EVALUATION OF MECHANICAL AND THERMAL PROPERTIES OF SHAPE MEMORY POLYMERS USING 4D PRINTING TECHNIQUE

M.Geetha[1], *P. Prasanna*[2]
[1]*PostGraduate Student, Department of Mechanical Engineering, Jawaharlal Nehru Technological University, Hyderabad, Telangana*
[2]*Associate professor, Department of Mechanical Engineering, Jawaharlal Nehru Technological University, Hyderabad, Telangana*

***Abstract*:** 4D printing, an emerging extension of additive manufacturing, enables the fabrication of smart structures that undergo controlled transformations when stimulated by external triggers such as heat, moisture, or light. Shape Memory Polymers (SMPs) are a prominent class of such smart materials, capable of recovering their original shape upon stimulation.

This study focuses on the development and evaluation of a composite SMP blend of Polylactic Acid (PLA) and Thermoplastic Polyurethane (TPU) in a 70:30 ratio, fabricated using fused deposition modeling (FDM)-based 4D printing. Unlike prior work centered solely on mechanical behavior, this research emphasizes a combined analysis of mechanical, thermal, and shape memory performance. Standard test specimens were printed under varying parameters of layer thickness, printing speed, printing temperature, and raster angle based on a Taguchi L9 orthogonal array. Mechanical properties such as tensile strength, flexural strength, impact resistance, and Shore D hardness were experimentally investigated. Thermal characteristics were analyzed using Differential Scanning Calorimetry (DSC) to identify glass transition, crystallization, and melting behavior. In addition, shape memory functionality was validated through hot water recovery tests.

The results indicate that the PLA/TPU blend achieved tensile strength up to 23.6 MPa, flexural strength of 4.8 MPa, impact strength of 59 J/m, and Shore D hardness values between 82–91, depending on processing conditions. Thermal transitions were observed at ~57 °C (Tg) and ~156 °C (Tm), confirming suitability for thermal actuation. Shape memory testing validated rapid recovery behavior, demonstrating the material's potential for applications in biomedical scaffolds, actuators, and adaptive load-bearing structures.

Keywords: **4D Printing, Shape memory polymers, PLA/TPU Blends.**

1. INTRODUCTION

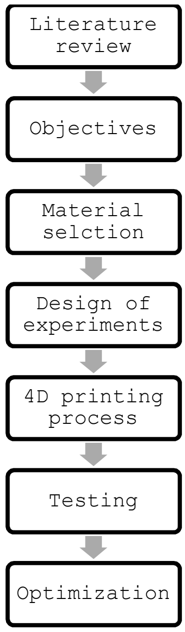
The concept of 4D printing was introduced by Skylar Tibbits in 2013, highlighting the integration of time as a functional dimension in additive manufacturing. Unlike traditional 3D printing, which produces static geometries, 4D printing employs smart materials capable of adapting their structure, properties, or shape in response to environmental stimuli such as heat, moisture, or light. This innovation has led to increasing interest in biomedical devices, aerospace, robotics, and adaptive architectural systems.

Among the various smart materials, Shape Memory Polymers (SMPs) are particularly promising due to their ability to temporarily fix a deformed shape and subsequently recover their original geometry upon activation. Polylactic Acid (PLA), a biodegradable and renewable polymer, is widely studied for 3D/4D printing due to its stiffness and biocompatibility. However, its brittleness limits functional adaptability. Thermoplastic Polyurethane (TPU), on the other hand, offers flexibility, toughness, and elasticity. A PLA/TPU blend thus combines rigidity with flexibility, enabling improved shape memory effects.

Recent studies have investigated the mechanical optimization of PLA/TPU blends fabricated using 4D printing techniques. However, many works have primarily focused on tensile and impact performance, with limited exploration of thermal transitions and experimental validation of shape memory behavior. This research aims to bridge that gap by comprehensively evaluating both the mechanical and thermal characteristics of PLA/TPU composites while explicitly demonstrating their shape memory effect.

The objective of this work is therefore twofold: (i) To optimize printing parameters such as layer thickness, speed, temperature, and raster angle to improve mechanical properties, and (ii) To validate thermal and shape memory behavior to establish the feasibility of PLA/TPU SMPs for advanced functional applications.

