

Thick-Section Photocuring of Putties, Gels, Sealants and Potting Compounds: Attenuation, Frontal Cure, Exotherm and Through-Cure Qualification

Juan Segurolo

3Dresyns by Resyner Technologies S.L.

ER-185 | Engineering Review | Version 0.2 | 11 September 2026

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

Statement of Significance

Photocuring ceases to be a surface-coating problem when the optical path becomes comparable with the attenuation length of the formulation. In a thick putty, gel, sealant or potting mass, the exposed surface can reach a high apparent cure state while an intermediate layer or core remains chemically and mechanically different. Increasing irradiance or exposure time does not guarantee that this gradient disappears, because absorption, scattering, photoinitiator depletion, photobleaching, oxygen transport, vitrification, heat generation and any secondary cure mechanism evolve during exposure.

ER-185 treats through-cure as a spatial qualification problem. The engineering question is not whether light can start polymerisation, but whether every region that carries a required function reaches an accepted final state without unacceptable thermal, dimensional or chemical gradients. The review separates ordinary Beer-Lambert attenuation from photobleaching-assisted cure fronts, and both from thermally self-propagating frontal polymerisation and dual-cure chemistry. No published thickness, dose, wavelength, photoinitiator level or temperature is transferred as a universal design rule.

Keywords: thick-section photocuring; through-cure; photobleaching; photofrontal polymerization; frontal polymerization; acrylate; methacrylate; exotherm; potting compound; sealant; depth-resolved conversion

Abstract

Direct depth-profiling studies of acrylate photopolymerisation show that conversion can vary strongly with depth when photoinitiator absorption, UV absorbers or pigmentation screen incident radiation [1]. Scherzer's evidence was obtained in thin acrylate coatings at micrometre-scale probe depths; ER-185 transfers only the depth-dependence mechanism, not that experimental geometry, to thick-section qualification. In suitable photobleaching systems, the optical state changes during exposure and permits a photochemical cure front to advance much farther than the initial penetration depth; Ebner and co-workers demonstrated through-cure to 52 mm in one specifically engineered (meth)acrylate system [2]. That result establishes feasibility, not a transferable 52 mm specification. Review literature describes photoinitiating systems and kinetic considerations for frontal photopolymerisation in composites and thick three-dimensional structures [3]. Dual-curing acrylate architectures provide a distinct multi-reaction route whose final state must be qualified independently [4].

ER-185 builds a qualification architecture around these coupled phenomena. It requires optical characterisation of the formulation and geometry, depth-resolved chemical or mechanical response, time-resolved thermal evidence where exotherm is consequential, and explicit differentiation among direct photochemical cure, photobleaching-assisted photofronts, thermally driven fronts and secondary cure. Photo-DSC can characterise reaction heat and kinetics, but its results depend on sample geometry, mass, atmosphere and temperature and therefore cannot substitute for a thick-part thermal map [5]. The final acceptance criterion is functional through-cure across the defined geometry and environmental range, not surface tack loss or a single top-surface conversion value.

1. Scope, terminology and ownership

ER-185 covers photocurable masses whose section thickness or optical path is large enough that the material state may vary materially with depth. Representative applications include putties, gels, sealants, encapsulants and potting compounds. The relevant geometry may be a slab, bead, fillet, cavity fill, annulus, deep recess or irregular three-dimensional volume.

Surface cure means the state measured near the illuminated boundary. **Depth-resolved cure** means a measured state assigned to defined positions below or away from that boundary. **Through-cure** means that all regions required for the intended function meet pre-defined acceptance criteria. It does not mean merely that no liquid is visible.

A **photochemical photofront** is an advancing optical reaction zone enabled by time-dependent optical changes such as photobleaching. A **thermal frontal polymerisation** front is sustained materially by reaction heat and heat transfer. These mechanisms may coexist in some systems, but they are not synonyms.

