청정소재제품기술

보 문

Fabrication and characterization of disposable golf tees using biodegradable polymer through 3D printing

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Abstract

Many studies have been conducted on the indiscriminate use of plastic due to the environment problems it has caused all over the world. This problem can be mitigated by using eco-friendly/biodegradable plastics that can be decomposed by microorganisms or enzymes. This study focused on addressing the plastic golf tees that are thrown away at golf courses. In order to replace conventional golf tees (ABS) with a more eco-friendly alternative, this study explored a biodegradable plastic and 3D printing method for producing golf tees. Among the biodegradable plastics, PLA (polylactic acid) was found to be a good candidate as an eco-friendly material because it is biodegradable by microorganisms. Thus, golf tees were prepared by using PLA via 3D printing, and the physical and chemical properties of the tees were evaluated. The amorphous region of PLA was confirmed through XRD. Also, FT-IR showed the unique peak of PLA without impurities. It was confirmed through an optical microscope that the specific surface area and roughness had increased. This structure plays a role in firmly fixing the golf tee when it is inserted into the ground. In addition, it was possible to improve the compressive load compared to ABS golf tees while also decreasing the compressive stretching.

Keywords : Polylactic acid, Acrylonitrile butadiene styrene copolymer, 3D printing

1. Introduction

Plastics, which are petroleum-based chemical products, have brought convenience to our daily lives with their excellent functions and affordable prices [1-3]. However, excessive disposal of plastics has led to serious environmental pollution, as they are difficult to decompose and release harmful microplastics. Also, incomplete combustion during incineration can also cause air pollution [3]. Plastics can be harmful to human health when they are mistaken as food by marine organisms and accumulate in their bodies.

The amount of plastic waste increased from 5.28 million tons in 2011 to around 6300 million tons million tons in 2015 [4,5]. Recycling methods include reuse, energy recycling, incineration and landfill are methods for disposing of plastic waste. Resource reuse through recycling is the most important, but it is difficult to secure demand and plastic is used for energy recovery instead of landfill, but there are problems such as demand decline and price decline due to the limitations of energy recovery facilities. Plastic waste is a challenge to recycle due to the variety of plastics collected and the cost of removing impurities and sorting. To overcome situation, various materials with plastic properties that can solve environmental pollution are being researched, including bioplastics as a representative material. Bioplastics are bio-based polymers made from resources such as biomass. They are attracting attention as a new environmentally friendly material that can replace petroleum-based polymers, which are the biggest environmental pollution problem.

Biodegradable plastics can decompose over time due to the presence of water, carbon dioxide, etc. Biodegradable plastics can be divided into two categories: biodegradable plastics are made from materials such as sugarcane, cornstarch, and potato starch, and carbon-reducing biodegradable plastics, which are made by mixing bio-plastics with conventional plastics. Other examples

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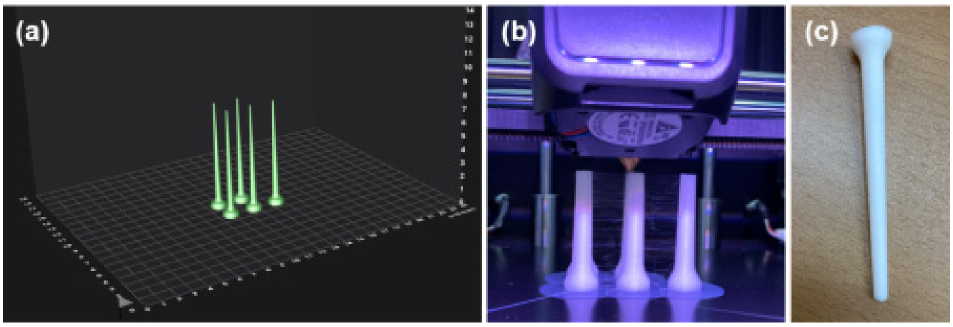

Figure 1. (a) G-Code generation, (b) PLA golf tee printing, and (c) output.

include biodegradable products made from cellulosic, biomass, biodegradable resins, and oxidizing agents mixed with catalysts and oxidizing agents. Polylactic acid (PLA) is an aliphatic polyester with ester bonds in its repeating unit, hydroxy and carboxyl groups, making it biodegradable and decomposable by microbes [6-8]. Bio-plastics are being considered as a solution to the environmental pollution caused by traditional plastics. The use of bio-plastics is growing in various industries and research on alternative materials is also being carried out using 3D printers. The printing conditions for PLA materials and improve the printing technology are being needed.

