

Sustainable photopolymer design towards a circular 3D printing

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Additive manufacturing has transformed prototyping and production, enabling rapid fabrication of complex geometries and customized components.¹ Among the various techniques developed so far, vat photopolymerization—employing liquid resins cured by light—has gained significant attentions due to its fine resolution and speed. The past three decades have witnessed the rapid progress in printer hardware and process optimization, but with the development of resin chemistry falling behind. Most commercial resins are derived from petrochemical (meth)acrylates and epoxides, which cure into permanently crosslinked networks. Not only are these materials non-renewable, they are also largely unrecyclable, representing a critical bottleneck in efforts to align additive manufacturing with the ongoing pursuit of a

circular materials economy.

Past efforts including the incorporation of dynamic covalent chemistry or mechanical recycling (grinding followed by re-extrusion) have enabled partial recycling but with limited fidelity, often requiring fresh reactive additives at each cycle.² This “snowballing effect” undermines true closed-loop operation. Moreover, the recycled materials do not match the mechanical and thermal properties of the initially synthesized ones.

Against this backdrop, the notion of “circular” resins is compelling: materials that can be repeatedly polymerized, depolymerized, and re-polymerized without substantial loss of performance or need for new feedstock. This necessitates the innovation of resin chemistry from the following several

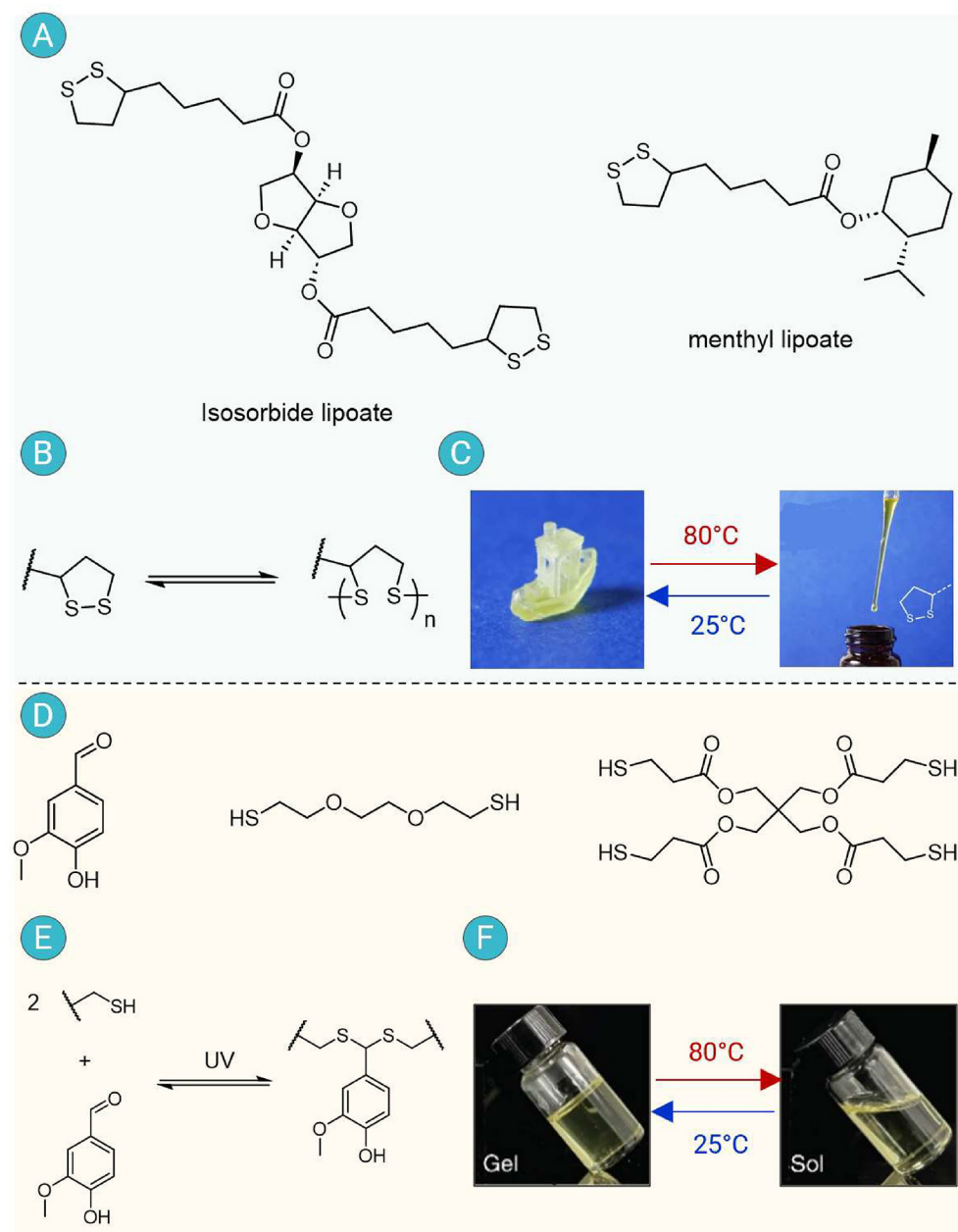


Figure 1. Overview of the design, dynamic equilibrium, and recycling for two circular photoresins (A) Chemical structures of formulated lipate photoresin including isosorbide lipate as a divalent cross-linker and menthyl lipate as a reactive diluent. (B) Dynamic equilibrium between cyclic disulfide and poly(disulfide)s. (C) Photographs showing a 3D printed object fabricated through photopolymerization of isosorbide lipate and menthyl lipate, and its depolymerization at 80°C to reform the lipate resin. Panels (A–C) adapted with permission from ref. 3, Springer Nature. (D) Chemical structures of formulated photoresin comprising vanillin, mono- and di-functional thiol compounds. (E) The reversible reaction among vanillin, thiols and dithioacetal. (F) Reversible sol-gel transition of the poly(dithioacetal) polymer networks. Panels (D–F) adapted with permission from ref. 4, American Association for the Advancement of Science.

aspects: (i) compatibility with rapid photopolymerization, (ii) efficient depolymerization back to reusable building blocks, (iii) tunability of mechanical properties, and (iv) ideally, derivation from renewable resources.

Recent breakthroughs have endeavored to reshape this landscape. Among many attempts are two recent studies, reported by Machado et al.³ (Figures 1A–C) and Yang et al.⁴ (Figures 1D–F), who independently presented two fully circular photopolymer resins. Both approaches achieve closed-loop recyclability while maintaining performance characteristics essential for industrial applications. Although their strategies differ—one leveraging renewable lipates with reversible disulfide linkages (Figures 1A–B), the other harnessing dissociative dithioacetal networks derived from bioaromatic aldehydes (Figures 1D–E), they converge on the same ambition, that is, to reconcile high-resolution additive manufacturing with sustainability.