ER-181 owns post-cure chamber field engineering for printed VPP parts. ER-186 owns light-curable adhesive assembly and bondline-specific questions. ER-027 retains detailed conversion metrology in the VPP corpus. ER-185 owns thick-section spatial cure and its qualification logic.

2. Why thickness changes the engineering problem

In a thin film, the incident radiation field may be similar across much of the reactive layer. As thickness increases, the material itself increasingly determines what radiation reaches deeper regions. Photoinitiator, absorbers, pigments, fillers, reaction products and the growing polymer network can all change the effective attenuation and scattering field.

The consequence is a coupled reaction-transport system. The top region can polymerise first, consuming initiator and monomer, changing refractive index and mobility and generating heat. Deeper regions experience a different photon flux, oxygen condition and temperature history. Even if they eventually polymerise, they need not reach the same conversion, network density, shrinkage or residual-species state. The qualification unit is therefore the complete section, not the illuminated face.

3. Attenuation is formulation and state dependent

Beer-Lambert attenuation is a useful starting model for a non-scattering absorber at fixed composition, but a reacting formulation is rarely fixed. Scherzer directly demonstrated depth-dependent conversion effects caused by strongly absorbing photoinitiator, UV absorber and pigment in acrylate systems [1]. This evidence establishes the need to measure depth response rather than infer it from incident intensity.

A thick formulation should therefore be characterised at the wavelength band actually used. Absorbance or transmission of the uncured formulation can identify obvious screening, but the relevant optical field may evolve during cure. Photobleaching can decrease absorption; coloured reaction products can increase it; phase separation, bubbles or filler redistribution can alter scattering.

An optical measurement at one path length should not be extrapolated blindly to a much thicker geometry. Nor should a clear resin be assumed optically simple if its initiator absorbs strongly in the source band.

4. Photoinitiator concentration has opposing effects

More photoinitiator can increase radical generation near the illuminated surface while simultaneously increasing absorption and reducing the fraction of incident light reaching depth. Too little initiator can improve optical penetration yet leave the deep region with insufficient radical generation. The optimum is therefore conditional on spectrum, molar absorptivity, quantum efficiency, formulation, oxygen state and geometry.

Ebner et al. explicitly demonstrated this competition in photobleaching (meth)acrylate systems [2]. Their work shows why photoinitiator concentration is not a monotonic control knob. The transfer rule is not their

optimum concentration. It is the requirement to optimise and verify the complete depth profile for the selected system.

5. Photobleaching-assisted photofrontal cure

Photobleaching can allow an initially absorbing formulation to become more transparent as the initiator is consumed or converted to less absorbing products. The active region can then move progressively deeper. In the Ebner study, a low-optical-density strategy combined with a photobleaching initiator enabled centimetre-scale curing, including a reported 52 mm specimen [2].

This is strong feasibility evidence for thick photochemical cure. It is not evidence that every TPO-L-containing acrylate will cure 52 mm, nor that the deepest region reaches the same state as the surface under another source, temperature or formulation.

Qualification should measure at least the start and end optical state where practical and must verify the resulting depth response. A visually solid specimen is insufficient because gelation can occur at a conversion below that required for final mechanical, chemical or thermal performance.

6. Thermal frontal polymerisation is a different mechanism

Acrylate polymerisation is exothermic. Frontal-photopolymerisation review literature treats photoinitiating systems and kinetic control as central to preparing composites and thick three-dimensional structures [3]. ER-185 therefore keeps any heat-supported propagation claim conditional on direct system-specific thermal and kinetic evidence rather than inferring it from the review alone.

The engineering attraction is obvious: a localized optical trigger can potentially initiate a much larger conversion volume. The engineering burden is equally important. Front velocity, peak temperature, heat loss, sample diameter, boundary conditions, filler loading and inhibitor state can determine whether the front propagates, stalls, oscillates or overheats.

ER-185 therefore uses the term *thermal frontal polymerisation* only when the evidence demonstrates a heat-supported propagation mechanism. A formulation that simply warms during UV exposure is not automatically undergoing frontal polymerisation.

