

Gas Barrier and Molecular Permeability in Vat-Printed Photopolymers: Diffusion, Sorption, Network State, Defects and Qualification

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Statement of Significance

Gas-barrier performance in a vat-printed photopolymer cannot be inferred from hydrophobicity, hardness, low water uptake or a successful pressure test. Molecular transport through a dense cured network is governed by the coupled sorption and diffusion of a defined penetrant, while real printed parts add thickness variation, incomplete conversion, layer interfaces, pores, pinholes, seals and post-processing history. Conversely, deliberately permeable photopolymers exploit high gas solubility, flexible network free volume, microporosity or functional fillers. This review separates dense-network permeation from leakage and porous flow, and proposes a qualification architecture for gas-transmission and permeability claims in VPP parts.

Keywords: vat photopolymerisation; gas permeability; gas barrier; gas transmission rate; permeance; diffusion; sorption; solution-diffusion; network state; free volume; crosslink density; hydrogen; oxygen; carbon dioxide; defects; membranes; qualification

Abstract

Vat photopolymerisation can fabricate both gas-permeable and gas-barrier polymer structures, but the underlying transport mechanisms and measurement quantities are often conflated. For dense homogeneous polymers, permeability reflects the combined ability of a penetrant to sorb into and diffuse through the network. Printed parts introduce additional pathways and state variables: conversion gradients, post-cure, residual species, water uptake, layer interfaces, shrinkage, voids, thickness and surface sealing. Direct VPP literature demonstrates highly gas-permeable printed PDMS-like networks, DLP-printed mixed-matrix membranes for H₂/CO₂ separation, and DLP-printed ionic-liquid-containing membranes with gas-specific permeability. Other VPP studies demonstrate tunable pressure-driven permeability through intentionally porous phase-separated membranes; those data are not equivalent to molecular gas permeability in dense barriers. This review defines the distinctions between gas transmission rate, permeance, permeability, leakage and porous flow; maps chemistry, network state and defect structure to expected transport behaviour; and proposes a minimum reporting and qualification framework. ISO 15105-1:2007, the developing ISO/DIS 15105-1 and ISO 15105-2:2025, together with ASTM D1434-23, provide method anchors for films and sheeting but do not by themselves validate a complete three-dimensional VPP article. 3Dresyn NPGB1 and 3D-ADD SAP1/SAP2 are included only as controlled manufacturer implementation examples spanning opposite transport-design directions.

1. Scope and evidence boundary

ER-54 addresses transport of gases through the cured photopolymer phase and through defects or designed porosity in VPP-fabricated specimens and parts. The central question is not simply whether a part “holds

pressure”, but which transport pathway controls the observed gas transfer under defined pressure, temperature, humidity, thickness, cure state and geometry.

The review is intentionally narrower than general chemical resistance, solvent uptake or microfluidic qualification. ER-41 controls immersion-driven chemical resistance and solvent uptake; ER-12 controls organ-on-chip material qualification; ER-30 controls oxygen transport only where it affects inhibition during printing; ER-72 controls environmental ageing; ER-86 (in preparation) controls extractables and leachables. ER-54 uses those variables only when they alter gas transport through the final cured article.

ER-89 controls leak testing and seal qualification of finished fluidic components and assemblies. ER-54 is restricted to molecular permeability and related transport through the material state; pressure loss in a component is not automatically a molecular-permeability measurement, and a permeability coefficient does not establish leak-tightness of a finished assembly.

Manufacturer documentation is treated as implementation evidence only. Product-specific permeability entries are not generalized to other formulations, gases, thicknesses, printers, cure states or geometries.

