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Research Article

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Hemp Reinforced Polylactic Acid (PLA) Composite Produced By Fused Filament Fabrication (FFF)

Eriyik Biriktirme Yöntemiyle Kenevirle Güçlendirilmiş Polilaktik Asit (PLA) Kompozit Filaman Üretimi

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ABSTRACT

Reinforcement of polymer matrix with natural fiber can provide an increase in mechanical properties of the related composite. Since thermoplastics, especially biocomposite materials are recyclable, they contribute to a sustainable ecosystem. In this study, 10% by weight hemp reinforced polylactic acid (PLA) matrix compounds were produced. Tensile test specimens were performed in two different infill patterns, parallel and +/- 45° cross, using the Fused Filament Fabrication (FFF) method from the developed biocomposite filaments. Ultimate tensile stress increases approximately 20%. It has been observed that the geometry of the infill pattern greatly affects the tensile strength. In addition, through optical and scanning electron microscopy (SEM) the produced composite filaments were examined. Surface interactions and homogeneous fiber distribution between PLA and hemp were investigated. As a result, hemp was used as a reinforcement material in the study. Homogeneous distribution is very important in the preparation of the compounds and a twin-screw extruder was used to achieve this. However, it has been observed that the interface between fiber and matrix is insufficient. This situation negatively affects structural performance. On the other hand, the addition of hemp decreases the thermal resistance and melting temperature and increases the glass transition temperature compared to pure PLA.

Key Words

Hemp reinforced polylactic acid composite, Fused filament fabrication, Additive manufacturing, Filament production.

ÖZ

Polimer matrislerin doğal elyaflar ile güçlendirilmesi mekanik özelliklerde artış sağlayabilir. Termoplastikler, özellikle biyokompozit malzemeler geri dönüştürülebilir olduğundan sürdürülebilir bir ekosisteme katkıda bulunurlar. Kenevir lifleri öğütülmüş ve boyutları küçültülmüştür. Bu çalışmada ağırlıkça %10 kenevir takviyeli polilaktik asit (PLA) matrisli hammadde geliştirilmiştir. Geliştirilen biyokompozit hammaddeden eriyik birleştirme yöntemi (FFF) kullanılarak iki farklı dolgu geometrisinde çekme numuneleri üretilmiş ve mekanik performansları araştırılmıştır. En yüksek çekme dayanımı ortalama %20 artış göstermiştir. Üretilen numuneler optik ve yüzey elektron mikroskobu (SEM) ile incelenmiştir. Ara yüzey etkileşimleri ve fiberlerin homojen olarak dağılması oldukça önemli olup, araştırılmıştır. Sonuç olarak çalışmada kenevir takviye malzemesi olarak kullanılmıştır. Bileşimlerin hazırlanmasında homojen dağılım çok önemlidir ve bunu sağlamak için çift vidalı ekstrüder kullanılmıştır. Ancak buna rağmen fiber ve matris arasındaki ara yüzeyin yetersiz olduğu gözlemlenmiştir. Bu durum yapısal performansı olumsuz etkiler. Öte yandan, kenevir ilavesi, saf PLA'ya kıyasla termal direnci ve erime sıcaklığını düşürür ve cam geçiş sıcaklığını arttırır.

Anahtar Kelimeler

Kenevirle güçlendirilmiş polylaktik asit kompozit, Eriyik filaman üretimi, Biyokompozit, eklemeli imalat, Filament üretimi.

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INTRODUCTION

Additive manufacturing technology has been developed under the name of rapid prototyping since the 1980s. The related development and research process has been continuing with an increasing trend and interest [1]. With the fused filament fabrication (FFF) method, three-dimensional forms can be done by printing computer-aided design (CAD) in two-dimensional layers. Although there are many different additive manufacturing methods, the FFF method is one of the most cost-effective and easiest to implement. [2]. The bio-resin polylactic acid (PLA) is the most widely used material in this technology [3-4]. As seen in Figure 1. PLA, a thermoplastic natural resin, can be printed at low temperature and provide sufficient adhesion force without heating on the printing table [5]. The fact that it does not emit any odor during the printing process in terms of occupational safety, and that it does not require dehumidification before printing, are the important factors in its widespread use [6].

Concerns in the field of sustainability have led to a shift from thermoset materials to recyclable thermoplastic materials. Although thermoplastic materials can be responsibly recycled at the end of their life, they degrade [7]. It is also quite an important sustainability issue, that the matrix and reinforcing material can be dissolved in nature and not produced from petroleum-derived materials [8]. Hemp has been used with petroleum-based thermoplastic resin like epoxy as an alternative to glass and carbon fibers [9].

