

Reactive Process Safety, Exotherm and Fire Risk in Photoresin Manufacture and Use

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Statement of Significance

Photopolymer resins are commonly discussed through printability, cure depth, mechanical properties and exposure control. A separate engineering question is whether the uncured or partially reacting material can remain inside a controlled reactive envelope during manufacture, storage excursion, thermal processing and use. This question cannot be answered by a flash point, a datasheet storage range, a differential-scanning-calorimetry onset temperature, or the fact that a finished part passed a flammability test. Reactive-process safety instead requires an evidence chain linking reactive inventory, initiation pathways, heat generation, heat removal, viscosity and transport changes, gas or vapour generation, containment, and credible deviations.

ER-176 defines that evidence chain for photoresin operations. It treats runaway polymerisation, incompatible mixing, heat accumulation and ignition as coupled but distinct hazards. It deliberately excludes occupational toxicology, finished-part flame-retardancy qualification, routine shelf-life/open-vat stability and generic process-management systems.

Abstract

Photoresin manufacture and use combine reactive unsaturated monomers or oligomers, photoinitiators, inhibitors, pigments, fillers, solvents and, in some systems, thermal initiators or second-stage curing chemistry. The same kinetic features exploited for rapid cure can create process-safety liabilities when reaction rate and heat generation rise faster than heat can be removed. This review develops a qualification framework for reactive safety across compounding, hold, storage excursion, post-cure and printer-adjacent operations. Primary and review evidence from radical-polymerisation runaway and inhibition studies shows that inhibitor state and loss of heat removal can materially change escalation behaviour [2,3]. Acrylic-acid runaway studies additionally show that secondary reaction pathways and fill state can alter pressure-generating consequences [1]. Calorimetric work on multifunctional acrylates also demonstrates autoacceleration during photopolymerisation, reinforcing that reaction rate cannot be assumed constant as conversion proceeds [6]. The review separates four questions that are often conflated: whether a formulation can self-heat or run away; whether volatile or decomposing species can generate pressure; whether vapours or liquids are ignitable; and whether an emergency intervention is technically defensible for the exact chemistry. It proposes a minimum evidence set based on composition state, calorimetry, kinetic interpretation, heat-transfer context, credible-deviation analysis and scale-specific acceptance criteria. No universal safe temperature, inhibitor concentration, batch size or emergency-quench recipe is proposed because those quantities are formulation- and equipment-specific.

Keywords: photoresin; reactive process safety; runaway polymerisation; exotherm; acrylate; inhibitor; calorimetry; thermal hazard; fire risk; scale-up

1. Scope, exclusions and state definitions

ER-176 owns the reactive-hazard problem from initiation to escalation. The relevant material states are: **as-received feedstock, compounded resin, held or stored resin, resin under light exposure, resin under deliberate thermal treatment, partially reacted material, and waste or residue that still contains**

reactive species. Each state may have a different inhibitor balance, dissolved oxygen content, thermal history, surface-to-volume ratio and degree of conversion.

The paper does not own routine shelf-life or open-vat stability, which asks whether performance remains within specification during intended storage or reuse. It does not own occupational exposure limits or dermatitis. It does not own flame-retardancy of the cured solid. It also does not prescribe a quality-management system. These adjacent subjects may provide boundary conditions, but none substitutes for reactive-hazard evidence.

2. Why reactive safety is a distinct engineering problem

The core process-safety question is dynamic: if an initiation event occurs, can the system reject the generated heat and remain bounded? A formulation may be stable for months under intended storage yet still have a severe excursion scenario after contamination, inhibitor depletion, unintended irradiation or heating. Conversely, a material with a low flash point may be manageable from a polymerisation standpoint if reactive initiation is strongly controlled, while its fire and vapour hazards remain significant. Treating these dimensions as one generic “chemical safety” property obscures the decision logic.

Acrylic monomers illustrate the distinction. NIOSH describes acrylic acid as readily polymerising and therefore shipped with inhibitor [4]. Ethyl acrylate is likewise described as polymerising readily unless inhibited and is also classified as a flammable liquid in the NIOSH Pocket Guide [5]. The relevant lesson for photoresins is not that every formulation behaves like neat acrylic acid or ethyl acrylate. It is that inhibition, reactivity and ignitability are separate state variables that must be established for the actual mixture.

