

Highly Specialised Photopolymer Resins for Extreme Service: High Temperature, Chemical Resistance, Flame Resistance, Gas Barrier, Electrical Insulation and Qualification

A State-Resolved Framework for Thermomechanical Retention, Chemical Exposure, Fire Behaviour, Permeation, Insulation and Service Ageing

Juan Seguro

3Dresyns by Resyner Technologies S.L.

Registered tax address: General Etxague 15B, 20003 Donostia / San Sebastián, Gipuzkoa, Spain

VAT number: ESB24827511

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

ER-160 · Engineering Review · Version 0.4 · 2 September 2026

Statement of Significance

Highly specialised photopolymer resins are often selected through one attractive label or peak value: high-temperature, chemical-resistant, flame-resistant, gas-barrier, electrically insulating or dimensionally stable. That practice hides the mechanisms that govern failure. Glass-transition temperature is not a continuous-use temperature; heat-deflection temperature is not thermal endurance; a 24-hour mass change is not chemical-service life; a small-flame classification is not heat release, smoke or finished-product fire safety; film permeability is not component leakage; and initial dielectric strength is not insulation reliability after heat, humidity, chemicals and surface contamination. This review replaces label-based selection with a state-resolved duty map. It connects resin identity, exposure physics, print conversion, washing, post-cure, residual stress, geometry, interfaces and ageing to separate acceptance decisions. Public 3Dresyns pages are used only as manufacturer-declared candidate information, including their own validation limits; they are not treated as independent evidence. The result is an operational framework for deciding when a monolithic specialty resin is defensible, when functions should be split between materials or coatings, and when a conventional polymer, ceramic or metal route is the safer engineering choice.

Abstract

Vat-photopolymerized thermosets can provide fine geometry and unusual combinations of stiffness, heat resistance, chemical durability, flame retardancy, gas transport and electrical insulation. They also retain linked liabilities: cure gradients, residual reactive species, high crosslink density, brittleness, stress, anisotropic defects, solvent uptake, additive migration, permeation, surface leakage and continuing network evolution. This qualitative engineering review defines six distinct extreme-service functions and the evidence required to close each one. It separates glass transition, heat deflection, decomposition onset, thermal expansion, creep and thermal endurance; distinguishes reversible sorption from swelling, extraction, stress cracking and chemical reaction; separates ignition, flame spread, oxygen index, heat release, smoke and toxicity; and distinguishes intrinsic permeability from defects, seals and total component leakage. Electrical insulation is assessed after the same thermal, chemical and humidity exposures that define service. Primary studies on high-temperature photopolymers, post-cure, solvent compatibility, gas transport and flame-retardant stereolithography are treated as bounded demonstrations rather than transferable recipes. An applied case compares three routes for a compact heated chemical-analysis sensor manifold and electrical housing. The resulting decision logic rejects an unsupported all-in-one resin, provisionally retains a modular printed route, and preserves a conventional route whenever pressure, fire or endurance evidence cannot be closed. The qualifying object is the aged material–process–geometry–interface system in its declared service sequence, not a resin name or an isolated initial coupon.

Keywords: vat photopolymerization; specialty photopolymer; high temperature; glass transition; heat deflection; creep; chemical resistance; environmental stress cracking; flame retardancy; cone calorimetry; gas permeability; leak testing; electrical insulation; thermal endurance; dimensional stability; qualification

1. Purpose, scope and governing distinctions

This paper makes highly specialised photopolymer resins selectable as industrial component systems. It has nine objectives. First, it translates *extreme service* into an ordered duty sequence rather than a collection of material adjectives. Second, it distinguishes the thermal quantities that are commonly collapsed into one temperature rating. Third, it separates chemical uptake, diffusion, swelling, extraction, reaction and stress-assisted cracking. Fourth, it separates small-flame behaviour, oxygen index, heat release, smoke and toxic effluent. Fifth, it distinguishes gas permeability through sound material from leakage through defects, joints or seals. Sixth, it treats electrical insulation as an aged system response. Seventh, it identifies coupled formulation, printing and post-cure trade-offs. Eighth, it demonstrates the framework through a component-scale route decision. Ninth, it defines linked evidence and change control for production.

ISO/ASTM 52900 provides additive-manufacturing (AM) vocabulary and process categories [1]. ISO/ASTM 52920 addresses qualification principles for industrial AM processes and production sites [2], while ISO/ASTM 52927 connects main AM characteristics to corresponding test methods [3]. These standards establish language and production-system expectations. They do not make a supplier adjective, a neat-resin property or one nominal printer recipe transferable to a finished component.

Six distinctions govern the review. **Thermomechanical retention** asks whether modulus, strength, toughness, creep resistance, dimension and interfaces remain acceptable under the real temperature–load–time history. **Chemical durability** asks what enters, leaves or reacts

with the network and what function remains during and after exposure. **Fire behaviour** asks how a specified specimen or product responds to a defined ignition and heat-flux scenario. **Gas barrier** asks for permeant-specific transport through material; **leak tightness** asks whether gas passes through discontinuities or assembled interfaces. **Electrical insulation** asks whether leakage, dielectric loss, surface behaviour and breakdown margin remain acceptable after environmental conditioning. **Dimensional stability** is a cross-cutting outcome of cure, stress, expansion, sorption, creep and ageing, not a seventh independent material label.

The scope covers component-scale stereolithography (SLA), digital light processing (DLP), masked stereolithography or liquid-crystal-display (LCD/MSLA) routes, their washing and post-cure, and hybrid printed-coated-assembled solutions. It includes high-crosslink-density acrylate, methacrylate, epoxy-acrylate, urethane-acrylate, maleimide, cyanate-ester, polyimide-precursor and flame-retardant candidate networks where public evidence exists. It includes rigid, tough or elastomeric barrier concepts only where they support an extreme-service decision. It does not supply proprietary formulations or printer settings.

Concrete, cement, geopolymers, regolith, building-scale deposition and macroscopic high-volume construction are excluded. So are universal continuous-use temperatures, chemical lists, fire classifications, permeabilities, dielectric limits or lifetimes. Pressure-retaining, high-voltage, transport, aerospace, medical, food-contact and fire-safety applications require the relevant product standards, regulatory controls and competent authority beyond this material framework.

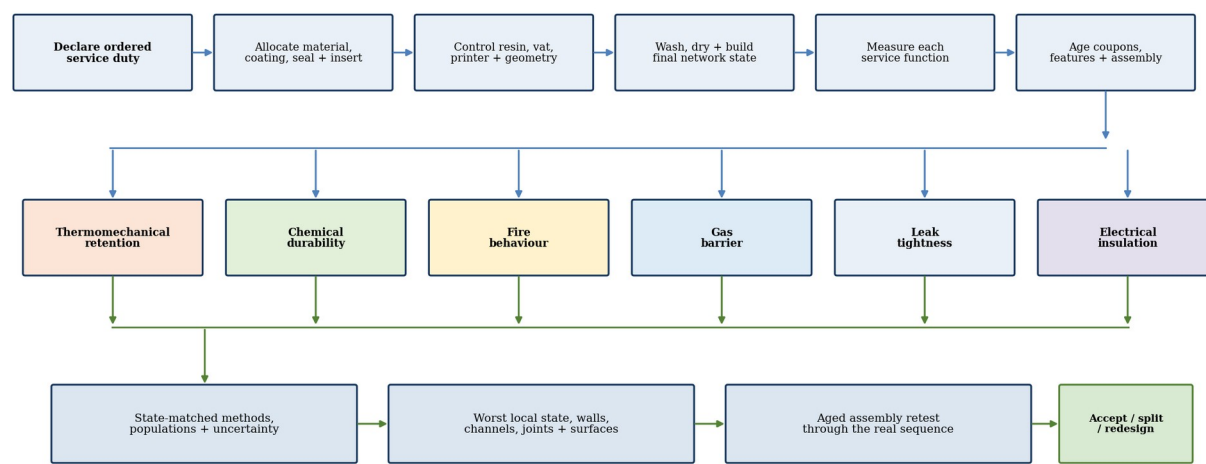
2. Define the complete duty before comparing resins

An extreme-service requirement is a time-ordered load case. It states the normal state, start-up, shutdown, cleaning, storage, transport, foreseeable upset and maintenance conditions. Each state records temperature, duration, heating and cooling rate, mechanical load, pressure or vacuum, chemical identity and concentration, humidity, radiation or light, electrical field, flame or heat-flux scenario, and dimensional or functional acceptance. A material that survives each stress separately can still fail when the sequence changes the network before the next stress arrives.

