

ORIGINAL RESEARCH ARTICLE

Enhancing the LPBF processability of PLCL powder by suppressing cold crystallization via thermal annealing

Xun Yuan¹, Xiaolu Zheng¹, Junchen Zhou¹, Xinli Wang¹, Feng Chen^{1,2}, Xiaoxiao Han^{1,2}, and Wei Zhu^{1,2*}

¹College of Mechanical and Vehicle Engineering, Hunan University, Changsha, China

²Intelligent Diagnostics and Therapeutic Equipment Innovation Center, Hunan University, Changsha, China

Abstract

Poly(L-lactide-co- ϵ -caprolactone) (PLCL) has emerged as a promising biocompatible copolyester, offering excellent structural flexibility alongside tunable shape-memory properties for advanced biomedical applications. However, its substantial crystallizable amorphous fraction makes it highly susceptible to cold crystallization during powder-bed preheating and laser-induced thermal cycling, resulting in severe powder caking and part warpage during laser powder bed fusion (LPBF). Herein, thermal annealing was used to reduce the crystallizable amorphous fraction available for cold crystallization of PLCL microspheres. Systematic evaluation revealed that annealing at 120 °C for 1 h nearly eliminated the cold-crystallization peak and increased XRD-derived crystallinity of the PLCL microspheres from 34.9% to 47.1%. Meanwhile, the annealed powder retained sufficient elevated-temperature mobility to support stable recoating at a nominal powder-bed preheating temperature of 100 °C, successfully mitigating part warpage during LPBF. At a selected volumetric energy density of 0.37 J/mm³, the printed specimens exhibited an apparent porosity of 11.7 ± 0.4%, a tensile modulus of 206.62 ± 61.39 MPa, and a tensile strength of 5.91 ± 0.72 MPa. The elongation at break reached approximately 180% at 37 °C. As a proof of concept, a PLCL scaffold with a triply periodic minimal surface (TPMS) architecture containing curved and overhanging features was successfully fabricated. These results support thermal annealing as a feasible pretreatment strategy for the LPBF processing of PLCL microspheres and provide a basis for future studies of temperature-responsive PLCL scaffolds.

*Corresponding author:

Wei Zhu
(zhuwei@hnu.edu.cn)

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1. Introduction

Poly(L-lactide-co- ϵ -caprolactone) (PLCL) is a promising biodegradable shape-memory copolyester for bone repair, owing to its tunable transition temperature, adjustable mechanical properties, and favorable biocompatibility.¹⁻³ PLCL is synthesized by copolymerizing L-lactide (L-LA) and ϵ -caprolactone (ϵ -CL), and its shape-memory transition properties can be adjusted primarily by changing the L-LA-to- ϵ -CL ratio.⁴⁻⁶ Increasing the ϵ -CL content enhances chain flexibility and lowers the glass-transition

temperature, thereby reducing the shape-recovery temperature and increasing deformability. In contrast, increasing the L-LA content generally increases the glass-transition temperature, stiffness, and crystallization capacity.^{6,7} These characteristics make PLCL a promising material for bone scaffolds intended for minimally invasive implantation and to facilitate bone regeneration. A PLCL scaffold can be programmed into a compact temporary configuration outside the body, delivered through a small surgical access, and subsequently recover its permanent geometry at body temperature.^{8,9} This behavior allows the scaffold to conform more closely to the defect boundary, reducing interfacial gaps and improving mechanical contact with the surrounding tissue.^{10,11} The recovery process may also generate transient mechanical cues at the scaffold–tissue interface, which could influence mechanosensitive cellular activities associated with osteogenic differentiation.^{12–14}

Bone scaffolds often require complex three-dimensional architectures, including interconnected pores, internal channels, and curved surfaces, to satisfy structural and functional requirements. Three-dimensional (3D) printing provides a suitable approach for fabricating such structures. The integration of shape-memory PLCL with 3D printing further enables four-dimensional (4D) printing, in which printed scaffolds undergo programmed shape changes over time in response to external stimuli.^{15–19} Commonly used 3D printing techniques for processing PLCL include fused deposition modeling (FDM) and direct ink writing (DIW).^{20,21} Although these techniques can produce porous PLCL scaffolds, their printing accuracy and geometric freedom are constrained by nozzle diameter, filament or ink rheology, interlayer bonding, and the continuous deposition of material strands. Additional support structures may also be required to fabricate complex overhangs, enclosed channels, and continuously curved surfaces.^{22,23} Laser powder bed fusion (LPBF) provides a support-free alternative by selectively fusing successive powder layers, while the surrounding loose powder supports the structure during fabrication.^{24,25} LPBF is therefore particularly suitable for fabricating scaffolds with interconnected pores, thin walls, complex overhanging architectures.^{26–29} In our previous work, spherical PLCL microspheres with a suitable particle-size distribution and satisfactory spreadability were prepared using an oil-in-water emulsion solvent-evaporation process.³⁰ As an initial proof of concept, strip-shaped specimens were fabricated from these microspheres using a substrate-assisted LPBF approach. The specimens exhibited shape-fixity and shape-recovery ratios exceeding 90%, with shape recovery triggered at 37 °C. Nevertheless, the powder remained difficult to process into complex unsupported structures. This limitation arose because the semi-

crystalline PLCL microspheres retained a substantial crystallizable amorphous fraction that underwent cold crystallization during powder-bed preheating and laser-induced thermal cycling. The resulting powder caking and part warpage compromised process stability. Regulating the initial crystalline state of PLCL powder to suppress cold crystallization during processing is therefore essential for the reliable LPBF fabrication of complex structures.

Thermal annealing provides a direct means of regulating the initial crystalline state of PLCL powder before printing.³¹ At an appropriate temperature below the melting onset, increased segmental mobility may promote the rearrangement and crystallization of L-LA sequences, thereby reducing the crystallizable amorphous fraction available for cold crystallization during subsequent LPBF processing.³² Suppressing this transition can reduce powder caking and crystallization-induced contraction, allowing the use of a higher powder-bed preheating temperature. The resulting decrease in thermal gradients slows melt cooling, promotes particle coalescence and interlayer bonding, and limits residual-stress accumulation and warpage. However, annealing may also alter particle-surface properties, interparticle cohesion, powder-bed uniformity, and the energy required for complete melting. Excessive annealing temperatures or holding times may cause particle adhesion, excessive crystal growth or perfection, and thermal degradation. The effects of annealing on PLCL crystallization, elevated-temperature powder spreading, and subsequent LPBF consolidation therefore require systematic investigation.

Accordingly, this study employed thermal annealing to reduce the crystallizable amorphous fraction available for cold crystallization in PLCL microspheres, thereby improving their LPBF processability. PLCL microspheres were annealed at 90 or 120 °C for different durations, and the resulting changes in thermal behavior, crystalline structure, particle morphology, and powder-bed uniformity were characterized. The elevated-temperature mobility and LPBF processing behavior of the annealed powder were subsequently evaluated. The microstructure, apparent porosity, and tensile properties of the printed specimens were analyzed, and a PLCL scaffold with triply periodic minimal surface (TPMS) architecture was fabricated as a proof-of-concept demonstration. Particular attention was paid to the relationship among annealing-induced crystallization, powder behavior, and the processing response of PLCL during LPBF.

2. Materials and methods

2.1. Materials

L-Lactide (L-LA; purity $\geq 99.5\%$, $M = 144.125$ g/mol) was

supplied by Daigang Biomaterial Co., Ltd. (Jinan, China). ϵ -Caprolactone (ϵ -CL; purity $\geq 99\%$, $M = 114.142$ g/mol), dichloromethane (DCM; purity $\geq 99.5\%$), and poly(vinyl alcohol) (PVA) were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Stannous octoate ($\text{Sn}(\text{Oct})_2$, purity $\geq 95\%$, $M = 405.12$ g/mol) was supplied by Adamas Reagent Co., Ltd. (Shanghai, China). Absolute ethanol (analytical grade) was purchased from InnoChem Science & Technology Co., Ltd. (Beijing, China).

