Preparation and Properties of Straw/PLA Wood Plastic Composites for 3D Printing

Jie Jiang1,2,*, Hai Gu1,2, Bin Li1,2 and Jie Zhang1,2

1School of Mechanical Engineering, Nantong Institute of Technology, Nantong, China
2Key Laboratory of 3D Printing Equipment and Application Technology of Jiangsu Province, Nantong, China

*Corresponding author: jiangjie@ntit.edu.cn

Abstract. Based on the single screw extruder, straw/PLA composites with different straw mass fraction, drawing temperature and screw speed were prepared with corn straw powder and PLA particles as raw materials, and FDM printing test was carried out to further study the influence of straw mass fraction, drawing temperature and screw speed on the mechanical properties of straw/PLA composites The results show that the tensile strength of the composite is the best when the straw content is 15%, the drawing temperature is 215°C, the screw speed is 60r/min; the flexural strength of the composite is the best when the straw content is 15%, the drawing temperature is 215°C, the screw speed is 70r/min; the hardness of the composite is the best when the straw content is 10%, the drawing temperature is 195°C, the screw speed is 70r/min.

Keywords: Polylactic acid, corn straw, wood plastic composite, single screw extruder, performance.

1. Introduction

3D printing technology is based on the basic principle of layering and stacking, which uses laser, electron beam and binder to stack powder materials, liquid materials and molten materials layer by layer to directly produce three-dimensional entities. 3D printing technology has the advantages of convenient, fast and not limited by the shape of target products. It is widely used in the fields of architecture, packaging, medical treatment, transportation, aerospace, military and other fields. Fused Deposition Molding (FDM) process has the advantages of relatively low cost, wide material sources, and simple post-processing. It is currently one of the most widely used 3D printing technologies and is used in medical and health, decoration, clothing, fertilizers, automobiles, electrical appliances and other fields.

Wood plastic composite is a new kind of composite material with high performance and high added value, which is made of plastic as the main raw material through proper treatment and different composite methods with various plastics. Using silane coupling agent (KH550) as plasticizer [1], plant fiber and polylactic acid wood plastic composites were prepared, and the effect of plant fiber content on the physical properties of the composite was studied. Feiwen Yang et al. [2] Used micron copper zinc particles to strengthen particleboard wood flour/polylactic acid wood plastic composites, and studied the effect of micro copper and zinc content on the structure and properties of the composite materials. The results showed that the composite had high gloss and antibacterial properties. Jianan Feng [3] and
others studied the mechanical properties and thermal stability of four kinds of rice straw fiber wood plastic composites by copolymerization of four kinds of rice straw fibers (sorghum, rice, corn and soybean) with PLA/PBAT. The results showed that the mechanical properties of soybean straw wood plastic composites were the best, and the thermal stability of corn straw wood plastic composites was the best. Tran Huu Nam et al. [4] dipped coconut shell fiber into 5% sodium hydroxide solution for 72h, and then prepared wood plastic composite with treated coconut shell fiber and PLA. The results showed that the shear strength and tensile strength of the treated coconut shell fiber were increased by 72.8% compared with that without treatment. Tran Huu Nam et al. [5] found that when the jute fiber content was 50%, the mechanical properties of jute/PBS biodegradable wood plastic composites were the best. Saidin w et al. [6] prepared wood fiber plastic (ZP102) polymer, and studied the effect of wood fiber content on mechanical properties. The results showed that when the wood fiber content reached 50%, the mechanical properties of the composite were improved.

In recent years, the preparation of environmentally friendly wood plastic composites from plant fiber materials and biodegradable plastics has become a research hotspot and an inevitable trend of material science development. PLA is polymerized from lactic acid. It is environmentally friendly, biodegradable and has excellent processability. It is the most commonly used material in FDM technology. At present, although some progress has been made in the preparation of polylactic acid based wood plastic composites, they are not fully suitable for FDM printing. In this paper, poly (lactic acid) (PLA) and straw powder were blended in a certain proportion to prepare silk materials for FDM process, and their properties were studied. Straw/PLA wood plastic composite has good biodegradability and is a kind of environment-friendly material. It is conducive to solve the problems of resource shortage and environmental pollution caused by straw burning, and has broad application prospects.