This research utilizes a tee made of biodegradable material, PLA, which has low environmental impact as it can be fully degraded after serving its purpose. Compared to the conventional ABS based Tee, which is widely used due to its low material cost and ease of post-processing in mass production through injection molding, the use of PLA reduces environmental concerns. However, the design limitations and high facility costs associated with ABS production through injection molding are drawbacks. Using PLA as an alternative material in the production of disposable products, which are currently facing restrictions and changes, is possible [9-12].

In this study, the solutions were presented with prioritizing environmental design and production were considered. X-ray Diffraction, FT-IR spectroscopy, Optical microscope, Thermo-gravimetric Analyzer, and Universal Testing Machine were carried out to compare the performance of conventional product.

2. Material and methods

2.1 Design of golf tee

The golf tee design was created using the 3D modeling program SketchUp to quantize the design. The top of the tee was designed to be broad and horizontal with a 12 mm width and 80 mm length so that the golf ball would fit easily. The top was designed to gradually become thinner from 5 mm to less than 1 mm at the bottom to ensure a secure fit in the ground.

2.2 3D printing of golf tee

The 3D modeling file was converted to STL (Standard Triangle Language) format and saved. The saved file was uploaded to Cubicreator4 Single (3DP-110) by G-Code Cubicone to convert it to G-Code. PLA and ABS were selected as the materials in the output options. The temperature was set differently for each material, with PLA at 210 ^{o}C and ABS at 240 ^{o}C. The values for wall thickness, infill, speed, and support were printed consistently.

The 3D printer equipment used in this study was the Single-3DP110F printer from Cubicone using FDM (Fused Deposition Modeling) method. The build size of this model is 20 mm x 190 mm x 200 mm, with a maximum nozzle temperature of 260 ^{o}C and a maximum heating bed temperature of 120 ^{o}C. It can print all materials with 1.75 mm filaments. The printing process starts with the bed moving in the x and y axis and the nozzle moving in the z axis. The filaments used were Cubicone PLA (PLA-PLUS) and ABS (ABS-A100). The density of PLA is 1.24 g m^{-3}, the nozzle temperature is around 200 ^{o}C, and the diameter is 1.75 mm. ABS filament is known for its excellent post- processing such as drilling and grinding and has good adhesion and uniform melting point. The nozzle used was 0.4 mm.

The manufacturing of golf tees has been optimized for 3D printing by converting the design into G-Code and setting the best printing conditions in Figure 1. The filament, made of a heat-resistant material using the extrusion layer method, is heated to temperatures of 210 ^{o}C for PLA or 240 ^{o}C for ABS, and preheated to allow the filament to flow smoothly through the nozzle. The build bed is also preheated to 65 ^{o}C to ensure proper adhesion of the printed object. The design of the golf tees is designed for commercialization and to avoid any inconsistencies in shape. Once the printing is ready, the filament is inserted into the extruder, and continuously supplied through a feeding device. As the filament passes through the hot nozzle, it adheres to the build bed, starting the layering process to produce the desired shape.

3. Results and discussion

The researchers used XRD (SmartLab, Rigaku, Japan) and FT-IR (Thermo Fisher Scientific US/is50, Thermo, US) to analyze the 3D printed golf tees made of PLA and ABS (Acrylonitrile Butadiene Styrene Copolymer) in Figure 2 and 3. The XRD results showed that the PLA golf tees had two characteristic main peaks at

