

Hemiacetal-Ester and N,O-Acetal Photoresins for Vat Photopolymerisation: Acid-Triggered De-crosslinking, Hydrolysis, Reprocessing, Polymer Recovery and Qualification

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Statement of Significance

Acetal-family junctions can make a light-cured thermoset vulnerable to a chosen acid, water or heat trigger without making every backbone bond reversible. Hemiacetal esters have enabled CLIP-printed polyurethane networks that yield purified polyurethane diols; CO₂-derived N,O-acetals have enabled thiol-ene VPP objects with controlled hydrolysis and hot-press reprocessing. ER-113 separates these outcomes and closes trigger, product identity, mass and next-use performance.

Keywords: vat photopolymerisation; hemiacetal ester; N,O-acetal; acid-triggered de-crosslinking; hydrolysis; polyurethane; thiol-ene; CLIP; reprocessing; recovered polymer; qualification.

Abstract

Hemiacetal-ester (HAE) and N,O-acetal junctions offer two routes to degradable VPP thermosets. HAE-terminated polyurethanes use methacrylate cure for geometry and dilute acid to release a reusable polyurethane diol after poly(methacrylic acid) removal. Oxazolidone N,O-acetals use thiol-ene cure; their exchange and hydrolysis depend on protic species, temperature, base, dynamic-bond fraction and topology. Direct evidence includes CLIP printing, vat working curves, 50 µm layers, acid dissolution, hot-press reprocessing and measured mechanical loss. O,O-acetals, ketals, HAE and N,O-acetals are not interchangeable, and dissolution, recovered polymer, reprocessing and monomer recovery are different endpoints.

1. Scope and boundaries

ER-113 owns VPP materials whose de-crosslinking, hydrolysis or exchange is governed by a HAE or N,O-acetal. It includes HAE polyurethane photoresins, oxazolidone N,O-acetals, methacrylate and thiol-ene fixation, acid/base additives, recovered-polymer purification and thermal reprocessing.

ER-41 retains liquid resistance; ER-59 dual cure; ER-63 generic covalent adaptable networks; ER-64 thiol-ene/yne VPP; ER-72 ageing; ER-74 generic cleavable networks; ER-80 in-can stability; ER-82 photobase chemistry; ER-92 residual-reactant hazard; ER-100 corpus architecture; ER-103 polyurethane VPP; and ER-112 thioester exchange [C1-C12]. ER-113 is the acetal-family chemical-identity and recovery gate.

O,O-, N,O- and hemiacetal-ester motifs differ in equilibrium and cleavage. HAE cleavage can release a polyurethane diol plus methacrylic-polymer byproduct; N,O-acetal hydrolysis can disconnect an oxazolidone network. Acid hydrolysis, thermal dissociation, exchange, dissolution and biodegradation are separate processes.

2. Identity and reaction gate

Motif	Print-fixing chemistry	End-of-use event	Claim withheld
HAE methacrylate end group	Radical methacrylate crosslinking	Acid cleavage to polyurethane diol + PMAA	Entire article returns to virgin resin
Oxazolidone N,O-acetal	Radical thiol-ene crosslinking	Dissociation/exchange or hydrolysis	Equivalent to O,O-acetal or N,S-acetal
Mixed dynamic/static network	Thiol-ene through all alkene sites	Partial connectivity loss set by topology	Cleavable-bond mol% alone predicts degradation
Hot-pressed CAN	Original photocure then thermal exchange	Network reprocessing	Mechanical properties fully recovered

Table 1. Acetal-family identity and outcome gate.

3. Direct evidence chain

3.1 HAE polyurethane photoresins and CLIP

Wu et al. prepared HAMA-terminated PPG/IPDI polyurethanes and photocrosslinked them at 365 nm with 1 wt% TPO [1]. Three liquid resins exhibited viscosities of 10–19 Pa s and were printed with an in-house CLIP system using 30 µm pixels. The polyurethane design produced elastic thermosets; the most extensible reached 250% strain at break and the highest ultimate tensile strength among the three was 2.1 MPa. These are formulation-specific values, not general HAE properties.

3.2 Acid de-crosslinking and polymer purification

Printed 2 × 4 × 4 mm HAE specimens dissolved within 1–3 h in 0.05 M HCl/methanol [1]. Controls retained at least 98% dry mass after two weeks in neutral or acidic water and at least 90% in methanol, although the authors attributed early methanol loss partly to swelling/extraction. HAE cleavage generated a polyurethane diol and 2.5–8.0 wt% calculated PMAA byproduct. Ion-exchange purification recovered 94–97% polyurethane, whereas the reported base-wash route gave 85% for resin B. This is functional-polymer recovery, not closed-loop regeneration of every original component.