Additives are used in thermoset and thermoplastic materials for various purposes such as increasing strength, retarding flame, increasing electrical conductivity [10]. Reinforcing with natural fibers provides an increase in mechanical properties [11-13]. Hemp, kenaf, flax, and jute are the most popular bio-additives [14]. Hemp has been used for this unique purpose since ancient times [15]. Interfacial bonds in reinforced composites are very important to achieve the desired improvement in mechanical properties [16]–[17]. Alkali treatment of hemp fiber increases tensile strength [19-20]. Although increasing the fiber ratio in fiber-reinforced plastics theoretically boosts the tensile strength in the fiber direction, it makes the material more brittle. In addition, since the fiber cost is higher, an optimum ratio should be determined by surveying the literature. Increasing the fiber ratio also reduces the melt flow index (MFI) value, making it difficult to extrude filaments and produce by the printer [21].

In this article, it has been studied about the production of biocomposite materials by the FFF method. 10% by weight of hemp was added to the PLA matrix and the change in thermal and mechanical properties was investigated.

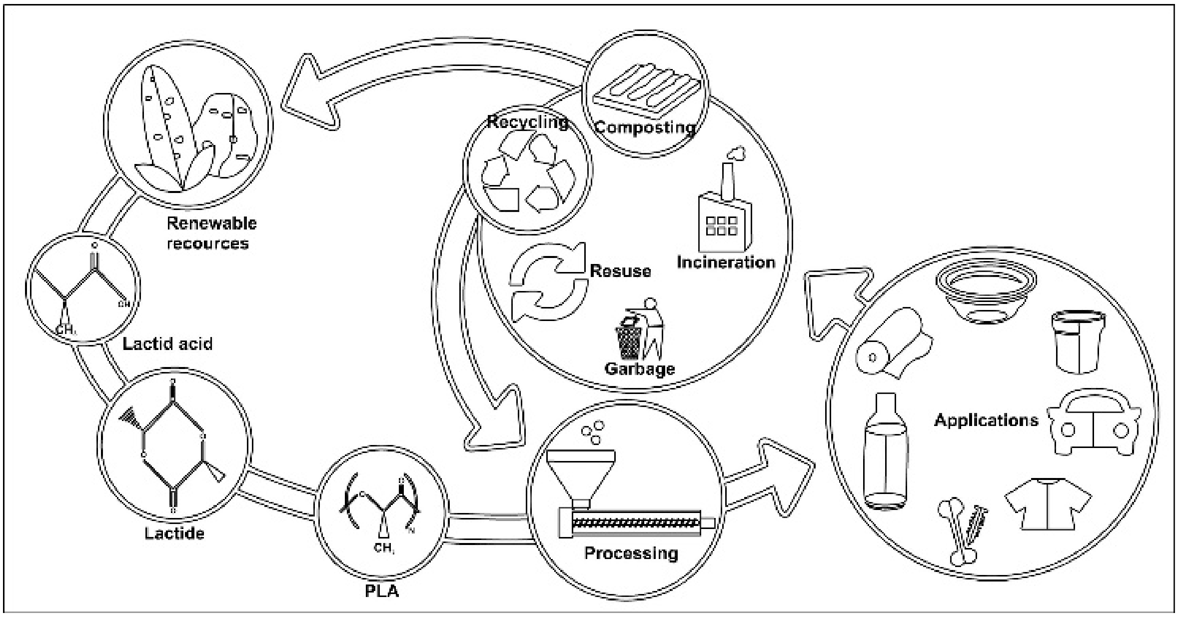

Figure 1. The life cycle of PLA.

Figure 2. Hemp reinforced PLA filament.

MATERIALS and METHODS

Materials

Natureworks company's Biopolymer 4043D PLA product was used as the resin. The density of the PLA is 1.24 gr/m^3, the melting temperature is 150-155 °C and the melt flow rate is 6.1 g/10min. It was modified with 10% of hemp by weight. Hemp fibers are produced from natural hemp obtained from Ketene Herbal Production and Textile Industry Trade company.

Grinding of fibers

Hemp fibers were first tried to be shredded in a griding mill. Unfortunately, an unsuccessful result was obtained. Hemp fibers were ground with the help of a shredder in the Retsch SM 100 device. The cropped hemp fibers were passed through a 500 µm sieve. Hemp fibers have an average density of 0.86 g/cm^3, a diameter of 10 - 400 µ, and a length of 100 - 1200 µ. No surface treatment has been applied to hemp fibers.

