Journal of Engineering and Technology

ISSN 2180-3811 eISSN 2289-814X https://jet.utem.edu.my/jet/index
DOI: https://doi.org/10.54554/jet.2025.16.2.011

# MECHANICAL PERFORMANCE AND SHAPE MEMORY BEHAVIOR OF 4D PRINTING POLYLACTIC ACID/BIOBASED THERMOPLASTIC POLYURETHANE

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**Article history:**
Received Date: 9 January 2025
Revised Date: 24 April 2025
Accepted Date: 9 June 2025

Keywords: 3D Printing, 4D Printing, Bio-Based Thermoplastic Polyurethane, Polymer Blend, Polylactic Acid

**Abstract**— Shape memory materials (SMMs) possess the unique ability to return to their original shape after deformation when exposed to external stimuli, making them highly desirable for applications such as biomedical devices and smart textiles. This study investigates the enhancement of polylactic acid (PLA) by incorporating bio-based thermoplastic polyurethane (bTPU) to improve flexibility and shape recovery. PLA/bTPU blends were prepared at varying weight ratios and characterized for mechanical properties, morphology, and shape memory behavior. Results showed that elongation at break increased dramatically from 7.66% in neat PLA to 944.14% in PLA60, indicating a substantial

improvement in ductility. Although tensile strength decreased from 43.26MPa (PLA) to 21.80MPa (PLA60), this trade-off was balanced by enhanced flexibility. Morphological analysis revealed a transition from brittle fracture in PLA to ductile, phase-separated “sea-island” morphology in PLA60, with continuous bTPU domains promoting energy dissipation. FTIR analysis confirmed the presence of functional groups associated with PLA and bTPU without new peak formation, indicating physical blending rather than chemical interaction. Shape recovery tests revealed that recovery improved from 48.25% in PLA to 81.48% in PLA60 under thermal stimulation at 85°C. These results suggest that PLA/bTPU blends offer improved mechanical resilience, elasticity, and shape memory behavior, making them suitable for sustainable 3D and 4D printing applications in fields requiring adaptable material performance. This research contributes to sustainable material engineering and supports the development of adaptable materials for aerospace, automotive, and bioengineering applications.

## I. Introduction

The increasing global emphasis on sustainable development has spurred interest in green manufacturing and the utilization of biodegradable, bio-based materials. Fused deposition modeling (FDM) has become a cornerstone of sustainable

production due to its material efficiency, design flexibility, and potential for reducing industrial waste [1]. Within this context, polylactic acid (PLA), a bioactive and biodegradable thermoplastic, is primarily produced from fermented plant starch, such as corn [2-3], making it a prominent choice due to its renewable nature, biodegradability, and notable mechanical strength and rigidity [4]. PLA's versatility in applications such as 3D printing is well-documented, however its inherent brittleness, marked by limited elongation at break and impact resistance, poses significant challenges in scenarios requiring flexibility and toughness [5-6].

To mitigate PLA's brittleness, researchers have explored toughening PLA by incorporating elastomeric polymers such as thermoplastic polyurethane [7]. TPU is a versatile class of thermoplastic elastomers, known for combining plastic and rubber-like properties, typically synthesized from petrochemical sources [8]. However, there is a growing interest in developing bio-based TPU alternatives using plant oils and renewable resources for polyol production, aiming to reduce the environmental footprint of traditional TPU manufacturing processes. The use of bio-based TPU (bTPU) offers a more environmentally friendly alternative and aligns with green manufacturing principles [8].

Prior studies have shown that introducing TPU improves shape memory behavior, making such blends ideal for 4D printing, where shape transformation under stimuli is required [9-11]. Shape memory polymers (SMPs) are central to 4D printing due to their ability to recover a pre-defined shape upon external triggers like heat [12-13]. PLA's shape memory effect (SME), though promising, requires enhancement for practical use. Integrating TPU into PLA has been shown to amplify shape memory effect (SME) by improving chain mobility and elasticity [10, 14-15].

The logical progression from PLA's brittleness to the

development of a flexible, durable, and shape-responsive PLA/bTPU blend forms the basis of this research. This study contributes directly to advancing green and additive manufacturing technologies. The insights gained support the development of eco-conscious smart materials for biomedical devices, soft robotics, and deployable systems, emphasizing not only functional performance but also environmental responsibility.

