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Anisotropic Properties of Polylactic acid–carbon Fiber Composites Prepared by Droplet spray Additive Manufacturing

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Received: 31 January 2019; Accepted: 21 February 2019; Published: 23 February 2019



Abstract: Anisotropic materials are important functional materials in many fields. The use of these materials is currently being expanded through the rapid development of additive manufacturing. However, there is still no universal method for fabricating two-dimensional anisotropic polymer composites. Here, polylactic acid–carbon fiber composites were prepared using the droplet spray method, and their mechanical and friction properties were studied. The tensile strength in the X–Y plane perpendicular to the direction of the droplet spray was significantly higher than that in the direction of droplet ejection. Similar trends were observed for the elongation at breaking and the impact strength. The friction coefficient was smallest in the X–Y plane. Scanning electron microscopy showed that carbon fibers were oriented in the X–Y plane, which enhanced the mechanical and friction properties in this plane.

Keywords: droplet spray; additive manufacturing; anisotropy; carbon fiber

1. Introduction

Anisotropy of polymer composites in fillers results in directional macroscopic properties [1,2]. One- and two-dimensional oriented anisotropic polymer composites have excellent properties, such as conductivity, thermal conductivity, magnetism, permeability and mechanical strengths, etc. [3–5]. They are widely used in biomedicine, electromagnetic shielding, stealth technology and aircraft fuselage materials [6,7]. In two-phase polymer composites, if one of the phases (e.g., the phase with high thermal conductivity) is uniformly dispersed without any orientation, the thermal conductivity is low at relatively low filler content. When the filler content is very high, an ideal thermal conductivity can be achieved; however, this might come with a loss in other material properties and/or an increase in cost. By contrast, a high thermal conductivity at low filler content can be achieved if the phase with high thermal conductivity is parallel to the direction of heat flow and forms a penetrating structure. The use of such anisotropic structures is an effective way to reduce the filler content while retaining the properties of the polymer filler [8].

Common methods for preparing one-dimensional oriented anisotropic polymer composites are shear force orientation [9,10], magnetic field orientation [11,12], electric field orientation [13–15], pre-orientation, thermal gradient self-assembly orientation of copolymers [16] and solvent evaporation-driven orientation [17]. By comparison, there are relatively few preparation methods for two-dimensional

oriented polymer composites, which can usually only be prepared using fiber cascades and other special methods.

For example, Sohn and Seo [16] obtained a lamellar microphase structure of PS-*b*-P4VP block copolymer by spin coating and annealing field treatment. Prefabricated fiber-liquid resin casting has also used to prepare one-dimensional and two-dimensional oriented polymer composites for engineering applications [17], typical FRP has been widely used, such as epoxy resin composites filled with glass fiber filled, Boron fiber filled phenolic resin.

Compared with the conventional methods described above, additive manufacturing—which generates three-dimensional entities by adding materials layer-by-layer through continuous physical stacking—has several advantages [18,19]. The main advantages of the additive manufacturing method are as follows: 1. It has a shorter production cycle. 2. It can manufacture complex parts without the limitation of traditional processing. 3. In the manufacturing process, it can save raw materials, and there is no waste nor recycling. 4. It has precise entity replication capability. Easir Arafat Papon et al. [20] studied the effects of carbon fiber reinforcement, nozzle geometry and bead lay-up orientations in fracture properties, void contents, and interfacial bonding. The results showed that there were significant improvements in fracture toughness and fracture energy for CF/PLA composites over pure PLA. Ning et al. [21] produced one- and two-dimensional anisotropic composites using two nozzles on the additive manufacturing machine to output long fibers and resins; however, the infiltration of the melt resin on the fibers was poor. Tekinalp et al. [22] blended resins and fibers with an average length of 3.2 mm and extruded them from nozzles with a diameter of 0.5 mm. Quan et al. [23,24] studied the microstructure of additively manufactured ABS resin composites, which they fabricated by adding short fibers, and continuous carbon fibers as the skeleton. They found that the short fibers led to a certain degree of one-dimensional orientation. They also analyzed the mechanism of orientation driven by shear force. However, despite these efforts, there is no universal preparation method for two-dimensional oriented anisotropic polymer composites.

