

Thermal Performance in Vat-Photopolymerised Polymers: HDT, Tg, Post-Cure and High-Temperature Qualification

Juan Seguro

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

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Statement of Significance

High-temperature performance in vat-photopolymerised polymers cannot be represented by a single temperature. Glass transition, heat-deflection temperature, viscoelastic softening, dimensional drift, thermal ageing and short-term survival under load probe different aspects of a cured network. This review treats thermal qualification as a state-dependent engineering problem in which formulation, conversion, post-cure, specimen geometry, loading mode and time at temperature must be reported together. The objective is to prevent nominal thermal ratings from being interpreted as universal service temperatures.

Keywords: vat photopolymerisation; high-temperature photopolymer; heat deflection temperature; HDT; glass transition temperature; Tg; DMA; DSC; post-cure; thermal ageing; hot lithography; SLA; DLP

Abstract

Thermal performance of VPP polymers emerges from network architecture and the cure history imposed by printing, washing and post-curing. HDT, Tg and dynamic-mechanical transitions are related but non-equivalent metrics, and their numerical values depend on test method, applied stress, heating rate, frequency, specimen state and conditioning. Recent work on hot-lithography, heat-assisted VPP, high-viscosity systems and high-Tg interpenetrating networks shows that print temperature and cure strategy can modify conversion, shrinkage, modulus and thermal response. This review develops a qualification framework that separates material transition temperatures from load-bearing service performance, distinguishes printing temperature from final-use temperature, and requires thermal ageing to be coupled with retained mechanical and dimensional measurements. A minimum reporting set is proposed for high-temperature VPP studies. Commercial 3Dresyns high-HDT grades are included only as implementation examples and not as evidence for universal high-temperature suitability.

1. Introduction

VPP thermosets are often selected for tooling, moulds, fixtures, fluidic components and engineering parts because crosslinked networks can retain stiffness beyond the temperature range of many commodity photopolymers. The phrase high-temperature resin, however, can describe several different phenomena. A material may exhibit a high calorimetric Tg but creep under load below that temperature; it may reach a high HDT under one specified stress but lose dimensional accuracy during a longer thermal dwell; or it may tolerate a brief process excursion that would not be acceptable as continuous service. Engineering qualification therefore requires the thermal metric to be tied to the stress, timescale and cured state in which it was measured. [1,2]

Photopolymer networks are unusually sensitive to cure history. Conversion can continue during post-curing, network heterogeneity can decrease or increase, and thermal exposure can produce physical ageing, additional reaction, stress relaxation or degradation. Sekmen and co-workers demonstrated the need to model curing-dependent thermo-viscoelastic and shrinkage behaviour rather than treating a photopolymer as a fixed elastic solid. Hot-lithography and heat-assisted VPP studies similarly show that resin temperature during fabrication can change rheology and final properties. These observations motivate a framework based on material state rather than a single catalogue temperature. [1,2,5]

2. Thermal metrics are not interchangeable

Domain	What is measured	Primary dependency	What it does not establish
Glass transition, Tg	Change in heat capacity or viscoelastic response associated with segmental mobility.	Method, heating rate or frequency, cure state and network heterogeneity.	A universal load-bearing service temperature.
HDT	Deflection of a standard specimen under specified flexural stress during heating.	Applied stress, geometry, heating protocol and specimen preparation.	Long-duration creep resistance or thermal stability.
DMA transition	Storage/loss modulus and tan delta versus temperature/frequency.	Frequency, strain amplitude, thermal history and fixture.	Chemical decomposition resistance.
Thermal decomposition	Mass loss or chemical degradation at elevated temperature.	Atmosphere, heating rate and chemistry.	Dimensional stability under mechanical load.
Service-temperature window	Application-specific retained function over time.	Load, duration, environment, geometry and acceptance criterion.	An intrinsic material constant transferable to every use.

Table 1. Engineering distinctions that must be preserved.

