

Silicone and Silicone-Like Elastomers in Vat Photopolymerisation: Polysiloxane Chemistry, Silicone-Free Functional Analogues, Thermal-Service Limits and Qualification

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Statement of Significance

Silicone is a chemical material-class term, whereas silicone-like is a bounded functional descriptor. Confusing them can transfer assumptions about thermal stability, low-temperature flexibility, compression set, permeability, fluid compatibility, weathering or biocompatibility without evidence. This review defines true silicone elastomers by a polysiloxane network, examines photochemical routes that make such networks compatible with vat photopolymerisation, and establishes a strict comparison framework for silicone-free photopolymers that reproduce selected tactile or mechanical functions. It also records the 3Dresyns composition boundary: its Silicone-Like products are declared silicone-free and are not direct silicone materials. Their generally lower temperature resistance must be qualified by exact grade and test state, not converted into an unsupported universal temperature limit.

Keywords: vat photopolymerisation; silicone elastomer; polysiloxane; poly(dimethylsiloxane); PDMS; silicone-like; silicone-free photopolymer; thiol-ene; dual cure; thermal-service limit; qualification.

Abstract

True silicone elastomers derive their material identity from crosslinked polysiloxane chains, most commonly poly(dimethylsiloxane), rather than from softness, Shore hardness or tactile feel alone. Vat photopolymerisation imposes low-viscosity, optical and rapid-gelation requirements that can conflict with the long flexible chains and reinforcing strategies used in conventional silicone rubber. Primary studies demonstrate several routes through this conflict, including thiol-ene crosslinking of vinyl- and thiol-functional polysiloxanes, simultaneous chain extension and crosslinking, sequential photo and thermal cure, and orthogonal silicone double networks. These routes prove that genuine silicone structures can be printed, but their reported properties remain formulation- and process-specific. Silicone-like photopolymers form a separate category: non-silicone networks may reproduce selected room-temperature functions such as softness, elastic deformation, shape recovery, tactile response or cushioning, yet functional overlap does not establish chemical identity or equivalence in heat resistance, compression set, tear propagation, permeability, fluid exposure, ageing or biological response. A defensible comparison must therefore proceed by declared function, controlled state and matched tests rather than by label. The proposed qualification stack combines chemistry verification, print-state control, tensile and tear response, time-dependent compression, cyclic durability, thermal ageing, fluid exposure and geometry-representative testing. Manufacturer statements are segregated from independent science. No proprietary formulation, product ranking, direct replacement claim or intended-use approval is provided.

1. Scope and boundaries

ER-102 owns the chemical-identity and transfer problem between true silicone elastomers and silicone-like vat photopolymers. It covers polysiloxane network chemistry, photochemical and staged-cure routes for printable silicones, VPP-specific processing constraints, the limits of functional analogy, thermal-service qualification and the evidence needed before a silicone replacement claim can be made.

ER-101 owns the generic mechanics of elastomeric and rubber-like photopolymers, including tear resistance, creep, stress relaxation, compression set and cyclic durability. ER-102 uses those quantities only to decide whether behaviour transfers across material classes. ER-39 owns the general fatigue and time-dependent-deformation gap; ER-68 to ER-70 own toughening, fatigue-crack growth and fracture toughness; ER-73 owns interlayer cohesion and anisotropy; and ER-90 owns frequency- and temperature-dependent damping [C1-C7].

The review does not disclose proprietary formulation, certify chemical composition, define a universal service temperature, rank commercial products or grant medical, food-contact, electrical, sealing or regulatory suitability. It does not treat every siloxane-containing hybrid as a silicone elastomer: the continuity and load-bearing role of the polysiloxane phase must be established.

2. Nomenclature gate: chemical identity before resemblance

Silicone elastomer denotes a crosslinked polymer in which siloxane chains form the relevant load-bearing network. PDMS is the most familiar example, with a flexible Si-O-Si backbone and methyl substituents. The low rotational barriers and high chain mobility associated with that backbone support very low glass-transition temperatures and broad elastomeric response, but exact properties depend on substituents, molar mass, crosslink density, filler, cure chemistry and ageing [1]. ISO 1629:2025 provides rubber nomenclature, and ISO 9924-3:2024 explicitly treats polysiloxane rubbers as a composition class for thermogravimetric analysis [S1,S2].