In this work, two-dimensional oriented anisotropic polymer composites were fabricated, which were based on deformation and shear-force driving of droplets during impact-spreading using droplet-spray additive manufacturing. The obvious anisotropy in the mechanical properties and friction property was investigated.

2. Materials and Methods

2.1. Materials

Raw materials were used as follows: Polylactic acid (PLA) from NatureWorks, Minnetonka, MN, USA (product name: 2003D). Dichloromethane ($\geq 99.8\%$) and carbon fiber (WD300) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). The carbon fibers had a diameter is 7 μm with an average aspect ratio of 5, and the original fiber had an anti-extension modulus of 230GPa and a tensile strength of 3.8 GPa. The experimental setup was a self-built spray printing system, as shown in Figure 1. Number 1 is the pneumatic device, number 2 is the cartridge, number 3 the spray needle, number 4 is the Z-axis manual adjusting table, number 5 is a high-voltage power supply, number 6 is the base board, number 7 is the control system, number 8 the X–Y electric platform, number 9 is the workbench and number 10 the computer. The needle used was a 30G stainless steel dispensing needle with an inner diameter of 0.7 mm.

The surface of the carbon fibers was treated with silane coupling agent KH-550. The sol concentration has a substantial impact on film formation; if the concentration is too high, the nozzle will be blocked easily, which makes the experiment less operable; if the concentration is too low, carbon fibers settle readily. Therefore, after analysis of several initial experiments, a PLA concentration of 0.3 mol/L was selected, and carbon fibers (10 wt% relative to the weight of polylactic acid) were added to the solution. The solution was then stirred magnetically for 2 h, followed by ultrasonic dispersion for 20 min at a frequency of 40 KHz and power of 250 W. The microdroplet injection system was then

opened and the parameters were adjusted. The distance between the nozzle and the substrate was 0.6 mm, the pressure was 1.2 kPa and the voltage was 1.0 kV.

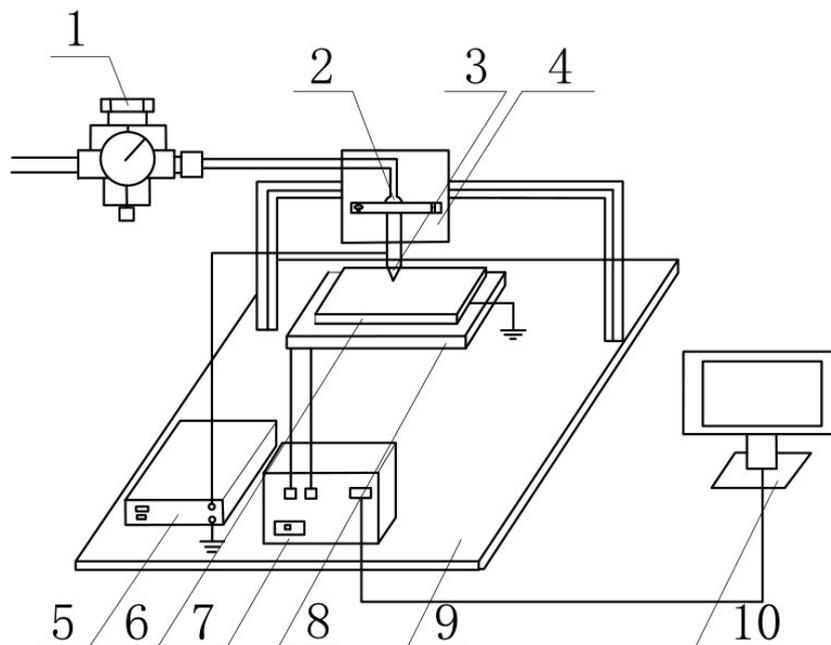


Figure 1. Schematic diagram of the printing system.

The horizontal plane perpendicular to the direction of injection was defined as the X–Y plane. The plane parallel to the direction of injection was defined as the Z plane. These orientations are shown in Figure 2.

