

Phenolic, Lignin-Derived and Bio-Aromatic Photopolymers for Vat Photopolymerisation: Native Polycondensation, (Meth)acrylate Functionalisation, Optical Attenuation, Volatile Evolution and Qualification

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Statement of Significance

Phenolic content does not identify one photopolymer network. A photoacid-catalysed novolak formulation can form a phenoplast by condensation, whereas eugenol-, guaiacol- or vanillin-derived (meth)acrylates form carbon-carbon networks that merely retain phenolic-derived aromatic structures. Lignin can be a low-level particulate reinforcement, a chemically modified macromolecular precursor or a source of isolated aromatic building blocks. ER-107 provides a state-resolved identity gate and qualification chain that prevents these systems from being grouped as one bio-based phenolic resin class.

Keywords: vat photopolymerisation; phenolic resin; novolak; phenoplast; lignin; vanillin; eugenol; guaiacol; methacrylation; photoacid; Hot Lithography; optical attenuation; volatile evolution; qualification.

Abstract

Phenolic and lignin-derived materials enter vat photopolymerisation through several chemically different routes. Primary studies demonstrate photoacid-triggered polycondensation of a pure novolak formulation by Hot Lithography without a binder or matrix polymer; stereolithography of eugenol-, guaiacol- and vanillyl-alcohol-derived (meth)acrylates; direct laser writing of vanillin acrylate networks; Hot Lithography of methacrylated lignin containing more than 30% lignin without reactive diluent; and low-level lignin reinforcement of a methacrylate SLA resin. The native phenolic route produces water and can form bubbles if reaction and evaporation overlap above the stable process window. Functionalised bio-aromatics instead undergo radical chain growth, so their cured network is not a phenoplast even when the precursor originated from a phenol. Lignin additionally introduces feedstock heterogeneity, chromophores, radical activity, aggregation and uncertain functionalisation. Renewable origin does not establish biodegradability, low hazard, low migration, reduced climate impact or chemical recyclability. This review separates chemical identity, biogenic-carbon accounting, optical processability, conversion, volatile balance, extractables, reaction-to-fire evidence and final duty.

1. Scope and boundaries

ER-107 owns the identity and qualification of native phenolic polycondensation and phenolic-, lignin- or bio-aromatic-derived photopolymer routes used in VPP. It covers novolak and resol distinctions, photoacid-triggered condensation, functionalised small-molecule bio-aromatics, methacrylated lignin, lignin-filled composites, optical attenuation, volatile evolution, conversion, residuals and final performance.

ER-08 retains biodegradation accessibility; ER-11 general bio-based design; ER-20 generic thermal qualification; ER-27 conversion metrology; ER-35 dispersion and sedimentation; ER-45 generic flame-retardant composites; ER-59 sequential dual cure; ER-61 gelation and vitrification; ER-64 thiol-ene/yne; ER-72 environmental ageing; ER-80 in-can radical stability; ER-91 evidence density and hazard; ER-92 residual-reactant hazard; ER-99 dispersant chemistry; ER-100 corpus architecture; and ER-106 other high-temperature thermoset families [C1-C16].

This review does not equate lignin with a phenolic resin, call a phenolic-derived acrylate a phenoplast, infer biodegradation from renewable origin, treat all technical lignins as interchangeable, or use char yield as proof of fire safety. Furan-derived systems are reserved for ER-108. Carbonised products are new materials and lose the original photopolymer identity.

2. Chemical-identity and renewable-content gate

Novolaks are commonly acid-catalysed phenol-formaldehyde products that require a curing agent for further network formation; resoles are commonly base-catalysed products able to self-condense when heated. Exact phenol-to-

formaldehyde ratio, catalyst, residual monomer and curing agent determine the real material. In the Hot Lithography proof of concept, a photoacid generator released acid that both promoted formaldehyde generation from the curing agent and catalysed novolak condensation [1].

A guaiacol methacrylate, vanillin diacrylate or eugenol-derived diacrylate is instead a functionalised molecule whose pendant vinyl group undergoes radical polymerisation. The aromatic precursor contributes stiffness, absorption and chemical functionality, but the load-bearing network is a (meth)acrylate network. Lignin reinforcement and methacrylated lignin are also separate: the former disperses lignin in another resin, whereas the latter covalently installs polymerisable functionality on an oxyalkylated lignin precursor [4,5].

