

Advanced Photocurable Acrylates and Thermoset Materials for Stereolithography: Cure-Dependent Viscoelasticity, Process–Property Relationships, and Post-Processing Effects

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Abstract

Background: The rapid expansion of stereolithography (SLA) and related vat photopolymerization techniques has placed increasing emphasis on understanding the links between resin formulation, processing parameters, post-processing, and the resulting mechanical and thermal properties of printed parts. This work synthesizes extant experimental findings and theoretical frameworks regarding acrylate-based photocurable systems, thermoset behavior under varying cure states, and the role of post-rinsing and post-curing in defining final performance. The aim is to present a cohesive, publication-ready examination of how resin chemistry and processing interplay to shape viscoelasticity, diffusional phenomena, mechanical strength, and the stability of printed components. (Schittecatte et al., 2023; Müller-Pabel et al., 2022).

Methods: The article integrates critical experimental observations and mechanistic interpretations from studies on resin formulation, printing orientation, post-processing solvents, and cure kinetics. Drawing on empirical data from stereolithography resin evaluations and established rheological and diffusion theory, this synthesis constructs a composite methodological narrative that links dynamic mechanical measurements, flexural testing, roughness and cytotoxicity assessments, and thermal analysis to interpret cure-dependent viscoelasticity and process-driven heterogeneity (Salmoria et al., 2009; Keßler et al., 2021; Lambart et al., 2022).

Results: Analysis shows that resin composition and printing parameters fundamentally alter crosslink density distributions, creating spatial heterogeneities that manifest as anisotropic mechanical response and cure-dependent viscoelastic relaxation. Post-rinsing solvent choice and post-curing regimen significantly affect surface topology, residual monomer content, and bulk mechanical properties; alternative rinsing solutions yield measurable differences in roughness and flexural strength (Lambart et al., 2022; Mendes-Felipe et al., 2018). Fully biobased photoactive acrylates and novel thermoset formulations provide routes to increased thermal stability while presenting challenges in cure control and diffusion-limited conversion (Miao et al., 2020; Park et al., n.d.).

Conclusions: Optimal part performance requires harmonizing resin chemistry, printing strategy, and post-processing. A rigorous emphasis on cure mapping, viscoelastic characterization across the cure window, and solvent-resin interaction studies is urged. The article concludes with a forward-looking research agenda emphasizing multiscale characterization, predictive curing models, and targeted post-processing protocols to reduce variability and improve functional reliability in SLA-printed components (Schittecatte et al., 2023; Müller-Pabel et al., 2022).

Keywords: stereolithography, photocurable acrylates, post-curing, viscoelasticity, resin formulation, post-rinsing

Introduction

Context and background. Vat photopolymerization, especially stereolithography (SLA), has established itself as a cornerstone manufacturing technique for highly detailed, functionally graded, and small-batch parts across biomedical, dental, aerospace, and consumer fields. The technique relies on photochemically initiated polymerization of liquid resins into highly crosslinked thermoset networks. The mechanical and thermal performance of SLA parts arises from a complex interplay among resin chemistry (monomer/oligomer identity, photoinitiator concentration, additives), process parameters (layer thickness, exposure dose, printing orientation), and post-processing steps (rinsing, post-cure exposure) (Schittecatte et al., 2023; Salmoria et al., 2009). Contemporary investigations reveal that even marginal changes in resin formulation or post-processing produce nontrivial shifts in flexural strength, modulus, surface roughness, and long-term stability. A deeper theoretical and experimental reconciliation of these variables is therefore urgent for both academic understanding and industrial application (Müller-Pabel et al., 2022; Mendes-Felipe et al., 2018).

Problem statement. Despite a growing body of empirical studies, there remains a marked fragmentation in the literature concerning how cure progression and post-processing treatments influence the viscoelastic response and ultimate mechanical properties of SLA materials. Researchers often report isolated results—e.g., orientation effects on flexural strength (Keßler et al., 2021), solvent impacts on surface features (Lambart et al., 2022), or cure-dependent modulus changes in epoxies (Müller-Pabel et al., 2022)—but comprehensive syntheses that integrate cure kinetics, diffusion-limited conversion, spatial heterogeneity, and post-processing chemistry across acrylate systems are scarce. Moreover, the advent of bio-derived acrylates and specialized thermosets (Miao et al., 2020; Park et al., n.d.) adds chemical complexity that challenges established assumptions about curing uniformity and mechanical predictability.

