

Recovery of Unreacted Monomers and Photoinitiators from Photoresin Waste: Separation, Identity and Requalification

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Abstract

Uncured photoresin waste, drag-out and wash streams can contain unreacted monomers, oligomers, photoinitiators, inhibitors and other formulation constituents. Detecting or extracting those species does not establish that they can be recovered as reusable feedstock. Published work demonstrates analytical extraction of residual photoinitiators from cured UV materials [1], chemical recovery and reprinting in deliberately recyclable photoresin systems [2], and resource recovery from photocured waste through coupled photooxidation-pyrolysis [3]. These routes are materially different from separating intact unreacted monomer and photoinitiator from heterogeneous production waste. ER-274 therefore treats direct component recovery as an evidence-limited separation problem. A credible claim requires stream identity, component-resolved mass balance, chemical identity and purity of each recovered fraction, inhibitor and degradation-state control, and requalification in a defined resin formulation. No universal distillation temperature, adsorbent, membrane, chromatographic process, recovered-fraction specification or blend ratio is supplied.

Keywords: photoresin waste; unreacted monomer; photoinitiator; recovery; separation; identity; purification; requalification; vat photopolymerisation

1. Significance, scope and ownership

The value of a recovered liquid depends on what it actually contains and what use is claimed for it. ER-274 owns recovery of intact or chemically assignable unreacted monomers and photoinitiators from uncured or partially cured photoresin waste streams, followed by identity and requalification. ER-74 owns cleavable and depolymerisable network chemistry. ER-111 and related chemistry-specific reviews retain their defined reversible-network routes. ER-198 owns end-to-end material circularity evidence [4]. ER-272 owns solvent-recovery mass balances. ER-275 will address purification and reuse of products generated by triggered depolymerisation; those products are not silently treated here as recovered original monomers.

1.1 Corpus boundary

ER-74 retains cleavable and depolymerisable network chemistry, ER-111 and related chemistry-specific reviews retain their defined reversible-network routes, and ER-198 retains end-to-end material-circularity evidence. ER-274 distinguishes recovery of pre-existing formulation components from chemical recycling of cured networks. ER-272 and ER-275 are current-series neighbours and are not used here as published evidentiary authority. A monomer produced by depolymerisation is a reaction product even if chemically identical to an original feedstock; its impurity history and qualification route remain different. Likewise, an extract containing a photoinitiator proves mobility and detectability, not a reusable photoinitiator fraction.

2. Start with the waste-stream state

Candidate streams include unused resin removed after a failed build, drained vat heel, filter residue containing liquid resin, solvent or aqueous wash liquid carrying uncured resin, and mixed cleaning residues. These streams differ in polymerisation history, light exposure, oxygen contact, water content, solvent composition, particulate loading and cross-contamination. A recovery study must freeze resin identity, lot, age, prior irradiation, temperature history, inhibitor state, wash chemistry and foreign-material exposure before assigning component yields.

3. Analytical extraction is not recovery

Photoinitiators can be extracted from cured polymer matrices for analytical purposes. For example, photoinitiator migration studies have used ethanol extraction followed by spectroscopic quantification [1]. Such experiments establish that a species can be mobilised and measured under defined conditions. They do not establish economic isolation, purity, retained initiating efficiency or compatibility with a new formulation. Similarly, chromatographic quantification of residual or eluted methacrylate monomers is an analytical measurement; collecting an instrument fraction is not yet a manufacturing recovery route.

4. Separation must be component-resolved

A useful recovery train separates at least four classes: carrier solvent or water; target monomer or reactive diluent; photoinitiator or sensitiser package; and non-target material such as oligomer, inhibitor, pigment, degradation product or cured particulate. Physical operations should be selected from measured properties - volatility, partitioning, solubility, molecular size, adsorption affinity or charge - rather than from generic labels. Because many acrylates and photoinitiators can undergo heat-, light- or radical-driven change, the separation process itself can alter the very species being recovered. Identity must therefore be re-measured after separation.

