4D PRINTING OF PLA AND PLA-BASED COMPOSITES FOR LOAD-BEARING APPLICATIONS

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Bachelor of Technology in Mechanical Engineering

Vignan’s Institute of Information Technology

September 2020

Submitted in partial fulfillment of requirements for the degree

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

at the

CLEVELAND STATE UNIVERSITY

December 2023

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ACKNOWLEDGMENT

First and foremost, I would like to thank my research advisor, Dr. Prabaha Sikder, for guiding me in this research project and academics during my master's program. His support and knowledge made it possible for me to present this work. I learned so much from him, professionally and personally; he has helped and supported me tremendously.

I would also like to sincerely acknowledge Dr. Josiah S Owusu-Danquah for providing me with the facility of his lab equipment. I sincerely thank Lakshmi Likitha Velivela for helping me with mechanical testing in this Research. I'm also very thankful to my lab mates Surendra Singh Sonaye, Vijay Kumar Bokam, Harsha Phaneendra, and Pawan Sriharsha for their constant support.

I want to thank Dr. Josiah S Owusu-Danquah and Dr. Mustafa Usta, who agreed to be part of my thesis committee.

I'm forever grateful to my parents for all the encouragement and support they gave me. Finally, I'm very thankful to my friends who stood up for me constantly, irrespective of the situation, and helped me achieve this.

Dr. Sikder's STARTUP supports this work.

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ABSTRACT

This research investigates the deformation recovery of 3D-printed Polylactic Acid (PLA) shape memory polymers (SMPs). The study delves into the influence of Fused Deposition Modelling (FDM) parameters, such as nozzle temperature, layer thickness, and printing speed, on the thermomechanical behavior of PLA SMP honeycomb structures. The research identifies optimal printing conditions using the Taguchi approach and explores the cyclic shape memory recovery behavior of the optimized PLA SMP under compression loads.

Additionally, the research includes a chapter on the extrusion and printing of uniform-diameter polylactic acid carbon fiber (CFR-PLA) composite filaments. The synthesis of CFR-PLA involves planetary ball milling for composite homogeneity. Extrusion parameters and 3D printing conditions are optimized, and mechanical testing, particularly tensile testing, reveals the composite's strength and flexibility. Fracture surface analysis highlights the behavior of carbon fibers during testing.

Altogether, these results advance our understanding of PLA shape memory polymers and CFR-PLA composites, offering insights into material properties, printing parameters, and potential applications in various industries, including robotics, aerospace, and biomedicine.

Keywords: Polylactic acid (PLA), Carbon fiber, 4D Printing, Milling, Extrusion.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW OF 4D PRINTING

1.0 Introduction

In the 1980s, the term "3D printing" first emerged, marking a significant advancement in the field of manufacturing. This technology allows researchers, manufacturers, and others to fabricate materials based on CAD modeling, utilizing a layer-by-layer approach. The ability to bring complex designs to life with ease made 3D printing particularly noteworthy. Over time, it has evolved and found applications in various fields, including product development, prototyping, biotechnology, and material science. Among the commonly used 3D printing techniques are fused deposit modeling (FDM), selective laser sintering (SLS), selective laser melting (SLM), stereolithography apparatus (SLA), binder jetting, and digital light processing (DLP). As technology progressed, 3D printing became more accessible, fostering a knowledge-sharing community between learners and professionals.

As technology continues to advance rapidly in all spheres, a new technology of 3D printing, known as "4D printing," emerged in 2013. Coined in a laboratory at the Massachusetts Institute of Technology (MIT)[1], 4D printing overcame certain limitations of 3D printing by introducing the ability to change the shape of rigid materials through external stimuli. In essence, 4D printing can be defined as 3D printing with an added time dimension. However, not all materials used in 3D printing can be employed in 4D printing, as they must be able to undergo shape changes in response to external factors such as temperature, humidity, magnetic fields, UV light, wind, and water, among others. These adaptable materials, referred to as intelligent materials, possess the ability to sense external stimuli and respond accordingly.

Currently, 4D printing remains a highly specialized technique, requiring specific optimization of material properties for different methods and printing machines. Suitable printing methods include Fused Deposit Modelling (FDM), Digital Light Processing (DLP), Direct Writing (DW), and Polyjet. Five key factors determine the reliability of 4D printing: the materials used, additive manufacturing processes, stimuli, modeling techniques, and interaction mechanisms.

Shape Memory Polymers (SMPs) are the most used materials in 4D printing. These materials can be programmed to deform and reform. FDM is frequently employed to print SMPs, as they can be printed at low temperatures, are user-friendly, and exhibit minimal warping compared to other polymers. Among the SMP family, one notable biodegradable and bio-sourced polymer is polylactic acid (PLA), which is compatible with natural reinforcements and possesses excellent light absorption properties like glass. PLA has been commercially available since it was first discovered in 1845 and exhibits comparable mechanical and physical properties, making it a preferred material due to its widespread availability.

Projections indicate a compound annual growth rate (CAGR) of 20% between 2018 and 2028 for 4D printing. According to a 2019 report, the global market for PLA in 3D printing is expected to grow significantly, and various 3D printing techniques, including fused filament fabrication (FFF) or fused deposition modeling (FDM), Digital Light Processing (DLP), Color Jet (CJP), MultiJet Printing (MJP), Stereolithography (SLA), Selective Laser Sintering (SLS), and Direct Metal Printing (DMP) are commonly used.

The applications of 3D bioprinting technology span diverse industries, offering benefits in rapid prototyping for the flexible and swift design and production of sophisticated and customized parts. Industries such as aerospace, automotive, robotics, construction, dentistry, prosthetics, orthotics, and regenerative medicine have all leveraged 3D printing to revolutionize their respective domains. Moreover, 3D printing has extended to the production of customized consumer goods, including furniture, toys, phone coverings, and fashion items.

4D printing is an expansion of 3D printing that introduces a fourth dimension, time, to create dynamic, self-transforming things or materials. Objects are constructed layer by layer utilizing various materials in traditional 3D printing. However, 4D printing takes this concept further by enabling these printed objects to change their shape or properties over time when exposed to specific environmental stimuli. The shape recovery ratio, representing the difference between the initial deformation and the rate of deformation change per unit of time, becomes a crucial parameter in this context.

Since its conception by Tibbits in 2013[2], 4D printing technology has surmounted several obstacles and limitations associated with 3D printing. Two critical distinctions between 3D and 4D printing are the use of intelligent materials, also known as stimuliresponsive materials, and smart design. Unlike 3D printing, where no shape-related changes are expected post-printing, 4D printing allows for greater creative flexibility and leverages smart materials programmed for specific alterations that occur after printing. Figure 1 illustrates the difference between 3D printing and 4D printing.

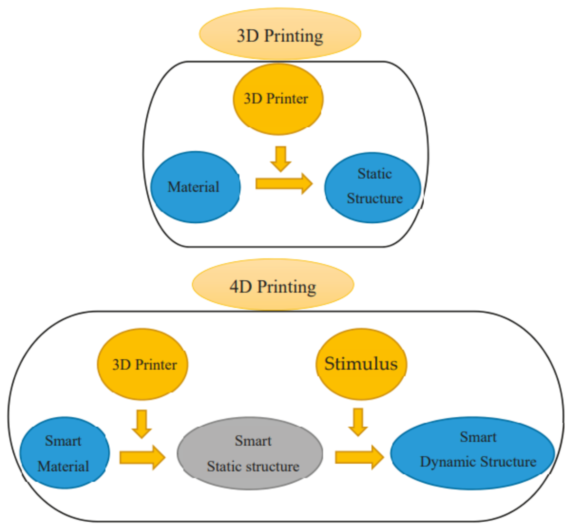


Figure 1. Difference between 3D and 4D Printing

4D printing technologies have far-reaching potential applications in architecture, medicine, food production, automobile manufacturing, and various other industries.

Shape memory polymers (SMPs) play a pivotal role in 4D printing, as they can revert to their original shape in response to stimuli, cycling between a rigid polymer state and an elastic state. This reversible shift in elastic modulus enables various shape changes. While several studies have explored the shape memory behavior of PLA, few have investigated how FDM settings affect these properties.

During the investigation of recovery [3]and material properties, stresses that correlate to a specified maximum load on PLA are discovered. These compressive stresses are the result of the force applied to each PLA sample during the experiment. It is important to note that the material architecture of the PLA sample led to a unique deformation response, causing each sample to slant, indicating both shear deformation and strain in the direction of loading (as seen in Fig. 2). As a result, capturing this material complexity in terms of stress effects and failure criteria becomes essential, requiring a comparison of simulation findings with experimental results.