Preparation of Hemp-PLA compound

Hemp fibers reinforced PLA resin bio-composite pellets were produced in a 20 mm twin screw extruder of Labtech Engineering brand. Bio-composite pellets with 10% hemp reinforced PLA matrix by weight were extruded at 190 °C and screw speed of 215 rpm. Water cooling is used during the process.

Preparation of Hemp-PLA filament

The produced compounds were extruded into 1.75 mm filament with the help of an extruder with a single screw and a single heating chamber. The error margin of the filament's diameter is around 5%.

It is considered that this situation may affect the tensile test results.

The produced filament cause difficulties while being wound on the reel. The filament was in a fragile structure. In Figure 2. broken filament during winding, and spool can be seen.

Production of Hemp-PLA composite tensile test specimens

As seen in Figure 3. D638 ASTM standard Type V sample was produced. Prints were taken in + - 45 and parallel fill geometries. The effect of geometry on tensile strength was also studied. To keep the integrity of the specimen during printing, two outer wall layers were used.

SEM and Optical Microscopy

Microstructure image analysis with scanning electron microscope was performed with Carl Zeiss 300VP device. İmaging operations were carried out on the fracture region of the tensile test's cracks. Imaging was performed at x500-1000-2500-5000-10000 magnification and 3kV energy. Before placement in the microscope, chamber samples were fixed on aluminum stubs with double-sided carbon tape and sputter-coated with 5nm gold. 200 times magnification was applied on the optical microscope as seen in Figure 4.

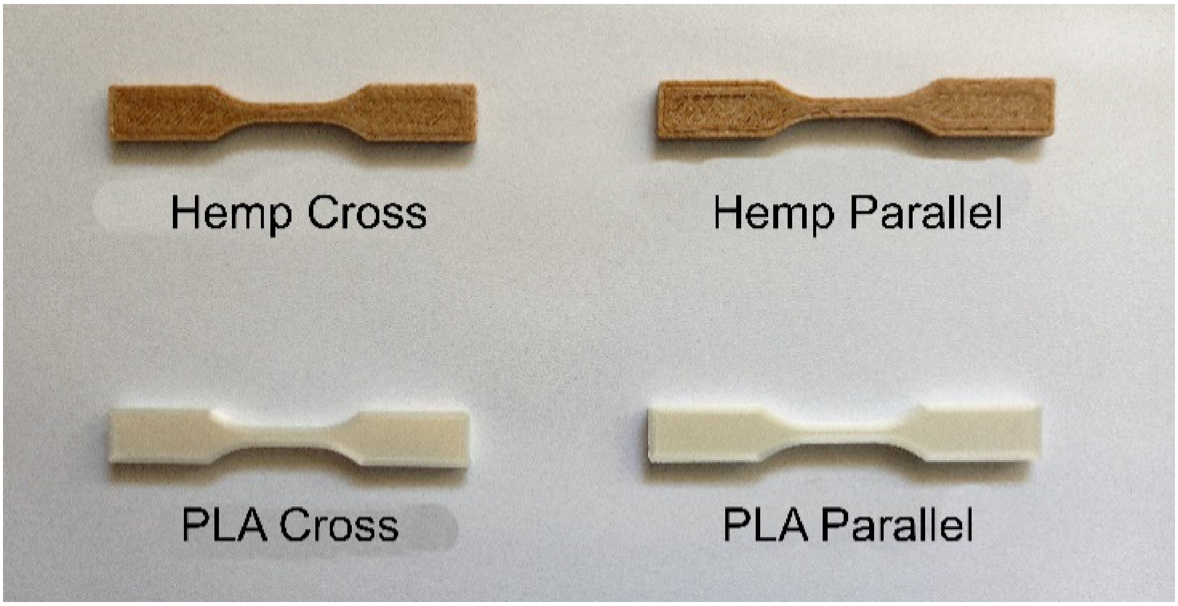

Figure 3. Tensile test specimens.

DSC and TGA

Differential Scanning Calorimetry (DSC) analysis was used to determine the glass transition temperature and melting temperature. The materials were heated to 300**°C**. Thermogravimetric analysis (TGA) is used to investigate thermal resistance.

Tensile Test

Tensile tests were performed according to the related standard [21]. 5 samples were used for each configuration. Instron 1114 testing machine was used with its data acquisition system at a constant crosshead speed of 0.5 mm/min.

