

Controlled Undercure in Radiation-Curable Pressure-Sensitive Adhesives: The Conversion Window, Residual Unsaturation as a Specification, and Migration from a Permanently Soft Layer

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Statement of Significance

A pressure-sensitive adhesive is not qualified by driving its photocure as far as possible. It must remain sufficiently compliant and dissipative to wet a counter-surface and develop tack while retaining enough cohesive network strength to resist shear, edge lifting, transfer and internal failure. In a radiation-curable PSA, cure therefore creates a bounded material-state problem rather than a simple maximisation problem. The useful state depends on formulation, coating weight, irradiation history, network formation and the measurement used to describe that state. Direct UV-PSA studies show that tack, peel adhesion and cohesive/shear performance can move in different directions as crosslinking advances [1-4]. Chemical conversion, gel fraction, residual carbon-carbon double bonds and residual monomer are likewise non-equivalent measurements [5-8]. ER-190 defines the evidence required to specify and requalify a deliberately bounded undercured PSA state without turning one published dose, conversion value, residual-unsaturation level or residual-monomer concentration into a universal target.

Keywords: radiation-curable pressure-sensitive adhesive; PSA; controlled undercure; conversion window; residual unsaturation; residual monomer; tack; peel adhesion; cohesion; shear strength; gel fraction; migration; UV crosslinking; qualification

Abstract

Radiation-curable pressure-sensitive adhesives occupy an unusual position in polymer processing: the released material must remain permanently soft enough to wet and adhere on contact while also carrying a crosslinked network sufficient to resist cohesive flow and failure. The optimum state is therefore not synonymous with maximum conversion or maximum crosslink density. Direct studies of acrylic UV-curable PSAs demonstrate that formulation, photoinitiator concentration, UV dose, exposure time and coating weight change tack, peel, shear, thermal response and shrinkage in coupled but non-identical ways [1-4,7]. Separate studies show that ATR-FTIR, gel fraction, calorimetry and residual-monomer analysis describe different parts of the cure state [5,6,8]. Residual carbon-carbon unsaturation can remain analytically detectable after useful network formation, while residual unreacted monomer is a distinct chemical population whose mobility and migration implications require separate measurement.

This review treats controlled undercure as an engineered, bounded network state rather than arbitrary incomplete curing. It develops a state-resolved qualification architecture linking incoming formulation, film thickness or coating weight, delivered radiant exposure, atmosphere and temperature to chemical conversion, gel/network formation, tack, peel, cohesion, residual unsaturation, residual monomer and application-specific migration evidence. No universal conversion window, residual-unsaturation specification, UV dose, photoinitiator level, coating weight or residual-monomer threshold is proposed. Structural-joint design and general bondline cure physics remain outside scope.

1. Scope, terminology and ownership

ER-190 addresses radiation-curable pressure-sensitive adhesive layers whose intended function depends on remaining permanently soft after cure. Its central question is how to define, measure and qualify a deliberately bounded cure state that preserves useful tack and wetting while creating enough network integrity for the intended cohesive duty.

Within the named sub-series *Radiation Curing Beyond Additive Manufacturing*, the same photochemistry, oxygen-inhibition, attenuation, interfacial and qualification principles are examined in films, coatings, inks and bulk-applied materials rather than only in printed layers. ER-190 focuses specifically on permanently soft radiation-curable pressure-sensitive adhesive films and coatings.

The phrase **controlled undercure** is used narrowly. It does not mean an accidentally unfinished reaction, an unknown exposure history or a failed cure. It means that the released PSA state is intentionally bounded below the maximum attainable conversion or crosslinking because the required adhesive function depends on retained mobility. That state is acceptable only when its chemistry, network response, adhesive performance and residual-species implications have been measured within a declared formulation and process window.

The controlled Gate 2 decision assigns ER-190 ownership of deliberate undercure/network state, tack/cohesion balance and the residual-unsaturation/migration question in permanently soft layers. Structural bonding of printed photopolymers belongs elsewhere. General light-curable adhesive formulation and bondline cure physics also belong elsewhere. ER-190 is therefore not a structural-joint design review and not a general review of all photocurable adhesives.

2. Why a PSA cannot be qualified by maximum cure

The defining behaviour of a PSA is interfacial contact under modest pressure without a separate liquid-to-solid cure step at the moment of bonding. That function requires the material to flow or deform sufficiently at the interface to create intimate contact while retaining enough cohesive integrity to avoid internal flow or transfer. Radiation curing changes both sides of that balance.

