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Research Article

Effects of Aging and Infill Pattern on Mechanical Properties of Hemp Reinforced PLA Composite Produced by Fused Filament Fabrication (FFF)

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Abstract

Additions of reinforcing natural fibers to polymer matrices provides an increase in mechanical properties. In addition, bio composite materials contribute to the sustainable ecosystem with their ease of recyclability. The effect of accelerated aging on the mechanical properties of PLA matrix biocomposite specimens has been observed in previous research. However, the effect of accelerated aging on the mechanical properties and the resulting mass loss of the material produced with fused filament fabrication (FFF) has been discussed for the first time in this study. Aging was applied to the biocomposite consisted of 10% hemp and PLA matrix produced at a constant rate, parallel to the tensile direction and cross (+/– 45°) angle, and the tensile stress and mass loss were examined. The aging effect has been observed even from the first week. Specimens with parallel printing to tensile direction showed a lower tensile performance than cross printing one. Since the structure in the laminates is quite durable, the adhesion performance in the laminate or through thickness direction has been low. Natural fibers are found so highly hygroscopic that chemical treatments will improve the interface and improve the mechanical properties.

Keywords: Hemp, Aging, Bio composite, Additive manufacturing

1 Introduction

The application areas for additive manufacturing, also known as 3D printing technologies, is expanding very rapidly [1]. Additive manufacturing methods, which started to be used in the late 1980s under the name of rapid prototyping, are developing steadily [2], [3]. 3D printing methods process computer-aided drawings sliced in two dimensions in layers in order to produce three-dimensional objects [4] and these, complex geometries that cannot be produced by traditional production methods can be produced in one piece [5]. Among the different 3D printing methods currently used, FFF has used widely due to its low cost, materials variety and availability and ease of use [6], [7]. FFF enables the production of functional prototypes using various thermoplastic raw materials and is the most widely used method among 3D printing technologies [8]. The most common raw materials used in FFF technique are acrylonitrile butadiene styrene (ABS)

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and polylactic acid (PLA)[3].

In 3D printing technologies, there are certain limitations in practice in terms of materials, processes, and performance [5]. Especially the lack of environmentally friendly, biodegradable, and bio-based printable materials is a major obstacle to the widespread adoption of 3D printing technology [9]. Researches on naturally-derived and renewable polymers instead of petroleum-based polymers with a sustainable environment-oriented approach attracts great attention [9]. Biomass obtained from marine, forestry, and agricultural sources which are the most abundant renewable raw materials on earth, has a promising potential as an alternative to fossil resources [10]. PLA, one of the polymer types, is a thermoplastic polymer obtained from renewable sources such as corn starch or sugar cane. Biodegradable and produced from biomass, PLA is in the form of "biopolymer".

Bio composite filaments made of natural fiber reinforced materials such as wood shavings, rice, coconut shell, hemp or flax fiber, with bio-based polymer matrix are used extensively in FFF due to their advantages mentioned before [11]. Bio-based composite is a completely environmentally friendly and sustainable composites made from bio-based materials [12]. Reinforcing biopolymer-based materials with natural fiber instead of synthetic fiber also provides significant advantages in terms of biodegradability, biocompatibility, and sustainability. Natural fiber-reinforced polymer composites have reached an important point in the research areas of polymer science and technology due to the environmental, social, and economic problems caused by synthetic reinforcements such as glass fiber, carbon fiber, and aramid fiber in recent years. Natural fibers are low-cost compared to conventional synthetic fibers. In addition, natural fibers offer good superior environmental performances [13], [14].

Bio composite filaments made of natural fiber reinforced materials with bio-based polymer matrix are used extensively in FFF devices due to their low cost, easy supply, high strength/weight ratio, good strength and flexibility modulus [15]. As the substitutes for petroleum-based synthetic filaments. From this point of view, wood shavings, rice, coconut shell, hemp or flax fiber, etc. plant-based materials are used for reinforcement [16]–[20].

The strength of the parts produced by the FFF method using bio composite filaments depends on the type of plant fiber, aspect ratio, and also the quality of the interface between the polymer matrix and the natural fiber [18], [19]. Besides economic and environmental advantages, bast fibers such as hemp, flax, and jute are often used due to their remarkable mechanical properties [21].

