Preparation and Performance Index Test of Continuous Glass Fiber Reinforced Filament- Polylactic Acid for 3D Printer

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Abstract. The "independent extrusion" 3D printer of Continuous Fiber Reinforced Thermoplastic Composites (CFRTPC) is gradually recognized by the market, but it cannot be widely used due to the limitations of printing materials. This paper focuses on the development of Continuous Glass Fiber Reinforced Filament- Polylactic Acid (CGFRF-PLA) for “independent extrusion” printing. The preparation device of Continuous Fiber Reinforced Filament (CFRF) was designed, and the effects of preparation process parameters such as temperature, speed and coupling agent on the performance index of CGFRF-PLA were studied by experiments, the best preparation process parameters were determined.

1. Introduction

Additive manufacturing (AM) is the most promising method for manufacturing complex structural parts [1]. Compared with traditional manufacturing methods, AM technology can shorten the design and manufacturing cycle, reduce production costs and improve competitiveness [2]. Among many AM technologies, fused deposition manufacturing (FDM) has attracted much attention due to its low cost and simple operation to use feature [3]. Polylactic acid (PLA), which is often used in FDM model making, is a kind of biodegradable material derived from renewable resources. As an environmentally friendly material, PLA is widely used in FDM. However, the strength of PLA is too low and the brittleness is too high, which limits its industrial application. How to improve the strength of PLA, reduce its brittleness and apply it to industrial products is one of the hot issues in the field of AM manufacturing. In recent years, many scholars have tried to apply CFRTPC, a method of preparing composite materials in the field of aerospace manufacturing, to the field of AM. At present, the research on 3D CFRTPC printing of "independent extrusion" is based on the printer and materials provided by Markforged Inc[4]. However, the sizing agent on the surface of CFRF is PA6, which can only effectively enhance the strength of CFRF-PA6. There is almost not CFRF for "independent extrusion" printing of other thermoplastic materials.

The research of fiber-reinforced FDM printing based on PLA mainly focuses on short fiber-reinforced [5]. However, the reinforcement of continuous fibers to PLA is mainly focused on the study of “co-extrusion” printing method. Nanya et al. [6] found that the interfacial strength between carbon fiber and PLA can be effectively improved by pretreating carbon fiber with polylactic acid sizing agent, the tensile strength and flexural strength of the continuous carbon fiber reinforced PLA were 13.8% and 164% higher than those of the original carbon fiber reinforced PLA, respectively. Heidari-Rarani et al. [7] showed that the tensile strength and flexural strength of continuous carbon fiber reinforced PLA specimens increased by 35% and 108% respectively compared with pure PLA. The
research of J.M. Chacón et al. [8] is based on the CFRTPC printers of markforged series, so the CFRTPC printers and the range of materials is limited.

In this study, a set of devices for preparing CFRF was designed. In order to overcome the material limitation during "independent extrusion" printing, the research on 3D printing of CFRTPC-PLA is supplemented. The influence of the preparation process parameters such as temperature and speed and coupling agent on the performance index of CFRF was studied through the experiments, and the best preparation process parameters of CFRF that can be used for FDM printing were determined. Furthermore, the diameter, roundness, stiffness, the tensile strength of monofilament and tensile/flexural strength of CFRF printing samples were measured to observe the effect of silane coupling agent on CFRF.

2. Preparation for experiment

The preparation device of CFRF was designed to prepare CGFRF-PLA, as shown in Figure 1. The surface of continuous pure filament can be coated with sizing agent through the device. The equipment mainly includes the following modules: continuous filament unwinding module, wetting coupling agent module, sizing agent feeding module, melting module, sizing module, cooling module and CFRF rewinding module, etc.