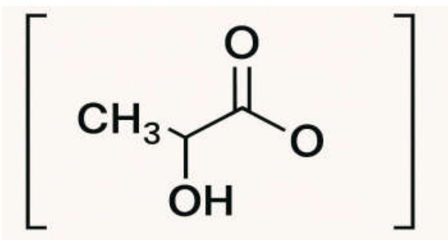
2. METHODOLOGY



3. MATERIAL SELECTION

Polylactic acid (PLA)

Polylactic PLA is a biodegradable thermoplastic made from renewable plant-based resources such as corn starch, sugarcane, and tapioca. The production process involves fermenting these feedstocks to generate lactic acid, which undergoes polymerization to form PLA. Its renewable origin and ability to degrade under certain conditions make PLA popular for uses like packaging, biomedical devices,



and additive manufacturing.

Figure 3.1 Chemical Structure of PLA

Thermoplastic polyurethane (TPU)

TPU exhibits excellent resistance to oils, greases, and solvents, making it suitable for demanding environments. It also offers superior impact strength, flexibility across a broad temperature range, and good adhesion to various substrates. TPU's recyclability and ease of processing further enhance its industrial relevance.

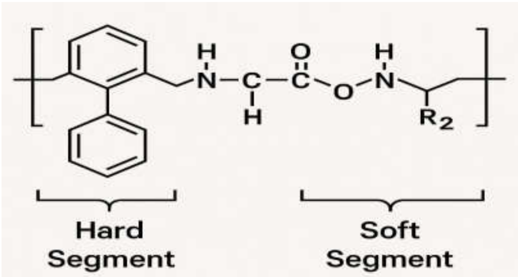


Figure 3.2 Chemical Structure of Thermoplastic Polyurethane (TPU)

Benefits of PLA/TPU Blends

Combining PLA with TPU results in a composite material that balances the strengths of both polymers. The inherent stiffness and ease of processing of PLA, when blended with the elasticity and toughness of TPU, create a material with enhanced flexibility and impact resistance. This synergy addresses PLA’s brittleness while preserving its biodegradability

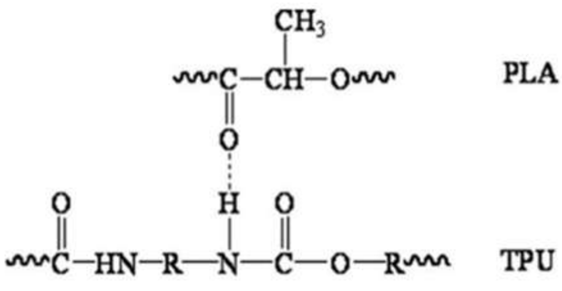


Figure 3.3 Hydrogen bonding between PLA and TPU

DESIGN OF EXPERIMENTS

To systematically evaluate the influence of multiple printing parameters on the mechanical properties of PLA/TPU (70:30) blend specimens, Specifically, the Taguchi method was chosen due to its efficiency in reducing the number of experimental trials while maintaining robust statistical accuracy. Among various orthogonal arrays, the Taguchi L9 orthogonal array was selected, which enables the analysis of four factors at three distinct levels. The parameters considered in this study include Printing Speed, Raster Angle, Layer Thickness, and Printing Temperature. This experimental design approach not only reduces the total number of required experiments from a full factorial 81 (3^4) to just 9 runs but also facilitates the identification of key factors and their optimal levels with minimal experimental effort.

Table 3.1 Design of Experiments

S no.	Printing Speed (mm/s)	Raster angle (º)	Layer Thickness (mm)	Printing Temperature (℃)
1	200	0	0.12	190
2	200	30	0.20	210
3	200	45	0.28	220
4	220	0	0.20	220
5	220	30	0.28	190
6	220	45	0.12	210
7	240	0	0.28	210
8	240	30	0.12	220
9	240	45	0.20	190

4. 4D PRINTING PROCESS

Figure 4.1: 4D Printing Process Mechanism

Selection of processing parameters

In the present study, PLA/TPU (70:30) blends were processed using Fused Deposition Modeling (FDM) to fabricate test specimens for mechanical and thermal evaluation. To ensure uniformity and minimize process-induced variability, certain printing parameters were maintained constant across all samples. These include extrusion speed, shell count, infill pattern, infill density, and bed temperature.

