



Research paper

## ***Influence of Freezing Time on Hardness and Impact Resistance of 3D-Printed PLA+***

 **Enes Aslan<sup>a,\*</sup>**

<sup>a</sup>Düzce University, Faculty of Engineering, Department of Mechatronics Engineering, Düzce, Türkiye.

\*Corresponding author: [enesaslan@duzce.edu.tr](mailto:enesaslan@duzce.edu.tr)

### **Article information:**

Received: 03/08/2025, Revision: 12/09/2025, Accepted: 30/09/2025

DOI: 10.29130/dubited.1757310

### **ABSTRACT**

This preliminary study investigates the effect of freezing duration on the impact and strength performance of 3D-printed PLA+ specimens produced with 50% and 100% infill densities in a honeycomb pattern using the FDM technique. Samples were stored at -80 °C for varying time intervals (up to 72 hours), and their dimensional changes, hardness, and impact resistance were evaluated. Results indicate that prolonged exposure to sub-zero temperatures caused a slight reduction in specimen diameter, likely due to material shrinkage. Conversely, hardness values increased with freezing time, reaching a maximum Shore D value of 85.78 for fully solid samples. Impact testing revealed that 100% infill density specimens absorbed more energy than 50% counterparts, with the highest impact strength (24.53 kJ/m<sup>2</sup>) observed after 72 hours of freezing. Visual analysis showed no significant variation in crack trajectory with freezing duration. Overall, the findings suggest that PLA+ retains and even improves its mechanical robustness under cryogenic conditions, making it a promising candidate for applications requiring durability in extreme environments.

**Keywords:** *Freezing time, 3D-printed PLA+, Impact Resistance*

### **I. INTRODUCTION**

Additive manufacturing technologies have gained widespread adoption among both professional and non-professional users over the past few decades. These systems operate on the fundamental principle of fabricating parts through a layer-by-layer deposition process (Pérez et al., 2020; Tofail et al., 2018). Compared to conventional manufacturing techniques, additive manufacturing offers several advantages, including rapid prototyping capabilities, the ability to produce geometrically complex structures, and greater user accessibility. According to the ISO/ASTM 52900 standard, additive manufacturing is categorized into seven primary process types: binder jetting (BJT), directed energy deposition (DED), material extrusion (MEX), material jetting (MJT), powder bed fusion (PBF), sheet lamination (SHL), and vat photopolymerization (VPP) (Buchanan & Gardner, 2019; ISO/ASTM, 2021; Tofail et al., 2018). In binder jetting, a liquid binder is selectively deposited to bond powder particles. Directed energy deposition employs focused thermal energy sources such as lasers, electron beams, or plasma to melt and deposit material. Material extrusion involves the continuous flow of thermoplastic material through a heated nozzle. Material jetting relies on the deposition of photopolymer droplets that are cured using ultraviolet (UV) light. In powder bed fusion, thermal energy selectively fuses regions of a powder bed to form solid layers. Sheet lamination creates objects by bonding and cutting successive layers of material sheets. Lastly, vat photopolymerization utilizes a vat of liquid photopolymer resin that is selectively cured through light-activated polymerization to form solid structures (ISO/ASTM, 2021). Almost all types of materials, including metal powders, polymers, glass, ceramics, and composites, can be utilised in AM technologies based on the desired application. For instance, metal powders require high energy to join together (DED, PBF), binder

liquids are necessary for ceramics and plastic particles (BJT), composite filaments need heat for melting (MEX), and resins need UV lights for curation (MJT, VPP) (ISO/ASTM, 2021).

Fused deposition modelling (FDM) system is one of the most popular systems used in additive manufacturing based on the MEX process. This is because of the ease of usage, which does not require competent users, economical, an abundance of manufacturers and also readily available stock materials. The working principle, this system uses a heated extrusion head where the filament is melted down, and then this molten material is extruded through the nozzle onto a build platform. After ejection, the polymer solidifies and creates the first layer. Subsequently, additional layers are deposited sequentially, each bonding to the one beneath (Çevik & Kam, 2020; Raghunath & Prashanth, 2020). Finally, the desired 3D structure was built.

Thermoplastic materials such as polylactic acid (PLA) (Farah et al., 2016; Jayswal & Adanur, 2023), polycarbonate (Bulanda et al., 2021), poly-caprolactone (Huang et al., 2020), acrylonitrile butadiene styrene (Azadi et al., 2021a) have been used with FDM systems. Prototypes and products can be manufactured using these materials and the system for the applications from healthcare to aerospace. PLA is one of the most preferred materials amongst other due to its easy processing, reusability, environmentally friendly and abundance for additive manufacturing technologies. PLA has been investigated in terms of many properties such as mechanical (Azadi et al., 2021b; Gonabadi et al., 2020), tribological (Raichur et al., 2024; Santo et al., 2024), biological (Grémare et al., 2018), physical and chemical. Additionally, its impact strength and energy absorbance capacity were also investigated in many researchers. For example, Ma et al. Have been produced different specimens with various pattern to investigate the impact capacity of PLA products. They observed that different patterns have different energy absorption capacity even if used the same material in their study (Ma et al., 2024). In another study Jia et al. create some products using PLA as base material with some toughening agents blends to investigate the mechanical and impact profiles (Jia et al., 2022). In order to find out the best production parameters Taguchi methodology used in the following study, the study optimized FDM 3D printing parameters for carbon fiber-reinforced PLA, demonstrating that print speed, infill density, and nozzle temperature significantly affect impact strength and hardness (Ansari & Kamil, 2022). Aydınli and Er also used Taguchi methodology for the optimisation study. They investigated the effect of steel powder on the mechanical and impact profiles of the samples, considering production parameters as well (Osman Er & Osman, 2024).

Understanding material behavior under sub-zero conditions is crucial for selecting suitable materials for applications operating in extreme weather environments, frozen food packaging, goods stored in cold environments. Although limited research has addressed this topic, most existing studies focus on incorporating various fillers into PLA and examining their performance at low temperatures. For instance, one study found that while linseed cake provides a plasticizing effect in PLA-based composites at room temperature, this effect diminishes below zero due to oil solidification; nonetheless, the composite's overall mechanical properties remain adequate for use in cold environments (Mysiukiewicz et al., 2020). In another study, cryogenic treatment has used to enhance the mechanical properties of 3D-printed Polylactic Acid (PLA). When PLA specimens were exposed to extremely low temperatures around  $-263\text{ }^{\circ}\text{C}$  using a cryocooler, the specimens strength increased by approximately 35% within 5 hours, with most of the improvement occurring during the first hour. They concluded that this enhancement related to crystallinity, improved molecular alignment, and possible interactions with the helium cooling medium (Gupta et al., 2025). Vaught et al. was also investigated the PLA and carbon fibre reinforced PLA samples using the cryogenic tensile testing system. Their aim is to find out the potential of additive manufacturing polymers for cryogenic applications They found that thermoplastics reveals significant improvements in mechanical performance. PLA shows a notable strength increase from 47 to 120 MPa when cooled, while carbon fibre reinforced PLA demonstrates an even greater 250% increase from 37 to 130 MPa. Both materials withstand multiple cryogenic thermal cycles, with neat PLA experiencing reduced room-temperature ductility but CF-PLA maintained its properties (Vaught et al., 2023). As another example of cryogenic applications in additive manufacturing with ABS polymers, one study examined the material's performance at low temperatures, emphasizing its use in producing complex supports and tools for diverse cryogenic purposes (Bartolomé et al., 2017).

