

# Phase-Change and Latent-Heat Materials in Printed Photopolymer Structures: Containment, Cycling and Thermal Management

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ER-270 · Engineering Review · Version 0.4 · 23 September 2026

## Abstract

Phase-change materials can add passive thermal buffering and latent-heat storage to printed photopolymer structures, but nominal PCM loading does not establish usable storage capacity. The qualified object must preserve a defined phase-transition interval, latent enthalpy, containment, heat-transfer path, mechanical integrity and cycle stability after printing and post-cure. This review develops a non-compensatory framework for photopolymer/PCM structures spanning directly dispersed and microencapsulated routes. It separates calorimetric storage capacity from leakage resistance, thermal conductivity, geometry-dependent charge/discharge rate and mechanical state. It also treats filler settling, optical attenuation, capsule damage, cure residuals, thermal expansion mismatch and phase-change cycling as coupled manufacturing variables. The central requirement is to qualify stored/released energy in the printed geometry after representative cycling, rather than extrapolating from neat PCM data or initial DSC values.

Keywords: phase-change materials; latent heat; thermal energy storage; photopolymer composites; microencapsulation; vat photopolymerization; thermal cycling; leakage; thermal management; additive manufacturing

## 1. Significance and scope

Photocurable matrices have been used with particulate and encapsulated phase-change materials in direct-ink-writing and vat-photopolymerization routes [1-4]. VPP studies demonstrate that PCM/resin composites can retain measurable latent heat after printing, while loading changes rheology, thermal conductivity, porosity and mechanics [2-4]. The review therefore treats the printed component as a coupled thermal-storage system whose usable energy and response time depend on material state, containment and geometry.

### 1.1 Corpus boundary

Published incumbents retain neighbouring ownership. ER-20 owns final-part thermal performance and thermomechanical qualification; ER-72 owns general environmental ageing; ER-170 owns accelerated-ageing validity; ER-181 owns post-cure process engineering; ER-204 owns transient thermal-history measurement during photopolymerisation; ER-244 owns mixing/settling/bubble state in resin vats; and ER-245 owns resin-vat temperature control. ER-270 owns intentional phase-change/latent-heat function in printed photopolymer structures: PCM identity, containment, latent enthalpy, conductivity, geometry, cycling and thermal-management verification. ER-266 retains supercapacitor energy storage and ER-265 battery components; those electrochemical storage mechanisms are not interchangeable with latent heat.

## 2. Latent heat is a state function, not a loading claim

Usable latent storage depends on the mass fraction that actually undergoes the intended transition and on the enthalpy measured in the final composite. Wei, Cipriani and Pentzer printed photocurable polymer-PCM composites and demonstrated thermal regulation over repeated melting/solidification cycles [1]. Er and co-workers later used VPP with lauric-acid/resin systems and reported that increasing PCM fraction raised latent enthalpy while reducing mechanical performance [2]. A formulation therefore needs both calorimetric and mechanical acceptance. ASTM E793-24 specifies DSC determination of enthalpies of fusion and crystallization, while ISO 11357-3:2025 specifies melting/crystallization temperatures and enthalpies for plastics [5,6]. These methods establish measurement discipline; they do not make neat-PCM results representative of the printed composite.

## 3. Containment route must be identified

Free or shape-stabilized PCM, microencapsulated PCM and chemically bound solid-solid PCM solve different leakage problems. Er and co-workers produced SLA photocurable-resin composites with microencapsulated PCM and measured increasing latent storage with MEPCM content [3]. Melendez and co-workers specifically used MEPCM suspensions in VPP to mitigate leakage risk and characterized capsule distribution after printing [4]. Evidence from one containment route cannot be transferred to another without verifying migration, capsule integrity and phase compatibility.

## 4. Printability couples rheology, optics and phase-change loading

PCM particles or capsules alter viscosity, sedimentation tendency and optical propagation. Higher loading can improve thermal storage while reducing cure depth, increasing scattering or changing recoating. Melendez and co-workers showed that base-resin viscosity affected the printable MEPCM fraction [4]. Qualification should therefore map storage performance against actual printability and dimensional fidelity rather than maximize PCM fraction in isolation.