2.2. Synthesis of PLCL copolymer

PLCL copolymer was synthesized via ring-opening copolymerization.^{33,34} Briefly, L-LA was placed in a flask and subjected to three vacuum–nitrogen purge cycles (10 min per cycle) using a Schlenk line to remove residual air and moisture. ϵ -CL was subsequently added at an L-LA/ ϵ -CL molar feed ratio of 75:25. The flask was heated in an oil bath at 140 °C until the monomers were completely melted, after which stannous octoate was added at a total monomer-to-catalyst molar ratio of 2000:1. Polymerization was carried out under a nitrogen atmosphere at 140 °C for 24 h. The product was dissolved in DCM and precipitated in absolute ethanol to remove unreacted monomers and residual catalyst. After filtration, the copolymer was dried under vacuum at 40 °C to constant weight and denoted as PLCL.

2.3. Preparation of PLCL microspheres

PLCL microspheres were prepared using an oil-in-water emulsion solvent-evaporation method.^{30,35} Briefly, PLCL was dissolved in DCM at a concentration of 0.01 g mL⁻¹ to form the oil phase. The solution was slowly added to an aqueous PVA solution (0.01 g/mL⁻¹) and emulsified at 9000 rpm for 10 min using a high-shear homogenizer. The dispersed oil droplets were stabilized by PVA, forming an oil-in-water emulsion. After emulsification, the mixture was continuously stirred to evaporate the DCM. The resulting microspheres were collected by centrifugation and washed repeatedly with deionized water to remove residual PVA. Finally, the microspheres were freeze-dried and sieved before further use.

2.4. Thermal annealing of PLCL

A loose layer of PLCL microspheres was placed in a ceramic crucible and annealed in a forced-air drying oven (WGL-45B, Tianjin Taisite Instrument Co., Ltd., China) under ambient-air conditions. The manufacturer-specified temperature fluctuation and temperature-distribution accuracy were ± 1 °C and $\pm 2.5\%$, respectively. The powder was introduced at room temperature, and the oven was set directly to 90 or 120 °C. After the target temperature was reached, the powder was held for 1, 2, or 3 h and then

allowed to cool naturally to room temperature inside the oven. The annealing temperatures were selected based on the first-heating differential scanning calorimetry (DSC) profile of the PLCL microspheres. The lower temperature of 90 °C was slightly above the cold-crystallization onset temperature (86.6 °C) but below the cold-crystallization peak temperature (99.5 °C), thereby allowing the effects of annealing within the cold-crystallization interval to be evaluated. In contrast, 120 °C was above the cold-crystallization peak but below the melting onset temperature (146.2 °C), providing greater segmental mobility to promote chain rearrangement and crystallization without inducing bulk melting. Temperatures below the cold-crystallization onset were not investigated because the reduced segmental mobility and slower crystallization kinetics were expected to produce only limited structural changes within the selected annealing duration. The annealed samples were named according to annealing temperature and time: A90-1h, A90-2h, A90-3h, A120-1h, A120-2h, and A120-3h. The unannealed microspheres were designated UA.

2.5. Powder characterization

The crystallization behavior of the PLCL microspheres was evaluated using DSC and X-ray diffraction (XRD). DSC measurements were performed using a DSC204F1 instrument (NETZSCH, Germany). The samples were heated from 0 to 180 °C under nitrogen at a heating rate of 10 °C min⁻¹. The first heating scan was analyzed because it reflects the thermal history of the microspheres.

XRD patterns were recorded using a Bruker D8 Advance diffractometer (Bruker, Germany) in continuous-scan mode over a 2θ range of 5–65°, with a scan rate of 2° min⁻¹ and a step size of 0.005°. The diffraction data were processed using Jade 9.0 software. Before peak deconvolution, the background was estimated and subtracted using the built-in background-correction function, followed by mild smoothing to reduce high-frequency noise without altering the peak positions or widths. Each diffraction pattern was fitted over the complete measured range using four crystalline reflections centered at approximately 14.8°, 16.7°, 19.1°, and 22.4°, together with one broad amorphous halo. The same number of fitting components and initial peak positions were used for all samples to ensure comparability. The crystalline peaks and amorphous halo were described using pseudo-Voigt functions, while their positions, widths, and intensities were allowed to vary during fitting. The goodness of fit was evaluated using the coefficient of determination (R^2), the weighted-profile residual (Rwp), and the distribution of the residuals. All fitted patterns satisfied $R^2 \geq 0.99$ and $Rwp \leq 10\%$, and the residuals were randomly distributed

around zero without systematic or peak-shaped features. A full width at half maximum (FWHM) of approximately 3° was used as the empirical threshold for distinguishing the relatively narrow crystalline reflections from the broad amorphous contribution. The XRD-derived crystallinity was calculated as follows³⁶:

$$X_c = \frac{A_{crystal}}{(A_{crystal} + A_{amorphous})} \quad (1)$$

where $A_{crystal}$ and $A_{amorphous}$ are the integrated areas of the crystalline peaks and amorphous halo, respectively.

The morphology of the PLCL microspheres was examined by scanning electron microscopy (SEM; MIRA4 LMH, TESCAN, Czech Republic). Powder-bed topography was characterized by confocal laser scanning microscopy (CLSM). A 50 mm × 50 mm × 5 mm substrate containing a groove 10 mm in width and 0.4 mm in depth was used for the spreading test. Each powder was spread into the groove and leveled with a blade to reproduce the powder-spreading process used in LPBF. For each annealing condition, three randomly selected areas were examined using CLSM. Each measured area covered approximately 2.5 mm × 2.5 mm. The S_a value of each area was calculated separately using ConfoMap, and the results are reported as the mean ± standard deviation of the three measured areas ($n = 3$ areas). Powder mobility at elevated temperature was evaluated qualitatively using a vial-tilting method. Approximately 5 g of each powder (UA, A90-1h, and A120-1h) was placed in an identical glass vial. The heated samples were maintained at 80 °C for 30 min, and each condition was evaluated once. The vials were then slowly tilted to approximately 45° to determine whether the powders moved freely along the vial wall or remained as cohesive plugs. Powder beds obtained after preheating were also photographed to assess agglomeration, recoater drag marks, displacement of previously formed layers, and surface continuity.

2.6. Scaffold fabrication

Scaffold specimens were fabricated using a Sharebot SnowWhite2 LPBF system. Before printing, the PLCL microspheres were dried at 40 °C for 12 h to minimize residual moisture. The dried powder was then loaded into the build chamber and preheated.

A qualitative stepwise preheating test was used to identify a suitable nominal powder-bed preheating temperature. The initial assessment at 80 °C included both UA and A120-1h; stepwise testing at 90 and 100 °C was continued only for A120-1h. Thus, nominal setpoints of 80, 90, and 100 °C were examined for A120-1h in 10 °C

increments. No additional user-defined holding period was imposed at any setpoint. Once the programmed nominal preheating temperature was reached, the machine automatically initiated the printing sequence according to its preset control procedure, and powder recoating proceeded automatically on a layer-by-layer basis. The number of recoating cycles was not prescribed as an independent experimental variable, and the exact number completed at each setpoint was not separately recorded. The observations included powder-bed spreading and caking and, where printing could proceed, recoater-induced movement of previously sintered layers and visible specimen warpage. When poor spreading, visible warpage, or layer movement was observed, the nominal preheating temperature was increased and the printing test was repeated. The lowest tested temperature that produced a stable, uniform powder bed without visible specimen warpage or recoater-induced layer movement was selected for subsequent printing. This test was used as a qualitative process-screening procedure.