## II. Experimental

### A. Materials Selection and Blending Ratios

This study employed commercially available polylactic acid (PLA) pellets (Ingeo 2003D, NatureWorks Co. Ltd, USA). Bio-based thermoplastic polyurethane (bTPU) used was LARIPUR 4525EG (Plastech Technical). PLA/bTPU blending ratios in Table 1 were systematically selected to evaluate the progressive influence of bTPU content on mechanical and shape memory properties. Previous studies suggest that TPU concentrations up to 30% can significantly enhance flexibility but may compromise tensile strength due to polymer phase separation [16-17]. In contrast, PLA50/TPU50 significantly reduces tensile strength and introduces printability issues such as voids, poor interlayer adhesion, and filament buckling due to increased melt viscosity and flow resistance [18]. Therefore, blend ratios up to 40% bTPU were chosen.

Table 1: Blending Ratios

| Sample | PLA (%) | bTPU (%) |
|---|---|---|
| PLA | 100 | - |
| PLA90 | 90 | 10 |
| PLA80 | 80 | 20 |
| PLA70 | 70 | 30 |
| PLA60 | 60 | 40 |

### B. Sample Preparation

PLA and bTPU were dried in an oven maintained at 50°C for 1 hours, in order to eliminate the moisture. PLA pellets were physically mixed with bTPU at different ratios. The mixtures underwent extrusion using a FILABOT EX6 extruder equipped with multi-zone temperature control. The designated temperatures for the

front, middle, and back zones were 185°C, 195°C, and 185°C, respectively, while the feed zone was maintained at 50°C. The extruded filaments were spooled by a FILABOT spooler and concurrently cooled via an integrated FILABOT airpath. The extruded filaments were spooled to achieve a consistent diameter (1.60-1.75mm ± 0.05 mm), critical for reliable FDM printing. A purging protocol using pure PLA between batches prevented cross-contamination. All filaments were manufactured using a Creality Ender-3 V3 SE printer via the FDM technique. All of samples were printed under the same parameters, which are detailed in Table 2.

Table 2: 3D Printing Parameters

| Parameter | Value |
|---|---|
| Nozzle temperature (°C) | 200 |
| Infill pattern | Grid |
| Layer height (mm) | 0.2 |
| Printing orientation | Flat |
| Printing speed (mm/s) | 50 |
| Plate temperature (°C) | 60 |
| Infill density | 100 |

## III. Characterizations

### A. Tensile Test

All printed samples underwent tensile test in line with ASTM D638 type 4 using Shimadzu Autograph AGS-X series universal testing machine. The testing was conducted at a strain rate of 5 mm/min. To ensure statistical validity, at least six samples were tested for each experimental group.

### B. Morphology Test

A Scanning Electron Microscope (SEM), model JSM 5600, was utilized to examine the morphologies of the PLA/bTPU polymer blend. The fracture cross-sections of the printed samples were cut into smaller pieces and mounted onto specimen stubs. To improve conductivity, the sample surfaces were coated with a thin layer of gold. The morphologies were observed at an accelerating voltage of 10.0 kV and a magnification of 500x.

### C. Chemical Behavior Test

Fourier Transform Infrared (FTIR) Spectroscopy was employed to analyze the functional groups of the 3D-

printed samples. Scanning was conducted across a wavenumber in the range of 4000cm$^{-1}$ to 400cm$^{-1}$ with a resolution of 4cm$^{-1}$.

### D. 4D Printing Shape Recovery Test

Cantilevers with dimensions of 25mm width, 70mm length, and 1mm thickness [12] were 3D-printed into a flat 180° shape to evaluate their shape memory properties. Each cantilever was first immersed in 85°C water for 3min, a temperature exceeding PLA's glass transition point, to induce deformation. This condition was selected based on Leist et al.'s findings, which showed a significantly higher recovery rate at 85°C (75.54%) compared to 65°C (42.92%), highlighting the effectiveness of higher temperatures in activating shape memory behavior. After cooling to room temperature in their deformed state, the bent angles were measured. A second immersion at 85°C for 3min to activate the shape recovery, and final angles were recorded to determine recovery efficiency.

## IV. Results and Discussion

### A. Tensile Properties

Figure 1 shows that pure PLA demonstrated the highest tensile strength at 43.26MPa, characteristic of its rigid and brittle molecular structure dominated by crystalline regions [2, 19][20-21]. The introduction of bTPU caused a progressive reduction in tensile strength [4, 16], with PLA90 exhibiting a 27.6% decrease to 31.32MPa. Interestingly, tensile strength values stabilized between 31.77MPa (PLA80, 20% bTPU) and 31.76MPa (PLA70, 30% bTPU), suggesting a transitional phase where TPU particles remained dispersed within the PLA matrix without significant phase separation [17, 22].