Literature gap and significance. The existing literature offers robust experiments examining individual variables (e.g., post-curing effects on thermal and mechanical properties for a specific resin; Mendes-Felipe et al., 2018), but lacks a unifying framework that connects resin molecular design to cure-dependent viscoelasticity and the pragmatic effects of post-rinsing solvents and post-curing schedules. There is also a need to reconcile older, foundational observations about polymer mobility and diffusion (e.g., Cross, 1965; Cox & Merz, 1958) with modern photocuring contexts where rapid conversion, vitrification, and diffusion limitation coexist. This article addresses this synthesis gap by assembling theoretical constructs and observed experimental trends into an integrated narrative, offering explicit mechanistic reasoning for process–property dependencies and pointing to methodologies capable of resolving outstanding uncertainties (Schittecatte et al., 2023; Müller-Pabel et al., 2022; Miao et al., 2020).

Objective and scope. The objective is to produce a comprehensive, theory-informed, and evidence-anchored treatise on the processing and post-processing determinants of mechanical and viscoelastic behavior in SLA-printed acrylates and thermosets. This article will: (1) analyze the role of resin composition and photopolymerization kinetics in defining cure heterogeneities and network formation; (2) discuss the mechanical consequences of printing orientation and layerwise curing; (3) evaluate the effects of rinsing solvents and post-curing regimens on surface and bulk properties; (4) integrate viscoelastic theory relevant to cure-dependent modulus evolution; and (5) prescribe experimental and modeling strategies for future research. All major claims are tied to experimental studies and theoretical references from the provided literature (Schittecatte et al., 2023; Keßler et al., 2021; Lambart et al., 2022; Mendes-Felipe et al., 2018; Müller-Pabel et al., 2022; Salmoria et al., 2009; Miao et al., 2020).

Methodology

Approach overview. This work is a synthetic research article that integrates experimental evidence from published studies with mechanistic

polymer physics to generate a comprehensive conceptual and methodological framework. The methodology is textual and analytical rather than experimental: it leverages reported datasets and detailed method descriptions to carry out meta-level reasoning about cure processes, diffusion constraints, post-processing chemistry, and viscoelastic outcomes. The emphasis is on constructing robust cause-effect linkages and articulating experimental designs capable of isolating and quantifying key phenomena.

Literature selection and criteria. Sources were chosen from the supplied reference list to ensure direct relevance to acrylate and thermoset behavior in SLA and related vat photopolymerization contexts. Priority was given to studies that reported quantitative mechanical or thermal measurements (e.g., flexural strength/modulus, dynamic mechanical data, thermal transitions), detailed post-processing protocols (e.g., rinsing solutions, post-curing durations), or in-depth analyses of cure-dependent viscoelastic properties (Mendes-Felipe et al., 2018; Lambart et al., 2022; Müller-Pabel et al., 2022; Salmoria et al., 2009). Foundational polymer physics and rheology sources (Cross, 1965; Cox & Merz, 1958) were used to link observed behavior to transport and rheological models that remain valid in glass-forming and vitrifying networks.

Analytical framework. The analysis follows a layered framework:

1. **Resin chemistry to network formation.** Examine monomer/oligomer functionality, crosslinking potential, and photoinitiator efficiency and their influence on conversion rates and crosslink density profiles (Schittecatte et al., 2023; Miao et al., 2020).
2. **Cure kinetics and diffusion limitations.** Apply concepts of reaction-diffusion coupling and mobility constraints in vitrifying systems to interpret conversion gradients and cure heterogeneities (Müller-Pabel et al., 2022; Cross, 1965).
3. **Process parameters and anisotropy.** Analyze how layer thickness, exposure dose, and printing orientation produce structural anisotropy and fractographic

differences, especially under flexural loading (Keßler et al., 2021).

4. **Post-processing chemistry.** Evaluate solvent-resin interactions during rinsing and the impact of post-curing thermal or UV exposure on residual monomer content, surface roughness, and cytotoxicity (Lambart et al., 2022; Mendes-Felipe et al., 2018).
5. **Viscoelastic measurements and interpretation.** Interpret reported dynamic mechanical analyses and relaxation behavior in the context of cure progression and crosslink evolution (Müller-Pabel et al., 2022; Shlykov et al., 2022).
6. **Integration and predictive insights.** Synthesize these components into process-property maps, proposing experimental protocols and modeling approaches for future studies.

Methodological assumptions and limitations.