3.3 CO₂-derived N,O-acetal VPP

Caliari et al. formed oxazolidone N,O-acetals and crosslinked diallyl monomers with multifunctional thiols [2]. Acidic species, including thiols and BAPO photoproducts, could promote premature dissociation; 0.5 wt% triethylamine suppressed the side reaction. With 0.5 wt% BAPO, 390 nm irradiation produced a 4.4 s gel point and complete double-bond-band consumption within 20 s in the controlled experiment. Vat tests supported 50 µm layers at 2.5 s exposure, grooves down to 100 µm and a printed gyroid, while the authors retained a need to improve z resolution with absorbers.

3.4 Tunable hydrolysis and reprocessing

N,O-acetal content and crosslink density jointly governed degradation [2]. A 100% N,O-acetal network degraded about 15% in neutral water and 85% in 1.0 M methanesulfonic acid after four days at 25 °C; at 60 °C it degraded completely within minutes under acid and within four days in neutral water. Hot pressing at 90 °C and 1 ton for 5 min reformed a film, but storage modulus at −10 °C fell from 2549 to 1926 MPa even though IR spectra and T_g were similar. Reprocessability therefore did not equal full mechanical recovery.

3.5 Adjacent mechanistic evidence

Coufal et al. examined hemiacetal-based dynamic systems and provided reaction-mechanism evidence outside a VPP qualification [3]. It supports the warning that equilibrium, water activity, catalyst and substituent identity matter, but it does not supply vat optics, working curves, printed geometry or recovered-resin performance.

4. Vat and shelf-state gate

Acid-labile resins must be qualified as complete formulations. Moisture, carboxylic acid, thiol acidity, photoinitiator fragments, base neutraliser and post-cure temperature can change the same bond later invoked for end-of-life. The N,O-acetal study required TEA to prevent cure-stage cleavage [2]; the HAE route used acid in synthesis and acid again for de-crosslinking [1]. Residual catalyst and acid capacity must therefore be measured, not inferred from recipe.

Control	Failure risk	Minimum evidence
Acetal identity	Wrong motif or cleavage products	NMR/FTIR, end groups, functionality and purity
Acid/base balance	Premature cleavage or blocked degradation	Species, loading, residual acidity/basicity and ageing
Water/solvent	Swelling confused with hydrolysis	Water content, uptake, dry mass and product analysis
Optical package	Poor z control or changed recovered-resin cure	Spectrum, Dp, Ec, lateral growth and spatial conversion

Table 2. Minimum controls for acetal-family vats.

5. Service and degradation qualification

Service stability and end-of-life activation must be separated. HAE thermosets showed stable rheological moduli to 150 °C in the reported scan yet an HAE thermal-dissociation onset around 170 °C [1]. N,O-acetal networks showed temperature- and acid-dependent dissociation, partial hydrolysis even in neutral water, and composition-dependent T_g [2]. ISO tensile, thermal and creep methods support retained-property mapping [S1–S6], but application temperatures, media and durations must be reproduced directly.

Hydrolysis studies require dry input mass, specimen dimensions, medium volume and composition, pH/acidity, temperature, agitation, time, swelling, soluble products and residual solids. A loss of dry mass is not by itself mineralisation or biodegradation. ISO 175:2010 and ISO 6427:2025 frame liquid exposure and extractables [S7–S8].

6. Recovery, reuse and environmental boundary

For HAE systems, report recovered polyurethane mass, molecular-weight distribution, hydroxyl end groups, residual PMAA, ion-exchange or wash losses and the identity of any new product made from the diol. For N,O-acetal systems, distinguish hydrolytic fragments from a hot-pressed network and compare each reprocessing cycle by chemistry, T_g, modulus, strength and geometry. ISO 14040:2006 and ISO 14044:2006 require a defined functional unit and inventory [S9–S10]; neither a 94–97% recovered-polyurethane yield nor a reformed film establishes environmental superiority.

7. Qualification architecture

Gate	Minimum evidence	Release question
Molecular identity	Acetal class, placement, functionality, acid/base species and impurities	Which bond and products are controlled?
Vat process	Rheology, spectrum, working curve, conversion and fidelity	Does the exact resin print reproducibly?
Service	Liquids, humidity, T _g , creep, thermal history and residual catalyst	Is cleavage acceptably latent?
Degradation	Trigger, kinetics, swelling, dry mass and soluble-product identity	Did the intended topology disconnect?
Recovery/reuse	Purity, yield, reformulation and next-use properties by cycle	What material was actually reused?
Environment	Energy, solvent, reagent, waste and functional-unit LCA	Is circularity auditable?

Table 3. Release gates for HAE and N,O-acetal VPP systems.

