

Effect of PCL content in 3D-printed resin blends on thermal behavior, surface hardness, and in vitro cell response

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Abstract. Commercial stereolithography (SLA) resins offer high print fidelity but limited ability to tune material response for biomedical applications. This study investigated the effect of polycaprolactone (PCL) content on SLA-printed BioMed Clear blends containing 5%, 10%, and 15% PCL, with PEG400 used as a plasticizer. Printed specimens were characterized by thermogravimetric and derivative thermogravimetric analysis, simultaneous heat-flow analysis, Shore D hardness testing, and a CCK-8 assay using PANC-1 cells. PCL-containing blends showed an endothermic event at 54-56 °C and lower apparent mass-loss onset temperatures (193-197 °C) than BioMed Clear (270.5 °C), while the dominant decomposition response remained near 390-420 °C. Shore D hardness decreased from 76.0 for BioMed Clear to 71.2, 57.3, and 45.3 for the 5%, 10%, and 15% formulations, respectively. Relative CCK-8 activity increased with PCL content and time, reaching 63.9% of the cell-only control for 15% PCL at 72 h. These findings show that PCL content modifies the thermal response and surface hardness of SLA-printed BioMed Clear blends and is associated with different in vitro cellular metabolic responses among the tested formulations. Further work is required to establish the underlying phase, surface, and long-term biological mechanisms.

Keywords: BioMed Clear; polycaprolactone; stereolithography; thermal analysis; Shore D hardness; PANC-1; CCK-8

1. Introduction

Tissue engineering relies on three-dimensional scaffolds that provide suitable structural and biological environments for cells [1,2]. Additive manufacturing enables controlled fabrication of complex scaffold geometries, and stereolithography (SLA) is particularly attractive because of its high resolution and ability to produce intricate structures [2-4]. A continuing limitation, however, is that commercially available SLA resins have largely fixed material properties, making it difficult to tailor their mechanical and biological response for specific experimental applications [4].

Polycaprolactone (PCL) is a semi-crystalline aliphatic polyester widely investigated for biomedical scaffolds because of its flexibility, low melting temperature, and established use in degradable polymer

systems [5,6]. PCL also has limitations, including hydrophobicity, limited cell-adhesive functionality, and slow hydrolytic degradation [6-8]. These characteristics have motivated blending PCL with other polymers or functional phases to modify surface, mechanical, and biological behavior [7-10]. Integrating PCL into SLA-compatible photopolymer systems is less straightforward because the thermoplastic PCL phase must coexist with a photocurable resin network [9-11].

For SLA-printed polymer blends, the relevant question is therefore not only whether the formulation can be printed, but also how blending changes the resulting material response. Photopolymerization, polymer compatibility, residual low-molecular-weight species, and post-curing can influence thermal transitions and mechanical properties [9,11]. Surface chemistry and topography can also influence cellular responses [7,8], while residual photoinitiators or other leachable species remain important considerations when interpreting in vitro assays [11,12]. Consequently, thermal, mechanical, and cell-based measurements should be interpreted together without assuming that any single measurement establishes biodegradation or biological suitability.

Although PCL-based scaffolds have been widely investigated using extrusion-based additive manufacturing, fewer studies have examined PCL-photopolymer systems processed by SLA [9,10,21-23]. In particular, data linking PCL concentration with thermal behavior, surface hardness, and short-term cellular response in a medical-grade SLA resin remain limited. A concentration-dependent study can therefore provide useful information on how the addition of PCL changes measurable properties of the printed blend.

Accordingly, this study investigated SLA-printed BioMed Clear-PCL formulations containing nominal PCL levels of 5%, 10%, and 15%, with PEG400 used as a plasticizer. The objective was to determine how formulation composition affected thermal behavior, Shore D hardness, and PANC-1 cellular metabolic activity after SLA processing. Thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), simultaneous heat-flow analysis, Shore D hardness testing, and a CCK-8 assay were interpreted together to identify concentration-dependent trends while limiting conclusions to the properties directly measured in this study.