Many researchers have been interested in the characterization of natural fiber-reinforced polymer matrix bio composites but using these in the FFF is quite newly drawing the attention. Aziz *et al.* Studied the mechanical properties of virgin and alkali-treated hemp fiber reinforced polyester composites. Alkali treated composites showed superior flexural strength and flexural modulus values compared to untreated composites [22].

Lu *et al.* produced hemp fiber-reinforced composites using a high-density polyethylene matrix recycled (HDPE) by compression moulding. The fiber volume ratio was between 20–40%. To improve the fiber-matrix interface, hemp fibers were soaked in 5% NaOH solution for 24 h at 60°C. After chemical treatment, the surface morphology and chemical composition of hemp fibers were analysed by Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). This study showed that hemp fiber-reinforced rHDPE composites can achieve a considerable mechanical performance such as tensile strength of 60 MPa with a fiber volume ratio of 40% [21].

In the study of Pickering and Aryan also evaluated the structure and mechanical performance of alkali-treated harakeke and hemp fiber reinforced d PLA composites produced with the dynamic sheet former method. Harakeke reinforced PLA matrix bio composites have been observed to have tensile strength up to 101.6 MPa and hemp reinforced PLA matrix bio composites up to 87.3 MPa. These was 90% and 60% higher than pure PLA. Minimum and critical fiber volume ratios were also determined [23].

Sair *et al.* investigated the effect of different fiber ratios (5, 10, 15, 20, 25, and 30) on water absorption, thermal conductivity and mechanical properties in hemp fiber reinforced rigid polyurethane (PU) composites. he results showed that the thermal conductivity of composites increased linearly with density while ones of 15% by weight have shown a 40% increase in tensile strength. The results showed that the polyurethane-hemp fiber composite offers good insulating properties compared to traditional insulating materials (glass wool, mineral wool, etc.) the material can provide a promising solution for building insulation [24].

Mazzanti *et al.* studied on the improvement of the fiber-matrix interface with alkali treatment and using scanning electron microscopy (SEM) for short hemp fiber reinforced PLA composite specimens with 3 and 6% fibers by weight produced by extrusion. They observed that alkaline treated hemp reinforced PLA composites had higher tensile properties than untreated ones i.e., with short hemp fiber of 3% in weight one achieves an increase 8.4% in tensile strength while 18.7%, and 6% short hemp fiber reinforcements achieve an increase up to 15.4 and 37.5% in tensile modulus [25].

Pappu *et al.*, using melt processing and injection molding techniques, produced sisal and hemp fibers with PLA for the first time. The obtained average tensile strength (46.25 ± 6.75 MPa), Young's modulus (6.1 ± 0.58 GPa), and specific tensile strength (38.86 ± 5.0) PLA reinforced by sisal and hemp fibers has shown significantly increased the impact strength. Overall, they have stated that hybrid composites perform well and have great potential for the use as an environmentally friendly alternative material in automotive, packaging, electronics, indoor and agricultural applications [26], [27].

Islam *et al.* have produced 30% by weight of alkali-treated and untreated long hemp fiber-reinforced PLA composites by film stacking and made them subjected to accelerated aging in four different time intervals (250, 500, 750 and 1000 h) using UV at 50°C and water spray. After accelerated aging, it was observed that tensile strength, bending strength, Young’s modulus, flexural modulus, and fracture toughness decreased while the impact strength of both treated and untreated composites increased [28]. Sarasini *et al.* examined the performance of injection moulded short basalt fiber, hemp fiber, and hemp/basalt hybrid fiber-reinforced high-density polyethylene (HDPE) composites. They have found that fiber reinforcements significantly increase the mechanical properties and crystallinity of composites [29].

Xiao *et al.* studied the use of thermoplastic bio composites with industrial hemp hurds in the FFF. They investigated the melt flow, rheology, physical, thermo-mechanical, and mechanical properties of bio composites produced by using the wastes. Poly butylene adipate-co-terephthalate (PBAT) and ethylene-methyl acrylate-glycidyl methacrylate terpolymer (EGMA) were used as a hardener and for harmonizing additive, respectively, in melt bonding and extrusion to produce the FFF filament. FFF printed standard specimens were compared to injection molded bio composites. The FFF filament exhibited a diameter tolerance within 0.02 mm and roundness variability below 0.03 mm, and hemp hurds loaded FFF printed parts below 30 phr showed higher impact toughness than commercial PLA filament. In addition, FFF printed specimens showed greater dimensional accuracy with increased hemp hurds loading [30].