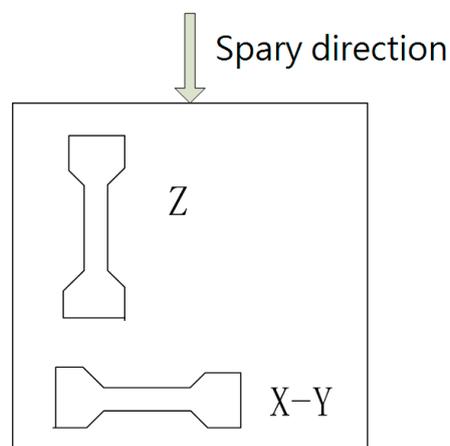


Figure 2. Diagram of the specimen.

2.2. Performance Testing Methods

2.2.1. Mechanical Property Testing

The tensile strength and elongation upon breaking of the films were tested using a WDW-5000N tensile tester (Shanghai Huai Instrument Equipment Co., Ltd., Shanghai, China). According to GB/T 1041-2008, the samples were cut into dumbbell shapes. To ensure the accuracy of the tensile results, five samples of each specimen were prepared. The two extreme values were removed and the average value was taken as the final result. Similarly, the bending properties were tested according to ASTM

D790-2003, and the impact properties were tested using a TY-4020-15J impact testing machine (Jiangsu Tianyuan Testing Equipment Co., Ltd., Yangzhou, China) according to GB/T 1043-2008.

2.2.2. Friction and Wear Testing

The orientation of carbon fibers has a significant effect on the friction and wear properties [25,26]. In this work, the tribological properties of specimens under dry friction were tested using an HSR-2M friction and wear tester. The sensor size was 1000 gf, the load was 2 N, the motor speed was 200 rpm, and the friction time was 30 min. Silicon nitride spheres (4 mm diameter) were used as friction coupling.

2.2.3. SEM Characterization

The samples were scanned using a Hitachi S-4800 scanning electron microscope (SEM, Hitachi S-4800, Tokyo, Japan) under ultrahigh pressure (EHT 5000V). A conductive adhesive spray was used to attach the sample to the base of the SEM.

3. Results and Discussion

3.1. Mechanical Properties

The tensile strength of the sample is shown in Figure 3. The tensile strength of PLA without carbon fibers differs only slightly (10%–20%) between the X–Y PLA and Z–PLA. The reason for this is that the bonding strength between layers is weaker than the strength of the PLA body, and the solvent blurs the interface between layers. This results in lower anisotropy than is commonly observed in 3D printing. For example, the difference in tensile strength in different directions of FDM (Fused Deposition Modeling) printing is generally more than 50% [27]. When carbon fibers were added to the PLA, the tensile strength in the X–Y plane was about 50% higher than that in the Z–plane. In addition, the carbon fibers change the tensile properties of the specimen. In the X–Y plane, the addition of carbon fibers increases the tensile strength by about 40%, whereas the strength in the Z–direction hardly changes. Moreover, the test standard deviation of the samples with carbon fibers is larger than that of pure PLA. This is mainly because of insufficiently uniform dispersion of fibers and their effect on the interfacial bond strength between layers.

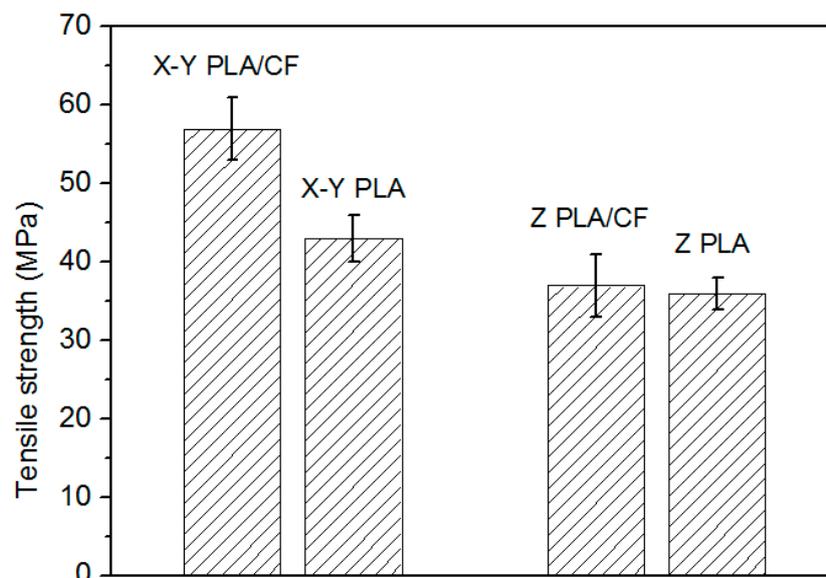


Figure 3. Tensile strength of the polylactic acid–carbon fiber (PLA–CF) specimens.