7. Exotherm is both signal and hazard

Reaction heat can be useful evidence of polymerisation and can assist deep cure, but it is not inherently beneficial. Thick sections have a lower surface-area-to-volume ratio and can retain more heat than thin test films. A formulation that is benign in a 1 mm layer can experience a materially different temperature history in a large potting volume.

Photo-DSC provides a controlled way to compare reaction heat and kinetics, and Bachmann et al. show that sample shape, mass, atmosphere and temperature affect interpretation [5]. A DSC heat-flow trace is nevertheless a small-sample measurement. It cannot by itself establish the peak temperature or gradient in a production-scale cavity.

Where exotherm can affect safety, boiling, void formation, shrinkage, component damage or network state, qualification requires time-resolved temperature measurements in representative geometries. Maximum credible fill volume, insulation, substrate conductivity, ambient temperature and start temperature become controlled variables.

8. Oxygen and exposed-surface state

Radical acrylate cure is sensitive to oxygen inhibition. In a thick mass the surface, walls and core can experience very different oxygen access. The illuminated top surface may be replenished by air while the core becomes oxygen-depleted; conversely, dissolved oxygen may delay initiation throughout a freshly mixed volume.

The result can be a superficial tacky layer over a better-cured interior, or a delayed start followed by rapid exotherm after oxygen is consumed. Oxygen effects should therefore be treated as a spatial and temporal boundary condition rather than a binary air-versus-inert label.

Any inerting, cover film, closed-cavity or vacuum strategy requires its own compatibility and process evidence. Eliminating oxygen inhibition at the surface does not prove deep cure.

9. Pigments, fillers and functional particles

Putties, sealants and potting compounds are often intentionally filled. Mineral fillers, fibres, pigments, conductive particles, flame-retardant packages and other additives can absorb or scatter the actinic field. Their distribution can also evolve during storage or dispensing.

A transmission measurement on the neat binder is therefore not representative of a filled commercial formulation. The relevant material state includes filler identity, particle-size or agglomerate distribution, concentration, dispersion, settling history and path length.

A change in colour or filler grade can require requalification even when the base resin and photoinitiator are unchanged. Through-cure is a formulation property only after the complete formulation state and source geometry are fixed.

10. Geometry and illumination access

Nominal thickness is not enough. A 10 mm transparent slab illuminated from two sides is not equivalent to a 10 mm deep blind cavity illuminated from one opening. Curved walls, metallic inserts, opaque housings and neighbouring components can create reflection, shadow and heat-sink effects.

The relevant optical path should be defined from every illuminated boundary to the critical point. If multiple sources or part rotation are used, their contribution should be documented. If the production geometry includes shadowed zones, a single photochemical mechanism may be incapable of closing the cure requirement regardless of surface dose.

Worst-case geometry is thus application specific: maximum depth, longest unilluminated path, highest attenuation formulation, most reflective or absorptive boundary, largest thermal mass and least favourable ambient condition may be different test cases.

11. Dual cure for dark or shadowed regions

Dual-curing acrylate systems combine more than one curing reaction within one material architecture [4]. For thick-section engineering, the relevant point is that a secondary reaction can change the route to final state where optical access is limited; its chemistry, trigger and completion must be demonstrated for the selected system rather than inferred from a generic dual-cure label.

This architecture can solve an optical-access problem, but it creates a second qualification problem. The second reaction needs its own reactive-group balance, catalyst or initiator state, latency, storage stability, temperature or humidity boundary, and completion evidence. The first reaction can change mobility and diffusion available to the second.

A dual-cure label therefore cannot be treated as proof of shadow cure. The darkest and most diffusion-limited production location must be measured after the full specified conditioning time.