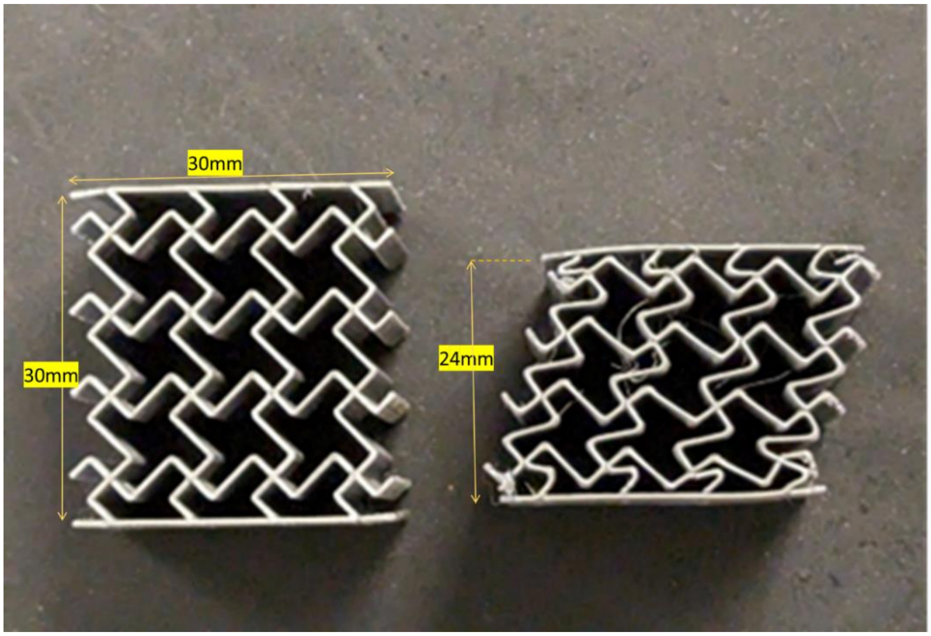


Figure 2. Shear deformation of the specimen

The shape memory effect of the samples was studied in this work by submerging samples in a water tank at a post-heating temperature of 65°C. The stress failure criterion was further investigated using finite element simulation in SOLIDWORKS software.

This research is expected to fill a gap in the specialized literature, as there are no comparable findings in this research area. Additionally, it will yield critical insights for 4D-printed structures intended for cyclic applications.

CHAPTER II

DEFORMATION RECOVERY OF ADDITIVELY MANUFACTURED POLYLACTIC ACID (PLA) SHAPE MEMORY POLYMERS

2.1 Introduction

Shape memory polymers (SMPs) are a type of intelligent, multifunctional material that can store and recover programmed deformations in response to external stimuli such as temperature, moisture, light, electricity, or magnetism [4-6]. SMPs have gained a lot of attention due to their potential to create multifunctional composites and devices that can be used in the fields of aerospace, biomedicine, and robotics. Compared to shape memory alloys, such as the well-known Nickel-Titanium, SMPs have lighter weight and can be produced at a lower cost. Their functional properties can also be easily tailored, thus allowing a more expansive room for application-specific designs[7].

The functional classification of a shape memory polymer is defined by the state of the material about the glass transition temperature (Tg). At temperatures higher than Tg, the SMP at a rubbery state can recover large magnitudes of induced deformations upon loading and unloading at a constant temperature, i.e., super elasticity. On the other hand, at temperatures below the Tg, substantial irrecoverable strains (or residual deformations) are induced in the material upon loading and unloading mechanically. However, these residual deformations are recovered once the material is heated above the Tg, signifying the one-way shape memory effect functionality. In some cases, the material can be programmed to remember two different shapes, one at a cold temperature and another at a high (hot) temperature[8]. Each change in temperature corresponds to a degree of shape recovery-this underlines the principle of the so-called 4D printing. Among the biodegradable and bio-sourced SMP family, Polylactic acid (PLA) is the most common. PLA has high tensile and flexural strengths and high elastic deformation, and it is widely available[9, 10].

Over the past years, different additive manufacturing (AM) technologies, also known as 3D printing methods, have been used to manufacture polymers successfully. AM offers several known advantages over traditional fabrication methods, including reduced material waste, enhanced design freedom, and the potential for rapid prototyping. The creation of patient-specific models for use in dentistry, prosthetics, and orthotics is being revolutionized in the field of medicine by 3D printing [11, 12]. According to the 2019 Grand View Research report, the worldwide PLA market for 3D printing would expand at an average compound annual growth rate (CAGR) of 20% between 2018 and 2028[13]. The most adopted techniques for 3D printing include Fused Filament Fabrication (FFF) or Fused Deposition Modelling (FDM), Digital Light Processing (DLP), Color Jet (CJP), MultiJet Printing (MJP), Stereolithography (SLA), Selective Laser Sintering (SLS). PLA-SMPs are frequently 3D printed using Fused deposit modeling as they print at a low temperature and are easy to use. Moreover, warping in FDM-fabricated polymers is substantially less than those fabricated from other techniques.

However, one of the main challenges of additive manufacturing is controlling the printing parameters to achieve a targeted material behavior. Existing experiments have looked at how FDM parameters affect the mechanical strength of PLAs [14-16], but only a few have investigated how these parameters affect the deformation recovery of PLA-SMPs. Barletta et al. [17] studied the shape memory properties of SMPs and observed that the activation temperature significantly influences the shape recovery time. Fundamentally, heating deformed SMPs to higher temperatures increased the magnitude of deformation recovery and reduced the recovery time. For complex-architecture structures, understanding the interplay of geometry and printing parameters on the long-term cyclic performance of the material is vital for the efficient design of smart structures [18].

To this end, this study focused on two objectives: first, quantifying the effect of FDM printing parameters on the thermomechanical behavior of PLA-SMP honeycomb structure, and second, assessing the cyclic shape memory recovery behavior of optimized PLA SMP subjected to compression loads. The study outline follows a brief description of the material fabrication process and experimental testing procedures given in Section 2, A discussion of results, emphasizing the effect of printing temperature, layer thickness, and printing speed on the deformation behavior of the SMP, are discussed in Section 3. The conclusions drawn from the study are given in Section 4.

2.2 Materials and Methods

2.2.1 Material and Specimen Fabrication

The fermentation of plant materials such as cornstarch, taro, and sugar cane results in the production of the PLA polymer. It is a pure polymer but may contain limited additives to modify various properties, including intramolecular flexibility, melt viscosity, and color or visual properties. Fillers and reinforcements can be added to the PLA matrix to enhance its essential characteristics. Carbon fibers, glass fibers, or nanoparticles, for instance, can improve the mechanical strength, stiffness, and heat resistance of PLA-based SMPs. The physical and mechanical properties of the PLA sample used in this study are reported in Table 1.

Table 1. Physical and mechanical properties of the PLA sample.

Properties	Value
Density	1.24g/cm^3
Tensile strength at the break at 20^{o}C	43Mpa [19]
Melting temperature	177^{o}C
Glass transition temperature	57^{o}C
Yield strength	Variable
Elastic Modulus	Variable

2.2.2 Design and Printing of the PLA SMP Structure

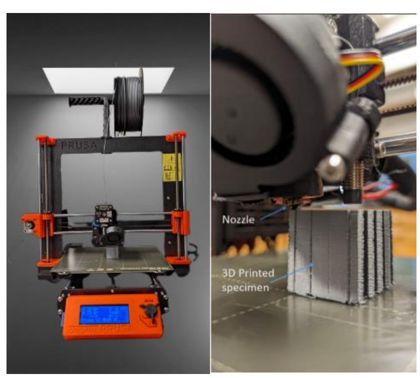


Figure 3. PRUSA i3 MK3S+

A 30 x 30 x 30 mm^3 sandwich structure was fabricated using PRUSA i3 MK3S+ (see **Figure 3**). Sandwich structures are efficient load-bearing components made up of a lightweight core, which separates two thin face sheets. The 3D printer integrates various technologies and features that add to its reliability and ease of use. **Figure 4** outlines the general steps involved in the FDM fabrication process. A computer-aided design (CAD) model was created in SolidWorks and fed into the printer as the input geometry. The printing process begins with the melting of a filament, which is deposited layer by layer on the printing platform through the nozzle. After the first layer gets deposited, the nozzle advances to build the next layer, and this process repeats until the entire object is produced. In the process of repeatedly melting and cooling, the layers bond together to form the printing component. Figure 3 shows a sample of the 3D Printed PLA with dimensions.

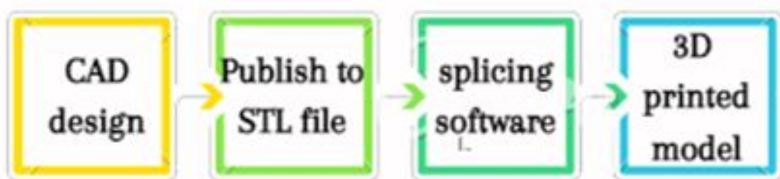


Figure 4. Stages in the FDM procedure for creating 3D printed parts.

The process parameters have an impact on the precision, effectiveness, and attributes of the material. Therefore, a thorough examination of several process variables is required to make reliable parts using FDM technology. By varying the printing parameters, different samples were fabricated, each expected to have a different mechanical response. Several studies in the past have shown that maximum strength is obtained when PLAs are manufactured using a 0° build orientation [20]. Thus, in our study, the build orientation was kept the same for all cases, and the parameters of interest were selected to be the nozzle temperature (T), printing speed (s), and layer thickness (t).