During printing, only the laser power (P) was varied, with values of 5.6, 7.4, 9.4, and 11.2 W. The scan speed (v), hatch spacing (s), and layer thickness (h) were fixed at 2000 mm s⁻¹, 0.1 mm, and 0.1 mm, respectively. The volumetric energy density (ED) was calculated as follows³⁷:

$$ED = \frac{P}{v \cdot s \cdot h} \quad (2)$$

The corresponding ED values were 0.28, 0.37, 0.47, and 0.56 J/mm³. For the UA microspheres, an additional substrate was installed in the build area to reduce warpage. Based on our previous optimization³⁰, the laser power, scan speed, hatch spacing, and layer thickness were set to 4.2 W, 600 mm s⁻¹, 0.05 mm, and 0.1 mm, respectively, corresponding to an ED of 1.40 J/mm³. After printing, the specimens were removed from the powder bed, and the excess loose powder was carefully removed. The specimens were subsequently classified and labeled according to the powder condition and ED.

2.7. Microstructure of printed specimens

The internal microstructure of the printed specimens was characterized by paraffin-assisted sectioning combined with multimodal optical microscopy. Paraffin embedding provides mechanical support for the porous specimens, allowing thin sections to be prepared without severe deformation or structural collapse. Specifically, the printed specimens (20 mm × 4 mm × 1.5 mm) were infiltrated and embedded with low-melting-point paraffin (melting point: 56 °C). After solidification, 10 μm-thick sections were cut along the build direction (Z-axis) using a rotary microtome

and mounted on glass slides. The sections were examined under a polarized-light microscope in bright-field (BF), dark-field (DF), and polarized optical microscopy (POM) modes to assess layer interfaces, pore structure, and crystalline features.

2.8. Mechanical properties and porosity of printed specimens

The tensile properties of the printed specimens were measured using a universal testing machine (AGS-X, Shimadzu, USA). Type 5B specimens were prepared according to ISO 527-2 and tested at either 25 or 37 °C at a crosshead speed of 2 mm min⁻¹. Tensile modulus, tensile strength, and elongation at break were determined from the stress-strain curves. The tensile testing was performed using three independently fabricated specimens ($n = 3$).

The apparent porosity of the printed specimens was measured using the Archimedes method with a precision balance equipped with a density determination kit. The dry mass of each specimen in air was first recorded as (m_1). The specimen was then immersed in deionized water under vacuum until no air bubbles were observed, ensuring that the internal pores were fully infiltrated. After gently removing excess surface water with water-saturated tissue, the saturated mass in air was recorded as (m_2). The apparent mass of the saturated specimen suspended in water was subsequently recorded as (m_3). At least three specimens were measured for each condition, and the apparent porosity (P) was calculated as follows³⁸:

$$P = \frac{m_2 - m_1}{m_2 - m_3} \times 100\% \quad (3)$$

2.9. Statistical analysis

Data are expressed as mean $\pm$ standard deviation. Where a single factor was statistically compared across more than two groups, one-way analysis of variance (ANOVA) was used, with $p < 0.05$ and $p < 0.01$ considered statistically significant.

3. Results and discussion

3.1. Effect of annealing on the crystallization behavior of PLCL microspheres

To evaluate the effect of thermal annealing on the crystallization behavior of the PLCL microspheres, DSC and XRD analyses were performed. As shown in Figure 1a and 1b, the UA samples exhibited a pronounced cold-crystallization peak (T_c) centered at approximately 100 °C, followed by a melting peak (T_m) centered at approximately 155 °C. The presence of this cold-crystallization peak

indicated that the PLCL microspheres contained a considerable fraction of crystallizable amorphous regions. During LPBF, the transient heat generated by laser scanning could induce cold crystallization in the heat-affected material before melting occurred. The resulting heat release and crystallization-induced contraction could amplify local thermal and strain heterogeneity, thereby promoting residual-stress accumulation and warpage of the printed specimens.³⁹ This peak was markedly suppressed after annealing at either 90 or 120 °C, indicating that a substantial fraction of the crystallizable chains had already crystallized during thermal annealing. Notably, the peak was almost completely eliminated in the A120 samples, whereas a weak step-like variation remained in the original cold-crystallization region of the A90 samples and showed no appreciable change with increasing holding time. These results indicated that annealing at 120 °C, above the cold-crystallization peak temperature, was more effective in allowing the crystallizable chains to reorganize and crystallize before subsequent heating.

The first-heating DSC curves were differentiated to identify the thermal-transition boundaries more clearly and to compare the stable preheating temperature window of the PLCL microspheres, defined as the interval between the cold-crystallization endset temperature ($T_{cc-endset}$) and the melting onset temperature ($T_{m-onset}$) (Figure 1c and 1d). The preheating temperature window was widened after annealing, with a more pronounced increase observed for the samples annealed at 120 °C. This change was attributed mainly to the thermal history introduced during thermal annealing rather than to a fundamental shift in the intrinsic thermal transitions of PLCL. During annealing, chain rearrangement and crystallization occurred near the annealing temperature. In the subsequent DSC scan, the resulting thermal-history effect appeared as a step-like heat-flow variation and altered the corresponding first-derivative curve. For the samples annealed at 90 °C, this heat-flow variation overlapped with the original cold-crystallization region. Structural changes therefore began at a relatively low temperature during reheating, which could increase the risk of thermal adhesion and agglomeration during powder-bed preheating. In contrast, after annealing at 120 °C, the main heat-flow variation was shifted toward the melting region. Although a broader preheating temperature window was obtained, the thermal event occurred well above the temperature range used for powder-bed preheating and was therefore less likely to impair powder spreading.

Quantitative thermal parameters extracted from the DSC curves were used to evaluate the effect of thermal annealing on the cold-crystallization behavior of the PLCL

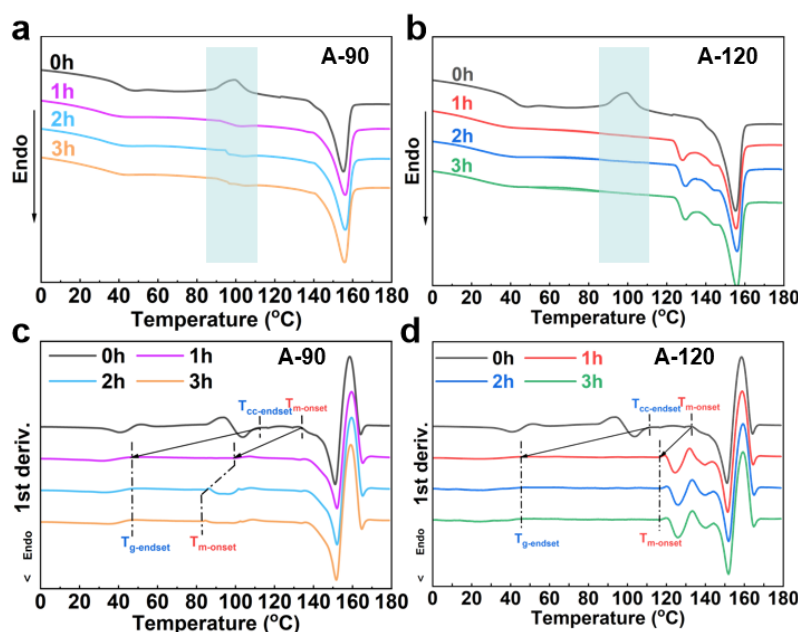


Figure 1. First-heating DSC curves of PLCL powder annealed at (a) 90 °C and (b) 120 °C for 0–3 h, with the corresponding first-derivative curves in (c) and (d).

Abbreviations: DSC: Differential scanning calorimetry; PLCL: Poly(L-lactide-co-ε-caprolactone).

