

Environmental Ageing and Property Retention in Vat Photopolymerisation: Resin Storage, Photooxidation, Hydrothermal Conditioning and State-Resolved Qualification

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Statement of Significance

A vat-photopolymerised part does not possess one permanent set of properties. Resin storage, printing, washing, post-curing, dry relaxation, moisture uptake, thermal exposure and light-oxygen ageing can each move the material to a different chemical and mechanical state. This review establishes a state-resolved qualification architecture that separates reversible conditioning from irreversible degradation, initial post-cure development from service ageing, and accelerated screening from a validated lifetime claim.

Keywords: vat photopolymerisation; environmental ageing; resin storage; physical ageing; photooxidation; photoyellowing; water sorption; hydrothermal conditioning; post-cure; accelerated weathering; property retention; recovery; service-life qualification

Abstract

Vat photopolymerisation converts a liquid formulation into a network whose measured properties continue to depend on time and environment after printing. The starting resin may age during storage; the green print may undergo additional reaction during washing and post-curing; the solid network may physically relax; water may reversibly plasticise the material or irreversibly promote hydrolysis, leaching and interfacial damage; and ultraviolet-visible exposure in oxygen can change chromophores, colour, surface chemistry and mechanics. These processes are frequently collapsed into broad claims such as stable, UV-resistant, non-yellowing or durable. The resulting data can be misleading when the initial material state, exposure boundary and recovery step are not declared. This review separates five states: stored resin, green print, post-cured baseline, environmentally aged specimen and recovered or reconditioned specimen. Direct VPP evidence shows that storage-aged resin can change realised geometry and mechanics even when bulk viscosity changes little; post-cure can improve stiffness while introducing shrinkage; dry physical ageing can increase modulus; water immersion can reduce stiffness without measurable surface hydrolysis; elevated-temperature hydrothermal exposure can produce severe cracking and mechanical loss; and wet-dry cycling can yield a different endpoint from continuous immersion. Weathering studies further show that photoinitiator chemistry, stabilisation, post-cure history and resin class control whether optical and mechanical degradation evolve together. The proposed framework requires an exact resin and process identity, a frozen initial condition, fully specified spectrum-dose-temperature-humidity history, state-resolved dimensional, optical, chemical and mechanical measurements, and an explicit recovery step before irreversible degradation is assigned. Reporting aids are proposed for property retention, dimensional retention and post-ageing recovery, but raw values and complete curves remain mandatory. Existing ISO methods cover weathering, water absorption, chemical immersion, tensile testing, dynamic mechanical analysis and colour measurement; none by itself establishes a transferable VPP service life. The central principle is: exposure time is not material age unless the starting state, mechanism and recovery path are known.

1. Scope and evidence-selection method

ER-72 is restricted to temporal and environmental evolution of vat-photopolymerised materials and their precursor resins. It addresses pre-print resin storage, post-print state definition, physical ageing, water and humidity exposure, hydrothermal conditioning, photooxidation, colour drift, reversibility and property retention. It does not provide universal lifetime values, formulation recipes or an accelerated-test conversion from laboratory hours to service years.

The evidence base prioritises peer-reviewed studies that identify the printing route, material state, exposure condition and at least one measured chemical, optical, dimensional or mechanical consequence [1-10]. Studies are used at the level they support: a colour study does not establish mechanical durability; a water-uptake study does not prove hydrolysis; and a post-cure study defines the initial state rather than service ageing. Shared evidence-to-decision and disclosure rules for this series are defined in RP-02 [R1].

Manufacturer documentation is included only as implementation context. Product labels and additive positioning do not establish service life, standardised weathering performance, non-yellowing under every spectrum or retained properties after an unspecified exposure.

2. Ageing is a state transition, not a single property

The term ageing is used for several physically different processes. Some continue network formation. Some reduce free volume without changing covalent connectivity. Some introduce a penetrant that lowers effective glass-transition temperature and modulus. Others break chains, oxidise chromophores, extract soluble species or damage interfaces. The same measured direction can therefore arise from opposite mechanisms: modulus may increase through continued cure or physical ageing, but it may also appear to increase after selective loss of a soft fraction; mass may increase by water uptake while molecular weight decreases by hydrolysis.

Table 1. Mechanism classes that must be separated in VPP ageing studies

Mechanism class	Typical observation	Evidence needed before interpretation
Resin-storage evolution	Change in print threshold, geometry, green strength, colour, viscosity or sedimentation before exposure of the solid.	Storage time, temperature, atmosphere, container/light history, spectroscopy/rheology and re-calibrated print response.
Continued cure and post-cure	Higher conversion, modulus or strength; shrinkage; reduced extractables; altered colour.	Initial conversion, post-cure spectrum/dose/temperature, dimensional change and matched unpost-cured control.
Physical ageing	Modulus or yield stress rises while ductility or relaxation capacity changes, without clear chemical scission.	Time below T _g , thermal history, DMA/DSC, recovery above T _g or after annealing, and chemistry control.
Reversible sorption or plasticisation	Mass gain, swelling, lower modulus or T _g ; partial recovery after drying.	Equilibrium criterion, water activity/medium, temperature, uptake-desorption cycle and recovered-state measurement.
Hydrolysis, leaching or irreversible network damage	Persistent mass loss, cracks, molecular change, retained softening or loss of strength after recovery.	Dry-basis mass balance, spectroscopy/chromatography, recovered-state mechanics and sectioned inspection.
Photooxidation and photoyellowing	Colour shift, haze, surface oxidation, embrittlement or loss of optical transmission.	Declared spectral power distribution, irradiance/dose, oxygen, temperature, colour method and chemical/mechanical co-measurement.
Interface and filler ageing	Debonding, crack initiation, sedimentation legacy, opacity or non-uniform property loss.	Interface imaging, through-thickness mapping, particle/filler state and comparison with unfilled matrix.