2. Materials and methods

2.1 Materials and blend preparation

PCL powder with an average molecular weight of 14,000 g/mol-1 was obtained from Merck-Sigma Aldrich (St. Louis, MO, USA). BioMed Clear, a medical-grade SLA photopolymer, was obtained from Formlabs (Somerville, MA, USA) [13]. PEG400 was included as a plasticizer in the blend system. Three PCL-containing formulations were prepared at the nominal levels used in the original experimental protocol (5%, 10%, and 15%), using 500 mL of BioMed Clear as the reference batch volume. Table 1 and Table 2 provide Biomed Clear material and PCL primary properties.

Table 1: Biomed Clear material properties

Material	Density, (g/cm ³)	Ultimate Tensile Strength (MPa)	Young's Modulus, (MPa)	Elongation, (%)	Hardness, (Shore- D)
Biomed Clear	1.09	52	2080	12	78

Table 2: PCL primary properties

Material	Molecular weight, (g/mol)	Density (g/cm ³)	Glass Transition (°C)	Melting T° (°C)	Tensile Strength (MPa)	Young modulus (GPa)
PCL	3,000-80,000	1.071-1.200	(- 65) - (- 60)	56-65	4-785	0.21-0.44

For each formulation, the required PCL powder was dissolved in dichloromethane (DCM) under magnetic stirring at 50 °C for 1 h. BioMed Clear was then added incrementally and stirring continued for 30 min. The mixture was examined by gas chromatography before printing to check removal of residual DCM. Figure 1 summarizes the preparation sequence.

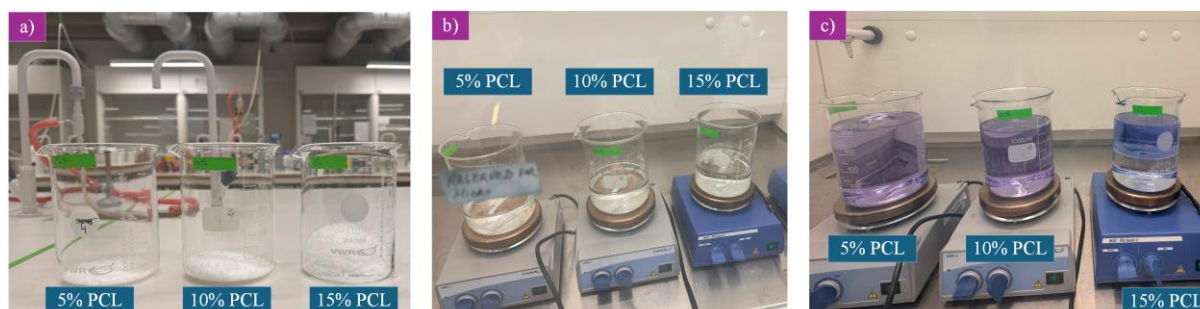


Figure 1. Preparation of the PCL-BioMed Clear formulations: (a) PCL mass measurement, (b) dissolution of PCL in DCM, and (c) incremental addition of BioMed Clear.

2.2 SLA 3D printing and post-processing

The blended resin was transferred to the SLA resin tank and specimens were printed using the settings summarized in table 3. Printed parts were washed in 99% isopropyl alcohol (IPA), dried, and UV post-cured according to the BioMed Clear post-processing procedure before characterization.

Table 3. SLA printing and post-processing settings reported for the study.

Parameter	Setting
Slicing software	PreForm v3.29
Layer height	100 μ m
Build orientation	0°
Wash	15 min in 99% IPA
Drying	5 min

2.3 Thermal characterization

Thermal characterization was performed with a simultaneous TGA/DSC 3+ system (Mettler Toledo, Switzerland). BioMed Clear and the three PCL-containing formulations were cryogenically milled before analysis to obtain a more uniform thermal response. Approximately 17 mg of material was placed in an alumina (Al_2O_3) crucible and heated from 25 to 800 °C at 10 K min⁻¹ under nitrogen flowing at 50 mL min⁻¹. The instrument recorded sample mass as a function of temperature, derivative mass-loss rate (DTG), and a simultaneous heat-flow signal. TGA curves were normalized to 100% of the initial mass at 25 °C to enable direct comparison of apparent onset temperature, dominant decomposition temperature, and residual mass at 800 °C.

The heat-flow signal was examined for low-temperature thermal events and interpreted together with the TGA/DTG response. Because the present analysis does not independently establish the molecular origin of every event, assignments were kept conservative: the approximately 54-56 °C event in the PCL-containing blends was treated as PCL-associated because it coincides with the reported melting range of semi-crystalline PCL [5,18], whereas other low-temperature events were reported descriptively.