To the best of our knowledge, there is a noticeable gap in the current literature regarding the energy absorption capacity of 3D-printed samples conditioned at sub-zero temperatures. While numerous studies have explored the mechanical, thermal, and tribological properties of PLA-based parts, the majority of these investigations have been conducted under standard or elevated temperature conditions. Although some

recent research has begun to address cryogenic treatment and low-temperature mechanical performance of PLA and its composites, these studies have primarily focused on tensile strength improvements, crystallinity changes, or material behavior during thermal cycling. However, very limited work has specifically examined the impact behavior or energy absorption characteristics of PLA specimens after exposure to sub-zero environments, particularly as a function of freezing duration.

Moreover, existing studies tend to concentrate on material-level modifications—such as the addition of fillers or toughening agents—or post-processing techniques like cryogenic treatment, without adequately considering how the freezing process itself (in terms of duration and temperature) affects the mechanical integrity and impact resistance of additively manufactured PLA parts. Another notable deficiency is the lack of comprehensive evaluations that combine multiple performance metrics, such as dimensional stability, hardness, and impact strength, after low-temperature conditioning. These parameters are crucial for assessing the reliability of 3D-printed components intended for use in outdoor or refrigerated environments, where they may be subjected to mechanical stress while in a frozen state.

Therefore, this preliminary study aims to address these gaps by systematically investigating the effects of freezing duration on the impact strength, dimensional accuracy, and surface hardness of FDM-printed PLA specimens. By doing so, this research seeks to contribute to the limited body of knowledge concerning the sub-zero performance of additively manufactured polymers and provide valuable insights for the design and deployment of PLA-based components in cold-weather or cryogenic applications.

## II. MATERIAL AND METHOD

### *A. Materials*

PLA+ is environmentally friendly and easy to use for additive manufacturing systems. Therefore, it is a preferred material for an extrusion-based manufacturing process. A commercial PLA+ filament branded as ESUN was used in this study. PLA+ filament is an enhanced version of pure PLA to improve toughness and strength. The filament wrapped around the spool, its diameter and density were 1.75 mm and 1.23 g/cm<sup>3</sup>. Based on the manufacturer's data sheet, the melt flow index was 5g/10 min at 190 °C/2.16 kg. This polymer is a thermoplastic polymer which glass transition temperature (around 60°C), and so the bed temperature was set at 50°C and the print temperature at 220 °C.

### *B. Methods*

Fused deposition modelling (FDM) system, also known as a material extrusion system, was used to manufacture test samples. The used system is branded the FlashForge Adventurer 5M Pro (China), which has a maximum printing speed of 600mm/s and multiple nozzle diameter options. The schematic representation of the FDM system was shown in Figure 1a. Prior to manufacturing, Charpy impact samples (based on the ISO 179-1: Plastics-Determination of Charpy Impact Strength standard) (ISO, 2023) and cylindrical samples were designed as CAD files using a CAD design software. The schematic Charpy impact test was presented in Figure 1b.

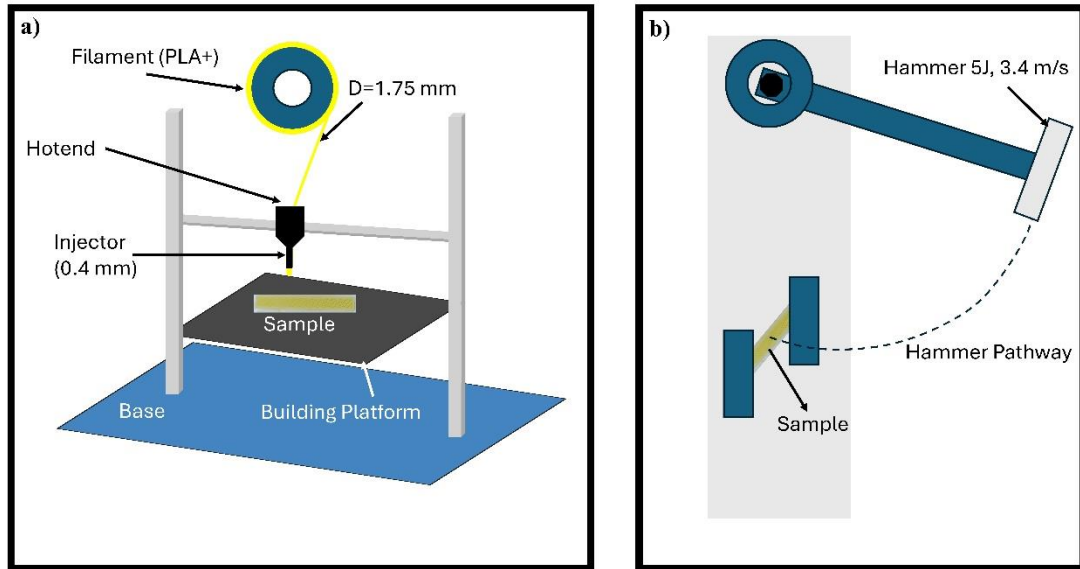


Figure 1. a) FDM system used for manufacturing, b) Charpy Impact test machine and manufactured samples.

The dimensions of the samples were; the cylindrical shape with 15 mm diameter and 10 mm height, and the Charpy sample (unnotched) were designed as 80x10x4 mm based on the standard (Figure 2a). After that, CAD files transform to the STL format. This file was transferred to another software Orca-Flashforge which is belong the FDM system to prepare file for printing process (Figure 2a). Properties as the nozzle temperature, bed temperature, printing speed, infill density and pattern can be set up via this software. At least three different samples were produced. The manufacturing parameters were presented in Table 1. The infill density was 50% and 100%, and the pattern was honeycomb. The produced samples for the analysis can be seen in Figure 2b.

Table 1. Manufacturing parameters.

