

Thermal Expansion and Thermomechanical Dimensional Stability in Vat-Printed Photopolymers

CTE, TMA, Cure-State Dependence, Orientation, Thermal Cycling and Material-Mismatch Qualification

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Statement of Significance

A resin can pass a Tg or HDT requirement and still fail a dimensional-tolerance requirement when temperature changes. Thermal expansion is a strain response, not a thermal-transition label, and the measured coefficient depends on specimen state, temperature interval, cure history and sometimes build orientation. ER-96 defines the evidence needed to separate reversible thermal expansion from cure shrinkage, viscoelastic relaxation, irreversible ageing and high-temperature softening in vat-printed photopolymers.

Keywords: thermal expansion; coefficient of thermal expansion; CTE; thermomechanical analysis; TMA; dimensional stability; thermal cycling; anisotropy; vat photopolymerisation; SLA; DLP

Abstract

Thermomechanical dimensional stability in vat-photopolymerised polymers is controlled by more than a single coefficient of thermal expansion (CTE). Linear expansion can vary with temperature, cure state and network mobility; the response can change near glass transition; repeated heating can reveal residual cure or irreversible strain; and the printed architecture can introduce orientation-dependent behaviour in some systems while other SLA systems show little or no measurable thermal-expansion anisotropy. Direct VPP evidence supports both sides of that boundary. Peterson et al. used thermomechanical analysis in a DLP-printed graded-crosslink system [1]. Sekmen et al. showed that thermo-viscoelastic behaviour and shrinkage depend on degree of cure and temperature in a commercial SLA/DLP photopolymer [2]. Klimtova and Vesely found no orientation-dependent thermal expansion in the SLA epoxy system they tested, despite strong anisotropy in FFF controls [3], whereas Nabavian Kalat et al. reported orientation-dependent thermal expansion and dimensional stability in an SLA shape-memory epoxy [4]. ER-96 therefore treats CTE as a conditioned material-state measurement rather than a universal datasheet constant. The qualification architecture combines specimen-state definition, TMA/dilatometry, temperature-window control, heating/cooling history, orientation comparison where justified, and component-level dimensional checks when inserts or dissimilar materials create CTE mismatch.

1. Scope and controlling boundaries

ER-96 owns the **reversible and thermomechanically conditioned dimensional-response layer** of vat-printed photopolymers. Its primary questions are how linear dimensions change with temperature, when a reported CTE is valid, whether the response is direction-dependent, and how thermal mismatch should be qualified in a component.

The scope is deliberately separated from neighbouring reviews. ER-20 controls Tg, HDT and general thermal-performance qualification. ER-31 controls cure shrinkage, residual stress and warpage created during or after polymerisation. ER-38 controls burnout, residue and shell interaction in investment casting. ER-39 controls creep, fatigue and stress relaxation. ER-43 controls multimaterial interface architecture. ER-47 controls thermal conductivity. ER-72 controls ageing and irreversible environmental degradation. ER-96 may use burnout or interface examples only to supply thermomechanical expansion/mismatch inputs, and may measure a transition or residual strain to interpret TMA data, but it does not absorb those neighbouring endpoints.

The central rule is that **CTE is not a synonym for dimensional stability**. A defensible dimensional-stability claim also requires the relevant temperature interval, conditioning state, cycle history, direction, geometry and allowable irreversible drift.

2. What a CTE measurement represents

For an approximately linear interval, the technical coefficient of linear thermal expansion describes change in length per original length per temperature change. In real crosslinked photopolymers, however, the apparent slope can vary with temperature because network mobility changes, especially near a glass transition. A single value should therefore be linked to the interval over which it was fitted rather than presented as an invariant molecular constant.

ASTM E831-25 defines a TMA method for the technical coefficient of linear thermal expansion of sufficiently rigid solid materials [S1]. ISO 11359-2:2021 likewise specifies TMA determination of linear thermal expansion for plastics and also addresses Tg by TMA [S2]. These standards provide measurement architecture, not a VPP-specific acceptance criterion.

The specimen must also remain mechanically suitable for the probe and temperature range. If the material softens enough for probe indentation, or if a transition produces strongly nonlinear deformation, the reported “CTE” can become method- and interval-dependent. The test record should therefore preserve probe/load conditions, specimen geometry and the actual fitted ranges.

3. Cure state is part of the thermomechanical material identity

Photopolymerisation does not end merely because a part has been removed from the printer. Residual functional groups, post-cure, thermal history and network mobility can alter subsequent thermomechanical response. Sekmen et al. measured thermo-viscoelastic properties as functions of temperature, degree of cure and frequency in a commercial photopolymer used for SLA/DLP, while separately modelling chemical shrinkage [2]. This is precisely why ER-96 separates **thermal strain after a defined cure state** from chemical shrinkage during cure.

