Development of PEEK Matrix Polymer Composite and Additive Manufacturing by Pellet Extrusion Method

Merve Bagci Bilgen and Alaeddin Burak Irez

Abstract Within the context of this study, it is intended to develop new biocompatible polymer-based composite materials. For this purpose, PEEK (polyether ether ketone) was used as the matrix of the composites, and carbon nanotube (CNT) was used as the reinforcement. The PEEK matrix and 1 wt. % CNTs were melt mixed in a twin-screw extruder to obtain the compound in the form of pellets. Then, using these pellets, composites were manufactured using a pellet extruder type 3D printer. After manufacturing, microstructure of the specimens was observed using optical microscopy, and mechanical characterization was performed through three-point bending tests and Charpy impact tests. The most noteworthy result of the microscopy was the absence of any discontinuity between the layers of the specimen for pure PEEK specimens. Furthermore, the mechanical improvement was not apparent by the CNT incorporation for the tested composites. In conclusion, pellet extrusion is thought as a promising tool for the manufacturing of biocompatible materials for biomedical applications.

Keywords Biocompatibility · Pellet extrusion · PEEK · CNT · 3D printing

Introduction

Technological advancements have a significant impact in all areas. In particular, in the manufacturing industry, modern methods are increasingly being used instead of conventional techniques. In this respect, additive manufacturing, also known as 3D printing, is a growing field. A three-dimensional printer is a machine that produces three-dimensional solid objects from a three-dimensional CAD (computer-aided design) file prepared in the digital environment. With three-dimensional printers, models designed in a digital environment can become objects that can be manipulated and examined in a short time [1]. Three-dimensional printer technologies work with the technique of stacking layers on top of each other. However, the methods of creating these layers may differ. For polymers, the most widely known of these methods are the ones that form solid objects by melting the plastic material [2]. The advantages of three-dimensional printers are as follows: the design is easily transferable/shared as it consists of digital data, the ability to make changes and corrections quickly, the ability to easily produce customized products, the efficiency in terms of investment and production, the price of the product can be calculated prior to production, and the use of recyclable materials, which is equivalent to producing a minimum of material waste [3]. There are many types of additive manufacturing methods, and the FDM (fused deposition modeling) additive manufacturing type is one of the most common ones because this technique is simple, cost-effective, and widely available for many different polymers [4]. Studies have been carried out on the FDM technique for a long time, and this method continues to be developed. Despite the advantages mentioned, the FDM technique has the following disadvantages: low extrusion speed and lack of enclosed workspaces to apply this technique to create a large prototype and processing thermoplastic materials such as PEEK (polyether ether ketone) through FDM is a difficult process due to the high melt viscosity. To overcome these challenges, the pellet extrusion technique was used in this project [5]. In pellet extrusion, instead of using the polymer in the filament form with a specific diameter and stiffness, the polymer pellets are fed directly into the extruder of the 3D printer. This offers freedom in the material composition, and it is possible to achieve customized material properties. In this study, PEEK matrix composites were developed to meet the requirements of a wide variety of applications. PEEK is a semi-crystalline thermoplastic used in high-performance engineering applications. Compared to

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other thermoplastics, PEEK has very good thermal stability and excellent resistance to chemicals, solvents, and hot water and can be used continuously for very long periods of time up to 250 °C in air. PEEK also has an important deformation capacity and excellent impact resistance. Besides, the crystalline nature of PEEK provides its high temperature resistance [6]. Similar to many other thermoplastics, the mechanical properties of PEEK can be enhanced by nano-reinforcements such as carbon nanotubes (CNTs) [7]. CNTs exhibit a very high elastic modulus of more than 1 TPa and a strength 10–100 times that of the strongest steel. CNTs also have excellent thermal and electrical properties [8].

Within the context of this study, it is intended to develop new biocompatible polymer-based composite materials that can be utilized in biomedical applications. To this end, PEEK was used as the matrix of the composites, and carbon nanotubes (CNT) were used as the reinforcement. The PEEK matrix and 1 wt% CNT were melt mixed in a twin-screw extruder to obtain the compound in the form of pellets. Then, from these pellets, the composites were fabricated using a pellet extruder type 3D printer. After fabrication, the microstructure of the specimens was observed by optical microscopy, and mechanical characterization was performed by three-point bending tests and Charpy impact tests.

