

Moisture Tolerance of Epoxy, Oxetane and Vinyl-Ether Cationic Photoresins

Phase state, ring opening, dark cure and storage boundaries

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Abstract

Water can act as a proton carrier, nucleophile, chain-transfer agent, hydrolysis reactant, plasticiser or separate phase in cationic photoresins. Its effect is therefore not represented adequately by one humidity value or by the statement that moisture inhibits cure. Epoxy, oxetane and vinyl-ether systems differ in monomer structure, basicity, miscibility, propagation route and network development, while formulation components change the amount and state of water that reaches the reactive species.

This review defines a comparative moisture-tolerance qualification architecture. It requires measurement of resin water content and phase state before exposure, chemistry-specific conversion during irradiation, post-irradiation dark evolution, thermal post-cure where used, and remeasurement after controlled conditioning or storage. Primary evidence covers all three monomer families, real-time water and monomer monitoring, cycloaliphatic-epoxy models, oxetane/epoxide combinations, dark cure and hybrid-network consequences. The evidence shows that water can accelerate, retard or redirect parts of the reaction depending on chemistry and state. It supports formulation-specific tolerance boundaries, not a universal water limit, humidity limit, drying instruction, monomer-family ranking, exposure compensation or shelf-life claim.

Keywords: cationic photoresin; moisture tolerance; water content; phase state; epoxy; oxetane; vinyl ether; ring opening; chain transfer; dark cure; storage boundary

1. Significance and scope

Cationic photopolymerisation is often described as insensitive to oxygen but sensitive to moisture. That shorthand is insufficient for qualification. Water can be dissolved in the resin, associated with a hygroscopic component, sorbed from air, concentrated at an interface or present as a separate phase. The same analytical water content can therefore correspond to different local reactive states.

ER-218 addresses the comparative qualification of moisture state across epoxy-, oxetane- and vinyl-ether cationic photoresins. It links measured water state to in-exposure reaction, dark evolution, post-cure and storage response. It does not restate the general cationic mechanism or prescribe a universal moisture value, drying condition, exposure adjustment, dark-cure time or shelf life.

1.1 Corpus boundary

ER-065 retains general cationic ring-opening photopolymerisation, photoacid generation, broad humidity effects, epoxy/oxetane network formation and dark-cure explanation. ER-218 owns state-resolved water measurement, comparative epoxy/oxetane/vinyl-ether response, exposure/dark/post-cure separation and formulation-specific moisture-tolerance boundaries. ER-081 retains in-can cationic stability, latency and premature polymerisation. ER-072 retains environmental ageing and property retention after hydrothermal conditioning. ER-170 retains accelerated-ageing factors and life-claim validity. ER-179 retains container, headspace, light transmission and storage-excursion disposition. ER-189 retains water removal, coalescence and film formation in waterborne UV-curable dispersions. ER-215 retains iodonium/sulfonium architecture in hybrid radical-cationic systems. ER-095 retains general photoinitiator migration and substitution.

2. Measure water content and phase state

Ambient relative humidity is an exposure condition, not a measurement of resin water. The qualification record should report water content by a validated method and state whether the formulation appears homogeneous, contains droplets or domains, or has water associated with a solid, polyol or other hygroscopic component. Sampling time and position matter because equilibration and phase separation may be slow.

A gravimetric water mass fraction can be defined as

$$w_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{m_{\text{formulation}}}$$

where $w_{\text{H}_2\text{O}}$ is the measured water mass fraction, $m_{\text{H}_2\text{O}}$ is water assigned by the declared analytical method and $m_{\text{formulation}}$ is the sampled formulation mass. The value does not identify spatial distribution or distinguish dissolved, bound and phase-separated water. Karl Fischer titration, near-infrared spectroscopy or another suitable method needs calibration and interference control for the actual chemistry.

3. Conditioning history is part of the specimen

Moisture uptake depends on temperature, humidity, exposed area, layer thickness, agitation, headspace and time. A formulation equilibrated in a sealed vial is not equivalent to a thin film exposed to humid air. Added-water experiments are also not automatically equivalent to sorption from the environment because mixing can create a different phase state.

The conditioning record should distinguish initial preparation, equilibration, sampling, exposure and later storage. When a relative-humidity condition is used, the resin water content should be measured or bounded rather than assumed from the chamber setting. Reversibility should be tested by controlled reconditioning only when that is part of the intended qualification question.