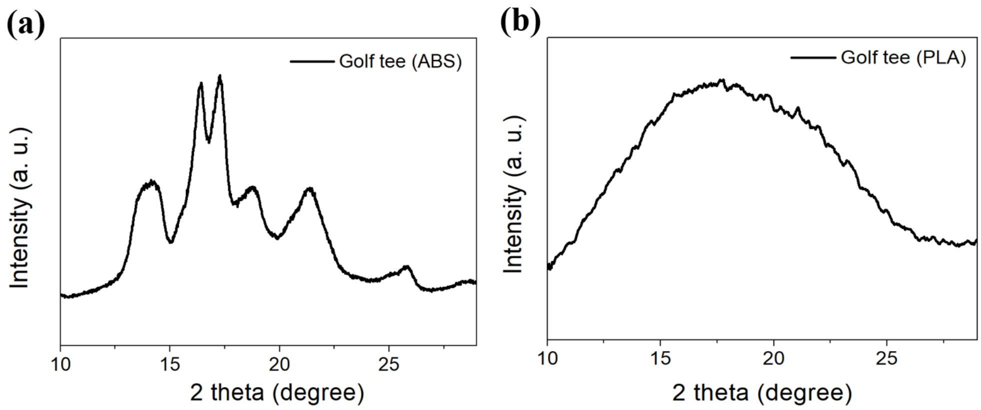

Figure 2. XRD graphs: (a) ABS-based golf tee and (b) PLA-based golf tee.

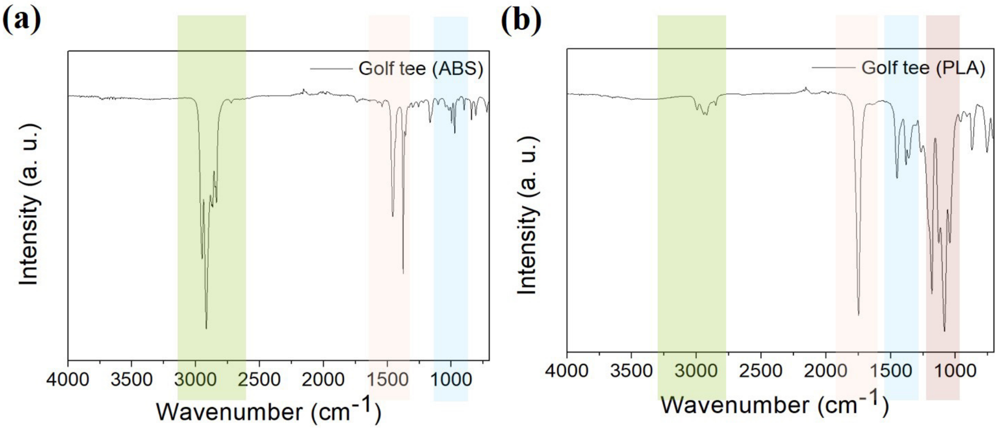

Figure 3. FT-IR analysis: (a) ABS-based golf tee and (b) PLA-based golf tee.

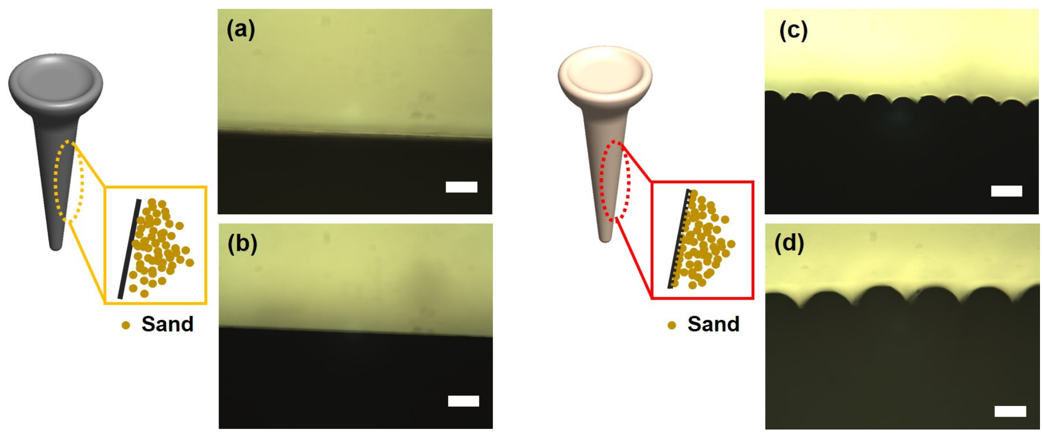

Figure 4. Optical microscope images: (a) ×10, (b) ×20 of ABS-based golf tee and (a) ×10, (b) ×20 of PLA-based golf tee.