3. Reactive inventory: what can generate or accelerate heat

A photoresin reactive inventory can include monofunctional and multifunctional (meth)acrylates, unsaturated oligomers, photoinitiators, thermal initiators, redox components, cationic species, inhibitors and stabilisers. Fillers, pigments and additives may appear chemically inert while still changing thermal conductivity, optical absorption, viscosity, gas disengagement or adsorption of stabilisers. Solvents and reactive diluents can change both heat capacity and vapour pressure.

The first qualification task is therefore compositional rather than calorimetric: identify which constituents can initiate, propagate, catalyse, inhibit, decompose or alter heat and mass transport. “Proprietary blend” is not a process-safety model. A supplier SDS is necessary for hazard communication but normally cannot demonstrate mixture-specific runaway behaviour, especially where the formulation differs from the neat substances on which much published hazard information is based.

4. Heat generation, heat removal and self-heating

Runaway is fundamentally an imbalance between heat generation and heat rejection. Polymerisation rate is temperature dependent; increasing temperature can increase reaction rate, which increases heat generation and can produce further temperature rise. Whether this feedback becomes self-accelerating depends on chemistry, conversion, inhibitor state, thermal mass, vessel geometry, agitation, heat-transfer area and the response of the cooling system. A review of free-radical polymerisation inhibition explicitly describes runaway escalation when reaction heat generation exceeds cooling-system heat-removal capacity [2].

Scale matters because reactive inventory tends to grow with volume while passive heat rejection is governed largely by area and temperature difference. This does not justify a universal scaling exponent for every process, but it does explain why a benign small beaker test cannot be transferred directly to a larger vessel. A scale-up decision must therefore compare the heat-release potential and rate against the actual heat-removal capability of the intended equipment under both normal and credible-deviation states.

5. Autoacceleration and loss of transport

Multifunctional acrylate photopolymerisation can exhibit autoacceleration. Tryson and Shultz reported autoacceleration for the multifunctional acrylates they studied but not for the monofunctional acrylate comparator [6]. Their abstract also reports substantial decreases in propagation and termination rate constants with conversion [6]. The mechanistic importance for process safety is broader than the specific monomers studied: functionality and conversion state can change the kinetic regime, while viscosity and diffusion constraints alter propagation and termination. Reaction rate therefore cannot safely be extrapolated as though the material remained a low-viscosity Newtonian liquid with constant kinetic parameters.

In filled photoresins, rising viscosity also affects convective mixing and local heat transport. A local initiation event in a poorly mixed zone can experience a different thermal trajectory from the bulk temperature indicated by a single vessel probe. Qualification should therefore ask whether the temperature measurement is representative of the most reactive or most thermally insulated zone, not merely whether a temperature sensor exists.

6. Inhibitors, retarders and stabilisation state

Inhibitors are not an intrinsic guarantee of safety. Their effectiveness depends on identity, concentration, oxygen availability where relevant, temperature, contamination and reaction pathway. In the MMA system reviewed by Maafa, hydroquinone is described as an inhibitor and 1,4-benzoquinone as a retarder, while the effectiveness of a hindered hydroquinone inhibitor is reported to depend on oxygen availability [2]. Ampelli and co-workers likewise showed different inhibition and retardation behaviour in their investigated MMA polymerisation system [3]. These results should not be universalised to all photoresins, but they demonstrate why the generic label “stabilised” is insufficient.

A defensible specification should therefore distinguish inhibitor identity from inhibitor function in the final formulation. Incoming raw-material concentration, dilution during compounding, adsorption or partitioning, oxygen dependence and thermal degradation can all alter the effective stabilisation state. If a formulation relies on an inhibitor for safe hold time, the inhibitor becomes a safety-critical compositional attribute rather than merely a shelf-life additive.

7. Initiation and incompatible-mixing scenarios

Credible initiation routes include unintended light exposure, thermal decomposition of initiators, contamination with radical-generating species, oxidants, reductants, acids, bases or metals where the chemistry is sensitive to them, and erroneous order of addition. The process-hazard analysis should not assume that only the intended photochemical route can initiate polymerisation.

The strongest evidence is formulation-specific compatibility testing under realistic concentrations and thermal conditions. Generic compatibility tables can identify hazards to investigate but do not close the question for a multicomponent resin. The key engineering output is a list of credible combinations that can raise reaction rate, lower induction time, consume inhibitor or create a second exothermic pathway. Acrylic-acid runaway work documents a Michael-addition pathway whose own exotherm can induce further polymerisation, demonstrating that a secondary reaction pathway can materially alter escalation [1].