The pace of movement of the print head or nozzle of a 3D printer during the printing process is known as print speed; its standard unit of measurement is millimeters per second (mm/s). The print quality, adhesion of layers, total print time, and handling of difficult features like bridging and overhangs are all impacted by the print speed selection [21]. The vertical distance between successive layers of material deposited during the printing process is known as layer thickness. It has a major effect on print speed and quality. While thicker layers speed up printing at the expense of potential resolution loss, thinner layers produce finer, more detailed prints [22]. Nozzle temperature can be referred to the temperature of the nozzle at which the filament is extruded out from the printer.

Here, the best set of parameters for an L27 array was determined using the Taguchi approach, which significantly lowers the complexity of experimentation. For each set of printing parameters, two specimens were printed, tested and averaged. **Table 2** shows the range of temperature, printing speed, and layer thickness considered in this study.

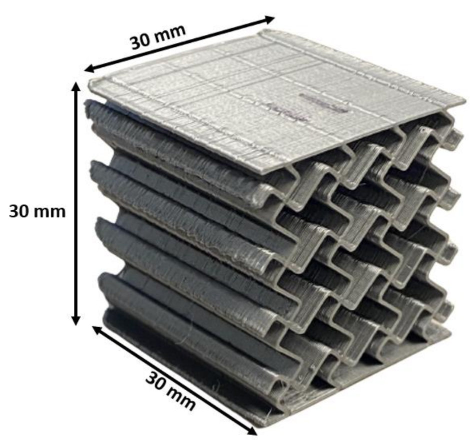


Figure 5. Sample 3D Printed PLA with dimensions.

Table 2. Printing parameters used for the study.

Sample	Nozzle Temp (C)	Layer thickness(mm)	Print Speed (mm/s)
1	190	0.2	30
2	190	0.2	60
3	190	0.2	90
4	190	0.15	30
5	190	0.15	60
6	190	0.15	90
7	190	0.1	30
8	190	0.1	60
9	190	0.1	90
10	210	0.2	30
11	210	0.2	60
12	210	0.2	90
13	210	0.15	30
14	210	0.15	60
15	210	0.15	90
16	210	0.1	30
17	210	0.1	60
18	210	0.1	90
19	230	0.2	30
20	230	0.2	60
21	230	0.2	90
22	230	0.15	30
23	230	0.15	60
24	230	0.15	90
25	230	0.1	30
26	230	0.1	60
27	230	0.1	90

Table 3. Nozzle Diameters of the Extruders.

Layer Thickness (mm)	Nozzle dia (mm)
0.2	0.4
0.15	0.3
0.1	0.2

2.2.3 Compression and Deformation Recovery Testing

The 3D printed PLA specimen was tested in a Universal Testing Machine (UTM), *Instron 3369* model, which has a high-precision load and data collection unit to measure the samples' compressive strength. **Figure 6** describes the general steps involved in the deformation recovery testing of the shape memory polymer samples. Before each test, the initial height of the printed samples was recorded, and then upon placement in the UTM machine, further subjected to a compression deformation of up to 14 mm. The deformation rate was set at 1 mm/min for all tested samples.

The force-versus-displacement data was retrieved from the *Blue Hill* Universal software interfaced with the UTM, and the yield stress, yield strain, and elastic modulus were obtained for each sample. The final deformed height was measured, and the total irrecoverable deformation, δirr was evaluated as the difference between the initial and final heights. Typical to most engineering materials, some small elastic rebound/ elastic recovery occurs after completely removing the applied mechanical loads. The deformed samples were heated to a temperature of 65^{o}C (which was above the PLA's glass transition temperature) using warm water, and the amount of deformation recovery was recorded after heating. Since this SMP material operated under the one-way memory effect, the height measured at the end of heating remained the same even after the temperature environment of the PLA was reduced from 65^{o}C to room temperature (22-23^{o}C).

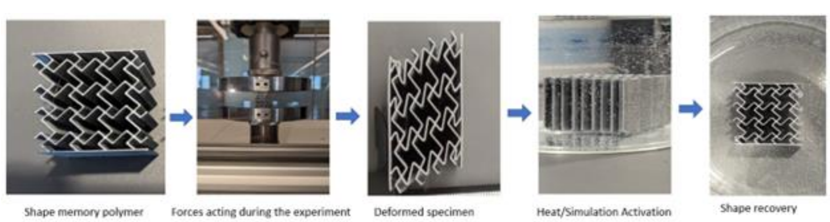


Figure 6. Schematic representation of the shape memory behavior of PLA

2.3 Results and Discussions

This section contains the results of our extensive investigation, which included the 3D printing and compression testing of 27 PLA samples with different printing conditions. The complex interaction between nozzle temperature, layer thickness, and compressive stress in 3D-printed PLA materials is clarified by these findings. Our analysis of the effects of these parameters yields crucial information for maximizing the structural integrity and mechanical performance of 3D-printed parts. Researchers and practitioners in the field of additive manufacturing will find these insights invaluable as they provide a greater understanding of how particular printing conditions affect PLA's compressive properties. This will allow for the custom design of 3D-printed products for a wide range of applications.

2.3.1 Effects of Printing Parameter Variations on Mechanical Properties

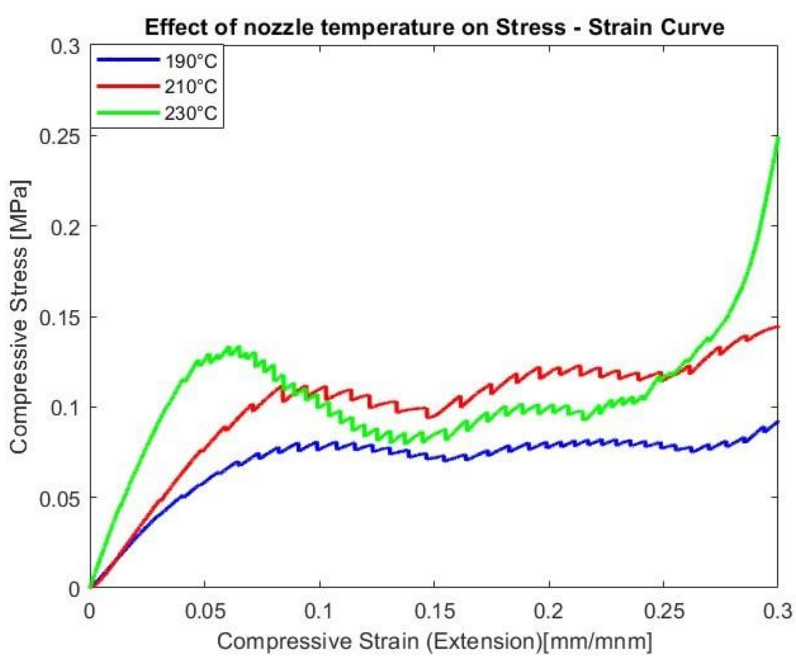


Figure 7 (a)

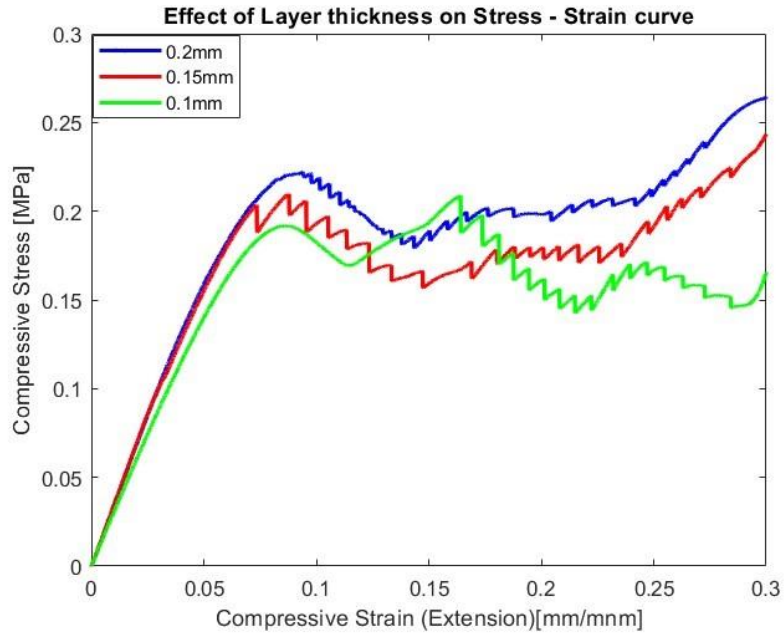


Figure 7 (b)