Properties/Units	Values
Material	PLA+
Printing Temperature (°C)	220
Bed Temperature (°C)	50
Number of Walls	3
Infill Density (%)	50/100
Infill Pattern	Honeycomb
Infill Angle (°)	45
Layer Height (mm)	0.2
Nozzle Diameter (mm)	0.4
Filament Diameter (mm)	1.75

Before initiating the experimental procedures, all samples were stored at -80 °C for varying durations of 12, 24, 36, and 72 hours (Figure 2c). Subsequently, the Charpy impact tests, as well as diameter and hardness measurements, were conducted. In addition, the same measurements were performed on the samples kept at room temperature. All experiments were conducted immediately after samples were taken from the freezer to avoid the temperature rise of the samples.

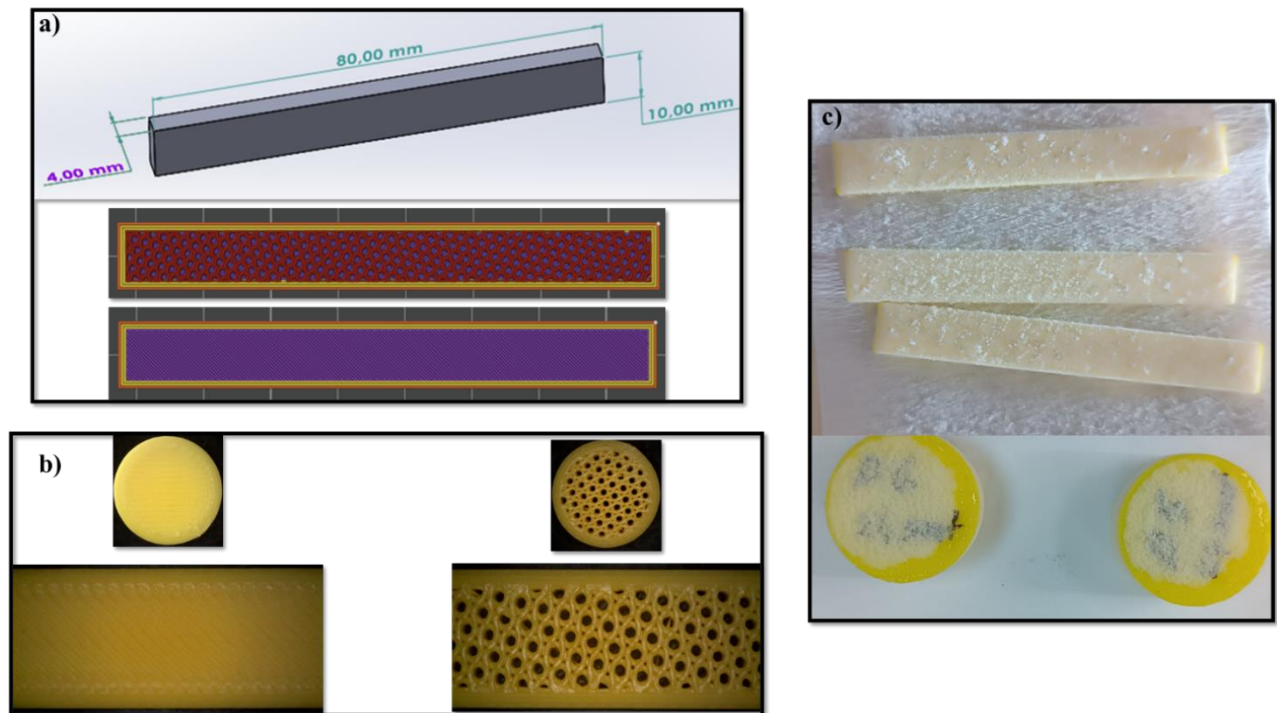


Figure 2. a) Images of modelled and sliced specimens, b) the fabricated real specimens c) examples of frozen samples 24 hours.

The cylindrical shapes were produced to evaluate the dimensional differences in diameter before and after freezing the samples at  $-80\text{ }^{\circ}\text{C}$  and also to identify the deviation between modelled and fabricated samples. The diameter measurement was performed with a digital calliper. Five different measurements from at least three samples were taken to determine the average diameter value. Hardness measurements were conducted on the lateral surfaces of the samples using a Shore D durometer, with readings taken from three distinct locations on each sample.

Charpy impact tests were conducted to investigate the impact toughness of the 3D printed samples. A pendulum-type impact testing machine (Xj 50w, China) with a maximum energy capacity of 5 J and a striker velocity of 3.4 m/s was used for all measurements. The specimens, which did not contain any notches, were placed horizontally between the supports, and the pendulum was released to strike the centre of each sample. To guarantee reliable and consistent results, each specimen was tested a minimum of three times. The energy absorbed during fracture was recorded directly from the machine's scale and used as an indicator of impact resistance. The digital views of broken samples after the Charpy impact experiment were taken by helping of a digital microscope (Dino Lite).

This study investigates the influence of cryogenic conditioning on the impact behavior of 3D-printed PLA+ specimens with different infill densities. In particular, the effects of prolonged exposure to  $-80\text{ }^{\circ}\text{C}$  on dimensional stability, hardness, and impact resistance were evaluated. Since PLA is widely used in additive manufacturing but is generally considered brittle at low temperatures, understanding its performance under sub-zero conditions is crucial for applications in cold environments. The experiments focused on measuring diameter changes, Shore D hardness, impact strength, and fracture behavior to determine how freezing duration and infill geometry affect structural integrity. The following section presents and discusses the results in detail.

### III. RESULTS AND DISCUSSION

The designed diameter of sample was set to 15 mm, the measured average diameter was 14.85 mm. The deviation between the real and designed samples was 1%. Samples were measured immediately after taken from the freezer. The diameter of samples was measured before and after freezing. Figure 3 presents measured diameter values for both samples 50% and 100% infill density. The results indicate that increasing duration in the freezer leads to a decrease in diameter for all samples. It shows that samples were shrunk in sub-zero conditions. The decreasing trend was observed for both infill densities. The

greatest shrinkage was determined at 24 hours of freezing with 0.58%. Additionally, the initial decrease in specimen diameter after 12 hours at  $-80\text{ }^{\circ}\text{C}$  is likely due to thermal contraction, a typical response of polymers at low temperatures. However, the slight increase observed after 23 hours may be caused by internal stress relaxation or structural rearrangement within the PLA. Over extended freezing periods, these changes can lead to minor dimensional recovery as the material stabilizes under cryogenic conditions.

