

Transient Thermal-History Measurement During Photopolymerisation

Exotherm, heat loss, local temperature and state attribution

Juan Seguro

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

ER-204 · Engineering Review · Version 0.3 · 16 September 2026

Abstract

Photopolymerisation couples a light-driven reaction to heat generation, heat transport and temperature-dependent kinetics. A measured temperature trace is therefore neither a direct measure of conversion nor a pure record of reaction enthalpy. It is the result of local heat generation, conduction into tooling and previously cured material, convection in liquid resin, radiation, changing material properties, source heating, sensor response and the location at which temperature is observed.

This review defines a measurement architecture for transient thermal history during photopolymerisation. Photo-differential scanning calorimetry, embedded sensors, infrared thermography and inverse heat-conduction models are compared by their measurands and perturbations. The review separates directly observed temperature and heat flow from inferred volumetric heat generation and inferred cure state. It examines spatial and temporal resolution, emissivity, sensor lag, contact resistance, boundary conditions and the non-uniqueness of inverse attribution. A validation hierarchy links calibrated temperature measurement to independent spectroscopy or calorimetry without assuming a universal heat of reaction. The result is a framework for reporting where and when temperature was measured, what model converted it into chemical information and which conclusions remain conditional. No universal cure-temperature or safety limit is proposed.

Keywords: photopolymerisation; thermal history; exotherm; thermography; photo-DSC; inverse heat conduction; degree of conversion; sensor response; heat transfer; measurement uncertainty

1. Significance and scope

Temperature affects viscosity, diffusion, propagation, termination, phase behaviour and transport. Photopolymerisation in turn generates heat and changes thermal properties. The feedback can be negligible in a thin, well-cooled film or dominant in a thick, rapidly reacting volume. The engineering question is not merely how hot a process became, but whether the measurement resolves the thermal history of the chemically active region and whether a claimed cause is supported.

A surface camera, a thermocouple and a photo-DSC do not observe the same quantity. Their traces should not be compared as though they were interchangeable temperatures.

1.1 Corpus boundary

ER-204 owns transient thermal measurement and attribution during photopolymerisation. ER-176 retains reactive-process safety, fire prevention and emergency controls. ER-181 retains post-cure process engineering. ER-185 retains thick-section formulation and cure guidance. ER-020 retains final-part thermal performance and thermomechanical qualification. ER-351 will own process-state heat-generation and transport models at a broader control level; ER-204 supplies the measurement foundation.

2. Energy balance and observable quantities

A local thermal balance can be written as:

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + \dot{q}_{\text{rxn}} + \dot{q}_{\text{opt}} + \dot{q}_{\text{other}}$$

where density ρ , heat capacity c_p and conductivity k may vary with temperature and conversion. $\dot{q}_{\text{rxn}}$ is the volumetric reaction-heat rate, while $\dot{q}_{\text{opt}}$ is the volumetric rate of absorbed optical energy not stored chemically. Boundary conditions determine conduction, convection and radiation losses.

Temperature T is directly observable only at the sensor's effective sampling volume and response time. Reaction heat and conversion are inferred unless separately measured. A good report identifies which terms are measured, imposed, fitted or assumed.

3. Photo-differential scanning calorimetry

Photo-DSC measures differential heat flow from a small sample under controlled thermal and illumination conditions. After baseline and optical corrections, the exothermic area can estimate reaction enthalpy. If a defensible total reaction enthalpy ΔH_{tot} is available, a calorimetric conversion proxy is:

$$\alpha H(t) = \frac{\int_0^t \dot{Q}_{\text{rxn}}(\tau) d\tau}{\Delta H_{\text{tot}}}$$

The denominator is not universal. Residual reaction after the measurement window, overlapping thermal events, oxygen, light attenuation and incomplete baseline correction can bias it. Jiang and Drummer used photo-DSC to analyse acrylate photopolymer cure kinetics, demonstrating the method's value under controlled small-sample conditions [1].

Transfer to a printer is limited by geometry, optical path, exposed area, thermal contact and heat loss. Photo-DSC is best treated as a controlled kinetic and enthalpy experiment, not a miniature printer.

4. Contact temperature sensors

Thermocouples, resistance sensors and fibre-optic probes can provide time-resolved local measurements. Their bead or sensing volume averages a region and perturbs both heat flow and possibly the optical field. Conductive leads create an additional heat path. Contact resistance and sensor encapsulation add lag.

A first-order response approximation is:

$$\tau \frac{dT_s}{dt} + T_s = T_m$$

where T_s is sensor temperature, T_m the local material temperature and τ is an effective time constant. Deconvolution can amplify noise and should be validated using a known transient. Quoting acquisition rate without sensor time response overstates temporal resolution.

Sensor placement should be verified independently, especially in thin layers. A sensor displaced by one layer thickness may sample tooling, liquid or cured material rather than the active zone.

5. Infrared thermography

Infrared cameras measure band-limited radiance from a visible surface and convert it to apparent temperature using emissivity, reflected-background and transmission assumptions. Liquid resin, transparent windows and changing cured surfaces can violate a constant-emissivity model. The camera may observe the vat exterior rather than the reacting region.

Thermography is powerful for spatial patterns and non-contact timing. It requires radiometric calibration, focus, pixel-footprint reporting, geometric correction for oblique views, frame timing and an emissivity strategy. A black reference patch can validate the camera but may not represent the resin. Multi-surface reflection should be considered in enclosed printers.