Table 4.2 Constant parameters for Printing

Parameters	Value
Extrude Speed	32 mm/s
Shell count	3
Infill Pattern	Triangle
Infill Density	20%
Bed Temperature	50°C

Table 4.3 Printing Factors with levels

Parameters	Level 1	Level 2	Level 3
Printing speed(mm/s)	200	220	240
Raster angle (º)	0	30	45
Layer Thickness (mm)	0.12	0.20	0.28
Printing Temperature(°C)	190	210	220

This design allowed systematic evaluation of parameter influence while minimizing the number of experimental trials.

Fabrication

Specimens were fabricated using Fused Deposition Modeling (FDM) on Elegoo Neptune 4 Max 3D printer. Test specimens were prepared according to relevant ASTM standards for each property evaluation. Care was taken to maintain consistent bed temperature, extrusion speed, and environmental conditions across all trials.

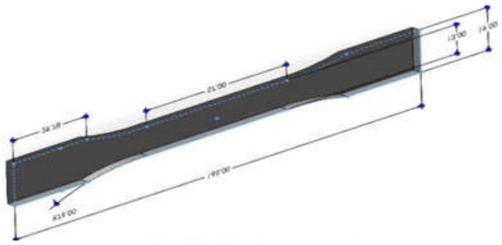


Figure: as per ASTM D256

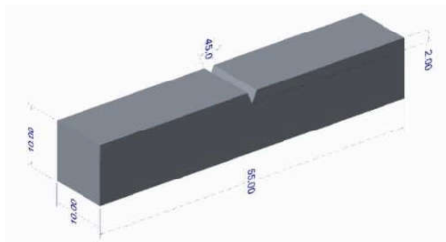


Figure: as per ASTM D638

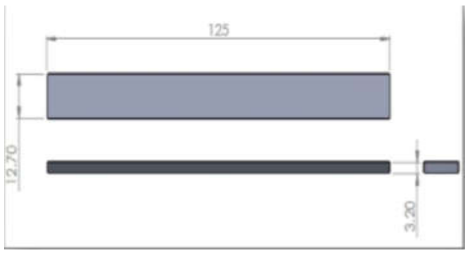


Figure: as per ASTM D790

Figure: as per ASTM D2240

5. TESTING

Mechanical Testing

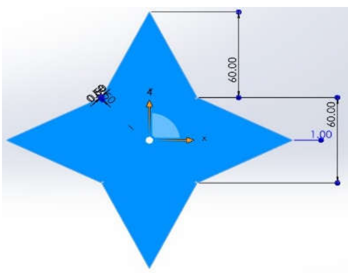
The following tests were conducted:

Tensile Test: Performed as per ASTM D638 to evaluate tensile strength and elongation.

Flexural Test: Conducted according to ASTM D790 using a three-point bending setup.

Impact Test: Carried out as per ASTM D256 (Izod configuration) to measure impact resistance.

Shore D Hardness Test: as per ASTM D2240, using a Shore D durometer to determine surface hardness.



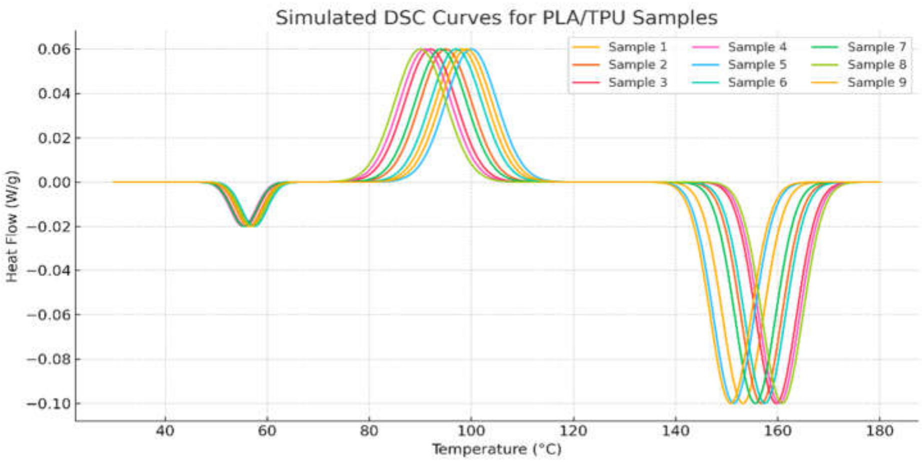
Sno.	Printing speed (mm/s)	Raster angle (º)	Layer Thickness (mm)	Printing Temp (°C)	Tensile Strength (MPa)	% Elongation	Impact strength (J/m)	Shore D Hardness	Flexural strength (MPa)
1	190	0	0.12	190	14.557	3.76	46.5	83	4.425
2	190	30	0.20	210	13.827	3.96	59.17	86	4.423
3	190	45	0.28	220	15.015	4.14	57.10	89	4.351
4	220	0	0.20	220	21.377	5.93	59.25	85	4.461
5	220	30	0.28	190	21.685	5.00	57.35	90	4.365
6	220	45	0.12	210	21.785	5.60	46.72	82	4.324
7	240	0	0.28	210	23.600	4.79	57.68	91	4.465
8	240	30	0.12	220	14.954	4.28	48.6	82	4.325
9	240	45	0.20	190	17.785	4.70	59.33	87	4.812