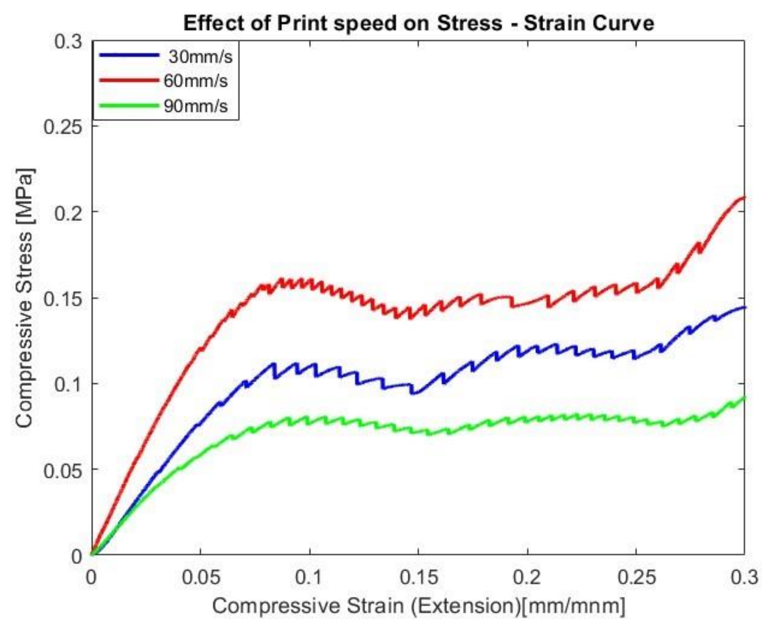


Figure 7 (c)

Figure 7. Effect of printing parameters on Compressive stress
7(a)Effect of nozzle temperature 7(b)Effect of layer thickness 7(c) Effect of Print speed

From the above representations, it was clear that nozzle temperature had a big impact on compressive stress. A steady and significant increase in compressive stress was seen as the nozzle temperature rose from 190°C to 230°C. The importance of nozzle temperature in determining the compressive strength of PLA components created via 3D printing is highlighted by this observation. The material was better able to tolerate compressive stresses as a result of the higher temperatures encouraging stronger interlayer bonding.

Second, it was discovered that layer thickness also played a significant role in determining compressive stress. The layer thickness, which varied from 0.1 to 0.2 mm, increased in direct proportion to the increase in compressive stress. Increased load-bearing capacity and overall structural robustness were facilitated by thicker layers. This finding emphasizes the direct relationship between layer thickness and compressive strength, showing that constructions with thicker layers are more robust and able to sustain higher compressive stresses.

Finally, an unusual pattern was observed when contrasting the print speed (30mm/s, 60mm/s, 90mm/s). Comparing 30mm/s to 60mm/s of print speed, there was a noticeable rise in compressive stress. Nevertheless, there was a sudden decrease in compressive stress when the print speed was raised to 90mm/s. This insight emphasizes how print speed optimization requires a careful balance. The print speed's first rise of 60mm/s mm indicates that it can support a higher load-bearing capability and maintain structural integrity. But the subsequent reduction at 90mm/s might be explained by too much material, which would hinder interlayer adhesion and weaken the structure.

All things considered, these results highlight how crucial nozzle temperature and layer thickness are in determining the compressive strength of PLA materials that are 3D printed. With regard to a variety of additive manufacturing applications, this knowledge offers insightful guidance for maximizing the mechanical performance and structural integrity of 3D-printed components.

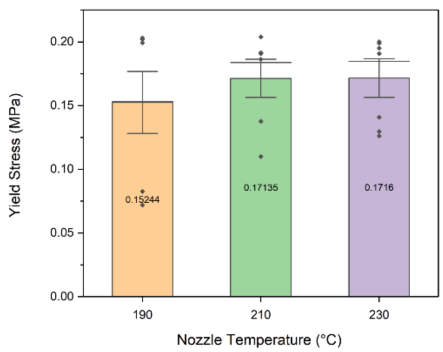


Figure 8 (a)

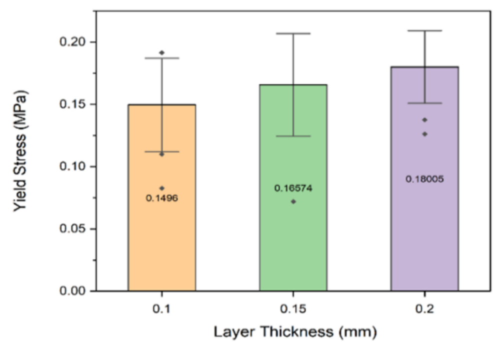


Figure 8 (b)

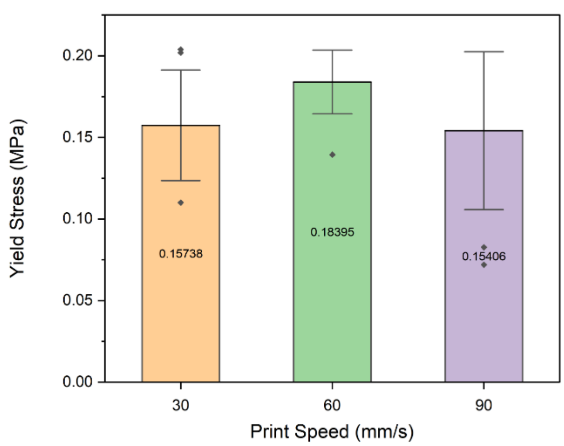


Figure 8 (c)

Figure 8. Effect of Printing parameters on the yield stress.
8(a) Effect or Nozzle temperature 8(b) Effect of Layer thickness 8(c) Effect of Print speed

Our 27 PLA sample compression test results have provided vital information about the connection between different printing parameters and compressive stress. These results provide insight into how PLA behaves mechanically in various scenarios.

Figure 8 (a) illustrates the noteworthy rise in yield stress, from 0.1524 MPa to 0.1716 MPa, as the nozzle temperature is elevated from 190°C to 230°C. Similarly, in Fig 8 (b), as the layer thickness varies from 0.1 to 0.2, there is an observable increase in yield stress, progressing from 0.1496 MPa to 0.18005 MPa. Additionally, in Fig 8 (c), when the printing speed is enhanced from 30 mm/s to 60 mm/s, the yield stress escalates from 0.15738 MPa to 0.18395 MPa. Conversely, an increase in print speed to 90 mm/s results in a decrease in yield stress to 0.15406 MPa.

M. Barletta at. el.[17] observed similar results, by conducting compression tests on samples while varying the printing speed, nozzle temperature, and layer thickness. They observed that thicker layers of 0.3mm and higher nozzle temperatures of 210°C increased the compressive stress when compared with 180^{o}C and 0.1mm. On the other hand, lower compressive strength was observed at the increased printing speed from 40 mm/s to 80 mm/s.

Dave, H. K., et al., explored the relationship between print speed and compressive strength; it indicates that compressive strength improves initially a bit as print speed increases. This tendency is restricted, though, to a particular point, usually at a print speed of 40 mm/min. After this, compressive strength begins to decline as print speed keeps rising, which is similar to our results [23]. The relationship between layer thickness and compressive strength in the study reveals that changes in layer thickness have a noticeable impact on compressive strength. It was observed that an increase in layer thickness leads to an improvement in compressive strength up to a certain point(0.2mm). However, once this optimal point is reached, further increases in layer thickness(>0.2mm) resulted in a reduction in compressive strength [24-27].

At the end of each complete load-unload, the dimensions of the deformed samples were measured. Due to the honeycomb structure of the PLA's core, it was observed that although only uniaxial compression load was applied, the corresponding deformation response indicated both vertical and shear/angular displacement. In particular, the average change in angle was ~ 12.5° for most samples as shown in **Figure 9** From the practical viewpoint, this indicates that the present PLA structure, even under a single mechanical load provides a bi-directional actuation, thus enabling the design of simple yet efficient actuators. For each set of printing parameters, the corresponding stress-strain curves were analyzed to determine the variation in the yield stress and elastic modulus. Figure 10 shows the load-versus-displacement response curve for the case of T=190 °C, s=30mm/s, and t=0.10,0.15,0.20mm. Since two specimens were fabricated for each set of printing parameters (T, s, and t), the average values of the yield stress and Young's modulus were calculated and used for this parametric study.

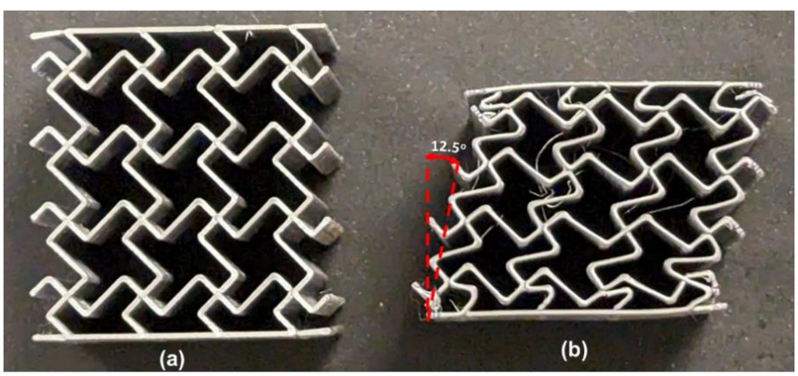


Figure 9. (a) Undeformed and (b) deformed state of the PLA showing both compression and shear deformation response.