2. Experiment

2.1. Materials
The main raw materials and reagents selected in this paper are shown in Table 1. All materials were used as received without further purification.

| Reagent name       | Specifications | Manufacturer                                      |
|--------------------|----------------|---------------------------------------------------|
| PLA particles      | 4032D          | Dongguan Shunjie Plastic Technology Co., Ltd., Dongguan, China |
| Corn stalk powder  | 300 mesh       | Tianjin Lianfeng Agricultural Products Co., Ltd., Tianjin, China |
| Coupling agent     | KH-550         | Nanjing Chuangshi chemical additives Co., Ltd., Nanjing, China |
| Surfactants        | PEG400         | Dongguan Weida Chemical Technology Co., Ltd., Dongguan, China |
| Flame retardant    |                | Tianjin Aoda fireproof material technology Co., Ltd., Tianjin, China |
| Toughening agent   | PS             | Dongguan Shanyi Plastics Co., Ltd., Dongguan, China |
| Heat stabilizer    | Calcium stearate | Fujian Yongchun Ju Xi Food Co., Ltd., Fujian, China |

2.2. Equipment
The experimental equipment and instruments are shown in Table 2.

| Experimental apparatus     | Model          | Manufacturer                                      |
|-----------------------------|----------------|---------------------------------------------------|
| Single screw extruder      | Diameter 1.75, 3mm | Self-made                                         |
| Electric constant temperature blast drying oven | 101-1B | Hunan Lichen Instrument Technology Co., Ltd., changsha, China |
| Precision power amplifier timing electric stirrer | JJ-1H 200W | Dongguan Xihua Testing Instrument Co., Ltd., Dongguan, China |
| Granulator                 | XH-433         | Dongguan Xihua Testing Instrument Co., Ltd., Dongguan, China |
At present, the single screw extruder on the market are all used for mass production of FDM wire, and the equipment size is large. The single screw extruder used in this paper is independently developed, as shown in Figure 1. The equipment has simple structure and small size, which is suitable for the trial production of new materials in the field of rapid prototyping. Compared with the traditional single screw extruder, it can save material, reduce cost and adapt to the current market demand for diversity of materials.

![Single screw extruder](image)

Figure 1. Single screw extruder.

2.3. Samples Preparation

2.3.1. Material configuration. Because the surface of the composites prepared by unmodified straw powder and polylactic acid is rough, silane coupling agent KH-550 can significantly improve the compatibility of corn straw powder and PLA, which is conducive to the combination of corn straw powder and PLA. KH-550 silane coupling agent alcohol solution was prepared with 10% ratio. 300 mesh straw powder was placed in an oven at 105°C and dried to a moisture content of less than 3%. The dried straw powder was added with 1.5% KH-550 silane coupling agent alcohol solution, and a proper amount of surfactant, flame retardant and toughening agent were added. The straw powder was placed on a precision power increasing timing electric stirrer and pretreated at 80°C for 3h. After the reaction is completed, it is dried at 105°C until the moisture content is less than 3%.

The straw powder 3D printing composite materials with 10%, 15% and 20% straw mass percentage were prepared. The straw powder after coupling modification was evenly mixed with polylactic acid and other additives in a high-speed mixer. After mixing, the mixture was dried, and finally granulated to prepare the composite material for wire drawing.

2.3.2. Preparation of corn straw/PLA wood plastic 3D printing composites. In this paper, straw polylactic acid wood plastic composite 3D printing material with diameter of 1.75mm was prepared. The effects of straw mass fraction, screw speed and drawing temperature on material properties were studied. The test results show that when the screw speed of the single screw extruder is lower than 50r/min, the extrusion die is easy to be blocked due to the slow extrusion speed, and it is difficult to pull out the wire; when the screw speed of the extruder is higher than 90r/min, the drawn wire is uneven due to the drawing speed, and the diameter is obviously less than 1.75mm, so the screw speed is selected between 60-80r/min. When the content of straw powder is more than 20%, the wire is difficult to be formed. Therefore, this paper studies the straw powder composite material with no more than 20%. When the drawing temperature is lower than 195°C, the material can not be melted and extruded. When the temperature is higher than 215°C, the material is easy to produce bubbles and it is difficult to pull out the uniform wire. Therefore, the wire drawing temperature is between 195-215°C.