Material label	Minimum identity evidence	Claims withheld
Photoacid-cured phenoplast	Novolak/resol identity, curing agent, PAG, condensation markers and volatile balance	Generic acrylate or volatile-free cure
Phenolic-derived (meth)acrylate	Molecular precursor, degree of functionalisation, vinyl conversion and network composition	Phenoplast identity and native phenolic reactivity
Methacrylated lignin resin	Lignin source, isolation, oxyalkylation, grafting degree and phase distribution	Uniform macromolecule or fully bio-based content
Lignin-filled composite	Technical lignin identity, loading, particle/aggregate state and matrix composition	Covalent lignin network participation
Carbonised derivative	Pyrolysis schedule, mass yield, carbon chemistry, porosity and defects	Retention of photopolymer identity

Table 1. Identity gate for phenolic and lignin-derived VPP routes.

3. Demonstrated VPP routes

3.1 Photoacid-triggered native phenolic polycondensation

Wolff et al. directly printed novolak-based phenolic formulations by Hot Lithography without an additional binder or matrix polymer [1]. The vat, platform and recoating unit were held at 80 °C and a 375 nm laser was used. Paraformaldehyde or trioxymethylene diacetate acted as curing agents, while an iodonium photoacid generator initiated acid-catalysed chemistry. The reported process window around 80-90 °C balanced reaction and bubble suppression. These values belong to the exact formulation, heated machine and geometry.

3.2 Natural-phenolic (meth)acrylate formulations

Ding et al. prepared an eugenol-derived diacrylate, guaiacol methacrylate diluent and vanillyl-alcohol dimethacrylate crosslinker [2]. A ternary formulation (GEV 60-20-20 mol%, 2 wt% TPO) was printed on a commercial 405 nm SLA machine for geometric evaluation. On separately photocured bulk specimens of the same formulation, storage modulus reached 3.40 GPa (DMA, 25 °C) and tensile strength 61.7 ± 5.1 MPa. These are not printed-specimen values. The results demonstrate functionalised bio-aromatic acrylates, not native lignin or phenolic condensation.

3.3 Vanillin-acrylate optical printing

Navaruckiene et al. studied vanillin dimethacrylate and vanillin diacrylate under UV/visible radical curing [3]. Direct laser writing demonstrated microstructured optical printing. The reported antimicrobial observation belongs to the tested film and assay and does not establish antimicrobial durability, leaching control or biomedical approval.

3.4 Methacrylated lignin without reactive diluent

Keck et al. oxyalkylated wheat-straw soda lignin with propylene oxide and then methacrylated the product [4]. The authors reported grafting of 90% of functional hydroxyl groups, double-bond conversion of at least 80% with the studied initiators, lignin content above 30%, and Hot Lithography without reactive diluent. This is a formulation-specific proof of concept.

3.5 Lignin-reinforced methacrylate composites

Zhang et al. solution-blended 0.2-1.0 wt% softwood kraft lignin into a methacrylate SLA resin [5]. Under their post-cure conditions, the 0.4 wt% formulation reached 49.0 MPa tensile strength versus 30.7 MPa for the control. This evidence concerns low lignin loading in a separate matrix and cannot be used to claim a universal reinforcement optimum.

4. Optical attenuation and photochemical state

Aromatic chromophores absorb across wavelength ranges that depend on substituents, oxidation and aggregation. Technical lignin can additionally scatter when phase-separated. The same species may attenuate the cure beam, quench radicals, donate electrons, act as an inhibitor or participate in photoinitiation. Cure-depth and working-curve data must therefore be measured on the complete formulation at controlled temperature, age and path length, not inferred from neat-monomer spectra.

Photoacid systems add a second constraint: PAG action spectrum, acid generation, thermal cleavage and diffusion of acid must be separated from condensation kinetics. In radical bio-aromatic systems, inhibitor level and residual phenolic hydroxyl groups can change latency and conversion. ER-80 retains generic in-can radical stability and ER-27 generic conversion metrology [C3,C11].

Control	Potential failure	Minimum evidence
Absorption/scattering	Shallow cure, feature broadening or depth-dependent composition	Complete-resin spectrum, working curve, feature transfer and through-thickness conversion
PAG or initiator state	Spectral mismatch, thermal initiation or residual photoproducts	Identity, action range, dose, temperature and residual analysis
Lignin phase state	Aggregation, sedimentation, local inhibition or mechanical defects	Source, size distribution, dispersion, time and build-position sampling
Inhibitor/phenolic activity	Premature cure or incomplete radical conversion	Stability window, conversion kinetics and aged-vat comparison

Table 2. Optical and photochemical controls for phenolic and lignin-derived vats.