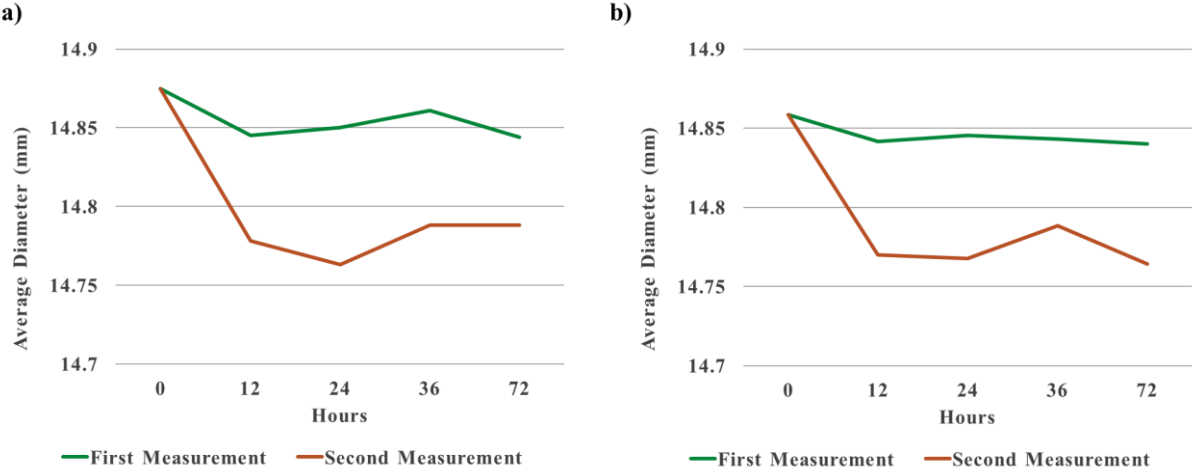


Figure 3. Average diameter values of a) 50% and b) 100% infill density samples, retained at different time intervals under room temperature and sub-zero conditions. (0 hours meaning that the samples were not put in the freezer)

The hardness values of the samples were measured immediately after taken from the sub-zero condition. The hardness value (Shore D) of the samples that keeping at the room temperature was 81.17 for 50% and 81.83 for 100% infill density. These values look similar with the literature (Teymoorzadeh & Rodrigue, 2015; Vishal et al., 2022). This small difference might be related with density of the sample. The measurements were taken from the lateral surfaces of the samples, which could have contributed to the variations. Since the samples had different infill densities, these differences likely affected the lateral dimension measurements.

Considering the frozen samples hardness values, the result presents that increasing time in the sub-zero environment increases of the hardness. For samples with 50% infill density, the average Shore D hardness values were recorded as 81.17, 82.5, 83.67, 83.67, and 83.78 for freezing durations of 0, 12, 24, 36, and 72 hours, respectively. A similar increasing trend was observed in specimens with 100% infill density, where the corresponding hardness values were 81.83, 82.5, 84, 83.83, and 85.78. Hardness measurements were performed to evaluate the effect of infill density and freezing duration on the mechanical behaviour of PLA specimens. The measurements can be seen in Figure 4.

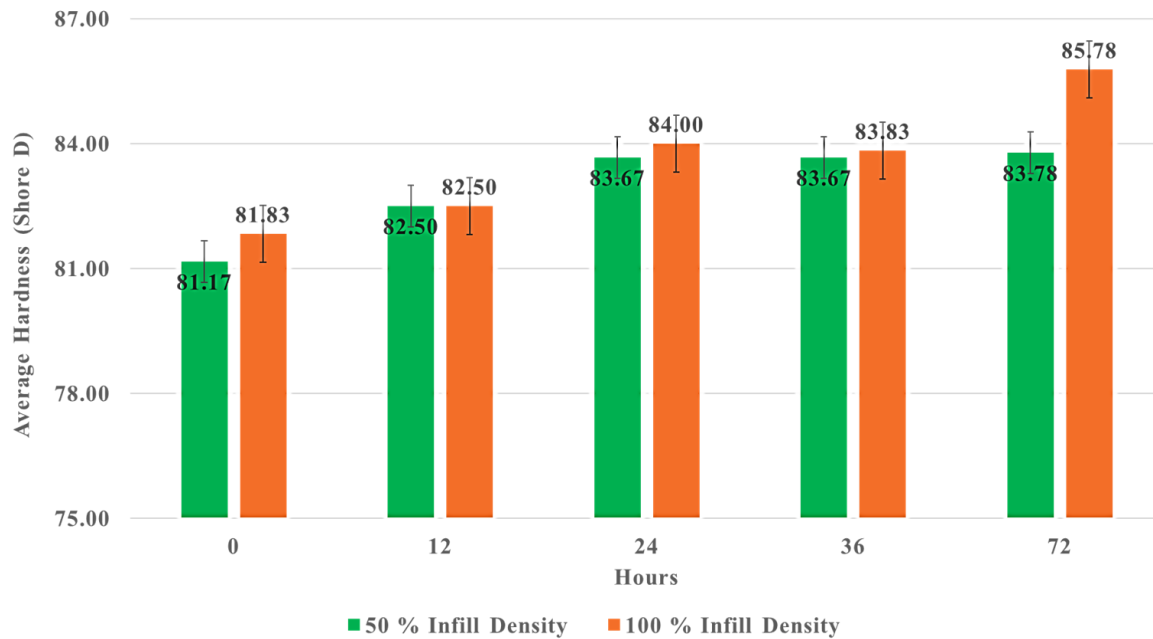


Figure 4. Average hardness values of 50% and 100% infill density samples, retained at different time intervals under room temperature and sub-zero conditions. (0 hours meaning that the samples were not put in the freezer)

Among all the tested conditions, the highest Shore D hardness value was obtained from the sample with 100% infill density that had been stored at  $-80\text{ }^{\circ}\text{C}$  for 72 hours, recording a value of 85.78. This result suggests that both a higher infill density and prolonged exposure to sub-zero temperatures contribute positively to surface rigidity. In contrast, the specimen with 50% infill density under the same freezing conditions exhibited a slightly lower hardness value of 83.78 Shore D. The observed trend indicates that while freezing enhances the hardness of PLA materials to a certain extent, infill density plays a more dominant role in determining the final hardness performance. These findings are consistent with previous studies reporting that higher infill levels reduce internal porosity, thereby improving mechanical resistance (Zhang et al., 2019). Other samples present the following hardness values: 81.17, 82.5, 83.67, 83.67, 83.78 for 50% infill density, and 81.83, 82.50, 84.00, 83.83, 85.78 for 100% infill density at 0, 12, 24, 36 and 72 hours, respectively.

