

Frontal Photopolymerisation in Additive Manufacturing: Ignition, Propagation, Heat Feedback, Stability and Geometric Control

A reaction-front qualification framework for distinguishing useful self-propagation from thermal runaway, quench and geometric loss

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Abstract

Frontal photopolymerisation replaces spatially repeated exposure with a self-propagating reaction zone sustained by reaction heat. That promise creates a qualification problem: ignition, propagation speed, peak temperature and heat loss are coupled, so a front that appears fast can also be compositionally nonuniform or geometrically unstable. This review separates ignition from sustained propagation, identifies the minimum thermal and conversion measurements needed to establish a stable front, and defines failure modes including quench, acceleration, fingering and overrun. The evidence base spans frontal-polymerisation fundamentals, phototriggered frontal systems and additive-manufacturing demonstrations.

Keywords: frontal photopolymerisation; additive manufacturing; ignition; heat feedback; propagation stability; geometric control

1. Significance and scope

Frontal photopolymerisation is useful only if a self-propagating reaction front can be ignited reproducibly and then remain thermally stable as geometry and boundary cooling change. The engineering significance is therefore the coupling between reaction heat, front velocity, conversion and shape retention rather than low external energy alone. Proprietary formulations and machine-specific tuning rules are outside scope.

1.1 Corpus boundary

ER-301 owns photo-initiated or photo-triggered frontal polymerisation as a coupled reaction-transport manufacturing mode. It excludes the general transient-thermal metrology owned by ER-204 and the general heat-generation models reserved for ER-351. ER-302 owns wavelength-orthogonal multistage photochemistry and is outside the frontal reaction-transport problem treated here.

2. Mechanistic basis

A propagating front exists only when local heat generation and transport raise adjacent material above the kinetic threshold faster than heat is lost. Photochemical input can define where the process starts, but once propagation begins the dominant state variables are conversion rate, exotherm, thermal diffusivity, boundary cooling and formulation-dependent kinetics [1,2].

3. State variables and process control

Ignition energy, initial illuminated volume and boundary temperature must be separated from front velocity. A process that needs continuous external exposure is not equivalent to autonomous propagation. Front velocity should be measured together with peak temperature and conversion behind the front, because the same velocity can arise from different thermal balances [1-3].

4. Principal failure modes

Quench occurs when heat loss or inhibitor load exceeds reaction feedback; acceleration occurs when increasing temperature steepens kinetics faster than heat can disperse. Lateral perturbations can generate curved or fingered fronts, and free surfaces can shift the balance through convective or radiative loss. Geometric acceptance therefore requires a map of the front trajectory rather than a single cure-time value. [2]

5. Measurement architecture

Useful measurements include synchronised temperature imaging or embedded thermometry, front-position versus time, post-front spectroscopy or conversion, density/shrinkage and dimensional inspection. Repeated runs should deliberately vary boundary cooling and section thickness to prove that the selected process window is stable rather than accidentally balanced [2,4].

6. Evidence hierarchy and transfer

The strongest evidence links a measured thermal trajectory to a reproducible conversion profile and finished geometry. Demonstrations of low external energy are secondary unless they also establish uniform state behind the front. Transfer between geometries must be requalified because surface-area-to-volume ratio changes the heat-loss field [1,3].

7. Qualification architecture

A frontal-process qualification package should record ignition conditions, front velocity, peak-temperature history, conversion behind the front and finished geometry over deliberately varied section thickness and heat-loss conditions. Negative controls should distinguish true autonomous propagation from exposure-assisted cure and should show the quench and acceleration boundaries. Transfer is justified only when the thermal trajectory and post-front conversion remain equivalent within the qualified geometry range.

8. Interpretation and decision logic

Decision logic should distinguish quench, stable propagation and thermal acceleration by combining front velocity with the thermal trajectory and the post-front conversion state. A wider operating window is justified only when geometry remains within tolerance while those three observables remain mutually consistent across repeated runs.

Table 1. Qualification matrix for frontal photopolymerisation in additive manufacturing.

State variable	Minimum evidence	Qualification purpose
Ignition	Light dose, initial heated volume	Separates trigger from propagation
Front speed	Position-time trace	Quantifies propagation stability
Thermal field	Peak and spatial temperature	Detects runaway or quench
Post-front state	Conversion and dimensions	Confirms complete, uniform cure

9. Diagnostic interpretation matrix

The diagnostic matrix for frontal photopolymerisation should separate insufficient ignition, propagation quench, stable self-propagation, lateral front instability and thermal acceleration. Interpretation therefore combines front-position data, thermal history, conversion and dimensional outcome rather than treating any one variable as proof of a qualified front.

Table 2. Diagnostic interpretation matrix for frontal-propagation instability.

Observed deviation	Competing mechanism	Discriminating check
Front stops	Heat loss or inhibition	Boundary-temperature and conversion map
Front accelerates	Thermal feedback instability	Temperature-rate correlation
Geometry broadens	Lateral heat spread	Front trajectory versus final edge
Weak region	Incomplete conversion	Spectroscopy behind front

10. Limitations and evidence gaps

Published frontal-polymerisation studies span radical, cationic and other reaction classes, and many are not vat-printing demonstrations. Quantitative propagation thresholds therefore cannot be transferred directly between chemistries. The review uses non-AM frontal systems to define physics, while requiring AM-specific evidence for geometric claims.

11. Conclusions

Frontal photopolymerisation should be qualified as a reaction-transport system, not as an exposure shortcut. A manufacturable front is one whose ignition, velocity, temperature, conversion and geometry remain jointly stable over the intended section size and boundary conditions.

References

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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

No new experimental dataset was generated for this review.