A property change is not an ageing mechanism. The mechanism must be assigned from the complete state history and matched controls.

3. The five-state qualification sequence

A defensible ageing result begins before printing. ER-72 defines five states that should be recorded separately:

- State R: stored liquid resin, including batch, age, storage temperature, headspace, light exposure, mixing and sedimentation history.
- State G: green printed object after printing and the declared wash, but before the final post-cure or conditioning step.
- State 0: the frozen post-cured and conditioned baseline against which ageing is normalised.
- State A(t): the specimen at a declared point during or immediately after environmental exposure.
- State Rec(t): the same specimen after a declared recovery, drying, rehydration, rest or thermal reconditioning step.

State A and State Rec answer different questions. State A captures the material as used in a wet, hot or irradiated environment. State Rec asks whether the change persists when the penetrant or temporary thermal history is removed. Omitting the recovery state can convert reversible plasticisation into an incorrect degradation claim; measuring only the recovered state can hide loss of in-service stiffness or dimensional control.

State G is recorded separately because post-cure development is measured from it, not from the print event: a modulus or dimensional change attributed to service ageing can originate in an incomplete transition from State G to State 0.

4. Resin storage and pre-print ageing

Liquid-resin ageing can alter realised parts even when conventional incoming-inspection values appear acceptable. Hedayati and co-workers stored a VAM resin at 50 ± 1 °C for 6, 12 and 48 days and found that the realised printed cylinder diameter increased from 12.9 mm for the non-aged resin to 14.4 mm after 48 days; relative to the nominal 12.7 mm ASTM D695 geometry, the final dimensional error was about 13%. Printed tensile and compressive responses also evolved, whereas cast controls showed no significant compressive change [6]. The study is important because it treats storage history as a printing variable rather than assuming that nominal formulation identity is sufficient. The dimensional result is specific to volumetric AM, where dose accumulates through a rotating vial and a shifted inhibition threshold or penetration depth acts on the whole object. In layerwise VPP, the same chemistry would act mainly through per-layer cure depth, so the qualitative mechanism transfers but the numerical magnitude does not.

Possible drivers in other formulations include inhibitor consumption, photoinitiator or co-initiator change, oligomer association, moisture uptake, sedimentation, oxygen equilibration, optical drift and, where demonstrated, dark reaction. Reference [6] measured and excluded detectable dark polymerisation and molecular-weight change for its system; the authors instead discussed oxygen and inhibitor state and optical drift, which were inferred rather than quantified directly. A viscosity measurement alone cannot exclude these changes. The relevant incoming record should include at minimum spectral absorbance at the print wavelength, high- and low-shear rheology where applicable, density, visible phase state, sedimentation or redispersion behaviour, water content where relevant and a calibration artefact printed under a frozen optical protocol.

A stored resin that still prints is not necessarily equivalent to its fresh state. Recalibration may recover geometry but not restore green-body mechanics, cure uniformity, extractables or final ageing response. ER-72 therefore treats recalibration as a control action, not proof of unchanged material identity.

5. Post-cure defines the baseline and can confound ageing

Post-curing frequently increases conversion and stiffness, but it can also produce shrinkage, residual stress, colour change and geometry-dependent gradients. Menargues and co-workers showed resin-specific post-cure responses in four rigid-family VPP resins and one flexible resin: the rigid systems gained mechanical performance with a dimensional penalty, while the flexible system showed dimensional stabilisation attributed by the authors to stress relaxation, although stress relaxation was not measured directly, and only limited mechanical reinforcement [5]. The study varied post-cure time at fixed 405 nm and 60 ± 2 °C and did not report irradiance or radiant exposure. A post-cure schedule is therefore part of the specimen definition, not a generic finalisation step.

A later increase in modulus during storage can reflect incomplete initial post-cure rather than environmental durability. Conversely, an aggressive post-cure can create a highly converted but stressed initial network that cracks or embrittles more rapidly during subsequent thermal or hydrothermal exposure. Ageing comparisons are valid only when State 0 has the same post-cure spectrum, irradiance, time, temperature, fixture condition, specimen temperature and delay before testing.

Conversion and extractables are useful baseline measurements but do not fully identify the state. Two specimens with similar final conversion may have different network heterogeneity, residual stress, chromophore concentration, free volume and moisture content. ER-72 therefore requires State 0 to be characterised by the properties relevant to the intended ageing claim, not by conversion alone.