Kim et al. showed in a defined acrylic PSA system that UV curing conditions altered rheological, thermal and adhesive performance [1]. Czech and co-workers independently showed that increasing UV crosslinking can reduce tack while increasing cohesive or shear performance, with peel adhesion responding differently and potentially passing through a system-specific optimum [2-4]. These studies do not establish one universal optimum. They establish the more important engineering point: **more cure is not a monotonic improvement variable for all PSA functions.**

A useful cure window must therefore be expressed against a vector of responses, not a single maximum. At minimum the released state must identify the adhesive functions that matter for the application and the failure modes that would make the layer unacceptable.

3. Tack, peel and cohesion are different measurands

Tack measures rapid adhesive interaction under a defined contact history. Peel resistance measures force during progressive interfacial separation under a declared geometry, rate and substrate condition. Cohesive or shear performance measures resistance to internal deformation or failure under sustained or imposed load. These responses share dependence on network state but are not interchangeable.

The UV-PSA literature used here repeatedly demonstrates this non-equivalence [2-4]. A formulation can gain cohesive strength while losing tack. Peel can increase, decrease or pass through a maximum depending on the competing effects of wetting, dissipation, interfacial interaction and cohesive integrity. A qualification programme that reports only tack cannot establish shear durability; one that reports only shear cannot establish rapid wetting or peel behaviour.

Accordingly, ER-190 treats the required response set as application-specific. The minimum vector contains only those properties needed to close the declared duty, but no single response may silently stand in for all of them.

4. Cure state is multidimensional

Chemical conversion describes consumption of reactive functionality under a defined analytical method. Gel fraction describes the fraction that remains insoluble under a declared extraction procedure. Network modulus or cohesive performance reflects the mechanical consequence of molecular architecture, interactions and time scale. Residual monomer describes a mobile or extractable chemical population. Residual carbon-carbon double bonds describe unreacted unsaturation that may be pendant, trapped, inaccessible, mobile or associated with species of different molecular size.

Do, Park and Kim used ATR-FTIR together with tack, peel and SAFT measurements to connect UV crosslinking chemistry with practical PSA behaviour [5]. The curing-properties study represented by [6] combined gel fraction, photo-DSC and FTIR-ATR and reported residual C=C in the cured network. Those measurements answer different questions. None authorises a one-to-one conversion between conversion percentage, gel fraction, cohesive strength and residual species.

A defensible PSA specification must therefore name the measurand. Statements such as 90% cured, fully gelled or low residual are incomplete unless the method, basis, sampling state and acceptance rule are defined.

5. Residual unsaturation is not automatically a defect

A permanently soft radiation-cured PSA can retain analytically detectable carbon-carbon unsaturation after a network sufficient for useful service has formed. The presence of residual C=C is therefore not, by itself, evidence that the adhesive is unfit. It is evidence that the chemical state is not identical to complete double-bond consumption.

This distinction matters because residual unsaturation can arise in several molecular contexts. A double bond may remain on a pendant group attached to a high-molecular-weight structure, on a soluble oligomer, on a low-molecular-weight monomer, or in a spatially inaccessible region of the network. Those states do not have equal mobility or migration potential. FTIR can indicate residual functionality but does not identify every mobile species or establish its release rate into a contacting medium.

ER-190 therefore permits residual unsaturation to become a specification only when its analytical method and relation to the required PSA state are demonstrated. A numerical residual-C=C value from one formulation is not a transferable acceptance threshold.

6. Residual monomer and migratable species are separate questions

Residual unreacted monomer is chemically distinct from residual unsaturation in the network. Czech, Bartkowiak and Krystofiak measured residual acrylic monomers in a defined solvent-free photoreactive PSA system and related them to adhesive-property and migration-related concerns [8]. Their results support the need to measure residual monomer where it matters; they do not establish a universal allowable concentration for all PSAs.

Migration additionally depends on molecular identity, concentration, network affinity, diffusion path, film thickness, contacting material, temperature, time and the analytical boundary used to define the receiving phase. A residual monomer concentration in the PSA is therefore not equivalent to a migration result. Conversely, a low residual-unsaturation signal does not prove that all mobile species are absent.

Where migration is safety- or function-critical, the qualification chain must distinguish at least three questions: what reactive or residual species remain, which of those species are extractable or mobile under the

relevant conditions, and what transfer actually occurs into the defined contacting phase over the declared exposure.

7. Formulation and photoinitiator state

The cure window belongs to a formulation, not to UV exposure alone. Reactive monomer and oligomer architecture, photoinitiator identity and concentration, chain-transfer behaviour, added crosslinker, stabiliser package and other constituents alter both reaction kinetics and the final viscoelastic state.

