

Poly(propylene fumarate) Photoresins for Stereolithography: Oligomer Identity, Reactive-Diluent Control, Temperature–Viscosity Coupling, Pulsed-UV Cure and Qualification

Juan Segurola

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

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Statement of Significance

Poly(propylene fumarate) (PPF) is an unsaturated polyester whose backbone fumarates support radical crosslinking while ester chemistry enables hydrolytic degradation studies. Direct stereolithography evidence spans continuous DLP and 308 nm excimer projection, but the resin is never PPF alone: oligomer molar mass and isomerisation, diethyl fumarate (DEF), initiator, temperature and exposure history jointly determine viscosity, cure depth, geometry and mechanics. ER-115 converts those dependencies into an auditable release architecture.

Keywords: vat photopolymerisation; stereolithography; continuous DLP; poly(propylene fumarate); diethyl fumarate; unsaturated polyester; excimer laser; resin temperature; viscosity; degradation; qualification.

Abstract

PPF photoresins have been processed by layerwise and projection stereolithography as PPF/DEF mixtures or PPF-rich systems. Primary studies show that oligomer number-average molar mass, PPF fraction and resin temperature control rheology; selected cDLP specimens exceeded 15 MPa ultimate tensile strength with elastic moduli of 178–199 MPa. A 308 nm pulsed-projection platform achieved micrometre-scale cure-depth control with 1 wt% BAPO, while initiator absorption, oxygen, interfaces, pulse fluence and bleaching altered the working-curve response. These data are platform-specific. HOS-cell attachment after 48 h, hydrolysable ester linkages and the term resorbable do not establish device biocompatibility, in-vivo resorption or safe degradation products. Qualification must freeze oligomer identity, DEF and initiator mass balance, temperature–viscosity state, temporal exposure, spatial cure, extractables, degradation products and use-specific biological evidence.

1. Scope and boundaries

ER-115 owns PPF oligomer identity, DEF-reactive-diluent composition, resin temperature, continuous-DLP or pulsed-excimer curing and PPF-specific degradation qualification. It does not own generic biodegradable scaffolds, every unsaturated polyester, biomedical approval or universal working curves.

ER-05 retains working-curve reproducibility; ER-06 biological-response qualification; ER-15 scaffold transport/degradation; ER-27 conversion; ER-30 oxygen inhibition; ER-32 storage/reuse; ER-36 rheology/recoating; ER-67 hydrogel VPP; ER-72 ageing; ER-74 generic cleavable networks; ER-86 extractables; ER-100 corpus architecture; and ER-110 itaconate-derived unsaturated polyesters [C1-C13]. ER-115 is the PPF chemical-identity and exposure-state gate.

PPF differs from polypropylene, poly(propylene carbonate), poly(propylene glycol), fumarate salt and small-molecule fumarate. DEF is both diluent and reactive unsaturated component, so a PPF/DEF network cannot be attributed to PPF alone.

2. Identity and formulation gate

Variable	Coupled consequence	Minimum evidence
PPF synthesis	Molar mass, fumarate/maleate content, end groups and residual catalyst	Route, NMR isomerisation, SEC method, dispersity and impurities
PPF:DEF fraction	Viscosity, double-bond density, cure threshold, extractables and network composition	Mass fractions, purity, conversion and residual DEF
Photoinitiator	Absorption/bleaching, radical rate, cure depth and photoproducts	Identity, loading, spectrum, ageing and extractables
Resin temperature	Strong viscosity and transport change; possible kinetic change	Vat temperature map, equilibration, shear history and open-vat time

Table 1. PPF-resin identity controls.

3. Direct primary evidence

3.1 cDLP oligomer and temperature study

Luo et al. prepared PPF by ring-opening copolymerisation of maleic anhydride and propylene oxide followed by base-catalysed isomerisation [1]. They compared number-average molar masses of 1.1, 1.7 and 2.0 kDa, PPF contents of 50 and 75 wt% in DEF, and temperatures from 25 to 55 °C. Zero-shear viscosity followed a linear Arrhenius relationship over the studied range. The matrix demonstrates that oligomer identity, concentration and print temperature cannot be collapsed into a single viscosity label.

