

Evidence for Material Circularity in Photopolymer Additive Manufacturing

Material-Loop Closure, Recovery Mass Balance, Recovered-Feedstock Identity and Property Retention

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ER-198 · Engineering Review · Version 0.1 · 14 September 2026

Statement of Significance

A photopolymer may be degradable, repairable, reprocessible or reprintable without closing a material loop. ER-198 defines the evidence needed to distinguish those claims. Its central requirement is an auditable chain from a declared quantity of targeted end-of-use material, through recovery and recovered-feedstock identification, to a new printed article whose relevant properties are compared with the corresponding virgin-material state. The framework prevents recovery yield, successful reprinting or retained properties from being used as substitutes for one another, and it prevents material circularity from being presented as an environmental benefit without a separate life-cycle assessment.

Abstract

Claims of circular photopolymer additive manufacturing often compress several different operations into one word. Network cleavage or dissolution demonstrates processability of an article, not recovery of a defined material fraction. Isolation of a liquid or oligomeric fraction demonstrates recovery, not its identity or suitability as feedstock. Fabrication of a second object demonstrates reprinting, not equivalence of composition, yield or performance. Similar properties after one cycle do not establish repeatability or an environmentally preferable system. Primary studies have demonstrated materially different loop architectures, including recovery of functional oligomers followed by replenishment of a complementary reactant [1], and depolymerisation of photocured lipoate networks to chemically characterised reprintable resin across repeated cycles [2]. These studies also expose why evidence must be route-neutral: fresh inputs, recovered species, purification losses, additives and changes in print behaviour differ between chemistries. ER-198 proposes a qualification architecture based on a declared loop boundary, targeted-material mass balance, recovered-feedstock identity, transparent make-up accounting, reprinting as an observed process step and state-matched property retention. It excludes life-cycle assessment and does not treat recyclability as proof of sustainability.

Keywords: photopolymer additive manufacturing; material circularity; closed-loop evidence; mass balance; recovered feedstock; reprinting; property retention; vat photopolymerisation

1. Scope and controlling identity

ER-198 owns only the evidence that an end-to-end material loop closes across any route: targeted-material mass balance, recovery yield and identity, documented reprinting as a loop step, and property retention. It neither performs nor re-owns life-cycle assessment. Energy use, auxiliary-input inventories, environmental comparison and sustainability conclusions remain with ER-017.

The following neighbouring boundaries are binding. ER-017 retains life-cycle assessment, functional units, system boundaries, inventory quality and uncertainty. ER-063 retains Covalent Adaptable Networks and Vitrimer Topology in Vat Photopolymerisation: Exchange Kinetics, Reprocessing and Dimensional Stability. ER-072 retains Environmental Ageing and Property Retention in Vat Photopolymerisation across resin storage, photooxidation, hydrothermal conditioning and state-resolved qualification; ER-198 is limited to

property retention across recovery-and-reprint cycles. ER-074 retains triggered disassembly, fragment identity and closed-loop qualification of that route. ER-111 retains dithiolane/lipoate Ring-Opening Disulfide Networks, Dynamic Exchange, Depolymerisation, Reprinting and Qualification; reprinting as a chemistry belongs to ER-111. ER-112 retains thioester-specific degradation, filler recovery and oligomer reuse. ER-113 retains acid-triggered de-crosslinking, hydrolysis, reprocessing and polymer recovery. ER-183 retains mechanical recycling. ER-071 uses closed-loop in the distinct process-control sense.

ER-198 is therefore route-neutral. Dynamic covalent chemistry is an enabling family, not the subject owned by this review.

2. Distinguishing circularity claims

The claimed operation should be named before evidence is selected:

1. **Repair** restores function without necessarily recovering feedstock.
2. **Reshaping or reprocessing** changes an existing network or article without necessarily returning it to a printable liquid.
3. **Deconstruction or dissolution** removes the original article form but does not establish recovery yield or recovered-material identity.
4. **Recovery** isolates a declared material fraction from the process stream.
5. **Reprinting** uses recovered material in a documented additive-manufacturing step.
6. **Material-loop closure** connects a defined input lot to recovery, identified feedstock, reprinting and retained function with all additions and losses accounted for.

These are nested only when the evidence actually connects them. A result at one stage cannot be used as evidence for a later stage.

3. Declare the loop before running it

A loop claim needs a boundary and a conserved target. The protocol should identify the printed input lot, the targeted material or functional groups, the recovery route, every separation or purification step, the recovered fraction, all fresh additions, the reprinting step and the state in which the new article is tested.