5. Temperature, rheology and volatile evolution

Heated-vat processing can reduce viscosity and enable otherwise solid or highly viscous precursors, but temperature also accelerates dark reactions, component loss and phase change. Report vat, recoater, platform and specimen temperature together with warm-up, residence time, rheology and reactivity drift. A formulation stable for a short coupon may change during a long build.

Condensation produces small molecules. Wolff et al. directly linked bubble formation to water evolution when the reaction window exceeded the stable regime [1]. Formaldehyde-generating curing agents and acetic-acid-forming pathways add further mass-balance requirements. A bubble-free exterior does not establish zero volatile evolution or a dense interior. Stage-resolved mass, gas identification and internal inspection are required.

6. Lignin heterogeneity and functionalisation

Lignin is not one molecule. Plant source, pulping process, sulfur content, molecular-mass distribution, hydroxyl functionality, ash, colour and storage oxidation can all alter reactivity and optical response. Oxyalkylation and methacrylation add their own substitution distributions and residual reagents. Batch identity therefore requires more than the word lignin or a nominal mass fraction.

Biogenic feedstock fraction, lignin mass fraction, bio-based carbon fraction and covalently incorporated fraction must be reported separately. A reactive-diluent-free formulation can still contain non-renewable atoms or reagents introduced during modification. Renewable origin does not establish biodegradability; ER-08 owns structural-accessibility limits and ER-11 the general bio-based design framework [C1,C2].

7. Conversion, network closure and extractables

Native condensation and radical chain growth need different conversion markers. For novolak cure, use chemistry-specific evidence for methylene-bridge formation, curing-agent consumption and remaining volatile-generating species. For (meth)acrylated bio-aromatics or lignin, quantify vinyl conversion, gel fraction and soluble species. One insoluble-fraction value does not identify every residual molecule or prove homogeneous conversion.

ISO 6427:2025 provides a conventional anchor for organic-solvent-extractable matter, while ISO 175:2010 remains current for effects of immersion in liquid chemicals [S8,S9]. Application-relevant extraction still requires compound-specific analytics. Residual formaldehyde sources, phenols, acids, PAG fragments, initiator photoproducts, unreacted (meth)acrylates and modification reagents require state- and route-specific attention. ER-92 retains generic residual-reactant hazard [C12].

8. Mechanical, thermal and dimensional qualification

ISO 527-1:2019, ISO 527-2:2025 and ISO 178:2019 provide tensile and flexural anchors [S1-S3]. Report specimen geometry, surface, build orientation, internal voids, post-cure and conditioning. Numerical results from a natural-phenolic network, methacrylated lignin or low-loading lignin composite must not be compared without identifying matrix, composition and test state.

ISO 11357-2:2020, ISO 11358-1:2022, ISO 6721-11:2019 and ISO 11359-2:2021 anchor glass-transition, mass-loss, dynamic-mechanical and thermomechanical measurements [S4-S7]. Aromatic content or char formation does not by itself establish service temperature. Shrinkage, volatile loss and thermal expansion must be separated across printing and post-cure.

9. Fire, smoke, char and carbonisation boundaries

Phenolic resins are often associated with favourable fire response and char, but performance depends on formulation, specimen, flux, atmosphere and method. ISO 5660-1:2015 with Amendment 1:2019 remains current for cone-calorimeter heat release, smoke production and mass-loss rate; ISO 5659:2026 addresses optical smoke density [S10,S11]. Neither a TGA residue nor aromatic content substitutes for those tests.

Carbonisation creates a carbonaceous derivative with different composition, porosity, dimension and properties. A high char yield can coexist with smoke, toxic effluent, cracking or loss of function. ER-107 withholds flame rating, low-smoke, low-toxicity and carbon-component claims unless directly measured on the exact final object.