The experimental findings revealed that cryogenic conditioning did not deteriorate the mechanical behaviour of PLA+ specimens; on the contrary, it enhanced both hardness and impact resistance. This phenomenon can be attributed to the reduced molecular mobility of the polymer chains at sub-zero temperatures, which leads to increased stiffness and potentially higher crystallinity. While polymers are typically expected to become brittle in such environments, the test results demonstrated an opposite trend, particularly for fully solid specimens. The observed shrinkage in diameter, although relatively small, may also have contributed to the densification of the structure, providing a more compact internal configuration that supported higher energy absorption during impact.

Figure 5 presents the absorbance and impact strength of the PLA+ samples for all tested times. At first glance, as expected, increasing infill density from 50% to 100% resulted in increased impact strength and absorbed energy. This result shows similarity with the literature (Osman Er & Osman, 2024). Samples with 100% infill density contain more material than those with 50%, meaning a greater volume of material occupies the same area. As a result, these samples were able to absorb more energy. The average highest impact strength value was  $24.53\text{ kJ/m}^2$ , which was observed in the 100% infill density sample, retained in the freezer for 72 hours. Conversely, for the sample with 50% infill density, the greatest impact strength ( $13.49\text{ kJ/m}^2$ ) was observed in the one stored in the freezer for 36 hours. A similar trend was noticed when considering the absorbance profile of the samples.

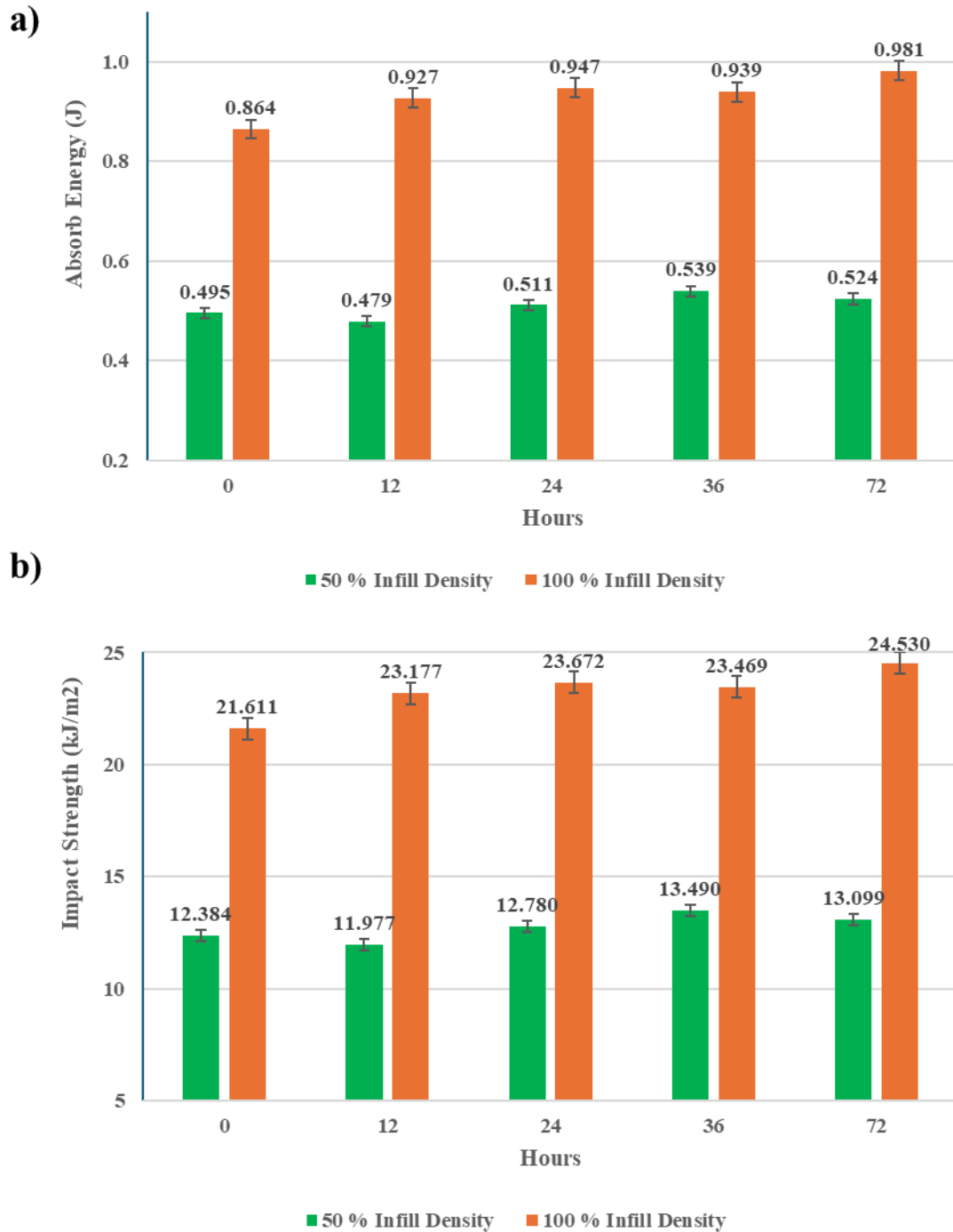


Figure 5. (a) Energy absorbance capacity, (b) Impact strength (kJ/m<sup>2</sup>) of 50% and 100% infill density samples, retained at different time intervals under room temperature and sub-zero conditions. (0 hours meaning that the samples were not put in the freezer)

Interestingly, the expected thing is that increasing storage time makes the sample more brittle, and so the absorbance energy and strength of the samples were decreased; however, in this study happened in vice versa. In other words, increasing time in the freezer at sub-zero temperatures increases strength and absorb capacity of 3D printed samples. This result is consistent with previous studies that reported an increase in mechanical strength. The observed behavior may be related to the rearrangement of polymer chains and the enhanced crystallinity caused by cryogenic exposure. Consequently, the samples stored for longer periods at subzero temperatures showed higher absorbed energy (Gupta et al., 2025). However, in the initial stages, a reduction in impact strength and energy absorption was observed in the 50% infill density specimens compared to room temperature conditions and the 12-hour mark. A similar trend was identified

in the 100% infill density samples, albeit at a later stage, specifically after 36 hours. After all, the increased absorption capacity and impact strength of the samples at other time points were observed for all samples. This phenomenon can be explained; initial reduction in impact strength and energy absorption can be attributed to increased brittleness of the polymer at the early stages of cryogenic exposure. At low temperatures, the polymer chains lose mobility, leading to reduced toughness and higher susceptibility to crack initiation. However, with prolonged exposure, structural reorganization and increased crystallinity occur, which enhance load transfer efficiency and improve the material's capacity to absorb energy. This explains the later increase in impact strength and absorbed energy observed in both 50% and 100% infill density samples (Chen et al., 2021; Nikonovich et al., 2023).

