

Reactive-Diluent Selection in Photocurable Formulations

Viscosity, conversion, shrinkage, network state and hazard trade-offs

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Abstract

A reactive diluent is not an inert viscosity reducer. It changes the liquid formulation, participates in cure and becomes part of the resulting network or residual-species population. Selection must therefore connect processing viscosity, compatibility, photoreactivity, achievable conversion, shrinkage, network state, volatility and hazard classification. Optimising any one of these dimensions in isolation can displace risk into another: a low-viscosity monomer can increase volatility or alter shrinkage; higher functionality can accelerate gelation yet restrict late conversion; a flexible spacer can reduce shrinkage in one formulation while reducing modulus; and lower nominal hazard cannot be inferred from a structural label alone.

This review presents a bounded selection architecture for photocurable formulations. It defines the material identity and specimen state needed for comparison, separates screening properties from formulation-level evidence, and treats viscosity, conversion, shrinkage and cured performance as coupled responses rather than intrinsic rankings. Direct studies show that reactive-diluent structure can change volatility, dilution efficiency, cure response and thermomechanical properties, but their numerical results remain system specific. The central recommendation is a staged comparison in a controlled base formulation, followed by verification under the intended process, post-cure and service state. Selection is a multi-criteria qualification decision, not a search for a universally best diluent.

Keywords: reactive diluent; photocurable formulation; viscosity; conversion; shrinkage; volatility; network state; hazard; qualification; multi-criteria selection

1. Significance and scope

Reactive diluents make viscous oligomer systems processable while remaining chemically involved in network formation. Their effects begin before exposure, continue through polymerisation and persist in the cured material. Consequently, the term *diluent* can conceal a large design responsibility.

This review addresses how to compare and select reactive diluents for radical photocurable formulations and how to transfer the same decision logic, with chemistry-specific modifications, to other photocuring families. It does not provide a commercial recipe, a universal concentration or a preferred supplier list.

1.1 Corpus boundary

ER-211 owns the formulation-level selection trade-off for reactive diluents. ER-027 owns conversion metrology and spatial cure heterogeneity. ER-031 owns cure shrinkage, residual stress and warpage. ER-091 owns historical evidence density and hazard classification of UV-curable monomers. ER-094 owns monomer structure-hazard relationships and limits of read-across. ER-172 owns incoming raw-material identity, inhibitor level, functionality distribution, impurity and lot equivalence. ER-182 owns network-state metrology. ER-212 owns oligomer molecular architecture. ER-219 owns volatile reactive-diluent loss, composition drift and requalification. ER-211 uses outputs from those subjects but does not replace their dedicated methods or acceptance decisions.

2. Define the candidate before comparing it

The minimum identity of a candidate includes chemical name, reactive-group family, nominal functionality, molecular-mass information, inhibitor package, purity or assay, relevant impurities, water content where applicable, supplier and lot. A commercial material described only as mono-, di- or tri-functional is not sufficiently defined for scientific transfer.

Identity should be separated from role. The same molecule may act as viscosity modifier, comonomer, flexibilising segment, polarity modifier or solubilising component depending on the rest of the formulation. A selection record should state the intended role and the base formulation in which it is tested.

3. Selection is a vector, not a rank

Let a candidate be described by a response vector

$$\mathbf{z} = (\eta, C, Sv, Tg, E, \epsilon b, Lv, H)$$

where η is viscosity under declared conditions, C is conversion, Sv is volumetric shrinkage, Tg is a glass-transition descriptor, E is modulus, ϵb is elongation at break, Lv is a volatility or mass-loss descriptor and H is the applicable hazard and exposure profile. No scalar score should be reported unless the weights, normalisation and decision context are declared.

Kury and co-workers evaluated viscosity, volatility, thermal stability, photoreactivity and thermomechanical response together, illustrating why dilution efficiency alone is incomplete [1]. Their salicylate-based systems are useful examples, not universal substitutes.