Thermal Testing

Differential Scanning Calorimetry (DSC) was employed to characterize the thermal transitions of the PLA/TPU blend. Samples were subjected to controlled heating cycles to determine glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm). These thermal properties were essential to evaluate the material's suitability for temperature-activated shape recovery.

Sno.	Printing speed (mm/s)	Raster angle (º)	Layer Thickness (mm)	Printing Temperature (°C)	Glass transition Tg (°C)	Crystallization Tc (°C)	Melting point Tm (°C)
1	190	0	0.12	190	57.2	98	153.2

2	190	30	0.20	210	56.4	95	156.8
3	190	45	0.28	220	55.7	92	159.7
4	220	0	0.20	220	55.3	91	160.3
5	220	30	0.28	190	56.8	100	151.4
6	220	45	0.12	210	57.5	97	157.5
7	240	0	0.28	210	55.5	94	155.6
8	240	30	0.12	220	57.0	90	160.9
9	240	45	0.20	190	56.6	99	150.8



Shape Memory Effect (SME) Testing

Shape memory behavior was validated by deforming printed specimens into a temporary shape and immersing them in hot water near the identified Tg range (~55–60 °C). Recovery of the original geometry was observed and recorded, confirming the shape memory capability of the PLA/TPU blend.

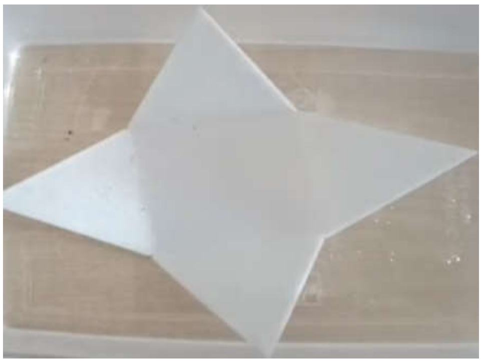


Figure 5.11 Fabrication

Figure 5.12 Programming

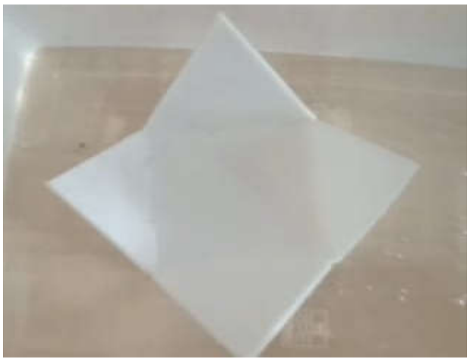


Figure Activation

6. OPTIMIZATION

The mechanical results were statistically analyzed using Analysis of Variance (ANOVA) to identify significant factors. Furthermore, Grey Relational Analysis (GRA) was applied to optimize multi-response outcomes, enabling the determination of parameter combinations that maximized tensile, impact, hardness, and flexural performance simultaneously.

Analysis of Variance (ANOVA)

Using the MINITAB statistical software, we performed the ANOVA analysis on the data for each response variable (Tensile strength, Impact strength, Flexural strength and Shore D Hardness)

Method Factor Coding (-1, 0, +1)

1. General Linear Model: Tensile Strength Vs Layer thickness, Printing temperature, Printing Speed, and Raster angle
2. General Linear Model: Impact Strength Vs Layer thickness, Printing temperature, Printing Speed and Raster angle
3. General Linear Model: Shore-D-hardness Vs Layer thickness, Printing temperature, Printing Speed, and Raster angle
4. General Linear Model: Flexural Strength Vs Layer thickness, Printing temperature, Printing Speed, and Raster angle.