6. Dry physical ageing and continued network evolution

Below the glass-transition region, an amorphous network can relax toward a lower free-volume state. This physical ageing can raise modulus or yield stress and reduce molecular mobility without creating additional covalent bonds. Schwarz and co-workers reported that dry storage of a printed elastomeric polyurethane for eight months increased initial stiffness E_0 , measured as a secant over approximately 0-5% strain, by about 10%, whereas 24 h of water immersion at 22 °C in darkness reduced it by about 15% relative to the dry-aged state. In that study the water-induced transition was complete within about 24 h, while the dry arm was sampled only at approximately one week and at eight months and therefore cannot resolve the early dry time scale [2]. The authors discussed physical ageing and hydrogen bonding from adsorbed moisture as possible contributors without adjudicating between them. The direction of change depended on state rather than on a universal ageing trend.

Neither of the two dry-ageing studies cited here sampled the early period densely enough to establish when relaxation or continued cure occurs. At minimum, the test schedule should include an early time point capable of capturing rapid relaxation or continued cure, followed by logarithmically spaced longer intervals. The absence of an early resolved trajectory in the available evidence is itself an argument for including that point rather than inferring it from a later endpoint.

Physical ageing and continued cure can overlap. A practical separation strategy combines conversion or residual-reactivity measurement with DMA/DSC, dimensional tracking and a controlled annealing or thermal-recovery step. If an apparent modulus increase reverses after heating above the relevant relaxation range without a change in conversion, physical ageing is a plausible contributor. If conversion and network density continue to increase, post-cure incompleteness or dark reaction must be considered.

7. Water sorption, hydrothermal conditioning and reversibility

Water exposure introduces at least four coupled effects: mass uptake, plasticisation, swelling stress and chemical transport. It may also extract residual species, hydrolyse susceptible bonds or debond fillers and interfaces. The relevant endpoint depends strongly on whether the part is intended to operate wet, return to a dry state, or cycle between both.

In the elastomeric polyurethane studied by Schwarz et al., 24 h of water immersion at 22 °C in darkness reduced initial stiffness relative to the dry-aged state but did not significantly alter failure strength or stretch, and FTIR did not indicate significant surface hydrolysis [2]. The conservative interpretation is reversible or partly reversible water-induced plasticisation, not chemical degradation. By contrast, Nugraha et al. reported severe hydrothermal damage at elevated temperature. Immersion at 75 °C raised moisture content to roughly three times the dry-fresh level, and tensile strength fell by about 59% after only one day; at the mildest condition tested, 28.5 °C for 90 days, tensile strength and hardness fell by 55.6% and 7.8% respectively [3]. Cracking was observed after immersion at both 50 °C and 75 °C, and FTIR absorption bands became progressively less distinct after 75 °C exposure. These two studies illustrate why mass uptake alone is not a damage metric and why temperature can change the controlling mechanism.

Continuous immersion and wet-dry cycling are not interchangeable. Ariyo and co-workers found that the maximum loading tested, 15 wt% of a 1:1 maple/oak wood-flour blend with particle size not exceeding 177 µm, fell from 19.63 to 5.13 MPa after continuous water absorption, whereas cyclic wet-dry exposure produced a later tensile value of 14.94 MPa [4]. The two endpoints are not a clean comparison of exposure modes: the continuously immersed specimens were tested wet after 288 h at 21 °C, whereas the cyclic specimens were tested dry after 840 h of immersion and five 24 h drying steps at 60 °C. Most of the difference is therefore attributable to moisture state at the moment of test, and possibly to thermal post-cure during drying, rather than to cycling itself. A qualification programme must include both an immediate wet-state measurement and a declared recovered-state measurement and state which one a retained-property figure represents.

Equilibrium must be demonstrated rather than assumed from a fixed 24-hour period. Specimen thickness, surface finish, post-cure, porosity, filler content and temperature control the transport timescale. Where Fickian fitting is used, the fit range, geometry and goodness of fit must be reported. Non-Fickian uptake, cracking or property-dependent transport invalidates a simple diffusion coefficient as a complete description.

8. Photooxidation, weathering and optical-mechanical co-degradation

Weathering combines radiation, oxygen and temperature, often with humidity or wetting. Zareanshahraki and co-workers compared three black, non-stabilised VPP resins with different chemistries under five post-cure routes, and weathered the UV-post-cured parts under the ASTM D7869 exterior exposure protocol [1]. Electron-beam post-curing produced considerable additional cross-linking to the point of embrittlement even at low doses of 0.05 to 1 Mrad, with a significant drop in elongation at break above 0.5 Mrad. The study does not establish a universal best post-cure, and because only the UV-only route entered the weathering arm it does not itself test a post-cure-weathering interaction; it does show that post-cure response is chemistry-dependent, which is why post-cure and weathering history must be declared together.

