

Single-Vat Multimaterial Vat Photopolymerisation by Photochemical Addressing

Wavelength Selectivity, Dose Encoding, Reaction Orthogonality and Crosstalk

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Statement of Significance

Single-vat multimaterial vat photopolymerisation replaces physical resin exchange with controlled photochemical addressing. Its central engineering problem is not whether two visibly different regions can be printed, but whether each commanded optical input creates the intended material state while suppressing unintended activation of every competing state. This review defines a route-neutral qualification architecture based on selectivity matrices, dose-state response surfaces, spatial crosstalk measurements and independent chemical and property verification. It deliberately excludes transferable formulation recipes and universal exposure settings.

Abstract

Multimaterial vat photopolymerisation can encode distinct polymer states within one liquid formulation by changing wavelength, dose or the photochemical pathway activated at each location. Direct primary studies demonstrate three relevant strategies: wavelength-selective radical and cationic curing from a multicomponent resin [1], grayscale control of local conversion and mechanical state in a single-cure resin [2], and dose-triggered switching between polymerisation mechanisms reported through a photobuffer-mediated system [3]. A recent hybrid epoxy–acrylate study further reports dual-projection fabrication of hard and soft domains from one resin [4]. These demonstrations do not by themselves establish robust material identity, reaction orthogonality or transferable process windows. ER-197 therefore treats multimaterial addressing as a classification and verification problem. It defines the commanded optical state, measured delivered excitation, reaction response, final material state and spatial location as separate quantities. A selectivity matrix records intended and unintended responses for every command–state pair. Qualification requires chemical evidence of reaction allocation, spatial measurement of crosstalk, property verification at homogeneous states and interfaces, and challenge conditions near decision boundaries. The method is intentionally non-prescriptive: no initiator identity, concentration, absorber loading, inhibitor level, exposure threshold or resin composition is proposed. The result is a defensible way to determine whether a one-vat or one-pot system is genuinely multimaterial rather than merely dose-varied or incompletely cured.

Keywords: vat photopolymerisation; multimaterial printing; wavelength selectivity; dose encoding; reaction orthogonality; crosstalk; selectivity matrix; grayscale DLP; qualification

1. Scope and controlling identity

ER-197 owns only photochemical material-state addressing, selectivity matrices, unwanted co-activation and proof of reaction orthogonality in single-vat or one-pot multimaterial VPP. This is the controlling ownership statement fixed by the author-countersigned sequence amendment and accepted consolidated allocation.

The following boundaries are binding. ER-004 retains spatial selectivity mechanisms in volumetric photopolymerisation. ER-043 retains interfaces and functionally graded networks after distinct material states have been created. ER-058 retains dual-colour photoinitiator design space for xolography. ER-077 retains

long-wavelength and superlinear photoinitiation, action spectra, photon upconversion and curing contrast. ER-197 does not reproduce those subjects and does not provide a formulation recipe.

2. What counts as a distinct material state

A change in colour, local conversion or modulus is not automatically a distinct material identity. The claim must declare what differs and how that difference is measured. Candidate state variables include reaction pathway, network composition, crosslink topology, conversion, glass transition, modulus, swelling response, transport response or another application-linked property.

Three levels should be separated:

1. **Optical command:** the wavelength band, dose or sequence requested by the print file.
2. **Chemical state:** the reactions and network components actually produced.
3. **Engineering state:** the resulting property distribution under a declared conditioning and measurement protocol.

Calling the output “multimaterial” is strongest when optical commands lead to chemically distinguishable networks and independently verified engineering states. A continuous conversion gradient within one reaction family may still be useful, but it should be described as dose-programmed property variation unless a defensible material-identity criterion is met.

3. Three addressing architectures

3.1 Wavelength-selective pathway activation

Schwartz and Boydston demonstrated a multicomponent resin containing acrylate and epoxide monomers with corresponding radical and cationic initiators [1]. Visible irradiation preferentially cured the acrylate component, whereas shorter-wavelength ultraviolet irradiation activated both reaction families. Chemical analysis, gel fraction and mechanical testing were used to distinguish the resulting states. The study establishes that wavelength can act as a material-state command, but it also shows that practical selectivity is asymmetric: one command may preferentially activate one pathway while another activates more than one.