6. Inferring internal heat generation

Zhang, Zhang and Zhao combined infrared measurement of a vat substrate with an inverse heat-conduction problem, a thermal–chemical model initialised by photo-DSC and ex-situ FTIR validation [2]. The study is a useful demonstration of state attribution from an accessible surface, and it explicitly exposes the role of geometry and assumptions.

An inverse solution is conditional because multiple internal heat histories can produce similar surface temperatures. Regularisation, parameter bounds and prior kinetic information reduce non-uniqueness but do not turn inference into direct observation. Training and validation exposures should be separated; agreement with the calibration case alone is insufficient.

7. Optical and non-reaction heating

Absorbed radiation can become heat through non-radiative relaxation even when it does not cause polymerisation. Projectors, windows, build plates and vats can also warm. A dark or non-reactive optical control is therefore needed when attributing a temperature rise to reaction heat. The control should match absorption and thermal properties as closely as practical without undergoing the target reaction.

Subtracting one trace from another is valid only if boundary conditions and thermal properties are comparable. Cure changes conductivity, heat capacity and contact, so subtraction may remain approximate.

8. Thermal–kinetic feedback

Photoinitiation may be light driven while propagation, termination, diffusion and reversible deactivation remain temperature dependent. Nwoko and co-workers showed temperature dependence in conventional and RAFT photopolymerisation and separated apparent propagation behaviour from benchmark kinetics at abstract level [3]. This supports a general caution: constant light input does not imply temperature-independent reaction rate.

When a kinetic model uses an Arrhenius term,

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right)$$

the fitted E_a is model and mechanism dependent. A temperature trace alone cannot identify the mechanism or distinguish propagation from termination changes.

9. Spatial and temporal resolution

Thermal gradients can be steeper than a sensor's sampling region and faster than its response. Report resolution as an effective measurement volume and bandwidth, not only as camera pixel size or sampling interval. Optical point-spread, thermal diffusion during one frame and numerical filtering all broaden the response.

A characteristic diffusion length over time t is approximately:

$$L_d \sim \sqrt{\alpha t}$$

where $\alpha = k/(\rho c_p)$. This scale helps judge whether a measured hotspot could remain local over the observation interval, but it is not a substitute for a geometry-specific model.

10. Calibration and validation hierarchy

A robust measurement chain uses:

- 1 temperature and heat-flow calibration with traceable standards where applicable;
- 2 sensor response tests under a known transient;
- 3 geometric and timing calibration;
- 4 optical controls for source and tooling heating;
- 5 repeated measurements under fixed initial temperature and boundary conditions;
- 6 independent conversion or chemical-state measurement; and
- 7 validation of any inverse model on conditions not used for fitting.

Independent spectroscopy need not agree numerically with calorimetric conversion because the measurands differ. The comparison should test predicted trends and defined endpoints rather than force identity.

11. Uncertainty and state attribution

Uncertainty sources include calibration, emissivity, reflection, sensor placement, lag, contact resistance, heat-capacity and conductivity inputs, source timing, optical absorption, baseline selection and inverse-model regularisation. Parameter correlation can make individual fitted values poorly determined even when the predicted surface temperature is accurate.

State attribution should be expressed in levels:

- 1 **observed:** calibrated temperature or heat-flow signal;
- 2 **derived:** temperature difference, integrated heat or corrected trace;
- 3 **model-inferred:** internal heat source or conversion;
- 4 **mechanistically assigned:** reaction pathway or rate-limiting step.

Each level requires additional evidence. Labels should not be collapsed in figures or conclusions.

12. Interpretation matrix

Observation	Supported interpretation	Unsupported leap
Surface temperature rises during exposure	Observed surface warmed	Entire rise is reaction exotherm
Photo-DSC exotherm integrates reproducibly	Heat-flow response is repeatable under cell conditions	Printer conversion follows the same curve
Embedded probe reports a peak	Sensor location experienced a filtered transient	Peak local resin temperature is exact without lag correction
Inverse model matches validation traces	Model predicts measured outputs within tested domain	Internal heat and conversion fields are unique
Higher temperature accompanies faster conversion	Thermal and chemical responses are coupled	Temperature caused the whole rate change

13. Minimum reporting set

Report formulation class without proprietary recipe; initial state; radiation spectrum, irradiance and timing; geometry and boundaries; sensor type, location, size, calibration and response; emissivity or contact assumptions; acquisition and filtering; raw and corrected traces; controls; heat-transfer and kinetic model equations; fitted and fixed parameters; independent validation; uncertainty; and whether each result is observed, derived or inferred.

14. Knowledge boundary

Direct internal temperature measurement in an optically active, moving layer remains difficult. Inverse methods can bridge inaccessible regions but are sensitive to model form and boundary conditions. Thermal properties can evolve with conversion, and sufficiently complete in-situ datasets for broad cross-material transfer remain limited.

15. Limitations

This review does not define safe operating temperatures, runaway criteria, cure recipes or fire controls. It does not qualify post-cure chambers or final thermal performance. Numerical examples from individual studies are not transferred as universal values.

16. Conclusions

A transient thermal trace is the response of a coupled reaction–transport–sensor system. Photo-DSC resolves controlled heat flow; contact probes resolve local filtered temperature; thermography resolves surface radiance; inverse models estimate inaccessible states. Defensible attribution requires controls for non-reaction heating, calibrated sensor response, declared boundary conditions and independent chemical validation. Separating observed, derived and inferred quantities prevents a useful temperature measurement from becoming an unsupported conversion claim.

References

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