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Electrical conductivity of graphene/Si_3N_4 doped PLA produced by fused filament fabrication

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Abstract

Today, the technological, scientific and industrial use of micro- or nano-scale products has rapidly expanded. Nanoparticles are added to metal, ceramic and polymer materials to produce nanocomposite materials. Polymer matrix nanocomposites have advantages over other materials in terms of weight, performance and price. As known from the literature, imparting electrical conductivity to thermoplastic materials such as polylactic acid (PLA) is possible. The industrial use of thermoplastic matrix has been the focus of nanocomposites due to its low cost, ease of production and recycling. Research on the use of 3D printers in the production of nanoscale-doped thermoplastics has been less common. 3D printing is an additive manufacturing method compared to traditional processing methods. Additive manufacturing is based on adding layer by layer to reduce production costs and reduce the production cycle. This study prepared nanocomposite material by adding nano-sized graphene and Si_3N_4 to PLA material at 0.5, 1, 2 and 3 wt. %. The prepared polymer matrix nanocomposite groups were produced using a fused filament fabrication (FFF-3D) printer and their electrical conductivity was examined at the five different points by the four-point probe method. According to the test results, the electrical conductivities of 1 and 2 % doped PLA are very close. But the 1 % doped samples is the composite group with the best conductivity with a value of 153.44 S/m. A value of 151.25 S/m followed this for 2 % doped PLA and 138.57 S/m for 3 % doped PLA. Thus, it was concluded that the electrical conductivity was reduced with the increased dope rate. Also, all samples' hardness was measured by the Shore D test. Although the increase in the hardness value of the samples did not affect as much as the increase in the dope ratio, the hardness values increased with the increase in the nanoadditive ratio.

1. Introduction

Bioplastic materials are a type of plastic that can degrade in nature. Polylactic acid (PLA) is a bioplastic material that is produced using natural plants such as corn and potatoes, which are abundant in starch and can be recycled after the end of the material's useful life [1]. PLA, used in the production of composite materials in various industrial sectors such as packaging, automotive and construction, was preferred due to its low cost, self-solubility in nature unlike petroleum-derived plastics and abundant availability [2].

Due to the insufficient properties of PLA, it is not used sufficiently in the production of functional materials. For this reason, nanocomposite materials produced with reinforcing materials added to PLA material at nano-size show superior properties compared to pure PLA material. Graphene material is a widely used reinforcement material in nanocomposite materials due to its superior conductivity and mechanical properties [3,4]. In a study by Gao et al., graphene was added to PLA material at 0, 5, 7 and 10 wt. % and 4 different composite groups were formed. They performed a tensile test to determine the mechanical properties of the samples in each composite group and concluded that the modulus of elasticity of the PLA material increased, while the tensile strength of doped PLA material increased up to 7 % [5].

There are many methods to produce PLA nanocomposite materials. Today, the use of additive manufacturing methods, which are innovative manufacturing methods, has increased. With additive manufacturing methods, part geometries created with computer-aided drawing programs (CAD) and converted to G-code with computer-aided manufacturing programs (CAM) using metal, ceramic or polymer materials can be produced by adding layer after layer. Producing models of complex geometric structures with additive manufacturing methods is possible. Among additive manufacturing methods, fused filament fabrication (FFF) is a widely used method for polymer materials and polymer matrix composites [3,4,6,7].

Ivanov et al. added nano-sized graphene and multi-walled carbon nanotubes to PLA material at different additive ratios and produced samples with FFF. They tested the thermal and electrical properties of the 3D printing material produced and it was observed that nano-reinforcements improved the thermal and electrical properties of pure PLA material [8].

In the literature, many studies investigate the effect of different fibre and/or nanoadditives on PLA matrix on mechanical properties. The biggest advantage of nano-size is its high surface-to-volume ratio. This increases the matrix and reinforcement interfacial bonding. Improvement in interfacial bonding affects thermal and electrical properties as well as mechanical properties. Graphene is a form of carbon atoms arranged in a two-dimensional hexagonal structure. Graphene conducts heat well and has superior mechanical properties. It was also preferred in our study because it has high electrical conductivity.

