DOI: 10.71762/yt6w-xe47

Research Paper

Study of the Effect of Biochar Addition to PLA on the Mechanical and Thermal Properties of 3D-Printed Samples

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Received: April 24, 2025; Accepted: June 20, 2025

Abstract

Biomass is a renewable material derived from plants and their residues, including straw husks, manure, and other organic waste. These materials contain excess carbon, such as biochar, which can be utilized in various industries to enhance efficiency, reduce production costs, and support environmental sustainability and recycling. In this study, the effects of adding biochar particles at weight ratios of 0%, 10%, 25%, and 40% to polylactic acid (PLA) were investigated in terms of tensile strength and differential scanning calorimetry (DSC) thermal analysis. X-ray diffraction (XRD) was used to identify the crystalline structure of the biochar. The results showed that increasing the biochar content significantly reduced the tensile strength of PLA. The tensile strength dropped from 56 MPa for pure PLA to 41, 14.3, and 8.5 MPa for 10%, 25%, and 40% biochar, respectively. Similarly, the tensile modulus decreased from 5.7 GPa for pure PLA to 5.1 GPa at 10%, 3.8 GPa at 25%, and 2 GPa at 40% biochar. Thermal analysis indicated that adding biochar to PLA led to a reduction in both the glass transition temperature (Tg) and melting temperature (Tm), while the degree of crystallinity increased.

Keywords

Polylactic Acid, Biochar, Tensile Test, Thermal Properties

1. Introduction

In recent years, growing environmental concerns and the limitations of fossil resources have significantly increased attention toward developing sustainable and eco-friendly materials [1-2]. In this context, polylactic acid (PLA), a biodegradable polymer derived from renewable sources such as corn starch and sugarcane, has gained a special place in various industries, including packaging, medicine, and additive manufacturing (3D printing) [3]. Due to its biodegradability, biocompatibility, and easy processability, PLA is recognized as one of the most widely used biopolymers [4]. However, limitations such as relatively low mechanical and thermal properties pose challenges to its use in some engineering applications [5]. To overcome these limitations, the addition of reinforcing agents and natural fillers to the polymer matrix has attracted attention.

Biochar, a carbon-rich, porous material obtained from the pyrolysis of biomass under low or no oxygen conditions, is considered a promising filler in polymer composites due to its unique properties

such as high thermal stability, biocompatibility, and wide availability [6]. Not only is biochar a sustainable and environmentally friendly material, but it can also act as a reinforcing agent in improving the mechanical and thermal properties of polymers due to its porous structure and high surface area [7]. Adding biochar powder to the PLA matrix can enhance not only mechanical properties such as tensile strength, elastic modulus, and impact resistance but also thermal stability and the heat performance of the produced filaments, crucial in 3D printing applications where mechanical and thermal properties are crucial [8].

Elnour et al. [9] added biochar particles to polypropylene and observed that although biochar had little effect on the mechanical properties, such as tensile strength and stiffness, it improved the thermal stability and thermal degradation resistance of polypropylene. She et al. [10] added biochar to gutta-percha and found that adding 2 wt.% biochar improved the tensile strength and water permeability resistance of gutta-percha. They also concluded that biochar increased the biodegradability of gutta-percha.

3D printing, as an emerging technology, requires raw materials with optimized mechanical and thermal properties to produce parts with dimensional accuracy and reliable performance [11]. PLA-based filaments are widely used in this technology due to their printability and biodegradability. However, improving the properties of these filaments by adding natural fillers such as biochar can pave the way for developing new, high-performance materials for the 3D printing industry [12].

This paper studies the effect of biochar powder on the mechanical and thermal properties of PLA-based filaments. For this purpose, biochar particles were added to the PLA matrix at 10, 25, and 40 wt.%. Tensile tests were conducted to evaluate the effect of biochar content on tensile strength and elastic modulus. Differential Scanning Calorimetry (DSC) was used to assess the effect of biochar on PLA's glass transition temperature and crystallinity. This study can be a valuable step toward developing high-performance, sustainable materials for advanced industries.

