use different machines, resins, optical models, exposure definitions and success criteria. Numerical values are retained only when tied to the source-specific system and are not proposed as transferable targets.

The descriptors m_t, r_b, W_H and R_H are proposed reporting aids. They have not been standardised or validated through an interlaboratory study. No current international standard is identified here as defining a tomographic VAM gel threshold, background-dose reserve or material operating window. ISO/ASTM 52900 supplies terminology and ISO/ASTM 52902 supplies geometric-capability context, not a material-window method.

The public 3Dresyns page was reviewed as manufacturer implementation context on 22 August 2026. Product content can change and must be rechecked at the date of any release. No product or regulatory suitability claim is made.

Declarations

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. Manufacturer documentation is separated from peer-reviewed evidence and is not presented as independent validation.

Data availability: No new experimental dataset was generated for this review.

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Standards and series framework

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