![Figure 1. The preparation device of CFRF.](image)

2.1. Materials and targets

In addition, the continuous fiber composite 3D printer is provided by Suzhou Bofei Yicheng Electromechanical Co., Ltd. And it can be seen that the diameter, roundness and stiffness of the CGFRF used for printing must meet certain requirements from Table 1. The CGFRF-PLA consumables prepared in this paper can be used for printing only in the range of parameter requirements. The continuous pure glass fiber (GF) is provided by Jiujiang Huachen Glass Fiber Co., Ltd. The diameter of sizing agent supplied by Shenzhen Esun Co., Ltd. is 1.75mm toughened PLA. The surface of glass fiber was treated with silane coupling agent (KH560, KH550), which can improve the wettability between GF and PLA, make the chemical reaction between GF surface and PLA, then form the binding layer of organic matrix - silane coupling agent - inorganic matrix. The detailed performance parameters of materials are shown in Table 2 and table 3.

| Categories                  | Technical parameter |
|-----------------------------|---------------------|
| Diameter/mm                 | 0.45±0.05           |
| Roundness/mm                | 0.01-0.02           |
| (150mm) Stiffness/mm        | >100                |

Table 1. Parameter requirements of CGFRF.
Table 2. Performance parameters of sizing agent PLA.

| Categories                          | Performance parameters |
|-------------------------------------|------------------------|
| Melt index (190℃/2.16kg)           | 2                      |
| Tensile strength (MPa)              | 60                     |
| Breaking elongation (%)             | 29                     |
| Flexural strength (MPa)             | 87                     |
| Flexural modulus (MPa)              | 3642                   |
| Printing temperature (℃)            | 205-225                |

Table 3. Performance parameters of GF.

| Categories                          | Performance parameters |
|-------------------------------------|------------------------|
| Glass category                      | E                      |
| Yarn category                       | C (Continuous fiber yarn) |
| Nominal diameter of single wire     | 9μm                    |
| Strands                             | 2                      |
| Ply diameter                        | 0.18mm                 |
| Twisted or not                      | Twisted                |
| Twist direction                     | S                      |

3. Effect of process parameters on the performance of CGFRF-PLA

3.1. Effect of temperature on the performance of CGFRF-PLA

The melt cavity temperature affects the viscosity of sizing agent PLA, and the viscosity of PLA decreases with the increasing of temperature. The viscosity of PLA plays a decisive role on the coating effect. Therefore, the appropriate melt cavity temperature is very important for the preparation of CFRF. The optimal temperature can be determined by changing the melt cavity temperature and observing the condition of the resin coated on the surface of the GF. First, find the best temperature range. The test temperature are 180 ℃, 190 ℃, 200 ℃, 210 ℃ and 220 ℃, respectively. The experimental phenomena are shown in Table 4.

Table 4. Effect of melt cavity temperature on the results

| Temperature  | phenomenon                                                                 |
|--------------|-----------------------------------------------------------------------------|
| 180/190℃     | The PLA on the surface of the fiber is less and the fiber often breaks.    |
| 200℃         | The PLA on the surface of the fiber increased, and occasionally the filament breaks. |
| 210℃         | The increase of PLA on the surface of the fiber is almost stable, and there is no breakage. |
| 220℃         | The diameter of CFRF at the outlet of the melt cavity is uneven, and there is no broken wire and overflow. |

It can be seen from the test phenomena in the table 4 that when the melt cavity temperature is between 180 and 210℃, the PLA on the surface of CGFRF-PLA at the outlet of the melt cavity is few, so it is difficult to successfully prepare continuous CGFRF-PLA. This is because the temperature is low, the tension of PLA melted in the melt cavity is large, and the fluidity is poor and the GF will be worn and broken when passing through, when the temperature is 220℃, it is so high that the fluidity of the sizing agent PLA is too large and the material overflows from the outlet of the melt cavity. It can be seen that the optimal melt cavity temperature is in the range of 210-220℃. In order to find the optimal melt cavity temperature, further test is carried out in the range of 210-220℃. The experimental phenomena are shown in Table 5.
Table 5. Test phenomena of the optimal temperature experiment.

| Temperature | phenomenon |
|-------------|------------|
| 210/212°C   | The increase of PLA on the surface of the fiber is nearly stable. |
| 214/216°C   | The PLA coating on the surface of the fiber is uniform. |
| 218°C       | The diameter of the CGFRF at the outlet of the melt cavity is uneven, and few PLA overflows from melt cavity. |
| 220°C       | The diameter of the CGFRF at the outlet of the melt cavity is uneven, more PLA overflows from melt cavity. |

It can be seen from the test phenomena in Table 7 that the optimal melt cavity temperature is 214±2°C. At this temperature, the PLA has good fluidity and good viscosity wrapped GF, which is suitable for the preparation of CGFRF-PLA.