2. Materials and Methods

2.1 Materials

In this study, Bio-flex F 6510 grade polylactic acid (PLA) granules, manufactured by Fkur (Germany), with a density of 1.3 g/cm³, a melting point of 170 °C, and a melt flow index of 9 g/min, were used as the polymer matrix. Biochar fertilizer, derived from high-quality plant-based materials, was used as the filler. This biochar, being biodegradable and cost-effective, can both reduce the cost of filament production and enhance the biodegradability of PLA filaments.

2.2 Preparation of composite filaments

To remove moisture, PLA granules and biochar were placed in a vacuum oven at 90 °C for 4 hours. After drying, the PLA/biochar composite granules were prepared via extrusion. For this purpose, mixtures containing 0, 10, 25, and 45 wt.% biochar were fed into a laboratory-scale twin-screw extruder (Werner & Pfleiderer), and the composite granules were produced. The extruder zones were set at 160, 170, 180, 190, and 190 °C, respectively. Table 1 shows the composition of the prepared composite samples. Finally, the composite granules were extruded using a single-screw extruder to produce filaments with a diameter of 1.75 mm.

Table 1. Composition of the prepared samples

Sample code	Biochar (wt.%)	PLA (wt.%)
PLA	-	100
PB10	10	90
PB25	25	75
PB45	45	55

2.3 3D printing

The prepared filaments were used in a 3D printer to print dog-bone-shaped specimens and 3 mm-thick sheets. The nozzle and bed temperatures were set to 200 °C and 60 °C, respectively. The nozzle speed was set to 50 mm/s, the layer height to 0.2 mm, and the infill density to 100%. A linear print pattern was used. Figure 1 shows the printed dog-bone specimens.

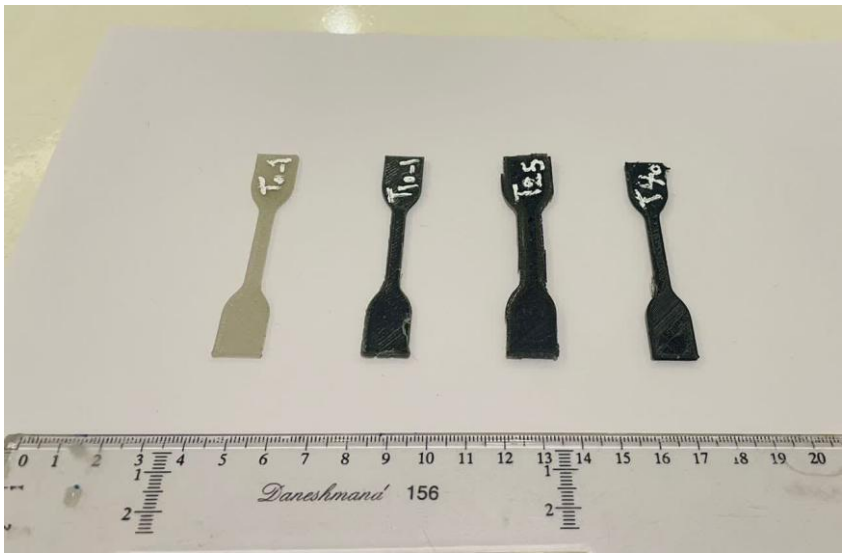

Figure 1. The printed dog-bone specimens

2.4 Characterization

X-ray diffraction (XRD) analysis was performed to investigate the structure and components of the biochar powder. The XRD test was conducted using a PHILIPS 1050 model device with Cu-Kα radiation. The scan was carried out over a 2θ range of 1 to 90 degrees, with a step size of 0.05° and a scan rate of 0.5°/min. Tensile tests were performed according to ASTM D638 using a HOUNSFIELD H50KS universal testing machine at room temperature with a crosshead speed of 5 mm/min. Mechanical properties such as tensile strength and elastic modulus were measured. For each sample type, three replicates were tested, and the average values were reported. Thermal properties were evaluated using Differential Scanning Calorimetry (DSC). The DSC test was carried out using a SANAF device (Iran) to determine glass transition temperature (Tg), melting temperature (Tm), cold crystallization temperature (Tc), and degree of crystallinity. The test was performed in the temperature range of 20 to 210 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1 XRD analysis

The X-ray diffraction (XRD) pattern presented in Figure 2 corresponds to the biochar fertilizer produced from plant residues through the "bio-carbonization" process. In this process, plant-based materials are decomposed at high temperatures under low-oxygen conditions and converted into carbon. The XRD graph provides critical information about the crystalline structure and chemical composition of the biochar. Several peaks are observed at different 2θ angles, indicating the presence of various crystalline phases in the biochar.