Grey Relational Analysis (GRA): Grey Relational Analysis (GRA) is a widely recognized technique used to determine the optimal conditions of various input parameters to achieve the best quality characteristics. Grey Relational Analysis (GRA) is a powerful method for optimizing processes and systems, especially when dealing with multiple variables and limited information. The process involves several stages:

- Data Pre-processing
- Normalizing
- Deviation Sequence
- Grey Relation Sequence
- Grey Relation Grade

Table 6.1 GRA Table

	Original values				Normalizing values			
Sno.	**Tensile Strength (MPa)**	**Impact strength (MPa)**	**Shore D Hardness**	**Flexural Strength (MPa)**	**Tensile Strength (MPa)**	**Impact strength (MPa)**	**Shore D Hardness**	**Flexural Strength (MPa)**
1	14.557	46.5	83	4.425	0.075	0.000	0.111	0.207
2	13.827	59.17	86	4.423	0.000	0.988	0.444	0.203
3	15.015	57.1	89	4.351	0.122	0.826	0.778	0.055
4	21.377	59.25	85	4.461	0.773	0.994	0.333	0.281
5	21.685	57.35	90	4.365	0.804	0.846	0.889	0.084
6	21.785	46.72	82	4.324	0.814	0.017	0.000	0.000
7	23.6	57.68	91	4.465	1.000	0.871	1.000	0.289
8	14.954	48.6	82	4.325	0.115	0.164	0.000	0.002
9	17.785	59.33	87	4.812	0.405	1.000	0.556	1.000
Max	23.6	59.33	91	4.812	1.000	1.000	1.000	1.000
Min	13.827	46.5	82	4.324	0.00	0.00	0.00	0.00

Deviation Sequence					Grey relation Coefficient				GRG	Rank
S. No	Tensile Strength	Impact Strength	Shore D hardness	Flexural Strength	Tensile Strength	Impact Strength	Shore D hardness	Flexural Strength		
1	0.925	1.000	0.889	0.793	0.351	0.333	0.360	0.387	0.358	8

2	1.000	0.012	0.556	0.797	0.333	0.976	0.474	0.385	0.542	5
3	0.878	0.174	0.222	0.945	0.363	0.742	0.692	0.346	0.536	6
4	0.227	0.006	0.667	0.719	0.687	0.988	0.429	0.410	0.628	4
5	0.196	0.154	0.111	0.916	0.718	0.764	0.818	0.353	0.663	3
6	0.186	0.983	1.000	1.000	0.729	0.337	0.333	0.333	0.433	7
7	0.000	0.129	0.000	0.711	1.000	0.795	1.000	0.413	0.802	1
8	0.885	0.836	1.000	0.998	0.361	0.374	0.333	0.334	0.351	9
9	0.595	0.000	0.444	0.000	0.457	1.000	0.529	1.000	0.747	2
Delta min	0.000									
Delta max	1.000	Theta= 0.5								

(Rank 1- Sample 7) Sample 7 has a raster angle of 1 and a printing speed of 3. The greatest Grey is achieved at a layer thickness of 3 and a printing temperature of 2. The best performance is achieved with a relational grade (GRG) of 0. 802.Shore Impact strength and Tensile strength are combined in this way.

Table 6.2 Grey Relation Grade and mean corresponding to the Design of Experiment

Printing speed (mm/s)	Raster angle (º)	Layer Thickness (mm)	printing Temp (°C)	GRG	S-N ratio	Means
200	0	0.12	190	0.358	8.92234	0.358
200	30	0.20	210	0.542	5.32001	0.542
200	45	0.28	220	0.536	5.41670	0.536
220	0	0.12	190	0.628	4.04081	0.628
220	30	0.20	210	0.663	3.56973	0.663
220	45	0.28	220	0.433	7.27024	0.433
240	0	0.12	190	0.802	1.91651	0.802
240	30	0.20	210	0.351	9.09386	0.351
240	45	0.28	220	0.747	2.53359	0.747

Table 6.3 Response table for means

Level	Printing Speed	Raster angle	Layer thickness	Printing Temp
1	0.4787	0.5960	0.3807	0.5893
2	0.5747	0.5187	0.6390	0.5923
3	0.6333	0.5720	0.6670	0.5050
Delta	0.1547	0.0773	0.2863	0.0873
Rank	2	4	1	3

Effect of parameters on mechanical properties

Influence of Layer Thickness

Changes in layer thickness have the greatest effect on the GRG increasing from 0.12 to 0.28. This indicates that the layer thickness possesses the greatest impact on boosting the tensile strength and impact the substance is a composite material made of a shape memory polymer that is strong.