The sizing temperature ensures the uniformity of diameter and the stability of roundness error of CGFRF-PLA. In order to find the proper sizing temperature, the test is carried out when the sizing temperature is in the range of 180-210 °C, and the experimental phenomena are shown in Table 6.

Table 6. Experimental phenomenon of the sizing temperature

| Temperature | phenomenon |
|-------------|------------|
| 180/185°C   | The CGFRF was slightly cooled and solidified at the sizing hole, and the CGFRF was broken. |
| 190°C       | Reduction of solidification and fracture. |
| 195/200°C   | There is not solidification phenomenon, CGFRF through the sizing module dose not break. |
| 205/210°C   | The flow of PLA on the CGFRF causes the diameter to decrease. |

According to the test phenomena in Table 6, it can be seen that CGFRF-PLA is frequently broken when the sizing temperature is between 180°C and 185°C, resulting in the failure of the preparation of CGFRF-PLA. With the increasing of the sizing temperature, the fracture phenomenon of CGFRF-PLA decreased. When the sizing temperature is between 195 and 200°C, CGFRF-PLA can stably pass through the sizing module without breaking. However, with the increasing of temperature, the PLA on the surface of CGFRF-PLA is less. The reason is that when the sizing temperature is too low, the CGFRF-PLA has cooled and solidified at the inlet of the sizing module, leading to the pulling of the CGFRF-PLA when passing through the sizing module. When the sizing temperature is too high, the sizing agent PLA on the surface of CGFRF-PLA melts and loses in the sizing module, resulting in the diameter of CGFRF-PLA too small and it is uncontrollable. Therefore, the sizing temperature of CGFRF-PLA is suitable in the range of 195-200°C.

3.2. Effect of speed on the performance of CGFRF-PLA

In order to ensure the supply of sizing agent PLA needed for the preparation of CGFRF-PLA, the feeding speed and the winding speed should meet a certain proportion relationship. Therefore, the theoretical velocity ratio of the two motors is calculated according to the preparation device of CFRF.

The diameter of extruder wheel of feeding mechanism is $D_1 = 11\, mm$, and the diameter of PLA is $d_1 = 1.75\, mm$. The diameter of the winding wheel of the winding mechanism is $D_2 = 85\, mm$, and the diameter of the wire outlet of the melting cavity is $d_2 = 0.55\, mm$. The diameter of glass fiber is $d_3 = 0.18\, mm$.

In the unit time, feeding volume $V_1 = \pi D_1 n_1 \cdot S_1$ is equal to the discharging volume $V_2 = \pi D_2 n_2 \cdot S_2$, that is

$$V_1 = V_2$$  \hspace{1cm} (1)

According to formula (2-1), the ratio of feeding speed to winding speed is $n_1 : n_2 = 2 : 3$. 

In order to obtain the optimal speed, further tests were carried out. In the experiment, the chamber temperature is 214±2℃ and the sizing temperature is within the range of 195-200℃. The test phenomena are shown in Table 7.

Table 7. Experiment phenomenon of speed matching.

| Winding speed(r/s) | Feed speed(r/s) | Phenomenon                                                                 |
|-------------------|----------------|---------------------------------------------------------------------------|
| 0.035             | 0.023-0.028    | The PLA on the surface of CGFRF-PLA at the outlet of melt cavity is less.  |
|                   | 0.029          | The PLA on the surface of CGFRF-PLA at the outlet of melt cavity is relatively low and tends to be normal. |
|                   | 0.030          | The coating of slurry PLA on the surface of CGFRF-PLA at the outlet of melt cavity is relatively uniform and without overflow. |
|                   | 0.031          | The coating of slurry PLA on the surface of CGFRF-PLA at the outlet of melt cavity is relatively all, but there is slight overflow. |
|                   | 0.032          | Excessive and uneven coating of slurry PLA on the surface of CGFRF-PLA at the outlet of melt cavity leads to serious overflow. |
| 0.04              | 0.027-0.032    | The PLA on the surface of CGFRF-PLA is less.                              |
|                   | 0.033-0.035    | The PLA on the surface of CGFRF-PLA at the outlet of melt cavity is less covered by PLA, and overflow occurs. |

