AN INVESTIGATION ON 3D PRINTED WALNUT SHELL-REINFORCED POLY (LACTIC ACID) COMPOSITE

Murat DEMİR[1], Ayberk SÖZEN[2], Yasemin SEKİ[1], Figen SELLİ[3]

[1] Dokuz Eylül University, Textile Engineering Department, İzmir, TURKEY
[2] Dokuz Eylül University, Marine Sciences and Technology, İzmir, TURKEY
[3] Eskişehir Technical University, Advanced Technologies Research and Application Centre, Eskişehir, TURKEY

Corresponding author: murat.demir@deu.edu.tr

Abstract: *In this current study, the producibility of 3D printed walnut shell composite is investigated. PLA granules and untreated ground walnut shells were mixed priorly and then extruded by using a single screw extruder to produce filaments for 3D printing. Then, pristine and walnut shell doped PLA filaments were 3D-printed by using the fused filament fabrication (FFF) method. The thermal decomposition behaviour of the filaments and the morphology of 3D printed parts are examined by Thermo-gravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively. SEM micrographs presented non-adhesion between the particle and the polymer and also non-homogeneous particle distribution. TGA data revealed that the moisture content of PLA increased, and both pristine and doped PLA filament can resist to extrusion processes which take place at 200C.*

Keywords: *PLA, 3D-printing, walnut shell, extrusion, additive manufacturing, reinforced PLA, Fused filament fabrication.*

1. INTRODUCTION

Additive manufacturing also referred to as 3D printing, has gained a lot of attention and popularity with the help of producing complex geometries without special tools in good accuracy, and ease of production for prototyping. Since the first idea was presented in the 1970s, many different technologies have been presented for additive manufacturing and Fused Deposition Modelling (FDM) is one of the most common used 3D printing technologies (Dip et al., 2020). In the working principle of FDM printers, filament form material is fed through a heated nozzle, and designed parts are produced by the deposition of molten polymers on the printing bed.

In FDM printers, the properties of 3D parts are mainly affected by printing parameters and polymers. Recently, there has been an outbreak of studies that focus on producing reinforced filaments for FDM printers. Most of those studies used different kinds of waste or fibres as additive materials and revealed a cost-effective, sustainable and environmentally friendly production chain for filament production (Balla et al., 2019; Royan et al., 2021).

The cost of filaments can be decreased by the addition of economical filler materials, which may improve the properties of the polymers. The use of fillers especially bio-based materials will assist in mitigating the environmental impact (Ahmed et al., 2020). The aim of this study to manufacture 3D printing of walnut shell reinforced PLA parts. For this purpose, the walnut shells were ground and mixed with PLA pellets. PLA/walnut shell mixture was extruded to produce filament and then 3D printed parts. The composite filaments and 3D printed parts were analysed by thermogravimetric analysis and scanning electron microscopy.

2. MATERIALS AND METHODS

2.1. Materials

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

2.4. Characterization of the PLA filaments and 3D-printed parts

To investigate the thermal stability of pristine and walnut shell doped PLA filaments, thermogravimetric analysis was conducted by using a Shimadzu DTG-60H instrument. The investigation was performed from room temperature to 600 C at a rate of 10 C/min. To prevent oxidation, the analysis was conducted under a nitrogen atmosphere. The microstructure of the 3D parts was analysed with Zeiss Sigma500 FESEM scanning electron microscope using the SE2 detector. Prior to placement in the microscope, chamber samples were fixed on aluminium stubs with double-sided carbon tape and sputter coated with 10nm gold. Imaging was performed at x500-1000-2500-5000-10000 magnification and 5kV energy.

2.5. Tensile tests

Tensile tests were performed according to the related standard (ASTM D638) with its data acquisition system at a constant crosshead speed of 1 mm/min.

3. RESULTS AND DISCUSSION

SEM micrographs are presented in Figure 3. When the SEM images were examined, it was observed that there was a problem of non-adhesion between the printed layers. Interfacial bonding is unsuccessful. There are gaps in the matrix due to the inability of ground walnut shells to adhere to the PLA matrix during filament production. The distribution of particles in the matrix is not homogeneous. Non-homogeneous structure of reinforced filament for the production of additive manufacturing has also been stated in different studies (Lee et.al., 2021; Singh et.al., 2022; Mazur et.al., 2022). to overcome this problem, some suggestions have been offered as smaller particle size, pre-treatment of reinforcing materials and post-treatment of produced 3D parts (Wang et.al., 2022; Chen et. al., 2022). The mechanical performance of the whole structure decreases due to the above-mentioned reasons.