Materials and Methods

In this study, the materials to manufacture the composites were provided by different companies. First, PEEK was supplied from Evonik® under the commercial name VESTAKEEP 2000 G in the form of pellets. It has a density of 1.3 (g/cm^3) and a melting temperature of 340 °C. Next, 0.7 wt% COOH-activated carbon nanotubes (CNT) were provided by Nanografi®, Turkey. The CNT has a density of 2.4 (g/cm^3), a surface area of 65 m^2/g, an outer diameter of 28–48 nm, and a length of 10–25 µm.

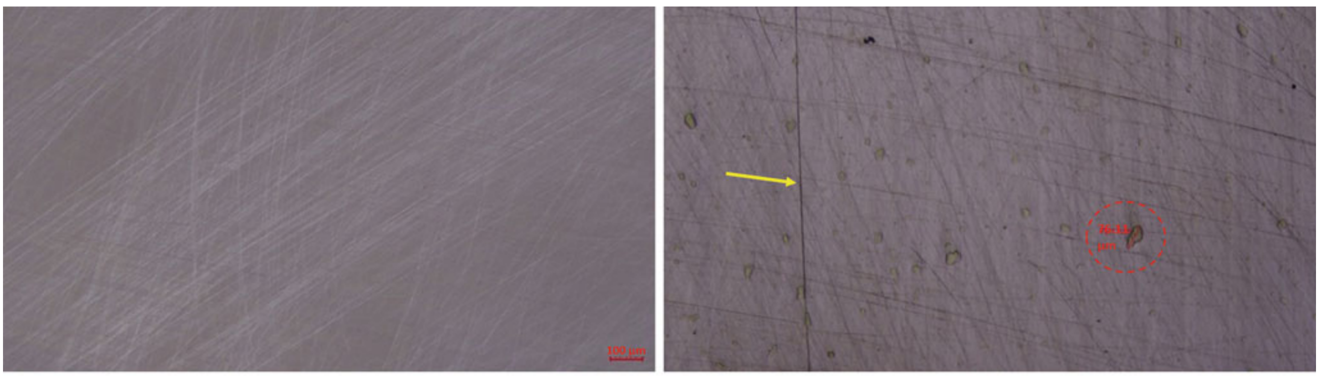
After the materials were procured, the composites were manufactured using the additive manufacturing technique of pellet extrusion. Due to the nature of this technique, the composite pellets must be obtained before the specimens are printed. Therefore, the composite pellets were obtained through an extrusion process. Prior to the extrusion process, the PEEK pellets were dried for 3 h in a vacuum oven at 150 °C to remove moisture that may have been trapped due to storage conditions. Then, the composite pellets were fabricated using a Kökbir Makina® co-rotating twin-screw extruder with an L/D ratio of 22, a screw diameter of 12 mm, and a screw speed adjusted to 60 rpm. The twin-screw extruder consists of six zones, and in order to reach the melting temperature of the materials used, the temperature values were set to 47.5 °C for the feed zone, 325 °C for the first zone, 330 °C for the second zone, 340 °C for the third and fourth zones, and 360 °C for the extruder exit. At the exit of the extruder, after the compound has cooled down, the composite is obtained in the form of a filament, and, with the help of a rotary cutter, it is transformed into granules. In the next step, using the pellets from the extrusion process, composites are manufactured using the Yizumi® SpaceA-900-500-S 3D printer. In this 3D printer, the screw diameter was 16 mm, and the screw speed was set to 200 rpm. Regarding the operational parameters of the 3D printer, the extruder temperature was 400 °C, the nozzle diameter was 2.5 mm, the layer thickness was 1.6 mm, and the printed material width was 3 mm. After the composites were fabricated, experimental characterizations were performed.