Because this article synthesizes published data across multiple resin systems and experimental setups, inter-study variability (differences in degree of conversion measurement methods, specimen preparation, and test conditions) is an acknowledged limitation. Where necessary, claims are framed with conditional language and supported by multiple references to establish generality. The analysis does not produce new experimental data; rather, it interprets and extends existing findings to generate testable hypotheses and prescriptive guidance for practitioners and researchers (Salmoria et al., 2009; Mendes-Felipe et al., 2018).

Analytical procedures. The following textual analytical steps were applied:

- Extract mechanistic descriptions and quantitative trends from the specified studies (e.g., the influence of rinsing solvents on roughness and flexural strength in Lambart et al., 2022; cure-dependent viscoelastic properties in Müller-Pabel et al.,

2022).

- Cross-reference reported observations with well-established polymer physics frameworks (e.g., the influence of vitrification on reaction rates and mobility, as discussed in foundational rheology literature and modern reviews).
- Develop integrated narratives that link molecular-scale processes (radical polymerization, network formation) with mesoscale heterogeneities (conversion gradients across layers) and macroscopic properties (flexural strength, modulus, roughness).
- Identify methodological gaps in the experimental literature and propose practical experimental designs (e.g., multi-length scale mechanical testing, spatially resolved conversion measurements) to address them.

Results

Resin formulation and process parameters drive final mechanical properties. The synthesis of experimental reports shows a clear and consistent pattern: resin formulation (monomer type, oligomer molecular weight, functionality, and presence of additives) and printing parameters (exposure dose, orientation, layer thickness) interact to determine the spatial distribution of conversion and thus the crosslink density. Specifically, acrylate systems with higher functionality or oligomer molecular weight generally yield networks capable of higher glass transition temperatures and stiffness when fully converted (Schittecatte et al., 2023; Miao et al., 2020). However, rapid conversion and early vitrification can trap residual monomer in less mobile regions, resulting in internal heterogeneities that affect macroscopic performance (Müller-Pabel et al., 2022).

Cure heterogeneity and anisotropic mechanical behavior. Empirical evidence indicates that printing orientation influences flexural strength and modulus in temporary dental materials and

other SLA products (Keßler et al., 2021). Orientation-dependent curing arises from two principal mechanisms: (1) layerwise exposure and stair-step geometry create microscale stress concentrators and anisotropic layer interfaces; (2) the photopolymerization front and local light intensity vary with the layer geometry and the presence of previously cured material, producing gradients in conversion across layer boundaries. Keßler et al. (2021) demonstrate that flexural strength and modulus differ significantly with printing direction, and fractographic analysis reveals failure modes reflecting interlayer adhesion strength and layer boundary defects. These findings collectively show that anisotropy is not merely geometric but also chemical—conversion gradients lead to weaker interfacial zones susceptible to crack initiation and propagation (Keßler et al., 2021; Salmoria et al., 2009).

Viscoelastic evolution across the cure window.

Cure-dependent viscoelastic properties in epoxy and acrylate networks have been evaluated through dynamic mechanical analysis and time-temperature superposition, revealing that modulus and damping are strong functions of conversion and crosslink density (Müller-Pabel et al., 2022). Müller-Pabel et al. (2022) emphasize that as conversion increases, the storage modulus transitions from liquid-like to rubbery and then to glassy behavior, with relaxation spectra shifting to higher frequencies. Importantly, near the gel point and during vitrification, mobility reduction causes a decoupling of reaction kinetics from bulk diffusion, which manifests as incomplete conversion in regions that become glassy early. This incomplete conversion contributes to long-term physical aging, residual stress, and property drift, findings corroborated by viscoelastic studies that examine cure kinetics along with mechanical behavior (Müller-Pabel et al., 2022; Cross, 1965).

Post-rinsing solvents significantly affect surface and mechanical properties.

Lambart et al. (2022) provide a detailed study of rinsing procedures for 3D-printed orthodontic appliance materials, evaluating alternative post-rinsing solutions and their impacts on roughness, flexural strength, and cytotoxicity. Their results clearly show that solvent selection during rinsing has measurable effects: aggressive solvents may extract unreacted monomers and plasticizers, reducing surface tack

and improving biocompatibility, but may also increase surface micro-roughness or embrittlement if they extract key oligomeric fractions or swell localized regions. Conversely, milder solvents may leave residual surface monomer leading to higher apparent smoothness but elevated cytotoxicity and lower flexural strength after in-service aging. These tradeoffs illuminate the criticality of selecting rinsing solvents that balance extraction efficiency with preservation of mechanical integrity (Lambart et al., 2022).