Table 1. Thermal parameters, XRD-derived crystallinity, and powder-bed areal roughness of PLCL microspheres subjected to different annealing conditions

Group	Cold-crystallization enthalpy, ΔH_{cc} (J g ⁻¹)	Melting enthalpy, ΔH_m (J g ⁻¹)	XRD-derived crystallinity (%)	S_a (μm)
UA	8.013	21.093	34.9	63.22 ± 0.58
A90-1h	—	—	41.7	62.19 ± 0.48
A90-2h	—	—	41.2	65.49 ± 3.68
A90-3h	—	—	40.7	61.67 ± 1.61
A120-1h	1.415	27.359	47.1	63.47 ± 5.16
A120-2h	1.722	27.888	46.2	70.97 ± 1.78
A120-3h	1.621	28.827	45.8	68.53 ± 1.77

Abbreviations: PLCL: Poly(L-lactide-co-ε-caprolactone); XRD: X-ray diffraction.

microspheres, and the results are summarized in Table 1. The UA samples exhibited a cold-crystallization enthalpy (ΔH_{cc}) of 8.013 J g⁻¹ and a melting enthalpy (ΔH_m) of 21.093 J g⁻¹. After annealing at 120 °C for 1, 2, and 3 h, ΔH_{cc} decreased markedly to 1.415, 1.722, and 1.621 J g⁻¹, whereas ΔH_m increased to 27.359, 27.888, and 28.827 J g⁻¹, respectively. The marked reduction in cold-crystallization enthalpy provided quantitative evidence that thermal annealing suppressed the cold-crystallization behavior of

PLCL. Quantitative DSC parameters were not reported for the A90 samples because the step-like heat-flow variation overlapped with the original cold-crystallization region, preventing reliable baseline determination and integration of ΔH_{cc} .

XRD was further used to assess the crystalline structure of the PLCL microspheres. As shown in Figure 2, the UA microspheres exhibited diffraction peaks at 2θ values of

approximately 14.8° , 16.7° , 19.1° , and 22.4° , corresponding to the (010), (110/200), (203), and (015) planes of α -form PLLA crystals, respectively. No distinct reflections associated with crystalline ϵ -CL sequences were detected, indicating that the crystalline regions were mainly formed by ordered L-LA sequences. After thermal annealing, these characteristic peaks became sharper and more distinct, suggesting an increase in crystalline order. The XRD-derived crystallinity calculated by peak deconvolution is summarized in Table 1. The largest increase was observed for the A120-1h samples, whose XRD-derived crystallinity reached 47.1%, compared with 34.9% for the UA samples.

3.2. Powder flowability

The morphology of the PLCL microspheres was examined by SEM to determine whether it was affected by thermal

annealing. As shown in Figure 3, the microspheres retained their overall spherical shape after annealing at 90 or 120 $^\circ\text{C}$ for 1–3 h. No obvious particle collapse, surface melting, or extensive interparticle fusion was observed under any of the annealing conditions. Thus, the selected annealing temperatures were sufficient to alter the crystalline structure of PLCL without causing macroscopic melting or loss of particle integrity.

Although SEM revealed no obvious changes in microsphere morphology after thermal annealing, the accompanying chain rearrangement and crystal evolution might have affected interparticle contact, friction, and cohesion. The surface topography of the spread powder beds was therefore measured to evaluate the effect of thermal annealing on powder-bed quality. The CLSM height maps in Figure 4 showed the distribution of peaks

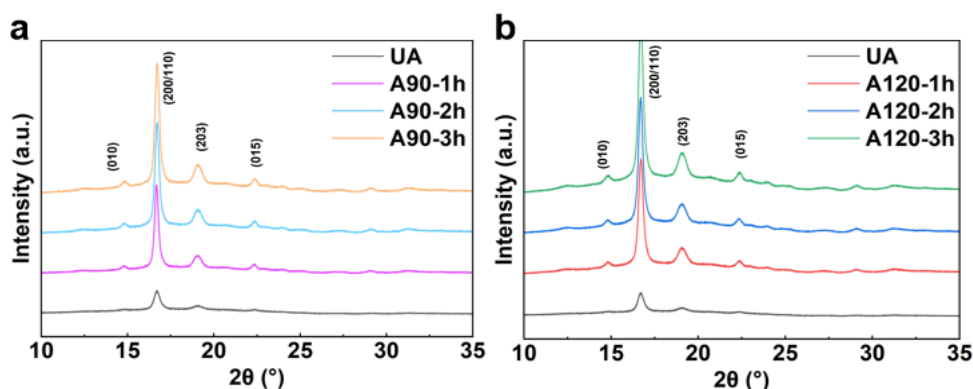


Figure 2. X-ray diffraction patterns of (a) PLCL powder annealed at 90 $^\circ\text{C}$ for 0–3 h and (b) PLCL powder annealed at 120 $^\circ\text{C}$ for 0–3 h
Abbreviation: PLCL: Poly(L-lactide-co- ϵ -caprolactone).

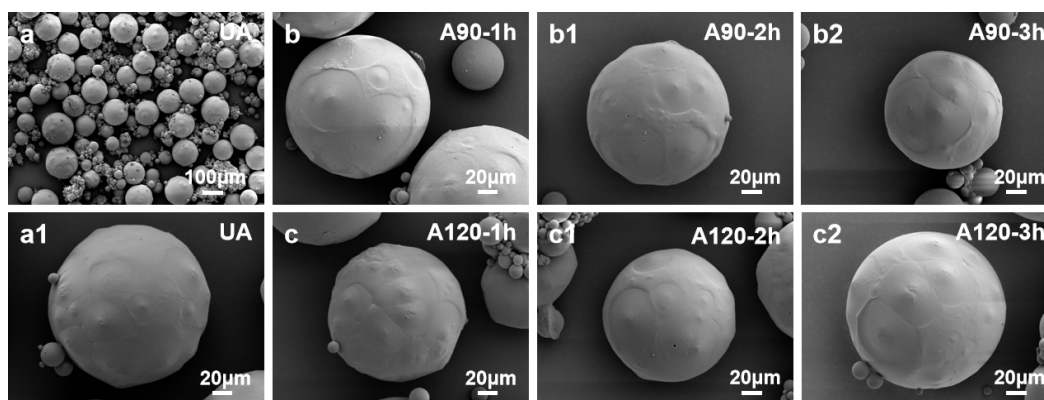


Figure 3. SEM images of PLCL microspheres: (a, a1) UA at low and high magnifications, respectively; (b, b1, b2) microspheres annealed at 90 $^\circ\text{C}$ for 1, 2, and 3 h, respectively; and (c, c1, c2) microspheres annealed at 120 $^\circ\text{C}$ for 1, 2, and 3 h, respectively
Abbreviations: PLCL: Poly(L-lactide-co- ϵ -caprolactone); SEM: Scanning electron microscopy.

and depressions across the powder-bed surfaces. The areal roughness (S_a) was used to quantify powder-bed uniformity.⁴⁰ A lower S_a value indicated a smoother and more uniform powder layer, although it did not directly represent the intrinsic flowability or packing density of the microspheres. The S_a values obtained under the different annealing conditions are presented in Figure 4 and Table 1. The UA powder bed exhibited an S_a value of $63.22 \pm 0.58 \mu\text{m}$. After annealing at 90°C for 1, 2, and 3 h, the S_a values were 62.19 ± 0.48 , 65.49 ± 3.68 , and $61.67 \pm 1.61 \mu\text{m}$, respectively. These values remained close to that of UA, indicating that annealing at 90°C had little effect on the uniformity of the spread powder layer. For the samples annealed at 120°C , the S_a values were 63.47 ± 5.16 , 70.97 ± 1.78 , and $68.53 \pm 1.77 \mu\text{m}$ after 1, 2, and 3 h, respectively. Although the mean value for the A120-1h samples was close to that of the UA samples, greater variation was observed among the measured areas for the A120-1h samples. These results suggested that, within the scope of the present local CLSM measurements, annealing at 120°C did not substantially alter the mean local surface roughness of the powder bed, although greater spatial variation was observed among the measured areas. Overall, annealing had only a limited effect on the surface roughness and spreading behavior of the PLCL microspheres under the investigated conditions.

To qualitatively assess the effect of annealing on powder mobility at elevated temperature, equal amounts of UA and annealed microspheres were placed in identical glass vials and heated under the same conditions at 80°C (Figure 5a). The vials were then slowly tilted to compare the movement

of the powders. The annealed microspheres flowed along the vial wall and gradually settled at the bottom. In contrast, the UA microspheres remained as a cohesive plug even when the vial was inverted, indicating pronounced thermal agglomeration. These observations suggested that annealing reduced the tendency of the PLCL microspheres to adhere and agglomerate at elevated temperature, thereby improving their mobility under powder-bed preheating conditions.