Another important observation was the different response between the 50% and 100% infill density specimens. At lower infill densities, the internal honeycomb structure contained voids that initially reduced strength at short freezing durations but later acted as energy-dissipating regions when the structure stiffened under cryogenic conditions. In contrast, fully solid samples showed a consistent improvement in both hardness and impact strength with increasing freezing duration, reaching their peak performance after 72 hours. These findings suggest that infill geometry plays a critical role in determining mechanical behaviour under cryogenic exposure, and optimizing this parameter could be a promising strategy for tailoring 3D-printed PLA+ components intended for low-temperature applications.

The 50% infill density introduces a significant number of internal voids, which act as energy-absorbing zones during impact. These voids can serve as a buffer layer that mitigates the initial shock of the impact event. At room temperature, this semi-hollow structure may not provide sufficient resistance due to the relatively low rigidity of the PLA matrix. However, when exposed to  $-80\text{ }^{\circ}\text{C}$ , the infill structure becomes more rigid, potentially enhancing the distribution and dissipation of impact energy across the specimen. This temperature-induced stiffening effect may explain the improved impact resistance observed under cryogenic conditions.

Interestingly, the fully solid (100% infill) PLA specimens demonstrated enhanced impact resistance following exposure to  $-80\text{ }^{\circ}\text{C}$ . Several factors may contribute to this unexpected outcome. At such low temperatures, molecular mobility is greatly reduced, which increases the stiffness of the material (Nikonovich et al., 2023). Although brittleness is typically expected under these conditions, the increased rigidity may inhibit localized deformation and delay crack initiation, thus allowing the specimen to absorb more impact energy. Moreover, extended cryogenic exposure may have promoted cold crystallization in the PLA, resulting in improved mechanical properties due to a higher degree of crystallinity (Gupta et al., 2025). Since the specimens were tested at room temperature immediately after removal from the  $-80\text{ }^{\circ}\text{C}$  environment, residual thermal stresses or transient structural stiffening may also have influenced the results. Taken together, these factors likely contributed to the improved impact performance observed in cryogenically conditioned PLA samples, even at full infill density. In addition, another possible explanation is the reduction in sample diameter, which indicates volume shrinkage. As the freezing duration increases, this shrinkage results in denser and more compact structures, thereby enhancing the samples' energy absorption capacity.

Figure 6 illustrates the fracture surfaces of the specimens following Charpy impact testing, highlighting clear differences in failure modes between honeycomb-filled and fully solid PLA samples. The honeycomb structures displayed irregular and winding crack paths, which reflect a more distributed absorption of impact energy across the cellular network. In contrast, the fully solid specimens tended to fracture along straighter and sharper paths, indicating a comparatively brittle failure mechanism. Despite these distinctions, both groups exhibited non-linear crack trajectories, suggesting that the failure process was governed not only by cryogenic stiffening of the polymer matrix but also by the inherent anisotropy introduced during the FDM printing process. Overall, the freezing duration did not appear to alter the crack propagation behavior significantly, as specimens stored for different times at  $-80\text{ }^{\circ}\text{C}$  demonstrated similar fracture patterns.

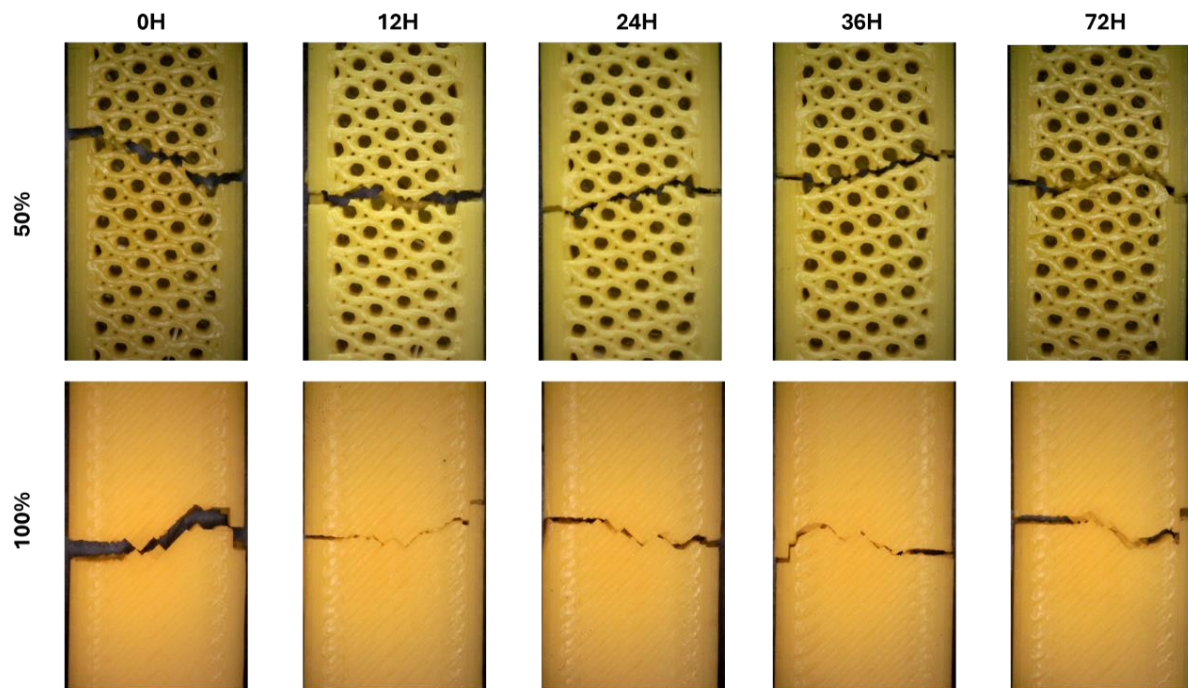


Figure 6. Fracture surfaces of PLA specimens with 50% honeycomb infill (top row) and 100% solid infill (bottom row) after Charpy impact testing. Visual differences in crack propagation patterns indicate the influence of infill geometry and internal structure on the failure mechanism.

#### IV. CONCLUSION

The effect of the freezing duration on the 3D printed PLA+ samples was considered in this study. 50% and 100% infill density samples with a honeycomb pattern design were manufactured using the FDM system. These samples were kept in the sub-zero conditions with different time-intervals. Then, dimensional differences, hardness and energy absorption capacity of the samples were investigated. The results show that, increasing time in the freezer decreases the diameter of the samples. It might be because of the samples were shrunk in sub-zero conditions. The decreasing trend was observed for both infill densities. The smallest diameter was measured as 14.76 mm. Conversely, the hardness value of the samples increases with time in the freezer. The highest Shore D hardness value was 85.78, obtained from the sample with 100% infill density kept at  $-80\text{ }^{\circ}\text{C}$  for 72 hours; the value was 83.78 Shore D for 50% infill density. Even if there are small differences in the hardness value between 50% and 100% density samples, infill density plays a more dominant role in determining the final hardness performance compared to the freezing experiment.