Post-curing regimes influence bulk conversion and thermal stability. Studies on post-curing (e.g., Mendes-Felipe et al., 2018; Salmoria et al., 2009) demonstrate that controlled exposure to UV and/or thermal treatments raises degree of conversion, increases glass transition temperature, and reduces extractables. Mendes-Felipe et al. (2018) evaluated a commercial Clear02™ resin, showing that post-curing leads to notable improvements in thermal stability and mechanical properties, attributable to increased crosslink density. Salmoria et al. (2009) similarly examined SOMOS 7110 and reported that laser manufacturing parameters and post-curing conditions modify mechanical performance. Importantly, post-curing must be optimized: insufficient post-cure leaves residual monomer and inferior properties; over-curing can introduce thermal stresses and potentially embrittle the network by over-constraining segmental mobility (Mendes-Felipe et al., 2018; Salmoria et al., 2009).

Biobased acrylates and novel thermosets present opportunities and challenges. The development of fully biobased, heat-resistant photoactive acrylates from aliphatic biomass (Miao et al., 2020) opens avenues for sustainable SLA materials with improved environmental credentials. These formulations, however, often have distinct reactivity profiles and thermal behavior compared to petrochemical analogs. Miao et al. (2020) report successful fabrication of heat-resistant photoactive acrylates, but also note the importance of tuning photoinitiator systems and cure schedules to ensure sufficient conversion and that the resulting networks achieve desired glass transition temperatures. Park et al. (n.d.) discuss mechanical and thermal properties of 3D-printed thermosets via stereolithography, underlining that thermoset chemistry must be co-optimized with processing to achieve targeted performance.

Diffusion, mobility, and the role of physical aging. Foundational literature on diffusion and mobility in amorphous solids and polymer matrices (Cross, 1965; Cox & Merz, 1958; Hancock et al., 1995) remains highly relevant for interpreting SLA cure phenomena. As polymerization proceeds and the network densifies, the mobility of unreacted species and chain segments decreases, leading to diffusion-limited reactions. This results in residual monomer trapped within glassy regions and a potential for long-term relaxation or physical aging phenomena (Hancock et al., 1995; Mapes et al., 2006). The practical consequence is that parts may experience property changes post-fabrication as trapped monomer slowly diffuses or as physical aging reduces free volume and alters mechanical response over time (Hancock et al., 1995; Mapes et al., 2006).

Correlations between rheological behavior and cure state. Classical rheological correlations (Cross, 1965; Cox & Merz, 1958) are useful when interpreting pre-gel resin flow and post-gel viscoelasticity. For example, Cross's pseudoplastic flow model helps explain how increasing conversion raises low-shear viscosity and alters flow behavior during recoating in layer-based processes. Understanding these rheological transitions is essential for designing printable formulations with stable flow behavior while maintaining reactivity (Cross, 1965; Cox & Merz, 1958).

Discussion

Interpreting the integrated evidence: synthesis and mechanisms. The corpus of literature synthesized above supports a mechanistic picture where resin chemistry, cure kinetics, and processing geometry combine to produce spatially heterogeneous networks whose mechanical properties cannot be deduced from bulk measures alone. Conversion gradients develop both through the thickness of individual layers and across the depth of the part due to light attenuation, oxygen inhibition, and diffusive constraints, yielding interlayer zones with reduced crosslink density. Such heterogeneities are directly implicated in anisotropic mechanical performance and characteristic fractographic signatures observed in flexural failure (Kessler et al., 2021; Salmoria et al., 2009).

Cure kinetics shape the viscoelastic landscape: early stages of polymerization exhibit liquid-like viscous behavior, while later stages reveal rubbery or glassy elasticity as crosslinking proceeds (Müller-Pabel et al., 2022). The transition to vitrification halts local mobility and arrests further conversion, producing a chemically frozen state that may still contain significant unreacted monomer. Thus, optimizing post-curing to push conversion beyond the vitrification window, where feasible, is necessary to reduce extractables and improve thermal stability (Mendes-Felipe et al., 2018).

Post-processing choices—particularly rinsing solvent selection—have been shown to materially affect surface topography and mechanical integrity. Lambart et al. (2022) demonstrate that solvent-resin interactions can be tuned to balance effective removal of unreacted species and preservation of mechanical robustness. This tradeoff is crucial for dental and biomedical applications where cytotoxicity and surface finish are paramount (Lambart et al., 2022).

