

Chemical Recycling of Acrylate and Methacrylate Photopolymer Networks: Bond Cleavage, Product Identity and Reuse

Qualification of chemical routes that convert crosslinked photopolymers into identifiable, reusable molecular feedstocks

Juan Seguro

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Correspondence: info@3Dresyns.com · www.3Dresyns.com

ER-452 · Engineering Review · Version 0.1 · 8 October 2026

Abstract

Conventional acrylate and methacrylate photopolymers derive dimensional stability from covalent crosslinking, which also obstructs melt reprocessing. Chemical recycling therefore requires either cleavable or exchangeable network chemistry, selective degradation conditions, and evidence that recovered products can re-enter a photocurable formulation without hidden accumulation of additives or by-products. This review defines a qualification framework for chemical recycling of photopolymer networks, separating bond cleavage from dissolution, product recovery from true closed-loop reuse, and reprintability from recovery of the original material state.

Keywords: chemical recycling; acrylate; methacrylate; photopolymer; covalent adaptable network; bond cleavage; depolymerisation; closed loop

1. Significance and scope

Photocured thermosets are difficult to recycle because crosslinks prevent conventional melt reprocessing. Recent reviews of vat-photopolymer recycling therefore focus on dynamic covalent chemistry, selective cleavage and reconstruction of printable feedstocks rather than simple comminution [1].

This review owns chemical conversion of cured acrylate and methacrylate networks into molecular or oligomeric feedstocks. ER-453 owns solvent-centred solvolysis as a unit operation; ER-454 owns thermochemical recovery.

2. Network architecture determines the recycling route

The network must be designed or characterised in terms of cleavable functionality. Permanent carbon-carbon backbones, ester linkages, imines, vinylogous urethanes and other dynamic motifs lead to fundamentally different degradation and exchange mechanisms.

Covalent adaptable networks illustrate how crosslinked materials can be made reprocessable by controlled bond exchange rather than by removing crosslinks entirely [2]. That principle is useful, but reprocessability and chemical recovery should not be conflated.

Network mapping should also identify non-cleavable backbone segments and any fraction expected to remain as insoluble residue. A route that recovers only a designed labile fraction should not be described as complete depolymerisation.

Cleavage selectivity should be evaluated as a reaction network rather than as disappearance of the parent network. Side products, residual crosslinked fragments and additive-derived species can determine whether the recovered stream is actually suitable for purification and reuse.

3. Bond cleavage must be chemically selective

A recycling reaction should identify which bond is targeted, which reagent or catalyst acts on it, and which competing bonds may also react. Loss of specimen mass is not evidence of selective depolymerisation.

Recent DLP-printable dynamic networks show that chemical degradation products can be converted into recycled resin precursors and returned to printing [3]. Such demonstrations make product identity and formulation reconstruction measurable rather than conceptual.

4. Product identity matters more than disappearance of the solid

Chemical recycling should quantify soluble, insoluble and volatile fractions and identify major recovered species. Unknown oligomers, residual catalyst, photoinitiator fragments and colour bodies can affect later cure even when nominal monomer recovery is high.

Purification belongs inside the recycling route. Extraction, precipitation, distillation or adsorption may be necessary to reach a defined feedstock state; recovery yield reported before purification can overstate useful circular yield.

Recovered feedstock should be compared with its virgin counterpart by identity, purity and functionality rather than by appearance. Spectroscopic or chromatographic evidence should be paired with mass balance and uncertainty.

Reaction selectivity should be checked against additives and embedded materials. A cleavage reagent that attacks pigments, fillers, metal inserts or secondary adhesives can create contamination that was absent from the original formulation.

Reagent recovery belongs in the process boundary. A chemistry that cleaves efficiently but consumes large solvent or reagent inventories can shift burden from polymer waste to liquid waste, so closed-loop claims should include reagent make-up, purge and regeneration.

5. Recovered feedstock must re-enter photopolymerisation

Reuse requires a defined formulation rule. If recovered material is blended with virgin monomer, fresh photoinitiator or crosslinker, the replenishment fraction should be reported so that closed-loop claims are not based on a small recycled contribution.

Photopolymerisation kinetics are sensitive to absorbers, inhibitors and reactive-functionality balance. Recycling cycles can therefore shift working curves, exposure latitude and final conversion even when viscosity remains acceptable.

Mechanical performance alone is insufficient to show recovery of the material state. Optical response, dimensional fidelity, cure depth and residual extractables can reveal impurity accumulation before bulk strength fails.

Axis	Measurement	Failure mode
Network	cleavable/dynamic bonds and conversion	generic thermoset treated as recyclable
Reaction	reagent, catalyst, selectivity	mass loss treated as selective cleavage
Products	identity, yield, impurity profile	soluble fraction treated as monomer
Reuse	recycled fraction and formulation additions	small recycled blend treated as closed loop
Cycles	cure and property retention	single recycle treated as durability

Table 1. Domain-specific qualification matrix for chemical recycling of acrylate and methacrylate photopolymer networks.

6. Device-level verification across recycling cycles

Device-level verification should print the same representative geometry with virgin and recovered formulations under controlled exposure and compare dimensional, optical and mechanical outputs.

Multiple recycling cycles are required when a route is described as closed loop. Track accumulation of non-reactive species, catalyst residues and colour as well as any progressive increase in virgin make-up.

Failure criteria should include loss of selective cleavage, declining recovered-feedstock purity, cure drift, inability to meet dimensional tolerance and unacceptable property loss after reprinting.

Device-level qualification should test at least one recycle loop from printed article through cleavage, separation, reformulation and reprinting. Chemical conversion alone does not demonstrate circularity unless the recovered material returns to a controlled photopolymer function.

7. Minimum qualification framework

Report network chemistry, conversion state, degradation reagent, catalyst, temperature, time, solid-to-liquid ratio, recovered fractions, analytical identity, purification steps and mass balance.

For reuse, report recovered-feedstock fraction, formulation additions, cure response, print settings, final-part properties and the number of completed recovery/reprint cycles.

8. Engineering conclusions

Chemical recycling of photopolymer networks is credible only when bond cleavage produces identifiable feedstocks that survive purification and demonstrably re-enter photocuring. Disappearance of a cured part is the beginning of the evidence chain, not its end.

References

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Competing interest

Juan Segurola is founder, CEO and CTO of 3Dresyns by Resynr Technologies S.L., which develops and commercialises photopolymer materials and related additive-manufacturing technologies. This review is an engineering analysis and does not constitute a product-performance claim or a device qualification.