Although 3D printing technologies allow the creation of complex geometries and hierarchical cells layer by layer, it is a very effective tool in the selection of infill patterns, ensuring the strength of the structure, reducing waste, the amount of support material, and reducing printing time. Tian *et al.* found studies that the geometry directly affect the structural strength of the specimens and that the amount of voids in the lamina is high in the cross infill pattern [5]. Schirmeister *et al.* investigated the effect of geometry and argued that it is inevitable that structural properties are lower than injection molding due to the nature of FFF technology. Increasing the filament flow between 5–10%, can result in minimize the gap between the technologies [31]. Apart from linear geometries, asymmetric and randomly distributed patterns can also be used as infill patterns in FFF. In addition, lowering the nozzle size also reduces the void structure in places where there are sudden dimensional changes such as corners and prevents the formation of stress concentrations [5].

Reinforcing with natural fibers provides an increase in mechanical properties of polymer composites. In addition, recycled bio composites materials contribute to the environmental sustainability [32]. The production of hemp fiber reinforced filaments with PLA by the FFF method was studied for the first time. The effect of accelerated aging on the mechanical properties of bio composite consisting of hemp fibers and PLA produced by film stacking was previously observed, but the effect of accelerated aging on these mechanical properties and the resulting mass loss was discussed for the first time in this study. Unlike the UV light accelerated aging made by Islam and others, in this study, the integrated effect of temperature, humidity, and salt on the mechanical properties was investigated. Additionally, the effect of infilling directions on mechanical properties was also given.

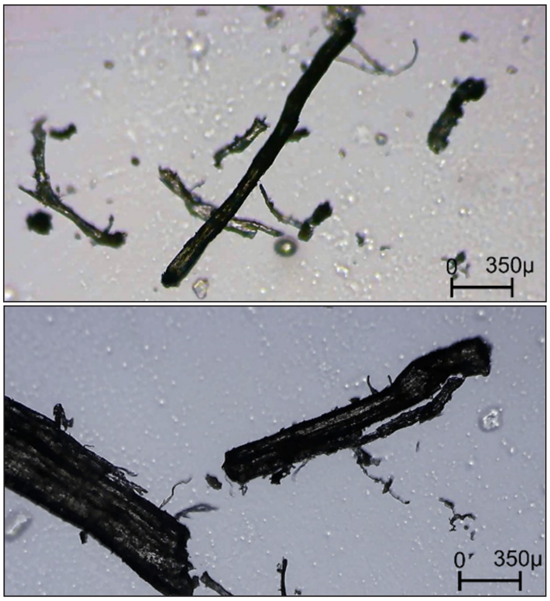


Figure 1: Optical microscope photo of hemp fibers.

2 Experimental

2.1 *Materials*

FKuR Kunstsoff company's Bio-Flex F7510 PLA product was used as matrix material. The density of the used PLA is 1.25 gr/m^3, the melting temperature is 155°C and the melt flow rate is 2–4 g/10 min. 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.

2.2 *Hemp fiber production*

Hemp fibers are produced from natural hemp by grinding in the Retsch SM 100 device. The ground 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 as seen in Figure 1. No surface treatment has been applied to hemp fibers.

2.3 *Preparation of hemp-PLA composite pellets*

Hemp fibers reinforced PLA matrix bio-composite pellets were produced in 20 mm twin screw extruder of Labtech Engineering brand. Bio-composite pellets with 10% hemp reinforced PLA matrix by weight were extruded at 180°C and screw speed of 200 rpm.

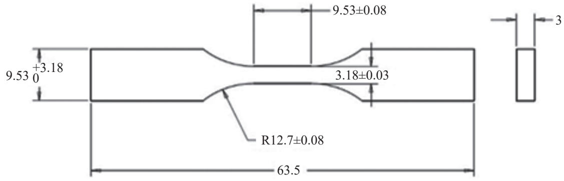


Figure 2: D638 ASTM standard type V tensile test sample.