The correct decision boundary is the delivered component. A high glass-transition temperature measured on a uniformly post-cured bar does not establish the core state of a thick housing. A favourable immersion mass change does not qualify a stressed thread. A flame-test plaque does not represent a thin down-facing wall containing supports or a bonded joint. A gas-transmission film does not detect a trapped wash channel or a damaged seal. An electrical plaque tested dry does not represent a chemically contaminated creepage path.

Table 1. Six service functions and the evidence that closes each decision

Function	Required outputs	Conditions that remain attached	Component-level closure	Invalid substitution
Thermomechanical retention	Modulus, strength, toughness, creep, strain, distortion and failure time	Temperature-load-time sequence; orientation; thickness; post-cure; atmosphere; uncertainty	Loaded final geometry passes normal, transient and aged duty	Tg, HDT or TGA onset alone
Chemical durability	Uptake/loss, swelling, extraction, cracking, retained mechanics and chemistry	Chemical identity; concentration; mixture; temperature; stress; agitation; time; recovery	Critical surfaces, joints and witnesses retain function through the service sequence	"No visible change" or 24-hour mass change alone
Fire behaviour	Ignition, afterflame, dripping, oxygen index, heat release, smoke and residue as required	Method; specimen thickness/orientation; conditioning; heat flux; ignition; colour/additives	Required material and finished-product fire evidence at minimum qualified section	"Flame retardant", UL-style label or LOI alone
Gas barrier	Permeability, transmission rate, diffusion lag and sorption for each permeant	Gas; purity; pressure; humidity; temperature; thickness; area; state	Stable wall transport below owner-set limit after ageing	One gas, one film or one dry value for all gases and parts
Leak tightness	Total/local leak rate and path under pressure/vacuum sequence	Tracer; differential pressure; temperature; seals; joints; detector; calibration	Final assembly passes calibrated leak test before and after service cycles	Low permeability as proof of no leak
Electrical insulation	Resistivity, permittivity/loss, leakage, breakdown distribution and thermal endurance	Voltage/frequency; waveform; electrodes; thickness; temperature; humidity; contamination; ageing	Assembly retains guard-banded insulation margin after coupled exposures	Initial dry dielectric strength or "insulating" label



Extreme-service acceptance belongs to the aged material-process-geometry-interface system, not to a resin label.

Figure 1. State-resolved route from service duty to an accepted extreme-service component.

The chain is deliberately reversible. If a housing leaks after heat cycling, analysis proceeds from the detected path to seal compression, joint movement, local wall strain, cure gradient, porosity, support damage, resin state and material lot. If insulation resistance falls after a cleaning cycle, the investigation separates absorbed liquid, ionic residue, surface contamination, microcracking and electrode geometry before changing bulk chemistry. A failure is traced to the earliest causal state rather than hidden by a replacement label.

3. Polymer-network identity and the states that must not be conflated

The liquid resin is a reactive formulation, not the final material. Its identity includes oligomers or prepolymers, reactive diluents, photoinitiators, photosensitizers, inhibitors, absorbers, pigments, fillers, flame-retardant species, adhesion promoters, stabilizers and adventitious water or contamination. Lot, storage temperature, light exposure, container headspace, age, mixing, filtration, refill and vat history can change print response. Functional additives may also absorb or scatter the printing wavelength, alter viscosity, partition to a surface or modify network conversion.

At least ten states are separated. The **received state** is the material in its container. The **conditioned liquid state** follows mixing, warming, degassing or filtration. The **vat state** includes time, temperature, contamination, recovered resin and exposure history. The **green state** is the just-built network with residual liquid and spatially variable conversion. The **washed state** has experienced solvent extraction and possible swelling. The **dried state** has lost some but not necessarily all wash fluid. The **photo-post-cured state** reflects wavelength, irradiance, geometry and oxygen access. The **thermally post-cured or annealed state** may form additional network, relax stress, volatilize species or distort geometry. The **assembled state** adds coatings, seals, fasteners, adhesives, conductors and dissimilar thermal expansion. The **service-conditioned state** contains the accumulated thermal, chemical, humidity, fire-screening, pressure and electrical history.

Conversion is spatial. A thin transparent bar exposed from all sides can reach a different network state from the centre of a pigmented or filled wall, a blind channel or a shadowed interface. Conversion is also not a sufficient descriptor. Crosslink topology, dangling chains, unreacted species, phase separation, free volume, residual stress and physical ageing can differ at similar conversion. Sarkar and co-workers demonstrated that changes in curing history alter network structure and measured properties within one photopolymer system [34]. The transferable lesson is the need to control and measure cure history, not a universal optimum dose.

Two-stage networks make the state distinction explicit. Kuang et al. demonstrated a high-speed printing concept in which a first reaction forms the printable shape and a second cure develops final thermoset performance [32]. Fridman, Alvarez and Palmese demonstrated a sequential maleimide/cyanate-ester interpenetrating-network route in which the printed state and high-temperature post-cured state have deliberately different network roles [30]. Such architectures can widen the process–property window, but they also create new obligations: second-reaction conversion, exotherm, volatilization, temperature uniformity, dimensional change and incomplete core transformation must be verified.

4. Thermal performance: six temperatures, no universal rating

Glass-transition temperature (T_g) marks a method-dependent region in which amorphous molecular mobility changes; it is not a single invariant service limit. ISO 11357-2 specifies differential-scanning-calorimetry determination of T_g [4], while ISO 6721-11 addresses dynamic mechanical analysis [5]. Onset, midpoint, heat-capacity step, storage-modulus drop, loss-modulus peak and tan-delta peak can produce different reported values. Frequency, heating rate, prior cure, moisture, specimen direction and thermal history remain part of the result.

Heat-deflection temperature (HDT) is the temperature at which a specified flexural deflection occurs under a specified stress and heating procedure. ISO 75-1 provides general test-method principles [6]. HDT is useful for comparing a defined specimen state, but it is neither a

no-load glass-transition temperature nor a long-term loaded-use temperature. A high-HDT brittle material can crack under thermal shock, notch stress or assembly preload before flexural deflection controls.

Thermomechanical analysis measures dimensional response. ISO 11359-2 covers coefficient of linear thermal expansion and T_g by thermomechanical analysis [7]. Expansion below and above transition, cure shrinkage, stress relaxation and anisotropy all affect seals and precision features. A small mean coefficient does not prevent warpage when cure or temperature is spatially nonuniform. Dissimilar inserts and coatings create interfacial shear even if each individual material is stable.

Thermogravimetry characterizes mass change under a controlled atmosphere and heating programme; ISO 11358-1 provides general principles [8]. An onset of mass loss is not an allowable service temperature. Mechanical relaxation, oxidation, embrittlement, outgassing, colour change or insulation loss can occur well before a selected mass-loss threshold. Conversely, a short dynamic TGA ramp does not reproduce months of oxygen diffusion and stress.

Creep and stress relaxation often govern extreme-service thermosets. The relevant question is not whether the specimen stays below T_g but whether time-dependent strain, seal load, fastener preload and local contact pressure remain acceptable. A high initial modulus can coexist with poor long-duration stability near a broad transition. Krizma and Suplicz measured temperature-dependent dynamic and creep behaviour of two commercial vat-photopolymer resins and then tested printed mould inserts [33]. Their route-specific result showed why a headline high-temperature label did not predict which insert deformed less or which one cracked under the tested moulding cycle.

Thermal endurance is a property-retention relationship over time, not the highest temperature survived briefly. IEC 60216-1 defines ageing procedures and evaluation principles for thermal endurance of electrical insulating materials and explicitly relies on an Arrhenius-type relationship only where the assumed mechanism remains valid [22]. Crossing a transition, changing oxidation regime, depleting stabilizer or opening cracks can invalidate extrapolation. A defensible programme selects functional endpoints, multiple temperatures, failure criteria and evidence that the degradation mechanism is stable.

The practical thermal record therefore includes at least: method-specific T_g values; storage modulus over the duty range; HDT at the stated stress; expansion and irreversible dimensional change; short- and long-duration creep; decomposition or volatilization evidence; thermal cycling; retained strength and toughness; seal or joint load; and functional response after ageing. No one number replaces that record.

5. High-temperature photopolymer strategies and their coupled losses

High-temperature performance can be pursued by increasing crosslink density, using rigid aromatic structures, introducing inorganic reinforcement, separating shape cure from property cure, or converting a precursor to a more thermally stable polymer. Each strategy shifts rather than removes constraints.