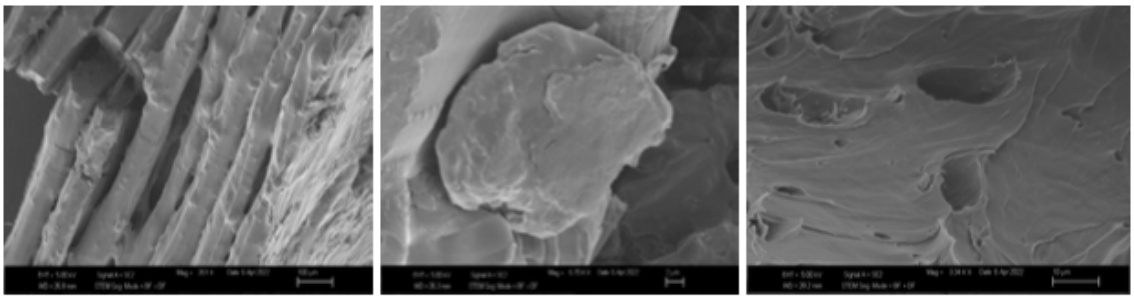


Figure 3. SEM images of 3D printed PLA-walnut shell

Figure 4 and Figure 5 show thermal analysis curves of pristine PLA and walnut shell-loaded PLA filaments. Walnut shell increased mass loss of PLA till 120°C which can be attributed to the water evaporations present in the filament. It increased by app. 17% due to the incorporation of hygroscopic natural cellulosic waste into PLA. 100% PLA and walnut shell-loaded PLA lost 1% of their mass at 224.58 and 131.95°C, respectively. The mass losses at 200°C which is generally extrusion temperature recorded as <1% and 1.5%, respectively. The addition of walnut shells into PLA decreased the maximum decomposition temperature by 11.5%. this is because of the lower thermal decomposition temperature of a walnut shell than PLA (Narlıoglu et al., 2021).

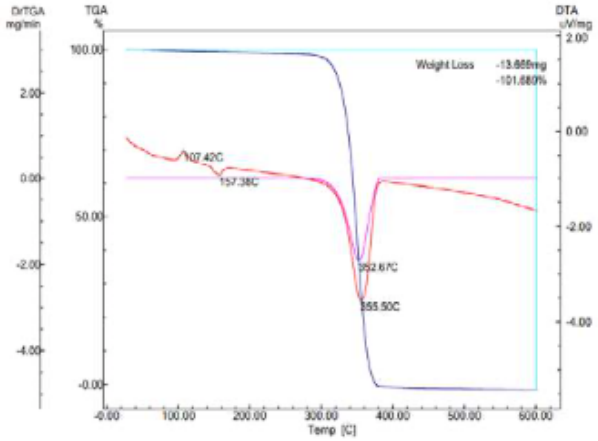


Figure 4. Thermal analysis curves of 100% PLA filament

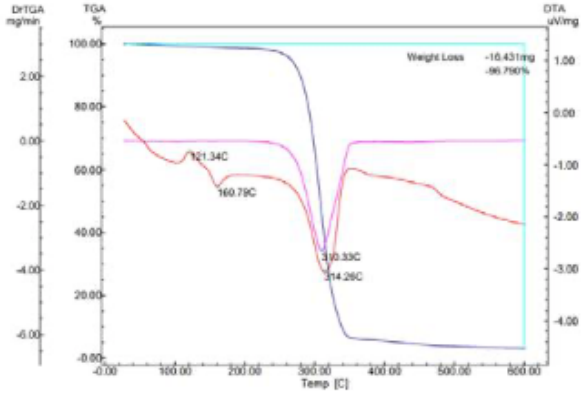


Figure 5. Thermal analysis curves of a walnut shell loaded PLA filament

The tensile test of the 3D parts produced from walnut shell reinforced PLA and pure PLA is illustrated in Figure 6. From figure 6, in accordance with the literature, 3D parts produced from walnut shell-reinforced PLA displayed a smaller tensile test result. Poor adhesion between PLA and walnut shell parts is counted as the main reason for the reduction of mechanical behaviours of 3D parts.