3.2 Dose-encoded conversion and property

Yue et al. used local grayscale intensity to control degree of cure in a single-vat, single-cure system [2]. The printed regions spanned soft and stiff states from the same formulation. This is direct evidence that dose can encode a local engineering response. It is not, by itself, proof of reaction orthogonality because the principal controlled variable is conversion within a common resin chemistry.

3.3 Dose-triggered switching between pathways

The official abstract of Ma et al. reports a different dose architecture: a photobuffer suppresses cationic polymerisation at lower exposure, then becomes saturated at higher exposure so that acid generation activates the second pathway [3]. Because only the official abstract and supplementary record were directly available in the present source set, ER-197 uses this study only to establish the existence of the reported architecture. It does not reproduce compositions, thresholds or performance values from it.

These architectures should not be collapsed. Wavelength selection, dose-dependent conversion and dose-triggered pathway switching create different qualification burdens and different failure modes.

4. The selectivity matrix

For optical commands C_i and candidate material states S_j , define the measured response in each matrix cell as $R_{ij} = M(S_j | C_i)$, where M is a declared chemical or physical measurement, not a nominal exposure setting. Diagonal entries represent intended response and off-diagonal entries represent co-activation. A useful selectivity statement therefore requires both:

- adequate response of the intended state; and

- bounded response of every unintended state.

The matrix must be built at the relevant spatial scale and after the declared post-processing state. A two-command system requires at least four measured command–response cells, not two successful coupons. If commands are sequential, order becomes an additional matrix dimension because the first exposure can alter absorption, diffusion, mobility or reactivity during the second.

No universal numerical acceptance ratio is proposed. The acceptable separation depends on the claimed material distinction, measurement uncertainty and application consequence.

5. Delivered excitation rather than nominal settings

Nominal wavelength, grayscale and exposure time are commands. The resin experiences a spatially distributed spectral irradiance integrated over time, modified by optics, attenuation, scattering, prior conversion and geometry. Qualification therefore records, as far as practicable:

- spectral distribution for each optical channel;
- irradiance and dose at the build plane under the declared geometry;
- spatial registration between channels or grayscale pixels;
- temporal sequence and delay between commands;
- layer thickness and cumulative exposure from neighbouring layers; and
- the optical state of the resin as conversion proceeds.

The dual-projector method in [1] required explicit alignment and calibration of the two projected images. That observation is transferable as a control requirement, not as a prescription for a particular optical layout.

6. Wavelength selectivity is a system property

Spectral separation between initiators or photosensitisers is necessary but not sufficient. The operative selectivity depends on the entire formulation and process: absorption tails, concentrations, optical path length, competing absorbers, initiation efficiencies, propagation and termination kinetics, oxygen inhibition, conversion-dependent mobility and any continuing dark or thermal reaction.

Consequently, an absorbance spectrum alone cannot prove material selectivity. The evidence chain should connect delivered wavelength to reaction-specific conversion and then to the claimed material property. The hybrid epoxy–acrylate study of Kim et al. reports a covalently bound hybrid monomer and wavelength-selective sensitisation used for hard and soft domains [4]. In this review, that paper is cited only for the result stated in its official abstract because the complete publisher text was not directly available in the present source set.

7. Dose encoding is not a scalar lookup table

Dose is often written as irradiance multiplied by time, but equal nominal dose need not produce equal state when intensity, exposure sequence, oxygen replenishment, temperature or reaction kinetics differ. A qualification surface should therefore retain irradiance and time as separate controlled variables until reciprocity has been demonstrated over the claimed range.

For a dose-programmed system, the minimum evidence is a measured mapping from optical command to conversion and property, including uncertainty and transition regions. Yue et al. found a region in which properties became too sensitive to conversion for convenient control [2]. This illustrates why a dramatic property span is not equivalent to a wide, robust operating window.

Layerwise printing adds cumulative exposure. A region may receive its intended dose in one layer and unintended contributions through subsequent or neighbouring projections. The relevant input is therefore the exposure history of a voxel or material volume, not only the command assigned to its nominal layer.

8. Reaction orthogonality must be demonstrated

Two reaction families are orthogonal for the claimed process only if each commanded pathway can be activated with acceptably limited activation or interference of the other under the complete printing and post-processing sequence. Evidence may combine:

- reaction-specific spectroscopy or chemical analysis;
- gel fraction or selective swelling interpreted with appropriate controls;
- thermal or mechanical signatures linked to independently characterised states; and
- control specimens receiving each command, both commands, reversed order and no command.