Figure 4 shows the elongation upon breaking of the specimen. The trend among specimens is similar to that for the tensile strength. The elongation at breaking of PLA without carbon fibers is

20% larger in the X–Y plane than in the Z–plane, which is mainly because of the weak bonding force between layers. By contrast, in the presence of carbon fibers, there is a large difference in elongation between the two directions.



Figure 4. At breaking of the polylactic acid–carbon fiber (PLA–CF) specimens.

The impact strength of the different specimens is shown in Figure 5. The general trend among specimens is similar to that of the tensile strength, but much more pronounced. The impact strength was 300% higher in the X–Y plane with carbon fibers than in the Z–plane without carbon fibers. This is because the carbon fibers confer impact resistance of PLA and the effect of fiber orientation. The impact strength in the X–Y plane with carbon fibers is about 140% higher than that in the Z–plane of the specimens with carbon fibers. This is because of the fiber orientation in the specimens. The impact strength in the Z–plane of specimens with carbon fibers is about 50% higher than that without carbon fibers; the impact strength of specimens without carbon fibers differs only slightly between the two directions.

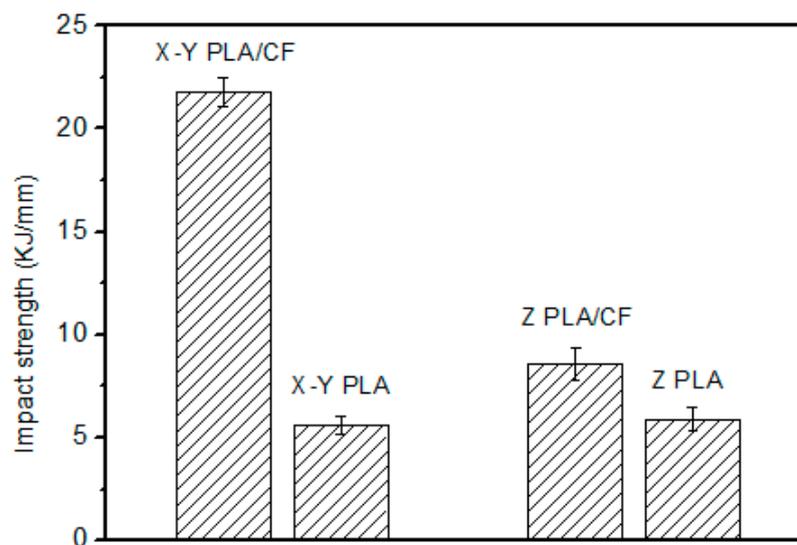


Figure 5. Strength of the polylactic acid–carbon fiber (PLA–CF) specimens.

3.2. Friction Properties

The friction and wear tests of PLA composites sliding against an Si_3N_4 ball were evaluated on a ball-on-disk tribo-meter (HSR-2M, Zhongke Kaihua Technology Development Co., Lanzhou, China)

at room temperature. The contact schematic diagram of the friction couple was shown in Figure 6. The Si_3N_4 ball, as a counterpart, was 4 mm in diameter. Before each test, the Si_3N_4 ball and the block samples were cleaned with cotton dipped in acetone. The friction coefficient was continuously recorded by an online data acquisition system attached to the tester.