2. Transport quantities that must not be conflated

Table 1. Gas-transport quantities and non-equivalences

Quantity / observation	Engineering meaning	What it does not establish
Gas transmission rate (GTR)	Steady-state amount of a specified gas transmitted through a declared specimen area and time under the method conditions.	Intrinsic material permeability unless thickness and method assumptions are appropriate.
Permeance	Transmission normalized by the driving pressure difference; it remains a specimen-level property.	Intrinsic homogeneous-material permeability when defects, multilayers or thickness uncertainty dominate.
Permeability	Thickness-normalized material transport coefficient for a homogeneous membrane under the declared gas, temperature, pressure and conditioning state.	Leak tightness of a finished 3D article or transfer to a different gas.
Leak rate	System-level gas loss through joints, pinholes, cracks, interfaces and/or bulk material.	Molecular permeability of the polymer phase.
Porous-flow permeability	Pressure-driven flow through connected pores or channels; Darcy-type behaviour may dominate.	Solution-diffusion transport through a dense polymer network.
Gas solubility / uptake	Amount of gas dissolved or absorbed in the material at a defined state.	Rate of transport through the material.
Selectivity	Relative transport of two species under a defined membrane and method.	Absolute barrier performance or mechanical integrity.

3. Dense-network transport: sorption and diffusion

For dense nonporous polymer membranes, the solution-diffusion framework separates two contributions. A gas first partitions into the polymer according to its thermodynamic affinity; it then migrates through transient free-volume elements created by molecular motion. Under the usual simplified assumptions, permeability is the product of a solubility contribution and a diffusivity contribution [1,2]. The decomposition is conceptually valuable because the same permeability can arise from very different combinations of gas affinity and molecular mobility.

Crosslinking generally constrains segmental mobility and can reduce accessible free volume, but the relationship is not a universal monotonic rule across chemistries. Polar groups can increase sorption for

condensable or interacting penetrants even while network densification decreases diffusivity. Elastomeric siloxane-rich networks can remain highly permeable because of their flexible backbone and free-volume characteristics. Therefore, chemistry labels such as “hydrophobic”, “silicone-like”, “highly crosslinked” or “monomer-free” are not substitutes for gas-specific measurement.

4. Direct VPP evidence: deliberately gas-permeable networks

4.1 Photocurable PDMS systems

Fleck et al. developed a DLP-SLA printable methacrylate-PDMS formulation and directly measured oxygen transfer through printed 100 μm films using a custom fixture [3]. The study established that high-resolution VPP and gas-permeable elastomeric behaviour can coexist, but the custom oxygen-transfer setup is not interchangeable with ISO 15105 or ASTM D1434 and should not be treated as a standardized permeability value.

A subsequent lower-viscosity PDMS formulation from the same group retained high-resolution DLP printability and reported gas permeabilities of 596 Barrer for O_2 and 3071 Barrer for CO_2 on 150 μm lv-PDMS membranes tested by a third-party laboratory according to ASTM D1434-82(R09)e1 [4]. Those values demonstrate the scale of gas transport achievable in a specific printed PDMS-derived network. They do not define a universal PDMS-like VPP range, because composition, conversion, extraction, membrane thickness, testing method and penetrant all matter.

4.2 Printed gas-separation membranes

Pustovarenko et al. formulated DLP-printable acrylate mixed-matrix membranes containing methacrylate-functionalised MIL-53(Al)- NH_2 and demonstrated H_2/CO_2 gas-separation behaviour [5]. Their work is particularly relevant to VPP because the filler was chemically integrated with the photocurable matrix; the study reports that the MOF-containing printed membrane increased permeability relative to the bare polymer at approximately constant selectivity. The same paper also notes that highly crosslinked DLP matrices can exhibit intrinsically low permeability and that poor filler-matrix interaction can introduce non-selective defects. Thus, a filler can alter both the intended molecular pathway and the unintended defect pathway.

Pulukkody et al. later demonstrated DLP printing of fluorinated poly(ionic liquid)-ionic liquid composite membranes and measured pure-gas permeability for HFC-32 and HFC-125 [6]. The more permeable gas differed because transport is gas-specific; the result supports the need to identify the penetrant rather than report a generic “gas permeability”.

5. Porous permeability is a different phenomenon

VPP can also manufacture intentionally porous membranes. Kirkebæk et al. used VPP combined with polymerisation-induced phase separation to tune porosity, pore size, hydrophobicity and pressure-driven membrane permeability by copolymer composition and micropatterning [7]. Their reported permeability is a liquid-flow membrane quantity in LMH/bar. It is scientifically useful for showing how VPP chemistry and architecture can control transport, but it is not equivalent to the molecular gas permeability of a dense film.