Czech, Bartkowiak and Mozelewska showed that unsaturated photoinitiator chemistry and concentration interact with UV dose and exposure time to change tack, peel and shear [2]. Related studies using multifunctional or additionable photoinitiator architectures likewise demonstrate that the response to irradiation depends on formulation design [3,4]. These observations justify recording formulation identity and photoinitiator state as controlled inputs. They do not justify transplanting one photoinitiator percentage into another resin family.

A change of monomer ratio, oligomer batch, photoinitiator grade, reactive crosslinker or stabiliser therefore has potential to move the qualified cure window even when the lamp setting is unchanged.

8. Delivered radiant exposure, not nominal lamp time

Exposure time alone is not the energy state received by a film. The delivered field depends on source spectrum, irradiance, distance, optics, ageing, geometry, attenuation, atmosphere and temporal history. For ER-190, these variables matter only to the extent that they alter the PSA state; the paper does not attempt to become a general radiation-source qualification review.

The direct PSA studies show that UV dose and time affect tack, peel and cohesion in formulation-specific ways [1-4,7]. Therefore a qualified record should preserve the actual exposure descriptor used by the process, the measurement basis for that descriptor and the relation between source command and film state. If only time is recorded, the evidence is bounded to the source configuration under which that time was demonstrated.

No irradiance, dose or exposure-time value from the cited studies is adopted as a universal target.

9. Coating weight and film thickness are part of the cure state

Mozelewska et al. directly show that composition, UV dose and coating basis weight interact in determining tack, peel, shear, SAFT and shrinkage [7]. This is a central qualification point. A thicker PSA layer changes optical path length, thermal mass, oxygen-access geometry and the amount of material through which the network must carry cohesive load. A process that is qualified at one coating weight is not automatically qualified at another.

Coating weight and physical thickness should not be conflated when density, solids content or substrate penetration can vary. The record should state whichever quantity is controlled and, where necessary, establish their relationship for the actual formulation and coating method.

A cure window is therefore at least a formulation-exposure-thickness state, not a lamp setting in isolation.

10. Oxygen and surface state

Radical photopolymerisation can be sensitive to oxygen near exposed surfaces. In a thin PSA film, the surface-to-volume ratio can make surface inhibition particularly relevant to tack and interfacial behaviour. The effect, however, depends on formulation, source, atmosphere, film thickness, exposure direction and surrounding interfaces.

ER-190 does not prescribe inerting as universally necessary. Instead, atmosphere is treated as a controlled process variable when evidence or process history shows that it materially changes the released PSA state.

The qualification record should distinguish a film cured against a liner, under air, under a second substrate or under a deliberately controlled atmosphere, because those boundary conditions are not automatically equivalent.

11. The conversion window is an evidence construct

A **conversion window** is useful only if both its lower and upper boundaries are tied to failure modes. The lower boundary can be limited by inadequate network formation, excessive cohesive flow, transfer, poor thermal resistance or unacceptable residual species. The upper boundary can be limited by loss of tack, reduced wetting, embrittlement, reduced peel energy or another application-specific loss of adhesive function.

The cited literature establishes the possibility of such competing trends but does not provide universal window limits [1-8]. A defensible window is therefore built experimentally for the actual formulation, coating weight, substrate/liner system and radiation process. Chemical and performance measurements are linked but retained as separate evidence streams.

Where no single conversion value is measured directly, the process can still be qualified through a controlled multivariate state description. What is prohibited is calling the state a conversion window while measuring only a lamp command or one adhesive property.

12. A measurement architecture for controlled undercure

A practical measurement stack can be divided into four layers.

Reaction-state measurements may include FTIR or another validated method for residual reactive functionality, calorimetry where appropriate, and related chemistry-sensitive methods. These describe reaction progress but not complete adhesive performance.

Network-state measurements may include gel/sol fraction, rheological or viscoelastic response, cohesive/shear performance and other methods that reveal whether an effective network has formed.

Adhesive-function measurements include tack, peel and application-relevant holding power or shear. Test geometry, substrate, surface state, dwell, rate, temperature and conditioning belong to the result.

Residual-species measurements include residual monomer, extractables or migration tests selected for the intended contact and risk. They cannot be replaced by FTIR residual-C=C alone.

The qualification argument becomes stronger when these layers converge on the same bounded state without being collapsed into one surrogate variable.

13. Failure modes and diagnostic separation

An undercured-looking failure is not automatically caused by low conversion. Low tack can result from excessive crosslinking, poor wetting, contamination or substrate incompatibility. Cohesive transfer can reflect insufficient network formation but can also depend on temperature, dwell and load. Poor peel can arise from too little interfacial contact, too much network stiffness, a weak interface or an inappropriate test geometry.

Residual species likewise require diagnostic separation. A high residual-monomer result can arise from formulation or insufficient reaction, but the appropriate correction cannot be selected without knowing the chemical identity and process state. Increasing dose may reduce one residual species while moving tack or peel outside the useful window.