8. Manufacturing scale: dosing, mixing and hold time

Compounding operations create transient states that may be more hazardous than the finished resin. Local initiator concentration can temporarily exceed the final formulation value during dosing. Poor mixing can produce zones of different inhibitor, pigment or reactive-diluent concentration. High-shear mixing may add heat. Vacuum degassing changes gas content and can affect boiling or vapour release. A hold period after addition but before filling may create the longest residence time at elevated temperature.

The safe process envelope must therefore be tied to sequence and equipment, not only final composition. At minimum, the batch record should identify order of addition, addition rate of safety-relevant components, maximum credible hold time, agitation state, temperature measurement location and response to cooling loss. A change in vessel scale, impeller, jacket performance or fill level can invalidate a previous heat-transfer assumption even if the formulation is unchanged. Acrylic-acid runaway studies report fill-level dependence in the consequences of gas and water generation, illustrating why fill state belongs in the transfer assessment [1].

9. Thermal post-cure and two-stage systems

Two-stage photoresins can separate shape creation from final network development. This can be valuable for high-temperature or high-performance materials, but it turns post-cure into a reactive operation rather than a simple conditioning step. The internal ER corpus already identifies reaction exotherm as potentially safety-critical for two-stage thermal cure; that observation defines an adjacent engineering need but is not used here as independent scientific validation.

Qualification must distinguish heat supplied by the oven or chamber from heat generated by the reaction. A programmed chamber temperature does not prove that the part or resin volume follows the same trajectory. Thick sections, stacked parts, fixtures or insulating geometries can create local thermal coupling and self-heating. Where a second-stage reaction is substantial, the thermal schedule needs evidence that includes the reactive mass and geometry actually processed.

10. Storage excursion and unintended initiation

An excursion should be evaluated as a change in chemical state, not only as time outside a labelled temperature band. Relevant questions include whether inhibitor was consumed, whether initiator decomposition advanced, whether viscosity or phase state changed, and whether the material returned to its original reactive behaviour after cooling. A visually normal resin may still have a changed induction period or exothermic response.

Unintended light exposure is a separate initiation route. The significance depends on spectral overlap, optical path length, photoinitiator concentration and the ability of the system to dissipate heat. Light exposure of a shallow film and exposure of a large optically attenuating volume are not thermally equivalent operations.

11. Fire and vapour hazard versus polymerisation hazard

Fire risk and runaway polymerisation can interact but should be assessed separately. A low-flash-point component can create an ignitable vapour atmosphere without any polymerisation runaway. Conversely, a strongly exothermic polymerisation can occur in a formulation whose overall vapour flammability is limited. Heat from runaway may then increase evaporation, decomposition or pressure and create secondary fire scenarios. Acrylic-acid runaway work also reports generation of water and gases associated with secondary reaction pathways, directly linking chemistry to pressure and containment consequences [1].

Therefore, a complete assessment asks at least four different questions: Can the material polymerise or decompose exothermically? Can that reaction self-accelerate under the intended scale and containment? Can vapours or decomposition products form an ignitable atmosphere? Can pressure generation exceed the capability of the equipment or venting arrangement? A single “flammable/non-flammable” label answers none of these completely.

12. Calorimetric and analytical evidence hierarchy

Screening DSC can reveal exothermic events and compare formulation states, but an onset observed under a particular scan rate is not a universal safe-temperature limit. ASTM E2070-23 addresses kinetic parameter estimation from isothermal DSC data and explicitly includes accelerating reactions such as thermoset curing within its applicability range [7]. The standard also states limitations on the thermal-curve forms to which the

methods apply. This illustrates a broader rule: kinetic parameters are meaningful only when the method assumptions are satisfied.

Reaction calorimetry provides heat-flow information under controlled mixing and dosing. Adiabatic or near-adiabatic methods can probe self-heating trajectories under low heat-loss conditions. Isothermal storage or hold tests can address induction periods at selected temperatures. Analytical methods can track inhibitor, conversion or decomposition products. None is universally sufficient alone. The evidence package should be chosen around the failure mechanism that would control the real operation.