4. Viscosity and process state

Report viscosity with temperature, shear rate or frequency, measurement geometry, conditioning and time after mixing. A single value at an unspecified temperature cannot support recoating, jetting or heated-vat decisions. Mixtures may be non-ideal; a useful descriptive model is

$$\ln \eta_{mix} = \sum_i \phi_i \ln \eta_i + \Delta_{mix}$$

where ϕ_i is a declared volume fraction and Δ_{mix} is an empirical interaction term. This expression is a fitted comparison tool, not a universal mixing law.

The NIST study of dimethacrylate dental composites found that resin viscosity affected the radiant exposure required to approach adequate polymerisation in those systems [2]. This supports measuring viscosity as part of cure qualification. It does not establish a universal exposure correction for vat photopolymerisation.

5. Compatibility and phase state

A candidate that reduces initial viscosity can still be unsuitable if it causes haze, crystallisation, sedimentation, microphase separation or time-dependent drift. Screen the complete formulation over the intended temperature window and storage interval. Record mixing order and thermal history.

Compatibility must include photoinitiator, absorber, pigment, filler, oligomer and other additives. Apparent clarity is not proof of molecular homogeneity, while a stable structured dispersion is not necessarily a failure. The relevant question is whether the phase state is controlled and compatible with optical transport, cure and service performance.

6. Reactive-group identity and functionality

Nominal functionality influences network formation but does not uniquely determine effective crosslink density. Steric accessibility, intramolecular cyclisation, unequal group reactivity, conversion and comonomer sequence all intervene. Acrylate and methacrylate labels also imply different kinetic tendencies, but formulation-specific measurement remains necessary.

The direct vat-polymerisation comparison by Kılıç and Camadanlı held triacrylate content constant and observed structure-dependent dilution, shrinkage and tensile responses [3]. The study shows that candidates with equal nominal functionality need not be equivalent. Its reported numerical changes apply only to the tested resin and process.

7. Conversion and mobility arrest

Conversion should be measured in the intended spectral, thermal and oxygen environment and at relevant depths or locations. A diluent can increase early mobility and rate while changing the conversion at vitrification, residual unsaturation or dark reaction. Conversion is not equivalent to gel fraction, crosslink density or modulus.

For a suitably normalised infrared band, a simplified conversion estimate is

$$C(t) = 1 - \frac{A_t/A_{r,t}}{A_0/A_{r,0}}$$

where A_t is the reactive-band area and $A_{r,t}$ is a stable reference-band area. Band selection, baseline, sampling depth and reference stability must be validated. Dimethacrylate-network measurements demonstrate that vitrification can change property evolution and leave continued conversion coupled to mobility [4].

8. Shrinkage and stress are related but distinct

Volumetric shrinkage may be expressed as

$$S_v = \frac{V_0 - V_c}{V_0}$$

where V_0 and V_c are uncured and cured volumes under declared conditions. Measurement timing matters because thermal contraction, solvent loss and post-cure can be superimposed.

Shrinkage does not uniquely predict residual stress. Stress depends on when the material acquires stiffness, constraint, geometry, temperature and relaxation. ER-031 retains that dedicated boundary. ER-211 requires shrinkage and stress-related evidence to be recorded separately and prevents a low-shrinkage result from becoming an unsupported low-warpage claim.

9. Network state and thermomechanical response

Reactive diluents become network strands, pendant groups, soluble residuals or combinations of these states. Compare gel fraction, swelling-derived descriptors, dynamic-mechanical response and residual extractables where relevant. No single result should be relabelled as crosslink density without a justified model.

Monofunctional candidates may reduce junction density in one system but can also raise conversion or introduce rigid segments. Multifunctional candidates may raise early network connectivity but increase heterogeneity or mobility arrest. The outcome depends on the coupled oligomer-diluent-initiator system [1,4].

10. Volatility and composition drift

Volatility must be measured over the intended time, temperature, surface-area and ventilation conditions. Vapour pressure, isothermal mass loss and process emissions answer different questions. Kury and co-workers showed large differences in mass loss among tested monofunctional diluents and connected volatility to possible composition change during processing [1].