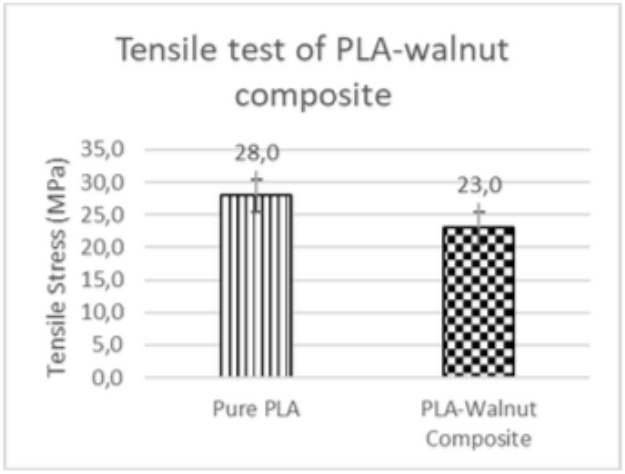


Figure 6. Tensile test results

2.2. Preparation of PLA/walnut shell composite filaments

Walnut shells are ground by using Retsch SM 100 grinding device. The grinding process was performed in order to decrease the size of the particle. The ground walnut shells were passed through a 63 µm sieve. No surface treatment has been applied to walnut shells. Laboratory type Flax brand Arya single screw extruder was used to turn PLA pellets and ground walnut shells into filaments. The extruder's zone temperature, screw and production speed are kept as 170 °C, 15 hz/h and 1.5 kg/h (50mm/sec), respectively. Walnut shell reinforced PLA filaments are produced in a diameter of 1.75 mm (±5%) in accordance with the fused filament fabrication technology. Figure 1 illustrates the production of walnut shell reinforced filament production. No surface treatment has been applied to the filament after production. The produced filaments are stored in vacuum bags to protect them from moisture.



Figure 1. PLA-walnut filament making

2.3. Production of 3d printed PLA composite parts

Printed samples were produced using a Creality Cr-200b brand and model printer. The printing temperature was set to 165°. Printing speed was kept as 40 mm/sec. The layer thickness was determined as 0.12 mm. Raft was used to adhere the products to the heated glass plate during printing. As the nozzle width, 0.4 mm was tried first, but because there were blockages. Production was made with 0.6 mm. Production of 3D parts with walnut shell reinforced filaments is illustrated in Figure 2.