RESULTS and DISCUSSION

SEM and Optical Microscopy

In the optical microscope examination, it was observed that the cross-fill geometry was better fused in the z-axis as seen in Figure 3.

Non-adherent structures were found in the sections taken from the fracture region of the cross-infill geometry. These adversely affect the mechanical and thermal properties. It was also determined that there were problems with homogeneity in the distribution of the fibers.

The hemp additive is not homogenously distributed in the matrix material at every location. This resulted in high standard deviations between samples in the tensile test [23]. By examining the SEM results, it was observed that the fiber lengths and diameters were quite different. This led to different results between the samples in the tests [24]. In addition, regions with weak interfacial interaction between the PLA matrix and hemp fibers were found, and regions with gaps between some surfaces were determined as seen in Figure 5. The fact that the interfacial transitions cannot be provided efficiently, reinforcement potential might not be founded as expected.

DSC and TGA

In the DSC test, the glass transition temperature increased from 59 °C to 65 °C, and the melting temperature decreased from 152 °C to 146 °C as given in Figure 7. One of the main reasons for this change is the extra extrusion step of the material while adding hemp fibers. On the other hand, the printing process causes the polymer to degrade.

By examining the TGA analysis, it is seen that the material loses its mass dramatically at 326 °C before the additive is added in Figure 6. This temperature decreased to 294 °C after the addition of additives. This shows that the thermal resistance of the material has decreased. It was not possible to deduce the additive hemp amount percentage by weight from this chart. Mass transitions are not clear.