This distinction is essential for printed scaffolds, membranes and foams. If connected pores dominate transfer, the effective transport may be orders of magnitude larger than transport through the polymer phase and may depend primarily on pore size, tortuosity and pressure-driven flow. A barrier paper must therefore demonstrate that the measured specimen is sufficiently dense and defect-free for a bulk-polymer permeability interpretation to be valid.

6. Liquid sorption evidence as an adjacent constraint

Stovall et al. studied permeability of liquid solvents through vat-photopolymerised acrylate elastomers based on n-butyl acrylate and hydroxyethyl acrylate [8]. Increasing HEA content increased permeability of the tested solvents and increased water uptake; the magnitude of solvent permeability also depended on polymer-solvent interactions described using Hansen solubility parameters. These are liquid-permeability data, not gas-transmission data. Their value for ER-54 is mechanistic: network composition and penetrant affinity can materially change sorption and transport, so humidity or absorbed liquid can alter the state in which a gas-barrier specimen is tested.

7. VPP-specific state variables

Table 2. VPP variables that can change measured gas transport

Variable	Mechanistic route	Minimum control
Degree of conversion	Changes network connectivity, segmental mobility and residual reactive species.	Declare print exposure and post-cure; use conversion evidence when comparison depends on cure state.
Crosslink density / architecture	Changes chain mobility, free volume and swelling response.	Do not infer from hardness alone; report formulation/network descriptor and mechanical/thermal state where relevant.
Water uptake / humidity	Can plasticise polar networks, occupy sorption sites and change free volume.	Condition specimens and report relative humidity or dry-state protocol.
Thickness	Directly changes transmission and is required when converting specimen-level permeance to material permeability.	Measure actual thickness at multiple locations.
Layer orientation / interfaces	Can create anisotropic defect populations or interlayer transport pathways.	Test at least one orientation relevant to service; inspect for interlayer defects.
Shrinkage / residual stress	Can generate microcracks, edge lifting or stress-assisted leakage.	Inspect before/after conditioning; separate crack leakage from bulk permeation.
Washing / extraction	Removes residual species and may swell or restructure the network.	Record solvent, duration, temperature, drying and mass/dimension recovery.
Post-cure temperature/time	Can raise conversion or alter free volume and residual stress.	Treat post-cure as part of the material state, not a cosmetic step.
Fillers / phase separation	Can create selective transport pathways or non-selective interfacial voids.	Characterise dispersion/interface and verify defect-free morphology.
Surface coating / seal	Can dominate effective barrier response even if the printed bulk is permeable.	Report coating chemistry, thickness, coverage and separate coated/uncoated controls.

8. Defect transport and finished-part leakage

A dense-film permeability measurement and a finished-part leak test answer different questions. A printed vessel may lose gas through threaded fittings, bonded joints, support-removal scars, trapped uncured resin channels, layer defects or pinholes even when the bulk photopolymer has low molecular permeability. Conversely, a thin defect-free film may show measurable molecular permeation while a thick finished component passes a short-duration pressure-hold test.

For barrier applications, the test architecture should therefore use two linked tiers: a material/specimen tier that quantifies gas transmission or permeability, and a component tier that measures leakage or retained pressure in the actual geometry. Failure localisation should be attempted whenever a component fails. A

component leak rate should not be back-calculated into material permeability unless the transport area, path length and absence of discrete leaks are established.