Machado et al. introduced a resin platform derived entirely from lipoic acid, a naturally occurring cyclic disulfide.³ By esterifying lipoic acid with renewable alcohols such as isosorbide and menthol, they produced multivalent crosslinkers and reactive diluents that undergo

radical-mediated polymerization under UV light (Figure 1A). Due to the dynamic character of strained disulfide linkages (Figure 1B), the resulting 3D printed networks can depolymerize back into their constituent materials at 80°C catalyzed by phosphazene/thiophenol (Figure 1C). The depolymerization can also proceed in the absence of catalyst, but requiring a higher temperature (i.e., 140°C). Subjecting the depolymerized mixture to a Digital Light Processing (DLP) printer allows to reproduce the complex object at room temperature (Figure 1C).

This system demonstrates several compelling achievements. First, the resins are processed on commercial DLP printers, presenting feature resolutions as fine as 100 µm without requiring additional opaquing agents. Second, printed objects are chemically depolymerizable in green solvents such as 2-methyltetrahydrofuran, with recovery yields up to 98% and in a high quality. This enables the recovered resins to be reprinted with negligible compromise in fidelity. Third, the system can afford materials of varying properties from soft, brittle to rigid and tough, through adjusting the ratio of crosslinker to diluent or substituting different alcohol-derived lipoates. This ensures customized design of different 3D printed objects, and meets distinct application requirements.

Despite its promise, the approach faces challenges. Trace oligomeric species persist after depolymerization, introducing minor impurities that could accumulate over multiple cycles. Catalysts such as phosphazenes, though effective, present cytotoxicity concerns, while some synthetic steps rely on hazardous solvents. Mechanical strength, though adjustable, remains lower than that of rigid commercial acrylics. Nonetheless, the system offers the first demonstration of renewable, fully depolymerizable photopolymer resins for additive manufacturing—an important milestone in aligning sustainability with practical utility.

In parallel, Yang et al. developed a dissociative network chemistry based on dithioacetal linkages formed between thiols and bio-based aldehydes such as vanillin (Figure 1D).⁴ Central to their design is the use of a photoacid generator (PAG), which accelerates thiol–aldehyde “click” reactions under UV light, enabling rapid gelation at room temperature suitable for 3D printing. Crucially, the dithioacetal bonds can dissociate back into thiol and aldehyde groups at 80 °C under mild acidic conditions (Figures 1E–F), and the dissociation kinetics can be controlled through simple neutralization. This mechanism allows printed networks to depolymerize into photoreactive oligomers that can be directly reprinted without adding fresh monomers.