Increasing functionality and crosslink density can raise modulus and transition temperature while reducing strain-to-failure and fracture tolerance. The same dense network can reduce solvent swelling but increase cure stress and sensitivity to a notch. Low-viscosity reactive diluents can restore printability but may lower final thermal performance, volatilize during post-cure or increase shrinkage. A formulation must be judged across liquid handling, cure, transformation and service, not only at the final polymer.

Aromatic polyimide routes illustrate the transformation burden. Hegde et al. demonstrated mask-projection stereolithography of all-aromatic polyimides through a processable precursor route [31]. The work establishes that nominally nonprocessable high-performance chemistry can be shaped photolithographically. It does not make shrinkage, conversion, imidization, solvent removal, voiding, colour, dimensional fidelity or mechanical performance transferable. The transformed state and its geometry are the engineering object.

Sequential networks can decouple the rapid gel needed for printing from the high-temperature reaction needed for service. Fridman et al. reported maleimide/cyanate-ester systems whose high-temperature post-cure produced high reported T_g and improved toughness within their compositions and methods [30]. The study also exposes why the word *post-cure* is inadequate: staged temperatures, secondary-network conversion, mass change, density change and dimensional retention are material-specific process variables.

Reinforcement can raise low-temperature stiffness or reduce expansion while adding optical scattering, sedimentation, viscosity, interface defects and stress concentration. The best reinforced resin below one temperature may lose matrix stiffness sharply at a higher temperature. The Krizma–Suplicz mould study is an especially useful warning: application deformation and failure reflected temperature-dependent modulus, creep, load, heat transfer and geometry together [33]. Reinforcement did not create a universal ranking.

The public 3Dresyns HDT1 page declares very high HDT for one candidate resin but also warns that rigid high-HDT photopolymers can be fragile and short-lived at temperature, recommending machined polyimide or moulded polyamide-imide or other conventional polymers when durable high-HDT performance is needed [28]. This manufacturer-declared limitation is technically important. A supplier's own peak value should open an evidence request, not close a route decision.

A high-temperature route is rejected early when the required post-cure cannot be delivered uniformly; when the green part cannot survive handling; when shrinkage or distortion consumes tolerance; when residual stress or brittleness undermines the load case; when outgassing contaminates the system; or when ageing evidence cannot cover the declared temperature–time–atmosphere range. Conventional PAI, polyimide, PEEK-class thermoplastics, ceramics or metals remain valid comparators rather than failures of AM ambition.

6. Chemical resistance is a coupled transport–reaction–stress problem

A liquid or vapour can sorb into a polymer, diffuse through it, plasticize it, swell it, extract soluble species, react with the network, catalyse hydrolysis or oxidation, deposit ionic contamination, or attack a filler, coating, adhesive or seal. These mechanisms have different time signatures and reversibility. “Chemical resistant” is therefore incomplete without chemical identity, purity, concentration, mixture, temperature, pressure, phase, agitation, exposure time, mechanical stress and recovery protocol.

ISO 175 describes immersion methods for determining effects of liquid chemicals on plastics [9]. It supports controlled changes in mass, dimensions, appearance and properties under stated conditions. A short immersion result does not establish continuous flow, vapour exposure, diffusion through a wall, alternating chemicals, pressure, stress or multi-year service. ISO 62 separately addresses water absorption [12]; water uptake can affect dimension, Tg, dielectric behaviour and reaction even when no gross damage appears.

Solubility parameters and polarity can guide screening, but they do not replace experiment. Erokhin, Gordeev and Ananikov compared interactions of 3D-printed polymers with liquids and developed solvent-compatibility maps for their specific materials and conditions [35]. The result supports structured screening and shows that printing-generated layers and polymer–liquid interactions matter. It cannot be transferred to an unidentified commercial resin, longer exposure, higher temperature or a stressed component.

Chemical uptake follows both thermodynamic affinity and transport kinetics. A favourable early mass change can mean slow ingress rather than equilibrium resistance. A small net mass change can hide simultaneous solvent uptake and additive extraction. Drying back to original mass can hide irreversible network damage. The minimum record therefore separates wet mass, dry-back mass, dimensions, hardness or modulus, strength/toughness, surface and fracture microscopy, extractables or chemical analysis where relevant, and functional outputs such as leak rate or insulation.

Mixtures defeat one-solvent intuition. Water can change the affinity and mobility of an organic solvent. A cleaning sequence can extract a stabilizer before the process chemical arrives. Oxidant concentration can fall at the surface while reaction products accumulate. Vapour can condense in a cold feature. A pH value does not identify the acid, base, buffer, salt, oxidizing power or solvent activity. Compatibility matrices retain exact formulation and temperature rather than grouping all acids, alkalis, fuels or solvents.

The public 3Dresyns CR UHT page provides manufacturer-declared 24-hour mass-change values for a named chemical panel under an ISO 175 framing and states that final performance depends on design, printing, post-cure, time and environment [29]. Those declarations can prioritize an independent test matrix. They do not establish long-term retained mechanics, stressed-joint integrity, mixture resistance or service life. The HCR1 page similarly declares combined heat, chemical, moisture and insulation functions while labelling values as indicative and requiring user validation [25]. Combining claims increases the number of endpoints that must pass; it does not create evidence by multiplication.

7. Stress cracking, extraction, joints and internal surfaces

Environmental stress cracking (ESC) can occur when a chemical that produces little damage in an unstressed specimen accelerates cracking under tensile stress. ISO 22088-1 establishes general guidance for ESC testing, and ISO 22088-3 defines a bent-strip method [10,11]. The stress source may be an external load, interference fit, screw torque, snap feature, adhesive cure, seal compression, thermal-expansion mismatch or residual print/post-cure stress. A flat immersion coupon cannot close those conditions.

The chemical qualification set includes unstressed material, controlled stressed specimens, printed features and assembled joints. Printed notches, layer transitions, support scars, threads and blind corners are deliberate challenge locations. Stress should be measured or calculated rather than described as “under load”. Failure observations retain crack origin and orientation. A specimen that survives while unloaded but cracks under an application-relevant strain is chemically incompatible with that duty.

Extraction matters even when the part retains shape. Residual monomer, photoinitiator fragments, stabilizers, dyes, flame retardants or low-molecular-mass species can enter the process fluid. The same loss can create free volume, embrittlement or changed fire behaviour. The analytical target comes from the application and formulation risk assessment. A gravimetric result cannot identify what migrated.

Washing is the first chemical exposure and must be inside the product genealogy. Solvent identity, purity, water content, bath age, temperature, agitation, time, flow access and drying affect both surface cleanliness and network state. Overwashing can extract or swell; underwashing can leave conductive, reactive or combustible residue. A later process-chemical test is uninterpretable if the starting wash state is uncontrolled.

Internal channels are not external plaques. They can receive lower post-cure dose, retain wash solvent, accumulate condensed chemicals and experience different stress. A channel that cannot be cleaned, dried and verified is a design no-go unless a validated indirect strategy provides equivalent assurance. Coatings can improve chemical or barrier performance, but pinholes, edge coverage, adhesion, cure, thermal mismatch and repair become controlled functions. A coating specification without inspectable continuity is not a risk reduction.

Table 2. Minimum chemical-exposure matrix for a printed extreme-service component

Exposure state	Specimen or feature	Measurements before, during and after	Failure information preserved
Wash and dry	Thin/thick coupons, blind channel and supported surface	Mass, residual solvent, dimension, surface chemistry/cleanliness and conversion proxy	Swelling, incomplete exchange, extractables, trapped liquid and cure inhibition
Single chemical screening	Unstressed coupon at service concentration and temperature	Wet/dry mass, dimensions, appearance, modulus/strength and chemistry as needed	Uptake, extraction, reaction, softening and dry-back irreversibility
Stress-assisted exposure	Bent strip, notched bar, thread, seal land or loaded feature	Applied strain/stress, crack-initiation time, growth, retained load and fracture origin	ESC threshold, orientation, support scar and residual-stress interaction
Mixture and sequence	Coupon and representative feature through cleaning/service/upset order	Property trajectory after each step, not only final state	Synergy, stabilizer depletion, precipitation, carry-over and mechanism change
Vapour/condensation	Temperature-gradient feature or closed volume	Sorption, condensation location, dimensions, insulation and corrosion at inserts	Cold-spot accumulation, surface leakage and interface attack
Aged assembly	Coated/joined/sealed final geometry	Leak, seal load, dimensions, retained mechanics, insulation and functional output	Joint, pinhole, crack, delamination, fastener and internal-surface failure

8. Fire behaviour: method-specific evidence, not one “FR” value

Fire performance is a scenario-dependent response. Ignition, flame spread, afterflame, glowing, dripping, heat-release rate, total heat release, mass loss, smoke, corrosive effluent and toxicity answer different questions. A formulation can improve one and worsen another. Mineral or phosphorus-containing additives may promote char or alter gas-phase reactions while changing viscosity, cure depth, brittleness, smoke or residue. “Halogen-free” describes composition relative to a boundary; it does not prove low smoke, low toxicity or superior fire safety.