Silicone-like does not define a backbone. It can describe a non-silicone photopolymer that resembles a selected silicone grade in one or more bounded functions. Relevant examples include softness, indentation hardness, elastic recovery, conformal contact, damping, cushioning or tactile feel. Because different chemistries can occupy the same value on one metric, that resemblance must not be generalized beyond the measured function.

Term	Permitted interpretation	Interpretations that require separate evidence
Silicone elastomer	Crosslinked polysiloxane is a load-bearing network; cure route and composition are declared	Exact heat limit, purity, extractables, medical suitability and service life
Siloxane-containing hybrid	A formulation contains an identified siloxane component	That the continuous network is silicone or that silicone properties dominate
Silicone-like	Selected functional resemblance under stated conditions	Siloxane composition, direct replacement, thermal equivalence or chemical equivalence
Rubber-like / elastomeric	Large recoverable deformation on a stated timescale and temperature	Silicone identity, low set, high tear resistance or long fatigue life
Shore A value	Indentation response using the stated method and conditioning	Matched modulus, tear, compression set, permeability or thermal ageing

Table 1. Nomenclature gate. A permitted description supports only the stated identity or function.

3. Why true silicone is difficult to print by VPP

Conventional silicone performance often relies on high-molar-mass chains, reinforcing silica and cure packages designed for casting or moulding. VPP instead requires a resin that recoats, remains optically processable, gels rapidly enough to survive separation forces and develops adequate green strength. Raising chain length or filler loading can increase viscosity and light scattering. Lowering molar mass can improve flow but shorten network strands and reduce extension or toughness. Wallin et al. described this as a central printability-mechanics conflict and reported a useful SLA viscosity regime below about 5 Pa s for their system, not as a universal printer limit [1].

Low surface energy creates further process consequences. Wetting of the build window, recoating behaviour, resin adhesion, support interaction and bonding to dissimilar substrates can differ from common acrylate resins. Optical attenuation, inhibitor concentration, photoinitiator solubility and spectral overlap control cure depth. The green body must survive printing before any slower secondary reaction has developed final properties. A successful cure curve therefore does not alone prove interlayer continuity, extraction state or final mechanical stability.

4. Photochemical routes to genuine silicone networks

4.1 Thiol-ene crosslinking of functional polysiloxanes

Thiol-ene chemistry is a prominent route because vinyl- and thiol-functional polysiloxanes can react rapidly under light while retaining a siloxane backbone. Zhao et al. used branched mercaptan-functional polysiloxane with vinyl-terminated PDMS and reported tunable DLP-printed silicones with formulation-specific elongation up to 1400% [2]. Yu et al. introduced dithiol chain extension into a related light-curing system and, after silica reinforcement, reported 525.5 kPa tensile strength and 601% elongation for the tested formulation [5]. These numbers demonstrate chemical design options, not a transferable silicone envelope.

4.2 Simultaneous chain extension and crosslinking

Sirrine et al. combined dithiol and diacrylate-functional PDMS oligomers so that photoactivated reactions increased effective chain length while crosslinking the network. The study reported gel fractions above 90% and an approximately twofold increase in tensile strain at break relative to the equivalent photocured 5300 g mol⁻¹ PDMS diacrylamide control, reaching the modulus and strain at break of a photocured higher-molar-mass precursor while retaining low pre-print viscosity [3]. The principle is important: resin viscosity can be governed by lower-molar-mass precursors, while network strand length develops during exposure. Conversion heterogeneity and stoichiometric imbalance remain qualification risks.

4.3 Sequential, orthogonal and double-network cure

Wallin et al. formed a photocured thiol-ene silicone network that trapped a slower condensation-cured silicone network. The orthogonal reactions separated shape formation from final mechanical development. Their silicone double networks combined $E_{100}\%$ below 700 kPa with strains approaching 400%, toughness near 1.4 MJ m⁻³ and strength near 1 MPa, and enabled cohesive bonding to dissimilar substrates [1]. As adjacent UV-assisted direct-ink-writing evidence rather than VPP evidence, Ji et al. used a photo and thermal two-stage strategy to create printable PDMS architectures followed by thermal crosslinking [8]. In every staged system, the time, temperature, atmosphere and delay between stages become part of the material state.

4.4 Other printable silicone and siloxane-hybrid routes

Click-chemistry stereolithography has also been used to produce soft, self-healing silicone structures [4]. Palaganas et al. prepared a photocurable siloxane composite for 3D printing [6], which illustrates why composition language must remain precise: a siloxane-containing composite or hybrid is not automatically equivalent to a continuous polysiloxane elastomer. More recent work continues to address low-durometer toughness in direct-ink-write silicones [7] and solvent-free DLP photoinitiation [9]. Each route must identify which network carries load and which phase controls the claimed property.