In the experimental characterizations, the effect of CNT reinforcement as well as the effect of printing direction was examined. The fundamental mechanical properties were identified by three-point bending (3PB) tests. The 3PB tests were performed using a Testometric testing machine according to ASTM D790 test standard, and the crosshead speed was imposed at 10 mm/min. Next, the impact strength of the composites was investigated using a Zwick Roell HIT5P Charpy Universal Tester according to ASTM 6110-10. Each characterization was done using at least five specimens and the standard deviations are given in the results. In addition, specimens from two different composite groups were sectioned and cold mounting was performed. Then, the mounted composites were polished for optical microscopy to observe the microstructure. In addition, scanning electron microscopy (using Tescan Vega 3 SEM) was conducted to observe the damage mechanisms on the fracture surfaces of the failed specimens.

The specimens for the bending tests are given in Fig. 1. The light-colored specimens are pure PEEK specimens, while the black specimens show the CNT-incorporated PEEK matrix composites. In addition, the printing direction can be seen in Fig. 1; Fig. 1b, d shows the longitudinal printing direction, while the others show the transversal printing direction.

a) b) c) d)

Fig. 1 Three point bending test specimens: (**a**) PEEK transversal, (**b**) PEEK longitudinal, (**c**) PEEK/CNT transversal, (**d**) PEEK/CNT longitudinal



(a) (b)

Fig. 2 Optical microscope images: (**a**) PEEK specimen, (**b**) PEEK/CNT composite

Results and Discussion

After the manufacturing steps, sections of the printed specimens were taken and then mounted into resin. After polishing the specimens, optical microscopy was performed to observe the microstructure of the composites. In some 3D printing techniques, voids and fusion problems between successive layers can be observed in the printed part, resulting in degradation of mechanical properties. On the other hand, as can be seen in Fig. 2a, there are some scratches due to polishing in the sectioned surface. Nevertheless, the extrusion of PEEK pellets does not have discontinuities, which is an advantage for this technique. After incorporation of CNTs, some manufacturing-related problems are observed as shown in Fig. 2b. In Fig. 2b, as indicated with a yellow arrow, a line between the layers is observed. Besides, inside the dashed circles, some agglomerated CNTs are observed.

After the observation of the microstructures, the mechanical properties of the printed part were studied by three-point bending tests. Additive manufacturing techniques can cause anisotropy in the manufactured specimens with respect to the feed direction of the printhead. Therefore, this effect must also be tested after fabrication. In this regard, specimens printed parallel to the printhead feed direction are referred to as longitudinal specimens, and specimens with an orientation perpendicular to the printhead feed direction are referred to as transverse specimens. After performing the tests, the flexural moduli as a function of the tested parameters are given in Fig. 3. According to Fig. 3, CNT incorporation reduced the stiffness of the composites for both printing directions. This may be associated with the agglomeration of CNTs in the printed specimens due to the intense van der Waals interactions between the carbon atoms and some manufacturing deficiencies [9].

In addition, the calculated flexural modulus in the pure PEEK specimens with transverse printing direction was found to be 15% higher than the values in the samples with longitudinal printing direction. The printing direction also affected the strength of the pure PEEK material as given in Fig. 4.

From Fig. 4, for pure PEEK specimens, the effect of printing direction is not significant. As shown in the microscopic images, the interfaces between successive layers are defect-free. Therefore, this may be the reason for the unchanged strength.

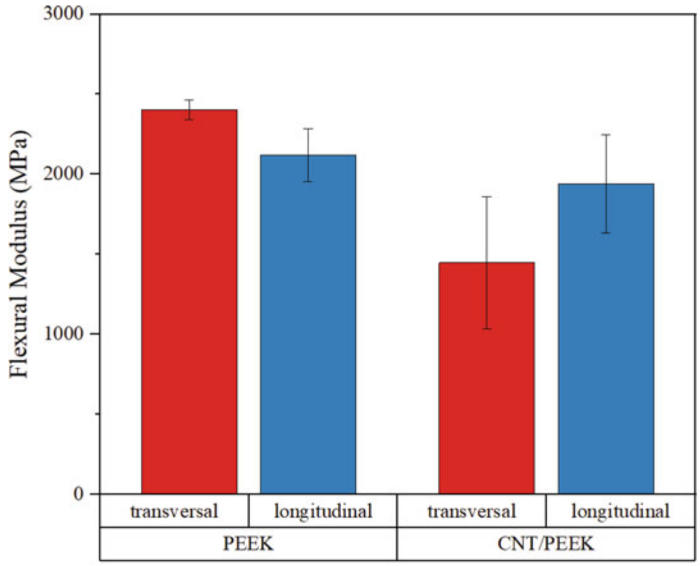


Fig. 3 Flexural moduli of the printed specimens with respect to CNT incorporation and printing direction