Technical implications and prescriptive recommendations. Based on the synthesized evidence, practitioners and researchers should consider the following prescriptive steps:

1. **Comprehensive cure mapping.** Employ spatially resolved conversion measurements (e.g., micro-FTIR mapping, Raman spectroscopy, or ToF-SIMS where appropriate) to quantify conversion gradients across layers and at surfaces. This mapping enables targeted adjustments to exposure and post-curing strategies to minimize weak interfacial zones (Kubicek et al., 2014; Mendes-Felipe et al., 2018).
2. **Process-formulation co-optimization.** Design resins with not only target bulk properties but also controlled reactivity profiles that mitigate rapid vitrification before sufficient conversion is achieved. This may entail balancing oligomer molecular weight, monomer functionality, and photoinitiator efficiency to obtain a desirable cure window (Schittecatte et al., 2023; Miao et al., 2020).

3. **Rinsing solvent selection and standardized protocols.** For medical and dental applications, establish rinsing protocols that remove extractables while minimizing deleterious extraction of structural oligomers. Comparative solvent studies akin to Lambart et al. (2022) should be routine in qualification workflows.
4. **Post-cure optimization.** Adopt controlled post-curing regimens that elevate conversion without introducing thermal stresses. Thermal ramping combined with staged UV exposure may yield more uniform conversion and reduce residual stresses than aggressive single-stage cures (Mendes-Felipe et al., 2018; Salmoria et al., 2009).
5. **Monitor for physical aging and long-term changes.** Given the propensity for physical aging and residual monomer-driven changes, particularly in vitrified regions, accelerated aging studies and monitoring of mechanical drift are recommended, especially for load-bearing or biomedical parts (Hancock et al., 1995; Mapes et al., 2006).

Limitations and counterarguments. The recommendations above are constrained by practical industry realities. For example, achieving uniform conversion by slowing photopolymerization may compromise throughput and economic viability for production. Additionally, some solvents effective at extracting monomer are hazardous or incompatible with clinical use; therefore, tradeoffs between extractability and biocompatibility can be complex. It is also possible that some resins with inherently high functionality are robust to modest heterogeneities due to redundancy in network formation; thus, blanket prescriptions must be tuned to specific chemistries (Schittecatte et al., 2023; Miao et al., 2020).

Future research directions. To accelerate progress and reduce variability in SLA outputs, future research should prioritize:

- **Multiscale characterization** combining nanoscale chemical mapping with

mesoscale mechanical testing to expose interfacial weaknesses and their causative chemistry.

- **Predictive cure models** that incorporate light transport, reaction kinetics, and diffusion limitations in a coupled simulation framework that can be parameterized for specific resin chemistries.
- **Green solvent development** for post-rinsing that balance extraction efficacy with safety and minimal impact on mechanical properties.
- **Tailored photoinitiator systems** that allow temporal control (e.g., two-stage initiators or photobase generators) to extend conversion before vitrification.
- **Adaptive printing strategies** such as gradient exposure or interlayer temperature control to mitigate interfacial defects created by abrupt transitions in conversion.

These directions align with the conceptual gaps identified in the literature and offer practical avenues for both academic inquiry and process improvement (Schittecatte et al., 2023; Müller-Pabel et al., 2022; Lambart et al., 2022).

Conclusion

This article synthesizes current understanding of how resin formulation, printing parameters, and post-processing choices govern the viscoelastic and mechanical behavior of SLA-printed acrylates and thermosets. Key conclusions include: (1) conversion gradients and cure-induced heterogeneities are central determinants of anisotropic mechanical performance and fractographic failure modes (Keßler et al., 2021; Salmoria et al., 2009); (2) viscoelastic properties depend strongly on cure state and network evolution, with vitrification creating diffusion limitations that entrap residual monomer and induce long-term property evolution (Müller-Pabel et al., 2022; Hancock et al., 1995); (3) post-processing—especially rinsing solvent choice and

post-curing regimen—has a measurable impact on surface roughness, flexural strength, and potential cytotoxicity (Lambart et al., 2022; Mendes-Felipe et al., 2018); and (4) the emergence of biobased acrylates and novel thermosets presents both opportunities for sustainability and challenges in cure control (Miao et al., 2020; Park et al., n.d.).

To realize the full potential of SLA for high-performance applications, the field must adopt rigorous cure mapping, process–formulation co-optimization, solvent selection protocols, and predictive modeling strategies that explicitly account for reaction-diffusion coupling and vitrification. By doing so, researchers and manufacturers can reduce variability, improve part reliability, and enable the broader adoption of photocurable materials in demanding applications.

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