Figure 10 shows that by keeping all parameters constant and varying only the layer thickness, both the Yield stress and Young's modulus increase with increasing layer thickness. Layer thicknesses considered ranged between 0.1 and 0.2 mm. At the layer thickness of 0.1 mm, the yield strength and Young's modulus were 0.185 and 2.45 MPa respectively; on the other hand, the thickest layer of 0.2 mm has the corresponding values of 0.209 and 2.85 MPa, respectively.

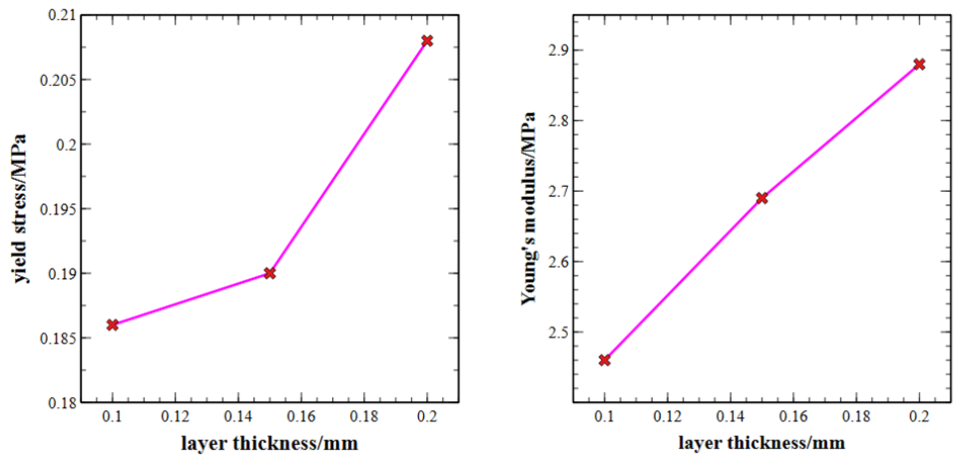


Figure 10. Variation of Material Properties with Layer Thickness

Although it is generally expected that a thin layer will bond better than a thick layer, it is worth mentioning that varying conclusions have been made in the literature concerning the influence of layer thickness on the overall strength of PLAs. For instance, previous studies showed that at the material level, i.e., based on tests conducted on dog-bone specimens subjected to uniaxial static tension, the impact of layer thickness on the mechanical properties of PLA varied as a function of the type of filament used to fabricate the PLA. For some cases, no clear effect on Young's modulus with layer thickness was observed, while for other PLA samples manufactured with Ultimaker filament, larger layer thickness resulted in increased modulus. However, the ultimate tensile strength always decreased with the layer thickness. Contrariwise, under similar experimental conditions,

[26] reported that specimens with larger building thickness experience higher ultimate tensile strength and reduced stiffness (Young's modulus).

The next parameter investigated was the printing speed. From **Figure 11** we observe that the mechanical properties (i.e., both Young's modulus and yield stress) decrease as the printing speed increases at a constant nozzle temperature and layer thickness.

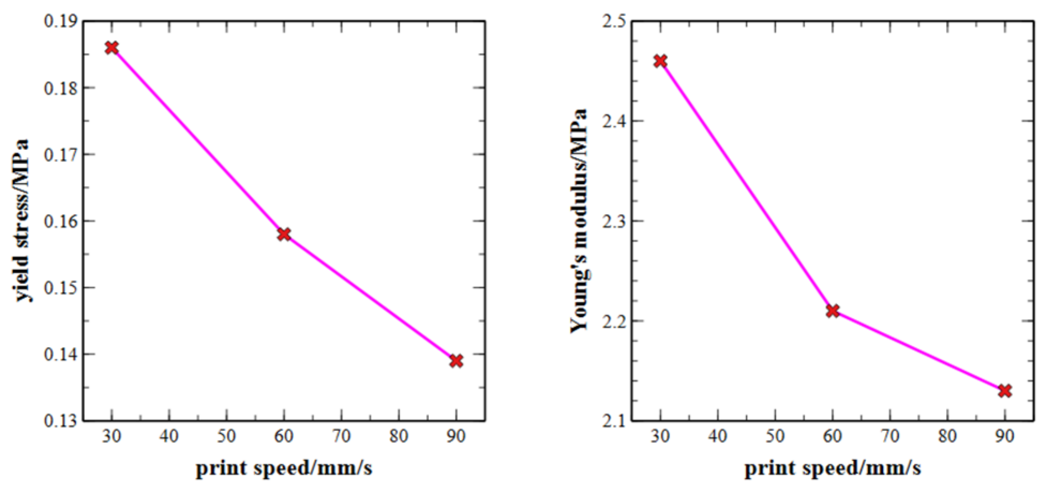


Figure 11. Variation of Material Properties with print speed

Here, when the print speed increased from 30 to 90 mm/s there was a marginal drop of 0.045 and 0.335MPa in the yield stress and Young's modulus values, respectively. High speeds reduce the average contact time and fusion between the deposited layers, thus leading to a decrease in the mechanical strength of the fabricated samples. Like the effect of the layer thickness, it is obvious from the results in **Figure 9** that the printing speed did not have a significant effect on the mechanical strength of the PLA structure.

Figure 12 shows that the mechanical properties vary significantly as a function of the nozzle temperature. There is a sharp drop in Young's modulus between T=190-

210°C, but closes and almost flattens from 210-230°C. Increasing nozzle temperature affects the flow characteristics which can allow for higher printing speed.

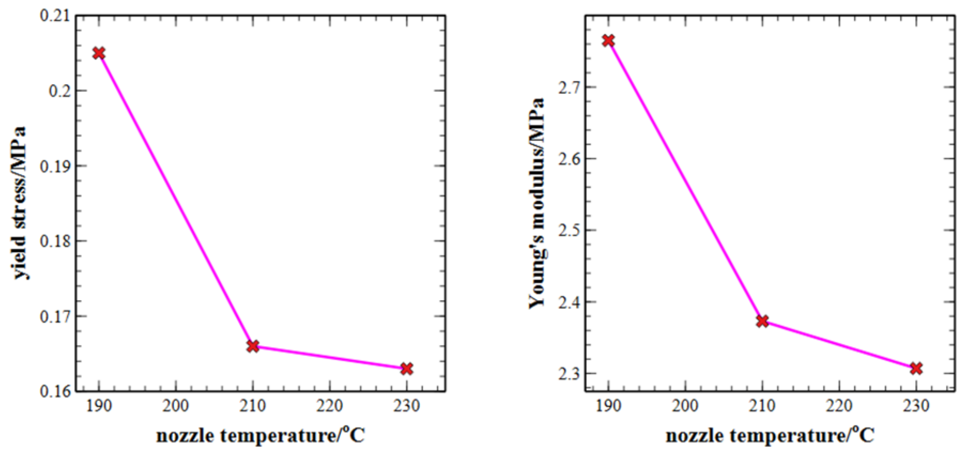


Figure 12. Variation of Material Properties with Nozzle Temperature

2.3.2 Cyclic Shape Memory Behavior Effect

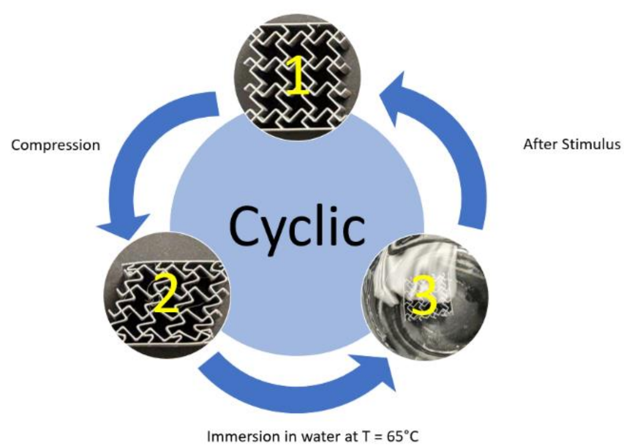


Figure 13. The Cyclic Process of PLA

The material's ability to survive many cycles of deformation and recovery is crucial, especially in applications involving repetitive stress on shape memory materials. Understanding the durability limits of a material is critical for design and engineering purposes. To study the cyclic shape memory effects, out of 27, sample no: 23 was selected randomly and subjected to five different cyclic shape memory effects. Figure.14 and 15 show the impact of cyclic shape memory. In the cyclic testing condition, the procedure outlined in Figure 13 was repeated five times for the optimized specimen, each measuring the yield stress and degree of recovery.

As shown in Figure 14, the recovery behavior reduces the material's ability to recover fully from deformation as the number of cycles increases. This behavior could be due to the progressive fracture development in the material during the compression test phase of each cycle. The noted deformation has a cracking noise heard during each testing phase of the experiment.