Butt et al. in their study investigated the effect of bed temperature and printing speed on the hardness of graphene-reinforced PLA materials produced by the FFF method. It was observed that the bed temperature and print speed in the produced samples affected the Shore D hardness [9].

Silicon Nitride (Si_3N_4) is a chemical compound of the element's silicon and nitrogen. The Si_3N_4, containing covalent bonding, is a thermodynamically stable ceramic. This material has been discussed in different studies on the thermal properties of nano-doped composites. In addition, it has been observed in many studies that it increases the efficiency of thermal processes by using it together with conductive nanoparticles [10]. The Si_3N_4 was used for the efficiency of the thermal process in FFF production.

Graphene, used in producing composite materials with electrical, thermal and superior mechanical properties, and Si_3N_4 with high wear resistance, used in turbine and automobile engine parts exposed to high temperatures, were used as nano-sized additives [10,11].

In this study, we added equal amounts of graphene and Si_3N_4 materials to the PLA matrix at 0.5, 1, 2 and 3 wt. %. Using the PLA/graphene/Si_3N_4 nanocomposite materials, samples were produced with FFF technology. The electrical conductivity and hardness of the samples produced with different additive ratios were tested.

2. Materials and methods

The matrix material in the study is PLA (Ingeo 3052D, melting temperature 200 °C, glass transition temperatures 55 – 60 °C), obtained from Eurotec. The properties of nano-doped materials, used for improvement, are graphene (purity > 99.9 %, thickness 5 nm, specific surface area 170 m^2/g, diameter 18 µm) and Si_3N_4 (purity > 99.9 %, size 10 µm). Materials are products of the Nanography company.

In the study, Si_3N_4 dimensions were reduced to nano-size by ball milling. After that graphene and Si_3N_4 were added to the PLA matrix by the twin-screw extruder at the rates specified in Table 1. Doped PLA matrix compounds were brought into filament form for use in the FFF method with a single-screw extruder. Sample production was carried out with the additive manufacturing method and the electrical conductivity and hardness of the samples were measured and compared.

2.1 Silicon nitride (Si_3N_4) size reduction

In order to reduce the size of Si_3N_4 with a grain size of 10 µm to nano-size, which is effective for thermal and electrical stability in the production of nanocomposites, the grinding process was carried out for 10 hours at 450 rpm using Restch PM 100 ball mill at Celal Bayar University Experimental Sciences Application and Research Center. During the grinding, 30 tungsten carbide (WC) balls with a diameter of 10 mm were used. The grain size was then analysed using a thermo-scientific Apreo S brand scanning electron microscope (SEM) at Ege University Central Research and Analysis Laboratory (MATAL). Figure 1 shows the SEM image of Si_3N_4 material after ball milling.

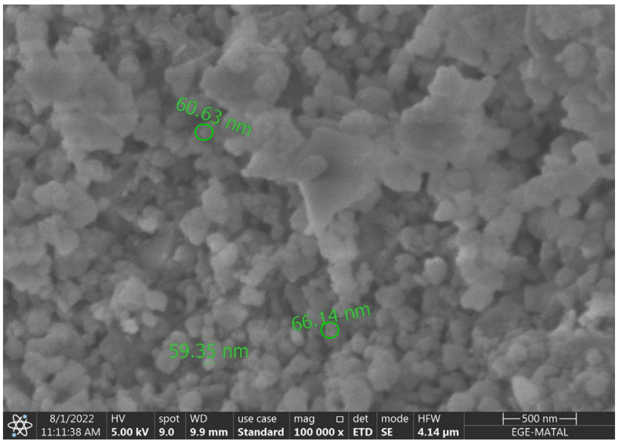

Figure 1. SEM image of Si_3N_4 material

The Si_3N_4 size, which was 10 µm at the beginning, was reduced up to 60 nm after grinding (Fig. 1). As a result of SEM analysis, it was observed that the size of Si_3N_4 decreased.

2.2 Composites production

The amounts of additives used to form nanocomposites according to the matrix material are shown in Table 1.