Peterson et al. used DLP grayscale exposure to create spatially varied crosslink densities and included thermomechanical analysis in their characterization [1]. The source supports a direct link between VPP process state and later material response, but it does not establish a universal CTE-versus-dose law for other formulations. Park et al. showed that SLA slice thickness and the resulting layer/interlayer morphology altered mechanical and thermal response, including the dynamic-mechanical glass-transition response, in printed thermosets [6]. This provides direct evidence that printing parameters can remain encoded in the delivered thermomechanical material state.

At minimum, a CTE comparison should hold constant resin batch/version, print orientation and exposure basis, wash state, drying, post-cure spectrum/dose, time between post-cure and test, and preconditioning. If those variables differ, the comparison is between material states rather than between nominal resin names.

Table 1. Thermomechanical quantities that must not be conflated.

Quantity	What it measures	Primary boundary
Linear thermal expansion / CTE	Reversible or technical length response over a specified temperature interval.	Not Tg, HDT or cure shrinkage.
Tg from TMA/DMA/DSC	A transition associated with changing molecular mobility, with method-dependent value.	Not an allowable dimensional drift by itself.
Chemical/cure shrinkage	Contraction associated with polymerisation and network formation.	Owned by ER-31 when used as a manufacturing-distortion endpoint.
Irreversible thermal strain	Residual dimensional change after a heating/cooling cycle.	Must be separated from reversible CTE; may indicate residual cure, relaxation or damage.
Thermal conductivity	Heat-flow transport property.	ER-47; does not determine expansion magnitude.
HDT	Deflection under specified load/temperature conditions.	ER-20; not a coefficient of expansion.

4. Orientation: a hypothesis to test, not an automatic correction factor

Layerwise manufacturing can create directional differences in cure history, interface density and geometry, but VPP thermal-expansion anisotropy is not universal. Klimtova and Vesely tested SLA epoxy specimens in four orientations by TMA and reported no difference in thermal expansion among the tested SLA orientations, in contrast with stronger anisotropy in FFF controls [3].

A later SLA study by Nabavian Kalat et al. reached a different material-specific result: flat- and edge-oriented shape-memory epoxy specimens showed different thermal expansion and dimensional stability, linked by the authors to layer surface area, layer count, microstructure and interlayer bonding [4]. These two sources are complementary rather than contradictory because they study different resins, geometries and process states.

Accordingly, ER-96 does not assume an XY/Z CTE ratio. Orientation should be included when the component geometry, print route or preliminary evidence makes it plausible, and a “no anisotropy detected” result is scientifically valid when supported by adequate uncertainty and test sensitivity.

5. Temperature interval, Tg proximity and cycle history

A CTE value taken well below Tg cannot automatically be extrapolated across Tg or into a high-mobility regime. Where the intended service interval approaches a transition, the expansion curve itself and the transition region matter more than one fitted slope. ISO 11359-2 explicitly couples TMA-based CTE and Tg determinations within the same general method family [S2].

Heating history also matters. A first cycle can contain residual cure, physical relaxation, moisture loss or other conditioning effects that are reduced on a later cycle. Reporting only the second-cycle slope can be appropriate for a stabilised state, but only if the first-cycle irreversible change is also recorded when service dimensional stability is the real engineering question.

A useful cycle record therefore separates heating slope, cooling slope, residual length change at the return temperature, and any change between cycles. This prevents a low fitted CTE from hiding unacceptable irreversible drift.

6. Material mismatch, inserts and constrained expansion

Thermal expansion becomes a stress problem when a printed polymer is bonded to an insert, coating, optical element, ceramic, metal or second polymer with a different dimensional response. ASTM E831 identifies thermal-stress risk in dissimilar-material bodies as one use of CTE data [S1].

For a bonded assembly, bulk coupon CTE is necessary but not sufficient. Geometry, bondline thickness, modulus versus temperature, cure stress, interfacial adhesion and the temperature-time cycle determine whether mismatch is accommodated or converted into distortion, debonding or cracking. ER-43 controls multimaterial interface architecture; ER-96 supplies the thermomechanical mismatch input rather than claiming interface durability from CTE alone.

Where dimensional tolerance is the final requirement, the component should also be measured across the actual thermal excursion. Coupon TMA and component dimensional metrology answer different levels of the evidence chain.

7. Investment-casting and high-temperature boundaries

VPP investment-casting patterns provide an important adjacent example because thermal expansion can load a ceramic shell during heating. Sameni et al. reported that adding powdered-wax filler to the studied VPP investment-casting pattern formulation reduced thermal expansion [5]. The result shows that expansion is formulation-dependent within this application class rather than a fixed consequence of the VPP process. ER-38 owns burnout, residue and shell interaction; ER-96 uses the example only to show why expansion cannot be reduced to Tg/HDT.