5. Mass balance and yield are not purity

For target component i , a basic component recovery may be expressed as $R_i = m_{i,\text{recovered}} / m_{i,\text{input}}$. The numerator requires measured concentration and recovered-fraction mass or volume; it is not the gross mass of a liquid fraction. Purity is a separate quantity, $P_i = m_{i,\text{recovered}} / m_{\text{fraction}}$. A high R_i can coexist with poor purity, and a very pure analytical fraction can represent negligible overall recovery. Both quantities require uncertainty and explicit treatment of material remaining in residues, filters, still bottoms or unmeasured fractions.

6. Photoinitiator recovery has an activity gate

Chemical identity alone does not establish photochemical function. A recovered initiator or sensitiser can contain photoproducts, oxidised species, isomers or co-extracted inhibitors. Requalification should therefore include identity/purity plus a functional photopolymerisation measurement under a defined formulation and wavelength. The comparison should control absorber content, optical path, oxygen condition and monomer composition. A recovered photoinitiator fraction should not be blended into production material merely because its UV-visible spectrum resembles that of the starting material.

7. Monomer recovery has an inhibitor and ageing gate

Recovered acrylate or methacrylate monomers can differ in inhibitor concentration, water, acid number, peroxide content, oligomeric material and thermal/light history. These variables can shift shelf stability and cure kinetics. Requalification should compare the recovered component with the specified virgin component using identity, purity, inhibitor and water measurements appropriate to the chemistry, followed by a matched resin comparison. A successful print is insufficient if viscosity, working curve, conversion, dimensional response or final properties have drifted.

8. Adjacent recycling studies define what this paper does not claim

Lopez de Pariza, Varela, Catt, Long, Blasco and Sardon demonstrated a deliberately recyclable polythiourethane photoresin system with chemical recycling and reprinting [2]. That evidence proves that closed-loop photopolymer chemistry can be designed, but it does not establish separation of intact monomer and photoinitiator from a conventional mixed waste stream. Zhang and co-workers studied photooxidation-pyrolysis of photocured waste and reported useful gas, liquid and solid products while degrading a model photoinitiator [3]. That route transforms cured waste and therefore belongs to resource recovery from reaction products rather than direct recovery of the original photoinitiator. These distinctions are essential to avoid relabelling chemical conversion as component recovery.

9. Non-compensatory release gates

Gate	Minimum evidence	Blocking failure
Waste identity	Resin/lot, age, prior light, wash chemistry and contamination	Unknown starting inventory
Target quantitation	Validated pre-separation monomer/PI concentrations	Recovery denominator missing
Component balance	All fractions and residues accounted	Gross liquid yield used as component yield
Identity/purity	Target identity plus non-target profile after separation	Analytical fraction assumed reusable
Stability state	Inhibitor, water and degradation markers as relevant	Recovered monomer ageing unresolved
Photochemical activity	Matched functional cure test for recovered PI	Spectrum substituted for initiation performance
Formulation bridge	Virgin-control comparison at declared substitution	Successful print called equivalence

10. Minimum experiment

A minimum direct-recovery study starts with a defined uncured photoresin and creates a traceable waste stream of known mass. Target monomers and photoinitiator are quantified before separation by validated methods. The separation train is then applied with all collected fractions weighed or volumetrically accounted. Each target fraction is re-analysed for identity, concentration, non-target components and relevant stability markers. Recovered components are then introduced into a controlled resin at a declared substitution fraction and compared with an otherwise identical virgin control using storage stability, viscosity, optical response or working curve, conversion and one final-part property. At least one repeated recovery or aged-stream challenge is needed before a serial circularity claim is made.

11. Knowledge boundary

No directly read peer-reviewed study was identified here that demonstrates routine recovery, purification and requalification of both intact unreacted monomers and intact photoinitiators from heterogeneous vat-photopolymerisation production waste. The adjacent literature supports analytical extraction, deliberately recyclable network chemistry and transformation of cured waste [1-3]. ER-274 therefore supplies an evidence architecture and minimum experiment, not a validated commercial separation process.

12. Conclusions

Recovery of unreacted monomers and photoinitiators is credible only when component identity survives a complete custody chain from waste stream through separation to requalified formulation. Extraction, detection, bulk liquid recovery and successful printing are different claims. The required evidence is component-resolved mass balance, purity, stability state and functional requalification, with residues and losses retained in the accounting. Until that chain is demonstrated, recovered fractions should be described as candidate secondary feedstocks rather than virgin-equivalent components.

References

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