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**Research Article**

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# An Investigation About Starch-Based Bio Composite Application for FDM Method

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**Abstract** In this study, it was aimed to investigate the changes in the mechanical properties and electrical conduction properties of the composite formed by adding graphite powder reinforcement materials to starch matrix biopolymers and removing the glycerol with hardening properties from the mixture. In addition, the use of the obtained bio-based composite in a three-dimensional printer with a "core -xy" type and screwed chamber extruder was carried out practically. 25% graphite powder reinforced starch composite exhibited the highest tensile strength according to neat starch. Also it was observed that obtained composite materials can be useful for the fused deposition modelling method.

**Keywords** Starch, Graphite Powder, Biocomposite

## 1. Introduction

In order to slow down and prevent environmental pollution, which has become one of the major problems of our age, the use of environmentally friendly materials that do not harm nature has become a necessity. Plastics are one of the most produced material groups in terms of ease of production and economy. Until the last two decades, synthetic plastics have had a wide range of uses. However, this global use is doing a lot of damage to our planet. Such use of petrochemical plastics has led to significant health problems. In order to prevent this situation, scientists have succeeded in producing bioplastics that can degrade in nature and do not harm health by doing different studies.

Although the use of synthetic plastics causes environmental pollution, they are also produced as harmful to health; this damage can be reduced considerably by using bioplastic material. Bioplastics (Biodegradable plastics) are polymers produced from renewable biological resources such as oil, starch, plant structures and food waste. Biodegradable polymers; due to the influence of environmental and biological decomposers (such as bacteria, fungi) such as the temperature and Ph values of the environment in which it is located, its internal structure is deteriorated and it is included in the cycle in nature in a much shorter time compared to other plastic derivatives. Acoording to Tabani [1], much attention is given today to developing green of green and sustainable materials to demonstrate the potential of biocompatible extraction-separation techniques in both laboratories and industrial sections. Thanks to the importance of green chemistry, nowadays, many scientists seek new extractants to preserve the environment and reduce the negative influence of human involvement. Worldwide, 325 million tons of fossil-derived plastics are produced. Bioplastics make up about 5 million tons of this production. Combinations of bioplastics with various reinforcing materials and agents have been produced in order to meet the desired mechanical properties.

As for the disadvantages of bioplastics, it may not be possible to produce all types in mass production because some of them are complex structure materials. In general, they do not have very high strength values. Plant-based bioplastics can bring with them the toxic substances they were exposed to while they were still plants in their pre-plant phase. It is not suitable for very long term designs and uses due to decomposition processes. It is very important to increase the strength of such bioplastics and to be able to produce them continuously.

Abbasi and Haeri [2] introduced the source and properties of biodegradable materials and discussed their analytical applications in liquid phase microextraction and sorbent-based microextraction techniques. The review also includes a comparison of new microextraction approaches with traditional methods to show their strengths. Duan et al [3] aimed to improve the properties of starch-based biodegradable plastics such as low mechanical properties and moisture sensitivity. For this reason, various natural fillers such as fibers, starch or cellulose crystals and laver were used as reinforcements and agents for bioplastics in the study. Moreover acrylate epoxidized soybean oil (AESO) material was used in the coating technique. Polyethylene was used to improve the connection between starch and AESO. At the end of these studies, they found a critical water content point between 16% and 18% in the plastics obtained. Kuz [4] investigated some characteristic properties of biopolymer and composite materials obtained by adding starch-based biopolymer carbon fiber and $TiO_2$ (Titanium Oxide). A decrease was observed in the compressive and fracture forces of the samples obtained in the mentioned study. Nevoralova and Krulis [5] focused on the preparation and characterization of chemically modified and plasticized biodegradable thermoplastic starch. They were produced by melt mixing methods by leaving the samples to dry in the form of a slurry mixture. Along with chemical interventions such as ethanol, sodium hydroxide solution addition and acetylation, organic additives such as green plant residues were also added to the mixtures. These controlled interventions and changing parameters have shown that the obtained plastic has a significant effect on the morphological structure and characteristic features. García et al [6] added copolymer pluronic F127 in certain proportions to the mixtures of corn starch and Chitosan (CTS) polymers obtained from crab shells separately and together. The changes in the morphological, thermal and mechanical properties of the packaging films obtained by gradually increasing the ratios were investigated. As a result of the tests performed, an increase in surface homogenization, an increase in water solubility, an increase in steam capacity and an increase in hardness were detected, and as a result of the tests performed with tensile samples, a decrease in the tensile strength of biopolymers was determined. Zhang et al. [7] presented a novel topology-optimization approach for designing biodegradable composites. Density-based approaches were used because of their mathematical completeness and ease of use.