A prominent peak appears between 26–28°, indicating the presence of graphite, which is known for its ordered crystalline structure. Smaller peaks in the range of 20–30° may represent silicates or other inorganic compounds. Comparing these peaks with reference patterns shows a match with copper oxide and copper nitrate crystalline phases, suggesting the presence of significant amounts of copper in the biochar. The presence of copper nitrate indicates that the biochar was produced using a "bio-carbonization process with nitrate-based fertilizers," where plant residues are heated with additives like sodium or potassium nitrate under low-oxygen conditions, resulting in nitrate-loaded biochar. Smaller peaks indicating the presence of carbide phases such as SiC (silicon carbide) or TiC (titanium carbide) are also observed. These compounds can enhance the mechanical and thermal properties of the biochar [13-14].

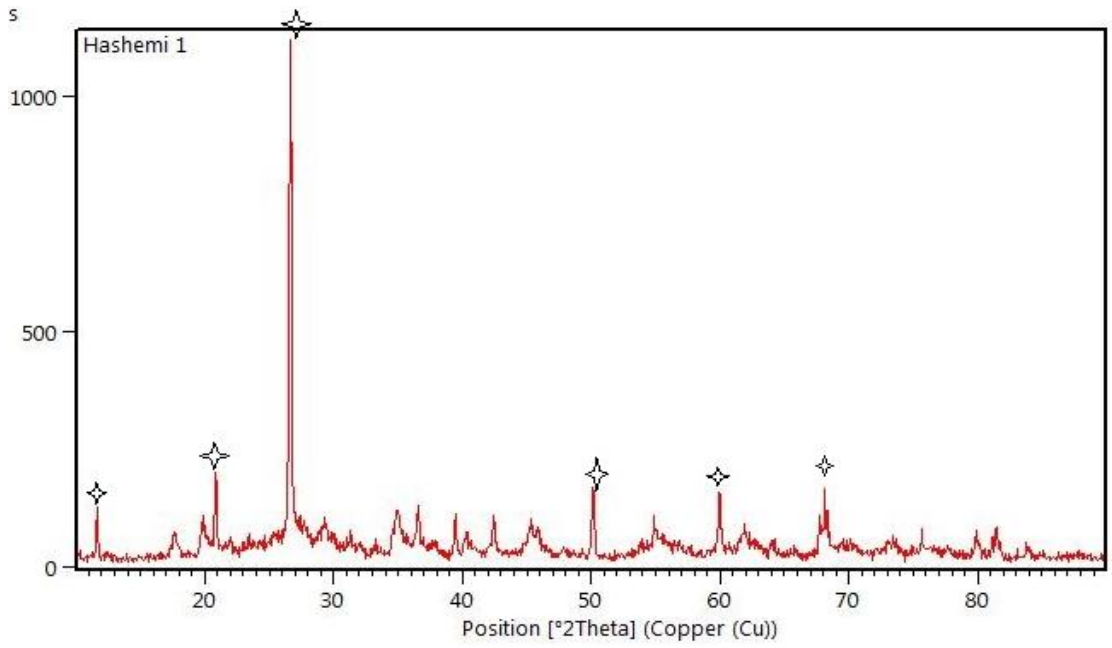

Figure 2. XRD pattern of biochar

3.2 Tensile test

The stress-strain curves and tensile strength data are shown in Figures 3 and 4. The neat PLA sample exhibited the highest tensile strength, around 50 MPa, and could stretch up to approximately 8% strain. Adding 10 wt.% biochar reduced the tensile strength to about 40 MPa and decreased strain to around 7%. With 25 wt.% biochar, tensile strength dropped further to 20 MPa, and strain declined to approximately 4%. The 40 wt.% biochar sample showed the lowest tensile strength (about 10 MPa) and strain (around 3%).