IEC 60695-11-10 specifies 50 W horizontal and vertical small-flame methods for comparing burning behaviour of defined solid or cellular specimens [16]. Its result is tied to specimen dimensions, conditioning, orientation and test procedure. ISO 4589-2 determines oxygen index at ambient temperature [17]. Oxygen index is useful for comparing a defined material state but does not reproduce a finished product’s ventilation, heat flux, enclosure, ignition source or geometry. ISO 5660-1 measures heat-release and smoke-production behaviour using the cone calorimeter [18]. These methods are complementary, not interchangeable.

Thickness is part of the result. A classification at a thick plaque cannot be assigned to the thinnest printed wall. Orientation and surface state can change melting, dripping and flame travel. Pigment, recycled resin, recovered vat material, post-cure, absorbed chemical and ageing can change burning. Printed porosity and layer interfaces can increase accessible area or create preferential paths. The qualification matrix uses the minimum wall, worst orientation and relevant conditioned states, with a laboratory competent for the selected standard.

Razzaq et al. demonstrated intrinsically flame-retardant phosphorus-containing shape-memory polymers manufactured by stereolithography and reported oxygen-index and vertical small-flame outcomes for their system [38]. Cai et al. demonstrated a bio-based photocurable flame-retardant resin for LCD printing and a functional triboelectric device [39]. These studies show credible chemical strategies and the possibility of combining printability with fire response. They do not establish performance for another resin, additive, printer, wall thickness, colour, aged state or product fire scenario.

The public 3Dresyns FR1 page declares a flame-resistant photopolymer candidate and states that fire performance depends on printer specifications and final application validation [26]. That page can initiate a defined test request. It cannot replace the test report, formulation/colour/version identity, specimen drawing, conditioning, raw observations, laboratory competence or finished-product assessment.

Fire retardancy is also a lifecycle and process-control issue. An additive that migrates, blooms, hydrolyses or is extracted may change performance over time. A covalently incorporated species can reduce migration but still alter network conversion or degradation products. Sanding and machining can generate additive-bearing dust. Fire testing produces hazardous smoke and decomposition products and belongs in controlled facilities, not routine print areas. The material safety data and task assessment govern handling independently of the desired fire classification.

A fire route is rejected when only a marketing class is available; when test thickness exceeds the intended minimum; when the required product standard is not addressed; when ageing or chemical exposure can remove the active species without retest; or when smoke, toxicity or heat release is decision-critical but unmeasured. Passing one small-flame screen is never described as a complete fire-safety approval.

9. Gas barrier, permeation, diffusion lag and leakage

Gas barrier is permeant-specific. In a homogeneous material, a common solution–diffusion description writes permeability P as the product of diffusivity D and solubility S . Under ideal steady conditions, flux scales approximately as $J = P \cdot \Delta p / l$, where Δp is the permeant partial-pressure difference and l is thickness. This relation is a screening model. P can vary with pressure, concentration, temperature, humidity, cure, free volume, crystallinity or network state; plasticization, dual-mode sorption, reaction and multicomponent transport can invalidate the simple assumptions.

ISO 15105-1 covers differential-pressure methods for gas-transmission rate in plastic film and sheeting [13]. ISO 15105-2 covers equal-pressure methods [14]. Their film boundary matters. A three-dimensional printed wall can contain cure gradients, layer-related voids, support damage, surface roughness and thickness variation. Film permeability can inform material selection only after specimen state, gas, pressure, humidity, temperature and thickness are mapped to the component decision.

Permeability is not leak rate. Permeation is molecular transport through nominally sound material. Leakage can pass through a crack, pore network, seal, threaded joint, bonded interface or unclosed support scar. ISO 20485 describes tracer-gas leak-testing techniques [15]. A component can use a low-permeability material and still leak badly through one defect; a deliberately gas-permeable membrane can be perfectly free of unintended leaks.

Fleck et al. characterized a gas-permeable, high-resolution PDMS-like resin for stereolithography [37]. That study is useful precisely because high permeability can be the intended function in one microfluidic component. Stovall et al. measured solvent permeability in printed acrylate elastomers and related transport to composition and polymer–solvent interaction [36]. Together they show that “barrier” is not a universal quality direction and that transport changes with chemistry and penetrant.

The public 3Dresyns NPGb1 page declares a non-polar gas-barrier candidate and one indicative hydrogen-permeability value under stated dry, 20 °C conditions; it also states that performance depends on geometry, wall thickness, humidity, processing and final cure [27]. That value remains a manufacturer declaration attached to its test state. It is not transferred to helium, nitrogen, mixed gases, elevated temperature, another thickness or an assembled seal. The page’s naming inconsistency between NPGb1 and NPCb1 is an additional reason to bind every purchase, certificate and test report to a controlled material identifier rather than a page heading alone.

Barrier testing should include initial transmission, time lag, steady state, desorption or recovery and repeat cycles where hysteresis is possible. Temperature and humidity are controlled on both sides. The gas composition and detection limit are stated. For multigas service,

each critical component or a justified mixture is tested because competitive sorption can change transport. For vacuum service, outgassing and permeation are separated from real leaks.

Component testing maps wall thickness and identifies joints. A calibrated tracer-gas test checks total assembly leakage before and after thermal, pressure, chemical and mechanical cycles. Local methods identify paths where required. A pressure-decay result is used only when volume, temperature, gas dissolution and instrument resolution make it sensitive enough. Passing a room-temperature leak test does not close hot leakage if expansion unloads the seal.

10. Electrical insulation after heat, humidity and chemicals

Electrical insulation is not the absence of a conductive filler. It is a system response governed by bulk and surface conduction, polarization loss, defects, geometry, voltage waveform, frequency, field enhancement, temperature, humidity, contamination and ageing. A resin can have high volume resistivity while a thin ionic film along a printed surface creates unacceptable leakage. A high dielectric strength measured during a short ramp can coexist with poor long-term endurance.

IEC 62631-2-1 covers relative permittivity and dissipation factor at technical frequencies from 0.1 Hz to 10 MHz [19]. IEC 62631-3-1 specifies a DC method for volume resistance and resistivity [20]. IEC 60243-1 addresses short-time electric strength at power frequencies [21]. These measurements answer different questions. Permittivity and loss influence capacitance and dielectric heating; resistivity addresses conduction under a defined field and time; breakdown is a statistical destructive outcome sensitive to electrodes, thickness and defects.

Temperature changes mobility and reaction rate. Humidity and absorbed chemicals can plasticize the network or transport ions. Flame-retardant additives, pigments and residual photoinitiator products can alter dielectric loss or conductivity. A chemical-resistant formulation is not automatically an electrical insulator after chemical exposure. The HCR1 public page declares combined chemical, heat and insulation functions but explicitly requires final validation [25]; independent testing must preserve that coupled boundary.

Geometry controls field. Sharp electrode edges, thin walls, trapped bubbles, layer interfaces, support scars, fastener holes and metallic inserts create local enhancement. Surface creepage paths depend on contour, contamination and condensation, not bulk thickness alone. Coatings and potting can improve the path while introducing adhesion, void and thermal-expansion risks. The electrical drawing therefore marks stressed volume, electrode geometry, creepage/clearance boundary and service contaminants.

The aged test sequence follows service order: cure and condition; establish initial resistivity, loss and breakdown population; expose to heat, humidity, chemicals and thermal cycling; measure leakage during exposure where relevant; recover under a stated protocol; and repeat electrical measurements. IEC 60216-1 provides a thermal-endurance framework when electrical or other properties are selected as the endpoint [22]. Extrapolation is rejected if degradation mechanism or transition changes across the test range.

An insulation claim closes only when the final assembly retains its margin under normal and foreseeable transient voltage, at the hottest and wettest relevant condition, after chemical and mechanical ageing, with measurement uncertainty and specimen variability. Regulatory insulation systems may require recognized materials, construction rules and certification that a standalone printed-resin study cannot supply.