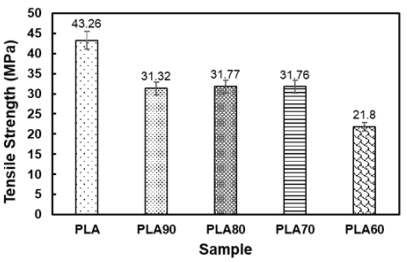


Figure 1: Tensile Strength of PLA and PLA/bTPU Blends

At 40% (PLA60), a dramatic 49.6% strength reduction to

21.8MPa occurred, indicating a critical percolation threshold where TPU domains likely formed continuous networks that compromised structural integrity. This trend aligns with previous studies of 3D printing PLA/TPU, where TPU concentrations above 30-40% caused accelerated modulus degradation due to interfacial incompatibility between polymer phases [4, 16, 18].

Figure 2 highlights elongation at break (%) improvements, reflecting increased flexibility and ductility with higher bTPU content [23]. Pure PLA exhibits limited elongation (7.66%) due to its inherent brittleness, while blends with 10% and 20% bTPU (PLA90 and PLA80) show modest improvements to 8.38% and 9.94%, respectively. A critical transition occurs at 30% bTPU (PLA70), where elongation surges to 118.68%, marking a shift from brittle to ductile fracture behavior. This aligns with studies showing TPU's soft segments and hydrogen bonding with PLA enhance interfacial adhesion, enabling energy dissipation during deformation [17, 24].

The most dramatic improvement appears in PLA60 (40% bTPU), achieving 944.14% elongation surpassing TPU's typical 500% threshold [25] as the blend adopts TPU's elastomeric characteristics through phase morphology optimization [26].

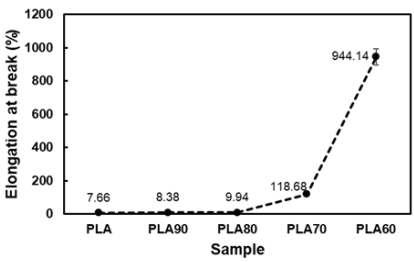


Figure 2: Elongation at Break of PLA and PLA/bTPU Blends

## B. Morphology Properties

Figure 3 illustrates the fractured cross-section morphologies of pure PLA and PLA blends. Pure PLA exhibits smooth surfaces, reflecting its brittle nature [3]. In contrast, PLA blends display rougher, ductile fracture characteristics, particularly PLA60, which shows significant plastic deformation and a "sea-island" morphology with numerous

"droplet-like" bTPU phase [4, 16, 27]. As bTPU content increases, larger and more continuous regions of bTPU were visible within the PLA matrix, consistent with findings from similar studies on PLA/TPU blends [16, 28, 29].

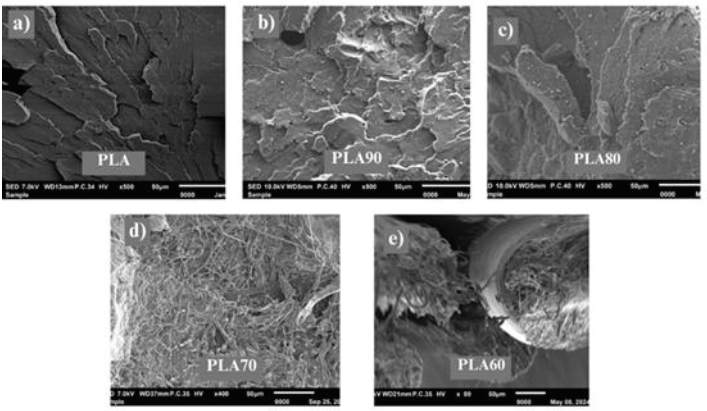


Figure 3: The Morphologies of PLA and PLA/bTPU Blends

This morphological evolution aligns with the mechanical data, where increasing bTPU content contributes to enhanced elongation at break. The formation of continuous bTPU-rich regions in higher blend ratios facilitates energy dissipation and crack deflection, mechanisms that are known to improve toughness and ductility [9]. These results correlate well with degradation studies, as prolonged thermal processing may induce chain scission in PLA, reducing molecular weight and promoting embrittlement in the neat sample. In contrast, the thermoplastic polyurethane (bTPU) phase resists degradation pathways due to its elastomeric nature, maintaining structural integrity and mitigating brittleness in the blends [11, 30]. Comparatively, similar studies on bio-based thermoplastic elastomer blends, such as PLA combined with PCL or PBS, have reported analogous improvements in ductility and impact resistance through phase separation and morphology control [31].

## C. Chemical Properties

Figure 4 shows the FTIR spectra of PLA and PLA/bTPU blends from 400 to 4000cm$^{-1}$.