Table 1. Amounts of materials doped to PLA material

Sample	Total dope amount, wt. %	Single dope amount, wt. %	
		silicon nitride	graphene
S1	0.5	0.25	0.25
S2	1	0.5	0.5
S3	2	1	1
S4	3	1.5	1.5

As shown in Table 1, four different nanocomposites (doped PLA matrix compounds) were produced. The dope ratios were realised as 0.5, 1, 2 and 3 wt. %. Graphene and Si_3N_4 were added in equal proportions in a twin-screw extruder.

2.3 Filaments and samples production

Compounds prepared with a single-screw extruder device were converted into a filament form at Dokuz Eylul University Marine Sciences and Technologies Institute. The raw material must be in filament form for production with the FFF method. The process parameters in filament production are 200 rpm constant screw speed and 195 °C die temperature.

Filaments were produced with a diameter of 2.85 mm (± 0.15 mm) in accordance with the feeding system of the FFF device to be used in sample production. The diameter was adjusted with air cooling and a spool puller. Diameter control was controlled instantaneously on the line with a micrometre. Figure 2 shows the filaments produced.

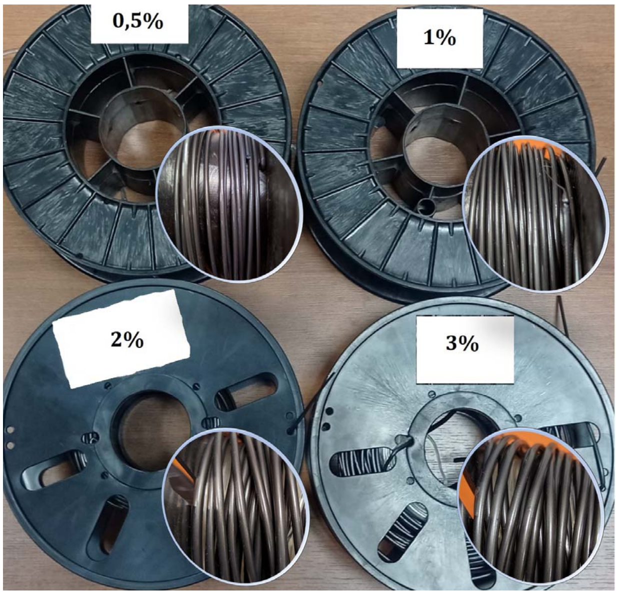

Figure 2. Filaments

In our study, the Ultimaker brand model 3 3D printer at Ege University Aviation Higher Education School was used to produce the test samples. Figure 3 shows the Ultimaker 3D printer.

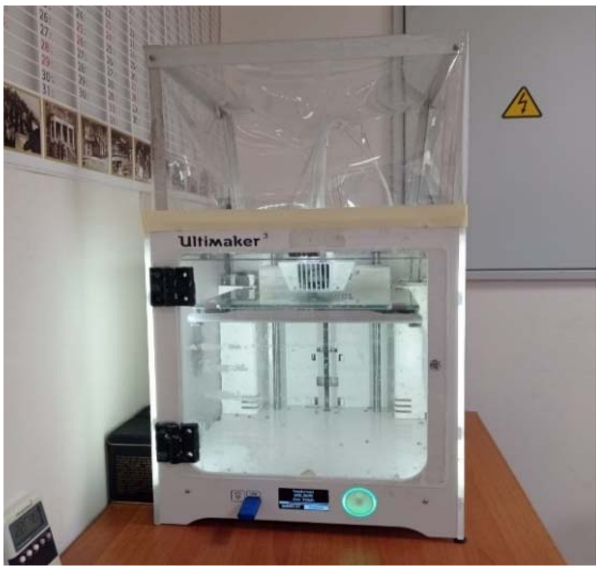

Figure 3. Ultimaker 3D printer

Table 2 shows the production parameters of the test specimens produced with the 3D printer. All samples were produced on glass plates.