ER-211 uses volatility as a selection criterion. The detailed handling-and-cure loss model, emissions, surface-state consequences and requalification after composition drift remain within ER-219. A low room-temperature mass loss does not establish negligible loss during heated processing.

11. Hazard, exposure and procurement screen

Hazard comparison requires current substance identity, classification data and safety data sheets for the actual supplied material. Mixture classification depends on the classified components, concentrations and applicable rules; it cannot be inferred from viscosity, bio-based origin, molecular mass or one structural motif [5].

The selection record should distinguish intrinsic hazard, exposure potential and risk controls. Lower volatility may reduce one inhalation pathway without removing skin sensitisation, irritation or other hazards. Final regulatory classification, workplace controls and waste obligations belong to competent jurisdiction-specific assessment. ER-091 and ER-094 retain the deeper hazard-evidence and read-across boundaries.

12. Interpretation matrix

Observation	Supported interpretation	Required follow-up	Unsupported leap
Lower viscosity at the test temperature	Better flow under that declared condition	Full rheology and process trial	Universal printability
Higher final conversion	More reacted groups in the sampled state	Gel, extractables and property measurements	Higher crosslink density by definition
Lower measured shrinkage	Smaller volume change in that method and interval	Stress and constrained-geometry testing	Lower warpage in every part
Higher modulus or glass-transition response	Changed network response in the tested state	Conversion, conditioning and service-temperature checks	Better toughness or durability
Lower isothermal mass loss	Lower loss in that test	Process-representative loss and composition checks	Non-volatile under all conditions
Less severe supplier classification	Different current classification evidence	Identity, concentration, SDS and exposure review	Intrinsically safe formulation

13. Minimum reporting set

Report candidate identity, supplier and lot; purity, inhibitor and relevant impurities; base formulation and replacement basis; mass and volume fractions; mixing order and thermal history; phase state; rheometer geometry, temperature and shear condition; exposure spectrum, irradiance, time and atmosphere; conversion method and sampling location; shrinkage method and timing; post-cure and conditioning; gel, swelling, extractables and dynamic-mechanical methods where used; volatility protocol; current classification and safety-data sources; replicate count, uncertainty and statistical treatment; and the decision rule used to select or reject a candidate.

Include both favourable and displaced responses. A formulation-level comparison should use a common base resin and matched process state. If equal-viscosity, equal-functional-group or equal-mass substitutions answer different questions, report them as separate experiments.

14. Knowledge boundary

Available studies establish that reactive-diluent identity and structure can influence viscosity, volatility, conversion behaviour, shrinkage and cured properties. They do not establish a transferable ranking of commercial diluents across oligomers, photoinitiators, spectra, filler states, post-cures and applications. The literature also does not justify deriving hazard or mixture classification from nominal functionality, renewable content or volatility alone. Candidate selection therefore requires formulation-specific comparison and current regulatory evidence.

15. Limitations

This review concentrates on selection architecture rather than exhaustive monomer chemistry. Most direct comparative studies cover a limited candidate set and one base formulation. Proprietary commercial identities and impurity distributions are often incompletely reported. Accelerated volatility tests may not reproduce open-vat handling, and bulk conversion can conceal gradients. Mechanical results depend strongly on specimen preparation and post-cure. The proposed response vector does not supply universal weights; these must come from the intended process, product and jurisdiction.

16. Conclusions

A reactive diluent should be qualified as a network-forming formulation component, not purchased as a viscosity number. The defensible workflow defines identity, compares candidates in a controlled base formulation, measures rheology under process conditions, verifies compatibility and cure, separates shrinkage from stress, characterises network and residual state, tests process-relevant volatility and reviews current hazard information. Equal nominal functionality does not imply equal behaviour, and one favourable response cannot stand in for the whole decision. The minimum-cost reliable strategy is staged screening followed by focused qualification of the few candidates that remain non-dominated across the declared criteria.

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