Table 7 shows the test phenomenon of the effect of speed on CGFRF-PLA molding. It can be seen that when the winding speed is 0.040r/s, no matter the feeding speed of sizing agent PLA is fast or slow, the sizing agent wrapped on the surface of CGFRF-PLA is less. This is because the volume of the melt cavity is certain and the winding motor speed is too fast, so the fiber bundles are not fully impregnated in the melt cavity. When the winding speed is reduced to 0.035r/s and the feeding speed of sizing agent PLA is from 0.023r/s to 0.03r/s, the sizing agent PLA wrapped on the surface of CGFRF-PLA at the exit of the thread increased and tends to be stable. When the feeding speed is between 0.023 and 0.028r/s, the PLA on the surface of CGFRF-PLA is less, because the feeding speed is so slow that the sizing agent PLA cannot fill the melt cavity. When the feeding speed of sizing agent PLA is higher than 0.031r/s, the feeding speed is much higher than the discharging speed, which causes the PLA to overflow from the melt cavity.

Therefore, when the feed speed is 0.030r/s and the winding speed is 0.035r/s, and the PLA on the surface of CGFRF-PLA is wrapped well without overflow. The actual speed ratio is \( n_1 : n_2 = 6 : 7 \).

In conclusion, the CGFRF-PLA material can be used for 3D printing when the following process parameters are adopted: melt cavity temperature is 214 °C± 2 °C, sizing temperature is 195-200 °C, the feeding speed of PLA is 0.030r/s, winding speed is 0.035r/s. The printing process of CGFRF-PLA is shown in Figure 2.

Figure 2. Printing test of CGFRF-PLA prepared.
3.3. Effect of coupling agent on the performance of CGFRF-PLA

The weak bonding between PLA and GF will significantly affect the mechanical properties of the component. In order to effectively transfer stress and obtain better comprehensive mechanical properties, the surface of GF was treated with silane coupling agent. In order to study the effect of silane coupling agent on the properties of CGFRF-PLA, three kinds of CGFRF-PLA (KH550, KH560 and untreated) were prepared. And the performance index was tested.

The diameter and roundness are measured by electron microscope (Leica DM6A). In order to get more accurate data, 50 sections of each are randomly selected for observation and measurement, the cross section of CGFRF-PLA is shown in Figure 3.

![Figure 3. CGFRF-PLA section.](image)

3.3.1. Diameter. First, select a point on the section as the end point of the line, and the other end point is any point of the circle. Then measure the length of a line and regard the maximum value as the first data. rotate 60° for each measurement and measure three times following the method. Take the average value of the three data as diameter \( d \) (mm) of CGFRF-PLA. 50 sections were selected for measurement. The measurement results were as follows.

Figure 4 shows the diameter distribution of CGFRF-PLA. It can be seen that the diameter distribution of CGFRF-PLA infiltrated by coupling agents KH560 and KH550 is concentrated at 0.45mm. The mean value and the median value of the fitting curve are basically coincide and they all meet the requirements. However, the diameter of CGFRF-PLA without coupling agent was smaller and mainly distributed at 0.43mm. The reason is that without silane coupling agent, the adhesion between GF and PLA is poor, resulting in less PLA wrapped on the surface of glass fiber.

![Figure 4. Diameter distribution of CGFRF-PLA.](image)
3.3.2. Roundness. The roundness of CGFRF-PLA was measured by two-point method. Half of the difference between the maximum diameter and the minimum diameter of the continuous glass fiber section was taken as the result. And 50 sections were selected for measurement. The measurement results were as follows.

![Figure 5. CGFRF-PLA roundness error distribution.](image)

Figure 5 shows the distribution of CGFRF-PLA. It can be seen that the roundness error distribution of CGFRF-PLA is mainly between 0.005 and 0.02mm, independent of the presence or absence of coupling agent infiltration, and the median value is 0.01-0.015mm. All kinds of CGFRF-PLA meet the printing requirements.

