Preparation and Mechanical Properties of Fiber Reinforced PLA for 3D Printing Materials

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Abstract: The cellulose prepared by means of TEMPO oxidation method and glass fibre was blended with PLA respectively, and were spun into enhanced PLA wires. This study evaluates the wire rods that is from extruder is suitable for FDM printing by various physical characterization tests to determine their feasibility as a 3D printing filament materials. The cellulose and glass fibre is blended with PLA and spun into the reinforced PLA filament respectively, which is applied to FDM printing technology. The results showed that the intensity of strike resistant of the reinforced PLA filament made from cellulose and PLA is 34% to 60% higher than the PLA filament, meanwhile the tensile strength is 43% to 52% higher than the pure one. The other enhanced PLA filament is 13% to 35% higher than the PLA filament in intensity of strike resistant , and the tensile strength is 54% to 61% higher than the pure one.

1. Introduction

3D printing is a technology which can produce 3D product based on the designed 3D model by the stacking of materials layer by layer in the 3D printing equipment ; which is known as the core technology of " the third industrial revolution" [1]. 3D printing material is the material basis of 3D printing, which is also a technical bottleneck to develop 3D printing further. At present, the raw materials suitable for FDM are only thermoplastic wire[2]. The shortcomings of pure thermoplastics made by FDM are insufficient strength, single function and weak carrying capacity[3]. Glass fiber is popular with most of people for its excellent property and cheaper [4]; research suggested that glass fiber is used to enhance the starch / PLA composites property, when the amount of glass fiber was 4%, the tensile strength of the composites can reach its critical value; Whose amount was over 4%, the enhancement effectiveness is weakened and the roughness of the fracture surface is reduced [5].
Nano-cellulose as a green material can meet the requirement of the current demand for new materials, which shows better performance on improving properties of the material. Someone found that the material casted by polyethylene glycol modified nano-cellulose and polylactic acid solution can enhance the degradation rate and lower its thermal stability[6]. There are also researchers using nano-cellulose as a composite filler preparation of nano-cellulose / polylactic acid composite, which showed that the composite filler can improve the crystallization ability of the polylactic acid in molten state and improve the mechanical properties of the material and improved the flexibility at the same time[7].

In this study, TEMPO oxidation method was used to prepare PLA fiber reinforced with PLA and the wire suitable for FDM was prepared by an extruder. Which was put in the FDM printer to print out the specific shape, whose mechanical properties was tested, so we can obtain the optimum choice of the reinforcing FDM printing material.

2. Preparation of wire samples

Laboratory materials and equipment: PLA(4032D Nature Works, USA); E-glass fiber powder (Fuhua nano new materials company); PBAT modified resin(Dongguan Renju Biological Materials Co., Ltd.); homemade microcellular cellulose; Miniature twin screw extruder(Model SJSZ-10A, Wuhan Ruiming Plastic Machinery Manufacturing Company); Drawing wire drawing machine (Model FQJS-160, Wuhan Ruiming plastic machinery manufacturing company).

The oxygen atoms of C = O in polylactic acid can form hydrogen bonds with the hydroxyl groups in cellulose, but the force is too small to form a sufficient cohesive force. The addition of an affinity solubilizer to both polylactic acid and nanofibers is one of the ways to improve the properties of the composites, PBAT modified resin as a solvent mechanism shown in Figure 1.

The process of wire manufacturing can be summarized as “Particle powder- Heating and melting- Machine out of the machine- Cooling hardening- Shape winding”.

In order to improve the performance of PLA used in FDM in practical use, we blended glass fiber and micro-nano cellulose with PLA particles to prepare enhanced PLA wires respectively. The pure PLA wires and reinforcing PLA wires were placed in the same 3D printer to print out a specific shape respectively, whose physical properties were tested; At the same time, the mechanical properties of the molding materials were observed when the different contents of the reinforcing fibers were added into
the two kinds of PLA respectively, and then we printed out a specific shape whose performance was test; The effect of the added microcellular cellulose content on the performance of PLA was also recorded.

Table 1. Preparation of Silk Specimen

|       | PLA/g | Microcellular cellulose /g | glass fiber /g | PBAT/g |
|-------|-------|-----------------------------|----------------|--------|
| First group | 200   | 0                           | 0              | 5      |
| Second Group | 200  | 10                          | 0              | 5      |
| Third group | 200   | 20                          | 0              | 5      |
| Fourth group | 200   | 0                           | 10             | 5      |
| Fifth group | 200   | 0                           | 20             | 5      |

The PLA, PLA / microcellular cellulose, PLA / glass fiber, which had been mixed up, were dried in an oven at 80 ° C for 8 hours and we should ensure to make the powder fully covered and grain completely dry achieving better performance in the preparation of filament.

The extruded PLA wire and PLA blends Reinforced wire can be harden after exposure to air for approximately 5 s, with the occurrence of a certain degree of contraction. The shape of the wire in the process of cooling will roughly determine the final shape of the wire in this section, so we should narrow the distance between filament machine to the extruder and the extruder. It is important to make the wire which was not completely cooled stereotypes and has a greater degree of toughness round the turntable used to collect the wire, so that the wire will be more intact wound on the turntable, whose thickness is more uniform, and it can make the subsequent FDM sample preparation process more convenient and efficient.