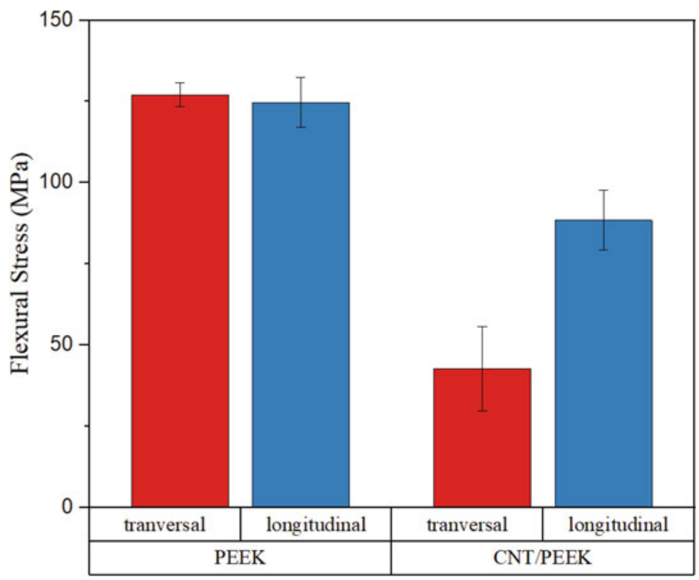


Fig. 4 Maximum flexural stress of the printed specimens with respect to CNT incorporation and printing direction

On the other hand, CNT incorporation again lowered the strength similar with stiffness. This reduction is more apparent for the transversally printed specimens. In addition, the standard deviation of the strength of CNT-reinforced specimens is larger than that of pure PEEK specimens. This may be the result of the inhomogeneity of CNT distribution. Finally, the elongation capacity of the printed parts was examined from bending tests and is given in Fig. 5. For pure PEEK specimens, it is clearly shown in Fig. 5 that longitudinally printed pure PEEK specimens can deform to failure by twice as much as transversely printed pure PEEK specimens. On the other hand, the decreasing trend of mechanical properties with the incorporation of CNTs did not change for the elongation at break. Discontinuities and inhomogeneities can cause stress concentration in the microstructure, leading to premature failure. In addition, longitudinally printed specimens may deform more than transversely printed parts. This is an expected result since transversely printed specimens have more layers.

After the three-point bending test, Charpy impact tests were carried out and results are given in Fig. 6. Upon examination of the results, it was found that the Charpy impact strength of the PEEK samples in the longitudinal printing direction was higher than the other samples. It was observed that the lowest impact strength was found in the transversal printing direction of the PEEK/CNT samples. It was expected that, due to the damping characteristics of CNTs, the impact resistance might

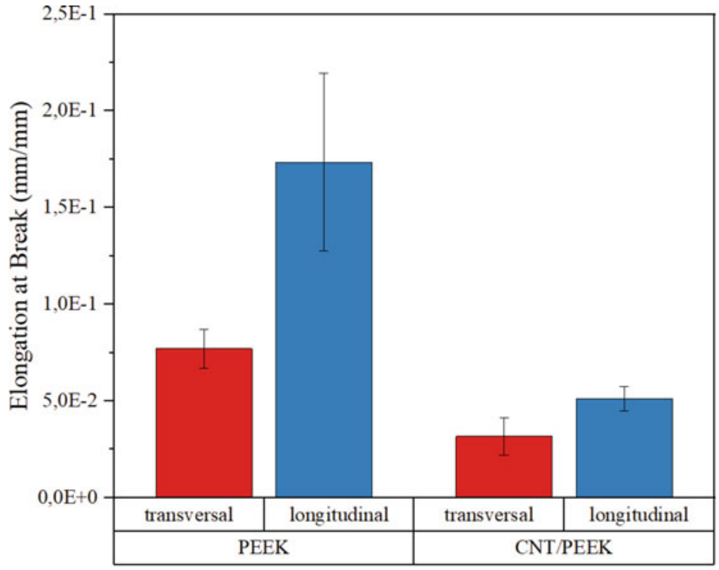


Fig. 5 Elongation at break of the printed specimens with respect to CNT incorporation and printing direction