3.3.3. Stiffness. The stiffness measurement refers to standard (GB/T 7690.4-2013). 5 sections of 150 mm CGFRF-PLA were randomly selected as samples, which were suspended on a stainless steel hook for at least 30s after standing. And the distance between the two ends 30 mm below the suspension point was taken as the stiffness index.

| Serial number | Distance/mm | 1   | 2   | 3   | 4   | 5   | Mean  |
|---------------|-------------|-----|-----|-----|-----|-----|-------|
| KH560         | 115         | 113 | 113 | 114 | 115 | 114.6|       |
| KH550         | 113         | 113 | 114 | 112 | 113 | 113  |       |
| None          | 113         | 112 | 114 | 113 | 112 | 112.8|       |

From table 8, it can be seen that the stiffness of CGFRF-PLA prepared by three processes is greater than 100mm. According to the mean value, the stiffness of CGFRF-PLA prepared by GF impregnation with coupling agent KH560 is the highest, but the difference is not significant. Each kind of CGFRF-PLA can be used for printing.

3.3.4. Mechanical properties. CGFRF-PLA is prepared for 3D printing. On the basis that the diameter, roundness and stiffness performance indexes of CGFRF-PLA meet the requirements, the mechanical properties of CGFRF-PLA and CGFRTPC-PLA printed with CGFRF-PLA also need to be studied. The tensile strength of CGFRF-PLA monofilament was tested, and the CGFRTPC-PLA standard sample [9] was prepared by using the printing parameters in Table 9. The tensile/flexural tests were carried out to analyze the effect of CGFRF-PLA on the mechanical properties of FDM printed samples. In each experimental group, five samples are prepared to obtain the average value of the target performance as the result. The tensile strength was tested by universal testing machine (xdl-100k, Xinhong testing machine factory, China). The tensile speed used in the measurement is 5mm/s.
Figure 6. CGFRTPC-PLA standard sample sample: (a) Tensile test sample; (b) Bending test sample

Table 9. Slice and print parameters.

| Name                        | Parameter       |
|-----------------------------|-----------------|
| Thickness                   | 3.2mm           |
| Printing layer height of base layer | 0.2mm       |
| Printing layer height of fiber layer | 0.2mm     |
| Substrate printing temperature | 215°C         |
| CGFRF-PLA printing temperature | 215°C        |
| CGFRF-PLA printing speed    | F500            |
| layers of fiber             | 3               |
| Number of loops in the same layer | 0-6          |

- Mechanical properties of CGFRF-PLA monofilament
  The tensile strength of CGFRF-PLA monofilament was tested under three different process conditions and universal testing machine was used for tensile test.

![Tensile curve of CGFRF-PLA monofilament.](image)

Figure 7. Tensile curve of CGFRF-PLA monofilament.

It can be seen from the tensile curve of CGFRF-PLA monofilament in Figure 7 that the tensile strength of CGFRF-PLA monofilament prepared by different coupling agents is not the same. The tensile strength of CGFRF-PLA monofilament infiltrated by coupling agent KH560 is better than that of other two. The tensile strength of CGFRF-PLA monofilament without coupling agent is the worst. The reason is that the chemical reaction between the coupling agent on the surface of glass fiber and sizing agent PLA, which can strengthen the bonding between the two materials. It can be seen from the results that the tensile strength of CGFRF-PLA monofilament treated with coupling agent KH560 is better than that treated with KH550, and the tensile strength of CGFRF-PLA monofilament is 379.81mpa, which is 115.87% higher than that of untreated CGFRF-PLA monofilament.