13. Decision gates for scale-up and operation

A formulation should not move to a larger reactive inventory merely because small-scale printing succeeded. A practical decision architecture is:

1. **Identity gate:** all safety-relevant reactive components and stabilisers are identified and controlled.
2. **Thermal-screen gate:** plausible exothermic events have been detected or bounded with a method appropriate to the chemistry.
3. **Kinetic gate:** where self-heating is credible, temperature dependence and induction behaviour are understood sufficiently for the intended hold and processing times.
4. **Heat-removal gate:** normal and credible-loss-of-cooling states have been compared with heat generation for the actual vessel, fill level and agitation state.
5. **Compatibility gate:** realistic contamination and order-of-addition scenarios have been screened where they can change initiation or inhibition.
6. **Scale gate:** the larger process does not rely on an unverified transfer of thermal behaviour from a smaller geometry.
7. **Emergency gate:** detection, isolation, venting or other response assumptions are supported for the exact equipment and chemistry rather than copied from another monomer system.

Failure of a gate is not proof that the formulation is unusable. It means the evidence is insufficient to claim a controlled reactive envelope at that scale and state.

14. Emergency disposition and the limits of generic recipes

Published inhibition studies and reviews show that emergency inhibition can be a technically meaningful subject in radical-polymerisation runaway scenarios [2,3]. They do not justify copying a shortstop recipe into a different resin. The required mixing time, inhibitor solubility, reaction stage, temperature, pressure, available headspace and decomposition pathway may differ. An emergency addition can itself create incompatibility, boiling, splashing or gas generation.

For that reason ER-176 does not publish a universal emergency-quench composition or dosing instruction. Emergency response belongs to the validated process design for the actual material and equipment. The scientific literature can establish mechanisms and candidate control principles; plant-specific engineering must demonstrate that the proposed intervention can reach and control the reacting mass within the available time.

15. Minimum reporting set for a defensible reactive-safety claim

A claim that a photoresin process is reactively controlled should report enough information to connect chemistry to equipment. At minimum this includes formulation class and safety-relevant components; inhibitor/stabiliser identity where relied upon; material state and thermal history; test method and sample mass; atmosphere and container condition; heating or irradiation protocol; observed exothermic events; basis for any kinetic interpretation; intended batch or reactive mass; vessel or chamber geometry; agitation and cooling state; credible deviations examined; and the acceptance criterion used to decide that the process remains controlled.

Statements such as “stable at 60 °C”, “DSC onset above 150 °C”, “non-flammable after cure”, or “contains inhibitor” are incomplete unless the measurement state, method, timescale and transfer to the intended operation are specified.

16. Limitations and evidence gaps

The strongest runaway literature is often based on commodity monomers, whereas commercial photoresins are multicomponent mixtures containing oligomers, reactive diluents, pigments, fillers and proprietary stabiliser packages. Mechanistic transfer from a neat monomer to a resin must therefore be explicit and bounded. The present review also does not establish safe-operating limits for any specific 3Dresyns formulation; those require formulation- and equipment-specific data.

Further work is particularly needed on large-volume photopolymer mixtures, highly filled resins, two-stage systems with substantial thermal cure, and waste streams containing partially reacted resin. These states can differ materially in heat capacity, thermal conductivity, optical attenuation, viscosity and inhibitor availability from the neat monomers that dominate classical runaway studies.

17. Conclusions

Reactive-process safety in photoresin manufacture and use is not reducible to a flash point, storage temperature, DSC onset or cured-part fire rating. The controlling question is whether the actual reactive mass, in its actual state and equipment, can remain bounded after credible initiation and deviation scenarios. Literature on acrylic acid, MMA and multifunctional acrylates establishes the relevance of runaway behaviour, inhibition state and autoacceleration [1,2,3,6]. Standards-based calorimetric methods provide useful kinetic tools but require their assumptions and applicability limits to be respected [7].

A defensible qualification therefore links composition, stabilisation, initiation pathways, calorimetry, kinetics, heat transfer, scale, containment and emergency logic. Where that chain is incomplete, the correct conclusion is not “safe” or “unsafe” in the abstract; it is that the reactive envelope has not yet been demonstrated for the intended operation.

Related Engineering Review boundaries

- ER-032 / ER-080 / ER-081: routine storage, reuse and open-vat stability.
- ER-091 to ER-095: occupational exposure, sensitisation and toxicological evidence.
- ER-160: extreme-service material systems, including cured-part flame-resistance qualification, and two-stage thermal-cure application context.
- ER-175: printer changeover and cross-contamination control.
- ER-178: solvent, wash-water and contaminated-waste management.
- ER-185: thick-section photocuring of putties, gels, sealants and potting compounds.

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Competing interests

The author is Founder and Scientific Director of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

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Data availability

No new experimental dataset was generated for this review.