In this paper, the orthogonal test method is used to select the material mass ratio, screw speed and drawing temperature as three influencing factors, which are respectively defined as factors a, B and C. each factor uses three levels, and the values of the levels are shown in Table 3.
Table 3. Controllable factors and levels.

| Factor level | Material mass ratio/% | Screw speed/r·min⁻¹ | Temperature/℃ |
|--------------|-----------------------|----------------------|---------------|
| 1            | 10                    | 60                   | 195           |
| 2            | 15                    | 70                   | 205           |
| 3            | 20                    | 80                   | 215           |

Without considering the interaction among the factors, the degree of freedom of the three factors and three levels is as follows:

\[ f_i = f_A + f_B + f_C = (3-1) \times 3 = 6 \]  \hspace{1cm} (1)

Therefore, the orthogonal table L₉(3⁴) is selected, and its degrees of freedom are as follows:

\[ f_2 = 9 - 1 = 8 \]  \hspace{1cm} (2)

Finally, three factors and three levels orthogonal experiment design scheme is obtained, as shown in Table 4. The composites were prepared according to the parameters in Table 4.

Table 4. L₉(3⁴) orthogonal table with three factors and three levels.

| Number | A/% | B/r·min⁻¹ | C/℃ |
|--------|-----|-----------|-----|
| 1      | 10  | 60        | 195 |
| 2      | 10  | 70        | 205 |
| 3      | 10  | 80        | 215 |
| 4      | 15  | 60        | 205 |
| 5      | 15  | 70        | 215 |
| 6      | 15  | 80        | 195 |
| 7      | 20  | 60        | 215 |
| 8      | 20  | 70        | 195 |
| 9      | 20  | 80        | 205 |

2.3.3. 3D printing performance test. This paper uses Einstart-3D printer of Hangzhou Xianlin 3D Technology Co., Ltd. the printing parameters are shown in Table 5.

Table 5. Printer parameters.

| Parameter                  | Value  |
|----------------------------|--------|
| Printing speed/mm·s⁻¹      | 50     |
| Extrusion speed/mm·min⁻¹   | 50     |
| Nozzle temperature/℃       | 195    |
| Fill line spacing/mm       | 0      |
| Printing layer thickness/mm| 0.15   |

In order to verify the 3D printing adaptability of straw polylactic acid wood plastic composites, print the test piece as shown in Figure 2 (a) (b) (c).
2.4. Characterization

2.4.1. Mechanical Properties. Tensile tests and flexural tests of the composites samples were conducted according to GB/T 10402-2006 and GB/T 1449-2005, respectively, using an electronic universal testing machine (WDW, Jinan Xinshijin testing machine Co., Ltd., Jinan, China). For each group, more than five replicates were used in the test and the data were recorded as mean. The tensile speed was 10 mm/min while the flexural test speed was 2 mm/min. Figure 2 shows the dimensions of the specimens for tensile and flexural tests.

2.4.2. Hardness. The hardness of the upper surface of the hardness test piece as shown in Fig. 2 (c) is measured with shore hardness tester type D equipment. Each test piece is measured 5 times and the average value is taken. The principle of shore hardness tester is that under the action of experimental force, the steel pressure needle with a certain shape is pressed into the surface of the sample. When the surface of the pressure foot completely fits with the surface of the sample, the end face of the pressure needle has a certain length L relative to the plane of the foot. The value of L is used to characterize the size of shore hardness. The smaller the L value is, the higher the shore hardness is, otherwise the lower the shore hardness is. The formula is as follows:

\[
HD = 100 - \frac{L}{0.025}
\]  

3. Results and Discussion

3.1. Experimental data
The tensile strength, flexural strength and hardness of 9 groups of experiments were recorded in Table 6.
Table 6. Tensile strength, flexural strength and hardness measurements.

| Number | A/% | B/r·min⁻¹ | C/℃ | σb/MPa | σs/MPa | HD  |
|--------|-----|------------|------|--------|--------|-----|
| 1      | 10  | 60         | 195  | 20.344 | 35     | 74.3|
| 2      | 10  | 70         | 205  | 23.688 | 72     | 80.8|
| 3      | 10  | 80         | 215  | 25.250 | 80     | 77.3|
| 4      | 15  | 60         | 205  | 25.969 | 88     | 70.8|
| 5      | 15  | 70         | 215  | 27.380 | 97     | 77.0|
| 6      | 15  | 80         | 195  | 22.840 | 70     | 77.8|
| 7      | 20  | 60         | 215  | 27.781 | 78     | 66.8|
| 8      | 20  | 70         | 195  | 21.844 | 69     | 75.3|
| 9      | 20  | 80         | 205  | 14.875 | 78     | 72.8|

3.2. Tensile strength

Calculate the mean value and range of single factor, as shown in Table 7. The mean main effect diagram is shown in Figure 3. The influence degree of tensile strength of the composite is C (temperature) > A (material mass ratio) > b (screw speed). The optimal test conditions are temperature 215℃, material mass ratio 15%, screw speed 60r/min, namely C3A2B1.