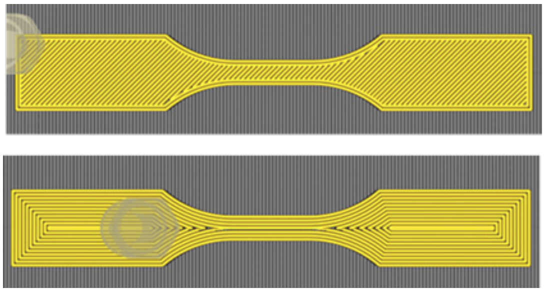


Figure 3: Infill patterns geometries, (upper +/–45°, bottom linear).

2.4 *Fabrication of hemp-PLA composite filaments*

Laboratory type Flax brand Arya single screw extruder was used to turn bio-composite compounds into filaments. The extruder's zone temperature is 205°C, screw speed is 15 Hz/h and production speed are 1.5 kg/h (50 mm/s). Biocomposite filaments with hemp fibers reinforced PLA are produced in a diameter of 1.75 mm (+/– 5%) in accordance with the FFF technology. No surface treatment has been applied to the filament after production. The produced filaments are stored in vacuum bags to protect them from moisture.

2.5 *Production of hemp-PLA composite specimens*

As seen in Figure 2, D638 ASTM standard Type V sample was produced. Bio-composite filaments were in two different infill patterns in Creality Ender 3 Pro FFF device shown in Figure 3. In the first infill pattern, the tensile force and the printing direction were in the same direction. As for the second infill pattern, to give an quasi-isostatic character to the specimens infilling directions were chosen as (+/–) 45°. In order to

Figure 4: Weathering test cabin.

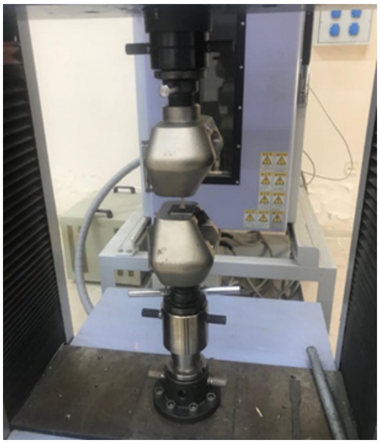


Figure 5: Weathering test cabin.

preserve the integrity of the specimen during printing, two wall lines were used on the outer layers. Such process parameters were 0.1 mm of layer thickness, 205°C of nozzle temperature, 40°C of bed temp (50 mm/s print speed. The printing process was carried out in a closed cabinet at 36°C to achieve a uniform cooling and constant distribution of the heat throughout the printer. The outside temperature was measured as 20°C.

2.6 *Testing*

2.6.1 Aging

According to the related standard (ISO 9227) the CC1000ip weathering chamber device (shown in Figure 4) from Ascott company was used for aging by the cyclic environmental conditions are programmed for the total period of 3 weeks with sampling weekly. In a day, three cycles of sprinkling, salt fog and drying were carried out. Temperature range in sprinkler mode is set between ambient temperature and + 60°C while the humidity is between 95–100% RH. In salt fog mode, the temperature range is set between ambient temperature and + 50°C. Salt mist spray rate was adjusted to 80 cm^2 between 0.5 and 2.5 mL/min. Drying mode temperature range is set between ambient temperature and + 70°C. Humidity is not controlled in drying mode.

2.6.2 Tensile test

Tensile tests were performed according to the related standard (ASTM D638) for the aged and control specimens. on an Instron 1114 testing machine that has 150 N load cells as seen in Figure 5, with its data acquisition system at a constant crosshead speed of 1 mm/min.

2.6.3 SEM

Microstructure analyses with scanning electron microscope were performed with Carl Zeiss 300VP device. Tensile tests were carried out on specimens of the tensile test's cracks. Imaging was performed at 500X–10000X magnification and 5 kV energy.

2.6.4 Mass loss

The loss of mass in the conditioned and unconditioned specimens with different infill directions after aging was measured with AND Brand HM-200 high precision balance.