The reasons for this reduction in tensile strength with increasing biochar content include: pore formation caused by biochar addition, which acts as stress concentrators and leads to premature failure; interfacial incompatibility between PLA and biochar; weak interfacial bonding, preventing proper stress distribution; and non-uniform distribution of biochar particles, leading to local stress concentrations and degradation of mechanical properties [15].

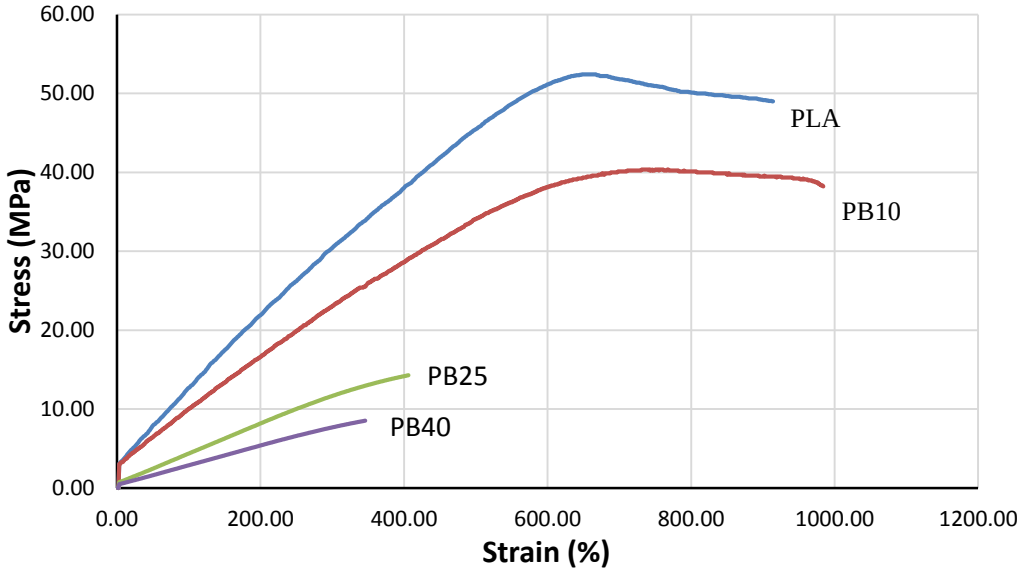

Figure 3. Stress-strain curve of the samples

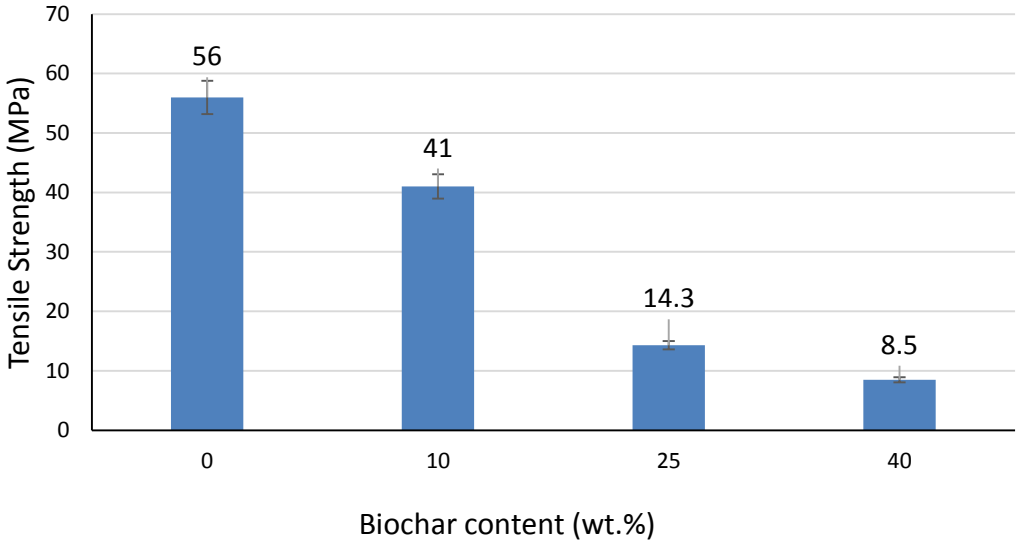

Figure 4. Tensile strength of the samples

The elastic modulus of the samples is shown in Figure 5. The neat PLA sample exhibited an elastic modulus of 5.7 GPa, indicating good stiffness. With 10 wt.% biochar, the modulus dropped to 5.1 GPa. With 25 wt.% biochar, it further decreased to 3.8 GPa, and finally, with 40 wt.% biochar, the lowest value of 2 GPa was reported. This decline is attributed to increased porosity and weaker interfacial bonding at higher biochar content.