Overall, thermal annealing altered the crystalline structure and elevated-temperature behavior of the PLCL microspheres without causing visible melting, particle collapse, or extensive interparticle fusion. Annealing at 120°C was more effective than annealing at 90°C in suppressing cold crystallization. Extending the annealing time from 1 to 3 h produced little further change in the DSC curves and crystallinity. The A120-1h samples were therefore selected for the subsequent experiments.

3.3. LPBF processing and microstructure of PLCL

The powder-bed preheating temperature was determined using the stepwise approach described above. The results are shown in Figure 5. At a nominal preheating temperature of 80°C , the UA microspheres showed pronounced caking and agglomeration, with a marked loss of powder mobility. The recoater could not form a continuous, uniform powder layer, and local powder accumulation and drag marks were observed on the bed surface. UA was therefore not further evaluated at 90 or 100°C . For the A120-1h samples, severe specimen warpage and movement of the previously sintered layer during recoating were observed at

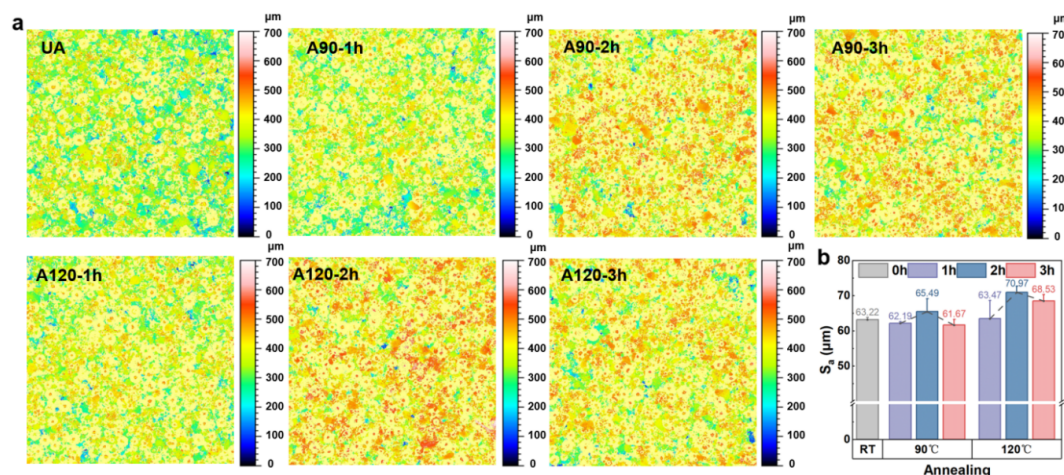


Figure 4. CLSM surface maps (a) and areal roughness S_a of blade-spread PLCL powder beds after different annealing treatments (b). Values are reported as the mean $\pm$ standard deviation from three randomly selected measurement areas for each condition ($n = 3$)
Abbreviations: CLSM: Confocal laser scanning microscopy; PLCL: Poly(L-lactide-co- ϵ -caprolactone).

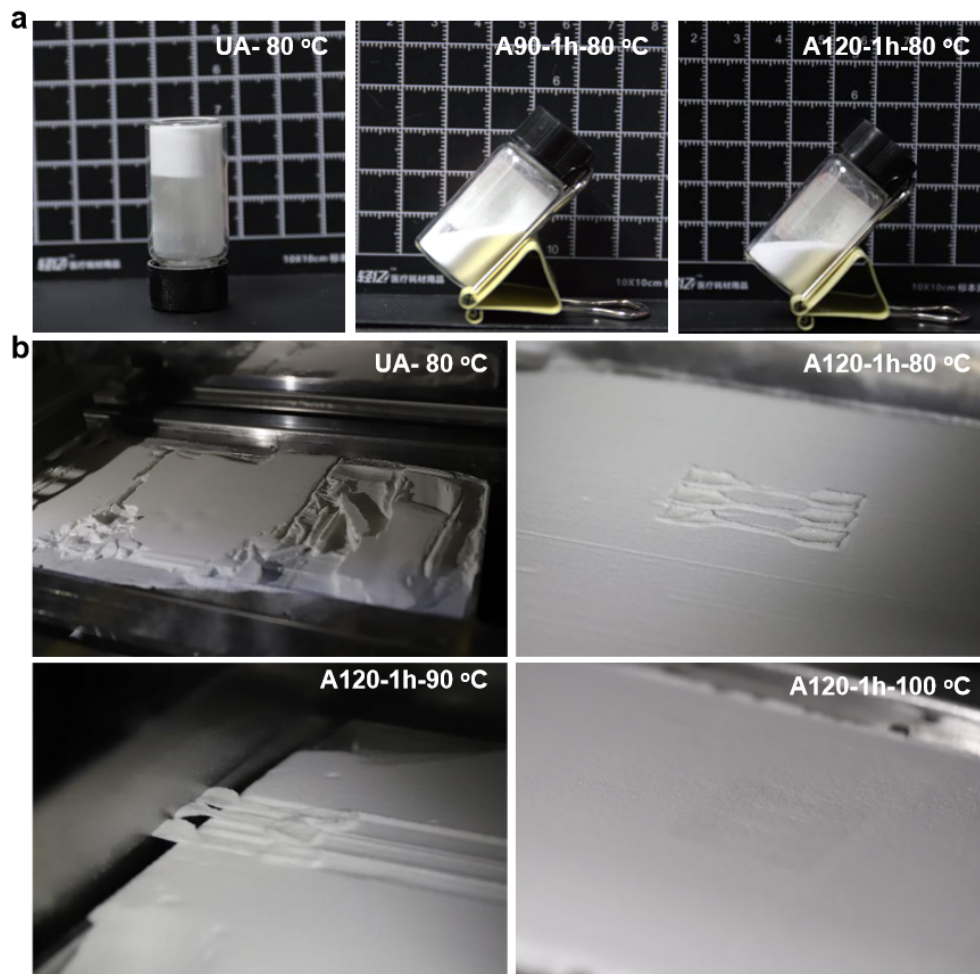


Figure 5. Qualitative vial-flow comparison of UA and annealed PLCL microspheres after heating to 80 °C (a) and powder-bed/part response during the stepwise preheat test (b)

Abbreviation: PLCL: Poly(L-lactide-co- ϵ -caprolactone).

80 °C. At 90 °C, warpage was reduced, but slight warpage and recoater-induced layer movement were still observed. At the nominal preheating temperature of 100 °C, the recorded powder temperature in the build chamber was 92 °C; the powder bed remained stable and uniform, with no visible specimen warpage or recoater-induced movement of the sintered layer. Therefore, 100 °C was selected as the nominal powder-bed preheating temperature for subsequent printing because it was the lowest tested setpoint that met both the powder-spreading and part-stability criteria.

The internal microstructures of the A120-1h specimens printed at different volumetric energy densities (EDs) were examined by bright-field (BF), dark-field (DF), and polarized optical microscopy (POM). The microstructure

of a UA specimen produced by substrate-assisted printing without powder-bed preheating was also examined for comparison (Figure 6). Despite the higher ED, the UA specimen exhibited a discontinuous internal structure containing irregular, interconnected pores of varying sizes. Numerous incompletely fused microspheres were observed, as indicated by the red circles, and only limited neck formation occurred between adjacent particles. In the DF image, the unevenly distributed scattering signals and locally bright regions were consistent with the presence of particle interfaces and microvoids. In comparison, the A120-1h specimens exhibited more continuous internal structures across the investigated ED range. Most of the original microsphere boundaries disappeared, while the remaining pores generally had smoother and more rounded profiles than those in the UA specimen.