9. Measurement architecture

Table 3. Minimum record for a defensible gas-permeability result

Layer	Required record	Reason
Material identity	Exact formulation/lot or controlled material ID; additives/fillers; storage history.	Defines what material was actually tested.
Print state	Printer/light source, layer thickness, orientation, exposure strategy, support/contact state.	Controls conversion and defect history.
Post-processing	Wash/extraction medium, time, drying, post-cure wavelength/dose/time/temperature.	Defines network and residual-species state.
Specimen geometry	Measured thickness map, exposed area, edge sealing, surface finish.	Required for permeance/permeability interpretation and leak exclusion.
Penetrant	Gas identity, purity/composition and, for mixtures, feed composition.	Transport is gas-specific.
Driving conditions	Upstream/downstream pressure or concentration, temperature and humidity.	Defines thermodynamic/kinetic test state.
Method	ISO/ASTM/in-house apparatus; sensor type; calibration; steady-state criterion.	Enables method comparability.
Reported quantity	GTR, permeance, permeability, time lag, selectivity or leak rate with units.	Prevents quantity conflation.
Defect control	Blank/leak test, replicate films, microscopy or integrity check where justified.	Separates molecular transport from pinhole/interface leakage.
Statistics	Replicates, central value, dispersion and uncertainty.	Defines reproducibility and confidence.

10. Standards: what they provide and what they do not

ISO 15105-1:2007 specifies differential-pressure methods for gas-transmission rate through plastic film and sheeting [S1]. It remains published, but ISO records show it at stage 90.92 and an ISO/DIS 15105-1 replacement is under development at enquiry close [S2]. A

recheck the status immediately before publication rather than presenting the 2007 edition as permanently current.

ISO 15105-2:2025 is the current equal-pressure method and was published in November 2025 [S3]. ASTM D1434-23 is active and uses a manometric approach to determine gas transmission rate, permeance and, for homogeneous materials, permeability [S4]. ASTM explicitly cautions that gas transmission is affected by moisture, plasticizer content and nonhomogeneities, and that the method does not address seals. Those cautions map directly onto VPP-specific concerns. The Fleck et al. [4] values discussed in §4.1 were measured under the historical ASTM D1434-82(R09)e1 method reported by that source; ASTM D1434-23 is the current edition and was not the method used in the 2023 study.

None of these standards, by itself, qualifies a complete printed pressure vessel, microfluidic device or hydrogen-containing component. They are film/sheet method anchors. Application release may require separate leak, pressure, burst, ageing, permeation, fire, chemical and regulatory testing depending on the service context.

11. Qualification matrix

Table 4. Qualification levels for VPP gas transport

Level	Evidence package	Permitted statement
A - screening	Defined specimen and gas; repeatable relative transmission or pressure-hold result.	Screening comparison only.
B - specimen permeation	Measured thickness/area, defined gas and state, calibrated method, replicate GTR/permeance.	Specimen-level gas-transmission statement under declared conditions.
C - material permeability	Level B plus homogeneous/defect-controlled specimen and justified thickness normalization.	Material permeability for the declared gas and state.
D - retained barrier	Level C repeated after relevant humidity, solvent, thermal, UV or pressure conditioning.	Retained permeability/barrier performance in the declared ageing window.
E - component qualification	Material evidence plus finished-part leak/pressure testing, joints/seals, geometry and service acceptance criteria.	Application-specific component qualification; no transfer beyond validated conditions.

12. Failure-mode and discrimination matrix

Table 5. Common observations and discriminating tests

Observation	Competing explanations	Discriminating evidence
High apparent gas transmission	High bulk permeability; pinholes; edge leakage; poor seal; thin region.	Repeat with new specimen; leak/blank test; thickness map; microscopy; alternate edge seal.
Pressure decays rapidly in vessel	Bulk permeation; fitting/joint leak; crack; support-removal defect.	Tracer/leak localisation; isolated material coupon; joint controls.
Barrier improves after longer post-cure	Higher conversion; reduced residual species; stress relaxation; incidental seal change.	Matched conversion/state data; same geometry/seal; replicate permeability test.
Barrier worsens at high humidity	Plasticisation; water-mediated sorption change; swelling-induced defects.	Dry/wet conditioning cycle; water uptake; thickness/dimension recovery; defect inspection.
Filler increases permeability unexpectedly	Selective pathway; interfacial free volume; non-selective voids; phase separation.	Morphology/interface characterisation; selectivity data; density/void assessment.
High O ₂ permeability but low CO ₂ or H ₂ trend differs	Gas-specific solubility/diffusivity balance.	Test each gas separately under matched conditions; avoid generic gas ranking.
Porous membrane shows huge permeability	Connected pore flow rather than dense-network solution-diffusion.	Pore-size/porosity data and pressure-flow scaling; report as porous membrane permeability, not dense-polymer gas permeability.