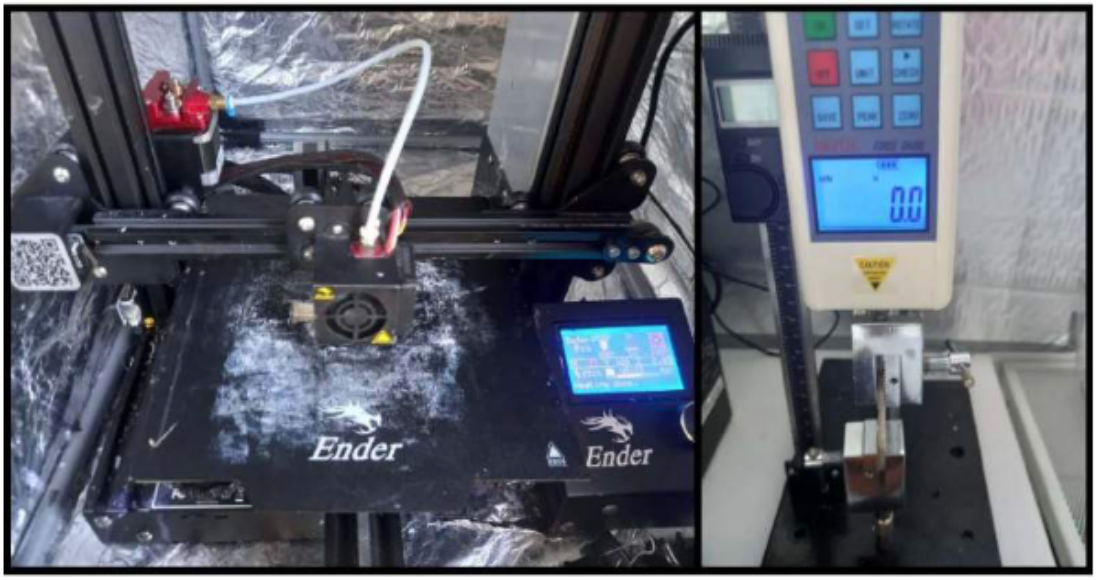


Figure 2. Tensile test printing and testing

4. CONCLUSION

This work aims to produce walnut shell reinforced PLA composite filament for 3D-printing. Walnut shells were ground firstly, mixed with PLA granules and then extruded to produce composite PLA filament. Pristine and walnut shell doped PLA filaments were 3D printed via FFF technology. Analysis results revealed that incorporating a walnut shell increased PLA's moisture content and decreased thermal degradation temperature. It is noticed that both of the filaments are thermally resistant to extrusion temperatures at about 200°C. SEM micrographs delamination of doped PLA parts and non-adhesion between particle and PLA. This is because no surface treatment was applied to the walnut shell. Accordingly, suitable chemical treatment and compatibiliser will be utilised to facilitate producibility and enhance filaments in the later stages of the study. For this reason, the strength values decreased in the tensile tests. While pure PLA was 28 MPa, this value decreased to 23 MPa when walnut was added. In addition, standard deviations in tensile tests are quite high since twin screw extruders are not used. Additives were not mixed homogeneously in the polymer. Despite the mechanical behaviour loss of walnut shell reinforced PLA compared to the pure PLA, including non-industrial wastes in the production process will contribute to the development of eco-friendly production methods. There is a need to improve the mechanical properties of the parts produced for this method, but as such, they can still be used in non-structural structures.

REFERENCES

Ahmed, W., Alnajjar, F., Zaneldin, E., Al-Marzouqi, A.H., Gochoo, M. & Khalid, S. (2020). Implementing FDM 3D Printing Strategies Using Natural Fibers to Produce Biomass Composite. *Materials*, *13*(4065), 1-23.

Balla, V. K., Kate, K. H., Satyavolu, J., Singh, P., & Tadimeti, J. G. D. (2019). Additive manufacturing of natural fiber reinforced polymer composites: Processing and prospects. *Composites Part B: Engineering*,174, 106956.

Chen, F., Ni, X., Liu, Y., Xia, X., & Gao, X. (2022). Preparation and properties of heat-treated esterified wood flour/polylactic acid composites for FDM 3D printing. *Journal of Materials Science*, 1-16.

Dip, T. M.; Emu. A. S.; Nafiz, M. N. H.; Kundu, P.; Rakhi, H. R.; Sayam, A.; Akhtarujjman, Md.; Shoaib, M.; Ahmed, M. S.; Ushno, S. T. et al.. (2020). 3D printing technology for textiles and fashion.*Textile Progress*,52(4), 167-260.

Lee, C. H., Padzil, F. N. B. M., Lee, S. H., Ainun, Z. M. A. A., & Abdullah, L. C. (2021). Potential for natural fiber reinforcement in PLA polymer filaments for fused deposition modeling (FDM) additive manufacturing: A review. *Polymers*, 13(9), 1407.

Mazur, K. E., Borucka, A., Kaczor, P., Gądek, S., Bogucki, R., Mirzewiński, D., & Kuciel, S. (2022). Mechanical, Thermal and Microstructural Characteristic of 3D Printed Polylactide Composites with Natural Fibers: Wood, Bamboo and Cork. *Journal of Polymers and the Environment*, 30(6), 2341-2354.

Narlıoglu, N., Salan, T., Alma, M.H. (2021). Properties of 3D-Printed wood sawdust reinforced PLA composites. *Bioresources*, 16(3), 5467-5480.

Royan, N. R., Leong, J. S., Chan, W. N., Tan, J. R., & Shamsuddin, Z. S. B. (2021). Current state and challenges of natural fibre-reinforced polymer composites as feeder in fdm-based 3D printing. *Polymers*, 13(14), 2289.

Singh, R., Kumar, R., Pawanpreet, Singh, M., & Singh, J. (2022). On mechanical, thermal and morphological investigations of almond skin powder-reinforced polylactic acid feedstock filament. *Journal of Thermoplastic Composite Materials*, 35(2), 230-248.

Wang, J.,Bai, J., Hua, H., Tang, B., Bai, W., & Wang, X. (2022). Characterization and Scalable Production of Industrial Hemp Fiber Filled PLA bio-composites. *Journal of Natural Fibers*, 1-12.