Photoyellowing can arise from photoinitiator fragments, residual photoinitiator, oxidation products and changes in the cured network. In the author's own earlier work on UV-cured acrylate clear coatings, discoloration was linked to photoinitiator type across 24 commercial photoinitiators using controlled CMC(CIELab) colour-difference measurement [8]. Bassenheim and co-workers later compared two

methacrylate matrices with varied photoinitiator and stabiliser design and showed that colour stability during dark thermal and hydrolytic storage could also be maintained by the oxidising additive cumene hydroperoxide [7]. Together these studies support a chemistry-first interpretation: discoloration originates in formulation chemistry and dark ageing, so a weathering result cannot be predicted from radiant dose without knowing the photoinitiator system. Neither study applied a light-ageing exposure, so neither bounds the additional contribution of photooxidation.

Application studies reinforce the need for a defined metric. Wallach and co-workers applied ISO 4892-2 accelerated ageing to printed orthodontic materials and found changes in colour and translucency, while coffee, tea and red wine produced larger changes than the accelerated exposure [9]. Kaynak Öztürk and co-workers subjected a single SLA-printed permanent-crown resin to 10,000 thermal cycles between 5 and 55 °C and found that colour change depended strongly on the shade of the resin cement beneath the 1 mm specimen, with all groups exceeding the clinically accepted Delta E00 limit even before thermocycling [10]. The study illustrates that apparent colour drift can be dominated by an adjacent layer rather than by the polymer itself and does not establish material-to-material differences, since only one printed resin was tested. These studies establish exposure- and assembly-specific optical drift; they do not define a universal aesthetic threshold or prove corresponding mechanical degradation.

Optical and mechanical ageing should be measured together when either is used as a durability surrogate. A colour-stable material can still embrittle, and a mechanically retained material can yellow. Surface spectroscopy, colour, haze or transmission, mass, dimensions and mechanics should be mapped to the same specimens or to matched specimens from the same build and position.

Table 2. Representative evidence for state-dependent ageing in vat-photopolymerised systems

Study	Exposure and material state	Supported engineering conclusion
Zareanshahraki et al. [1]	Three VPP resin chemistries; five post-cure routes; ASTM D7869 weathering applied to the UV-post-cured specimens.	Post-cure response is chemistry-specific; EB cross-linking can embrittle, but the weathering arm did not compare post-cure routes.
Schwarz et al. [2]	Printed elastomeric polyurethane; water exposure and up to eight months dry storage.	Water softening and dry physical ageing can move initial stiffness in opposite directions; the rapid 24 h transition belongs to immersion, not dry ageing.
Nugraha et al. [3]	Bio-based printed photopolymer; dry ageing and 90-day immersion at 28.5, 50 and 75 °C.	Elevated-temperature hydrothermal exposure can produce cracking and major property loss; exact values and material state must remain condition-specific.
Ariyo et al. [4]	SLA composite with up to 15 wt% maple/oak wood flour; continuous immersion tested wet versus wet-dry cycling tested dry.	The endpoint difference is strongly confounded by moisture state and drying history; immediate wet and recovered states must both be reported.
Menargues et al. [5]	Rigid and flexible VPP resins under UV post-cure.	Post-cure sets the initial state and can trade mechanical gain against dimensional change; stress relaxation in the flexible resin was proposed, not measured directly.
Hedayati et al. [6]	VAM resin stored at 50 °C for 6-48 days, then printed.	Liquid-resin storage can change VAM dimensions and mechanics; the qualitative state-history lesson transfers, not the volumetric-AM magnitude.
Bassenheim et al. [7]	3D-photoprintable dental formulations with two methacrylate matrices and varied photoinitiator, stabiliser and oxidising-additive design under dark storage.	Colour stability is a formulation-system property; neither this study nor [8] bounds the additional contribution of light ageing.
Segurola et al. [8]	UV-cured clear coatings; controlled photoyellowing and colour measurement.	Photoinitiator chemistry and residual fragments can control discoloration.
Wallach et al. [9]	Printed orthodontic materials; ISO 4892-2 ageing and beverage exposure.	Beverage media produced larger optical changes than the accelerated exposure; one exposure does not represent all service media.

Study	Exposure and material state	Supported engineering conclusion
Kaynak Öztürk et al. [10]	One printed permanent-crown resin; four cement shades; 10,000 thermocycles between 5 and 55 °C.	Colour drift can be dominated by cement shade and assembly optics; a single-resin study cannot support material-to-material comparison.

9. Exposure design and the limits of acceleration

An accelerated exposure is useful only when it accelerates the same dominant mechanism as service. Higher temperature can move a polymer through T_g, increase oxygen or water transport, change equilibrium uptake, accelerate hydrolysis, volatilise species or activate dark cure. A single Arrhenius extrapolation is invalid when the mechanism or state changes across the temperature range.

For optical ageing, report the source type, spectral power distribution, irradiance at the specimen, radiant exposure, specimen or black-panel temperature, chamber air temperature, relative humidity, wet or condensation cycle, oxygen condition, mounting geometry and distance. Calendar time alone is not an exposure quantity. For hydrothermal ageing, report water or medium composition, pH, ionic strength, dissolved oxygen where relevant, specimen-to-liquid ratio, agitation, temperature, refresh schedule and equilibrium or endpoint criterion.