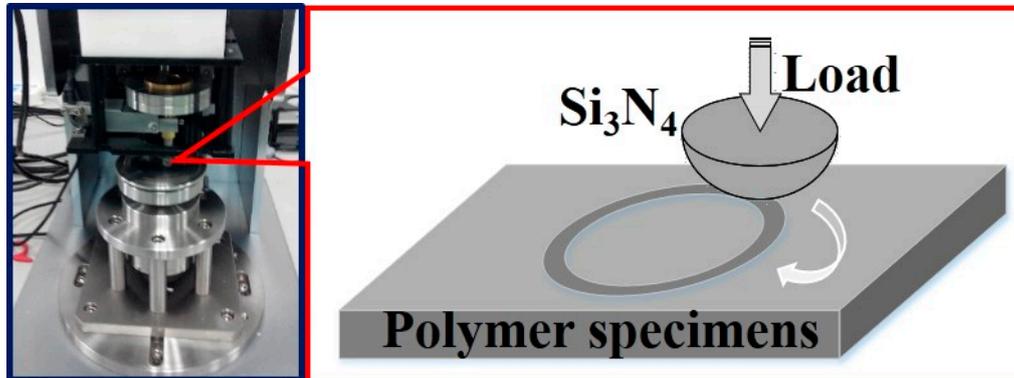


Figure 6. Equipment picture and contact schematic diagram for measuring friction.

The wear resistance of PLA is relatively poor, and there are few reports on the investigation of its friction and wear properties. To investigate the anisotropy of fibers after orientation in polylactic acid, the tribological properties of the fibers were measured. The friction coefficients (Figure 7) of the X–Y PLA–CF and Z–PLA–CF specimens are smaller than those of the X–Y PLA and Z–PLA specimens, which indicates that carbon fibers can reduce the friction coefficient of PLA; the friction coefficients of the X–Y PLA–CF specimens are smaller than those of the Z–PLA–CF specimens, and the friction coefficients of the X–Y PLA specimens are smaller than those of the Z–PLA specimens, indicating that microdroplet injection induces anisotropy.

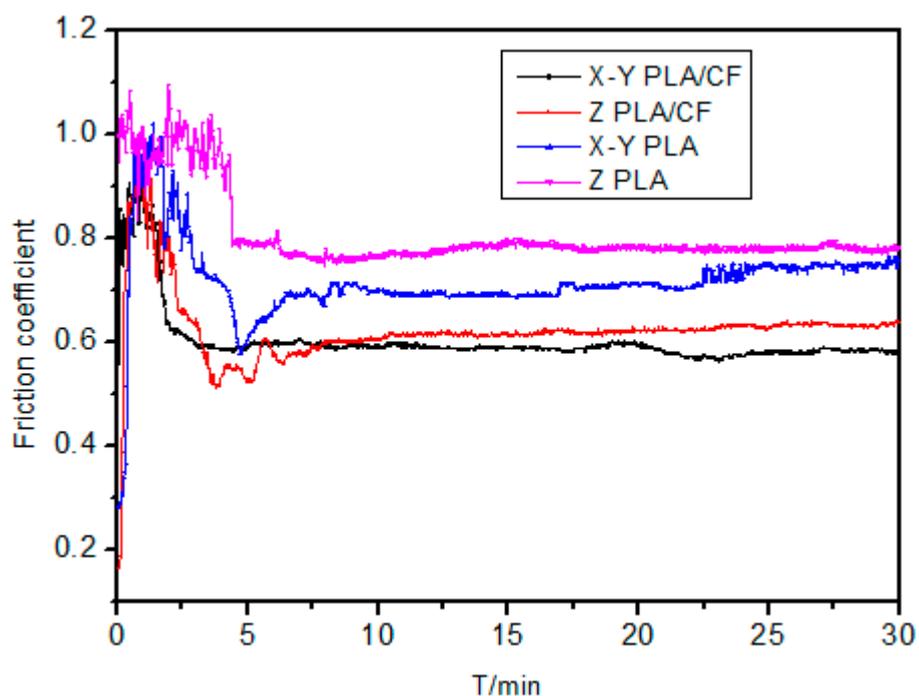


Figure 7. Friction coefficient of the poly(lactic acid)-carbon fiber (PLA-CF) specimens.

3.3. SEM Results

Figure 8 shows a distribution diagram of short carbon fiber in the X–Y plane of the sample, and Figure 8 shows a cross-sectional image of the X–Y sample after the tensile test. The carbon fibers had a

degree of orientation and were randomly distributed in the X–Y plane, as shown in Figure 8. Under tension (Figure 9), more carbon fibers are pulled out and are either oriented horizontally or inclined, which demonstrates that they are disorderly distributed in the plane perpendicular to the X–Y plane. Comparing Figures 8 and 9, it can be considered that the long-diameter directions of carbon fibers are mostly in the X–Y plane, and are randomly distributed in the x–y plane, forming a two-dimensional anisotropy. Carbon fiber has high strength and good lubricating property. The two-dimensional anisotropy also partly explains the results of the above-mentioned mechanical and friction tests.