Peaks at 2993cm$^{-1}$ and 2941cm$^{-1}$ correspond to asymmetric and symmetric C–H stretching, while 1748cm$^{-1}$ represents C=O stretching. The ether bond appears at 1180cm$^{-1}$, and the C–O bond at 1079cm$^{-1}$. The peak at 1454cm$^{-1}$ is linked to the C–H bond in the methyl group (–$CH_3$) of PLA. Bands at 864cm$^{-1}$ and 752cm$^{-1}$ signify amorphous and crystalline PLA states, respectively. The 3000-3500cm$^{-1}$ range suggests hydrogen bonding, though it is absent in PLA/bTPU blends due to low bTPU content, indicating physical mixing rather than chemical bonding [6, 10] which aligns with the SEM observations showing the droplet morphology.

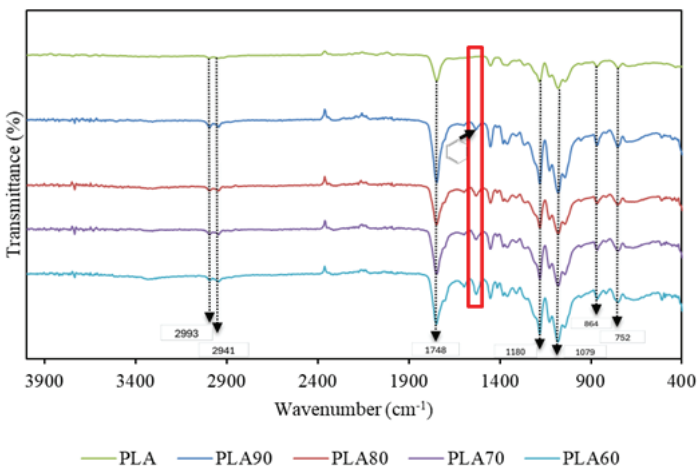


Figure 4: FTIR Spectra of PLA and PLA/bTPU Blends

**D. Shape Memory Properties**

Figure 5 shows a clear increasing trend with higher concentrations of bTPU, indicating enhanced shape memory performance. Pure PLA exhibits the lowest recovery at 48.25%, likely due to its high stiffness and limited molecular mobility. As the composition shifts to PLA90 and PLA80, recovery improves to 53.64% and 59.77%, respectively, suggesting increased flexibility and better phase interaction. A more significant jump is

observed in PLA70 (73.23%), highlighting a balance between structural integrity and elasticity. PLA60 achieves the highest recovery at 81.48%, likely due to a more pronounced reduction in crystallinity and an increase in amorphous regions, which facilitate chain mobility and energy storage. This trend suggests that higher concentrations of bTPU improve shape recovery by enhancing elasticity and reducing internal stresses. This findings align with prior studies on PLA/TPU blends, highlighting bTPU's role in improving PLA's shape memory properties [10].

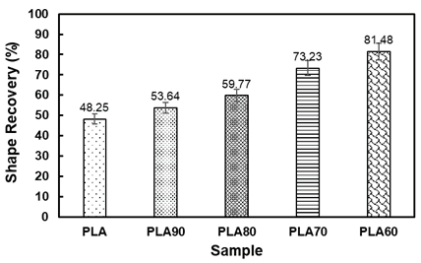


Figure 5: Shape Recovery Percentage of PLA and PLA/bTPU Blends

## V. Conclusions

In this study, PLA/bTPU blends significantly enhanced the material's flexibility and shape memory performance. The elongation at break increased markedly from 7.66% in pure PLA to 944.14% in PLA60, while tensile strength decreased from 43.26MPa to 21.80MPa. Shape recovery efficiency improved with higher bTPU content, reaching 81.48% in PLA60 compared to 48.25% in neat PLA. Morphological analysis revealed greater ductility and energy dissipation due to phase separation, while FTIR confirmed physical blending without new chemical interactions.

Among all compositions, PLA70 offered the most balanced properties in terms of mechanical strength, ductility, printability and shape memory. However, increasing bTPU content beyond 40% introduced challenges such as void formation and reduced print quality due to higher melt viscosity. These limitations suggest the need for further investigation into the use of compatibilizers or alternative processing methods to improve phase dispersion and reduce printing defects.

Overall, these findings contribute to the development of sustainable materials engineering, supporting the creation of adaptable materials for diverse sectors such as aerospace, automotive, and biomedical engineering. The use of bio-based materials aligns with the broader goal of reducing reliance on petrochemicals and promoting sustainability in manufacturing processes. As the field of 4D printing continues to evolve, materials like PLA/bTPU blends are poised to play a significant role in creating innovative products with dynamic properties.

## VI. Acknowledgement

The authors express their gratitude to the Kulliyyah of Engineering, International Islamic University Malaysia (IIUM), and the Asian Office of Aerospace Research and Development (AOARD) for their financial support provided through the collaborative research grant (FA2386-22-1-4041) in partnership with Sungkyunkwan University, South Korea.

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