Acceleration should be demonstrated by mechanism equivalence. At minimum, compare chemical signatures, crack morphology and property ranking at more than one severity level. If elevated temperature produces a different oxidation product, uptake regime, crack path or failure mode, it should be treated as a separate screening condition rather than converted into service years.

The exposure sequence also matters. UV followed by water may not equal water followed by UV because one step can change permeability, chromophores or residual stress. Combined exposures should be tested directly when the intended use combines radiation, heat and moisture.

10. Geometry, build orientation and through-thickness gradients

Ageing rate is geometry-dependent. Thin specimens have short diffusion paths and high surface-to-volume ratio; thick parts may retain dry cores while their surfaces oxidise or swell. Lattices, channels and sharp corners amplify local exposure and stress. A coupon result is therefore transferable only when the relevant transport and stress scales are represented.

Build orientation can influence initial conversion, layer interfaces, surface roughness, pore pathways and crack direction. Ageing may magnify these differences by preferentially attacking low-conversion regions or interfaces. The minimum orientation record should specify the build direction, layer plane, loading direction, exposed surface and specimen location in the build. Sectioned spectroscopy, hardness or imaging is required when a surface-to-core gradient is plausible.

For filled or pigmented systems, scattering and absorption can create a cure-state gradient before ageing begins. Water or heat can then debond the filler-matrix interface, change refractive matching or initiate cracks. The unfilled matrix and a matched filled formulation are needed to separate network ageing from interface ageing.

11. Reversibility, recovery and irreversible damage

A recovery protocol should be designed around the intended service question. A wet-use device may need performance in the equilibrium-wet state, whereas a tool exposed briefly to solvent may be judged after recovery. ER-72 recommends reporting both whenever practical. Drying temperature, vacuum, humidity, rest time and endpoint must be frozen because aggressive drying can itself anneal, oxidise or further cure the network.

Irreversible degradation should not be assigned solely because the immediate aged property differs from State 0. Stronger evidence includes persistent loss after recovery, new chemical products, dry mass loss, chain scission, altered gel fraction, cracks or a non-recovering dimensional change. Conversely, complete property recovery does not prove that no chemical change occurred; compensating physical ageing or additional cure can mask damage. Chemical and mechanical evidence should therefore be interpreted together.

Recovery can also be property-specific. Modulus may return while elongation, fracture resistance, colour or dimensional stability remains altered. A single recovery percentage should never replace the full property vector and failure mode.

12. Proposed reporting descriptors

The following quantities are reporting aids, not standardised material constants. Raw values, uncertainty and complete curves remain mandatory.

12.1 Property-retention ratio

$$R_{age,P(t)} = P_A(t) / P_0$$

P_0 is the property at the frozen State 0 baseline and $P_A(t)$ is the property at the declared aged state. The property, test method, hydration state, temperature, rate, orientation and failure definition must be identical. Ratios above one are possible and do not automatically indicate improved durability; continued cure or physical ageing may be responsible. $R_{age,P}$ is the state-resolved environmental-ageing form of the broader property-retention convention $R_{P,n}$ used elsewhere in this series; the state and normalisation basis must always accompany the symbol.

12.2 Recovered-property ratio

$$R_{rec,P(t)} = P_{Rec}(t) / P_0$$

$P_{Rec}(t)$ is measured after the declared recovery protocol. Report $R_{age,P}$ and $R_{rec,P}$ together. A recovered ratio near one indicates restoration of that property only; it does not prove restoration of molecular structure, fracture resistance, colour or lifetime. $R_{rec,P}$ is a post-exposure reconditioning ratio normalised to the frozen State 0 baseline of this review. It is different from the rest-recovery ratio $R_{rec}(t)$ used in ER-67, which is normalised to an initial mechanical state within a loading sequence, and the two must not be compared or pooled.

12.3 Fraction of apparent change recovered

$$F_{rec,P(t)} = [P_{Rec}(t) - P_A(t)] / [P_0 - P_A(t)]$$

This fraction is meaningful only when the denominator is sufficiently different from zero and the direction of change is declared. Values outside 0-1 can occur through over-recovery, continued cure or additional damage. Use it only with the three raw values and uncertainty.

12.4 Mass, dimensional and optical change

$$\Delta m_{\text{dry}}(t) = [m_{\text{dry},t} - m_{\text{dry},0}] / m_{\text{dry},0} \quad R_{\text{dim},i}(t) = L_{i,t} / L_{i,0}$$

Wet mass gain and dry mass change answer different questions and should not be mixed. For a specimen that only loses dry mass, the removed fraction $f_{\text{sol}}(t)$ used in ER-74 is the sign-inverted form of $\Delta m_{\text{dry}}(t)$; this relationship does not hold when mass gain, deposition or incomplete recovery occurs. Dimensions should be reported by axis when swelling or shrinkage is anisotropic. Colour should use a declared CIELAB or CIEDE2000 method [S9,S10], with instrument geometry, illuminant, observer, background and surface condition stated. No universal ΔE acceptance value is asserted by ER-72.

12.5 Apparent diffusion parameters

An apparent diffusion coefficient may be reported only when the specimen geometry, boundary condition and uptake curve support the selected model. The fit interval, residuals and equilibrium assumption must be shown. Cracking, swelling-dependent transport, leaching or two-stage uptake invalidates a simple Fickian descriptor as a complete mechanism.