16° and 19° with the literature value (JCPDS No. 00-054-1917) [13], while the ABS golf tees showed characteristic broad peak at 2θ of 20° (JCPDS No. 00-064-1623) [14].

The results of FT-IR analysis showed that the PLA-based golf tee was well manufactured as there were no impurities present. This was confirmed by observing the unique peak of PLA at 3,000 cm^{-1} for -CH stretching, 1,780 and 1,680 cm^{-1} for C=O stretch, 1,500 cm^{-1} for C=H stretching and 1,180 cm^{-1} [15,16]. The absorption characteristics of the ABS-based golf tee are C-H stretch around 3,000 cm^{-1}, 1,602 cm^{-1} (C ═N), 1,500 - 1,400 cm^{-1} (-C-H bending in phenyl ring), and 800 - 650 cm^{-1} (C=C stretching) [17-19].

Optical microscopy (Figure 4) was used to analyze the surface of the manufactured PLA-based golf tee and ABS-based golf tee. The results showed that the PLA-based golf tee had a rough surface compared to ABS, which is due to its FDM layering structure. This roughness increases the golf tee's non-planar area and makes it more firmly supported when inserted into grass or soil. The difference in surface roughness between the two

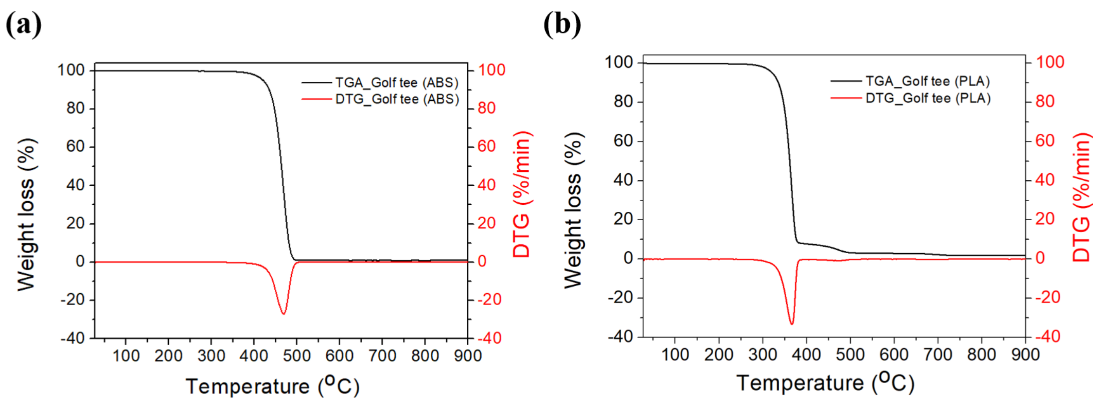

Figure 5. TGA and DTG graphs: (a) ABS-based golf tee and (b) PLA-based golf tee.