2.4 Shore D hardness

Shore D hardness was measured in accordance with ASTM D2240-15 using 10 mm $\times$ 10 mm $\times$ 10 mm printed specimens. Measurements were obtained with a manual Shore D durometer (Model LD-YJ; serial no. 40041982) mounted on an operating stand. The indenter was lowered onto the specimen

surface and maintained in contact for 10 s before recording the reading. Three specimens were tested for each formulation, and five measurements were taken at different positions on each specimen to account for local variation. Table 4 summarizes the specifications of Shore D hardness test machine used for this study.

Table 4: Shore D hardness tester specifications

Specification	Value
Model	HBD100-0
Indenter	Konus 30
Depth of indentation	0-2.5 mm
Test pressure	50 N
Measurable	0.55-44.5 N

2.5 CCK-8 assay

Circular scaffold discs 10 mm in diameter were printed for testing in 24-well cell plates. Before cell culture exposure, the discs were treated with 70% ethanol and exposed to ultraviolet light as part of the preparation and sterilization procedure. PANC-1, human pancreatic adenocarcinoma cells were maintained in Dulbecco's Modified Eagle Medium supplemented with 10% fetal bovine serum and 1% penicillin-streptomycin at 37 °C and 5% CO₂. A total of 10,000 cells were seeded onto each scaffold in the 24 well cell culture plate. The tested scaffold groups were the 5%, 10%, and 15% PCL formulations; controls comprised media plus cells (M+C), media plus scaffold (M+S), and blank media. Each condition was performed in triplicate.

Cellular viability was assessed with Cell Counting Kit-8 (CCK-8, Dojindo) at 24, 48, and 72 h. At each time point, 10 μ L of CCK-8 reagent was added to 100 μ L (10% v/v) of culture medium and incubated for 4 h. Absorbance was measured at 450 nm. Background absorbance from the relevant scaffold-only or blank control was subtracted, and the corrected signal was expressed relative to the M+C control, defined as 100%. Because inferential statistical results were not available in the dataset used for this manuscript, CCK-8 differences are reported descriptively rather than as statistically significant.

3. Results and discussion

3.1 Thermal response

The TGA curves (Figure 2) show a clear difference between BioMed Clear and the PCL-containing formulations. BioMed Clear exhibited an apparent onset of mass loss at approximately 270.5 °C and a dominant decomposition temperature of 419.67 °C. The PCL-containing blends showed lower apparent onsets of 197.0, 196.7, and 193.0 °C for the 5%, 10%, and 15% formulations, respectively. The lower-temperature mass loss demonstrates that the blended formulations introduced thermally less stable constituents or local environments, but the onset cannot be assigned exclusively to PCL because PEG400, formulation-dependent curing, and other low-molecular-weight constituents may also contribute.

The Biomed Clear material demonstrated an initial degradation temperature of roughly 270.5°C, with maximum degradation happening at 419.67°C, as summarized in Table 6. The values demonstrate the higher thermal stability of Biomed Clear, aligning with prior research on photopolymerizable methacrylate-based resins, recognized for creating strong crosslinked networks during polymerization, resulting in delayed thermal decomposition. The residual mass at 800°C was noted to be 1.29%, indicative of little char formation, characteristic of crosslinked polymers degrading in inert nitrogen environments.