Table 7. Analysis table of tensile strength range.

| Parameter       | A/%  | B/r·min⁻¹ | C/℃  |
|-----------------|------|-----------|------|
| Mean value 1    | 23.094 | 24.698     | 21.676 |
| Mean value 2    | 25.396 | 24.304     | 21.511 |
| Mean value 3    | 21.500 | 20.988     | 26.804 |
| Extreme difference | 3.896 | 3.710       | 5.293 |
| patch           | 2    | 3          | 1     |

Figure 3. Effect curve of tensile strength.

3.3. Flexural strength

Calculate the mean value and range of single factor, as shown in Table 8. The mean main effect diagram is shown in Figure 4. The influence degree of the flexural strength of the composite is C (temperature) > A (material mass ratio) > b (screw speed). The optimum experimental conditions are as follows: drawing temperature 215℃, material mass ratio 15%, screw speed 70r/min, namely C3A2B2.
Table 8. Analysis table of flexural strength range.

| Parameter          | A/%   | B/r·min⁻¹ | C/℃   |
|--------------------|-------|-----------|-------|
| Mean value 1       | 72.667| 77.333    | 68.333|
| Mean value 2       | 85.000| 79.333    | 79.333|
| Mean value 3       | 75.000| 76.000    | 85.000|
| Extreme difference | 12.333| 3.333     | 16.667|

Figure 4. Effect curve of flexural strength.

3.4. Hardness

Calculate the mean and range of single factor, as shown in Table 9. The mean main effect diagram is shown in Figure 5. The influence degree of the composite hardness is B (screw speed) > A (material mass ratio) > C (temperature). The optimum test conditions are as follows: screw speed is 70r/min, drawing temperature is 195℃, and material mass ratio is 10%, namely B2A1C1.

Table 9. Hardness range analysis table.

| Parameter          | A/%  | B/r·min⁻¹ | C/℃ |
|--------------------|------|-----------|-----|
| Mean value 1       | 77.47| 70.63     | 75.80|
| Mean value 2       | 75.20| 77.70     | 74.80|
| Mean value 3       | 71.63| 75.97     | 73.70|
| Extreme difference | 5.83 | 7.07      | 2.10 |
| patch              | 2    | 1         | 3    |

Figure 5. Effect curve of hardness.
4. Conclusions
3D printing straw/PLA wood plastic composites were prepared by single screw extruder. Firstly, the straw powder was modified, and then the straw polylactic acid wood plastic composite wire was prepared. The surface of the silk is smooth, which can meet the basic requirements of FDM printing, and the printing effect is ideal. The effects of straw mass fraction, screw speed and drawing temperature on the tensile strength, bending strength and hardness of straw PLA wood plastic composites were further studied. The results showed that straw/PLA wood plastic composites were not only suitable for FDM printing, but also had good mechanical properties and hardness.

Acknowledgments
This work was financially supported by the Priority Discipline Construction Program of Jiangsu Province (No. 2016-9), Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (No. PPZY2015C251); and the project supported by the Nantong Science and Technology Commission of China (Nos. CP12016002 and JCZ18034).

References
[1] Lingxiao Liu, Maohai Lin, Zhang Xu, et al, Polylactic Acid-based Wood-plastic 3D Printing Composite and its Properties, J. BioResources. 2019, 14 (4) 8484-8498.
[2] Yang F, Zeng J, Long H, et al, Micrometer Copper-Zinc Alloy Particles-Reinforced Wood Plastic Composites with High Gloss and Antibacterial Properties for 3D Printing, J. Polymers. 2020, 12 (3): 621.
[3] Jianan Feng, Weixing Zhang, Lei Wang, et al, Performance Comparison of Four Kinds of Straw/PLA/PBAT Wood Plastic Composites, J. BioResources. 2020, 15 (2), 2596-2604.
[4] Nam T H, Ogihara S, Tung N H, et al, Effect of alkali treatment on interfacial and mechanical properties of coir fiber reinforced poly(butylene succinate) biodegradable composites, J. Composites Part B Engineering. 2011, 42 (6): 1648-1656.
[5] Nam T H, Goto K, Yamaguchi Y, et al, Improving mechanical properties of high volume fraction aligned multi-walled carbon nanotube/epoxy composites by stretching and pressing, J. Composites Part B Engineering. 2016, 85: 15-23.
[6] Saidin W, Wagiman A, Ibrahim M. Development of Wood-Based Composites Material for 3D Printing Process, J. Applied Mechanics & Materials. 2013, 315: 987-991.