13. 3Dresyns implementation boundary

The controlled August 2026 3Dresyns TDS corpus contains both barrier-oriented and permeability-enhancing implementation routes. 3Dresyn NPGb1 is positioned as a non-polar gas-barrier SLA/DLP/LCD resin; its current controlled public technical documentation is TDS revision 1.3, August 2026 [M1]. That TDS includes a hydrogen-permeability entry referenced to ISO 15105-1. Because a product-specific number depends on specimen state, thickness and method execution, ER-54 does not use that single entry as evidence of generic barrier performance across geometries or gases.

3D-ADD SAP1 Bio and 3D-ADD SAP2 are positioned in the opposite design direction: manufacturer documentation describes them as additives for increasing fluid sorption, permeability, breathability and

microporosity in compatible 3Dresyns. Their current controlled public documentation is TDS revision 1.3, August 2026 [M2-M3]. They are included to illustrate that “permeability” may be an intended function rather than a defect; no quantitative gas-transport performance is inferred without gas-specific testing.

The 3Dresyns examples therefore define an implementation design space, not a scientific ranking. Any public product claim should name the gas or fluid, specimen geometry, cure/post-processing state, temperature, humidity, pressure conditions, method and reported quantity.

14. Research and standardisation priorities

- a VPP-specific round-robin comparing gas permeability of identical printed resins across printers and post-cure states;
- orientation-resolved transport studies to determine whether layer interfaces create meaningful anisotropy;
- paired density/microscopy/permeation methods that distinguish bulk solution-diffusion from microvoid leakage;
- conversion and free-volume mapping linked directly to gas permeability before and after post-cure;
- humidity-dependent H₂, O₂, CO₂ and water-vapour transport in representative acrylate, methacrylate and siloxane-rich VPP networks;
- ageing studies under solvent cleaning, hydrothermal exposure, UV and cyclic pressure;
- validated thin-wall and curved-specimen methods that represent actual printed vessels and channels;
- separate reporting conventions for GTR, permeance, permeability, porous flow and component leak rate;
- qualification of coatings and multilayers without falsely attributing their barrier response to the printed bulk;
- clear applicability rules for adapting ISO 15105 and ASTM D1434 to additively manufactured geometries.

15. Conclusions

Gas transport in vat-printed photopolymers is a coupled material-state and manufacturing problem. In a dense network, gas permeability reflects penetrant sorption and diffusion; in a real printed object, microvoids, layer defects, edges, seals and coatings may dominate the measured loss. In deliberately porous VPP membranes, pressure-driven pore flow is a separate transport regime and must not be reported as if it were dense-polymer permeability.

The VPP literature already demonstrates both extremes: highly gas-permeable printed PDMS-derived materials and DLP-printed functional membranes for gas separation, while highly crosslinked acrylate matrices can suppress permeability unless selective fillers or interfaces change the transport pathway. The data also show why gas identity matters: oxygen, carbon dioxide, hydrogen and fluorinated gases interact differently with a given polymer network.

A defensible barrier claim should therefore contain: exact material and cure state + measured specimen geometry + defined gas + pressure/temperature/humidity + named measurement method + correctly identified quantity + defect/leak control + replicate uncertainty + ageing where relevant. A finished-part qualification adds component-level leak and pressure evidence on top of the material measurement; it does not replace it.

Limitations

This review is a literature-based engineering synthesis and reports no new permeation experiments. Direct VPP gas-permeability literature remains much smaller than the broader membrane-science literature. Several retained studies concern purpose-designed membranes rather than bulk structural resins. Liquid-permeability and gas-uptake studies are used only where they clarify sorption/transport distinctions and are not

quantitatively transferred to gas barrier claims. ISO 15105-1:2007 is currently published but under revision; Its status was checked for this release.

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 documentation is included only as implementation context and is separated from independent scientific evidence.

Data availability

No new experimental dataset was generated for this review. Scientific statements derive from the cited literature and standards; manufacturer examples derive from controlled 3Dresyns documentation.

Company information

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Standards

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