3D printing, a general term in additive manufacturing and is also defined as solid free form manufacturing, refers to a printing method that creates a 3D object by depositing material layer by layer under computer control to build a physical part or structure [8]. With the increase in the use of 3D printer technology (especially Fused Deposition Modelling method), which can manufacture using plastic raw materials for more than 20 years, the importance of the selection of the material to be used in production has increased at the same rate. Polymer filaments are commonly used in 3D printers using additive manufacturing technology such as FDM Technology. Bioplastic materials and composite materials are produced from these filaments. These filaments can be in various diameters in accordance with the diameter of the printing nozzle and in different mixtures according to the desired properties. The use of starch-based bioplastics in the food industry, which is one of the production methods, and the effect of additives such as glycerol, chitosan, citric acid, which are used to increase the functionality of these plastics, on bioplastics were mentioned by Cheng, et al. [9]. They observed that one of the limiting factors for the use of bioplastics is poor mechanical properties. Traditional production methods such as extrusion and casting and modern bioplastic production methods such as 3D printing are also examined. Ji et al. [10] carried out a deeper insight to predict the precision and textural quality of printed products through the molecular structure of starch, and presented useful information for designing personalized starch-based food products by 3D printing. Chen et al. [11] investigated the relationship between rheological properties and printability of three types of starch-based staple food (potato, rice and corn starch) for hot-extrusion 3D printing (HE-3DP). In their study, Damian et al [12] found that Poly Vinyl Alcohol (PVOH) component can be produced by a method called melt modification, which provides a similar melting of corn starch. It was found that very good quality 3D printing filaments could be obtained from these thermoplastics. In the study of Günay et al [13], the effect of some variable parameters in the printer's process on the mechanical properties of PLA+ samples produced with 3D manufacturing technology called melt stacking modeling (FDM) was investigated. These variables are the fill rate of the scan angle and the extrusion speed. In this direction, tensile test samples were prepared and necessary tests were carried out. In the results, it was concluded that the parameter that has the most effective on the tensile strength is the fill rate. Although the studies continue, there is still a need for detailed technical information about the use of bioplastics and composite structures in three-dimensional printers and the elimination of weaknesses.

Since there is a polymer binder such as glycerine in the structure of starch-based simple bioplastics obtained from corn starch, they are flexible and unstable. It is very important to increase the strength of such biopalstics and to be able to produce them continuously. In this study, the changes in the mechanical properties and electrical conductivity of the polymer formed by adding graphite powder to starch matrix biopolymers and removing glycerol from the mixture were analyzed. This polymer mixture was produced in a three-dimensional printer with a "core -xy" type and screwed chamber extruder. Characterization analyzes of the produced samples were carried out with the help of tensile test, microscopy and electrical conductivity conduction tests.