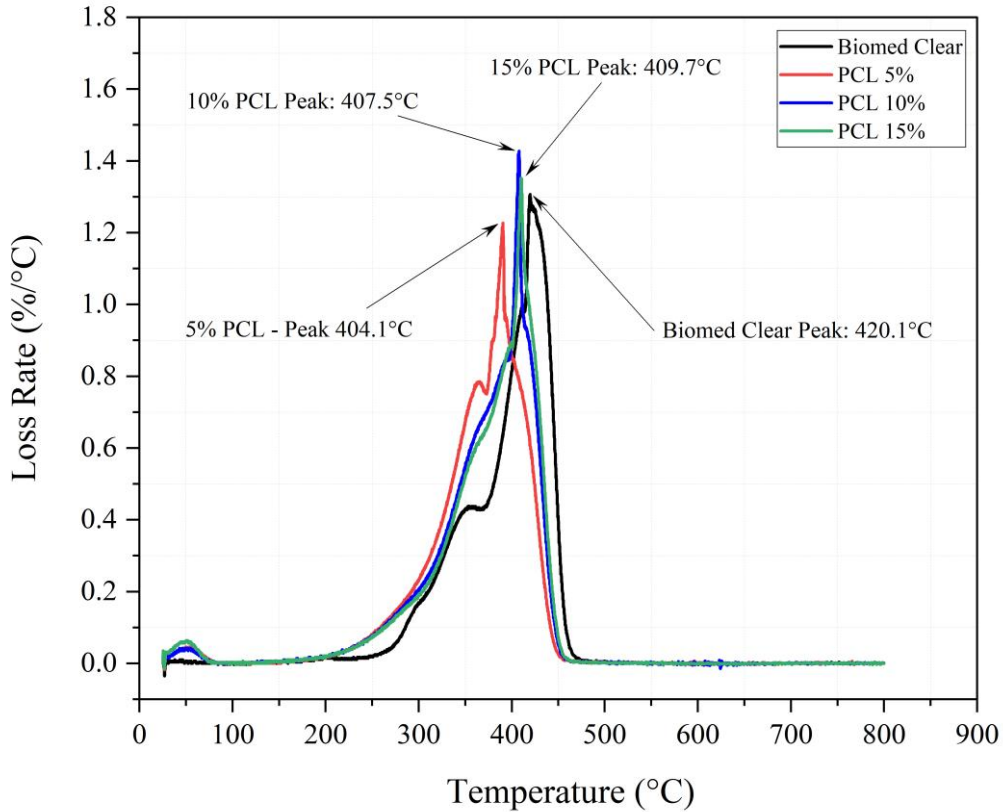


Figure 3. Derivative thermogravimetric profiles of BioMed Clear and the PCL-containing formulations.

This study supports a two-stage thermal decomposition mechanism:

- Stage I (100-300°C): Characterized by the initial degradation of PCL, which may involve preliminary melting, volatilization, and partial breaking of ester bonds.
- Stage II (350-450°C): This stage corresponds to the degradation of the Biomed Clear matrix, as indicated by the dominant DTG peak.

Differential thermal analysis was utilized to examine the thermal transitions and stability of Biomed Clear and its blends with PCL at different concentrations (5%, 10%, and 15%). The heat flow curves indicated a series of thermal events that offer important perspectives on the physical and chemical properties of the materials subjected to thermal stress. The findings align with the established thermal characteristics of polymeric systems and provide deeper understanding into the impact of PCL integration in the Biomed Clear matrix.

The simultaneous heat-flow signal provided complementary information on lower-temperature transitions. BioMed Clear showed events near 42.3 and 52.3 °C. Their precise molecular origin cannot be established from the present dataset, so they are reported as low-temperature thermal events rather than definitively assigned as glass transition or post-curing. In contrast, all PCL-containing formulations exhibited an endothermic event between approximately 54 and 56 °C, consistent with the melting range of semi-crystalline PCL [5,18]. The persistence of this feature after SLA processing demonstrates that a PCL-associated thermal signature remained detectable in the printed blends.

Additional events occurred at approximately 93.3, 82.0, and 79.7 °C for the 5%, 10%, and 15% PCL formulations, respectively. Their origin cannot be assigned conclusively from the available measurements. Because the experiments were performed under nitrogen and no dominant TGA mass-

loss event occurred at these temperatures, the additional events are not interpreted as oxidative degradation. Figure 4 and table 6 summarize the observed heat-flow response.

Table 6. Summary of thermal events of differential thermal analysis

Material	Temperature (°C)			
	Glass transition (T _g)	PCL melting (T _m)	Post-curing (cross-linking)	Initial degradation
Biomed Clear	42.33		52.33	
BC-PCL 5%		55.67		93.33
BC-PCL 10%		54.33		82.00
BC-PCL 15%		54.67		79.67