4. Water can alter several reaction steps

Water may change acid solvation, proton transfer, initiation, active-monomer formation, propagation, chain transfer and termination. It can also change viscosity and miscibility, which alter transport and local composition. A higher instantaneous conversion can coexist with shorter chains, different hydroxyl content or a changed network.

Soucek and Chen observed a non-monotonic humidity response in defined cycloaliphatic-epoxy and epoxy/polyol coatings and proposed different roles for water at low, intermediate and high conditions [2]. Koseki and Ohtsuka directly compared epoxy, oxetane and vinyl-ether derivatives in a cationic ink system and found chemistry-dependent reaction-rate responses while curing speed decreased in the tested inks [1]. These findings reject a one-sign model of moisture.

5. Conversion alone does not define the product state

Functional-group conversion is necessary but insufficient. Water-mediated chain transfer or hydrolysis can change molecular architecture without an obvious loss of endpoint conversion. Phase separation, vitrification and network heterogeneity can further decouple conversion from modulus, dimensional response or extractable species.

For a declared spectral band, conversion may be expressed as

$$\alpha(t) = 1 - \frac{A(t)/A_{ref}(t)}{A(0)/A_{ref}(0)}$$

where $\alpha(t)$ is conversion, $A(t)$ is the reactive-band area and $A_{ref}(t)$ is a validated internal reference. Water and hydrolysis products must not interfere with either band. Lin and Stansbury used near-infrared spectroscopy to monitor water and vinyl-ether response in real time, demonstrating the value of following both species rather than inferring water behaviour from monomer conversion alone [3].

6. Viscosity, miscibility and phase state can change the apparent response

Water can lower viscosity in one formulation, create domains in another, or partition into a polar component. These physical changes alter diffusion and local acid or monomer concentration. A cure-rate change cannot be assigned uniquely to a chemical mechanism unless viscosity and phase state are controlled or measured.

Ge and co-workers examined water in a visible-light-initiated methacrylate/epoxy hybrid and measured kinetics, crosslinking structure and dynamic mechanical properties [5]. Their work supports pairing kinetics with product-state evidence. It does not provide a moisture limit for a neat epoxy, oxetane or vinyl-ether photoresin.

7. Separate exposure, dark evolution and thermal post-cure

Cationic activity may continue after light is removed, but the rate depends on temperature, mobility, acid state and vitrification. A later thermal treatment can restore mobility and advance reaction through a different history. Measurements should therefore define at least the end of irradiation, one or more isothermal dark times, and the state after any declared thermal post-cure.

Let the state vector be

$$\mathbf{S}(t) = (\alpha(t), w_{H_2O}(t), T(t), P(t))$$

where α is chemistry-specific conversion, w_{H_2O} is measured water content, T is specimen temperature and P is the observed phase-state descriptor. Golaz and co-workers separated UV intensity, temperature and dark-curing effects in a defined cycloaliphatic epoxy [4]. That study supplies a measurement architecture, not a water-tolerance threshold.

8. Epoxy response is formulation-specific

Cycloaliphatic epoxies can show water-assisted proton transport or chain transfer at one condition and strong retardation at another. Polyols, hydroxyl functionality, acid strength, counterion, resin hydrophilicity and film geometry shift the observed response. The non-monotonic behaviour reported by Soucek and Chen is therefore a property of their tested systems and protocol [2].

Koseki and Ohtsuka also found that epoxy derivatives did not respond identically to water [1]. Qualification must retain exact epoxide identity and functionality rather than using “epoxy” as a sufficient category. A pass requires both reaction-state evidence and a product-state criterion relevant to the intended material.

9. Oxetane response changes in mixtures

Oxetanes can have different induction and propagation behaviour from epoxides, and their response changes when epoxide or another reactive component is added. Koseki and Ohtsuka included oxetane derivatives in a direct comparison of water effects across cationic ink chemistries [1]. Pang and co-workers showed that oxetane response depended on structure, initiator solubility and combination with epoxide or acrylate in their NIR- and UV-sensitive systems [6]. The first study supplies moisture-specific evidence in its defined ink system, while the second is direct-adjacent evidence for mixture dependence; neither permits transfer of an oxetane-only result to a different oxetane/epoxide formulation.