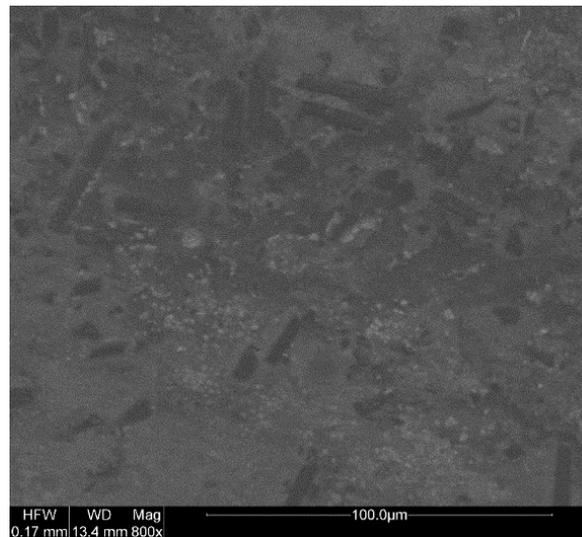


Figure 8. X–Y plane of the polylactic acid–carbon fiber specimen.

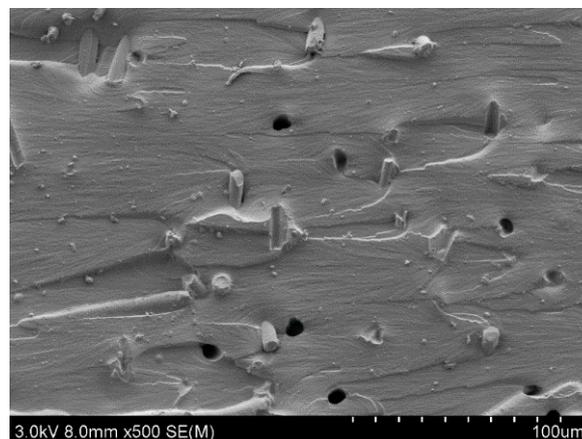


Figure 9. Tensile fracture cross-section of the X–Y polylactic acid–carbon fiber specimen.

4. Conclusions

Polylactic acid–carbon fiber composites were fabricated by using the microdroplet spray method. The mechanical properties, frictional properties and the microscopic surface of the composites were tested. The main conclusions are as follows:

- (1) The SEM images show that carbon fibers were oriented in the X–Y plane perpendicular to the direction of injection.
- (2) This orientation of carbon fiber enhanced the material anisotropy and resulted in superior, directional properties, such as strength.
- (3) The carbon fiber reduces the coefficient of friction of the printed material, and the oriented carbon fiber further enhances this effect.

This work reports that it is critically important to understand the thermo-mechanical behaviors of 3D printing materials with carbon fiber, particularly anisotropy in some properties for the use of the emerging manufacturing technique, 3D printing, in a wide variety of engineering applications.

Author Contributions: Investigation, Y.L. and Q.D.; writing—original draft preparation, Y.L. and Q.D.; validation, H.Z.; data curation, T.W.; methodology, M.Z.; formal analysis, Y.Z.

Funding: This research was funded by the Key Scientific Research Projects of Higher Education of Henan Province of China, grant number 19A430014, Scientific and Technological Research Projects of Henan Province, grant number 192102210215 and the Young Key Teachers Projects in Henan Higher Education Institutions, grant number 2018GGJS113.