The selected printed specimens had ultimate tensile strength above 15 MPa and elastic moduli of 178–199 MPa [1]. These values were described in relation to trabecular bone, but material-range overlap is not functional equivalence to bone and does not qualify a scaffold. Tensile results require state, geometry and method closure [S1-S2].

3.2 308 nm projection photocuring

Beke et al. studied purified PPF and a 7:3 w/w PPF:DEF blend with 1 wt% BAPO using 20 ns XeCl-laser pulses at 308 nm and 100 Hz [2]. The reported PPF weight-average molar mass was 4600 Da by SEC–MALS. The article reports formulation- and exposure-dependent microstructure depths under its pulsed-laser setup. These setup-specific values are not optical penetration depths and cannot be transferred as a fixed working curve. During exposure, photoinitiator consumption can change the optical field, so total fluence alone does not define a universal cure-depth relation.

3.3 Pulse, threshold and defect boundary

At 20 mJ cm⁻² per pulse, the PPF:DEF blend began curing at a reported total fluence of 1000 mJ cm⁻² with 35 µm depth, whereas pure PPF began at 120 mJ cm⁻² with 18 µm depth [2]. Pulse fluence above 100 mJ cm⁻² caused bubble formation. Interface scattering and reduced oxygen at the quartz boundary broadened pillars, while non-uniform deep irradiation contributed to cratered tops. Total fluence therefore does not preserve the temporal, interfacial or defect state.

3.4 Mechanical state under projection

Nanoindentation on selected pillars gave 2.0 ± 0.5 GPa for PPF and 2.8 ± 0.9 GPa for PPF:DEF under the reported geometry and Oliver–Pharr analysis [2]. These local indentation moduli cannot be substituted for the cDLP tensile moduli in [1]. Farkas et al. separately reported four orders of stiffness variation by laser-parameter modulation [3]. Exposure-controlled stiffness is therefore also an exposure-controlled material state, not a free grading variable; thermal state requires its own method closure [S4].

3.5 Geometry and cell-evidence boundary

The excimer study produced floating two-dimensional and 2.5-dimensional grids, including a 3.5 s exposure of 350 pulses at 100 Hz for one PPF case [2]. The authors observed adherent HOS cells and no dead-cell signal in analysed samples after 48 h. This is preliminary cell-line evidence on the studied surface; it does not close extract chemistry, degradation products, sensitisation, implantation, chronic response or device performance [S7–S11].

4. Exposure-state and spatial-cure gate

Control	Why it matters	Release output
Continuous source	Intensity, wavelength, absorber and temperature set kinetics and depth	Working curve plus conversion and geometry
Pulsed source	Pulse fluence, width, number and repetition rate can change bleaching, heating and bubbles	Full temporal exposure vector, not total fluence alone
Interface	Oxygen, quartz/resin scattering and attachment alter local cure	Freestanding and interface-specific fidelity
Post-process	Wash and post-cure alter residual DEF, conversion and mechanics	Mass balance, spatial conversion and final-state properties

Table 2. Exposure-state controls for PPF stereolithography.

5. Degradation and biological qualification

Backbone ester bonds make hydrolysis plausible, but crosslink density, residual DEF, geometry, water transport and local pH determine the realised pathway. A release study must report initial dry mass, specimen dimensions, medium, temperature, pH, agitation, swelling, dry residual mass, molecular-mass change and identified soluble products [S5–S6] [S9–S10]. Resorbable, degradable and biodegradable are not interchangeable labels. Spatial capability claims require controlled test artefacts rather than a single scaffold image [S3].