Likewise, ceramic VPP parts after debinding/sintering have a different material identity from the as-printed photopolymer network. Ceramic CTE after sintering belongs to the ceramic phase and microstructure, not to the photopolymer binder. ER-96 is therefore limited to vat-printed photopolymer states and polymer-containing assemblies unless an explicitly defined intermediate state is being measured.

8. Minimum qualification architecture

Define the delivered material state. Record resin version/batch, build orientation, exposure basis, wash/dry/post-cure, conditioning and specimen age.

Measure the dimensional curve, not only one number. Preserve length-versus-temperature data, fitted intervals and transition regions.

Separate reversible and irreversible response. Include cooling and repeat cycles when dimensional stability is claimed.

Test orientation where justified. Do not impose a directional correction without evidence.

Escalate to component-level measurement for constrained or multimaterial designs. CTE mismatch is an input to stress and distortion, not a complete failure prediction.

Table 2. Suggested ER-96 qualification record.

Domain	Minimum record	Decision enabled
Specimen state	Batch/version, orientation, layer thickness, exposure, washing, drying, post-cure, conditioning.	Reproducible material identity.
TMA / dilatometry	Instrument, probe/load, atmosphere, heating/cooling rate, geometry, temperature interval.	Traceable expansion curve.
CTE reporting	Fitted interval(s), uncertainty/repeats, direction, cycle number.	Comparable coefficient within stated bounds.
Transition context	Tg or softening indication where relevant to fitted interval.	Avoids extrapolating a low-temperature slope through a transition.
Cycle stability	Return-to-temperature residual strain and repeat-cycle change.	Separates reversible expansion from permanent drift.
Component validation	Critical dimensions over service cycle; insert/substrate identity if present.	Links material data to final tolerance.

9. Reporting rules

Do not report a CTE without the temperature interval and specimen state. Do not translate Tg or HDT into dimensional stability. Do not assume VPP anisotropy from manufacturing method alone. Do not report a first-heating slope as reversible expansion when residual cure or relaxation is visible. Do not transfer a coupon CTE directly into a multimaterial stress or lifetime claim without component-level mechanics.

If a datasheet value is used, the report should state the test method and conditioning basis when available. If those conditions are unknown, the value is a screening input rather than a qualification result.

10. Research gaps and priority experiments

Published VPP thermomechanical studies remain sparse compared with the number of commercial claims that use terms such as dimensional stability, high temperature or low shrinkage. A priority evidence gap is therefore a matched multi-resin study that measures TMA curves, repeat-cycle residual strain and component dimensions from the same print/post-cure states rather than comparing unrelated datasheet values.

A second gap is the interaction between **water uptake and thermal expansion**. Hygroscopic swelling can change baseline dimensions and plasticise a network, so ER-96 recommends conditioning or humidity control when moisture-sensitive materials are compared. Water sorption itself remains outside this paper; the point here is to prevent an uncontrolled moisture state from being misread as thermal expansion.

A third gap is scale transfer. TMA specimens are intentionally small and unconstrained, whereas service parts may contain thin walls, ribs, bonded inserts or spatially varying cure. Direct dimensional metrology over temperature should therefore accompany coupon TMA for precision assemblies. The required result is not merely a lower CTE but an acceptable dimensional excursion and return-to-baseline behaviour.

Finally, orientation should be investigated with enough repeats to distinguish a true directional effect from specimen-to-specimen scatter. The published contrast between negligible orientation dependence in one SLA epoxy [3] and clear orientation dependence in another [4] makes this an experimentally testable variable, not a platform-wide assumption.

11. Conclusions

Thermal dimensional qualification of vat-printed photopolymers requires more than a Tg/HDT value and more than one CTE number. The relevant evidence is a conditioned length-versus-temperature response linked to cure state, temperature interval, cycle history and direction.

Direct VPP evidence shows why orientation must be tested rather than assumed: one SLA system showed no measurable thermal-expansion anisotropy under the tested conditions [3], while another showed clear orientation-dependent expansion [4]. That formulation-specificity is the central engineering lesson.

ER-96 therefore treats CTE as one parameter inside a broader dimensional-stability architecture. Reversible expansion, irreversible drift, transition proximity and material mismatch remain separate evidence layers.

Scientific literature

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Version note

Version 0.3 is a literature-based release incorporating independent review corrections and prepared for independent delta review. No universal CTE value, orientation correction factor or service-temperature limit is assigned to any 3Dresyns resin. No Zenodo, DOI-registration, Shopify or public-release action is authorised by this document.