## 2. Materials and Method

### 2.1. Materials and Sample Preparation

The matrix material used in this study was based on a commercially available corn starch was supplied by Kenton Ltd. The proportions of materials required for the preparation of high-strength, starch-based, glycerin-free 100% biodegradable plastic that can be used in a three-dimensional printer have were calculated. Glycerin, which is a hardener, has been removed in order to reduce the elasticity modulus and increase the hardness. The preparation processes of starch-based simple plastic with added graphite were carried out using a precision balance (KN Master brand). The 60ml distilled water (PURELAB Option-Q) was added into the beaker. 10gr Corn Starch was added and the mixture was stirred continuously with a glass rod. The mixing was very slow and using a glass rod for (5 min) until it becomes homogeneous. 5.12 g acetic acid (acetic acid (glacial, ≥99.85%, 537020, Sigma Aldrich) as plasticizer was added. 10% and %25 wt. Graphite powder (Merck 104206) was added to the mixture and mixing was continued until the viscosity of the mixture reached a gel-like consistency. With the casting method, the mixture was poured into Polystyrene foam molds and added to the printer's chamber and printing samples were taken.

### 2.2. Tensile Test

Tensile tests of the prepared Bioplastics were carried out on the Zwick Z010 ProLine 10kN device. In order to see the difference of graphite-added plastic from graphite-free bioplastic, a graphite-free bioplastic sample was also subjected to tensile test and only the effect of graphite on tensile strength was observed. The tests were carried out with a preloading force of 5N and a speed of 100mm/min by clamping the specimens from two different ends of the specimens in the tensile jaws in the vertical movement axis.

### 2.3. Electric Conductivity Test

RXN-303D 0-30V DC 0-3A single output laboratory type power supply was used to measure electrical conductivity after bioplastics were obtained. After the two ends of the plastics were sanded with very fine sandpaper to reduce a layer of approximately 0.5 mm, oscilloscope crocodile probes were connected to the sanded surfaces and the internal resistance of the plastics and the ampere values passing over them were measured by applying 1V, 5V, 12V, 24V voltages, respectively. The obtained values were reported by the graphs.

**2.4. Microscopic Observation**

After the graphite-added bioplastics were produced, their morphological structures were visualized under Nikon brand light microscopes. Nikon MA-100 inverted industrial metallurgical microscope and ADL Olympus microscope were used together with NIS Elements Br software. Micro internal structures were examined at 0x, 100x, 200x and 500x zooms, respectively.

**3. Results and Discussion**

Reinforcement materials have caused visible changes in the change of mechanical properties of biopolymers. The samples were subjected to different tests in order to learn exactly how much and how the reinforcement materials worked. There was no problem in terms of viscosity and extrusion process in the use of the obtained bioplastics in FDM technology in three-dimensional printers.

**3.1. Microscopic Examination**

The micro-structures of the starch-based 10% Graphite powder-reinforced bioplastic sample's surface topography are seen in Figure 1.

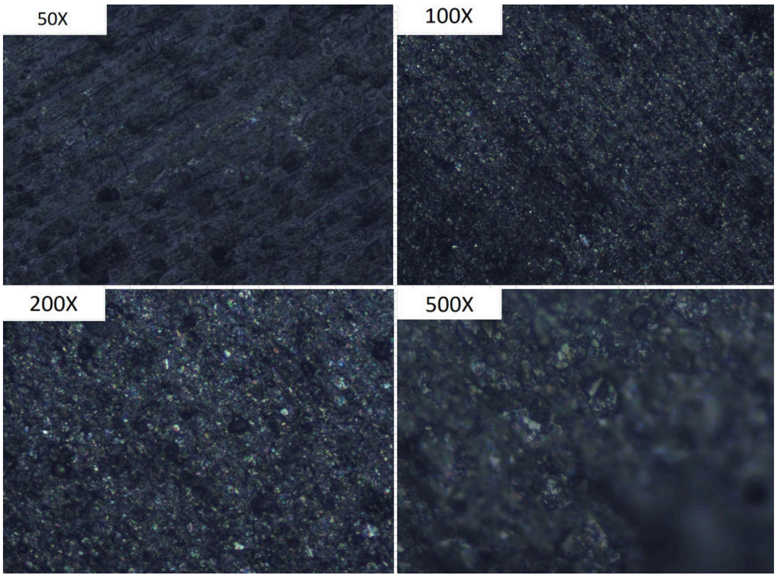


*Figure 1: 50X, 100X, 200X and 500X zoom view of graphite-reinforced bioplastic under microscope, respectively*

The structure formed by intertwining of graphite and starch can be seen in the image. Partial agglomeration of graphite was also observed. In Figure 1 200X and 500X, as can be seen in the images under focus, the lattice-like structures formed by the graphite powder glow under the light by creating reflection.