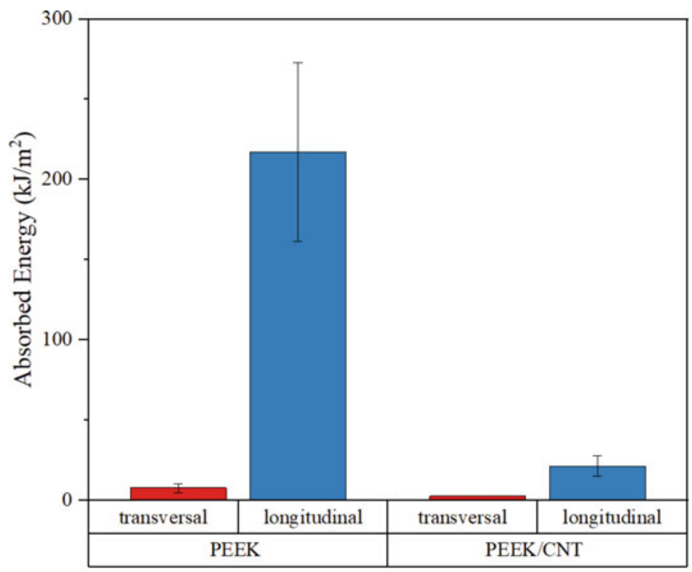


Fig. 6 Charpy impact test results with respect to CNT incorporation and printing direction

have been improved. However, as with the bending tests, no improvement was observed in the impact resistance of the composites. This may be due to manufacturing issues.

After completing the mechanical characterizations, SEM fractography was performed on the failed specimens. In Fig. 7, the fracture surface of the pure PEEK specimen is given, and a smooth fracture surface is considered an indicator of ductile behavior. In addition, no discontinuities were observed in the microstructure, which is consistent with the optical microscopy.

Conclusion

In this study, a composite material was developed for use in biomedical applications. The novelty of this study is the manufacturing of this composite by the additive manufacturing technique of pellet extrusion. As reinforcing agents, CNTs were incorporated into the PEEK matrix by twin-screw extrusion. Then, the composite in pellet form was used by the 3D printer to fabricate the specimens for mechanical characterizations. From microstructural observations, no discontinuity was

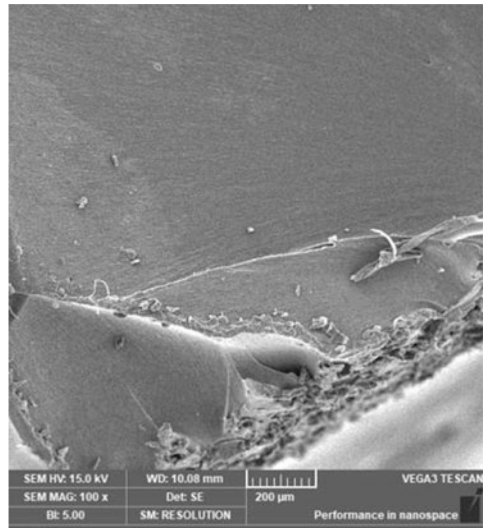


Fig. 7 SEM fractography of pure PEEK specimen

observed for the pure PEEK specimens. However, the CNT addition resulted in some homogeneity issues. This is probably associated with the high van der Waals forces between the carbon atoms and the π-π interactions. For these reasons, the expected improvement in mechanical properties was not observed. In addition, the effect of the printing direction was also investigated, and anisotropy in the specimens with respect to the printing direction was observed. These results were obtained on a laboratory scale, and it is expected that eliminating the deviations by using more advanced manufacturing facilities, these composites can be promising in the development of biomedical implants.

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