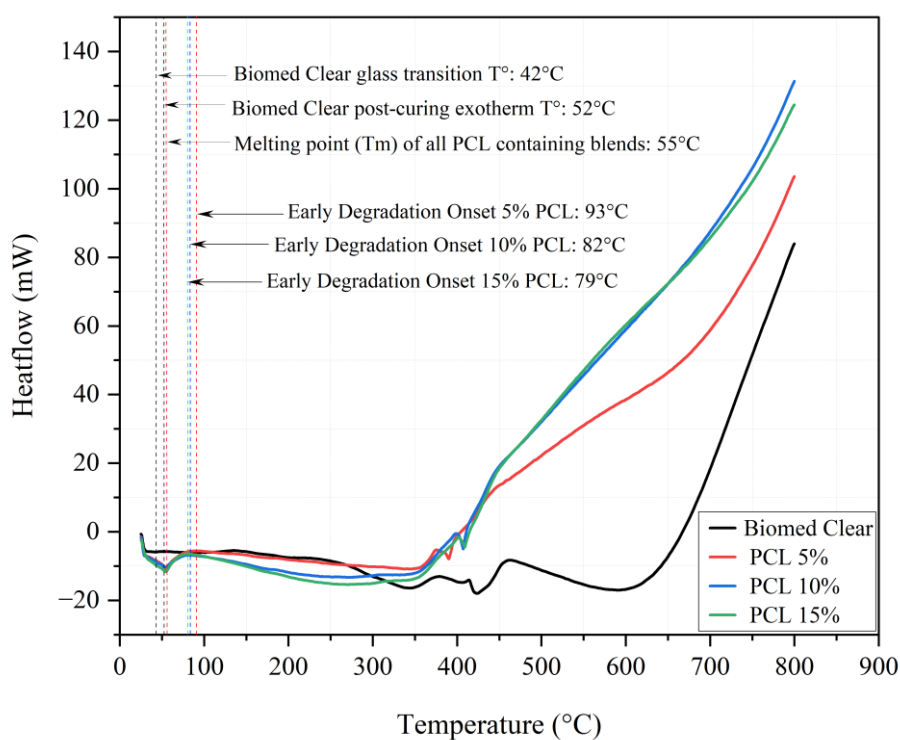


Figure 4. DTA curves with thermal events

Two distinct thermal events were observed for Biomed Clear alone. The initial event was an endothermic transition at approximately 42.3°C, corresponding to the glass transition temperature (T_g) of the Biomed Clear polymer matrix. This finding corresponds with literature for methacrylate-based resins, where the glass T_g generally ranges from 30 to 50°C, contingent upon crosslink density and monomer structure. The existence of a T_g indicates that, while being a crosslinked photopolymer, Biomed Clear maintains a degree of molecular mobility at higher temperatures. This mobility correlates with segmental motion in areas of the polymer network that are less densely crosslinked or contain defects.

Taken together, the thermal results show three robust features. First, the blended formulations exhibited substantially lower apparent onset temperatures of mass loss than unmodified BioMed Clear. Second, all PCL-containing formulations retained a PCL-associated thermal event near 54-56 °C. Third, the dominant high-temperature decomposition event remained within approximately 390-420 °C, close to the BioMed Clear response. These observations demonstrate formulation-dependent thermal behavior

after SLA processing, but they do not establish physiological biodegradation, detailed phase morphology, or the isolated contribution of PCL relative to PEG400 and other formulation factors.

The observed 54-56 °C event agrees closely with the well-established melting range of semi-crystalline PCL [5,18], supporting its use as the most confidently assigned low-temperature feature in the blends. Published studies of PCL and mixed polymer systems also show that the main decomposition response can vary with formulation, polymer interactions, and heating conditions [14,16,17]. For that reason, the lower apparent TGA onset observed here is best treated as a formulation-specific thermal response rather than as a universal decomposition temperature for PCL.

3.2 Shore D hardness

Shore D hardness decreased monotonically with increasing nominal PCL content (figure 5). BioMed Clear measured 76.00 ± 0.00 , compared with 71.20 ± 0.33 for 5% PCL, 57.33 ± 0.13 for 10% PCL, and 45.26 ± 0.95 for 15% PCL. Relative to BioMed Clear, the 15% formulation therefore showed a reduction of approximately 40% in Shore D hardness. This is the clearest concentration-response relationship observed in the study.