Impact of Printing Speed

Variations in printing speed have the greatest impact on the GRG. The second most significant factor is between 200 and 240. Its influence on although remarkable, GRG is less important than hardness.

Impact of Printing Temperature

On shape memory, this is the third most important factor. The GRG value rises with printing temperature increases, but the GRG value begins to decline when the temperature reaches 2200°C reduces.

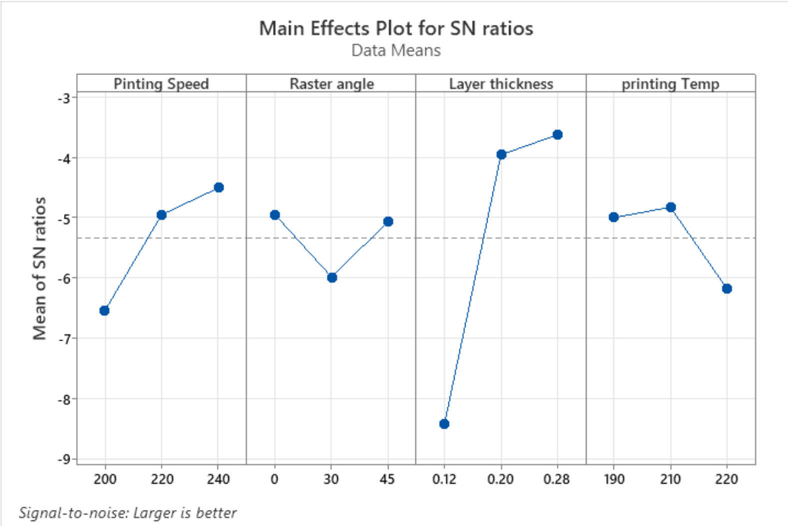
Impact of Raster Angle

The fact that this Parameter has the least impact on GRG means that the variations in the Raster angle from 0^0 to

45^0, the initial GRG increases to 300, but at greater raster angles (45^0) diminishes.

Optimal Solution

The optimal printing Speed, based on the means, is level 3 (0.64) because it shows the highest mean value, which typically indicates better performance. Similarly, to the printing speed. The graph below shows the mean response for the different levels of reinforcement



(1, 2, and 3), using data from the table.

Layer Thickness Level:3 Raster Angle Level :1

Printing Speed Level:3 Printing Temperature Level:2

The maximum overall SN ratio, which suggests the best performance according to the SN ratio analysis, will result from this combination of circumstances.

Effect of parameters on Thermal properties

Effect of Printing Speed

Glass transition temperature(Tg) increased slightly with printing speed, peaking at 240 mm/s due to improved PLA phase continuity and reduced chain mobility restrictions is Decreased with increasing speed, indicating that higher deposition rates reduce thermal residence time and hinder ordered crystallization. Tm remained relatively stable, with minor variations reflecting differences in crystalline perfection.

Effect of Raster angle

Glass transition temperature (Tg) slightly decreased with higher raster angles, reflecting increased amorphous phase dominance and TPU chain mobility.

Crystallization temperature(Tc) showed a decreasing trend as raster angle increased, indicating disruption in crystal nucleation.Tm remained largely unaffected, suggesting minimal impact of raster angle on PLA crystalline stability.

Effect of Layer Thickness

Glass transition temperature(Tg) is highest at 0.12 mm, where improved interlayer bonding and reduced TPU interference were observed is decreased with increasing layer thickness, suggesting slower crystallization in thicker deposits. Melting temperature(Tm) is Peaked at 0.20 mm, indicating optimal crystalline packing at balanced cooling conditions.