3 Results and Discussion

Tensile strength values after weathering and control specimens are shown in Figure 6. From the results, the tensile strength can reach 19.7 MPa in the control group parallelly infilled, while it was 28.0 MPa in the cross-infilled. Islam *et al.* similarly, a decrease of 10% in the tensile strength of plates with 30% of hemp in weight produced by stacking was observed after rapid aging [28]. After 3 weeks of aging samples parallelly infilled, tensile strength decreases by 50% to 10 MPa. As for the samples cross infilled after 3 weeks

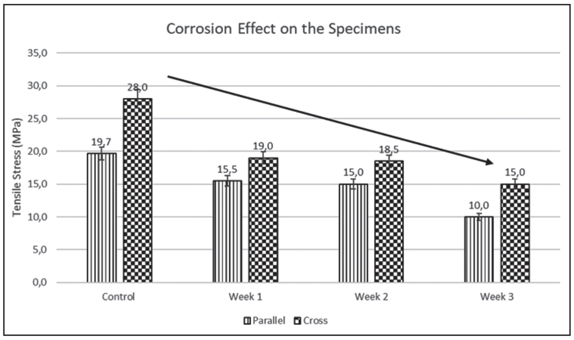


Figure 6: Tensile strength values after weathering and control specimens.

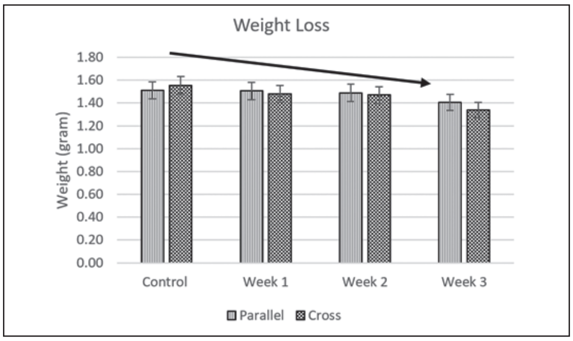


Figure 7: Mass loss graph in post-weathering and control specimens.

of aging, tensile strength decreased by 47% to 15 MPa. It is expected that printing in the tensile direction will allow stronger product than those of printed in crossed direction. When the samples were weathered, a decrease in their in the tensile direction than the tensile strength was systematically observed. Changes in tensile strength are almost the same at all the directions whether after and before aging. However, crossed ones show drastically change in time domain during the aging.

In Figure 7, the mass losses were also observing throughout the aging. This result is quite consistent as PLA is a bio composite that is easily degradable in nature. Same with the decrease in tensile tests, mass losses were accelerated after the 2nd week. While 1.51 grams was measured in the control samples parallelly infilled, the mass decreased to an average of 1.40 grams with a loss of 8% after 3 weeks of aging. average of 1.56 grams in the control samples cross-infilled decreased to an average of 1.34 g with a loss of 16% after 3 weeks of aging. The rate of mass loss in samples cross infilled is considerably higher than that of samples produced with a parallelly infilled because of the effect of the contact areas. To better interpret these effects, samples were examined under optical and SEM microscopes.

Tian *et al.* found in their studies that different geometry directly affects the structural strength of the samples and the number of voids in the lamina is high in the samples cross-infilled [5]. In this study, similarly the number of voids is quite high in samples cross infilled. However, it was observed that the bonding between layers was better than those of with cross infilled ones. This resulted in an increase in the strength

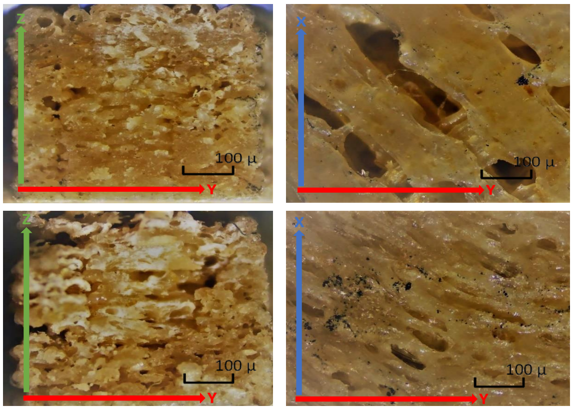


Figure 8: Optical microscope images of 3D printing specimens (Upper +/– 45, bottom parallel).

value and a higher tensile strength was obtained in the cross-infilled specimens.

In Figure 8, the view of the control groups of the cross and parallel infilled samples and the cross section at the break point is well-observed. The specimen is apparently parallel to tensile direction to what appears to be perfectly smooth from top view, but when the sections are examined, the opposite situation is in question while maintaining homogeneous adhesion between layers on through z-axis. It was found that adhesion between layer those printed in parallel geometry are sufficient. For this reason, the cross part's tensile test worked as a holistic structure, although not much on a layer basis, and the moment of inertia increased considerably compared to the other type. Eventhough, it is deeply robust on the basis of the related structures, parallel printed geometry has been able to act independently and provide a low network strength. Considering the weathering performance, the effect of geometry is seen to be quite high. The bonds in the Z axis are largely broken after the first weathering period. For this reason, there is a decrease in cross life in the first week.