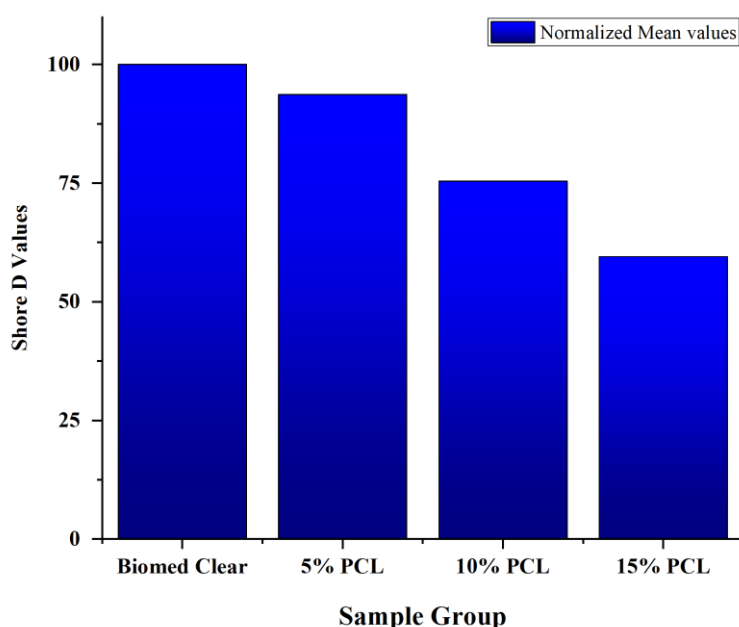


Figure 5. Shore D hardness of BioMed Clear and PCL-containing formulations.

The progressive reduction in Shore D hardness is consistent with reports in which increasing PCL content produces a softening effect when blended with more rigid polymers [19,20]. In the present study, the decrease was substantial: the 15% PCL formulation was approximately 40% lower in Shore D hardness than unmodified BioMed Clear. The monotonic trend across all four formulations makes surface hardness the clearest concentration-response relationship in the dataset.

PEG400 was also included as a plasticizer and may contribute to the measured hardness response. Because PEG400 was not isolated as an independent factor, the change should be attributed to the overall BioMed Clear-PCL-PEG400 formulation rather than exclusively to PCL. In addition, Shore D hardness is an indentation-based surface measurement and should not be treated as a direct measurement of Young's modulus, tensile strength, fracture toughness, or fatigue behavior. Within that limitation, the results show that the blend formulation provides a practical route for modifying surface hardness after SLA printing.

The direction of the hardness trend is consistent with previous polymer-blend studies. Reduced Shore D hardness when PCL was incorporated into a more rigid PLA-based system, while comparable

softening tendency in PHBH/PCL blends is reported [19,20]. These systems differ from the present photocurable BioMed Clear matrix, so their absolute hardness values are not directly transferable. Nevertheless, the common direction of change supports the interpretation that increasing the flexible polymer fraction can reduce indentation resistance in otherwise more rigid polymer matrices.

3.3 PANC-1 cellular metabolic activity

The CCK-8 assay showed consistent concentration- and time-dependent ordering among the three PCL-containing formulations (figure 6). At 24 h, relative CCK-8 activity was 5.0%, 9%, and 22% for the 5%, 10%, and 15% formulations, respectively. At 48 h, the corresponding values were 14.6%, 23.4%, and 42.4%, increasing at 72 h to 24.2%, 32.1%, and 63.9%. At every time point, the 15% formulation produced the highest corrected cell viability (CCK-8) signal, followed by 10% and 5% PCL.

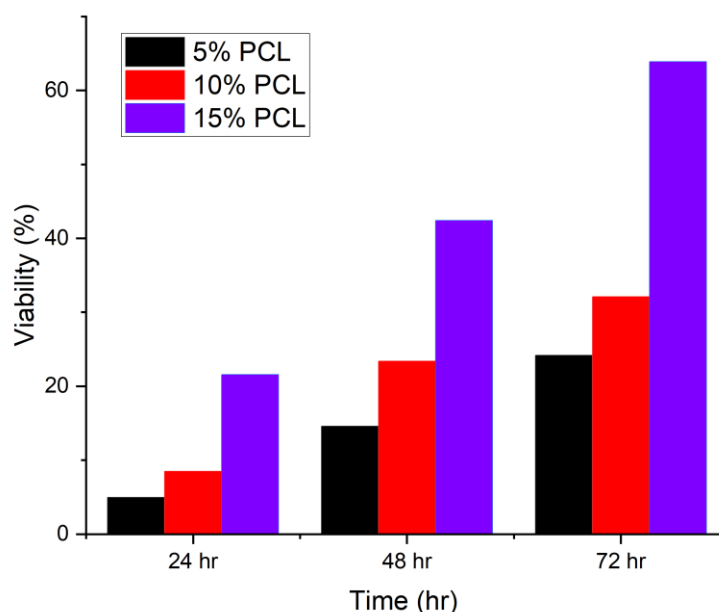


Figure 6. Relative PANC-1 CCK-8 activity on the 5%, 10%, and 15% PCL formulations at 24, 48, and 72 h. Values are normalized to the cell-only control (100%).