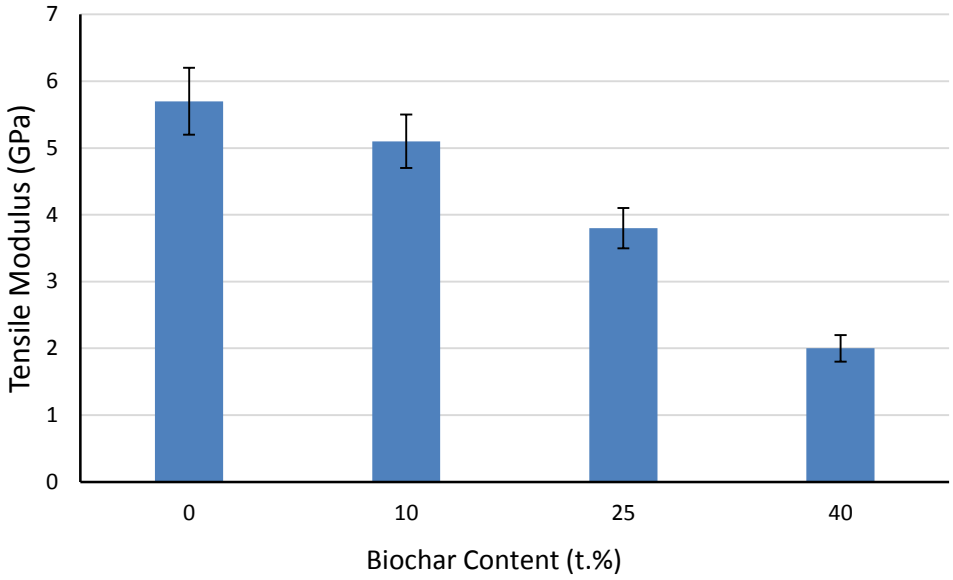

Figure 5. Elastic modulus of the samples

3.3 Thermal analysis

DSC tests were conducted to evaluate the thermal behavior and weight loss trends of the samples. The DSC curve for the samples is shown in Figure 6, revealing three key thermal events: the first endothermic peak corresponds to the glass transition temperature (T_g), the exothermic peak represents cold crystallization (T_c), and the second endothermic peak represents the melting temperature (T_m). The degree of crystallinity (χ) was calculated using the following equation:

$$\chi(\%) = \frac{(\Delta H_m - \Delta H_c)}{\Delta H_m^c} \times 100 \quad (1)$$

Where ΔH_m , ΔH_c and ΔH_m^c are the melting enthalpy, the cold crystallization enthalpy, and the enthalpy for 100 crystalline PLA of 93 J/g, respectively.

The DSC data are summarized in Table 2. Upon adding 10 wt.% biochar, T_g decreased from 70℃ for pure PLA to 64℃ for PB25. This drop is attributed to the porous and irregular structure of biochar, which weakens its interaction with the PLA matrix, thereby increasing the free volume and polymer chain mobility. No further change in T_g was observed beyond 10 wt.%.