Mechanical contrast alone cannot identify the reaction pathway uniquely. Different conversion, residual monomer, plasticisation or post-cure history can produce similar property differences. The chemical measurement and engineering measurement answer different questions and should not be substituted for one another.

9. Crosstalk has several forms

Crosstalk is any unintended response outside the commanded material state. At least four forms should be tested separately:

1. **Spectral crosstalk:** one optical channel activates a nominally non-target photochemical pathway.
2. **Dose crosstalk:** cumulative or scattered light moves a neighbouring region across a response boundary.
3. **Chemical crosstalk:** mobile initiators, acids, radicals, inhibitors or monomers migrate across the intended boundary.
4. **Process crosstalk:** post-cure, heat, washing or storage changes the contrast created during printing.

The 2019 MASC study reported that thermal processing could increase cationic conversion but also reduce multimaterial resolution [1]. This is an example of process crosstalk: a later operation can strengthen one state while eroding spatial distinction.

10. Spatial verification

A qualification artefact should contain homogeneous regions for every commanded state, isolated transitions, narrow features, repeated boundaries in multiple orientations and features placed at different build-field positions. Measurements should distinguish:

- command registration error;
- optical blur or scattering;
- chemically broadened transition zones;
- conversion and property gradients within nominally uniform regions; and
- post-processing changes in boundary position or contrast.

Reported resolution should state the measurand. Optical pixel pitch, chemical transition width and functional feature size are different quantities. The ownership and neighbouring boundaries stated in §1 govern this review.

11. Challenge conditions and robustness

Nominal successful prints are insufficient. The selectivity matrix should be challenged near the decision boundaries and across plausible variation in delivered excitation, resin state and geometry. Replication should include independent resin preparations and, where transfer is claimed, more than one build position or equipment instance.

Robustness is demonstrated when state classification remains correct within the declared uncertainty under those variations. It is not demonstrated by selecting one exposure pair after observing the result. A predeclared classification rule and blinded or automated evaluation reduce that risk.

12. What may remain proprietary

Scientific qualification does not require publication of a commercially actionable recipe. A public report can disclose:

- the addressing architecture;
- the state definitions and measurands;
- the experimental comparisons required;
- the form of the selectivity and crosstalk evidence; and
- the limitations and uncertainty of the conclusion.

It need not disclose component identities, concentrations, absorber packages, inhibitor levels, spectral tuning, exposure windows or compensation rules when those are proprietary. Withholding those details narrows reproducibility and transfer claims, so the article must not imply that an undisclosed formulation can be reconstructed or that its operating window is universal.

13. Minimum qualification claim set

A defensible single-vat multimaterial claim should state:

1. the optical commands and measured delivered excitation;
2. the chemical or structural criterion defining each state;
3. the engineering property criterion linked to each state;
4. every cell of the command–state selectivity matrix;
5. the spatial transition and crosstalk measurands;
6. the post-processing state at which classification is made;
7. uncertainty, replication and tested variation; and
8. the precise limits of transfer to other machines, geometries or resin states.

Without this set, a printed demonstration may establish feasibility but not qualified addressing.

14. Conclusions

Single-vat multimaterial VPP is best treated as a controlled mapping from optical commands to chemical states and from chemical states to engineering properties. Wavelength selection can address different reaction families [1], while grayscale dose can program conversion and mechanical state [2]. Emerging work reports both dose-triggered pathway switching [3] and hybrid wavelength-selective hard–soft printing [4], but the present review uses those two sources only within their directly available abstract-level evidence.

The key evidence object is a selectivity matrix that includes intended response and unwanted co-activation for every command–state pair. Reaction orthogonality requires chemical evidence; property contrast alone is insufficient. Spatial and process crosstalk must be measured after the complete exposure and post-processing history. This architecture supports rigorous qualification without publishing proprietary formulation or tuning details.

Related Engineering Review boundaries

The controlling ownership statement and all neighbouring boundaries are stated once in §1 and govern the whole review.

References

The accompanying source ledger maps S1 to reference [1], S2 to [2], S3 to [3] and S4 to [4].

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. The review intentionally withholds commercially actionable formulation and tuning details. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated. Source-access states and claim limits are recorded in the accompanying source ledger.

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