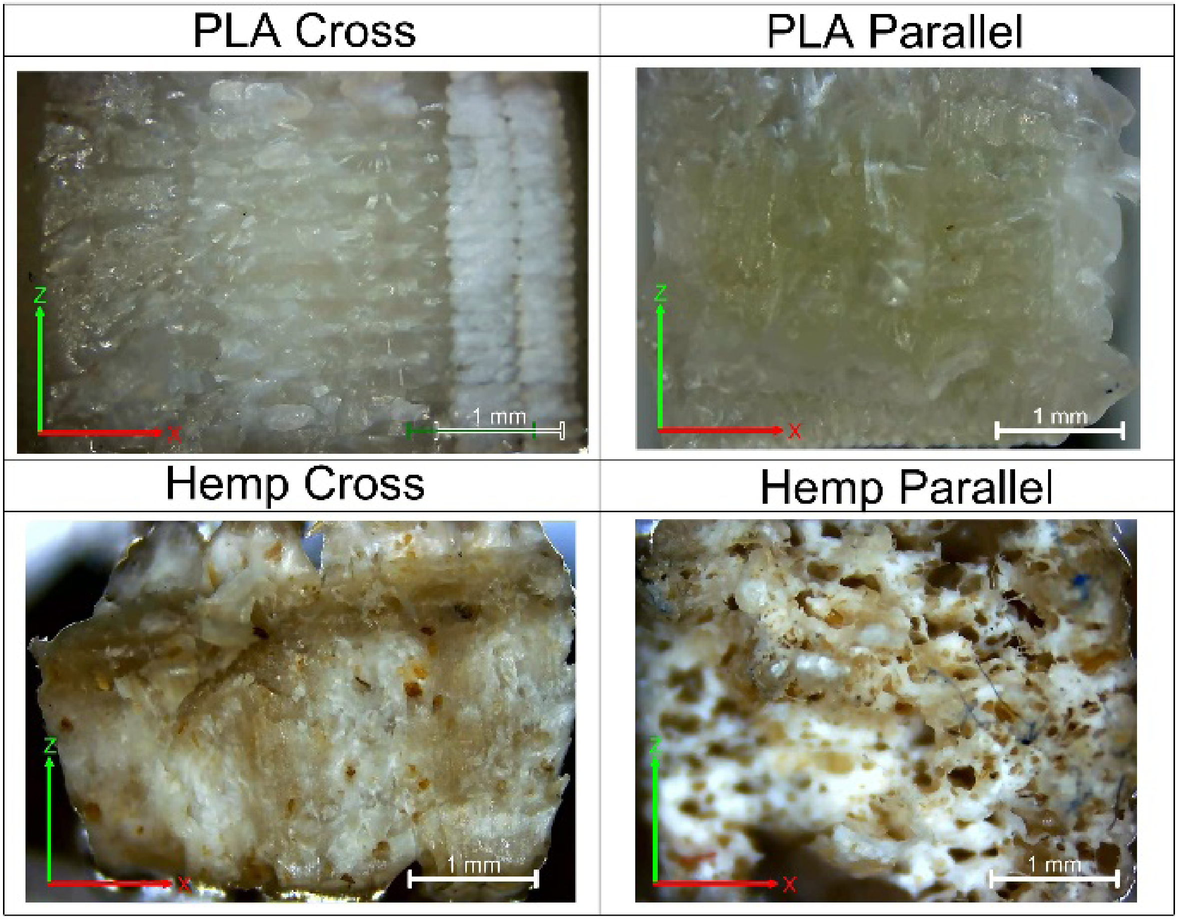

Figure 4. Optical microscope images.

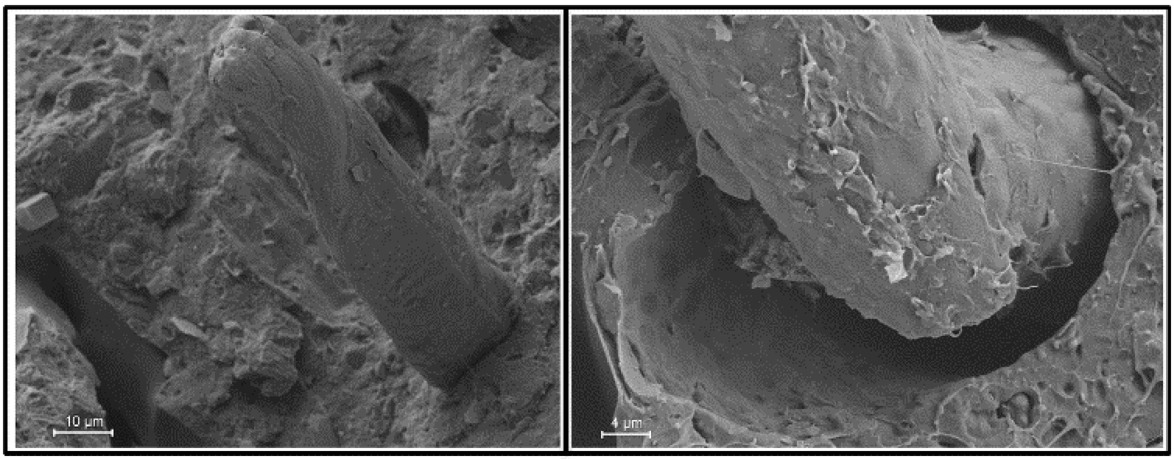

Figure 5. SEM images.

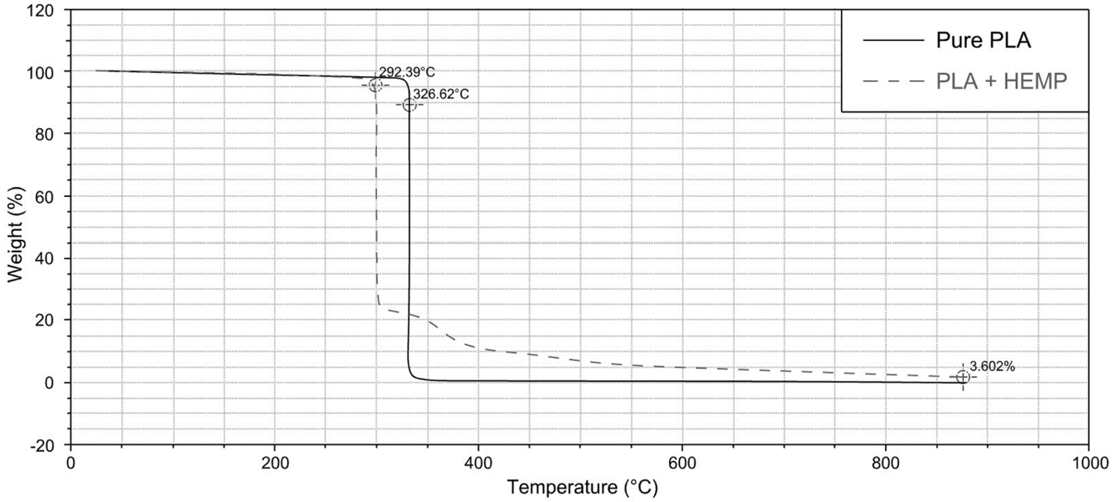

Figure 6. Thermogravimetric (TGA) analysis results.