Effect of Printing Temperature

Glass transition temperature(Tg)is highest at 210 °C, with a slight decrease at 220 °C due to TPU softening and increased chain mobility. Crystallization temperature(Tc) is Peaked at 210 °C, suggesting balanced crystallization kinetics at this temperature. Melting temperature(Tm) remained mostly stable, with a small increase at 220 °C linked to improved crystalline perfection.

7 RESULTS AND DISCUSSION

Mechanical Properties

- The mechanical test results demonstrated that the PLA/TPU (70:30) blend exhibited a good balance of strength and flexibility under different printing conditions.
- Tensile Strength: Ranged between 13.8 MPa and 23.6 MPa, with the highest strength observed at a layer thickness of 0.28 mm, printing speed of 240 mm/s, raster angle of 0°, and temperature of 210 °C.
- Flexural Strength: Varied from 4.3 MPa to 4.8 MPa, indicating adequate stiffness while maintaining toughness.
- Impact Strength: Recorded between 46 J/m and 59 J/m, with higher values at moderate raster angles and higher printing speeds.
- Shore D Hardness: Values were in the range of 82 to 91, showing that TPU addition provided flexibility without compromising hardness.
- These results are consistent with existing literature while highlighting the influence of process parameters on the mechanical performance of the blend.

Thermal Analysis (DSC)

The Differential Scanning Calorimetry (DSC) analysis confirmed the thermal transitions of the PLA/TPU blend.

- Glass Transition Temperature (Tg): Observed around 55–57 °C, corresponding to the onset of mobility in the amorphous phase.
- Crystallization Temperature (Tc): Detected between 98–102 °C, indicating partial ordering during cooling.
- Melting Temperature (Tm): Recorded in the range of 155–160 °C, associated with crystalline PLA domains.

These thermal transitions establish the feasibility of using thermal activation (hot water or controlled heating) to trigger the shape memory response.

Shape Memory Effect (SME)

Shape memory testing validated the functional responsiveness of the printed specimens. When deformed into a temporary geometry and exposed to hot water near Tg (~60 °C), the samples recovered their original shape within a short duration. This confirms that the PLA/TPU blend demonstrates effective thermo-responsive shape memory behavior, making it suitable for adaptive and biomedical applications.

Optimization of Printing Parameters

The statistical analysis using ANOVA indicated that layer thickness and printing speed were the most significant factors affecting tensile and impact strength. Raster angle and temperature also influenced performance but to a lesser extent.

Grey Relational Analysis (GRA) revealed the optimal combination of parameters as:

Layer thickness: 0.28 mm

Printing speed: 240 mm/s

Raster angle: 0°

Printing temperature: 210 °C

This combination provided the best overall mechanical performance, with a Grey Relational Grade (GRG) of 0.802, which was superior to other tested conditions.

Comparative Discussion

While prior studies have focused primarily on mechanical optimization of PLA/TPU SMPs, the inclusion of thermal analysis and direct SME validation in this research demonstrates a more holistic evaluation. The integration of DSC results with shape memory recovery testing provides experimental proof of thermo-responsive actuation, positioning this material system as a strong candidate for biomedical scaffolds, deployable structures, and adaptive actuators.

8 CONCLUSIONS

Thermal Properties – Glass Transition (Tg): Found between 55.3°C and 57.5°C, reduced from neat PLA due to TPU plasticization, which lowers activation temperature for shape recovery.

- Thermal Properties – Crystallization (Tc): Ranged from 90°C to 100°C, with lower values indicating TPU's interference in PLA chain packing, producing finer crystallites that enhance recovery elasticity.
- Thermal Properties – Melting Temperature (Tm): Ranged from 150.8°C to 160.9°C, showing TPU had minimal influence on PLA crystalline stability.
- Shape Memory Recovery: Achieved >90% recovery ratio within ~10 seconds at 70–80°C, with stable performance over multiple cycles and only minor residual strain in hinge regions.
- Shape Memory Mechanism: Validated the dual-segment SMP mechanism—rigid PLA crystalline phase for shape fixing and soft TPU amorphous phase for actuation.
- Application Potential: Suitable for biomedical devices, soft robotics, adaptive structures, and responsive consumer products, offering an optimal balance of stiffness, flexibility, and thermal responsiveness.
- Scientific Contribution: Established clear parameter–property relationships in 4D printed PLA/TPU SMPs, showing process control can enhance both functional performance and actuation efficiency.

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