5. Silicone-like, silicone-free functional analogues

A silicone-free photopolymer can be engineered to occupy part of the same functional space as silicone without containing a siloxane network. Flexible urethane, acrylate or other organic segments, moderated effective crosslink density, entanglement, physical association and architected geometry can produce soft-touch response, elastic deformation, resilience or cushioning. ER-101 reviews those generic network-design routes. ER-102 restricts the comparison to what has actually been matched.

The 3Dresyns public Silicone-Like collection currently presents two hardness anchor routes, Hard SR Shore A70 and Soft SR Shore A30, and states that they are silicone-like photopolymer systems, not direct silicone materials [M1]. For this manuscript, the author additionally declares that these products contain no silicone. This is a manufacturer and author statement, not an independent compositional assay and not a disclosure of proprietary chemistry.

The permitted claim is therefore narrow: the products are intended to provide selected silicone-like mechanical or tactile functions. No conclusion about equivalence in heat resistance, low-temperature behaviour, tear, compression set, fluid compatibility, gas permeability, weathering, electrical insulation, extractables or biocompatibility follows from the name. Those domains require matched tests on the exact printed and post-cured grade.

6. The functional-equivalence ladder

Level	Evidence required	Claim boundary
1. Descriptive resemblance	Documented feel, flexibility or shape recovery under stated conditions	May say silicone-like only for that observation
2. Metric match	Matched hardness, modulus or recovery method with uncertainty	May claim similarity only for the measured metric and state
3. Mechanical-function match	Tensile, tear, set, relaxation and cyclic evidence in relevant geometry	May claim bounded mechanical substitution
4. Environmental-function match	Thermal ageing, fluids, humidity, UV/ozone and permeability as applicable	May claim substitution only within the tested environment and duration
5. Intended-use qualification	Application-specific safety, lifetime, compliance and failure evidence	May support the defined use; not a material-wide equivalence claim

Table 2. Functional-equivalence ladder. Evidence at one level does not automatically satisfy the next.

7. Thermal-service limits

Thermal resistance is not a single number. Relevant limits can arise from glass-transition approach, modulus loss, stress relaxation, compression set, oxidation, chain scission, additional cure, volatile loss, discoloration, dimensional change, interfacial failure or unacceptable drift in the device function. A short heat-deflection impression or one thermogravimetric onset cannot define long-term elastomer service.

The flexible siloxane backbone gives appropriately formulated silicone rubbers an unusually low glass-transition region and can support broad temperature use [1]. That material-class advantage does not fix the service range of every silicone. Fillers, side groups, catalysts, crosslink chemistry, oxygen, load, thickness and duty cycle still matter. Conversely, matching a silicone grade at room-temperature Shore hardness does not reproduce its temperature dependence.

Under the author and manufacturer boundary applied here, 3Dresyns Silicone-Like products are silicone-free photopolymers and generally have lower resistance to elevated-temperature service than appropriately selected true silicone systems. This is a directional comparison, not a numeric rating and not a universal statement about every silicone comparator. A maximum-use temperature for a specific product must come from current grade-specific

documentation and a test programme reproducing load, duration, atmosphere and acceptance criteria. ISO 188:2023 anchors accelerated heat ageing, while ISO 11346:2023 addresses lifetime and maximum-use-temperature estimation [S8,S9].

8. Qualification matrix for silicone versus silicone-like transfer

Property domain	Minimum matched evidence	Common false transfer
Chemical identity	Declared composition plus appropriate analytical verification where required	Similar feel means silicone composition
Hardness and tensile	Same method, geometry, rate, temperature, orientation and conditioning	Same Shore A means same modulus or strength
Tear and flaw tolerance	Matched tear geometry, cut, thickness, rate and crack path	High elongation means high tear resistance
Compression retention	Compression set and stress relaxation at service strain, time and temperature	Visual recovery means retained sealing force
Cyclic duty	Amplitude, frequency, waveform, temperature, cycle count and retained properties	Several demonstration cycles prove fatigue life
Thermal service	Ageing and property retention over relevant load, atmosphere, time and temperature	TGA onset or material-class reputation defines service limit
Fluids and environment	Mass, volume and property change in exact media; UV/ozone/humidity as relevant	Silicone-like name transfers chemical compatibility
Component function	Printed geometry, interfaces, dimensional tolerances and functional acceptance test	Coupon similarity guarantees part substitution

Table 3. Minimum evidence for transferring a function from a silicone comparator to a silicone-like printed part.