2.1 Glass transition

Tg is a network transition, not a pass/fail service limit. DSC detects changes in heat capacity, whereas DMA derives transition behaviour from the temperature dependence of viscoelastic moduli and loss. The two methods can yield different numerical values without either being incorrect. For VPP, the chosen definition should therefore be stated explicitly together with cure and conditioning history. [9,10]

2.2 Heat-deflection temperature

HDT is valuable because it introduces mechanical load, but the result belongs to the specified stress and test geometry. ISO 75 therefore should be cited with the stress condition rather than reduced to an isolated temperature. A higher HDT can support screening for heated tooling or fixtures, but it does not remove the need to test creep, dimensional stability or cyclic exposure under the intended duty cycle. [8]

3. Cure state and post-cure are thermal variables

The printed green state, washed state and fully post-cured state are different polymer states. Residual reactive groups can increase conversion during post-cure; elevated-temperature post-cure may further alter crosslink density and stress state. Reporting only the final thermal value without the post-cure wavelength, irradiance or duration and temperature makes comparison difficult. Thermal qualification should therefore treat post-cure as part of specimen preparation, not as an incidental laboratory detail. [1,2,5]

Variable	Mechanism	Expected consequence	Reporting requirement
Build exposure	Sets initial conversion and network gradient.	Changes modulus, residual functionality and post-cure response.	Wavelength, exposure strategy, layer thickness.
Resin temperature	Changes viscosity and reaction/transport behaviour.	Can alter printability, conversion and stress development.	Vat temperature and whether actively controlled.
Wash protocol	Removes uncured material and can extract mobile components.	Changes surface state and potentially plasticisation.	Solvent, time, drying.
Light post-cure	Raises conversion and may change network heterogeneity.	Can increase stiffness/Tg but also embrittle.	Wavelength, time, irradiance when available.
Thermal post-cure	Promotes further reaction and relaxation.	May shift Tg/HDT and dimensional state.	Temperature, ramp, dwell, atmosphere.
Conditioning	Water, solvent or humidity can plasticise networks.	Can reduce Tg/modulus relative to dry state.	Medium, temperature and duration.

Table 2. Process variables that can move a reported thermal result.

4. Heated VPP and hot lithography

Printing at elevated temperature should not be confused with high-temperature service. Sameni et al. showed that hot-lithography printability depends jointly on vat temperature and mixture design. Weng and co-workers used a linear-scan VPP system to process ultra-high-viscosity resin, demonstrating how thermal assistance can expand the processable rheological window. Lim et al. later showed that heat-assisted VPP can alter physical and mechanical characteristics of dental resins. These studies establish process-temperature effects; they do not imply that a resin printed hot will necessarily serve at the same or a higher temperature. [3,4,6]

5. Network design for elevated thermal resistance

Higher thermal resistance generally requires restriction of segmental mobility through aromaticity, functionality, crosslink density, rigid comonomers or interpenetrating-network design. This creates a familiar VPP trade-off: network designs that raise Tg or HDT can increase liquid viscosity, reduce conversion at a fixed optical dose, raise cure stress or lower toughness. Recent high-Tg sequential interpenetrating-network work based on maleimide and cyanate-ester chemistry illustrates the value of separating resin-processability design from final network design. [7]

6. Time, load and environment define service performance

A short HDT ramp and a multi-hour thermal dwell answer different questions. For fixtures, moulds and pressurised fluidic parts, creep and stress relaxation may dominate before chemical degradation begins. For repeated cycles, thermal expansion mismatch and fatigue can accumulate even when peak temperature remains below the reported Tg. High-temperature qualification should therefore combine a transition metric with application-relevant mechanical retention and dimensional metrology.

Application question	Useful screening metric	Required follow-on evidence	Typical overclaim to avoid
Will the part remain stiff during brief heating?	Tg/DMA and HDT.	Modulus or deflection under representative load/time.	Tg equals maximum use temperature.
Will a mould retain geometry over repeated cycles?	HDT plus dimensional scan.	Cyclic thermal exposure, creep and retained dimensions.	One HDT test predicts mould life.
Will a fluidic part survive hot media?	Tg/HDT and chemical compatibility.	Immersion plus pressure/leak/dimension testing at temperature.	Dry thermal rating proves hot-fluid suitability.
Will a fixture survive a process excursion?	Short-term thermo-mechanical test.	Representative dwell, load and recovery.	Brief survival establishes continuous service.
Will properties remain after ageing?	TGA/DSC/DMA baseline.	Retained tensile/flexural/dimensional properties after ageing.	No visible damage means no degradation.