11. Vat photopolymerization, washing and post-cure as functional processes

Specialty chemistry must first share a process window with the light engine. Absorbing aromatic groups, pigments, phosphorus species, stabilizers and fillers can compete with the photoinitiator or scatter light. Increasing additive concentration to improve fire or barrier behaviour can reduce cure depth, raise critical exposure, worsen lateral growth or increase sedimentation. Increasing reactive diluent to restore viscosity can reduce the final network property. The valid region is an overlap between liquid stability, optical working response, feature formation, separation/replenishment, washability, post-cure and final service performance.

Printer commands are not measured exposure. Wavelength label, exposure time and nominal intensity omit spectrum, spatial field, divergence, temperature, interface transmission and ageing. A formulation-dependent working curve is a system measurement, not a portable material constant. Thick and thin features may require incompatible doses. Overcure that closes a channel can also trap wash chemistry and create a later electrical or chemical failure.

The vat is a time-dependent reactor and reservoir. Recovered resin can contain exposed oligomer, cured debris, moisture, contaminants or changed additive distribution. Flame retardants or barrier modifiers can sediment or partition. A refill does not reset history. Release rules define mixing, temperature, hold time, filtration, top-up, maximum reuse, sampling and rejection. Sentinel functional tests are selected from causal sensitivity, not convenience.

Washing removes accessible surface resin but also exposes the green network to a penetrant. Bath concentration, saturation and temperature alter extraction. Blind cavities may retain both uncured resin and solvent. Drying time cannot be specified without geometry, solvent and detection. A mass plateau can help but may not prove a clean internal surface. The wash route is qualified with representative channels and worst-case orientations.

Post-cure develops property and can simultaneously consume tolerance. Light wavelength, irradiance, temperature, time, atmosphere, fixture, chamber position and load are controlled. For a two-stage resin, thermal schedule and reaction exotherm may be safety-critical. A longer or hotter cure is not automatically better: it can cause stress, oxidation, embrittlement, volatilization, yellowing or seal-land distortion. The final state is defined by bounded process variables and functional evidence, not the phrase “fully cured”.

Dimensional compensation is applied only to stable, causal bias. Software scaling cannot correct lot-varying conversion, asymmetric cure, changing residual stress or chemical swelling. Geometry is measured after every transformation that consumes tolerance and again after service conditioning. The dimensional datum is tied to temperature and humidity.

12. Multi-objective conflicts and the case for modular routes

The all-in-one extreme-service resin is an attractive but high-burden hypothesis. High crosslink density can improve Tg and reduce equilibrium sorption yet increase brittleness and cure stress. Flexible segments can improve impact tolerance and seal conformity while increasing permeation and creep. Flame-retardant additives can improve one combustion response while increasing viscosity, optical attenuation, moisture sensitivity, smoke or dielectric loss. Inorganic fillers can reduce expansion or permeability while creating interfaces, sedimentation and electrical field concentration.

The correct optimization target is not the largest property count on a datasheet. It is accepted service function per complete manufacturing cell, including failed builds, washing, post-cure, finishing, coatings, assembly, inspection, destructive qualification and ageing. A monolithic part can reduce joints but couple every function to one formulation and one process window. A modular design adds interfaces but allows each zone to use a more appropriate material, test and replacement strategy.

Modularity is not automatically superior. A coating can delaminate; a seal can relax; a conventional insert can concentrate stress; a joint can leak; and extra parts add tolerance and labour. The advantage exists only if functions become independently controllable and inspectable. The system-level test remains mandatory.

Table 3. Route options, credible advantages and decisive no-go gates

Route	Credible advantage	Coupled burdens	Decisive evidence	No-go condition
Monolithic specialty photopolymer	Fine integrated geometry, fewer joints and one build genealogy	One chemistry must close cure, heat, chemicals, fire, barrier, insulation, brittleness and ageing	Worst-section cure plus aged component tests for every claimed function	Any critical function relies only on a label, film, initial plaque or inaccessible internal state
Two-stage high-temperature network	Printing reaction separated from final property-forming reaction	Green handling, staged thermal cure, exotherm, volatilization, shrinkage and core conversion	Reaction-state mapping, thermal uniformity, dimension, creep, toughness and ageing	Secondary cure cannot be delivered or verified through final geometry
Filled or flame-retardant resin	Potentially lower expansion, altered fire response or barrier pathway	Viscosity, scattering, sedimentation, interfaces, stress concentration, smoke and property drift	Local composition, working window, minimum-thickness fire/transport tests and retained mechanics	Functional additive destroys print window or cannot remain homogeneous and stable
Printed body plus coating/seal/insert	Functions allocated to independently chosen zones; repair or replacement possible	Pinholes, edge coverage, adhesion, seal relaxation, joint leakage and thermal mismatch	Interface inspection, local and total leak, adhesion after cycling and assembled function	Coating continuity or joint condition cannot be inspected or qualified
Conventional high-performance polymer, ceramic or metal	Mature processing, temperature/pressure margin and established standards may dominate	Machining/tooling, mass, lead time and geometric limitations	Application-specific certified stock/process data and finished-part tests	AM geometry adds no verified value sufficient to justify its qualification burden

13. Measurement architecture, populations and uncertainty

Every result begins with a requirement, specimen drawing and state label. The drawing records orientation, layer or exposure relation, thickness, supported faces, internal surfaces, post-cure access, notches, electrodes, seals, coatings and datums. The state label records resin lot and vat history, build file, wash, dry, photo/thermal cure, conditioning and exposure sequence. Replicates span independent lots, builds and build positions rather than repeated readings on one specimen.

Thermal measurements use more than one technique when the decision requires it. DSC and DMA Tg values are named by method and evaluation point [4,5]. HDT retains stress and specimen condition [6]. TMA retains axis, preload and heating history [7]. TGA retains atmosphere, heating rate and selected onset definition [8]. Creep tests use application-relevant stress and temperature and report full time response rather than one endpoint. Thermal cycling measures both reversible motion and permanent set.

Chemical tests retain exact mixture preparation, concentration, temperature, volume-to-surface ratio, agitation, refresh, evaporation control and exposure order. Wet measurement time and dry-back protocol are fixed. Mechanical and dimensional endpoints are measured with guard bands. ESC specimens retain strain and surface orientation [10,11]. When internal surfaces govern, sacrificial or witness geometries reproduce optical and wash access; their correlation to the part is established rather than assumed.

Fire reports identify standard edition, laboratory, specimen thickness, orientation, conditioning, colour/formulation, print direction, support/finish and observations. A classification is not averaged across failed specimens. Cone-calorimetry data preserve heat flux, ignition, heat-release curve, total heat, smoke and residue. The selected endpoints correspond to the product hazard analysis; extra fire numbers do not compensate for a missing relevant scenario.

Gas-transport reports retain permeant, purity, humidity, partial pressures, temperature, thickness map, area, preconditioning, time lag, steady-state criterion and calibration [13,14]. Leak reports retain tracer, test pressure, temperature, background, detector sensitivity and reference-leak traceability [15]. Permeability and leak-rate units are never interchanged. The component record maps test paths to joints and walls.

Electrical reports retain electrode material and geometry, specimen thickness, conditioning, voltage waveform/ramp, frequency, time, surrounding medium and failure criterion [19–21]. Breakdown is summarized as a distribution with censored or abnormal failures handled transparently. Insulation resistance is recorded over electrification time. Surface and volume paths are separated when the fixture permits.

Measurement uncertainty includes calibration, repeatability, specimen preparation, thickness, temperature, humidity, load, timing, gas composition, pressure, electrical field, operator and between-lot/build variation. Acceptance uses a predeclared guard band. A value inside the uncertainty interval around a limit is not converted to a pass by rounding or selective repetition.

Statistical power follows the failure consequence and variability. A small research set can demonstrate a mechanism but rarely estimate a production tail. Qualification populations cover the intended process window and challenge its edges. Production monitoring uses variables causally connected to failure, such as resin viscosity at a defined history, optical working response, post-cure temperature field, mass-loss or conversion proxy, sentinel creep, wash residual, wall thickness, leak rate or insulation resistance.

14. Ageing, occupational safety and lifecycle boundaries

Ageing combines stressors in a justified order. Heat can accelerate oxidation and relax stress. Humidity can lower Tg or conductivity margin. Chemicals can extract a flame retardant or plasticize a seal. Pressure and thermal cycling can open a leak path. Voltage can drive ionic contamination. Ultraviolet light can continue cure or cause photo-oxidation. A factorial screen can identify interactions, but final qualification reproduces the credible service sequence rather than testing isolated coupons only.