**3.2. Electric Conductivity Examination**

The current values of the produced Biopolymers were tested under voltages of 1V, 5V, 12V, 24V. It was observed that there is no electrical conduction in the starch polymer as seen in Figure 2.

Then, 10% graphite reinforced bioplastics were subjected to a certain electrical current and electrical conductivity results are shown in Figure 3. A voltage-current graph was created under these voltages and given in Figure 4. Only, 11.7% graphite reinforced bioplastic did not generate any electric current due to its internal resistance under 1V voltage applied. When the voltage was applied as 5V, an electric current of about 0.05Ampered progressed over the bioplastic. Then, a voltage of 12Volt was applied, which caused a current of about 0.1Amper to flow through the bioplastic. When a voltage of 24Volt was applied, a current of 0.258A was able to progress through the bioplastic.

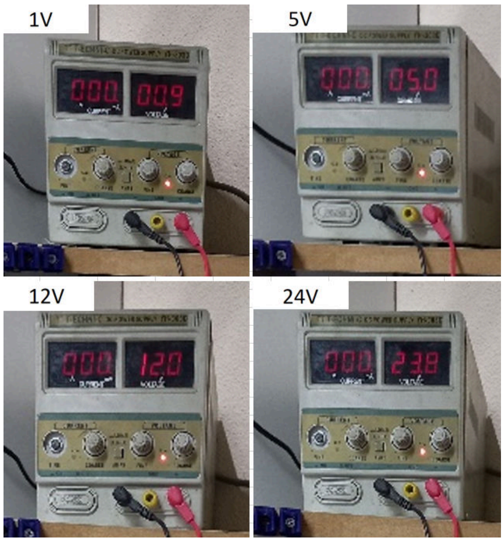


*Figure 2: Electrical conductivity results of starch bioplastic for different voltage values*

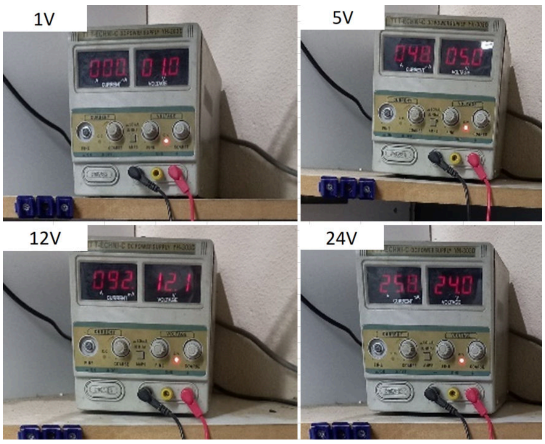


*Figure 3: Electrical conductivity results of %10 graphite reinforced bioplastic for different voltage values*