Biological evaluation begins with a risk-management plan for the final manufactured state [S7]. In-vitro cytotoxicity [S8] cannot replace degradation-product identification [S9–S10], extractables or chronic use-specific evidence. Absorbable-device guidance further requires a time-resolved biological and material evaluation rather than a single cell-attachment image [S11].

6. Failure-mode interpretation

- Viscosity is acceptable at 55 °C: verify thermal history, inhibitor reserve and cooling drift before transferring the process.
- PPF content is stated: retain DEF, initiator, residual catalyst and maleate/fumarate balance; PPF wt% is not full identity.
- Total fluence matches: retain pulse width, pulse fluence, repetition rate and oxygen/interface state.
- Cure depth grows: inspect bleaching, lateral broadening, cratered tops and gas formation rather than fitting one curve blindly.
- Indentation modulus is high: do not substitute it for tensile, compressive, fatigue or scaffold-level performance.
- Cells adhere at 48 h: withhold device biocompatibility, implantation and degradation-product safety.
- The network hydrolyses: identify products and withhold in-vivo resorption and environmental biodegradation until directly proven.

7. Minimum workflow

- Freeze PPF synthesis route, fumarate isomerisation, molar-mass distribution, end groups, residual catalyst and batch.
- Freeze PPF:DEF, initiator, inhibitor, absorber, impurities, water and exact vat temperature.
- Measure viscosity versus shear rate and temperature after controlled equilibration and ageing.
- Close spectrum, intensity or pulse vector, conversion, cure depth, lateral growth, bubbles and interface effects.
- Close washing and post-cure by residual DEF, spatial conversion, mass change and final-state properties.
- Close degradation by products and kinetics; close biological response on the final material under a risk plan.
- Revalidate every molecular-mass, concentration, temperature, optical-source or geometry change.

8. Conclusions

PPF is a credible stereolithography resin class because its unsaturated polyester backbone combines radical network formation with a hydrolysable chemical architecture. Direct studies support cDLP processing, temperature-dependent viscosity control and rapid 308 nm projection of selected PPF/DEF formulations.

The evidence also prevents simplification. DEF participates in the network; oligomer mass and isomerisation change the vat; BAPO absorption and bleaching reshape cure depth; pulse parameters influence defects and stiffness; and local indentation, tensile properties and scaffold function are different endpoints.

ER-115 therefore releases no universal PPF formulation, exposure, mechanical property, biodegradation rate, biocompatibility or clinical suitability. The exact final material must close chemical identity, temperature–rheology state, spatial cure, residuals, degradation products and biological risk.

Limitations

This qualitative engineering review is not a systematic meta-analysis. Direct evidence combines one cDLP oligomer/temperature study and two related excimer-projection studies; their sources, geometries and mechanical methods are not pooled. No proprietary recipe, universal exposure, safe processing temperature, sterilisation validation, full extractables profile, in-vivo degradation, toxicological qualification, regulatory approval, life-cycle assessment or clinical-performance claim is supplied.

Author contributions

Juan Segurola: conceptualisation, evidence synthesis, boundary definition, engineering interpretation, manuscript preparation and final author verification.

Competing interests

The author is founder and CEO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated. Scientific statements derive from cited primary literature and official standards.

Company information

3Dresyns by Resyner Technologies S.L. · General Etxague 15B, 20003 Donostia / San Sebastián, Gipuzkoa, Spain · VAT ESB24827511 · info@3Dresyns.com · www.3Dresyns.com

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Related Engineering Review boundaries

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- [C2] Segurolo, J. Biological Response in Photopolymer Additive Manufacturing. ER-06. Zenodo or controlled version (2026).
- [C3] Segurolo, J. Transport, Degradation and Mechanical Evolution in Vat-Printed Tissue-Engineering Scaffolds. ER-15. Zenodo or controlled version (2026).
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- [C5] Segurolo, J. Oxygen Inhibition and Free-Surface/Interfacial Cure in VPP. ER-30. Zenodo or controlled version (2026).
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