

Electron-Beam versus Photoinitiated Curing of Acrylate Formulations

Network Formation Without a Photoinitiator, Depth-Dose Coupling and Requalification Boundaries

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Statement of Significance

Electron-beam curing can initiate acrylic network formation without a deliberately added photoinitiator, but that difference does not make an electron-beam process a direct substitute for an optically qualified cure. Electron energy deposition, dose rate, penetration, atmosphere and formulation state determine a reaction and network history that cannot be reduced to a universal conversion from optical radiant exposure to absorbed dose. ER-188 defines a bounded comparison and a requalification framework. It distinguishes the justified absence of photoinitiator-derived species from the unjustified claim that the cured material contains no residual or mobile species.

Abstract

Photoinitiated and electron-beam curing can both polymerise acrylate formulations, yet they deliver initiation energy through different physical routes. Optical curing depends on spectral absorption, photoinitiator chemistry and light attenuation, whereas electron-beam curing deposits ionising energy through a depth distribution governed by accelerator and material conditions. Direct primary studies show that EB dose, dose rate and accelerating voltage can affect conversion, gel/sol composition and network response; that equivalent nominal initiation energy does not make photo- and EB-initiated polymerisations chemically or kinetically equivalent; and that filler state, thickness, substrate and formulation can change route-specific outcomes [1-4]. ER-188 converts this evidence into a conservative qualification framework. A UV-qualified formulation transferred to EB is treated as a new material-process state requiring verification of composition, depth response, network state, residual chemistry and intended-use performance. No universal EB dose, penetration depth, UV-to-EB conversion, oxygen-immunity claim or automatic regulatory advantage is proposed.

Keywords: electron-beam curing; acrylates; photopolymerisation; absorbed dose; dose rate; network formation; photoinitiator; requalification

1. Scope and ownership

ER-188 addresses the engineering consequences of replacing photoinitiated curing with electron-beam initiation in acrylate formulations. Its central question is not which technology is generally superior. It is what changes in the material-process state when network initiation no longer depends on an intentionally added photoinitiator, and what evidence is needed before a formulation or product qualified under one route can be accepted under the other.

Within the named sub-series *Radiation Curing Beyond Additive Manufacturing*, ER-188 examines the same photochemistry, oxygen-inhibition, attenuation, interfacial and qualification principles in coatings and films rather than only in printed layers. It does not extend its evidence or claims to inks or other bulk-applied materials not addressed by the controlled sources.

The review owns photoinitiator-free EB initiation, depth-dose coupling, dose-rate effects, oxygen response and transfer/requalification boundaries. ER-083 and ER-084 retain general photocuring taxonomies. ER-095

retains photoinitiator migration and substitution. Electron-beam powder-bed fusion of metals belongs to ER-146 and supplies no direct evidence for radiation curing of acrylate coatings or films.

The primary evidence base comprises four directly controlled sources [1-4]. Their formulations, thicknesses, accelerators, atmospheres and dose ranges are study-specific. This review uses them to establish distinctions and qualification needs, not universal processing windows.

2. The initiation routes are physically different

In a photoinitiated formulation, photons must reach an absorbing species capable of generating the reactive intermediates that start polymerisation. Spectral output, photoinitiator absorption, formulation attenuation, scattering, optical path and oxygen at exposed interfaces all participate in the delivered cure state.

In electron-beam curing, energetic electrons deposit energy through interactions with the irradiated material. A deliberately added photoinitiator is not required in the systems considered here [1,2]. Absorbed dose, dose rate and accelerating voltage are therefore not optical equivalents expressed in different units. They are EB process coordinates with different physical meanings.

Frison et al. showed in a defined aromatic epoxy-diacrylate film that dose and dose rate affected conversion, gel/sol composition and viscoelastic or network response, while accelerating voltage governed electron penetration [1]. The study also showed that sufficiently energetic irradiation can activate chemistry beyond simple acrylate double-bond conversion [1]. This is direct evidence against treating conversion as a complete description of network identity.

3. No universal UV-to-EB conversion exists

Matching an optical energy measure to an EB dose does not establish equivalent initiation, conversion or network state. Schissel, Kloepper and Jessop compared five acrylate formulations using an explicit equivalent-initiation-energy approach [2]. EB curing proceeded without photoinitiator [2]. Conversion responses depended on initiation route and monomer chemistry [2]. The two routes also require different depth-energy descriptions; that is a methodological consequence of their different energy-delivery mechanisms, not a reported formulation dependence.

The significance is methodological. A conversion factor derived for one density, thickness, spectrum, photoinitiator, atmosphere and geometry is a model result for that system. It cannot be promoted to a universal relationship between kGy and optical radiant exposure. Even where bulk conversion appears similar, the routes may differ in initiation distribution, side reactions, soluble fraction, crosslink topology and through-thickness state.

Transfer should therefore begin with a new process map, not a unit conversion. The record should separately identify optical spectral exposure for the photoinitiated state and absorbed dose, dose rate, voltage, scan or pass configuration and atmosphere for the EB state.