## 5. Thermal conductivity and latent capacity are separate axes

A material can store substantial latent heat yet charge and discharge too slowly because the polymer matrix and many organic PCMs are poor thermal conductors. Conductive additives, thin walls, fins or topology can reduce thermal resistance, but added non-PCM mass dilutes gravimetric latent heat and can alter cure. Thermal conductivity and effective latent enthalpy must therefore be reported separately and combined only in geometry-specific transient tests.

## 6. Geometry determines useful thermal response

DSC on a milligram sample establishes transition temperature and specific enthalpy but not the time required for a printed component to absorb or release useful heat. Wall thickness, surface area, internal channels, contact resistance, convection and boundary conditions determine the transient response. Thermal management qualification should compare the intended geometry under specified heat flux or temperature history and record both energy and time-domain metrics.

## 7. Cycling must challenge containment and matrix integrity

Repeated phase transitions impose volume change, interfacial shear and thermal expansion mismatch. Capsules can crack or debond; free PCM can migrate through porosity; the photopolymer matrix can fatigue, craze or continue to post-cure. Wei, Cipriani and Pentzer reported repeated-cycle performance for their printed composites [1], but cycle counts and materials remain route-specific. A service claim requires a declared cycle profile, dwell, temperature extrema and post-cycle calorimetry/leakage/mechanical inspection.

8. Transition temperature and hysteresis must match the use case

The melting interval, crystallization interval, supercooling and thermal hysteresis determine when stored energy is available. A high latent enthalpy outside the operating temperature window is not useful. Qualification should report onset, peak and end temperatures for heating and cooling under a declared DSC method and should verify that the larger printed geometry follows the intended thermal window under realistic ramp rates. Heating/cooling rate, specimen mass, calibration and atmosphere should therefore be declared under the selected DSC method [5,6].

9. Non-compensatory qualification matrix

| Gate             | Required evidence                                                           | Blocking failure                                         |
|------------------|-----------------------------------------------------------------------------|----------------------------------------------------------|
| G1 PCM state     | Identity, phase-transition window and final-composite enthalpy measured     | Neat-PCM datasheet substituted for printed-composite DSC |
| G2 Containment   | Leakage/migration and capsule or stabilization integrity demonstrated       | No post-print containment evidence                       |
| G3 Print state   | Rheology, dispersion, cure and geometry remain within qualified window      | Thermal loading maximized while printability drifts      |
| G4 Heat transfer | Conductivity/diffusivity and geometry-dependent transient response measured | Latent heat used as sole thermal-performance metric      |
| G5 Cycling       | Representative phase-change cycles with retained calorimetry and integrity  | Initial-state result extrapolated to lifetime            |
| G6 Mechanics     | Structural integrity maintained through thermal cycles                      | Thermal function accepted despite cracking/debonding     |

10. Minimum reporting set

Report PCM chemistry and grade, encapsulation or stabilization route, PCM fraction on a clearly stated mass/volume basis, photopolymer composition category, printer/wavelength, layer and exposure conditions, mixing history, rheology, specimen orientation, cure/post-cure, DSC method and transition temperatures, melting/solidification enthalpy, thermal conductivity/diffusivity, density/porosity, leakage method, mechanical state, cycle profile and retained properties. For thermal-management demonstrations, report geometry, boundary conditions, sensor locations, heat flux or imposed temperature history and uncertainty.

11. Knowledge boundary

The cited evidence establishes that photocurable polymer/PCM composites can retain latent-heat function after additive manufacturing and that loading, containment route, rheology, conductivity, mechanics and cycling can interact. It does not establish a universal PCM fraction, transition temperature, latent enthalpy, leakage limit, conductivity target, cycle life or thermal-management benefit. DSC values from neat PCM or an uncycled composite do not establish usable storage in the final printed geometry. Qualification therefore remains specific to the printed composite state, containment architecture, declared calorimetric method, geometry, boundary conditions and representative cycling history.

12. Conclusions

A printed phase-change structure is qualified only when latent storage, containment, heat-transfer rate, mechanics and cycling all remain acceptable in the same final state. High PCM fraction or a large DSC peak cannot compensate for leakage, unprintability, inadequate thermal conductance or cycle damage. The strongest evidence connects formulation and print state to final-component calorimetry and transient thermal response after representative cycling.

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