13. Minimum qualification architecture

Table 3. Minimum evidence architecture for an environmental-ageing or property-retention claim

Domain	Minimum record or measurement	Conclusion enabled
Material identity	Resin batch/version, age, storage history, colour/filler/additive state and relevant incoming checks.	Defines the precursor state and prevents silent formulation drift.
State G, green print	Printer, wavelength, irradiance, exposure, layer/orientation, vat history, calibration artefact, post-wash dry mass, green dimensions and any green-state property used later as a control.	Defines the realised green object and cure gradient, and fixes the condition from which post-cure development is measured.
State 0	Wash, post-cure, delay, temperature/humidity, conversion or cure-state evidence and baseline property vector.	Creates the only valid normalisation baseline.
Exposure	Spectrum or medium, dose/time, specimen temperature, humidity/wet cycle, oxygen, pH and geometry.	Defines the environmental load rather than calendar time alone.
Transport and mass	Wet and dry mass, equilibrium criterion, thickness and uptake/desorption history.	Separates sorption from persistent material loss.
Chemistry	Spectroscopy, chromatography, gel/sol fraction or other mechanism-relevant evidence.	Distinguishes plasticisation, oxidation, hydrolysis, leaching and continued cure.
Dimensions and optics	Axis-resolved dimensions; colour, haze or transmission under a declared method.	Captures function-relevant drift and gradients.
Mechanics	Application-relevant tension, compression, DMA, fracture or cyclic test at matched state and rate.	Quantifies retained function without substituting one property for another.
Recovery state	Declared drying/rest/rehydration/annealing protocol followed by repeated measurements.	Separates reversible conditioning from persistent change.
Acceptance and uncertainty	Predefined endpoint, replicate plan, confidence/uncertainty and failure-mode rule.	Supports a bounded engineering decision rather than retrospective threshold selection.

14. Failure modes and interpretation errors

Table 4. Common interpretation failures in VPP ageing qualification

Observation	Interpretation error	Required response
Stored resin still prints	Resin assumed chemically and functionally unchanged.	Recheck spectrum, rheology, calibration, green state and final properties.

Observation	Interpretation error	Required response
Modulus rises after storage	Called improved durability.	Separate continued cure and physical ageing; measure conversion, Tg and ductility.
Wet modulus falls	Called hydrolysis or degradation.	Measure recovery after drying and look for chemical change or dry mass loss.
Mass uptake is low	Material called hydrothermally stable.	Measure cracks, interface damage, Tg, dimensions and mechanics; small uptake can accompany large damage.
Colour remains stable	Mechanical and chemical stability inferred.	Measure oxidation and mechanical retention independently.
Colour changes	Mechanical failure assumed.	Treat optical drift as its own endpoint unless co-degradation is demonstrated.
High-temperature exposure accelerates change	Hours converted directly into service years.	Demonstrate mechanism equivalence and a valid acceleration model.
Coupon retains properties	Complex part lifetime inferred.	Address thickness, surface-to-volume ratio, orientation, stress and transport geometry.
Property recovers after drying	Original network state declared fully restored.	Check chemistry, fracture, colour and repeated-cycle response.
UV-protection additive used	Universal UV resistance or non-yellowing claimed.	Rebuild cure calibration and test the complete formulation under a declared weathering method.

15. Standards and method boundary

ISO 4892-2:2013 with Amendment 1:2021 defines xenon-arc exposure methods, while ISO 4892-3:2024 addresses fluorescent UV lamps [S1,S2]. ISO 4892-2:2013 is currently flagged for revision and must be restated at the time of any future test report. These standards define apparatus and exposure practice; they do not specify a VPP lifetime, a universal dose or an acceptance threshold. ISO 62:2008 addresses water absorption and requires care when non-Fickian behaviour or soluble loss occurs [S3]. ISO 175:2010 addresses immersion in liquid chemicals but does not by itself separate reversible sorption from network damage [S4].

Tensile properties should be measured under a declared current method such as ISO 527-1:2019 and, where appropriate to the specimen type, ISO 527-2:2025 [S5,S6]. ISO 527-1:2019 is currently flagged for revision, and the 2025 edition of ISO 527-2 renames specimen types 1A/1B as A1/A2, so historical data must state which edition and nomenclature apply. DMA and DSC provide complementary state information under ISO 6721-11:2019 and ISO 11357-2:2020 [S7,S8]. Colour coordinates and differences should be reported using the declared CIELAB and CIEDE2000 procedures in ISO/CIE 11664-4:2019 and ISO/CIE 11664-6:2022 [S9,S10].

No single published ISO or ASTM document qualifies environmental lifetime of a vat-photopolymerised material across resin storage, printing, post-cure, weathering, sorption, recovery and retained function. The nearest published polymer-part document, ISO/ASTM 52924:2023, is scoped to thermoplastics consolidated by powder-bed fusion or material extrusion in the as-built condition and therefore covers neither photopolymerisation nor post-exposure retention. A standards-based test remains an exposure or measurement method; service-life assignment still requires a product-specific mechanism, stress state, environment and acceptance case.