4. Depth-dose coupling replaces optical attenuation, but not with a constant

Optical cure depth is limited by absorption and scattering within the formulation and by the spectrum-dependent response of the initiator. EB energy deposition is also depth-dependent, but the governing mechanism and control variables are different. Electron penetration changes with accelerating voltage and with the density, composition and thickness of the irradiated article [1,2].

Penetration is not identical to adequate cure. A beam may deposit energy through a declared thickness while still producing an inadequate reaction or network state. Wei et al. compared UV- and EB-cured graphene composite films and found that the two routes diverged with filler loading: the EB-cured films cured uniformly between upper and lower surfaces and their cure depth was unaffected by graphene content, while the UV-cured films were non-uniform and their cure depth fell as graphene content rose [3]. Because this

evidence is available at abstract level, ER-188 uses it only to support the need for formulation-specific depth verification.

A qualification specimen should represent the actual density, filler state, substrate, thickness and beam access of the product. Thin-film results do not automatically transfer to thick sections, pigmented systems, multilayers or assemblies containing high-density inclusions.

5. Dose, dose rate and voltage are distinct controls

Absorbed dose describes energy deposited per unit mass. Dose rate describes how rapidly that energy is delivered. Accelerating voltage influences electron energy and penetration. Holding one coordinate constant does not hold the others constant, and equal total dose does not guarantee equal reaction history.

The Frison study directly supports this separation because conversion and network descriptors changed with both dose and dose rate in the investigated formulation [1]. The practical implication is that a process specification containing only a target dose can be incomplete. It may omit a rate-dependent kinetic or thermal history and may not ensure the required depth distribution.

The minimum EB process record should therefore identify the measurement basis for dose, dose-rate condition, accelerating voltage, number and arrangement of passes, line speed where relevant, beam-window and product geometry, atmosphere, product temperature and dosimetry location. This list is proposed qualification logic. It is not a universal recipe taken from a single source.

6. Conversion is not network equivalence

Acrylate double-bond conversion is useful, but it cannot by itself establish equality of cured states. Two conditions with similar conversion can differ in soluble fraction, crosslink distribution, trapped species, chain architecture, relaxation response or depth uniformity. Frison et al. explicitly connected EB conditions with gel/sol composition and viscoelastic/network properties [1]. Schissel et al. showed that initiation route and formulation influenced conversion under their comparison protocol [2].

ER-188 therefore proposes a state-resolved comparison. At minimum, route transfer should distinguish:

1. conversion or reacted-function measure;
2. gel and soluble fractions under a declared extraction method;
3. mechanical or viscoelastic response in the intended state;
4. through-thickness uniformity;
5. residual and reaction-product profile relevant to intended use;
6. final functional performance on the actual substrate or assembly.

Acceptance criteria must be claim-specific. This review supplies no universal conversion, gel fraction, modulus or residual limit.

7. What “without a photoinitiator” does and does not mean

For an EB formulation to which no photoinitiator is deliberately added, photoinitiator residues and photoinitiator-derived photoproducts are absent by formulation design. This can remove one defined source category from a chemical-risk assessment and is the direct complement to the photoinitiator migration problem owned by ER-095.

It does not establish that the cured article contains no residual or mobile species. Unreacted acrylates, oligomeric fractions, additives, impurities, irradiation products, substrate-derived species and products of unintended side reactions may remain relevant. Frison et al. show why the last category cannot be ignored: energetic EB conditions can activate chemistry beyond the targeted acrylate functionality [1].

Accordingly, “photoinitiator-free” is a compositional statement, not a synonym for non-migrating, non-toxic, food-contact compliant, medical-grade or low-extractable. Any such claim requires its own analytical, toxicological and regulatory evidence in the final material state.

8. Oxygen response must be demonstrated

Oxygen inhibition is commonly associated with radical photocuring at an exposed surface, but ER-188 does not assign blanket oxygen immunity to EB curing. Oxygen response depends on initiation rate, energy deposition, formulation, surface exposure, atmosphere and the endpoint being measured. An apparently dry surface does not prove through-thickness network equivalence or acceptable residual chemistry.

The qualification design should compare relevant surfaces and depths under the actual atmosphere. Where nitrogen or another controlled atmosphere is used, concentration, flow, enclosure, line speed and product geometry should be recorded. A change in atmosphere is a process change even if nominal absorbed dose remains constant.

No universal oxygen threshold is derived from the present evidence set.

9. Formulation, filler and substrate remain part of the cure system

EB removes the need for an optical photoinitiator, but it does not make formulation architecture irrelevant. Reactive functionality, molecular weight, viscosity, filler or pigment, additive package and substrate can alter energy deposition, reaction, network formation and final performance.

Wei et al. provide route-specific evidence from graphene-containing films [3]. Bisio et al. evaluated an EB-curable acrylic coating with an acrylated tannic-acid adhesion promoter across formulation, network incorporation, metal substrate and coating performance [4]. Together, these sources support treating the formulation and substrate as controlled parts of the EB process rather than assuming that accelerator settings alone determine success.