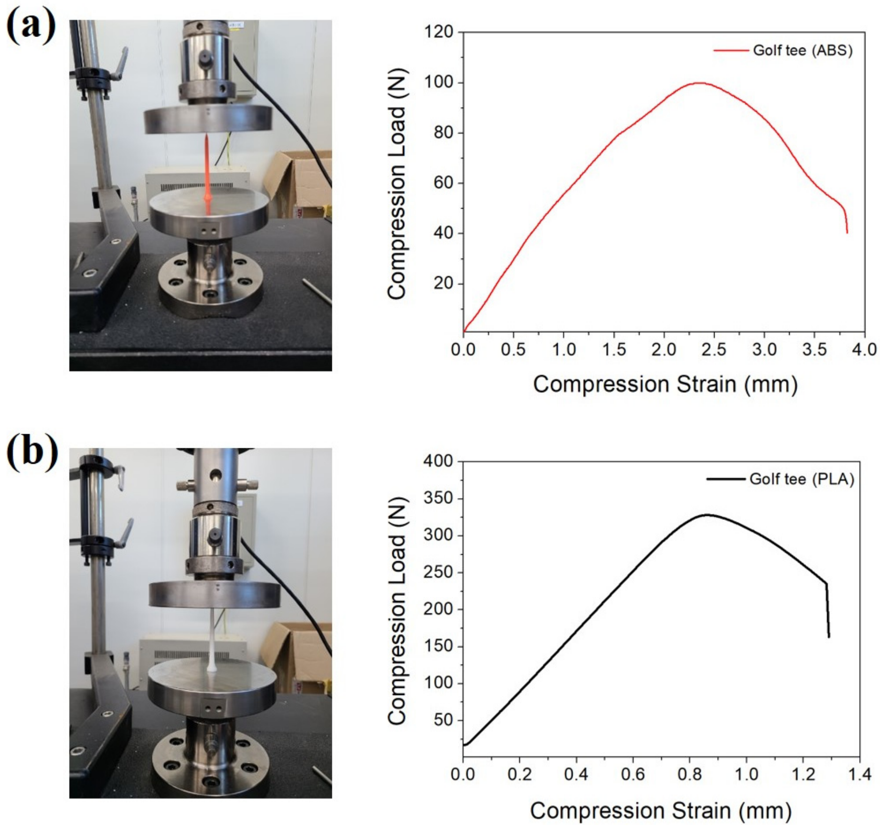

Figure 6. Real images of measurement and load-compression curves: (a) ABS-based golf tee and (b) PLA-based golf tee.

materials can be attributed to several factors. Firstly, PLA has a relatively low melting point and a fast crystallization rate. As a result, PLA solidifies quickly during the FDM process, leading to rapid formation of layers on the surface. Additionally, thermal conductivity plays a role in surface roughness. ABS is more thermally conductive than PLA, which means it distributes heat more uniformly among the stacked layers and dissipates heat quickly. Lastly, the output conditions during printing can also affect surface roughness. Both PLA and ABS may exhibit different surface qualities depending on printing parameters such as printing speed, layer height, and temperature. In conclusion, the rougher surface of PLA compared to ABS can be attributed to its fast crystallization rate, lower thermal conductivity, and the influence of printing conditions.

The TGA and DTG (Mettler-Toledo, TGA/DSC1) graphs obtained by conducting combustion experiments on the samples used in this study from room temperature to 900 °C min^{-1} with a heating rate of 10 °C min^{-1} are shown in Figure 5. The combustion process can be broadly divided into two regions. The first region, from around 30 °C to 100 °C, corresponds to the evaporation of water, while the second region, from around 400 °C, shows a rapid decrease in mass due to the combustion reaction of carbon [20,21]. After 500 °C, the combustion process ends and there is no further weight change. Golf tees made from PLA exhibit a drop in mass near the carbon combustion region of 320 °C and losing mass completely at close to 400 °C [22,23].

The strength of the manufactured objects was tested using an tensile testing machine and the force corresponding to the deformation was recorded in Figure 6. The unique characteristics of PLA and ABS, which were produced using 3D printer filaments, were confirmed by conducting tests while keeping their shape identical. The maximum compression force and compression strain of the golf tees were measured using UTM (Universal Testing Machine, Instron 5982) with a 10 kN load cell at a compression rate of 5 mm min^{-1}. The graph, with the X-axis set to compression strain (mm) and the Y-axis set to compression force (N), shows the strength characteristics of the golf tees. The highest compression force for the PLA-based golf tee was 328 N, which is about three times higher than the ABS-based golf tee (100 N), indicating improved durability. On the other hand, due to the high compression strength, the compression strain tends to decrease.

4. Conclusion

This study used a 3D printer utilizing the FDM method and compared the properties of natural friendly PLA material to the commonly used ABS material for Golf Tees, which pose environmental pollution problems. Optimal production was carried out to substitute ABS with PLA, and the precision of the produced Golf Tees was measured considering the characteristics of commercialized Golf Tees. 3D design program was used to design and manufacture functional shapes based on the measurement of dimensional precision. The results of the analysis in this study showed that the XRD analysis of the Golf Tees produced by the 3D printer confirmed the characteristic main peaks of PLA-based golf tee and FT-IR analysis confirmed that it was well produced without impurities. Results of analyzing surface characteristics using optical microscope showed that compared to conventional golf tees, the non-planar and roughness of the surface increased, allowing it to firmly hold in the ground when inserted. Compression load characteristics showed that PLA and ABS based golf tee had 328 N and 100 N, respectively. It showed that PLA had higher compression force over 3 times that of ABS.

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