12. Cure depth is not equivalent to functional through-cure

A depth-of-cure test often identifies a boundary between visibly or mechanically solid material and uncured liquid. That is useful for screening but may not match the final requirement. Mechanical modulus, residual monomer, glass transition, swelling, electrical insulation, adhesion to an insert, thermal conductivity or chemical resistance can each reach acceptable values at different reaction states.

ER-185 therefore separates three gates: gel/shape retention, chemical conversion state and application-specific function. A specimen can pass the first and fail the latter two.

The measurement method must be selected from the failure mode. FTIR or Raman can provide chemical conversion information, extraction can probe soluble fraction, DSC/DMA can probe thermal/network state, hardness or indentation can map mechanical gradients, and destructive sectioning can expose otherwise inaccessible regions. No one method proves every endpoint.

13. Depth-resolved sampling and metrology

Depth-resolved measurements should preserve spatial registration. Slicing a cured block into layers is useful only if cutting does not materially change the measured state or contaminate adjacent regions. Surface-sensitive spectroscopy needs a defined probe depth. Extraction from a bulk specimen can average away a thin under-cured core.

A practical qualification can combine orthogonal measurements: one chemically sensitive method, one mechanical or thermal response, and direct inspection for voids or interfaces where relevant. The number and position of depth points should be chosen before seeing the result.

Scherzer's depth-profiling work illustrates the central principle: cure must be interrogated at the depth where the claim is made [1]. The exact apparatus is not mandatory; spatial correspondence is.

14. Thermal and conversion gradients can decouple

A hotter region is not necessarily the most completely cured region. Local optical intensity, oxygen, diffusion and vitrification can all change reaction progression. Conversely, a dark core can become hot through heat conduction without receiving enough radical-generating light to follow the same network pathway as the surface.

This matters especially when comparing direct photocure with thermal frontal or dual-cure systems. Equal final temperatures do not prove equal reaction histories. Equal bulk conversion does not prove equal spatial network structure.

The process record should therefore preserve both thermal history and final depth-resolved response where either can be non-uniform.

15. Bubbles, shrinkage and internal defects

Thick reactive masses can trap air during dispensing, evolve volatile material or generate bubbles if local temperature rises sufficiently. Polymerisation shrinkage can create internal stress or pull away from a housing, insert or substrate. A propagating thermal front can also create a steep moving temperature gradient.

These defects are not secondary cosmetic issues. A void can alter optical propagation during cure and later reduce mechanical, dielectric or barrier performance. Interfacial separation can create a new oxygen path or thermal resistance.

Qualification should therefore include the actual dispensing, degassing and fixture route, not only a pre-degassed laboratory cuvette.

16. Process-window development

A robust process study varies the parameters that control the relevant mechanisms rather than maximising one nominal input. At minimum the design should consider source spectrum, incident irradiance, exposure sequence, formulation optical state, temperature, initial material temperature, section geometry, fill volume, boundary materials and atmosphere.

For photobleaching systems, photoinitiator concentration and optical-density evolution are central. For thermal fronts, heat loss and maximum temperature are central. For dual cure, the second reaction's trigger and completion conditions are central.

The accepted window should be defined by simultaneous constraints: adequate depth-resolved cure, acceptable peak temperature, absence of unacceptable voiding or distortion, required functional response and repeatability.

17. Scale-up, transfer and change control

Scale-up is not a linear multiplication of exposure time. Increasing thickness changes optical attenuation and thermal retention. Increasing lateral size can reduce edge cooling. Moving from a transparent mould to an opaque housing changes optical access and heat transfer. A larger batch can alter starting temperature and dispensing time.

Changes that can trigger requalification include photoinitiator or absorber concentration, pigment/filler grade, source spectrum or optical power, cavity depth, fill volume, housing material, wall thickness, surface reflectivity, dispense temperature, ambient temperature, inerting, cover film, secondary-cure catalyst and storage age.

Transfer between machines or sources should compare the variables that control the demonstrated mechanism. Matching a nominal wavelength or wattage is not sufficient.