The printing process was carried out in a closed cabinet at 36°C in order to achieve a uniform cooling and constant distribution of the heat throughout the printer. In addition, the outside temperature was measured as 20°C. However, from the geometry, the middle of the sample cooled faster, the ends cooled later (Figure 9).

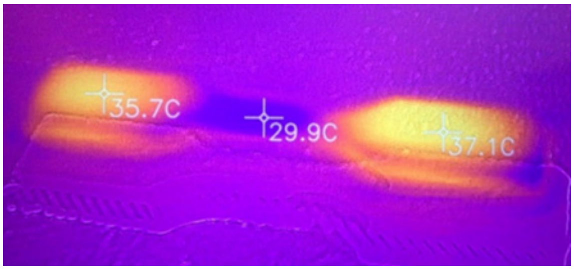
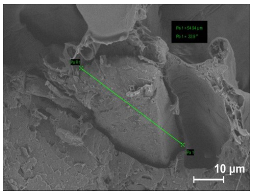
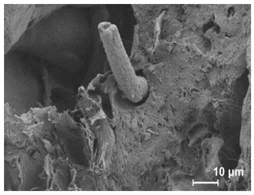
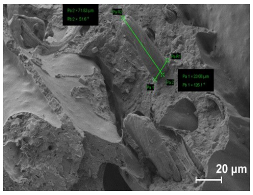
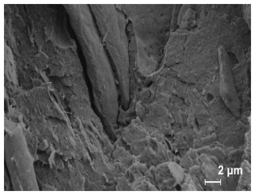
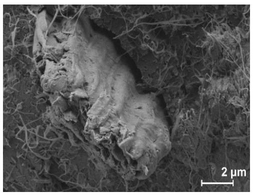
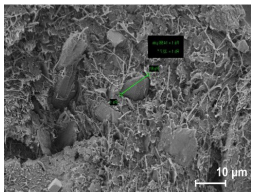
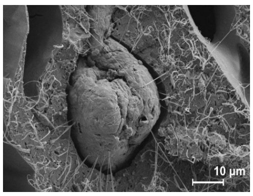
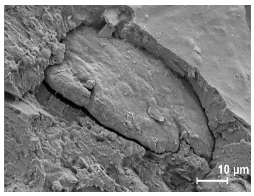


Figure 9: Thermal image of the cooling in the sample after FFF printing.

Microstructure analyses of damaged sections were performed on the specimens tested according to the ASTM D638 standard. When the images in Table 1 are examined, in the images obtained as a result of the analysis, voids created by the fibers in the rupture region are encountered. The voids created by the fibers represent the defects in the fiber-matrix interface assembly. Due to the lack of surface treatment of the fibers, voids have formed around the fibers. The necessity of interface improvement has emerged once again [25]. Fibrilation occurred in the PLA matrix with aging. With the increase in aging time, fibering increased. Fibrilation is an indicator of the degradation of the matrix material due to aging. Detection of degradation in the matrix material supports the decrease in mechanical test results.

Table 1: SEM images of different type of geometry and weathering time

	Paralel	**Cross**
Control Group		
1 week		
2 week		
3 week		

4 Conclusions

Infill pattern geometry highly affects the tensile strength and weathering performance. It is very important that the laminates adhere to each other, and the laminate works holistically. Since PLA is a biopolymer, and weathering effect is seen from the first week. Control group's tensile strength drop dramatically from 28/19.7 MPa to 10/15 MPa after 3 week period. Extension of the weathering time is suggested by the authors for future studies. Although ruptures between the layers in the Z axis are observed from the first week. The observation of this dissolution in the lamina becomes clear from the 3rd week. Since hemp is used as reinforcement material in studies related, its homogeneous distribution is very important. Even though the compounds were produced with double screw extrusion, non-homogeneous local areas were detected in the observations made with optical microscope and SEM. This situation affects the structural performance. In order to ensure homogeneous distribution and since natural fibers are highly hygroscopic, it is expected that chemical treatments will improve the interface and increase the mechanical properties. There is no doubt that aging increases impact strength. For this reason, the change in impact strength in weathered specimens can be examined for future studies.

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