16. Scope boundaries within the Engineering Review series

ER-20 addresses Tg, HDT, DMA, decomposition and service-temperature interpretation. ER-72 uses temperature as an ageing variable and asks how properties evolve with time; it does not replace thermal-property qualification.

ER-32 addresses photopolymer storage, reuse and the open-vat state, including the same sealed high-temperature storage evidence used here. ER-32 owns the vat-management question - light leakage, oxygen ingress, contamination, evaporation, selective depletion and repeated printing from an open vat - as test requirements. ER-72 uses stored-resin evidence only to define State R as the precursor condition of an ageing claim and does not qualify vat reuse or open-vat operation.

ER-31 addresses cure shrinkage, residual stress and warpage generated during manufacture. ER-72 includes those variables only as part of the State 0 baseline or as drivers of later cracking.

ER-33 addresses washing, drying, extraction and dimensional response during post-processing. ER-72 begins after the declared baseline has been established, except when post-processing history is the controlled initial-state variable.

ER-39 addresses fatigue, creep and time-dependent deformation under mechanical loading. ER-72 does not convert static environmental retention into fatigue life or long-term creep performance.

ER-41 addresses chemical resistance and solvent uptake under defined media. ER-72 focuses the time-state-recovery architecture across multiple environmental mechanisms and does not replace medium-specific chemical-resistance qualification.

ER-44 addresses photoabsorbing fillers, optical response and cure-depth control, and already defines optional colorimetry and xenon-exposure gates while explicitly disclaiming photochemical-ageing durability. ER-72 uses the same standard method families but applies them inside the state-resolved architecture, requiring optical drift to be co-measured with chemical, dimensional and mechanical endpoints on matched specimens. ER-72 does not infer print-depth performance from ageing colour data, and ER-44 does not establish durability from optical measurement.

ER-17 addresses life-cycle assessment and environmental interpretation. ER-72 reports material durability evidence and makes no claim that longer retention automatically reduces environmental impact.

ER-74 addresses cleavable and depolymerisable networks for triggered disassembly and recovery. ER-72 addresses unintentional or service-relevant evolution and does not classify controlled end-of-life cleavage as ageing.

ER-22 addresses ophthalmic photopolymer materials and sets the device-class requirement list for optical quality, surface, ageing and biocompatibility. ER-72 supplies the state-resolved ageing method that such a requirement list presupposes; neither infers the other's acceptance criteria.

17. 3Dresyns implementation boundary

3Dresyns offers clear and black UV-protection additives and a bio-based non-yellowing additive positioned for formulation-level optical-stability control [M1-M3]. 3Dresyns also lists an in-can stabiliser additive documented as increasing the long-term stability of resin in liquid form, from months to several years [M4]. These products are implementation variables, not independent evidence of a universal service lifetime, a standard weathering classification or retained mechanics after a particular exposure.

The UV-protection additives alter the spectral state of the complete resin, and their documentation states that overdosing slows printing speed and, for the clear grade, depth of cure [M1,M2]. The non-yellowing additive is documented as not affecting print speed [M3], which does not by itself establish that the cured-state optical and mechanical baseline is unchanged. Any use therefore requires a new wavelength-specific calibration, conversion check, dimensional validation and property baseline before ageing begins. A stabiliser that improves liquid shelf stability may also change induction time or cure kinetics and must not be described as extending printed-part lifetime without separate solid-state data.

The following expressions should not be used for a 3Dresyns formulation without formulation- and workflow-specific evidence:

- UV-proof or immune to photooxidation;
- non-yellowing under every light source, temperature or use environment;
- one-year or multi-year printed-part lifetime from an in-can shelf-life statement;
- hydrolytically stable from low short-term water absorption alone;
- weathering-qualified without a declared ISO/ASTM exposure and acceptance endpoint;
- unchanged after ageing when only one property was measured.
- outdoor durability without a declared exposure method and acceptance endpoint.

A future public ageing claim should identify the exact material version, printer, optical settings, post-cure, initial conditioning, specimen geometry, exposure method, recovery protocol, measured endpoints, uncertainty and tested duration. Manufacturer data remain first-party implementation evidence unless independently reproduced.

18. Design rules

- Freeze State 0 before beginning the ageing clock.
- Record liquid-resin age and storage history as part of material identity.
- Separate post-cure development from service ageing.
- Measure both immediate exposed state and recovered state whenever reversibility matters.
- Use dry-basis mass to distinguish uptake from persistent material loss.
- Pair optical, chemical, dimensional and mechanical measurements; no single surrogate is universal.
- Declare spectrum, dose, temperature, humidity, oxygen and medium composition, not exposure time alone.
- Do not use accelerated hours as service years without mechanism-equivalent validation.
- Represent the intended geometry, thickness, orientation and surface condition.
- Report trajectories and failure modes, not only first and last values.
- Recalibrate any formulation changed by stabilisers, UV absorbers, pigments or ageing modifiers.