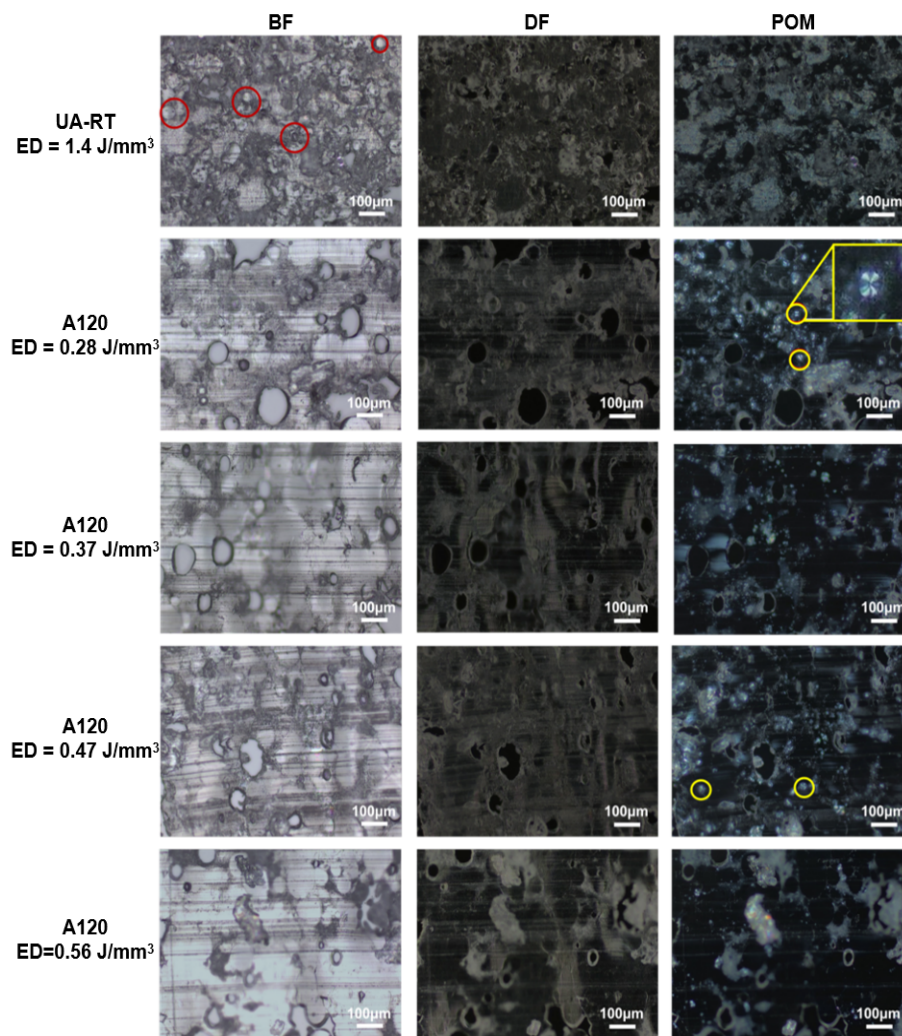


Figure 6. Bright-field (BF), dark-field (DF), and polarized optical microscopy (POM) images of the UA specimens fabricated using a low-temperature substrate without powder-bed preheating (UA-RT) at an ED of 1.40 J/mm^3 , and A120-1h specimens fabricated at a nominal powder-bed preheating temperature of 100°C and EDs of 0.28 , 0.37 , 0.47 , and 0.56 J/mm^3 .

Increasing the ED generally promoted microsphere melting and interparticle fusion, although no continuous improvement in densification was observed at higher EDs. Overall, the A120-1h specimens printed with powder-bed preheating showed markedly better structural continuity than the UA specimen printed without preheating, despite the substantially lower EDs used.

The POM images provided further qualitative information on the crystalline structure of the printed specimens. The UA specimen showed relatively weak and heterogeneous birefringence, whereas the A120-1h specimens exhibited more distinct and broadly distributed birefringent regions. Maltese-cross-like extinction patterns were observed in some regions, consistent with the

formation of spherulitic structures. These observations suggested that the thermal history introduced by thermal annealing, together with the slower cooling and greater chain mobility provided by powder-bed preheating, promoted the development of more ordered crystalline domains during solidification.

3.4. Mechanical properties and porosity of printed specimens

The mechanical properties and apparent porosity of the A120-1h specimens are shown in Figure 7. Overall, the mechanical properties initially improved and then declined with increasing ED, with the best performance obtained at 0.37 J/mm^3 (Figure 7a-7c). As the ED increased from

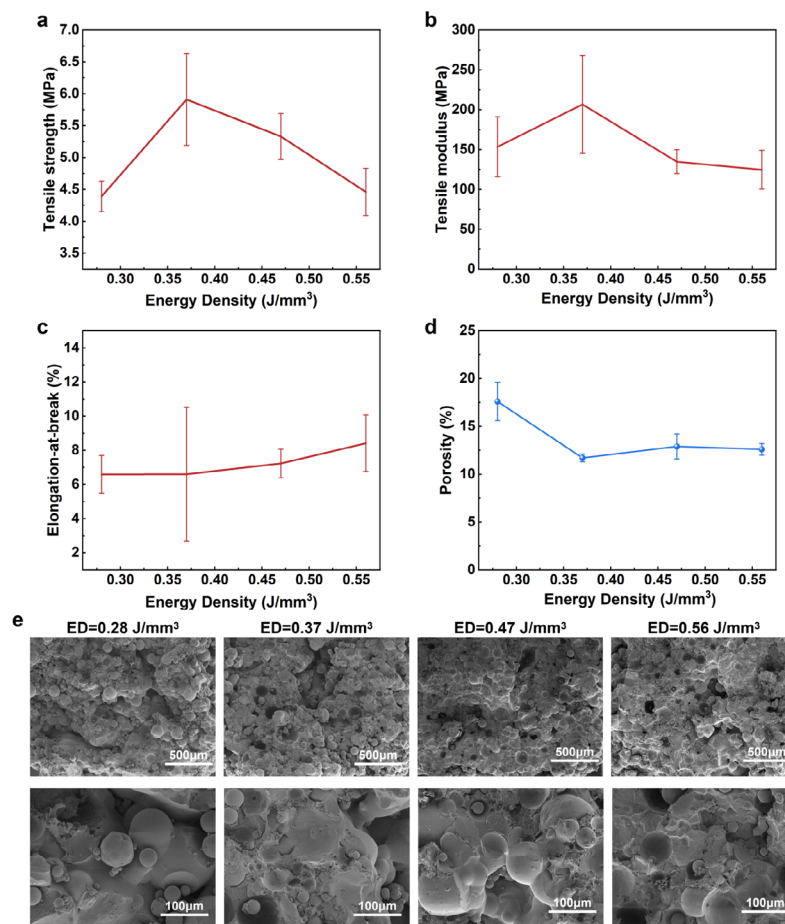


Figure 7. Mechanical properties, apparent porosity, and fracture morphologies of A120-1h specimens fabricated at different energy densities: (a) tensile strength, (b) tensile modulus, (c) elongation at break, (d) apparent porosity, and (e) fracture-surface SEM images
Abbreviation: SEM: Scanning electron microscopy.

0.28 to 0.37 J/mm³, the tensile strength increased from 4.39 to 5.91 MPa, while the tensile modulus increased from 153.46 to 206.62 MPa. At EDs of 0.47 and 0.56 J/mm³, the tensile strength decreased to 5.33 and 4.46 MPa, respectively, and the corresponding tensile moduli decreased to 134.76 and 124.72 MPa. The elongation at break ranged from 6.59% to 8.41% and showed no clear dependence on ED. The apparent porosity remained below 18% across the investigated ED range (Figure 7d). It decreased from 17.6% at 0.28 J/mm³ to a minimum of 11.7% at 0.37 J/mm³ and then remained between 12.6% and 12.9% at higher EDs. These results suggested that an ED of 0.37 J/mm³ provided the most favorable fusion and load-bearing continuity. Further increases in ED produced no additional densification and might have increased local structural heterogeneity. The residual voids observed on the fracture surfaces were consistent with the measured porosity (Figure 7e).