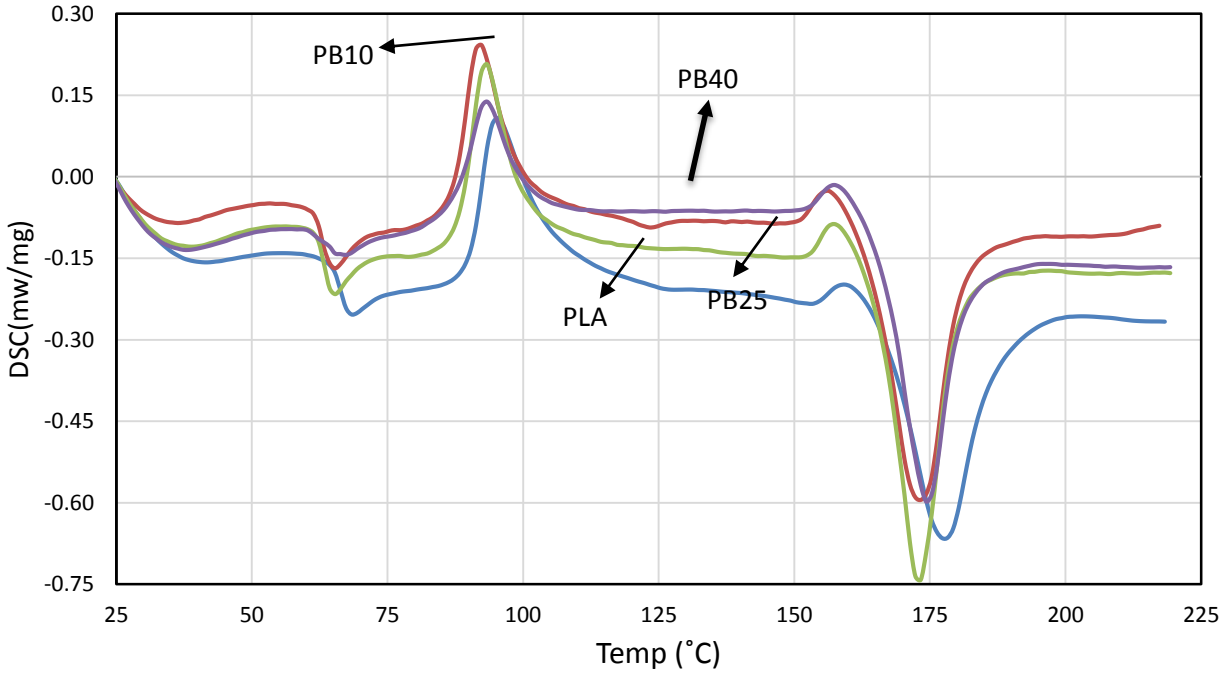

Figure 6. DSC scan of the samples

Cold crystallization temperature (T_c) also decreased from 94℃ for pure PLA to 91℃ for PB10, likely due to nucleation effects of the biochar particles. Further additions had no significant impact on T_c. By incorporating the biochar particles into the PLA matrix, T_m decreased; however, crystallinity increased. This seemingly contradictory behavior has been reported in previous studies [16-17]. Increased crystallinity suggests that biochar particles acted as an effective nucleating agent, with their porous, heterogeneous structure providing sites for PLA crystallization. However, the lower Tm indicates that the resulting crystals were smaller or less perfect (thin lamellae), requiring less energy to melt.

Table 2. DSC test data

Sample	T_g (℃)	T_c (℃)	T_m (℃)	ΔH_c (J/g)	ΔH_m (J/g)	χ (%)
PLA	70	94	177	22.62	31.65	9.7
PB10	64	91	174	20.83	34.86	15
PB25	64	92	172	21.01	34.23	14.2
PB40	65	92	175	14.11	23.41	10

4. Conclusion

In this study, the effect of adding biochar particles at weight ratios of 0, 10, 25, and 40% on the mechanical and thermal properties (DSC) of polylactic acid (PLA) was investigated. X-ray diffraction (XRD) was used to identify the crystalline structure of biochar. The results showed that the tensile strength and elastic modulus of PLA decreased with increasing biochar content. The tensile strength of pure PLA was 56 MPa, which dropped to 41 MPa at 10 wt.% biochar, 14.3 MPa at 25 wt.%, and 8.5 MPa at 40 wt.%. Similarly, the elastic modulus of pure PLA, initially 5.7 GPa, decreased to 5.1 GPa at 10 wt.%, 3.8 GPa at 25 wt.%, and 2 GPa at 40 wt.% biochar. Thermal analysis revealed that adding biochar reduced the glass transition temperature (T_g) from 70°C (for pure PLA) to 65°C (for 40 wt.% biochar) and the melting temperature (T_m) from 177°C to 172°C (at 25 wt.% biochar). At

the same time, the degree of crystallinity increased from 9.7% in pure PLA to 15% in the sample containing 10 wt.% biochar.

5. References

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