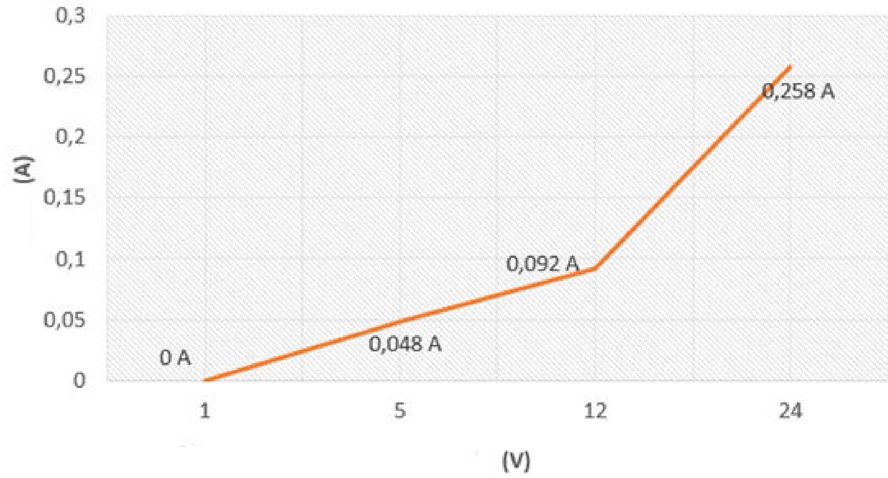


*Figure 4: %10 Graphite reinforced starch composite current-voltage graph*

In order to measure the electrical conductivity of 25% Graphite Powder reinforced bioplastic, 1V, 5V, 12V, 24V voltages were applied to the sample and photographic views of results are shown in Figure 5. The outputs were measured as 0.014A, 0.112A, 0.384A, 0.802A, respectively. This showed that the electrical conductivity of 25% graphite powder reinforced bioplastic is quite high (Figure 6). However, during the measurements, with the increase of the current passing through the sample, excessive heating and smoke output were observed more intensely, the sample approached the ignition temperature.

When the electrical conductivity of 25% graphite powder reinforced bioplastic was tested, it was concluded that the bioplastic has electrical conductivity gain, but there may be a heating problem.

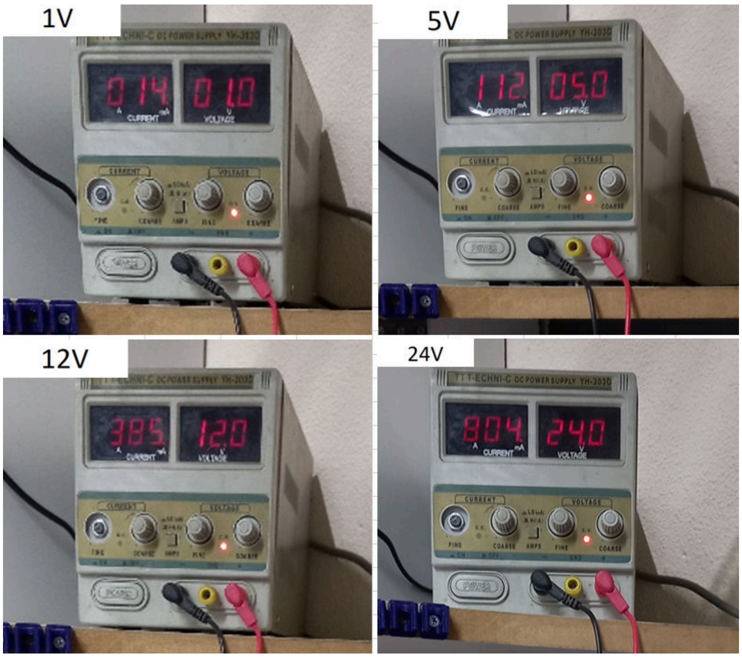


*Figure 5: Electrical conductivity results of %25 graphite reinforced bioplastic for different voltage values*

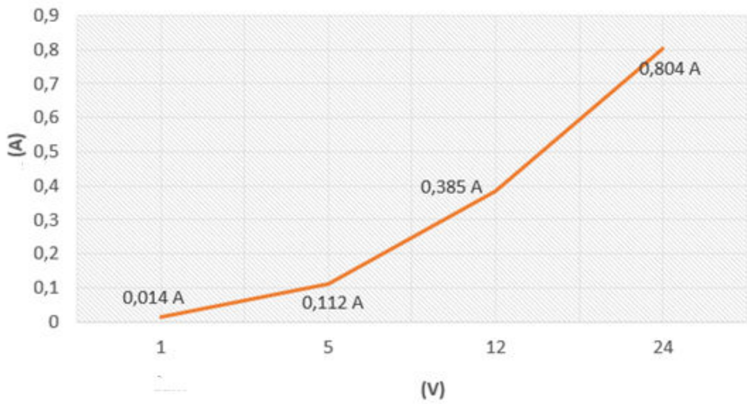


*Figure 6: Electrical conduction graph of 25% graphite powder reinforced bioplastic.*