The material properties also significantly reduce, as shown in Figure 15 as the number of cycles increases. In other words, after repeated cycles, the material was less effective in returning to its previous shape. Since the material cannot recover fully, it goes beyond reasonable doubt that its mechanical properties will also experience a significant reduction after each cycle due to fracture development. More to this point, the deficit in each recovery percentage corresponds to a certain amount of deformation stored in the material, which could be expressed as a strength reduction factor. According to the study[3], the diminished recovery ability may be due to the increasing development of fractures inside the material during the compression test phase of each cycle. As a result of many deformation and recovery cycles, the material suffers fractures or cracks.

% Recovery = (h1/h2)×100%

Where h1 = height of the deformed sample after the compression testing

h2 = height of the structure after stimulation at 65 ^{o}C

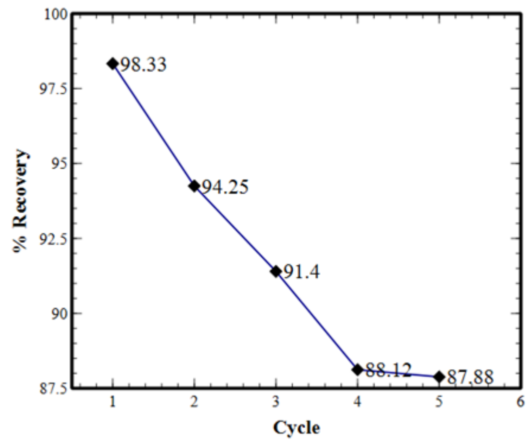


Figure 14. % Recovery vs. number of cycles

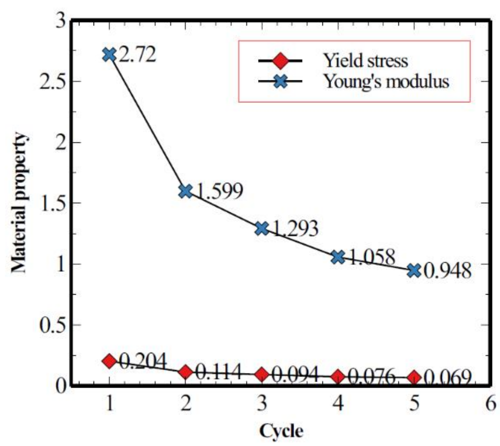


Figure 15. Material property vs. number of cycles

2.4 Conclusions

In this work, we have investigated the intriguing realm of Shape Memory Polymers (SMPs), specifically Polylactic Acid (PLA), and how different 3D printing factors affect them. PLA is a fascinating material for 4D printing applications because of its capacity to recall and regain its shape when exposed to temperature fluctuations. We have gained insights into how essential printing parameters affect the mechanical properties of PLA by compressing 27 PLA samples under various printing settings.

Our results demonstrate that the compressive strength of PLA is significantly impacted by nozzle temperature, layer thickness, and printing speed. Interestingly, a more considerable compressive stress was obtained with an increase in nozzle temperature, suggesting that interlayer bonding plays a crucial role in determining material strength. There is a direct correlation between layer thickness and compressive strength. Thicker layers have been proven to improve overall structural robustness and load-bearing capability. Nonetheless, it is vital to consider the careful balance needed to achieve the ideal layer thickness because too thick a layer may prevent interlayer adhesion.

The material's ability to recover from deformation over a number of cycles was demonstrated using cyclic shape memory tests, which showed a decreasing recovery ability as the number of cycles grew. This result implies that the material may acquire fractures due to repeated cycles. These findings highlight the importance of comprehending the material's limitations when using shape memory materials under repeated stress.

Our research advances knowledge of the connection between printing settings and the mechanical properties of PLA SMPs that are 3D printed. The structural integrity and mechanical performance of 3D-printed components can be significantly enhanced by using these insights. With potential uses in robotics, biology, and aerospace, they further broaden the scope of 4D printing technology. Shape memory polymer-based innovative structures can now be engineered and designed novelly, increasing their efficiency and dependability in practical use.

CHAPTER III

EXTRUSION AND PRINTING OF UNIFORM-DIAMETER POLYLACTIC ACID CARBON FIBER COMPOSITE FILAMENTS

3.1 Introduction

Made from renewable materials like maize starch or sugarcane, polylactic acid (PLA) is a thermoplastic polymer that is both biodegradable and bioactive. PLA is in high demand because of its environmental friendliness and is frequently utilized in a variety of industries, including 3D printing, food packaging, and the biomedical sector. Along with qualities like transparency, high rigidity, and strong thermal stability, PLA stands out for being a versatile option for sustainable material solutions.

Carbon fiber reinforcement (CFR) is the method of making composite materials by adding carbon fibers to polymer matrices. Carbon fibers are renowned for their remarkable strength and lightweight. They are carbon atoms extracted from organic polymers such as pitch or polyacrylonitrile (PAN). Carbon fibers are added to polymers such as PLA and function as reinforcing agents, thereby improving the material's mechanical properties.

Because of its exceptional stiffness, heat resistance, and strength-to-weight ratio, CFR composites are widely used in the aerospace, automotive, and sports equipment industries. Commercially available CFs have high Young's modulus values between 200 and 500 Gpa and tensile strengths between 3 and 7 Gpa[30].

The combination of the benefits of carbon fibers with PLA is known as Carbon Fiber Reinforced Polylactic Acid, or CFR-PLA. CFR-PLA achieves notable gains in mechanical performance while maintaining PLA's biodegradability because of the addition of carbon fibers. Because it is stronger, stiffer, and more heat-resistant than conventional PLA, this composite material can be used in a variety of applications. CFR-PLA is a material that can be used to make biodegradable packaging materials and lightweight structural components for aircraft. CFR-PLA is valuable to the consumer goods, automotive, and aerospace industries because it meets environmental standards and facilitates the development of high-strength components. As a result of the PLA and CFR integration, high-performance composites and biodegradable materials can now be combined, opening a world of possibilities.

Numerous studies on PLA and PLA composites 3D printing have been published. Tian et al.'s research [28] focused on recycling 3D-printed continuous carbon fiber-filled PLA composites and repurposing recycled raw materials for additional 3D printing. Wang et al.'s research [29] used PLA and kenaf fiber filaments to investigate the 3D printing of green composites. According to Maloch et al. [30], two fundamental process parameters influencing 3D printing are the layer thickness and the extrusion nozzle's temperature. The independent effects of every processing parameter on the mechanical properties of FDM pieces were examined by Alafaghani et al. [31]. In their investigation of the tensile strength of a 3D-printed work piece, Chen et al. [32] discovered that the extruder speed, extruder head temperature, fill rate, and thickness of fill can all have an impact on the part quality. Though numerous, the majority of these works concentrated on printing PLAs through a laborious trial-and-error process. In addition, there is slight process improvement for the 3D printing of CFR-PLA composites [33].

Planetary ball milling is a solid-state method in which the matrix material and reinforcement particles can be mixed homogenously to form composites [34]. Subsequently, we used the milled PLA-CF powders in a single screw filament extruder to form uniform-diameter 3D printable filaments. In previous studies, the composite was formed during the printing process [35]. Conversely, 3D printing is an additive manufacturing method that builds the part piece by piece using the idea of layer-by-layer production. This allows for the flexibility of subtractive manufacturing or the development of complex geometries in a single step without machining. When compared to conventional manufacturing methods, this lowers costs, production times, and material waste. Using thermoplastic filaments as feedstock material, fused filament fabrication, or FFF, is one of the most straightforward and widely used 3D printing processes. In accordance with the part's design, the filament is extruded out of a nozzle and deposited layer by layer [36].

This work created uniform-diameter PLA CF filaments by combining extrusion and ball milling. The filaments were then utilized in 3D printing equipment to create standard, unique constructions for testing mechanical qualities.

3.2 Materials and Methods

3.2.1 Materials

The polylactic acid material is employed in this study to change the additive carbon fiber to enhance the material's strength. PLA powders were procured from Huaqing (Xi'an) Natural Ingredients Co., Ltd. The commercially available milled CF PX35 powders (Ø 7.27µm, and density 1.81 g/cm3) used as the reinforcing material were procured from ZOLTEK (Missouri, USA).

3.2.2 Milling of PLA – CF

PLA pallets are mixed with the carbon fibers in 10% volume using planetary ball milling. The PLA pallets and the carbon fibers are weighed and transferred to stainless steel vials. The PLA and CF powders were mixed in a set in a high-energy planetary ball milling device (MSE Supplies LLC, Arizona, USA). The milling parameters used are shown in Table 4. The milling time, Speed, and ball-powder ratio are varied. For instance, at first, the milling speed was kept constant at 200 rpm and the milling time was varied for 2, 4, and 6 h. Next, the milling time was fixed for 4 hours, and the speed varied at 300, 400, and 500 rpm. The Ball powder ratio is 2:1 and 5:1[37].