19. Research priorities

The most urgent need is an interlaboratory state-definition protocol for VPP ageing. Studies should share a minimum State 0 record, use matched immediate and recovered measurements, and report chemistry and mechanics on the same exposure series. This would allow reversible sorption, physical ageing and irreversible degradation to be separated without assuming that one property represents the entire network.

A second need is liquid-resin ageing science. Shelf-life studies should connect molecular and optical evolution to realised cure depth, geometry, green-body mechanics, post-cure conversion and final ageing response. Conventional viscosity and visual inspection are not sufficient release tests for every resin class.

A third need is mechanism-aware acceleration. Multi-severity weathering and hydrothermal studies should test whether chemical products, transport regime and crack morphology remain constant before any Arrhenius or dose-based lifetime extrapolation is attempted. Geometry scaling and oxygen/water diffusion should be integrated into the model rather than treated as specimen scatter.

Finally, ageing data should be linked to application-specific function. Optical devices require transmission, haze, colour and surface quality; structural parts require fracture and fatigue evidence; wet devices require equilibrium-wet mechanics; and sacrificial or recyclable systems require a separate end-of-life state. A universal durability score would conceal these differences.

20. Conclusions

Environmental ageing in VPP is not one process and cannot be represented by one property. The same part may stiffen through physical ageing, soften through reversible water plasticisation, shrink through post-cure, yellow through photoinitiator chemistry, crack through hydrothermal damage or change geometry because the liquid resin aged before printing. These mechanisms can overlap and sometimes compensate in the measured endpoint.

The minimum defensible evidence chain is:

stored resin state -> printed green state -> frozen post-cured baseline -> declared exposure -> immediate aged state -> declared recovery state -> coupled chemical, optical, dimensional and mechanical interpretation

Existing standards provide valuable exposure and measurement methods, but no standard converts laboratory hours into a universal VPP service life. A claim should therefore remain bounded to the exact resin, process, State 0, specimen, environment, recovery protocol and measured function. The central engineering principle is: exposure time is not material age unless the starting state, mechanism and recovery path are known.

Limitations

This review is literature-based and does not introduce a new experimental dataset. The cited studies use different resin chemistries, printers, post-cures, specimen geometries, exposure methods and endpoints; numerical values are therefore not directly transferable. Several application studies use dental or composite materials and support method logic rather than universal acceptance limits. No universal acceleration factor, lifetime, colour threshold, retained-property threshold or preferred stabiliser is proposed. Standards and live manufacturer documentation were checked on 22 August 2026 and require re-verification if release is delayed.

Author contributions

Juan Segurola: conceptualisation, literature synthesis, engineering framework, writing and critical review.

Competing interests

The author is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. Manufacturer examples are segregated from peer-reviewed evidence and are not presented as independent validation of ageing, lifetime or environmental-durability claims. Reference [8] is the author's own earlier work, carried out at Manchester Metropolitan University before the founding of Resyner Technologies S.L.; it is cited as primary literature on photoinitiator-derived discoloration and is not presented as independent corroboration.

Data availability

No new experimental dataset was generated for this review. Scientific statements derive from the cited literature and standards; manufacturer examples derive from the cited public product documentation.

Company information

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Standards and series framework

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 - [S2] ISO 4892-3:2024. Plastics - Methods of exposure to laboratory light sources - Part 3: Fluorescent UV lamps. International Organization for Standardization. [Source](#).
 - [S3] ISO 62:2008. Plastics - Determination of water absorption. International Organization for Standardization. [Source](#).
 - [S4] ISO 175:2010. Plastics - Methods of test for the determination of the effects of immersion in liquid chemicals. International Organization for Standardization. [Source](#).
 - [S5] ISO 527-1:2019. Plastics - Determination of tensile properties - Part 1: General principles. International Organization for Standardization. [Source](#).
 - [S6] ISO 527-2:2025. Plastics - Determination of tensile properties - Part 2: Test conditions for moulding and extrusion plastics. International Organization for Standardization. [Source](#).
 - [S7] ISO 6721-11:2019. Plastics - Determination of dynamic mechanical properties - Part 11: Glass transition temperature. International Organization for Standardization. [Source](#).
 - [S8] ISO 11357-2:2020. Plastics - Differential scanning calorimetry (DSC) - Part 2: Determination of glass transition temperature and step height. International Organization for Standardization. [Source](#).
 - [S9] ISO/CIE 11664-4:2019. Colorimetry - Part 4: CIE 1976 L*a*b* colour space. International Organization for Standardization. [Source](#).
 - [S10] ISO/CIE 11664-6:2022. Colorimetry - Part 6: CIEDE2000 colour-difference formula. International Organization for Standardization. [Source](#).
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- Manufacturer documentation.** [M1] 3Dresyns. 3D-ADD UVP1, clear UV protection additive. [Source](#); [M2] 3Dresyns. 3D-ADD UVP2, black color UV protection additive. [Source](#); [M3] 3Dresyns. 3D-ADD NY1 Bio, non yellowing Bio based and Biocompatible additive. [Source](#); [M4] 3Dresyns. 3D-ADD STAB1, in can stabilizer additive of 3D resins. [Source](#). Public product documentation accessed 22 August 2026.