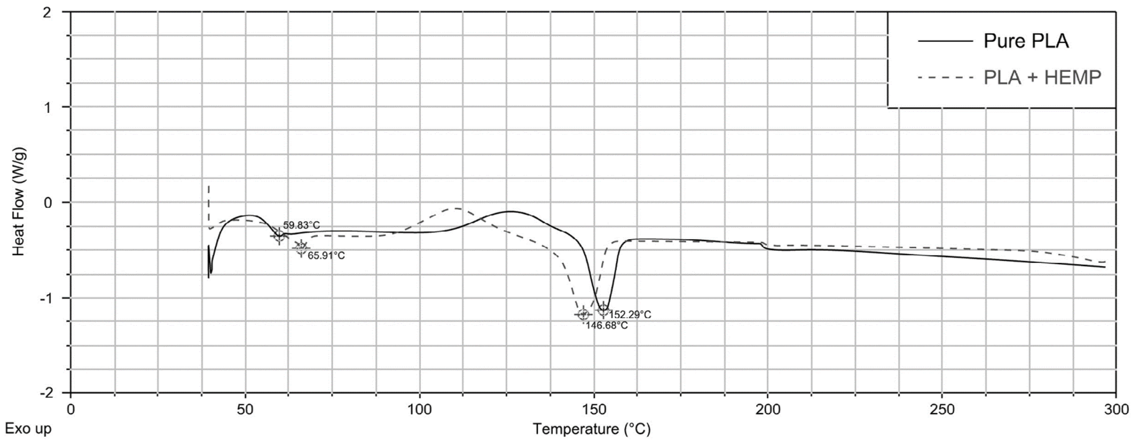

Figure 7. Differential scanning calorimetry (DSC) analysis results.

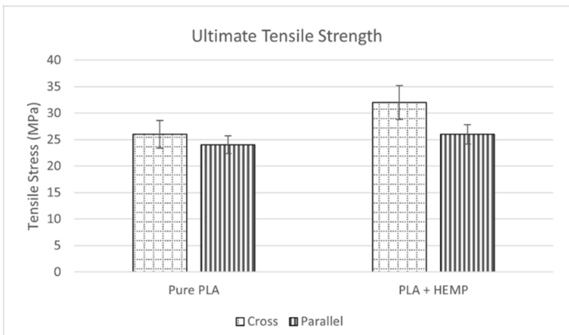

Figure 8. Tensile test results.

Figure 9. Benchmark test.

Tensile Test

By examining the tensile test in Figure 8., it was concluded that hemp additive positively affects the tensile properties of the material. Infill geometry has a surprisingly high impact on tensile performance. The tensile strength for the cross-fill geometry increases from 26 MPa to 32 MPa (23% increase). The standard deviation was 5.3 MPa for pure PLA and 6.2 MPa for Hemp reinforced PLA. For parallel fill geometry, this variation is less. There is a result that its changes from 24 MPa to 27 MPa (12% increase). The standard deviation was 3.3 MPa for pure PLA and 3.7 MPa for Hemp reinforced PLA. These results are quite low when compared to 10% short glass fiber reinforced PLA. Even without heat treatment, values of 50 MPa on average were seen in the previous study [25]. In another study, fiber-reinforced PLA composite was produced by using continuous fibers by additive manufacturing method (FFF) and 66% improvement was observed in mechanical properties [26]. By using continuous carbon fiber this rate could increase to 225% [27]. Continuous fibers provide a better performance, but it should be noted that the production technique is more complicated and costly. Poor performance of parallel geometry is unexpected. Material anisotropy provides high strength in the fiber direction. Although each layer was quite strong in parallel printed samples, the adhesions between the layers in the Z-axis were weak as overall laminate performance. The benchmark test, was at an acceptable level, as can be seen in Figure 9.

Table 1. Maximum Stress Values.

Materials	Infill Pattern	Tensile Stress
Pure PLA	-/+45	26 MPa
	0/90	24 MPa
PLA+HEMP	-/+45	32 MPa (%23 increase)
	0/90	27 MPa (%12 increase)

CONCLUSION

Infill pattern geometry has a significant effect on tensile performance. Hemp reinforcement increases tensile strength by only 10-20% depending on geometry. It could be used as an alternative reinforcement material to glass fiber where medium strength is required. Its homogenous dispersion and surface bonding are critical in the matrix. For future studies, applying chemical and alkaline surface treatment will contribute to this phenomenon and increase the mechanical properties.

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