CCK-8 is based on cellular reduction of WST-8 and is commonly used as an indirect measure of viable cell number and metabolic activity. It does not directly quantify cell adhesion, morphology, spreading, or surface coverage. The present data therefore support a formulation-dependent difference in short-term metabolic response rather than a direct claim of improved adhesion. The 15% PCL formulation produced the highest signal among the tested scaffolds, but even at 72 h its value remained below the cell and media-only reference, which is important when interpreting the magnitude of the biological response.

The increasing CCK-8 signal with PCL concentration occurred alongside the reduction in Shore D hardness, but the experimental design does not establish a causal relationship between these two observations. Surface chemistry, topography, PEG400, curing behavior, and residual constituents may also influence cell response. Furthermore, unmodified BioMed Clear was not included as a scaffold group in the CCK-8 experiment, so the current dataset demonstrates differences among the three PCL-containing formulations rather than biological superiority to BioMed Clear itself.

Previous work has shown that cell response on PCL-containing scaffolds can be sensitive to surface chemistry and surface modification [7,8]. Those studies also emphasize why the current CCK-8 trend should not be attributed to PCL concentration through a single mechanism. The present SLA-printed blend differs from electrospun or surface-treated PCL systems in resin chemistry, curing, surface morphology, and the presence of PEG400. The literature therefore provides qualitative context for the

observed concentration-dependent cellular response, while the mechanism remains outside the scope of the available measurements.

3.4 Cross-property comparison and formulation implications

A useful feature of the present dataset is that the four material formulations were evaluated across several complementary measurements. Table 5 brings together the principal thermal and hardness results and, where available, the 72 h CCK-8 response. The comparison highlights that increasing nominal PCL content was accompanied by a progressive decrease in Shore D hardness, while the dominant DTG peak remained within a relatively narrow high-temperature range. In contrast, the apparent TGA onset shifted markedly when PCL-containing formulations were compared with unmodified BioMed Clear.

The Shore D response showed the strongest monotonic concentration dependence. Hardness decreased from 76.00 for BioMed Clear to 71.20, 57.33, and 45.26 for the 5%, 10%, and 15% PCL formulations, respectively. This indicates that the formulation strategy can substantially alter surface indentation resistance while retaining SLA processability. The thermal results complement this observation by showing that the blended materials also differ in low-temperature transitions and in the temperature at which measurable mass loss begins.

The biological assay showed a parallel concentration ordering among the three PCL-containing groups, with the 15% formulation giving the highest CCK-8 signal at 24, 48, and 72 h. This parallel trend is noteworthy but should not be interpreted as evidence that lower hardness directly caused the higher cellular metabolic response. Cell-material interactions can also depend on surface chemistry, roughness, wettability, residual constituents, and curing state. The present dataset therefore supports formulation screening and comparison rather than a mechanistic link between a single material property and cell behavior. Table 7 Cross-property summary of the tested formulations.

Table 7. Cross-property summary of the tested formulations.

Formulation	TGA onset (°C)	DTG peak (°C)	Residue at 800 °C (%)	Shore D	CCK-8 at 72 h (%)
BioMed Clear	270.5	420.1	1.29	76.00 ± 0.00	
5% PCL	197.0	404.6	1.20	71.20 ± 0.33	24.2
10% PCL	196.7	407.5	0.99	57.33 ± 0.13	32.1
15% PCL	193.0	409.7	0.38	45.26 ± 0.95	63.9

The main contribution of these combined measurements is the demonstration of a reproducible composition-property trend across the investigated formulations. The study does not identify an optimum formulation for a specific tissue, because such a conclusion would require application-specific mechanical targets, direct surface characterization, broader biological evaluation, and degradation testing. Instead, the results establish a practical experimental basis for selecting BioMed Clear-PCL blend ratios for subsequent application-specific development.