9. VPP state variables that can invalidate comparison

- Formulation or grade identity, batch, storage history and mixing state, including the age of any multi-part or staged-cure system.
- Printer architecture, wavelength, irradiance, exposure strategy, layer thickness, separation mechanics and resin temperature.
- Optical dose-response, green strength, viscosity or recoating behaviour, and any filler-induced scattering or sedimentation.
- Build orientation, support strategy, surface damage, interlayer continuity, feature thickness and local overcure or undercure.
- Wash medium, time, agitation, drying, swelling history and residual solvent before mechanical or thermal testing.
- Post-cure spectrum, dose, temperature, atmosphere and delay; for dual cure, the complete sequence and evidence of final conversion.
- Conditioning time, humidity, test temperature and specimen age, including continued dark cure or physical ageing.
- Exact comparator grade and cure state. Silicone is a family, so an unspecified silicone control is not a reproducible comparator.

10. Core test architecture

Identity and state come first. Where composition is consequential, analytical methods should verify the claimed polymer class rather than infer it from hardness or infrared peaks in isolation. ISO 9924-3:2024 provides a composition-oriented thermogravimetric framework for polysiloxane rubbers, but a complete identification may require complementary spectroscopy, extraction or elemental methods chosen for the actual formulation [S2].

Mechanical comparison should use the same conditioned state. ISO 37:2024 anchors tensile stress-strain, ISO 34-1:2022 anchors defined tear configurations, ISO 48-4:2018 anchors Shore hardness, ISO 815-1:2019 anchors compression set and ISO 3384-1:2024 anchors compression stress relaxation [S3-S7]. The standard name alone is insufficient: specimen, method option, thickness, orientation, rate, temperature, dwell and recovery interval must be reported.

Environmental comparison should retain functional properties after exposure, not report exposure survival alone. ISO 188:2023 addresses accelerated ageing and heat resistance, ISO 11346:2023 addresses lifetime estimation, ISO 1817:2026 addresses effects of liquids and ISO 1431-1:2024 addresses ozone cracking [S8-S11]. Applicability to a photocured non-rubber network must be justified, and deviations must be declared.

11. Failure-mode interpretation

Observation	Possible explanation	Next discriminating test
Matched Shore A, different sealing force	Different compression modulus, relaxation or geometry sensitivity	Compression curve plus constant-deflection relaxation

Observation	Possible explanation	Next discriminating test
Good room-temperature match, rapid hot drift	Different network mobility, oxidation, post-cure or crosslink stability	Property retention during and after controlled heat ageing
High extension, low notch tolerance	Insufficient crack blunting or weak interlayer path	Standard tear plus crack-path and orientation analysis
Apparent recovery, growing permanent set	Viscoelastic flow, incomplete cure or damage accumulation	Recovery-time sweep and multi-cycle retained dimensions/force
Fluid swelling differs from comparator	Different solubility parameter, crosslink density or extractable fraction	Mass, volume and mechanical retention in exact fluid
Silicone identification is ambiguous	Hybrid or discontinuous siloxane phase rather than silicone network	Orthogonal compositional and network-continuity analysis

Table 4. Diagnostic matrix. The listed mechanisms remain hypotheses until discriminating evidence is obtained.

12. 3Dresyns implementation boundary

The public 3Dresyns collection uses Silicone-Like for two visible hardness anchor routes: Hard SR Shore A70 and Soft SR Shore A30. It explicitly describes them as silicone-like photopolymer systems rather than direct silicone materials and states that final suitability depends on geometry, strain, post-curing and actual mechanical demand [M1].

The author declaration for ER-102 is stricter: these 3Dresyns Silicone-Like formulations contain no silicone. The declaration is made to prevent chemical misclassification. It does not reveal composition, replace independent analysis or imply that every non-silicone constituent has been publicly identified. Product-specific claims must remain aligned with current technical and safety documentation.

The expected engineering position is functional similarity with limits. Selected room-temperature deformation, recovery, feel or hardness functions may resemble silicone comparators, while elevated-temperature resistance is generally lower. The exact boundary cannot be supplied by the collection name. It must be established for the selected grade, printer state, post-cure, geometry, load, duration and failure criterion. No direct silicone-replacement claim is authorised by this reviewed document.