The tensile behavior of the A120-1h specimens was also evaluated at 37 °C to simulate their mechanical response under physiological conditions. As shown in Figure 8, the elongation at break increased from approximately 6%–8% at 25 °C to approximately 180% at 37 °C. These results showed that the printed specimens retained substantial deformability at physiological temperature, which could facilitate their compression and deployment during minimally invasive implantation.

3.5. Fabrication of TPMS scaffolds

As a proof of processability, a TPMS scaffold containing complex curved surfaces and overhanging features was fabricated using the A120-1h samples at a preheating temperature of 100 °C and an ED of 0.37 J/mm³. As shown in Figure 9, the printed scaffold visually reproduced the designed curved topology and interconnected pore structure while maintaining its overall structural integrity.

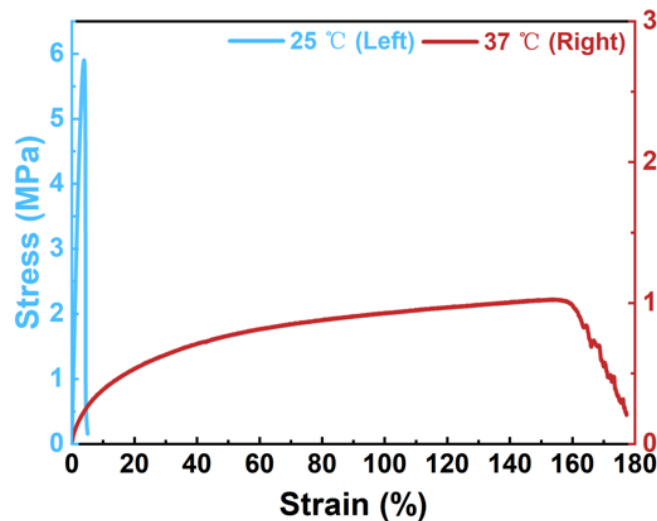


Figure 8. Stress–strain curves of the printed A120-1h specimens tested at 25 and 37 °C

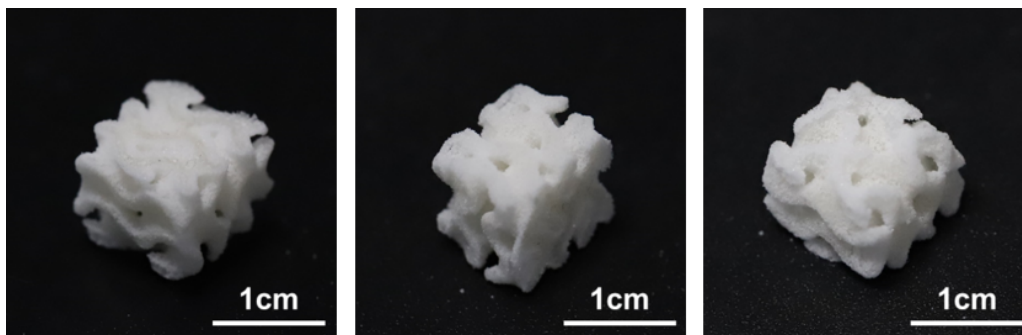


Figure 9. Photographs of a representative TPMS scaffold fabricated using A120-1h microspheres under the optimized processing conditions
Abbreviation: TPMS: Triply periodic minimal surface.

4. Conclusion

Thermal annealing markedly enhanced the LPBF processability of PLCL microspheres by regulating their initial crystalline state and suppressing cold-crystallization behavior. On the one hand, the annealed microspheres tolerated a higher powder-bed preheating temperature without severe caking or agglomeration and retained sufficient powder mobility, resulting in a stable powder bed and improved particle fusion and structural integrity. On the other hand, suppressing cold crystallization reduced crystallization-induced contraction during thermal cycling, thereby limiting dimensional instability, residual-stress accumulation, and specimen warpage. Under the selected nominal preheating temperature of 100 °C and an ED of 0.37 J/mm³, PLCL powder was successfully used

to fabricate a scaffold with a complex TPMS architecture. Overall, this study provides an experimental and processing basis for the future development of shape-memory PLCL bone scaffolds.

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Conflict of interest

The authors declare they have no competing interests.

Author contributions

Conceptualization: Feng Chen, Xiaoxiao Han, Wei Zhu

Data curation: Xun Yuan, Xiaolu Zheng, Xinli Wang

Formal analysis: Xiaolu Zheng

Funding acquisition: Xiaoxiao Han, Wei Zhu

Investigation: Xun Yuan, Xinli Wang

Methodology: Xiaoxiao Han

Project administration: Wei Zhu

Supervision: Xiaolu Zheng, Junchen Zhou, Wei Zhu

Validation: Xun Yuan, Junchen Zhou

Visualization: Xun Yuan, Junchen Zhou

Writing—original draft: Xun Yuan

Writing—review & editing: Xun Yuan, Xiaoxiao Han, Wei Zhu

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data

The data that support the findings of this study are available from the corresponding author.

References

1. Du Y, Xing L, Hou P, *et al.* Dual stimulus response mechanical properties tunable biodegradable and biocompatible PLCL/PPDO based shape memory composites. *Colloids Surf A Physicochem Eng Asp.* 2022;648:129244.
doi: 10.1016/j.colsurfa.2022.129244
2. Liu Q, Lou P, Sun Z, *et al.* Bio-based elastomers: design, properties, and biomedical applications. *Adv Mater.* 2025;37(22):2417193.
doi: 10.1002/adma.202417193
3. Xiang Z, Zhang J, Zhou C, *et al.* Near-infrared remotely controllable shape memory biodegradable occluder based on poly(l-lactide-co- ϵ -caprolactone)/gold nanorod composite. *ACS Appl Mater Interfaces.* 2023;15(36):42341–42353.
doi: 10.1021/acsami.3c09852
4. Zheng F, García-García A, Moreno-Benítez I, Ruiz-Rubio L, Pérez-Álvarez L, Vilas-Vilela JL. Shape-memory polymers for tissue engineering applications. In: *Stimuli-Responsive Materials for Tissue Engineering.* Weinheim, Germany: Wiley-VCH; 2024:91–148.
doi: 10.1002/9783527838882.ch3
5. Gong L, Zhang Y, Xu E, Lu H, Duan J, Bao J. Construction of fully biodegradable poly(L-lactide-co-caprolactone) random copolymer/poly(D-lactide) blend: crystallization, toughness, and biodegradability. *Polym Eng Sci.* 2026;66(6):4560–4574.
doi: 10.1002/pen.70520
6. Zhao Y, Liu H. Application of PLCL as a biodegradable polymer in biomedical engineering. *J Mater Sci Mater Med.* 2026;37(1):46.
doi: 10.1007/s10856-026-07016-3
7. Wei L, Chen Q, Zhou D, *et al.* Fabrication of poly(D,L-lactide-co- ϵ -caprolactone) with elastic-memory function and controlled biodegradability. *Int J Polym Mater Polym Biomater.* 2026;75(2):183–193.
doi: 10.1080/00914037.2025.2540845
8. Chirume WM, Guo C, Zheng D, *et al.* Advanced additive manufacturing in orthopedics: a comprehensive review of biomaterials, structural design, biological functions and clinical technology applications. *RSC Adv.* 2026;16(13):11668–11685.
doi: 10.1039/d5ra09513a
9. Ding A, Tang F, Alsberg E. The emerging 4D printing of shape-memory thermomorphs for self-adaptative biomedical implants. *Adv Funct Mater.* 2025;35(28):2418348.
doi: 10.1002/adfm.202418348
10. Pfau MR, Grunlan MA. Smart scaffolds: shape memory polymers (SMPs) in tissue engineering. *J Mater Chem B.* 2021;9(21):4287–4297.
doi: 10.1039/d1tb00607j
11. Zhang Y, Zhao F, Qiao A, Liu Y, Chen M. Rational design and functionalization of melt electrowritten 4D scaffolds for biomedical applications. *Nano-Micro Lett.* 2026;18(1):144.
doi: 10.1007/s40820-025-01986-9
12. Wan X, Liu Z, Li L. Manipulation of stem cells fates: the master and multifaceted roles of biophysical cues of biomaterials. *Adv Funct Mater.* 2021;31(23):2010626.
doi: 10.1002/adfm.202010626
13. Liu J, Wang X, Wu Z, *et al.* Dynamic stimulation of piezoelectric scaffolds enhances osteogenesis-related biological responses via electro-mechanical sensitive channels and cytoskeletal remodeling. *Biomaterials.* 2026;329:123938.
doi: 10.1016/j.biomaterials.2025.123938