The dissociative strategy provides extraordinary flexibility. By varying the thiol crosslinkers, the team fabricated materials spanning elastomers, glassy polymers, and semi-crystalline polymers. The materials exhibit extremely high mechanical toughness, which exceeds that of most recyclable photopolymers reported previously. Some formulations show elongation at break of over 1000% while still maintaining high strengths, which are suitable for engineering applications. Importantly, the recycling efficiency remains near 100% across multiple cycles, affording the reprinted objects of comparable properties to the original ones.

The ingenuity of this approach also consists in the following aspects. The printing process can proceed in the absence of solvents or postcuring, and printing performance is insensitive to humidity. Furthermore, by neutralizing the catalyst, the depolymerized oligomers remain stable for storage and subsequent reuse. However, reliance on PAGs introduces potential cost and toxicity considerations, and the chemistry, though bio-inspired, is less directly renewable than the lipoate systems. Nevertheless, the ability to combine closed-loop recycling with tunable high-performance properties represents a transformative step in photopolymer chemistry.

Placed side by side, the two studies illustrate both complementary strengths and divergent trade-offs. The lipoate platform relies on radical ring-opening of strained disulfides, whereas the dissociative network design employs stepwise thiol–aldehyde photochemistry. Both chemistries are reversible through exerting kinetic control over temperature, UV light, and/or catalysts. Yang et al. achieve near-ideal closed-loop recycling with virtually

unchanged resin composition and properties across several recycling cycles.⁴ Machado et al. approach similar efficiencies but face slight deviations due to incomplete depolymerization and oligomer carryover.³ Both outperform earlier dynamic covalent approaches that required fresh additives. The dissociative platform spans a wider mechanical range, including crystalline and glassy regimes with exceptional toughness. Lipoate resins primarily produce flexible or soft materials, but are being improved through increasing cross-link density and introducing hydrogen-bonding interactions. Lipoates offer a renewable and potentially biodegradable route, though synthesis currently involves non-benign reagents. Dissociative networks minimize waste and solvent use but depend on PAGs and neutralization agents. Both approaches have demonstrated compatibility with standard DLP setups, but industrial adoption also hinges on cost, ease of monomer synthesis, and safe handling of catalysts and byproducts.

These advances mark a paradigm shift in additive manufacturing. The capacity to repeatedly recycle photopolymer resins without compromising resolution or mechanical properties paves the way for sustainable 3D printing across diverse sectors. Biomedical scaffolds, consumer goods, and aerospace components could all benefit from closed-loop resins, reducing both waste and dependence on virgin petrochemicals. They challenge the assumption that high-performance thermosets must be inherently irreversible, instead demonstrating that reversibility and robustness can coexist. Moreover, they signal a broader convergence between additive manufacturing, green chemistry, and circular economy principles—fields that have often advanced independently.

In conclusion, the reports by Machado et al.³ and Yang et al.⁴ collectively represent a watershed moment for sustainable additive manufacturing. By harnessing distinct chemistries—renewable lipoate disulfides and dissociative dithioacetal networks—both groups achieve the elusive goal of circular photopolymer resins. Challenges remain in scaling, purity, and infrastructure, but the conceptual breakthrough is undeniable. As the additive manufacturing industry matures, such circular resin systems will be indispensable for aligning technological innovation with environmental stewardship. In this convergence of chemistry and sustainability lies the blueprint for a genuinely circular 3D printing paradigm.

REFERENCES

- Gibson I., Rosen D. W., Stucker B. (2010). *Additive manufacturing technologies: Rapid prototyping to direct digital manufacturing*. Springer US: Boston, MA. DOI:10.1007/978-1-4419-1120-9
- Pariza X. D., Varela O., Catt S. O., et al. (2023). Recyclable photoresins for light-mediated additive manufacturing towards loop 3D printing. *Nat. Commun.* **14**:5504. DOI:10.1038/s41467-023-41267-w
- Machado T. O., Stubbs C. J., Chiaradia V., et al. (2024). Renewably sourced, circular photopolymer resin for additive manufacturing. *Nature* **629**:1069–1074. DOI:10.1038/s41586-024-07399-9
- Yang B., Ni T., Wu J., et al. (2025). Circular 3D printing of high-performance photopolymers through dissociative network design. *Science* **388**:170–175. DOI:10.1126/science.ads3880

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AUTHOR CONTRIBUTIONS

Both authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

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