The food-metal-packaging context of [4] does not establish food-contact compliance, migration safety or general equivalence for other substrates. It demonstrates the need for application-specific evaluation.

10. Requalification when transferring a UV formulation to EB

A formulation qualified under UV should be treated as a new material-process state when transferred to EB. Removing the photoinitiator changes composition. Retaining it changes the chemical species exposed to ionising radiation. Adjusting reactive diluent, inhibitor, pigment or stabiliser to accommodate EB changes the formulation again.

A bounded transfer programme should:

1. define the intended claim and the accepted UV reference state;
2. lock the composition of the proposed EB formulation;
3. establish dose, dose rate, voltage, atmosphere and geometry controls;
4. verify depth-dependent conversion and network state;
5. compare soluble/residual chemistry using methods appropriate to the claim;
6. compare mechanical, adhesion and functional performance on the intended substrate;
7. evaluate ageing and environmental exposure where the claim depends on them;
8. define acceptance criteria, deviations and future change triggers.

This sequence is proposed by ER-188 as qualification logic. It is not presented as a validated universal protocol.

11. Failure modes and discriminating measurements

An inadequate EB-cured state can arise from insufficient absorbed dose, unsuitable dose rate, inadequate penetration, shadowing or non-representative dosimetry, atmosphere variation, formulation heterogeneity, substrate effects or a reaction pathway that differs from the expected acrylic network formation. Similar symptoms can have different causes.

A soft or tacky surface should not automatically be assigned to low total dose. Surface chemistry, oxygen, contamination and formulation may be involved. A brittle film should not automatically be assigned to overcure; formulation, depth gradient, substrate constraint and thermal history may also contribute. A failed adhesion result may reflect interfacial chemistry rather than bulk conversion.

Discriminating measurements can combine dosimetry, depth-resolved spectroscopy, extraction/gel analysis, thermal or viscoelastic measurements, surface analysis, microscopy and application-specific testing. The chosen set should distinguish the competing mechanisms relevant to the declared failure, not merely generate more measurements.

12. Change control

Potential requalification triggers include monomer or oligomer identity, functionality distribution, inhibitor or stabiliser, additive or filler, photoinitiator removal or retention, pigment state, coating weight, density, thickness, substrate, accelerating voltage, beam current, line speed, pass configuration, atmosphere, dosimetry system, equipment window condition and post-cure or thermal history.

Not every change requires complete repetition. A bridging argument is acceptable when retained tests can detect the affected failure modes and when the rationale is documented. Nominally unchanged dose is not sufficient evidence if the change can alter penetration, rate, chemistry or depth uniformity.

13. Minimum reporting

A reusable report should identify formulation composition and lot state, absence or presence of deliberately added photoinitiator, specimen and substrate, density and thickness, accelerator and voltage, absorbed-dose method and location, dose rate or line conditions, number of passes, atmosphere, temperature, conversion method, depth sampling, gel/sol or residual method and the functional tests tied to the claim.

The report should distinguish measured results from modelled energy deposition, and both from assumptions. It should state whether values apply to the surface, a bulk average or a depth-resolved location. It should also state what the experiment does not qualify.

14. Evidence limitations

The four-source evidence core is sufficient for a bounded critical review but not a systematic comparison of EB equipment, formulations or applications. Two sources are full primary journal articles, one is a full primary conference proceeding and one is used at publisher-record and abstract depth [1-4].

The available evidence does not support universal EB dose, dose rate, voltage, penetration depth, oxygen condition, conversion target, residual limit or UV-to-EB equivalence rule. It also does not establish automatic food-contact, medical or regulatory suitability.

15. Conclusions

Electron-beam curing can initiate acrylate network formation without a deliberately added photoinitiator, thereby removing photoinitiator-derived residues and photoproducts from the formulation pathway. That is a specific and potentially valuable difference. It is not proof that every other residual, extractable or migrating species is absent.

Direct evidence shows that absorbed dose, dose rate, accelerating voltage, formulation and cure route can affect conversion, gel/sol composition, depth response and network properties [1-4]. Consequently, equality of nominal energy or bulk conversion does not establish material equivalence.

The defensible transfer rule is therefore conservative: a UV-qualified formulation moved to EB is a new material-process state. Its composition, energy deposition, depth response, network state, residual chemistry and intended-use performance must be demonstrated under the actual production conditions. ER-188 supplies the framework for that demonstration while refusing universal process windows and automatic regulatory conclusions.

Related Engineering Review boundaries

ER-083 and ER-084 own general photocuring taxonomies. ER-095 owns photoinitiator migration and substitution. ER-188 owns the complementary photoinitiator-free EB case and its route-transfer qualification. ER-146 concerns electron-beam powder-bed fusion of metals and is unrelated.

References

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. This review does not claim that any 3Dresyns product is qualified for electron-beam curing, food-contact, medical or regulated use.

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Data availability

No new experimental dataset was generated for this review.