Table 2. Production parameters of the samples

Parameter	Value
Layer height, mm	0.1
Raster angle, °	± 45
Fill density, %	100
Bed temperature, °C	80
Nozzle temperature, °C	205
Nozzle diameter, mm	0.6
Print speed, mm/s	70

Butt et al. in their study, observed the highest hardness value in PLA samples with graphene doped at 70 mm/s print speed for 190 °C nozzle temperature and 80 °C bed temperature [9]. For this reason, print speed and bed temperature are determined as shown in Table 2.

All samples were drawn with the Fusion 360 CAD program. Sample drawings saved in stereolithography (STL) format in the CAD program were converted into G-code in the CURA CAM program. The samples are shown in Figure 4.

Figure 4. Samples

2.4 Electrical conductivity test

In this study, the measurements of electrical conductivity were performed on four different nanocomposites (doped PLA matrix compound samples) using by four-point probe method. Figure 5 shows the placement of the probes on the surface of the nanocomposite sample being tested. A constant voltage (V) was applied to the sample through the outer contacts using a DC power source and then the current across the inside contacts was measured. Keithley model 2182A a DC voltage source/picoammeter was used for all measurements. The same probe ranges were used to measure the electrical conductivity of the samples. Thus, varying readings that can be caused by different probe ranges were avoided.

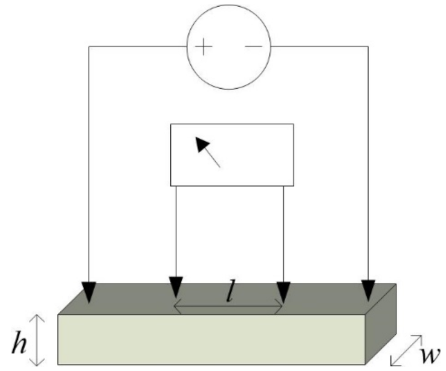

Figure 5. Schematic diagram of test setup for measuring sample electrical resistivity with the four-point probe method

2.5 Hardness test

The hardness measurements of all samples were made with the Shore D durometer. Measurements were made on the surface where the printing was completed for all samples with different dope amounts. Hardness measurements of all samples were carried out according to ASTM D2240 standard [12]. Measurements were made according to the Shore D scale.

All measurements were done 5 times in the middle of the samples, in different places away at least 6 mm from each point that was measured before.

3. Results and discussion

Figure 6 depicts a graph of the electrical conductivity of four different nanocomposite samples at room temperature. Minimal and maximal values are shown in the graph for each sample set.

Measurements were taken from 5 different regions of the printing surfaces that ended from all samples. The matrix material (pure PLA) did not show any conductivity. The standard deviation (SD) values performed at 5 points in all samples were between 2.6 and 1.2 as shown in Table 3. Obtained findings are sufficient for interpretation. Conductivity values are comparable for all samples.

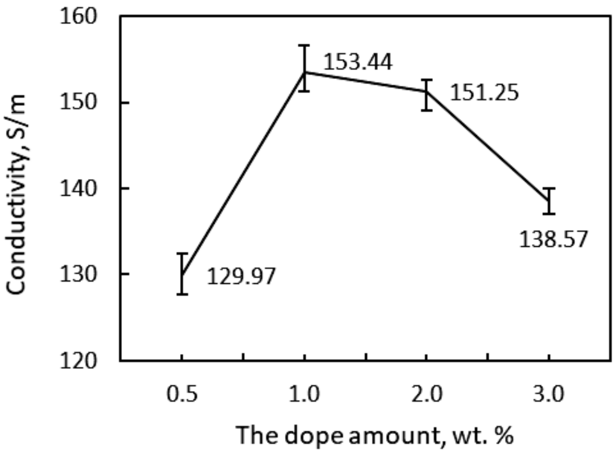

Figure 6. Electrical conductivity measurements of samples of four different nanocomposites

The nanocomposite with 1 wt. % dope amount exhibited the highest electrical conductivity of 153.44 S/m at room temperature. In contrast, nanocomposite with 0.5 wt. % dope amount exhibited the lowest electrical conductivity of 129.97 S/m. The electrical conductivity increased with rising doping amounts ranging from 0.5 to 1 wt. %.