- Mechanical properties of printing samples by FDM
  The tensile strength of CGFRF-PLA monofilament is the highest with treated by coupling agent KH560. However, due to the small cross-sectional area of the composite monofilament, it is necessary to further test the performance of CGFRF-PLA reinforced materials in FDM printed samples.
Three kinds of reinforced materials were used to prepare printed samples. 5 groups of experiments were conducted using different CGFRF-PLA, and there were 7 samples in each group. Three layers of CGFRF-PLA reinforced materials are laid, and CGFRF-PLA layers are evenly distributed in printed samples. The number of turns is increased from 0 to 6 in each layer. The following figure lists the tensile/flexural test data (each value is the average value of the test results of the same five groups of samples as the result). The number of turns is related to the volume fraction of CGFRF-PLA.

It can be seen from the Figure 8 that the tensile/flexural strength of CGFRF-PLA printed samples treated with coupling agent is higher than that without coupling agent. In addition, the effect of KH-560 is better than KH-550, and with the increasing of CGFRF-PLA, the tensile/flexural strength become larger obviously. The tensile/flexural strength were 94.97Mpa and 113.80Mpa, respectively, which was were 126.42% and 115.77% higher than that of untreated CGFRF-PLA printed samples. The reason is that the use of coupling agent can improve the interfacial adhesion between glass fiber and PLA resin material, which can better play the reinforcement effect of glass fiber, and the effect of different coupling agent is different. with the increasing of the volume fraction of CGFRF-PLA, the reinforcement effect of coupling agent is more obvious.

4. Conclusion

In this study, a preparation device of CFRF based on "independent extrusion" FDM CFRTPC printer was designed. The preparation process parameters of CGFRF-PLA were studied, and the influence of process parameters on the performance index of CGFRF-PLA was analyzed. The conclusions are as follows.

The results showed that when the melt cavity temperature was 214±2°C, the sizing temperature was 198±2°C, the winding speed was 0.035r/s and the feed speed was 0.03r/s, the performance index of CGFRF-PLA was the best and it can meet the requirements of FDM printing. The use of coupling agents KH550 and KH560 can enhance the diameter, roundness and stiffness of CGFRF-PLA, and increase the tensile strength of CGFRF-PLA monofilament. But, the effect of KH560 is better. The tensile strength of CGFRF-PLA is 375.01MPa, and the tensile/flexural strength of printing samples prepared by CGFRF-PLA are respectively 94.97Mpa and 113.80Mpa.

References
[1] Y. Song, Y. Li, W. Song, K.Y. Lee, V.L. Tagarielli, Measurements of the mechanical response of unidirectional 3D-printed PLA. Mater. Des. 123 (2017) 154–164.
[2] X. Wang, M. Jiang, Z. Zhou, J. Gou, D. Hui, 3D printing of polymer matrix: a review and prospective, Composites: Part B 110 (2017) 442–458.
[3] J.M. Chacón, M.A. Caminero, E. García-Plaza, P.J. Nuñez, Additive manufacturing of PLA
structures using fused deposition modelling: effect of process parameters on mechanical properties and their optimal selection, Mater. Des. 124 (2017) 143–157.

[4] MarkForged, MarkForged MarkTwo, https://Markforged.Com/.

[5] Devin Young, Nelson Wetmore, Michael Czabaj, Interlayer fracture toughness of additively manufactured unreinforced and carbon-fiber-reinforced acrylonitrile butadiene styrene, Additive Manufacturing. 22 (2018) 508–515.

[6] Nanya Li, Yingguang Li, Shuting Liu, Rapid prototyping of continuous carbon fiber reinforced polylactic acid composites by 3D printing. Journal of Materials Processing Technology, 2016. 238: p. 218-225.

[7] M. Heidari-Rarani, M. Rafiee-Afarani, A.M. Zahedi, Mechanical characterization of FDM 3D printing of continuous carbon fiber reinforced PLA composites. Composites Part B: Engineering, 2019. 175: p. 107147.

[8] J.M. Chacón, et al., Additive manufacturing of continuous fibre reinforced thermoplastic composites using fused deposition modelling: Effect of process parameters on mechanical properties. Composites Science and Technology, 2019. 181: p. 107688.

[9] ASTM D3039/D3039M, ASTM standard test method for tensile properties of polymer matrix composite materials. Book ASTM Stand. 15 (2012) 1–10.

[10] ASTM D790, ASTM standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials. Book ASTM Stand.10 (2010) 1–11.