14. Wu H, Yang S, Li J, *et al.* Current status and challenges of shape memory scaffolds in biomedical applications. *MedComm Biomater Appl.* 2024;3(3):e95.
doi: 10.1002/mba2.95
15. Wan X, He Y, Liu Y, Leng J. 4D printing of multiple shape memory polymer and nanocomposites with biocompatible, programmable and selectively actuated properties. *Addit Manuf.* 2022;53:102689.
doi: 10.1016/j.addma.2022.102689
16. Ding A, Tang F, Alsberg E. 4D printing: a comprehensive review of technologies, materials, stimuli, design, and emerging applications. *Chem Rev.* 2025;125(7):3663-3771.
doi: 10.1021/acs.chemrev.4c00070
17. Li J, Liang Z, Li T, Wan Q, Huang X, Kan Q. A comprehensive review on 4D printing and applications of thermo-induced shape memory polymers. *Int J Smart Nano Mater.* 2025;16(1):24-83.
doi: 10.1080/19475411.2025.2458833
18. Yu K, Yao Y, Zhang W, *et al.* Defects, monitoring, and AI-enabled control in soft material additive manufacturing: a review. *Virtual Phys Prototyp.* 2025;20(1):e2588456.
doi: 10.1080/17452759.2025.2588456
19. Khoo ZX, Teoh JEM, Liu Y, *et al.* 3D printing of smart materials: a review on recent progresses in 4D printing. *Virtual Phys Prototyp.* 2015;10(3):103-122.
doi: 10.1080/17452759.2015.1097054
20. Kirillova A, Yeazel TR, Asheghali D, *et al.* Fabrication of biomedical scaffolds using biodegradable polymers. *Chem Rev.* 2021;121(18):11238-11304.
doi: 10.1021/acs.chemrev.0c01200
21. İlhan R, Gumus OY, Lekesiz H. Biodegradable nanocomposite filament based on PLA/PCL/CNCs for FDM 3D printing: production, characterization and printability. *Polym Compos.* 2026;47(5):4737-4759.
doi: 10.1002/pc.70459
22. Zeenat L, Zolfagharian A, Sriya Y, Sasikumar S, Bodaghi M, Pati F. 4D printing for vascular tissue engineering: progress and challenges. *Adv Mater Technol.* 2023;8(23):2300200.
doi: 10.1002/admt.202300200
23. Xie Y, Han J, Dai X, *et al.* A review on biodegradable materials of sustainable soft robotics and electronics. *Adv Sci.* 2026;13(15):e10320.
doi: 10.1002/advs.202510320
24. Hajnys J, Ma QP, Vandzura R, *et al.* A review on support-free printing with powder bed fusion method. *Prog Addit Manuf.* 2026;11(1):717-733.
doi: 10.1007/s40964-025-01373-1
25. Radhakrishnan HRG, Chithamparam P, Thiagamani SMK, Muthukumaran A, Ayrilmis N. Advancing cardiac tissue engineering with smart biopolymers: from fabrication strategies to 4D printing and organoids. *Polym Adv Technol.* 2025;36(7):e70280.
doi: 10.1002/pat.70280
26. Cong S, Gu H, Wei C, *et al.* Advancements and challenges in overhang structure fabrication during laser powder bed fusion: a comprehensive review. *Virtual Phys Prototyp.* 2025;20(1):e2567382.
doi: 10.1080/17452759.2025.2567382
27. Yao S, Jiang D, Uglov VV, Ma F, Chen Y, Wang L. Comprehensive review on additive manufacturing of porous biomedical titanium alloys: structural design, surface modification and applications. *Int J Bioprint.* 2026;12(3):026160143.
doi: 10.36922/IJB026160143
28. Machotová J, Pagáč M, Svoboda R, *et al.* Effect of PA12 powder recycling on properties of SLS 3D printed parts including their hygroscopicity. *Eur Polym J.* 2024;220:113432.
doi: 10.1016/j.eurpolymj.2024.113432
29. Yang W, Zhong Y, He C, *et al.* Electrostatic self-assembly of pFe₃O₄ nanoparticles on graphene oxide: a co-dispersed nanosystem reinforces PLLA scaffolds. *J Adv Res.* 2020;24:191-203.
doi: 10.1016/j.jare.2020.04.009
30. Zheng X, Yang Y, Zhou J, Yuan X, Cheng X, Zhu W. Development of physiological temperature responsive shape memory polymer for bone tissue engineering. In: Ge SS, Yuan W, Chang H, Wang Y, Samani H, He H, eds. *Social Robotics + BioMed. Lecture Notes in Computer Science.* Vol 16435. Singapore: Springer; 2026:141-150.
doi: 10.1007/978-981-95-7538-1_13
31. Fu X, Jia W, Li X, *et al.* Phase transitions of the rapid-compression-induced mesomorphic isotactic polypropylene under high-pressure annealing. *J Polym Sci B Polym Phys.* 2019;57(11):651-661.
doi: 10.1002/polb.24820
32. Wang X, Wang Z, Xiang S, Peng M, Li G, Huang Y. Developing polypropylene copolymer powder with a wide sintering window for laser powder bed fusion via extrusion and in-blend annealing. *Addit Manuf.* 2024;86:104188.
doi: 10.1016/j.addma.2024.104188
33. Fernández J, Etxeberria A, Sarasua JR. Synthesis, structure and properties of poly(L-lactide-co-ε-caprolactone) statistical copolymers. *J Mech Behav Biomed Mater.* 2012;9:100-112.
doi: 10.1016/j.jmbbm.2012.01.003
34. Zhang M, Chang Z, Wang X, Li Q. Synthesis of poly(l-

- lactide-co- ϵ -caprolactone) copolymer: structure, toughness, and elasticity. *Polymers*. 2021;13(8):1270.
doi: 10.3390/polym13081270
35. Yao H, Zhu W, Zhu X, *et al.* Development of hydroxyapatite/polycaprolactone composite biomaterials for laser powder bed fusion: evaluation of powder characteristics, mechanical properties and biocompatibility. *Polymers*. 2024;16(6):731.
doi: 10.3390/polym16060731
36. Ju X, Bowden M, Brown EE, Zhang X. An improved X-ray diffraction method for cellulose crystallinity measurement. *Carbohydr Polym*. 2015;123:476-481.
doi: 10.1016/j.carbpol.2014.12.071
37. Buhairi MA, Foudzi FM, Jamhari FI, *et al.* Review on volumetric energy density: influence on morphology and mechanical properties of Ti6Al4V manufactured via laser powder bed fusion. *Prog Addit Manuf*. 2023;8(2):265-283.
doi: 10.1007/s40964-022-00328-0
38. Karimi M, Asadi-Eydivand M, Abolfathi N, Chehrehsaz Y, Solati-Hashjin M. The effect of pore size and layout on mechanical and biological properties of 3D-printed bone scaffolds with gradient porosity. *Polym Compos*. 2023;44(2):1343-1359.
doi: 10.1002/pc.27174
39. Han W, Kong L, Xu M. Advances in selective laser sintering of polymers. *Int J Extrem Manuf*. 2022;4(4):042002.
doi: 10.1088/2631-7990/ac9096
40. Tan LJ, Zhu W, Sagar K, Zhou K. Comparative study on the selective laser sintering of polypropylene homopolymer and copolymer: processability, crystallization kinetics, crystal phases and mechanical properties. *Addit Manuf*. 2021;37:101610.
doi: 10.1016/j.addma.2020.101610