8. Failure-mode interpretation

- A printed article dissolves in acidic methanol: identify recovered polymer and PMAA; do not call every original component recovered.
- A neutral-water control loses mass: separate extractables, swelling/drying artefacts and true bond hydrolysis.
- TEA improves photocure: verify long-term acid/base balance and whether the intended degradation trigger remains effective.
- A 50 µm layer prints in 2.5 s: retain spectrum, intensity, resin composition and Jacobs curve; do not transfer exposure blindly.
- A hot-pressed film reforms: report the measured modulus loss and do not equate similar T_g/IR with full property recovery.
- Dynamic-bond fraction rises: topology and crosslink density can reverse a simple composition–rate trend.

- Hydrolytic degradation occurs: withhold biodegradation, safety and environmental claims without their own evidence.

9. Minimum workflow and priorities

- Freeze acetal class, backbone/end-group placement, functionality, purity and all acid/base contributors.
- Measure complete-vat rheology, spectrum, working curve, conversion, lateral/z growth and dark ageing.
- Map service liquids, humidity, temperature, creep and retained chemistry before selecting an end-of-life trigger.
- Close degradation by dry mass and product identity, not visual disappearance.
- Close purification by recovered-polymer yield, end groups, molecular weight and residual byproduct.
- Requalify vat behaviour, geometry and properties for every reused or reprocessed material cycle.
- Inventory solvents, acid/base, ion exchange, wash water, energy and waste before environmental comparison.

10. Conclusions

HAE and N,O-acetal photoresins demonstrate that acid-labile or hydrolysable junctions can coexist with useful VPP processing. Direct studies support CLIP and vat printing, polymer purification, composition-controlled degradation and thermal reprocessing.

The same evidence establishes hard boundaries: HAE recovery leaves a PMAA stream; N,O-acetal cure depends on acid/base control; hydrolysis depends on topology as well as bond fraction; and reprocessing can retain Tg while losing modulus.

ER-113 therefore releases no generic acetal performance, safe-service window, biodegradability or environmental superiority. Each claim must close identity, trigger, mass, recovered products and next-use performance.

Limitations

This qualitative review is not a systematic meta-analysis. Direct VPP evidence currently rests on distinct HAE polyurethane and oxazolidone N,O-acetal platforms. Numerical values are formulation- and method-specific and are not pooled. No proprietary recipe, universal exposure, safe-service temperature, toxicological qualification, biodegradation result, LCA, regulatory approval or universal recycling claim is supplied.

Author contributions

Juan Segurola: conceptualisation, evidence synthesis, boundary definition, engineering interpretation, manuscript preparation and final author verification.

Competing interests

The author is founder and CEO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated. Scientific statements derive from cited primary literature and official standards.

Company information

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[S9] ISO 14040:2006. Environmental management - Life cycle assessment - Principles and framework. Edition 2; confirmed current in 2022. <https://www.iso.org/standard/37456.html>

[S10] ISO 14044:2006. Environmental management - Life cycle assessment - Requirements and guidelines. Edition 1; confirmed current in 2022. <https://www.iso.org/standard/38498.html>

Related Engineering Review boundaries

[C1] Segurola, J. Chemical Resistance and Solvent Uptake of Vat-Printed Photopolymers. ER-41. Zenodo or controlled version (2026).

[C2] Segurola, J. Sequential Dual-Cure Networks in Vat Photopolymerisation. ER-59. Zenodo or controlled version (2026).

[C3] Segurola, J. Covalent Adaptable Networks and Vitrimers Topology in Vat Photopolymerisation. ER-63. Zenodo or controlled version (2026).

[C4] Segurola, J. Thiol-Ene and Thiol-Yne Photopolymerisation in VPP. ER-64. Zenodo or controlled version (2026).

[C5] Segurola, J. Environmental Ageing and Property Retention in Vat Photopolymerisation. ER-72. Zenodo or controlled version (2026).

[C6] Segurola, J. Cleavable and Depolymerisable Networks in Vat Photopolymerisation. ER-74. Zenodo or controlled version (2026).

[C7] Segurola, J. In-Can Stability and Premature Polymerisation in Radiation-Curable Formulations. ER-80. Zenodo or controlled version (2026).

[C8] Segurola, J. Photobase-Mediated and Base-Catalysed Photocuring in Vat Photopolymerisation. ER-82. Zenodo or controlled version (2026).

[C9] Segurola, J. Residual Reactants, Impurities and Manufacturing Conversion as Hidden Drivers of Photopolymer Hazard. ER-92. Zenodo or controlled version (2026).

[C10] Segurola, J. From Individual Reviews to a Qualification Corpus. ER-100. Zenodo or controlled version (2026).

[C11] Segurola, J. Polyurethane, Polyurea and Urethane-Acrylate Photopolymers for Vat Photopolymerisation. ER-103. Zenodo or controlled version (2026).

[C12] Segurola, J. Thioester-Containing Photoresins for Vat Photopolymerisation. ER-112. Zenodo or controlled version (2026).