From a formulation-design perspective, the results also show that the largest property shift occurred between the 5% and 15% PCL conditions rather than as a minor perturbation around the BioMed Clear baseline. This gives the concentration series practical value as an initial screening window: the formulations span a broad range of Shore D hardness while retaining a detectable PCL-related thermal feature. Future work can use this range to select narrower compositions for application-specific mechanical, surface, or biological optimization without assuming that the highest PCL content is universally preferable.

3.5 Limitations and scope of interpretation

Across the existing dataset, increasing nominal PCL content was associated with three concurrent trends: retention of a PCL-associated thermal event near 55 °C, progressive reduction in Shore D hardness, and higher PANC-1 CCK-8 activity among the PCL-containing formulations. The hardness trend is especially clear, decreasing from 76.00 for BioMed Clear to 45.26 for the 15% PCL formulation. The

biological trend likewise increased consistently from 5% to 15% PCL at each measured time point. Together, these results show that the composition of the blended SLA material influenced both its thermal/material response and the output of the short-term cell assay.

The observations should nevertheless be interpreted as associated formulation-dependent changes rather than as a single causal pathway. Thermal analysis does not establish hydrolytic degradation, Shore D does not represent bulk mechanical stiffness, and CCK-8 does not directly measure adhesion. The combined dataset is most useful for identifying how the tested formulations differ and for defining which composition-dependent effects merit further study, rather than for assigning a specific tissue-engineering mechanism.

Several limitations define the scope of the conclusions. First, PEG400 was part of the blend system but was not independently evaluated, so the contribution of PCL cannot be completely separated from the total formulation effect. Second, unmodified BioMed Clear was not included as a scaffold group in the CCK-8 experiment; consequently, the biological data demonstrate differences among the PCL-containing formulations rather than superiority to BioMed Clear. Third, hardness is the only direct mechanical measurement reported, and it represents surface indentation resistance rather than bulk stiffness or strength.

A further methodological consideration is that the exact contribution of each formulation component cannot be separated without independent PCL, PEG400, and resin controls. The present paper therefore treats nominal PCL concentration as the organizing formulation variable while recognizing that the measured response belongs to the complete blended system. This distinction is particularly important when interpreting the hardness and CCK-8 trends.

The CCK-8 dataset is interpreted descriptively because inferential statistical results were not available, and the assay itself reflects short-term metabolic activity rather than direct adhesion or morphology. Similarly, the thermal results describe behavior under programmed heating and cannot be translated directly into physiological degradation. These limitations do not alter the measured concentration-dependent trends, but they define the appropriate level of inference and prevent broader claims regarding general cytocompatibility, resorption, or tissue-specific performance.

4. Conclusions

SLA-printed BioMed Clear-PCL blends showed clear concentration-dependent differences across the existing thermal, hardness, and CCK-8 datasets. PCL-containing formulations retained an endothermic event at approximately 54-56 °C consistent with a PCL-associated transition and exhibited lower apparent mass-loss onset temperatures than unmodified BioMed Clear, while the principal DTG decomposition event remained near 404-420 °C. Shore D hardness decreased systematically from 76.00 for BioMed Clear to 45.26 for the 15% PCL formulation, demonstrating substantial formulation-dependent softening after SLA processing.

Among the three PCL-containing scaffold groups, relative PANC-1 CCK-8 activity increased with both PCL concentration and culture time, reaching 63.9% of the cell-only control for the 15% formulation at 72 h. Taken together, the results establish BioMed Clear-PCL-PEG400 blending as a practical route for modifying the measurable thermal response and surface hardness of SLA-printed specimens while producing formulation-dependent differences in short-term cellular metabolic activity. The conclusions are intentionally limited to these measured properties and do not imply physiological biodegradation, direct cell adhesion, or tissue-specific suitability.

Data availability

All data analyzed in this study are presented in the manuscript. Raw data can be made available upon reasonable request.

Author contributions

Y Wakjira: Conceptualization, data curation, formal analysis, investigation, methodology, software, validation, visualization, and writing - original draft. H G Lemu: Conceptualization, methodology, project

administration, resources, supervision, and writing - review and editing. H R Hagland: Methodology, resources, supervision, validation, and writing - review and editing.

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