The targeted material may be total organic polymer, a defined monomer family, a functional oligomer fraction, a filler, or another explicitly measurable constituent. Selecting the target after observing what was recoverable creates a favourable but non-predeclared denominator. The target and acceptance rules should therefore be fixed before the recovery experiment.

The unit of analysis is a traceable batch. Material taken from unrelated experiments or pooled without recorded provenance cannot support a batch-level closure statement.

4. Mass balance is not recovery yield

Recovery yield describes the isolated recovered fraction relative to a stated denominator. A loop balance must additionally account for the material entering products, sampling, residues, wash streams, purification fractions, volatilisation and any unresolved loss. The accounting identity can be written without prescribing a chemical route:

targeted input = recovered target + target retained in other outputs + measured losses + unresolved balance.

The unresolved balance must be reported rather than assigned to recovery. Wet mass, solvent-containing mass and dry target-equivalent mass are different quantities. A yield based on an isolated liquid is not comparable with a yield based on quantified reactive functionality unless the conversion between them is validated.

Lopez de Pariza and co-workers recovered chemically characterised thiol-terminated oligomers and used them in subsequent print cycles [1]. Machado and co-workers measured recovery of reprintable lipoate resin

and compared its composition with the initial formulation across repeated cycles [2]. ER-198 uses these examples to show that recovery and identity are separate measurements, not to establish a universal acceptable yield.

5. Recovered-feedstock identity

The recovered fraction must be identified at the level required by the reprinting claim. Depending on the route, evidence may include:

- functional-group quantification relevant to the next polymerisation;
- spectroscopic comparison with the declared feedstock;
- molecular-mass or distribution measurements;
- composition or purity measurements;
- residual catalyst, solvent or degradation-product assessment; and
- optical or rheological properties that affect printability.

No single technique establishes identity in every system. A spectrum showing an expected band may confirm a functional group while missing changes in molecular-mass distribution, stoichiometry or impurities. Conversely, similar rheology does not prove chemical identity.

The comparison should distinguish identity, similarity and fitness for use. Recovered feedstock may be fit for a bounded reprinting application without being chemically identical to virgin feedstock. That narrower claim is preferable to treating a successful print as retrospective proof of identity.

6. Fresh inputs and the snowballing test

Every fresh reactive component, catalyst, initiator, stabiliser, solvent, processing aid and make-up fraction introduced after recovery must be recorded. Fresh material does not automatically invalidate a loop, but it changes what has closed.

Three quantities should remain separate:

- the fraction of the targeted original material recovered;
- the fraction of the next print formulation derived from recovered material; and
- the amount and role of fresh material required per cycle.

In the polythiourethane example, recovered functional oligomers were combined with fresh complementary reactant after functional-group quantification [1]. In the lipoate example, the authors explicitly contrasted routes that require accumulating fresh reactive species with a resin designed for repeated depolymerisation and reprinting [2]. The engineering question is not whether either route is labelled closed-loop, but whether its inflows, retained material and accumulating inventory are transparent.

A process that requires progressively more fresh resin may still recover material, yet its repeated-cycle behaviour differs from a loop whose inventory remains bounded. This is a mass-accounting distinction, not an environmental verdict.

7. Reprinting must be observed

Recure in a mould, film casting and additive reprinting are not interchangeable demonstrations. If the claim is photopolymer additive-manufacturing circularity, recovered feedstock must pass through a declared printing process and produce a deliberately selected geometry.

The report should state whether recovered material was printed alone or blended, whether process settings differed from the virgin baseline, and whether those changes were predeclared. Print completion alone is insufficient. At minimum, the reprinted state should be evaluated for cure behaviour, dimensional or feature fidelity appropriate to the process, and absence of gross defects that would conceal loss of function.

Both primary studies used recovered material in subsequent printing steps and characterised relevant print or material behaviour [1,2]. Their routes differ, so ER-198 does not transfer their formulations or settings.

8. Property retention requires state matching

Virgin and recovered-material articles must be compared at equivalent conditioning, geometry, build orientation, post-cure history and test method. Otherwise the cycle variable is entangled with specimen preparation.

The property set should be chosen from the intended engineering function, not from whichever measurement changes least. Mechanical modulus alone cannot establish retained behaviour when strength, strain, thermal transition, swelling, optical response or dimensional accuracy is material to the claim.

Results should be reported as distributions with uncertainty and replicate structure. “Similar” requires a declared rule. Failure to detect a difference is not proof of equivalence unless the test was designed with adequate resolution for a predeclared equivalence margin.

The two primary studies report retained or comparable properties after recovery and reprinting while also documenting composition, network or print-related evidence [1,2]. That conjunction is stronger than property comparison alone.