13. Minimum qualification workflow

- Define the requested function and comparator. Name the exact silicone grade, cure, geometry, environment and acceptance criterion.
- Gate chemical language. Use silicone only when a load-bearing polysiloxane network is established; use silicone-like only for bounded functional resemblance.
- Freeze material and VPP state, including batch, printer, exposure, orientation, wash, drying, post-cure and specimen age.
- Match the basic mechanical state with hardness and complete tensile curves under the same conditioning, not one catalogue endpoint.
- Add tear, compression set, stress relaxation and cyclic measurements when the function involves sealing, cushioning, repeated deformation or flaw-sensitive geometry.
- Measure heat ageing and property retention over the relevant load, atmosphere, temperature and duration. Do not infer service limits from TGA alone.
- Add exact fluid, humidity, UV, ozone, permeability or electrical tests only when those functions are part of the substitution claim.
- Test the printed component after coupons and monitor retained force, dimensions, leakage, damage or other functional output.
- State the qualified window and exclusions. Similarity outside the measured property, state and duration remains unproven.
- Keep intended-use, biocompatibility, regulatory and safety qualification separate from engineering similarity.

14. Research and standardisation priorities

- A shared terminology standard separating silicone, siloxane-containing, silicone-hybrid, silicone-like and rubber-like printable materials.
- Round-robin composition and mechanical testing of true silicone and silicone-free analogue grades under matched VPP states.
- Time-temperature maps for compression set, stress relaxation and retained force, rather than single short heat exposures.
- Direct relationships between chemistry, conversion gradient, interlayer continuity, extractables and long-term elastomer performance.

- Matched tear, fatigue-crack growth and component-damage studies across true silicone and non-silicone soft photopolymers.
- Public reporting of comparator grade, cure state, specimen age, wash and post-cure so silicone-equivalence claims can be reproduced.
- Grade-specific lifetime models that distinguish thermal decomposition, oxidative ageing, modulus drift and functional failure.
- Clear manufacturer disclosure when silicone-like products are silicone-free, preventing downstream assumptions about chemistry or service temperature.

15. Conclusions

True silicone VPP is chemically achievable. Thiol-ene functional polysiloxanes, simultaneous chain extension and crosslinking, staged photo and thermal cure, and orthogonal double networks show how printable resin requirements can be separated partly from final silicone mechanics. The literature also shows that no single architecture eliminates the need to control viscosity, photochemistry, green strength, conversion, interlayer continuity and post-cure state.

Silicone-like is a different and narrower proposition. A silicone-free photopolymer may reproduce selected silicone-like functions, but neither Shore hardness nor tactile resemblance transfers polysiloxane identity or the full package of thermal, chemical, compression, tear, permeability, ageing or biological performance. Equivalence must be built property by property and state by state.

For 3Dresyns, the boundary is explicit: the Silicone-Like products discussed here contain no silicone and are not direct silicone materials. They are intended as functional analogues and, in general, have lower elevated-temperature resistance than appropriately selected true silicone systems. That directional statement is not a temperature specification. Grade-specific documentation and application-representative validation remain controlling. ER-102 therefore closes with a comparison framework, not a replacement claim.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use different polysiloxanes, fillers, photoinitiators, printers, cure schedules, specimens and test conditions, so reported numerical values are not pooled or ranked. Manufacturer composition and performance statements are clearly segregated from independent science. No proprietary formula, independent chemical assay of 3Dresyns products, universal temperature limit, lifetime model, intended-use qualification or regulatory conclusion is presented.

Author contributions

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

Competing interests

The author is founder and CEO of 3Dresyns by Resyner Technologies S.L. Manufacturer sources and author declarations are segregated from independent scientific evidence. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated for this review. Scientific statements derive from the cited primary literature and standards. The review package includes a QA report and a source-ledger summary for independent full-manuscript review.

Company information

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Version note

v0.3 preserves the approved v0.2 scientific text and closes the final micro-delta gate. Independent review returned APPROVE, confirmed the restored Version note, found zero regressions and recorded one pre-existing non-blocking P3 typography observation. This release introduces no scientific change.

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Related Engineering Review boundaries

- [C1] Seguro, J. Fatigue and Time-Dependent Deformation in Vat-Printed Thermosets: A Qualification and Evidence-Gap Note. ER-39. Zenodo (2026). Concept DOI: 10.5281/zenodo.22048050. <https://doi.org/10.5281/zenodo.22048050>
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Manufacturer implementation source

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