When considering the absorbance capability of the samples, the results indicate that full infill density samples present more absorbance performance as expected. This situation happens due to a greater volume of material occupying the same area. The results also show that increasing time in the freezer at sub-zero temperatures increases strength and absorb capacity of 3D printed samples. The greatest impact energy was 0,981 J and impact strength was 24.53 kJ/m<sup>2</sup> on the samples (100 % infill density), which stay in the freezer for 72 hours. The smallest impact strength and absorption capacity were determined for the samples of 50% infill density stored at  $-80\text{ }^{\circ}\text{C}$  at 12 hours, 11.977 kJ/m<sup>2</sup> and 0,479 J, respectively. From the visual inspections of the fractures, it can be concluded that the freezing duration had no significant influence on the crack trajectory, as all specimens exhibited a similar fracture pattern.

This preliminary investigation also demonstrates that 3D-printed PLA+ specimens possess sufficient mechanical robustness to be considered for use in applications requiring impact resistance under extreme environmental conditions. The observed performance suggests that PLA+, when processed under appropriate printing parameters, may serve as a viable material for functional components exposed to low-temperature or harsh weather environments.

All results can be concluded as followings;

- Samples shrank slightly at sub-zero temperatures due to thermal contraction and stress relaxation.
- Hardness increased with longer freezing time, with 100% infill showing the highest values.
- Impact strength and energy absorption improved after prolonged cryogenic exposure, despite an initial decrease.
- Infill density strongly influenced performance, with solid specimens outperforming honeycomb ones.
- Shrinkage contributed to denser structures, enhancing energy absorption.
- Fracture paths differed by infill type but were not affected by freezing duration.

Future studies could focus on extending cryogenic exposure times beyond 72 hours to better understand long-term effects on mechanical performance. In addition, investigating other infill geometries, different polymer blends, and reinforced PLA composites would provide a broader perspective on cryogenic durability. Fracture mechanisms will be deeply investigated using SEM images. Testing under cyclic freezing–thawing conditions could also reveal the resistance of materials to thermal fatigue, which is relevant for aerospace, automotive, and outdoor structural applications.

Moreover, complementary mechanical tests such as tensile strength, compression resistance, and wear/tribological behaviour should be conducted to provide a more complete evaluation of the performance of PLA+ under cryogenic environments. These additional tests will help to determine how cryogenic conditioning affects not only impact and hardness but also long-term durability, surface performance, and load-bearing capability. Furthermore, evaluating PLA+ components under real service conditions, such as cold-chain packaging or aerospace parts exposed to fluctuating cryogenic temperatures, would strengthen the practical relevance of this study.

## DECLARATIONS

**Acknowledgements:** The author do not wish to acknowledge any individual or institution.

**Author Contributions:** All parts of the study were conducted by the Author.

**Conflict of Interest Disclosure:** The author/authors declare no conflict of interest.

**Copyright Statement:** The author(s) retain the copyright of their work published in the journal, which is licensed under the CC BY-NC 4.0 license, allowing others to share and adapt the work for non-commercial purposes with appropriate attribution.

**Funding/Supporting Organizations:** This research received no external funding.

**Ethical Approval and Participant Consent:** This study does not involve human or animal participants. All procedures followed scientific and ethical principles, and all referenced studies are appropriately cited.

**Plagiarism Statement:** This article has been evaluated for plagiarism and no instances of plagiarism were detected.

**Availability of Data and Materials:** Data sharing is not applicable to this study.

**Use of AI Tools:** The author declares that no Artificial Intelligence (AI) tools were used in the creation of this article.

## REFERENCES

Ansari, A. A., & Kamil, M. (2022). Izod impact and hardness properties of 3D printed lightweight CF-reinforced PLA composites using design of experiment. *International Journal of Lightweight Materials and Manufacture*, 5(3), 369–383. <https://doi.org/10.1016/j.ijlmm.2022.04.006>