9. Repeated cycles, drift and attrition

One recovery-and-reprint sequence demonstrates a loop step. It does not establish repeatability. Repeated cycles should track:

- cumulative recovered fraction and unresolved loss;
- fresh-input accumulation;
- composition and impurity drift;
- changes in molecular distribution or reactive functionality;
- cure and print-window drift;
- property retention under state-matched testing; and
- specimens lost to sampling or failed processing.

Cycle numbering must follow material lineage rather than calendar order. If only a selected fraction proceeds to the next cycle, the excluded fraction remains part of the balance.

Attrition can be hidden when each cycle is normalised to the material that survived the preceding one. Reporting both per-cycle and cumulative retention prevents an apparently stable percentage from obscuring shrinking material inventory.

10. Route-specific evidence without route ownership

Different chemistries create different recovery species and risks. Exchange-mediated oligomer recovery may require functional-group rebalancing. Depolymerisation to monomer-like species may require purity and recomposition controls. Filler recovery requires separation and filler-state measurements. Mechanical recycling requires particle history and reprocessing controls.

ER-198 does not prescribe or rank these chemistries. Its contribution is the common evidence architecture applied after a route has been chosen. Chemistry-specific mechanisms and performance claims remain with their controlling ERs.

11. Circularity is not life-cycle assessment

Closing a material loop does not by itself demonstrate lower energy use, lower emissions, reduced hazard, lower resource depletion or superior environmental performance. Recovery may require solvents, heat,

catalysts, purification, transport or fresh reactants. Those burdens may be justified, but they must be assessed rather than inferred.

ER-198 may report the inputs and outputs required to make a later assessment possible. It must not aggregate them into a sustainability conclusion. Functional units, counterfactual systems, allocation rules, inventories, impact categories and uncertainty remain with ER-017.

Likewise, renewable feedstock and recyclability answer different questions. A renewably sourced resin may have an incomplete material loop, and a petrochemical resin may have a well-evidenced recovery loop. Neither descriptor substitutes for the other.

12. What may remain proprietary

A public qualification report can disclose the loop boundary, measurement classes, material-accounting structure, identity criteria, reprinting evidence and property-retention conclusion without disclosing a commercially actionable formulation or recovery recipe.

Component identities, concentrations, catalysts, processing conditions, purification sequences and compensation rules may remain proprietary. When they are withheld, claims of independent reproducibility and transfer must be narrowed accordingly. The report must still disclose enough aggregate information to show which fresh inputs, losses and recovered fractions were counted.

13. Minimum evidence set

A defensible material-loop claim should include:

1. a predeclared target material and batch boundary;
2. input, recovered, residual, lost and unresolved mass categories;
3. a recovery yield tied to a stated denominator and material state;
4. evidence identifying the recovered feedstock;
5. complete accounting of fresh reactive and auxiliary inputs;
6. documented additive reprinting using the recovered fraction;
7. state-matched printability and engineering-property comparisons;
8. per-cycle and cumulative results where repeatability is claimed;
9. uncertainty, replication and treatment of failed or sampled material; and
10. a statement separating material circularity from environmental performance.

Any omitted element should narrow the claim explicitly. A route can be promising while the end-to-end loop remains only partially demonstrated.

14. Conclusions

Material circularity in photopolymer additive manufacturing is an evidence chain, not a material label. Deconstruction, recovery, identity, reprinting and property retention are distinct propositions. The chain closes only when they refer to the same traceable material lineage and when fresh inputs, losses and unresolved balance are visible.

Primary studies demonstrate that recovered functional oligomers can support subsequent printing [1] and that chemically characterised photocurable resin can be recovered and reprinted across repeated cycles [2]. Their different architectures reinforce the need for route-neutral accounting rather than a universal chemical prescription.

The proposed framework supports strong but bounded claims while protecting proprietary formulation know-how. It does not establish life-cycle benefit, sustainability or universal transfer to other chemistries and manufacturing conditions.

Related Engineering Review boundaries

The controlling ownership statement and all neighbouring boundaries are stated once in §1 and govern the whole review.

References

1. Lopez de Pariza X, Varela O, Catt SO, Long TE, Blasco E, Sardon H. Recyclable photoresins for light-mediated additive manufacturing towards Loop 3D printing. *Nature Communications*. 2023;14:5504. <https://doi.org/10.1038/s41467-023-41267-w>
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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. The review intentionally withholds commercially actionable formulation and processing details. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated. Source-access states and claim limits are recorded in the accompanying source ledger.

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