ISO 4892-1 provides general guidance for laboratory light-source exposure of plastics [23]. Laboratory exposure supports comparative ageing but does not create a universal outdoor or indoor lifetime. Spectrum, irradiance, specimen temperature, moisture and recovery remain attached. Thermal acceleration under IEC 60216-1 similarly requires a defensible relation and stable degradation mechanism [22]. When accelerated conditions cross Tg, boil an absorbed liquid, change oxygen availability or create a different reaction, the extrapolation is rejected.

Failure endpoints are functional. A component can retain tensile strength and fail because a seal land creeps, a coating pinholes, insulation resistance falls, gas transmission rises or a fire-active species migrates. Measurements are taken at intervals sufficient to see trajectory and mechanism. Recovery after removing the stress is reported because reversible plasticization and irreversible reaction have different consequences.

The liquid resin, wash solvent, additives, dust and fire-test effluent receive task-specific hazard assessment. NIOSH's safe desktop vat-photopolymerization guidance describes controls for resin handling, printing, cleaning and post-processing [24]. It is a hazard-control resource, not a declaration that a particular industrial cell or formulation is safe. Supplier safety data, exposure assessment, ventilation verification, skin/eye protection, spill response, fire controls and waste classification remain formulation- and jurisdiction-specific.

Sanding, drilling or machining a cured specialty resin can release polymer and additive-bearing particles. Heating and fire testing can release decomposition products. Mixing flame retardants or fillers can create inhalable dust or contamination. Controls follow the hierarchy: eliminate unnecessary handling, use closed transfer and local containment, verify engineering controls, establish work practices, then select personal protective equipment. "Cured", "bio-based", "halogen-free" or "natural" is not a hazard exemption.

Lifecycle review includes shelf and vat waste, wash-fluid management, energy-intensive post-cure, rejected builds, destructive test burden, coating replacement, repair, separation of inserts, and disposal of additive-containing material. A longer-lived modular assembly can be preferable to a nominally recyclable resin that fails early; conversely, a coating that cannot be repaired or separated can increase waste. Environmental claims require a declared functional unit and evidence, not feedstock adjectives.

15. Applied example: heated chemical-analysis sensor manifold and electrical housing

15.1 Requirement and failure boundaries

The illustrative component is a compact manifold/housing for an industrial chemical-analysis sensor mounted beside a process skid. It routes a low-volume sample or purge stream, supports a replaceable sensing insert, carries insulated electrical terminals and closes against a serviceable seal. The owner defines normal and transient temperature, pressure/vacuum, gas composition, cleaning chemicals, humidity/condensation, voltage, required fire evidence, allowable dimensional drift, leak limit and service interval. No numerical value in this example is universal; the point is to show how the requirements become tests and route gates.

The critical failures are: creep or distortion that unloads the seal; chemical swelling or stress cracking at a threaded port; extractables that contaminate the measurement; permeation or a defect leak that changes sample composition; surface conduction after humid chemical exposure; ignition or unacceptable fire response at the minimum wall; and a post-cure gradient that leaves an internal channel in a different state from the external coupon. Pressure containment and electrical/fire compliance are treated as system responsibilities, not inferred from the material framework.

The output sheet contains: delivered state; duty sequence; critical surfaces and joints; candidate allocation of body, barrier, seal and insulation; mandatory transformations; invalidation gates; test methods; evidence gaps; surviving routes; and no-go rationale. This makes the selection reproducible and reviewable.

15.2 Candidate routes and invalidation gates

Route A is a monolithic printed body made from a nominal all-in-one high-temperature, chemical-resistant, flame-resistant, gas-barrier and insulating resin. It offers the fewest joints and the most integrated channels. It is rejected at screening unless one controlled formulation and printer/post-cure route supplies evidence for every function in the worst local state. A high Tg or HDT does not close creep; a 24-hour chemical mass change does not close stressed ports; a film permeability does not close leakage; a flame classification at another thickness does not close the housing; and dry insulation does not close contaminated service.

Route B uses a printed chemically resistant structural body, a separately qualified seal, and an inspectable barrier or protective coating only where the body cannot meet the permeation or chemical requirement. A recognized or conventionally produced electrical/fire enclosure surrounds the terminal zone if the product standard demands it. The printed body retains geometric value in the low-volume manifold, while fire and insulation claims are not forced onto every wetted surface. This route is provisionally retained if the coating can cover and be inspected at every critical path, seal compression remains stable after thermal/chemical cycles, and the complete assembly passes leak and electrical tests.

Route C uses a machined or moulded high-performance polymer, ceramic or metal manifold with a separately printed non-pressure bracket, flow guide or disposable sensing feature. It sacrifices some integration and may add machining or joining. It is the default when pressure/temperature margin, long thermal endurance, recognized fire construction or chemical history dominates and the printed body

offers no verified compensating advantage. The 3Dresyns HDT1 page's recommendation to consider conventional polyimide or PAI for durable high-temperature duty supports keeping this comparator open [28].

15.3 Evidence plan and provisional decision

The first gate maps the complete duty and removes unnecessary multifunctionality. The second gate prints witness walls, channels, seal lands and stressed-port features at the worst build positions. Cure and wash access are verified. The third gate measures thermal state, creep and dimensional change; chemical uptake/extraction and ESC; permeation and total leakage; initial and conditioned insulation; and method-specific fire response at the minimum section. The fourth gate ages assembled parts through the declared heat–chemical–pressure–humidity sequence and repeats leak, seal-load, dimension and electrical tests.

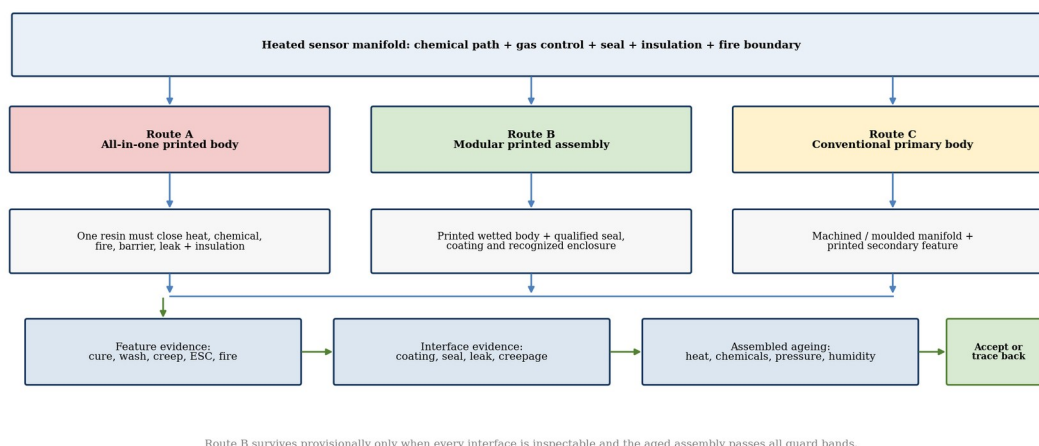


Figure 2. Route-selection logic for the heated manifold and electrical housing.

The provisional decision is Route B only when AM geometry materially improves the low-volume fluidic function and every interface is accessible to control. Route A remains a research hypothesis until combined evidence closes all functions. Route C is preferred whenever a recognized enclosure or conventional pressure/thermal material reduces total qualification burden more than integration reduces parts. This is not a product recommendation; it is the auditable result of the stated gate logic.

The example also demonstrates that a no-go is useful information. Rejecting an inaccessible coated channel before tooling, or moving the electrical/fire boundary to a recognized enclosure, can be more valuable than forcing one resin to carry every adjective. The framework rewards verified service performance, not material novelty.

16. Qualification genealogy and change control

A qualified extreme-service component links nine records. The **requirement record** contains the ordered duty, limits, failure consequences and guard bands. The **material record** identifies formulation/version, lot, safety data, storage and manufacturer declarations. The **vat record** captures conditioning, reuse, contamination and hold history. The **build record** captures printer, light engine, calibration, file, orientation, position, supports and thermal state. The **post-process record** captures drainage, wash, dry, support removal, photo/thermal cure and finishing. The **interface record** captures coating, seal, adhesive, fastener, conductor and conventional insert. The **exposure record** captures temperature, load, chemicals, humidity, gas, pressure, voltage and fire specimens in order. The **test record** preserves methods, raw data, uncertainty, failures and correlations. The **disposition record** links each accepted or rejected part to authorized evidence.