Table 3. From thermal metric to application-level qualification.

7. Minimum qualification architecture

A defensible thermal datasheet or publication should report the polymer state and method with every temperature. At minimum, the reader should know whether the specimen was green, washed, light-post-cured or thermally post-cured; whether it was tested dry or conditioned; and which load, rate and geometry were used. If the application is at elevated temperature, the relevant duty cycle should be recreated rather than inferred from the transition temperature alone. Tensile-property retention should identify the exact current ISO 527 part and specimen/test conditions used [11].

Block	Minimum information	Reason	Interpretation limit
Printing	VPP process, wavelength, layer thickness, vat temperature.	Defines initial network state.	Cannot transfer across arbitrary printers without validation.
Post-processing	Wash, light cure, thermal cure, drying.	Thermal properties are cure-state dependent.	A temperature without cure history is incomplete.
Thermal method	DSC/DMA/HDT/TGA standard, stress, rate, frequency.	Defines what temperature means.	Different methods are not directly interchangeable.
Conditioning	Dry/wet state, medium, humidity, time.	Captures plasticisation and ageing.	Dry data may not represent wet service.
Mechanical retention	Property before/after thermal exposure.	Connects transition to function.	Peak temperature alone does not prove retention.
Dimensional retention	Reference dimensions and post-exposure change.	Critical for tooling and precision parts.	Visual inspection is insufficient for precision claims.
Duty cycle	Temperature, load, dwell, cycles and environment.	Defines application qualification.	Supports only the tested use window.

Table 4. Minimum reporting set for high-temperature VPP.

3Dresyns implementation examples

The 3Dresyns portfolio contains high-HDT materials that illustrate how a commercial thermal designation can be connected to a controlled test method without turning that value into a universal service claim.

- 3Dresyn Biorigid R190D90 is documented by the manufacturer with heat-deflection temperature up to approximately 190 °C at 0.45 MPa under ISO 75. It is an implementation example of a high-HDT rigid VPP grade, not evidence that every geometry remains functional continuously at 190 °C [M1].
- 3Dresyn R290D90 ESD is documented by the manufacturer with heat-deflection temperature up to approximately 290 °C at 0.45 MPa under ISO 75. The number remains attached to the specified HDT condition and is not a universal continuous-use temperature [M2].
- 3Dresyn VAM HDT1 Bio provides a manufacturer-documented example of high-HDT material positioning for volumetric printing. Platform-specific processing and final-part thermal qualification remain necessary [M3].

These examples are based on controlled 3Dresyns product documentation. They are commercial implementation examples only; the literature review and methodological conclusions above do not depend on their product claims.

8. Conclusions

- Tg, HDT, DMA transitions, decomposition temperature and service temperature are distinct engineering quantities.
- VPP thermal performance is cure-state dependent; printing, washing and post-curing must be part of the reported specimen definition.
- Printing at elevated vat temperature expands processability but is not evidence of high-temperature service.
- HDT should always be reported with stress and method, and application qualification should add time-dependent load and dimensional retention.
- Thermal ageing should be followed by retained-property testing rather than judged by appearance alone.
- Commercial high-HDT values are useful screening data when tied to the specified method, but final geometry and duty cycle require validation.

Limitations

This is an engineering perspective rather than a meta-analysis. Thermal values are not pooled across materials because methods, cure states and resin chemistries differ. Product examples are not independently re-tested here.

Author contributions

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

Competing interests

The author is affiliated with 3Dresyns by Resyner Technologies S.L. Commercial 3Dresyns materials are identified only as implementation examples supported by controlled product documentation. They are not treated as independent peer-reviewed evidence and no proprietary formulation composition is disclosed.

Data availability

No new experimental dataset was generated for this review. Scientific statements are attributed to the cited literature and standards; commercial examples are separated from the independent evidence base.

Company information

Legal company name: 3Dresyns by Resyner Technologies S.L. Registered tax address: General Etxague 15B, 20003 Donostia / San Sebastián, Gipuzkoa, Spain VAT number: ESB24827511 Contact email: info@3Dresyns.com Company website: www.3Dresyns.com

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