Acknowledgments: The authors gratefully acknowledge the financial supports from the Key Scientific Research Projects of Higher Education of Henan Province of China (19A430014), Scientific and Technological Research Projects of Henan Province (192102210215) and the Young Key Teachers Projects in Henan Higher Education Institutions (2018GGJS113). We also thank Adam Brotchie, from LiwenBianji, Edanz Group China (www.liwenbianji.cn/ac), for editing the English text of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kim, J.W.; Lee, D.G. Effect of fiber orientation and fiber contents on the tensile strength in fiber-reinforced composites. *J. Nanosci. Nanotechnol.* **2010**, *10*, 3650–3653. [[CrossRef](#)] [[PubMed](#)]
2. Kim, J.W.; Lee, J.J.; Lee, D.G. Effect of Fiber Orientation on the Tensile Strength in Fiber-Reinforced Polymeric Composite Materials. *Key Eng. Mater.* **2005**, *297–300*, 2897–2902. [[CrossRef](#)]
3. Gong, S.; Zhu, Z.H.; Meguid, S.A. Anisotropic electrical conductivity of polymer composites with aligned carbon nanotubes. *Polymer* **2015**, *56*, 498–506. [[CrossRef](#)]
4. Shemelya, C.; De La Rosa, A.; Torrado, A.R.; Yu, K.; Domanowski, J.; Bonacuse, P.J.; Martin, R.E.; Juhasz, M.; Hurwitz, F.; Wicker, R.B.; et al. Anisotropy of thermal conductivity in 3D printed polymer matrix composites for space based cube satellites. *Addit. Manuf.* **2017**, *16*, 186–196. [[CrossRef](#)]
5. Wazzan, A.A. Effect of fiber orientation on the mechanical properties and fracture characteristics of date palm fiber reinforced composites. *Int. J. Polym. Mater. Polym. Biomater.* **2005**, *54*, 213–225. [[CrossRef](#)]
6. Goh, G.D.; Yap, Y.L.; Agarwala, S.; Yeong, W.Y. Recent Progress in Additive Manufacturing of Fiber Reinforced Polymer Composite. *Adv. Mater. Technol.* **2019**, *4*, 1800271. [[CrossRef](#)]
7. Fotovvati, B.; Namdari, N.; Dehghanghadikolaei, A. Fatigue performance of selective laser melted Ti6Al4V components: state of the art. *Mater. Res. Express* **2018**, *6*, 012002. [[CrossRef](#)]
8. Fereiduni, E.; Yakout, M.; Elbestawi, M. Laser-Based Additive Manufacturing of Lightweight Metal Matrix Composites. In *Additive Manufacturing of Emerging Materials*; AlMangour, B., Ed.; Springer: Cham, Switzerland, 2019; pp. 55–109.
9. Mao, C.; Huang, J.; Zhu, Y.; Jiang, W.; Tang, Q.; Ma, X. Tailored Parallel Graphene Stripes in Plastic Film with Conductive Anisotropy by Shear-Induced Self-Assembly. *J. Phys. Chem. Lett.* **2012**, *4*, 43–47. [[CrossRef](#)] [[PubMed](#)]
10. Huang, J.; Zhu, Y.; Jiang, W.; Yin, J.; Tang, Q.; Yang, X. Parallel Carbon Nanotube Stripes in Polymer Thin Film with Remarkable Conductive Anisotropy. *ACS Appl. Mater. Interfaces* **2014**, *6*, 1754–1758. [[CrossRef](#)] [[PubMed](#)]
11. Steinert, B.W.; Dean, D.R. Magnetic field alignment and electrical properties of solution cast PET–carbon nanotube composite films. *Polymer* **2009**, *50*, 898–904. [[CrossRef](#)]
12. Wang, D.; Song, P.; Liu, C.; Wu, W.; Fan, S. Highly oriented carbon nanotube papers made of aligned carbon nanotubes. *Nanotechnology* **2008**, *19*, 075609. [[CrossRef](#)] [[PubMed](#)]
13. Martin, C.A.; Sandler, J.K.W.; Windle, A.H.; Schwarz, M.K.; Bauhofer, W.; Schulte, K.; Shaffer, M.S.P. Electric field -induced aligned multi-wall carbon nanotube networks in epoxy composites. *Polymer* **2005**, *46*, 877–886. [[CrossRef](#)]
14. Ramón-Azcón, J.; Ahadian, S.; Estili, M.; Liang, X.; Ostrovidov, S.; Kaji, H.; Shiku, H.; Ramalingam, M.; Nakajima, K.; Sakka, Y.; Khademhosseini, A.; Matsue, T. Dielectrophoretically Aligned Carbon Nanotubes to Control Electrical and Mechanical Properties of Hydrogels to Fabricate Contractile Muscle Myofibers. *Adv. Mater.* **2013**, *25*, 4028–4034. [[CrossRef](#)] [[PubMed](#)]