10. Qualification architecture

Block	Minimum evidence	Release question
Feedstock identity	Phenolic/lignin source, derivatisation, composition, impurities and age	Is the starting material reproducible and correctly named?
Vat state	Temperature, viscosity, phase/dispersion, absorption and working life	Does the material remain printable during the full build?
Photochemistry	PAG/initiator action, dose, conversion and dark reaction	Which reaction fixes the printed geometry?
Volatile closure	Mass balance, gas identity, bubble/void inspection and post-cure	Is condensation or reagent loss controlled?
Final network	Chemical conversion, gel/extractables, morphology and dimensions	What network and residual state actually remain?
Properties	Mechanical, thermal, ageing and chemical retention	Do claims survive the declared environment?
Fire/sustainability	Method-specific fire data and auditable renewable/LCA definitions	Are high-char or bio-based claims bounded correctly?

Table 3. Release architecture for phenolic and lignin-derived VPP materials.

11. Failure-mode interpretation

- The heated vat prints initially but drifts during a long build: measure temperature, residence-time stability, volatility and dark reaction before changing dose alone.
- The native phenolic part contains bubbles: separate condensation kinetics from water or curing-agent product evolution and lower gradients or path length.
- A lignin-filled resin cures only near the surface: map absorption, scattering, aggregation and local conversion on the full formulation.
- A bio-aromatic acrylate is called phenolic resin: rename it by the polymerising functionality and final network rather than feedstock origin.
- Methacrylated lignin shows high nominal conversion: verify substitution distribution, gel fraction, soluble species and through-thickness state.
- TGA shows high residue: do not infer flame, smoke or toxicity performance without method-specific fire testing.
- A low lignin loading increases tensile strength: retain the exact matrix, loading and post-cure and do not extrapolate a universal optimum.
- Renewable content is high: quantify the accounting boundary and withhold biodegradability, recyclability and LCA benefit until separately demonstrated.

12. Minimum workflow and research priorities

- Freeze phenolic or lignin source, derivatisation, substitution, curing agent, initiator/PAG, impurities, inhibitor, water and storage state.
- Map rheology, absorption, scattering and working life at the actual vat temperature and build duration.
- Identify the geometry-fixing reaction and use route-specific conversion markers rather than one generic cure metric.
- Close volatile mass balance and inspect internal bubbles or voids across representative thicknesses and nodes.
- Record mass and x/y/z dimensions after printing, washing and each thermal or photochemical post-cure step.
- Quantify gel fraction, extractables and compound-specific residuals for the final conditioned state.
- Report lignin batch and modification distributions and distinguish feedstock, mass and bio-based-carbon fractions.
- Use tensile, flexural, DMA, DSC, TGA and TMA data only within their declared methods and test states.
- Measure heat release, smoke and effluent response directly before assigning fire or low-smoke claims.
- Develop reference materials that separate native phenolic condensation, functionalised bio-aromatic networks and lignin-filled composites.

13. Conclusions

Phenolic and lignin-derived VPP materials form a family of feedstock origins, not one polymer chemistry. Native photoacid-triggered novolak condensation, radical curing of isolated bio-aromatic (meth)acrylates, methacrylated lignin and low-loading lignin composites create different networks and process risks.

Primary evidence confirms direct binder-free phenoplast Hot Lithography, commercial-machine SLA of natural-phenolic acrylates, direct laser writing of vanillin acrylates, reactive-diluent-free Hot Lithography of methacrylated lignin and mechanical reinforcement by small lignin additions. Every result remains bounded by exact source, derivatisation, formulation, temperature, optical system and post-cure.

ER-107 closes with a state-resolved chain covering feedstock identity, vat stability, photochemistry, volatile evolution, conversion, residuals, geometry, final properties, fire testing and sustainability accounting. Renewable origin, aromaticity or high char cannot replace direct evidence for biodegradability, safety, fire performance or environmental benefit.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited systems use different phenolic and lignin sources, modification routes, initiators, curing agents, temperatures, printers, wavelengths, geometries, post-cures and test methods. Numerical values are not pooled or ranked. No proprietary formulation assay, universal printing window, fire certification, toxicological qualification, life-cycle model or regulatory approval is provided.

Author contributions

Juan Seguro: 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 the cited primary literature and official standards. The review package includes QA and source-boundary records for independent review.

Company information

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- [S11] ISO 5659:2026. Plastics - Smoke generation - Determination of optical density by a single-chamber test. Edition 1. <https://www.iso.org/standard/86322.html>

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Version note

v0.2 closes the v0.1 independent review findings without changing the frozen ER architecture. All corpus entries use deposit-neutral wording and ER-91 is explicitly anchored; the Ding values are assigned to separately photocured bulk specimens; and the five standards titles plus ISO 527-1 status are corrected. Independent review returned APPROVE on 31 August 2026.