Figure 16. Milling Setup

Table 4. Milling parameters

Ball diameter	5 mm
Vial Volume	100 ml
Ball to powder weight ratio (BPR)	2:1
Ball and vial material	Stainless Steel
Temperature	Ambient

We also tried the wet milling of the materials by stirring the PLA particles in ethanol for 1 hour and then adding the Carbon Fibers to the PLA and stirring overnight. The mixture is transferred to the flat plate and kept in the oven for 24 hours. We used the composite for the extrusion of the filament.

3.2.3 Extrusion of PLA CF Filaments

A flawless filament that extrudes at a consistent diameter is essential to the 3D printing process. The temperature and pressure inside the extrusion barrel are crucial factors determining the filament's quality. The milled PLA CF composites are placed in the oven at 70°C for 30 minutes to make sure that there is no moisture left [38] in the materials [PLA - CF]. PLA CF milled powders were supplied through the hopper to a single screw extruder (Filabot, EX6, Barre, USA). The nozzle diameter of the extrusion screw was 1.65 mm, with a length/diameter (L/D) ratio of 24/1 and a diameter of 1.6 mm. Depending on the pressure buildup inside the barrel, the screw speed was adjusted, with an average of 5 rpm. The temperatures of the barrel were set at the temperatures of 30°C at the feed and the heaters H1, H2, and H3 were set to 170°C, 175°C, and 180°C respectively. H3 is the heater at the nozzle, H2 is at the center of the barrel and H1 is adjacent to the hopper. The filament extruded out of the nozzle is passed through the airpath through the winder to spool the filament (Filabot, EX6, Barre, USA). The speed of the fans was set to 50rpm. For continuous spooling of filaments with uniform diameter and the lowest tolerances possible, i.e., without breaking. The winder's speed was meticulously adjusted in accordance with the extrusion rate. The PLA CF composite mixture is continuously fed through the hopper to ensure the extrusion rate and the spooling process are undistorted. Any disturbance during the whole process leads to inconsistency and breakage in the filament. The extrusion process is stopped by adding the purging materials to the hopper and getting the temperatures down. The spool is stored in the oven at 70°C before we start the 3D printing process.

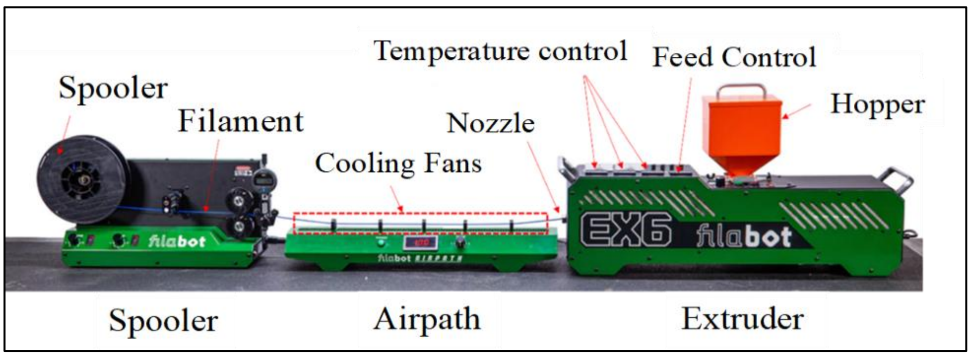


Figure 17. Extruder setup

Figure 18. Extruded PLA CF Filament

3.2.4 3D Printing of PLA CF

We used a PRUSA Mk3s+ 3D printer to print the tensile samples out of the extruded filaments. The nozzle temperature is set to 230°C, the build plate temperature is set to 60°C, and the print speed is set to 60mm/s. The nozzle diameter is 0.15mm. In this study, we have evaluated the tensile strength of the extruded PLA CF. The parameters we varied previously are mentioned in Table 2.

3.2.5 Mechanical Property Analysis

Tensile tests were performed on the printed tensile specimen. ISO 572-2 was followed for the tensile testing. Specimen dimensions are shown in the figure. 3D printing of the specimen is shown in the figure. The tensile tests were conducted using an Instron 3369 universal testing machine (UTM) equipped with a 50KN load cell, as seen in Fig 20.

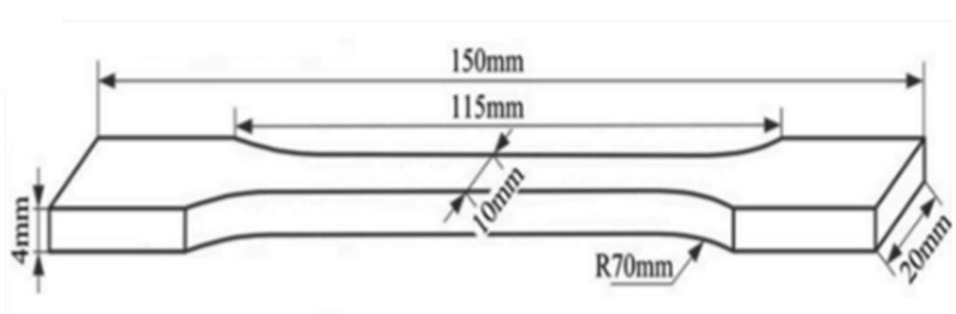
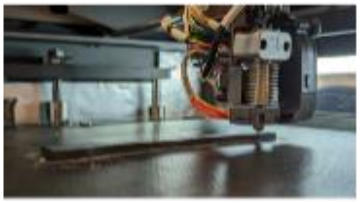


Figure 19. 3D printing of the specimen


3D Printing of Tensile specimen


Printed Tensile specimen


(a) Before testing (b) After testing

Tensile testing

Figure 20. Tensile testing

3.3 Results and Discussion

3.3.1 Milling Duration Effect on the Composite

Planetary ball milling, a highly effective mechanical process utilized for material synthesis, involves the rotation of grinding jars filled with balls around a central axis. This dynamic motion imparts kinetic energy to the materials within, fostering high-energy collisions between the grinding balls and the processed particles. Consequently, this interaction leads to significant deformation and refinement of the materials at the nanoscale. The duration of planetary ball milling plays a pivotal role in shaping the characteristics of the resulting composite materials. In shorter durations, such as the initial 2 hours, some degree of mixing and refinement occurs, though it may need to achieve complete homogeneity. As the milling time is extended to 4 and 6 hours, there is a noticeable improvement in mixing and deformation, resulting in enhanced homogeneity and reduced particle sizes. Prolonged milling durations contribute to achieving better homogeneity and lead to finer particle sizes, influencing the composite's mechanical properties. The resulting composites exhibit improved mechanical characteristics, making them well-suited for various applications. This nuanced understanding of the intricate relationship between planetary ball milling and milling duration is pivotal for tailoring composite materials with specific properties, with implications spanning various fields, from materials science and nanotechnology to advanced manufacturing processes [36, 39].

Figure 21. PLA CF composite in the SS vial.

3.3.2 Effect of Screw Speed on Filament Quality

In extrusion, the screw speed is an essential factor influencing filament quality. Higher screw speeds typically translate to increased extrusion rates, allowing for the processing of larger volumes of material within a given timeframe. However, excessively high speeds may lead to challenges such as heightened temperatures and insufficient cooling, potentially compromising the quality of the extruded filament.

Conversely, lower screw speeds offer a different set of advantages, providing more precise control over the extrusion process. This can be particularly beneficial when aiming for enhanced filament consistency. The optimal screw speed is critical for achieving a homogenous melt, ensuring an even distribution of additives or fillers throughout the filament. Maintaining the correct temperature is equally crucial, as elevated speeds generate more friction and heat, requiring careful temperature control to prevent overheating or insufficient melting.

The impact of screw speed extends to filament diameter and overall consistency. Variations in screw speed can introduce fluctuations in filament diameter, affecting the uniformity of the final product. Moreover, the relationship between screw speed and temperature is intricate, and adjustments must be made to strike a balance between achieving the desired extrusion rate and maintaining the quality of the filament.

Different materials may exhibit distinct responses to changes in screw speed, demanding a nuanced approach to extrusion parameters. Balancing the extrusion rate, melt homogeneity, temperature control, filament diameter, and material characteristics is essential for producing high-quality filaments tailored to specific applications and materials using the Filabot EX6.

3.3.3 Effect of Temperature of the Extruder on the Filament

During the extrusion process, the extruder's temperature profoundly influences the characteristics of PLA (polylactic acid) filament. When the extruder temperature is elevated, PLA experiences a reduction in viscosity, leading to smoother flow and improved distribution of molten material. This results in a more uniform filament of higher quality. On the contrary, lower extruder temperatures may increase PLA viscosity, potentially causing challenges in extrusion and contributing to uneven flow, which can compromise filament consistency. Striking a balance is crucial to avoid nozzle clogging issues. Maintaining an optimal temperature range is paramount for achieving a homogeneous melt in PLA, preventing inconsistencies in color or streaks in the filament. Elevated temperatures contribute to better layer adhesion in PLA, essential for the structural integrity of 3D-printed objects, while lower temperatures may result in weaker layer adhesion. Temperature variations can also impact the rate of extrusion and filament diameter, requiring careful control for dimensional consistency. To prevent thermal degradation, it's essential to avoid excessive temperatures that could compromise the mechanical properties of PLA. In 3D printing, where PLA is widely utilized, precise temperature control ensures accurate layer deposition, reduces the risk of defects, and contributes to overall print success. Additionally, for colored PLA filaments, maintaining consistent temperatures is vital for color stability in the final printed objects. Proper cooling considerations, such as adjusting fan speed, become crucial to achieving clean and well-defined features in PLA prints, as PLA tends to solidify rapidly. Controlling the extruder temperature is a critical aspect of optimizing PLA filament extrusion, impacting filament quality, printability, and the overall success of 3D printing processes.