Table 4. Minimum linked records for extreme-service resin qualification

Record	Mandatory content	Release evidence	Change that reopens qualification
Requirement and duty	Normal/start-up/shutdown/cleaning/upset sequence; geometry; load; temperature; chemicals; gas; voltage; fire; limits	Approved duty map, comparator and guard bands	New chemical, temperature, duration, pressure, voltage, fire scenario, wall or lifetime
Material and liquid state	Controlled product/version, composition disclosure appropriate to risk, lot, age, storage, viscosity/optical response and safety data	Released lot and bounded manufacturer information	Supplier/formulation, pigment, flame-retardant or filler level, container, storage or age
Vat and build	Mixing, temperature, reuse/top-up, printer/light field, file, orientation, supports, position and deviations	Controlled build record plus representative process witnesses	Vat/window, light engine, firmware/slicer, layer, dose, orientation, support or reuse rule
Wash, dry and post-cure	Solvent/bath, flow/access, drying, spectrum, irradiance, temperature, time, fixture and load	Clean/dry geometry with state/conversion and dimension evidence	Solvent, bath age, equipment, cycle, cure source, thermal schedule, fixture or load density
Interfaces	Coating material/process, continuity, seal lot/compression, adhesive, fastener, insert and conductor geometry	Inspected interfaces with adhesion, seal-load, leak and electrical evidence	Coating/seal/adhesive/insert supplier, thickness, cure, joint design, torque or repair
Thermal and dimensional	DSC/DMA/TMA/HDT/TGA as relevant, creep, cycling, toughness and final dimensions	Method-resolved initial and aged retention at worst local state	Duty temperature/time/load, section, atmosphere, post-cure or acceptance method
Chemical and fire	Exact exposure sequence, ESC, extraction, minimum-thickness fire methods and conditioned variants	Retained function plus method-specific fire report	Chemical/mixture, cleaning order, stress, colour/additive, thickness, fire method or conditioning

Record	Mandatory content	Release evidence	Change that reopens qualification
Barrier, leak and insulation	Gas transmission, local/total leak, resistivity/loss/breakdown, humidity and contamination	Aged assembly passes transport, leak and electrical guard bands	Gas/humidity/pressure, seal, voltage/frequency, electrode, creepage path or test fixture
Disposition and monitoring	Raw data, uncertainty, failures, deviations, authorized limits, serialization and trend	Traceable accept/reject decision and monitoring plan	Statistical drift, unexplained failure, supplier/process change or evidence outside validated range

Change control follows causal variables. A pigment change can alter cure and fire response. A new photoinitiator lot can alter conversion and extractables. A cure-chamber lamp replacement can alter spectrum and depth uniformity. A coating-thickness change can alter barrier, dimension and stress. A cleaning-fluid substitution can alter swelling and insulation. No change is minor merely because the CAD and product name remain the same.

Equivalence requires evidence. A supplier letter, similar datasheet or matching mean value is insufficient when distributions, geometry or ageing can differ. The equivalence plan identifies affected mechanisms, selects sentinel and full tests, defines acceptance before testing and documents the authorized decision. Failed or ambiguous equivalence remains a new configuration.

Production monitoring is not a shortened qualification ritual. It uses sensitive causal controls and periodic functional verification. Trends in viscosity, working response, post-cure temperature, wash residual, wall thickness, sentinel creep, leak rate or insulation can warn before final failure. Control limits come from a capable validated process and remain distinct from engineering specification limits.

17. Discussion, route trade-offs and conclusions

Specialised photopolymers create genuine industrial opportunity. They can combine fine internal geometry with thermoset networks, local barriers, electrically insulating structures and fire-modified chemistry in production quantities too small for dedicated moulding. Two-stage cure and aromatic precursor routes expand the accessible chemical space. Primary literature demonstrates credible mechanisms for high-temperature networks [30–32], printed high-temperature tooling [33], solvent compatibility [35], penetrant transport [36,37] and flame-retardant stereolithography [38,39]. The evidence is substantial enough to justify engineering trials, but too state-specific to justify universal service labels.

The central trade-off is coupling. Properties that appear complementary on a selection page can be antagonistic in formulation and service. Crosslink density can improve Tg and reduce sorption while worsening brittleness and residual stress. Flexibility can protect a seal while increasing creep and gas transport. A flame-retardant species can influence cure, smoke, migration and insulation. A coating can create an excellent barrier but move risk to adhesion and pinholes. The best route is the one that makes these conflicts measurable and repairable.

Manufacturer information has a legitimate but bounded role. The HCR1, FR1, NPGb1, HDT1 and CR UHT pages identify candidate functions and, importantly, state processing or final-validation dependencies [25–29]. Their values and adjectives remain declarations tied to named versions and stated conditions. They are not independent qualification. The framework does not discount them; it converts them into precise verification questions.

Standards also have bounded roles. A standard method improves comparability only when its specimen, conditioning and measured quantity match the decision. Tg methods do not deliver service life. ISO 175 does not close every chemical sequence. Oxygen index, small-flame and cone-calorimeter tests are not interchangeable. Film gas transmission is not leak tightness. Electrical plaque tests do not close creepage and contamination in a housing. Method names therefore appear beside, not instead of, the service boundary.

Nine conclusions follow.

- **Extreme service is a sequence, not a label.** Normal operation, transients, cleaning, storage, maintenance and foreseeable upset must be ordered because one exposure can condition failure under the next.
- **No single thermal number is a continuous-use rating.** Tg, HDT, expansion, decomposition, creep and endurance describe different mechanisms and retain their methods, loads and times.
- **Chemical resistance requires both transport and retained function.** Uptake, extraction, swelling, reaction and ESC are separated, and dry-back mass cannot erase irreversible damage.
- **Fire evidence is method-, thickness- and state-specific.** Small-flame behaviour, oxygen index, heat release, smoke and toxicity answer different questions; one pass is not finished-product fire approval.
- **Permeability and leakage are different failure paths.** A permeant-specific material value cannot qualify cracks, interfaces or seals, and a leak-free assembly can intentionally contain a permeable membrane.
- **Electrical insulation is qualified after the environment.** Heat, humidity, chemicals, contamination, cure gradients and geometry can dominate over an initial dry plaque value.
- **Printing, washing and post-cure create the material.** Resin, light engine, vat history, geometry and transformation are one controlled system; “fully cured” is not a measurable state by itself.
- **Functional splitting is an engineering route, not a compromise.** A printed body, coating, seal and conventional enclosure may produce lower total risk than an unsupported all-in-one resin, provided their interfaces are qualified.
- **A conventional route remains an active comparator.** When pressure, temperature, fire recognition or long endurance dominate, polyimide/PAI, thermoplastics, ceramics or metals may offer lower qualification burden and higher confidence.

The framework is designed to expose unsupported assumptions before they are hidden behind *high temperature*, *chemical resistant*, *flame retardant*, *gas barrier*, *insulating* or a favourable isolated number. A specialised photopolymer route is technically credible only when the full geometry receives a controlled network state, every critical function has a matching method and population, interfaces remain observable, uncertainty fits the decision, and the aged assembly passes the declared service sequence.