The required moisture experiment must therefore be conducted on the actual mixture. Reporting the oxetane fraction without the epoxide identity, initiator system, water state and optical history is insufficient.

10. Vinyl ether is an essential independent branch

Vinyl ethers undergo cationic addition rather than ring opening, and water can participate in side reactions and hydrolysis pathways that differ from cyclic ethers. ER-218 retains novelty only if vinyl-ether evidence and state-resolved water measurement remain explicit.

Lin and Stansbury monitored water and vinyl-ether monomer simultaneously and distinguished hydroxyl-containing and non-hydroxyl systems [3]. Koseki and Ohtsuka included vinyl-ether derivatives in their comparative ink study [1]. These studies establish that vinyl ether cannot be represented by an epoxy or oxetane moisture rule. They do not establish a universal ranking of the three families.

11. Establish a storage boundary by remeasurement

Storage tolerance requires a defined initial state, a conditioning interval and remeasurement. The response set should include water content and phase state, appearance or homogeneity, viscosity where relevant, cure kinetics, dark evolution and at least one cured-network or property endpoint. A sample that recovers cure rate after drying may still have undergone irreversible hydrolysis or composition change.

An acceptance boundary should be expressed for a specific formulation and package-independent laboratory condition. Container and headspace qualification remain with ER-179, while premature in-can reaction remains with ER-081. ER-218 asks only whether the material state after moisture conditioning remains equivalent enough for the declared cure and network criteria.

12. Interpretation matrix

Observation	Supported interpretation	Not established
Chamber RH increased	Environmental moisture activity changed	Resin water content or phase state
Measured water content increased	The sampled resin contained more water	Uniform dissolution or local reactive concentration
Initial cure rate increased	One kinetic interval accelerated	Acceptable network, storage state or final conversion
Endpoint conversion decreased	That functional-group endpoint was lower	Cause, chain architecture or reversibility
Dark conversion continued	Active chemistry persisted under that history	Universal dark-cure time or complete network formation
Performance recovered after conditioning	The tested endpoint was reversible under that protocol	Absence of hydrolysis or universal storage tolerance

13. Minimum reporting set

Report epoxy, oxetane and vinyl-ether identities and functionality; all reactive diluents, polyols, photoinitiator, sensitiser, counterion and additives; initial water content, measurement method, calibration and uncertainty; phase-state observation and sampling position; conditioning humidity, temperature, time, exposed area, thickness, headspace and mixing; viscosity or miscibility evidence needed for interpretation; source spectrum, wavelength, irradiance, exposure and specimen temperature; chemistry-specific analytical bands; conversion during irradiation, dark times and thermal post-cure; product-state method; storage interval; replicates and acceptance criteria.

Every numerical comparison must retain monomer identity, formulation composition, measured water state, phase state, geometry, irradiation, temperature, time and analytical endpoint. Humidity, added-water percentage and measured resin water content must not be used interchangeably.

14. Knowledge boundary

ER-218 does not duplicate ER-065: general photoacid generation, cationic mechanism, broad humidity effects and general dark cure remain outside this review. Primary evidence establishes only that measured water can affect epoxy, oxetane and vinyl-ether formulations differently; that dissolved, associated and phase-separated states require distinction; and that irradiation, dark evolution and thermal post-cure are separate states [1–6]. It does not establish a universal water limit, humidity limit, drying condition, shelf life, monomer-family ranking, exposure compensation or post-cure schedule.

15. Limitations

The sources span inkjet formulations, coatings, dental hybrids and laboratory-model systems. Water was introduced or controlled by different methods. Five of the six sources were inspected at full-text depth, while one was inspected at publisher-abstract depth. Dark-cure evidence is not always paired with moisture variation, and one oxetane study is direct-adjacent rather than moisture-specific. Numerical transfer among chemistries or applications is not justified.

16. Conclusions

Moisture tolerance in cationic photoresins is a state-resolved, formulation-specific property. Resin water content and phase state must be measured rather than inferred from ambient humidity. Epoxy, oxetane and vinyl ether require separate evidence, and mixtures require testing as mixtures. Conversion, dark evolution, thermal post-cure and final network response are distinct endpoints. A defensible boundary is established by controlled conditioning and remeasurement, not by a universal moisture number.

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