Table 3. Electrical conductivity measurement results and SD values

Sample	Electrical conductivity, S/m	SD, S/m
S1	129.9674	2.00165
S2	153.4392	2.67487
S3	151.2520	1.34101
S4	138.5680	1.26857

As the doping amount increased from 0.5 to 1 wt. %, the electrical conductivity increased and then declined with the dope amount higher than 1 wt. %. Several studies have shown that the electrical properties of nanocomposites depend not only on the dope amount, type and process but also on the initial dispersion and initial processing history of the nanoparticles [13-15]. The following comments can be made considering the possible reasons for such a decline in conductivity.

In some cases, the electrical conductivity of the nanocomposite material may decrease after certain doping amounts of graphene and Si_3N_4 due to the formation of agglomerates or clusters of these materials. This can lead to a decrease in electrical conductivity because the agglomerates or clusters act as insulators and block the flow of electrons through the material [16]. On the other hand, the effect of adding graphene and Si_3N_4 materials to the PLA matrix of more than 2 wt. % on the resulting nanocomposite material's electrical conductivity depends on the material's dispersion in the PLA matrix compound.

In addition, the annealing processes applied to the polymeric composites after production also affect the electrical conductivity. For example, Cipriano et al. investigated multi-walled carbon nanotube (MWCNT) and carbon nanofiber (CNF) filled polystyrene composites [17]. They observed an increase in conductivity with different annealing times and temperatures.

The hardness measurements of all samples are shown in Table 4.

Table 4. Shore D hardness measurement results and SD values

Sample	Shore D hardness	SD
S1	71.0	0.94
S2	74.7	0.84
S3	78.3	0.91
S4	82.0	0.79

The increase in the nano-dope amount increased the hardness value. Increasing hardness value did not show parallel properties with electrical conductivity. Adding particles to the polymers inhibits the dislocation motion and strengthens the material [18,19]. The resistance to dislocation movement created by the nanoadditive in the matrix increased the hardness. All minimal and maximal values for hardness measurement results are shown in the graph for each sample set in Figure 7.

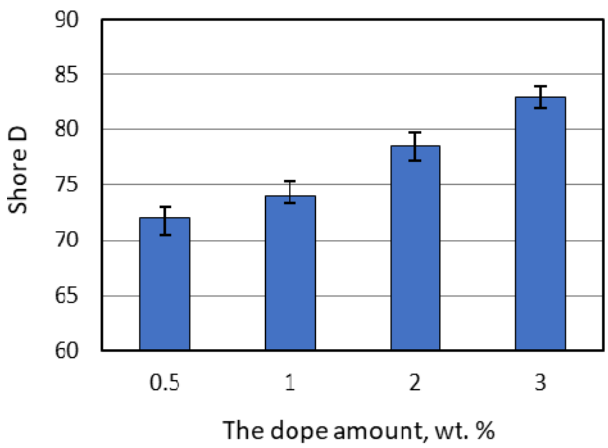

Figure 7. Hardness measurements of samples of four different nanocomposites

4. Conclusion

In our study, the manufacturability of a new nanocomposite material by adding additives to the sustainable and environmentally friendly PLA material by additive manufacturing and the improvement of the electrical conductivity of PLA material were investigated.

In line with the investigations, graphene and Si_3N_4 materials with superior electrical and mechanical properties were used as additives.

There was no problem in the 3D printing of the test specimens with the FFF-3D printer of the filaments produced in line with the experimental studies.

The electrical conductivity of graphene and Si_3N_4 reinforced PLA material with different doping amounts were tested and compared among themselves. It was concluded that the electrical conductivity of PLA material changed with the change in doping amount. The sample with the lowest conductivity was found to be 0.5 wt. % doped PLA. After the 1 wt. % doped PLA sample, it was observed that the electrical conductivity gradually decreased as the doping amount increased. Therefore, 1 wt. % doped graphene/Si_3N_4/PLA nanocomposite material was selected as the optimum material due to its superior electrical conductivity.

The effect of layer height and nozzle temperature on electrical conductivity can be investigated in future studies. In addition, studies can be carried out on the effect of the annealing process on electrical conductivity after production with FFF.

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