3.3.4 Effect of the Cooling Rate

The cooling rate during the extrusion of PLA filament plays a pivotal role in determining the material's characteristics and the success of 3D printing processes. A higher cooling rate results in rapid solidification of the molten PLA, contributing to enhanced dimensional stability and minimizing issues such as sagging and stringing during extrusion. Optimal cooling is essential for achieving finer details in prints, ensuring sharp edges and clean layer transitions that enhance overall print quality. However, striking the right balance is crucial, as excessively rapid cooling may compromise layer adhesion, especially in intricate designs or small layers. Gradual cooling is essential to prevent warping and internal stresses within printed objects. Adjusting fan speed is a practical means of controlling the cooling rate, with higher fan speeds contributing to faster cooling, which is particularly beneficial for intricate designs and overhangs. Achieving an optimal cooling rate is a delicate balance that influences the material's solidification, print quality, and the prevention of defects, ultimately contributing to the dimensional accuracy and success of PLA filament extrusion in various 3D printing applications[36].

3.4 Morphology Analysis of Extruded PLA CF Filament

The morphology analysis of extruded PLA carbon fiber (CF) filament is crucial to evaluating the composite material's structure and properties. Utilizing techniques such as scanning electron microscopy (SEM) enables a detailed microstructure examination, offering insights into carbon fibers' distribution, orientation, and interaction within the PLA matrix. Analysis of fiber dispersion and alignment provides information on the uniformity of fiber distribution, impacting mechanical properties. At the same time, cross-sectional SEM allows for an assessment of layering and the integration of carbon fibers into the PLA matrix. Additionally, measuring fiber length and aspect ratio is essential for understanding reinforcement efficiency, with longer fibers generally contributing to improved mechanical characteristics. Identification of voids, defects, and thermal properties through differential scanning calorimetry (DSC) further complements the morphological assessment. Ultimately, this comprehensive analysis aids in correlating microstructural features with mechanical performance, contributing to a holistic understanding of the extruded PLA CF filament and its suitability for various applications.

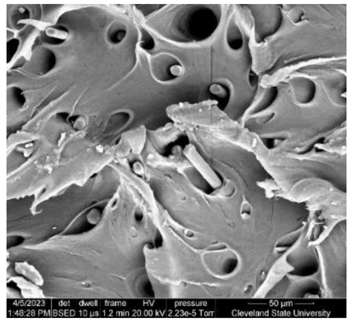


Figure 22. SEM image of extruded PLA CF filament

3.5 Effect of Printing Parameters on the Specimen

The trio of printing parameters, nozzle temperature, print speed, and layer height, plays a significant role in shaping the outcomes of 3D printing processes. Nozzle temperature directly influences material flow, with higher temperatures facilitating smoother extrusion but also posing challenges like stringing and over-extrusion. The temperature setting is critical for achieving proper adhesion between layers; too low a temperature may compromise bonding, while excessively high temperatures can lead to poor layer adhesion and structural integrity issues. Matching the nozzle temperature with the filament's recommended range is essential for optimal performance. Print speed dictates the pace at which the nozzle traverses the print area, directly impacting print time. While higher speeds reduce printing duration, they may introduce inaccuracies and compromise layer alignment. Slower print speeds, on the other hand, enhance detail and resolution, crucial for intricate designs. The choice of speed also affects cooling, influencing layer adhesion and mitigating issues like warping. Layer height, determining the thickness of each printed layer, plays a crucial role in defining resolution and surface finish. Smaller layer heights offer finer details but extend print time, while more enormous layer heights may sacrifice detail for speed. Selecting an appropriate layer height is essential for achieving dimensional accuracy along the Z-axis. Striking a balance among these parameters, considering material compatibility, printer specifications, and the specific requirements of the print job, is paramount for optimizing 3D printing outcomes.

Based on the previous results of PLA we discussed in Chapter 2, we optimized and selected the optimum printing parameters out of the 27 different variations. The nozzle temperature is set at 230°C, the print speed is set at 60 mm/sec and the layer height is set at 0.15mm.

3.6 Mechanical Testing

The results of the tensile testing conducted on the PLA CF (polylactic acid carbon fiber) composite offer a comprehensive insight into the material's mechanical behavior. The stress-strain curve, as illustrated in Figure 23 serves as a fundamental representation of the composite's response to applied tensile forces. The tensile strength, identified as the maximum stress endured by the material before failure, was determined to be 32.49MPa, providing crucial information about the composite's ability to withstand external forces. The elongation at break, representing the material's ductility, was measured at 2.16%, indicating the percentage increase in length before specimen failure and contributing valuable insights into the material's deformation characteristics. A detailed analysis of the fracture surface further unveiled that the carbon fibers pulled out from the PLA during the tensile testing which resulted in the breakage.

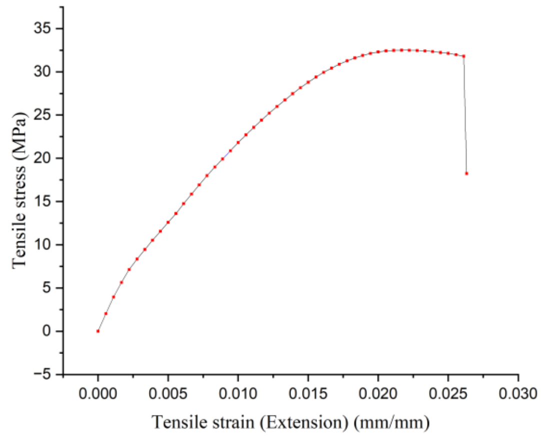


Figure 23. Stress-Strain curve of PLA CF tensile test

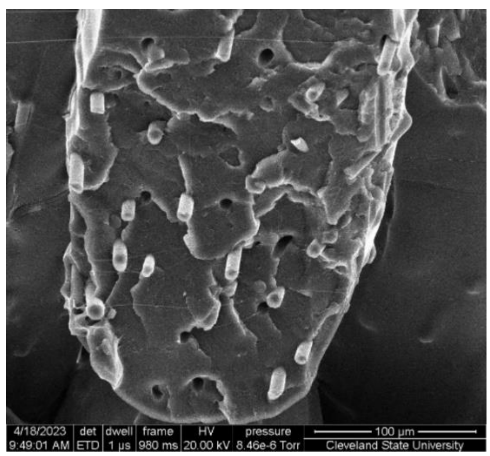


Figure 24. SEM image of broken PLA CF tensile sample

3.7 Conclusion

In conclusion, this study delves into Carbon Fiber Reinforced Polylactic Acid (CFR-PLA), a composite material synthesized by incorporating carbon fibers into PLA matrices. The amalgamation of PLA's biodegradability with carbon fibers' exceptional strength, stiffness, and heat resistance heralds a versatile material capable of applications in diverse sectors, from biodegradable packaging to lightweight structural components for aerospace. The research methodically explores the intricate processes of planetary ball milling and extrusion to fabricate uniform-diameter PLA CF filaments for 3D printing. The duration of planetary ball milling emerges as a critical factor, impacting the homogeneity and mechanical properties of the resulting composite. The subsequent extrusion of PLA CF filaments, influenced by parameters like screw speed and extruder temperature, is meticulously detailed, emphasizing the significance of these variables in achieving filament consistency and quality. The 3D printing process is further analyzed, highlighting the pivotal role of printing parameters—nozzle temperature, print speed, and layer height—in shaping the final specimen's characteristics. Based on a thorough optimization process, specific parameters are recognized for producing high-quality PLA CF specimens.

Mechanical testing, particularly tensile testing, becomes the focal point in assessing the performance of the PLA CF composite. The obtained stress-strain curve provides a comprehensive snapshot of the material's behavior under tensile forces, showcasing a tensile strength of 32.49 MPa and an elongation at a break of 2.16%. These results underscore the composite's ability to withstand external forces while offering insights into its ductility and deformation characteristics. Fracture surface analysis reveals the mechanical response, indicating carbon fibers' pullout during testing.

In essence, this study contributes to understanding PLA CF composite fabrication. It sheds light on the interplay between various processing parameters and their influence on the material's mechanical performance. The developed insights hold promise for advancing the utilization of CFR-PLA composites in diverse industrial applications, marking a significant step towards sustainable and high-performance materials in the evolving additive manufacturing landscape.

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