ER-190 therefore requires a mechanism-discriminating investigation rather than a default instruction to cure more.

14. Qualification by bounded process state

The minimum controlled record for a radiation-curable PSA should bind:

1. formulation identity and component lots;
2. photoinitiator/crosslinker identity and concentration basis where relevant;
3. coating method and coating weight or thickness;
4. substrate, liner and atmosphere/boundary state during cure;
5. radiation source identity, spectrum and delivered-exposure descriptor;
6. process temperature and other state variables shown to matter;
7. chemical/network-state measurements selected for the formulation;
8. tack, peel and cohesive/shear measurements selected for the duty;
9. residual-monomer/extractable/migration evidence where relevant;
10. conditioning, ageing and service-representative checks required by the intended use.

The record is not a universal recipe. It is the identity of the state for which the PSA claim has evidence.

15. Change control and requalification triggers

Requalification should be considered when a change can move the cure-state balance. Examples include a new monomer or oligomer source, photoinitiator grade or level, crosslinker, stabiliser, pigment or other additive; a changed coating weight; a new liner or substrate; a changed source spectrum or irradiance field; an altered exposure sequence; changed atmosphere; changed temperature; or a new residual-species or migration claim.

The depth of requalification depends on the demonstrated sensitivity of the system. A change that is shown not to move the relevant state may be bridged with focused evidence. A change that affects the reaction, network, film geometry or contacting environment can require a larger qualification repeat.

No percentage-change rule is universal. The trigger is the possibility that the evidence supporting the released state no longer transfers.

16. Migration and regulated-use boundaries

Migration is an application-specific transfer problem. Food contact, medical contact, pharmaceutical use and other regulated applications impose evidence requirements that are not established by a generic PSA cure study. ER-190 therefore does not translate residual-monomer or adhesive-performance data into a regulatory acceptance conclusion.

A material can meet tack, peel and cohesion requirements while failing a residual-species requirement, and the reverse can also occur. The complete released state must meet all requirements relevant to the intended duty. Where the PSA is part of a regulated product, responsibility for the finished-product qualification remains with the applicable manufacturer and regulatory framework.

The review provides no universal migration limit and no declaration of suitability for a regulated use.

17. Reporting and publication discipline

A useful engineering report separates measured results from inferred mechanism. It states the exact formulation state, process conditions and test method for each result. Study-specific optima remain attached to the study. Low residual, high conversion, good tack and fully cured are not acceptable standalone descriptors without measurement basis.

For comparative work, raw or appropriately normalised response curves are preferable to a single selected optimum because the trade-off among tack, peel and cohesion is itself the engineering object. Where an equivalence claim is made after a change, the acceptance margin and uncertainty rule should be declared rather than inferred from overlapping mean values alone.

ER-190 is part of the **Radiation Curing Beyond Additive Manufacturing** sub-series. That label does not change the evidence standard: every public claim remains bounded to the actual formulation, process, film geometry and measurement state.

18. Conclusions

Controlled undercure in a radiation-curable pressure-sensitive adhesive is not a defect category. It is a deliberately bounded network state required when permanent softness and interfacial wetting must coexist with sufficient cohesive integrity. Direct UV-PSA studies demonstrate why the useful state cannot be selected by maximising cure: tack, peel and cohesive/shear response are non-equivalent and can move in competing directions as formulation and irradiation change [1-4].

Chemical conversion, gel fraction, residual carbon-carbon unsaturation and residual monomer likewise describe different aspects of the material state [5,6,8]. Residual C=C can remain measurable without proving migration or failure; residual monomer and actual migration require separate analytical treatment. Coating weight, formulation identity and delivered irradiation are coupled process variables [2,7].

The defensible engineering output is therefore not a universal conversion percentage or UV recipe. It is a qualified state window that binds formulation, film geometry, radiation history, reaction/network evidence, tack-peel-cohesion performance and any required residual-species or migration measurements. Changes that can move that state require bridging evidence or requalification. Structural-joint design and general bondline cure remain outside this review.

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Related Engineering Review boundaries

- ER-165 retains structural bonding and joint qualification of printed photopolymer substrates.
- ER-186 retains formulation and general bondline-cure engineering for light-curable adhesives.
- ER-086 and ER-095 retain extractables/migration-method and exposure/biological-risk boundaries relevant to regulated-use interpretation.
- ER-190 owns only the bounded undercure/network-state problem in radiation-curable pressure-sensitive adhesive layers.

Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. The paper is an engineering review and qualification framework, not an independent product comparison. No proprietary formulation, product ranking or universal operating window is provided.

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Data availability

No new experimental dataset was generated for this review.