### 3.3. Tensile Test Results

As a result of the tensile test of non-reinforced starch matrix bioplastic at 100mm/min speed with 0.1N preload, it is seen that the maximum tensile strength Fmax is 48.8N (Figure 7).

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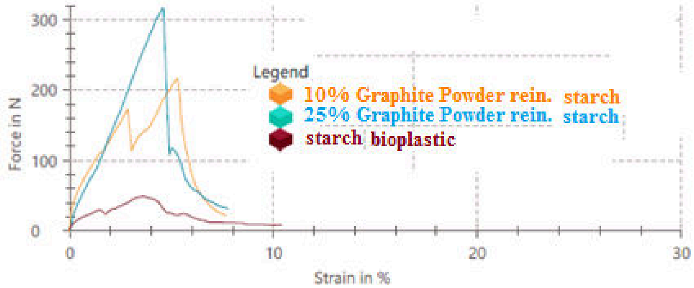
Pre-load : 5 N
Test speed : 100 mm/min

**Test results:**

| $L_0$ mm | $F_{max}$ N | $F_{max}$ N/mm² | $F_{Break}$ N | $F_{Break}$ N/mm² | dL at $F_{max}$ mm | dL at break mm |
|---|---|---|---|---|---|---|
| 91,04 | 216 | 215,96 | 21,5 | 21,45 | 4,8 | 7,0 |
| 58,08 | 317 | 317,02 | 31,6 | 31,62 | 2,7 | 4,5 |
| 58,73 | 48,8 | 48,83 | 7,97 | 7,97 | 2,1 | 6,1 |

**Series graph:**




**Statistics:**

| Series n = 3 | $L_0$ mm | $F_{max}$ N | $F_{max}$ N/mm² | $F_{Break}$ N | $F_{Break}$ N/mm² | dL at $F_{max}$ mm | dL at break mm |
|---|---|---|---|---|---|---|---|
| $\bar{x}$ | 69,28 | 194 | 193,94 | 20,3 | 20,35 | 3,2 | 5,9 |
| s | 18,84 | 135 | 135,44 | 11,9 | 11,86 | 1,4 | 1,2 |
| ν [%] | 27,20 | 69,84 | 69,84 | 58,29 | 58,29 | 44,88 | 21,26 |

It was observed that the tensile strength of the starch-based bioplastic was low and the elongation at break was high. There was an increase in tensile strength after the graphite powder reinforcement. The distribution of graphite powder in the structure caused an increase in the mechanical strength of the starch-based bioplastic. This can be attributed to the reinforcement being well wetted by the matrix and having good interface strength.

## 4. Conclusion

In this study, in order to increase the electrical and thermal conductivity of starch-based bioplastics and at the same time improve the strength values of this bioplastic, Graphite material, one of the most interesting materials of the last 10 years in terms of engineering and a research topic in many disciplines, was chosen. The effect of graphite powder on starch-based bioplastics is emphasized.

It has been determined that a maximum of 25% graphite powder-reinforced bioplastic material is suitable in the tests carried out for its application in three-dimensional printer manufacturing.

Adding more graphite powder created a blockage problem in the nozzle part of the 3D printer and was found to be unsuitable for printing.

As can be deduced from our study, electrical conductivity has been added to starch-based bioplastic composite materials (FDM method), which has made it possible to manufacture with three-dimensional printer technology. At the same time, the mechanical strength of the bioplastic was increased by removing glycerol from the starch-based bioplastic material and adding graphite powder.

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