- Azadi, M., Dadashi, A., Dezianian, S., Kianifar, M., Torkaman, S., & Chiyani, M. (2021a). High-cycle bending fatigue properties of additive-manufactured ABS and PLA polymers fabricated by fused deposition modeling 3D-printing. *Forces in Mechanics*, 3, 1–11. <https://doi.org/10.1016/j.finmec.2021.100016>
- Azadi, M., Dadashi, A., Dezianian, S., Kianifar, M., Torkaman, S., & Chiyani, M. (2021b). High-cycle bending fatigue properties of additive-manufactured ABS and PLA polymers fabricated by fused deposition modeling 3D-printing. *Forces in Mechanics*, 3(April), Article 100016. <https://doi.org/10.1016/j.finmec.2021.100016>
- Bartolomé, E., Bozzo, B., Sevilla, P., Martínez-Pasarell, O., Puig, T., & Granados, X. (2017). ABS 3D printed solutions for cryogenic applications. *Cryogenics*, 82, 30–37. <https://doi.org/10.1016/j.cryogenics.2017.01.005>
- Buchanan, C., & Gardner, L. (2019). Metal 3D printing in construction: A review of methods, research, applications, opportunities and challenges. *Engineering Structures*, 180, 332–348. <https://doi.org/10.1016/j.engstruct.2018.11.045>
- Bulanda, K., Oleksy, M., Oliwa, R., Budzik, G., Przeszlowski, Ł., Fal, J., & Jesionowski, T. (2021). Polymer composites based on polycarbonate (PC) applied to additive manufacturing using melted and extruded manufacturing (MEM) technology. *Polymers*, 13(15), Article 2455. <https://doi.org/10.3390/POLYM13152455>
- Çevik, Ü., & Kam, M. (2020). A review study on mechanical properties of obtained products by FDM method and metal/polymer composite filament production. *Journal of Nanomaterials*, 2020(1), Article 6187149. <https://doi.org/10.1155/2020/6187149>
- Chen, D., Li, J., Yuan, Y., Gao, C., Cui, Y., Li, S., Liu, X., Wang, H., Peng, C., & Wu, Z. (2021). A review of the polymer for cryogenic application: Methods, mechanisms and perspectives. *Polymers*, 13(3), 1–29. <https://doi.org/10.3390/polym13030320>
- Farah, S., Anderson, D. G., & Langer, R. (2016). Physical and mechanical properties of PLA, and their functions in widespread applications—A comprehensive review. *Advanced Drug Delivery Reviews*, 107, 367–392. <https://doi.org/10.1016/j.addr.2016.06.012>
- Gonabadi, H., Yadav, A., & Bull, S. J. (2020). The effect of processing parameters on the mechanical characteristics of PLA produced by a 3D FFF printer. *The International Journal of Advanced Manufacturing Technology*, 111(3–4), 695–709. <https://doi.org/10.1007/s00170-020-06138-4>
- Grémare, A., Guduric, V., Bareille, R., Heroguez, V., Latour, S., L'heureux, N., Fricain, J. C., Catros, S., & Le Nihouannen, D. (2018). Characterization of printed PLA scaffolds for bone tissue engineering. *Journal of Biomedical Materials Research - Part A*, 106(4), 887–894. <https://doi.org/10.1002/jbm.a.36289>
- Gupta, A., Kumar, N., Sachdeva, A., Sharma, G. K., Kumar, M., & Verma, R. (2025). Effect of cryogenic treatment on the mechanical properties of 3D-printed polylactic acid part. *Cryogenics*, 145, Article 104000. <https://doi.org/10.1016/j.cryogenics.2024.104000>
- Huang, B., Aslan, E., Jiang, Z., Daskalakis, E., Jiao, M., Aldalbahi, A., Vyas, C., & Bártolo, P. (2020). Engineered dual-scale poly ( $\epsilon$ -caprolactone) scaffolds using 3D printing and rotational electrospinning for bone tissue regeneration. *Additive Manufacturing*, 36, Article 101452. <https://doi.org/10.1016/j.addma.2020.101452>
- ISO/ASTM. (2021). *Additive manufacturing: General principles — Fundamentals and vocabulary* (ISO/ASTM 52900:2021). <https://www.iso.org/standard/74514.html>
- ISO. (2023). *Plastics — Determination of Charpy impact properties — Part 1: Non-instrumented impact test* (ISO 179-1:2023). <https://www.iso.org/standard/84393.html>
- Jayswal, A., & Adanur, S. (2023). Characterization of polylactic acid/thermoplastic polyurethane composite filaments manufactured for additive manufacturing with fused deposition modeling. *Journal of Thermoplastic Composite Materials*, 36(4), 1450–1471. <https://doi.org/10.1177/089270572111062561>
- Jia, S., Zhao, L., Wang, X., Chen, Y., Pan, H., Han, L., Zhang, H., Dong, L., & Zhang, H. (2022). Poly (lactic acid) blends with excellent low temperature toughness: A comparative study on poly (lactic acid) blends with different toughening agents. *International Journal of Biological Macromolecules*, 201, 662–675. <https://doi.org/10.1016/j.ijbiomac.2022.01.126>
- Ma, Q., Rejab, M. R. M., Song, Y., Zhang, X., Hanon, M. M., Abdullah, M. H., & Kumar, A. P. (2024). Effect of infill pattern of polylactide acid (PLA) 3D-printed integral sandwich panels under ballistic impact loading. *Materials Today Communications*, 38, Article 107626. <https://doi.org/10.1016/j.mtcomm.2023.107626>
- Mysiukiewicz, O., Barczewski, M., & Kloziński, A. (2020). The influence of sub-zero conditions on the mechanical properties of polylactide-based composites. *Materials*, 13(24), 1–12. <https://doi.org/10.3390/ma13245789>

- Nikonovich, M., Costa, J. F. S., Fonseca, A. C., Ramalho, A., & Emami, N. (2023). Structural, thermal, and mechanical characterisation of PEEK-based composites in cryogenic temperature. *Polymer Testing*, 125, Article 108139. <https://doi.org/10.1016/j.polymertesting.2023.108139>
- Osman Er, A., & Osman, M. A. (2024). Ergiyik filament ile imalat yönteminde kullanılan PLA ve çelik katkılı PLA filament malzemelerin mekanik ve fiziksel özelliklerinin incelenmesi. *Journal of the Faculty of Engineering and Architecture of Gazi University*, 39(2), 1285–1301. <https://doi.org/10.17341/gazimmfd.1276420>
- Pérez, M., Carou, D., Rubio, E. M., & Teti, R. (2020). Current advances in additive manufacturing. *Procedia CIRP*, 88, 439–444. <https://doi.org/10.1016/j.procir.2020.05.076>
- Raghnunath, K. R., & Prashanth, N. (2020). Influence of material density & model orientation on the mechanical strength & surface morphology of FDM based 3D printed specimens. *AIP Conference Proceedings*, India, 2283(1), Article 020090. <https://doi.org/10.1063/5.0026999>
- Raichur, S., Ravishankar, R., & Kumar, R. R. (2024). Tribological studies of nanoclay-reinforced PLA composites developed by 3D printing technology. *Journal of The Institution of Engineers (India): Series D*, 105(1), 517–525. <https://doi.org/10.1007/s40033-023-00500-y>
- Santo, J., Pradhik, V., Kalakoti, S., Saravanan, P., & Penumakala, P. K. (2024). Effect of composite processing technique on tribological properties of 3D printed PLA-graphene composites. *Tribology International*, 198, Article 109895. <https://doi.org/10.1016/j.triboint.2024.109895>
- Teymoorzadeh, H., & Rodrigue, D. (2015). Biocomposites of wood flour and polylactic acid: Processing and properties. *Journal of Biobased Materials and Bioenergy*, 9(2), 252–257. <https://doi.org/10.1166/jbmb.2015.1510>
- Tofail, S. A. M., Koumoulos, E. P., Bandyopadhyay, A., Bose, S., O'Donoghue, L., & Charitidis, C. (2018). Additive manufacturing: scientific and technological challenges, market uptake and opportunities. *Materials Today*, 21(1), 22–37. <https://doi.org/10.1016/j.mattod.2017.07.001>
- Vaught, L., Gonzalez, E., Meyer, J. L., & Polycarpou, A. A. (2023). Rapid qualification of fused filament fabrication thermoplastics for cryogenic applications. *Polymer Testing*, 129, Article 108288. <https://doi.org/10.1016/j.polymertesting.2023.108288>
- Vishal, K., Rajkumar, K., Sabarinathan, P., & Dhinakaran, V. (2022). Mechanical and wear characteristics investigation on 3D printed silicon filled poly (Lactic Acid) biopolymer composite fabricated by fused deposition modeling. *Silicon*, 14(15), 9379–9391. <https://doi.org/10.1007/s12633-022-01712-9>
- Zhang, P., Hu, Z., Xie, H., Lee, G.-H., & Lee, C.-H. (2019). Friction and wear characteristics of polylactic acid (PLA) for 3D printing under reciprocating sliding condition. *Industrial Lubrication and Tribology*, 72(4): 533-539. <https://doi.org/10.1108/ILT-11-2016-0280>