Table 2. Data of different materials in the extruder

|               | Feeding port temperature /°C | Cavity temperature /°C | Extrusion temperature /°C | Extrusion speed /r/min |
|---------------|------------------------------|------------------------|----------------------------|------------------------|
| PLA           | 153                          | 159                    | 135                        | 19.8                   |
| Plus microcellular cellulose | 160                        | 170                    | 140                        | 13                     |
| Plus glass fiber | 160                        | 180                    | 150                        | 15                     |

First, we finished the preparation of PLA wire, acquiring the data in Table 2 after certain test. In the extrusion process, it was found that the color of the PLA wire seemed to be transparent, and the temperature and moisture of PLA particles can cause the appearance of intermittent bubbles inside wire. The cooling rate of wire is faster ,the surface resembling the texture of tempered glass is very smooth and higher hardness. It also possesses higher brittle, which make it bend difficulty after cold-formation, but we can break it off at the bubble part.

Adding the micro-nano cellulose can make the originally close to the transparent color of PLA wire darker. In the process of gradual addition of 4% blend of micro-nano-cellulose PLA, there appearing white granular inside wire; With the amount of wire increasing the color becomes darker but the
final wire sample is beige. It is very clear that the elastic toughness of micro-nano-cellulose blended PLA wire is much better than the original pure PLA wire one via the naked eye observation; The hardness will be correspondingly enhanced while the roughness of wire surface is decreasing.

The surface roughness of glass fiber blended PLA wire material is higher when it is extruded. There will be visible white glitches appearing in the wire surface while the speed of final wire forming color varying is faster than the PLA blending micro-nano-cellulose wire, whose wire surface is rougher than the PLA wire and PLA blended micro-nano-cellulose wire. The color of glass fiber blended PLA wire is close to light gray and its brittleness is relatively higher than PLA. In addition the reinforcing PLA wires are superior to PLA wire in strength, hardness and other aspects.

3. Performance test sample preparation
The shape of the performance test specimen was prepared according to the tensile test of 1B in GB/T1040-2006 and the impact resistance test specimen of GB/T1040-1992. Experimental FDM printer is I3-2020 desktop-level 3D printer, the 3D printing process to control and monitor the software is Repetier Host 1.0.6. The temperature of the nozzle is 220 ℃, the working platform’s temperature is 50 ℃, the filling angle is 45 ℃, the filling type is filled with 100% entity, the filling interval is selected as 0%.

Figure 3. Performance test sample
Figure 4. Tensile specimen

4. Treatment of sample and Test of performance
After the preparation of all the samples, the sample in accordance with national standards was resting in certain condition for a period of time. The impact property of the material was measured on the pendulum impact test machine and tensile strength properties were tested in the computer control electronic universal testing machine. The results are shown as follow.
Figure 5. Impact strength data of the specimen

![Impact strength data](image1)

Figure 6. Tensile strength data of the specimen

![Tensile strength data](image2)

Figure 7. Stress-strain curves of tensile specimens

![Stress-strain curves](image3)

Figure 7 shows that the stress-strain curve of the reinforced PLA wire added with the fiber increases with the increase of the load and the strain gradually increases. When the stress reach critical value, the wire is broken and the stress decreases was pulled off. Compared to the PLA wire, the yarn
yield limit of the fiber was increased, and the stress applied to the fiber was also increased in the case of the same strain.

![Average elastic modulus (E)](image)

**Figure 8.** Average elastic modulus (E)

5. Conclusion

The enhancement effect of cellulose on PLA wire was evaluated from the two aspects of macro and micro. In terms of macro, the appearance, touch and other aspects is considered. First, pure PLA wire is higher brittle. Second its strength and toughness are not particularly good. Third it will be fracture or deformation irreversibly when bended seriously. So that the density of final 3D printing specimen is not high, whose silk lines are obvious. After adding 4% microcellular cellulose, the wire material’s toughness and the bending capacity are both greatly improved while its brittleness is lowered but the elasticity is greatly improved at the same time. When adding 8% microcellular cellulose, there is significant increase in hardness, which caused breaking or cutting it off more difficult. When adding 4% glass fiber, there is increase in hardness while the toughness decreased but its brittleness is slightly increasing. When adding 8% glass fiber, comparing with 4% of the wire, its brittle and hardness have greatly improved while bending and curling appears more blunt.

The perspective of mechanical properties is emphasized on , the result of the effect of different cellulose content on the PLA wire is shown. First the micro-nano-cellulose and glass fiber all can improve the impact resistance of wire and tensile strength; In terms of impact strength, the micro-nano-cellulose can provide good toughness so that the impact strength of the sample is more excellent; when its content ranging from 4% to 8%, the content of blended micro-nano-cellulose is positive correlation with the impact resistance strength of the pieces. As for the tensile strength, the glass fiber has a positive effect on the sample while the content of glass fiber ranging from 4% to 8% , whose variation in increase of tensile strength is not obvious.

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