References

- [1] ISO/ASTM 52900:2021. *Additive manufacturing - General principles - Fundamentals and vocabulary*. Edition 2; confirmed in 2025. <https://www.iso.org/standard/74514.html>
- [2] ISO/ASTM 52920:2023. *Additive manufacturing - Qualification principles - Requirements for industrial additive manufacturing processes and production sites*. Edition 1. <https://www.iso.org/standard/76911.html>
- [3] ISO/ASTM 52927:2024. *Additive manufacturing - General principles - Main characteristics and corresponding test methods*. Edition 1. <https://www.iso.org/standard/81802.html>
- [4] ISO 11357-2:2020. *Plastics - Differential scanning calorimetry (DSC) - Part 2: Determination of glass transition temperature and step height*. Edition 3; confirmed in 2025. <https://www.iso.org/standard/77310.html>
- [5] ISO 6721-11:2019. *Plastics - Determination of dynamic mechanical properties - Part 11: Glass transition temperature*. Edition 2; confirmed in 2024. <https://www.iso.org/standard/74988.html>
- [6] ISO 75-1:2020. *Plastics - Determination of temperature of deflection under load - Part 1: General test method*. Edition 4; confirmed in 2026. <https://www.iso.org/standard/77576.html>
- [7] ISO 11359-2:2021. *Plastics - Thermomechanical analysis (TMA) - Part 2: Determination of coefficient of linear thermal expansion and glass transition temperature*. Edition 2. <https://www.iso.org/standard/81835.html>
- [8] ISO 11358-1:2022. *Plastics - Thermogravimetry (TG) of polymers - Part 1: General principles*. Edition 2. <https://www.iso.org/standard/79999.html>
- [9] ISO 175:2010. *Plastics - Methods of test for the determination of the effects of immersion in liquid chemicals*. Edition 3; confirmed in 2026. <https://www.iso.org/standard/55483.html>
- [10] ISO 22088-1:2006. *Plastics - Determination of resistance to environmental stress cracking (ESC) - Part 1: General guidance*. Edition 1. <https://www.iso.org/standard/34861.html>
- [11] ISO 22088-3:2006. *Plastics - Determination of resistance to environmental stress cracking (ESC) - Part 3: Bent strip method*. Edition 1. <https://www.iso.org/standard/34874.html>
- [12] ISO 62:2008. *Plastics - Determination of water absorption*. Edition 3; confirmed in 2021. <https://www.iso.org/standard/41672.html>
- [13] ISO 15105-1:2007. *Plastics - Film and sheeting - Determination of gas-transmission rate - Part 1: Differential-pressure methods*. Edition 2; confirmed in 2020. <https://www.iso.org/standard/41677.html>
- [14] ISO 15105-2:2025. *Plastics film and sheeting - Determination of gas-transmission rate - Part 2: Equal-pressure method*. Edition 2. <https://www.iso.org/standard/91001.html>
- [15] ISO 20485:2017. *Non-destructive testing - Leak testing - Tracer gas method*. Edition 1; ISO catalogue stage 90.60 (close of review); the systematic review opened on 2022-10-15 and closed on 2023-03-05. <https://www.iso.org/standard/68190.html>
- [16] IEC 60695-11-10:2013, including Corrigendum 1:2014. *Fire hazard testing - Part 11-10: Test flames - 50 W horizontal and vertical flame test methods*. Edition 2.0; stability date 2028. <https://webstore.iec.ch/en/publication/2938>
- [17] ISO 4589-2:2017. *Plastics - Determination of burning behaviour by oxygen index - Part 2: Ambient-temperature test*. Edition 2; confirmed in 2022. <https://www.iso.org/standard/60786.html>
- [18] ISO 5660-1:2015, including Amendment 1:2019. *Reaction-to-fire tests - Heat release, smoke production and mass loss rate - Part 1: Heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement)*. Edition 3; confirmed in 2026. <https://www.iso.org/standard/57957.html>
- [19] IEC 62631-2-1:2018. *Dielectric and resistive properties of solid insulating materials - Part 2-1: Relative permittivity and dissipation factor - Technical frequencies (0.1 Hz to 10 MHz) - AC methods*. Edition 1.0. <https://webstore.iec.ch/en/publication/34510>
- [20] IEC 62631-3-1:2023. *Dielectric and resistive properties of solid insulating materials - Part 3-1: Determination of resistive properties (DC methods) - Volume resistance and volume resistivity - General method*. Edition 2.0. <https://webstore.iec.ch/en/publication/62314>
- [21] IEC 60243-1:2013. *Electric strength of insulating materials - Test methods - Part 1: Tests at power frequencies*. Edition 3.0; stability date 2029. <https://webstore.iec.ch/en/publication/1101>
- [22] IEC 60216-1:2025. *Electrical insulating materials - Thermal endurance properties - Part 1: Ageing procedures and evaluation of test results*. Edition 7.0. <https://webstore.iec.ch/en/publication/72550>
- [23] ISO 4892-1:2024. *Plastics - Methods of exposure to laboratory light sources - Part 1: General guidance and requirements*. Edition 4. <https://www.iso.org/standard/83801.html>
- [24] National Institute for Occupational Safety and Health. *Safe Desktop Vat Photopolymerization 3-D Printing*. DHHS (NIOSH) Publication, January 2025. <https://www.cdc.gov/niosh/media/pdfs/2025/01/Safe-3D-Printing.pdf>
- [25] 3Dresyns. *3Dresyn HeatChemRes HCRI is a Heat & Chemical Resistant 3D Resin with Excellent Insulating Properties*. Accessed 2 September 2026. <https://www.3dresyns.com/products/3dresyn-heatchemres-hcr1-is-a-heat-chemical-resistant-3d-resin-with-excellent-insulating-properties>
- [26] 3Dresyns. *3Dresyn FR1 Flame Resistant Rigid Resin (Fire & Flame Resistance)*. Accessed 2 September 2026. <https://www.3dresyns.com/products/3dresyn-fr1-for-fire-and-flame-resistance>
- [27] 3Dresyns. *3Dresyn NPGB1 Non-Polar Gas Barrier Resin*. Accessed 2 September 2026. <https://www.3dresyns.com/products/3dresyn-npgb1-is-our-non-polar-gas-barrier-resin>
- [28] 3Dresyns. *3Dresyn HDT1 for Ultra-High Deflection Temperature above 290 °C*. Accessed 2 September 2026. <https://www.3dresyns.com/products/3dresyn-hdt1-for-ultra-high-deflection-temperature-290-c>
- [29] 3Dresyns. *3Dresyn CR UHT Chemical Resistant Ultra Hard Resin (Acids & Mild Alkalis)*. Accessed 2 September 2026. <https://www.3dresyns.com/products/chemical-resistance-uhrt-ultra-hard-and-tough>
- [30] Fridman, A., Alvarez, N.J. and Palmese, G.R. *High-Tg Vat Photopolymerization Materials Based on In Situ Sequential Interpenetrating Polymer Networks of Maleimide and Cyanate Ester Monomers*. *Polymers* 17(23) (2025) 3179. <https://doi.org/10.3390/polym17233179>
- [31] Hegde, M., Meenakshisundaram, V., Chartrain, N., Sekhar, S., Tafti, D., Williams, C.B. and Long, T.E. *3D Printing All-Aromatic Polyimides Using Mask-Projection Stereolithography: Processing the Nonprocessable*. *Advanced Materials* 29 (2017) 1701240. <https://doi.org/10.1002/adma.201701240>
- [32] Kuang, X., Zhao, Z., Chen, K., Fang, D., Kang, G. and Qi, H.J. *High-Speed 3D Printing of High-Performance Thermosetting Polymers via Two-Stage Curing*. *Macromolecular Rapid Communications* 39 (2018) 1700809. <https://doi.org/10.1002/marc.201700809>
- [33] Krizma, S. and Suplicz, A. *Applying High-Performance Resins in Stereolithography Printing to Produce Prototype Injection Moulds*. *Scientific Reports* 15 (2025) 39652. <https://doi.org/10.1038/s41598-025-23249-8>
- [34] Sarkar, S., Lin-Gibson, S., Chan, E.P., Chiang, M.Y. and Baker, P.J. *Quantifying the Sensitivity of the Network Structure and Properties from Simultaneous Measurements during Photopolymerization*. *Soft Matter* 13(21) (2017) 3975-3983. <https://www.nist.gov/publications/quantifying-sensitivity-network-structure-and-properties-simultaneous-measurements>
- [35] Erokhin, K.S., Gordeev, E.G. and Ananikov, V.P. *Revealing Interactions of Layered Polymeric Materials at Solid-Liquid Interface for Building Solvent Compatibility Charts for 3D Printing Applications*. *Scientific Reports* 9 (2019) 20177. <https://doi.org/10.1038/s41598-019-56350-w>
- [36] Stovall, B.J., Rafalko, C.J., Cassidy, H.J., Zimudzi, T.J., Nyoni, H. and Hickner, M.A. *Permeability of 3D Printed Acrylate Rubbers*. *Journal of Applied Polymer Science* 142(18) (2025) e56814. <https://doi.org/10.1002/app.56814>
- [37] Fleck, E., Sunshine, A., DeNatale, E., Keck, C., McCann, A. and Potkay, J. *Advancing 3D-Printed Microfluidics: Characterization of a Gas-Permeable, High-Resolution PDMS Resin for Stereolithography*. *Micromachines* 12(10) (2021) 1266. <https://doi.org/10.3390/mi12101266>
- [38] Razaq, M.Y., Rupp, H., Balk, M. and Schadewald, A. *Stereolithographic 3D Printing of Intrinsically Flame-Retardant Shape-Memory Polymers*. *Advanced Materials Technologies* 10(3) (2025) 2400045. <https://doi.org/10.1002/admt.202400045>
- [39] Cai, Z., Chen, Y., Geng, S., Xiao, J., Chen, T., Fei, M., Qiu, R. and Liu, W. *Photocurable 3D Printing of Flame-Retardant Bio-Based Polymers for Customized Triboelectric Nanogenerators*. *Communications Materials* 7 (2026) 14. <https://doi.org/10.1038/s43246-025-01028-2>