15. Du, F.; Fischer, J.E.; Winey, K.I. Effect of nanotube alignment on percolat ion conductivity in carbon nanotube/polymer composites. *Phys. Rev. B Condens. Matter*. **2005**, *72*, 121404. [[CrossRef](#)]
16. Sohn, B.; Seo, B. Fabrication of the multilayered nanostructure of alternating polymers and gold nanoparticles with thin films of self-assembling diblock copolymers. *Chem. Mater.* **2001**, *13*, 1752–1757. [[CrossRef](#)]
17. Yan, X.L. Research on two-dimensional layout problem of anisotropic materials. Ph.D. Thesis, Wuhan University of Technology, Wuhan, China, June 2013. (In Chinese)
18. Dehghanghadikolaei, A.; Ibrahim, H.; Amerinatanzi, A.; Hashemi, M.; Shayesteh Moghaddam, N.; Elahinia, M. Improving corrosion resistance of additively manufactured nickel–titanium biomedical devices by micro-arc oxidation process. *J. Mater. Sci.* **2019**, *54*, 7333–7355. [[CrossRef](#)]
19. Ibrahim, H.; Jahadakbar, A.; Dehghan, A.; Moghaddam, N.S.; Amerinatanzi, A.; Elahinia, M. In Vitro Corrosion Assessment of Additively Manufactured Porous NiTi Structures for Bone Fixation Applications. *Metals* **2018**, *8*, 164. [[CrossRef](#)]
20. Papon, E.A.; Haque, A. Fracture toughness of additively manufactured carbon fiber reinforced composites. *Addit. Manuf.* **2019**, *26*, 41–52. [[CrossRef](#)]
21. Ning, F.D.; Cong, W.L.; Hu, Y.B.; Wang, H. Additive manufacturing of carbon fiber-reinforced plastic composites using fused deposition modeling: Effects of process parameters on tensile properties. *J. Compos. Mater.* **2017**, *51*, 1–12. [[CrossRef](#)]
22. Tekinalp, H.L.; Kunc, V.; Velez-Garcia, G.M.; Duty, C.E.; Love, L.J.; Naskar, A.K.; Blue, C.A.; Ozcan, S. Highly oriented carbon fiber–polymer composites via additive Manufacturing. *Compos. Sci. Technol.* **2014**, *105*, 144–150. [[CrossRef](#)]
23. Quan, Z.Z.; Zachary, L.; Amanda, W.; Yu, J.Y.; Qin, X.H.; Mark, M.; Jonghwan, S.; Joon-Hyung, B.; Youngseok, O.; Tsu-Wei, C. Microstructural design and additive manufacturing and characterization of 3D orthogonal short carbon fiber/acrylonitrile-butadiene-styrene preform and composite. *Compos. Sci. Technol.* **2016**, *126*, 139–148. [[CrossRef](#)]
24. Quan, Z.Z.; Wu, A.; Michael, K.; Qin, X.H.; Yu, J.Y.; Jonghwan, S.; Joon-Hyung, B.; Byung-Sun, K.; Tsu-Wei, C. Additive manufacturing of multidirectional preforms for composites: opportunities and challenges. *Mater. Today* **2015**, *18*, 503–512. [[CrossRef](#)]
25. Nak-Ho, S.; Suh, N.P. Effect of fiber orientation on friction and wear of fiber reinforced polymeric composites. *Wear* **1979**, *53*, 129–141. [[CrossRef](#)]
26. El-Sayed, A.A.; El-Sherbiny, M.G.; Abo-El-Ezz, A.S.; Aggag, G.A. Friction and wear properties of polymeric composite materials for bearing applications. *Wear* **1995**, *184*, 45–53. [[CrossRef](#)]
27. Chacón, J.M.; Caminero, M.A.; García-Plaza, E.; Nunez, P.J. Additive manufacturing of PLA structures using fused deposition modelling: Effect of process parameters on mechanical properties and their optimal selection. *Mater. Des.* **2017**, *124*, 143–157. [[CrossRef](#)]