18. Minimum reporting set, limitations and conclusions

A thick-section photocure record should state at least: formulation identity and version; filler/pigment state; photoinitiator system; source type and spectral band; incident irradiance and exposure sequence; geometry and maximum optical path; boundary materials; starting and ambient temperatures; atmosphere; fill volume; thermal history where consequential; depth-resolved measurement positions; conversion or network-state method; functional acceptance criteria; defect inspection; repeatability; and change-control triggers.

The literature supports several strong but bounded conclusions. Depth-dependent conversion is real and can be driven by initiator absorption, absorbers and pigments [1]. Photobleaching can enable very deep cure in specifically engineered systems, including the 52 mm demonstration of Ebner et al. [2]. Frontal-photopolymerisation review literature supports treating photoinitiating system and kinetics as explicit design variables for thick structures [3]. Dual-curing acrylate reviews support treating multi-reaction architectures as a distinct cure strategy whose final state requires independent qualification [4]. Photo-DSC can quantify reaction heat and kinetic response under controlled small-sample conditions but does not replace production-geometry thermal measurement [5].

The resulting engineering rule is simple: through-cure is a spatial final-state claim. It is valid only when the critical depth and geometry have been measured under the complete qualified formulation, optical, thermal and environmental state. A cured surface, a nominal lamp dose or one published cure depth cannot establish that claim.

Related Engineering Review boundaries

ER-027 retains detailed conversion-metrology ownership within the VPP corpus.

ER-181 owns post-cure chamber dose delivery, chamber geometry, rotation, shadowing, atmosphere and thermal coupling for printed VPP parts.

ER-176 owns reactive-process safety, including exotherm and fire-risk qualification; ER-185 uses thermal history only to qualify thick-section cure and does not reopen ER-176 safety ownership.

ER-186 owns formulation and cure of light-curable adhesives across 2D, 2.5D and 3D assemblies, including bondline-specific optical access and dark-zone control.

References

- [1] Scherzer, T. Depth Profiling of the Degree of Cure during the Photopolymerization of Acrylates Studied by Real-Time FT-IR Attenuated Total Reflection Spectroscopy. *Applied Spectroscopy* 56(11) (2002) 1403-1412. DOI: [10.1366/00037020260377698](https://doi.org/10.1366/00037020260377698).
- [2] Ebner, C.; Mitterer, J.; Eigruber, P.; Stieger, S.; Riess, G.; Kern, W. Ultra-High Through-Cure of (Meth)Acrylate Copolymers via Photofrontal Polymerization. *Polymers* 12 (2020) 1291. DOI: [10.3390/polym12061291](https://doi.org/10.3390/polym12061291).
- [3] Petko, F.; Świeży, A.; Ortyl, J. Photoinitiating systems and kinetics of frontal photopolymerization processes - the prospects for efficient preparation of composites and thick 3D structures. *Polymer Chemistry* 12(32) (2021) 4593-4612. DOI: [10.1039/D1PY00596K](https://doi.org/10.1039/D1PY00596K). [Review]
- [4] Konuray, O.; Fernández-Francós, X.; Ramis, X.; Serra, À. State of the Art in Dual-Curing Acrylate Systems. *Polymers* 10(2) (2018) 178. DOI: [10.3390/polym10020178](https://doi.org/10.3390/polym10020178). [Review]
- [5] Bachmann, J.; Gleis, E.; Schmölzer, S.; Fruhmman, G.; Hinrichsen, O. Photo-DSC method for liquid samples used in vat photopolymerization. *Analytica Chimica Acta* 1153 (2021) 338268. DOI: [10.1016/j.aca.2021.338268](https://doi.org/10.1016/j.aca.2021.338268).

Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. The article discusses technology categories relevant to the company's technical domain but makes no comparative product recommendation.

Data availability and AI-assistance statement

No new experimental dataset was generated. Generative AI assisted drafting, literature organisation and pre-review control but is not an author. Juan Segurola retains responsibility for the final article.