PRODUCTION OF CONTINUOUS CARBON FIBER REINFORCED POLYAMIDE FILAMENTS FOR MICROWAVE ADDITIVE MANUFACTURING

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ABSTRACT

Additive manufacturing, also known as three-dimensional (3D) printing, has been developed for more than 30 years for potential applications in aerospace, automotive and medical treatment. Benefiting from the computer-aided design, numerical and automatic control, the 3D printing becomes a burgeoning method and may lead to a revolution in the manufacturing industry. Continuous carbon fibers are promising reinforcement materials to improve stiffness and strength properties of the 3D printed plastics. Traditional additive manufacturing methods of fused filament fabrication (FFF) have a slow printing speed of small diameter continuous carbon fiber reinforced thermoplastic (CFRTP) filaments, because of the low efficiency and contact needed heat transfer disadvantages of the resistive heating approach. The microwave additive manufacturing by using instantaneous, selective and volumetric microwave heating, can fabricate large diameter CFRTP filaments with higher speed than the state-of-the-art printing methods. In this paper, the production process of large diameter continuous carbon fiber reinforced polyamide filaments is introduced. The polyamide sizing agent is applied to improve the bonding strength between carbon fiber and matrix resin. Carbon fiber volume frication and voids of the filaments are investigated.

1. INTRODUCTION

Advanced carbon fiber reinforced thermoplastic polymer composites are widely applied in aerospace and automotive industries, because of high impact resistance, advantages regarding recyclability and repairability as compared with thermoset composites. Usually, traditional ways to process such fiber-reinforced thermoplastic composites are based on autoclave and hot pressing forming technologies [1]. However, there are serious problems that restrict the development of current technologies. For example, 1) impossible to form complex composite structures, such as complex lattice truss or bionic parts; 2) difficult to achieve manufacturing of complete parts, therefore mounting holes need to be drilled after forming; 3) long manufacturing cycle and high energy consumption, as huge amount of time and energy are wasted on heating gas medium in oven. The above bottlenecks should be addressed to manufacture complex composite structures, improve performance and cut down cost.

Recently, a particular 3D printing method of fused filament fabrication (FFF) has been investigated to manufacture composite materials [2, 3]. Various ways were developed to improve mechanical properties of these composites printed by such FFF method. For example, Li et al. [4] researched continuous carbon fiber reinforced thermoplastic (CFRTP) composites printed by in-nozzle impregnation to improve tensile strength. The experimental results indicate that the FFF printed CFRTPs have higher Yong's modulus than the plastic one fabricated by stereo lithography (SLA) [5]. By using recycled continuous carbon fiber, the measured bending strength of the CFRTP composite is improved [6]. Impact strength of printed CFRTP increases as layer thickness increases in flat testing samples [7]. The average specific strength of 3D printed continuous Kevlar fiber reinforced Polylactide composite is comparable to the conventional production process [8]. Hu et al. [9] studied the mechanical properties of 3D printed continuous carbon fiber reinforced composite, and indicated that the small layer thickness and low printing speed can increase the flexural strength of printed part. Besides the research works of mechanical characterization of printed samples, the dimension of the CFRTP filaments with continuous carbon fibers and high carbon fiber volume content that were used for printing until now is less than 0.4 mm. For example, CFRTP filaments used by Markforged are about 0.35 mm diameter [10] and another filament reported by Liu et al. is about 0.4 mm (44% fiber volume content) [11]. Matsuzaki et al. can print 1.4 mm diameter filaments, but the filament has only 6.6% carbon fiber volume content [5].

Table 1. Different 3D printing methods of fiber reinforced composites

Printing method	Represented works	Continuous fiber reinforced	Printing speed	Volumetric heating	Non-contact heat transfer
Resistive heating	[12]	√√	×	×	×
Laser bonding	[13]	√√	√	×	×
UV light printing	[14]	√	√√	×	√√
Microwave printing	this work	√√	√√	√√	√√

The above-mentioned research works and achievements prove the considerable efforts in the ongoing development of composite 3D printing. However, the challenges of slow printing speed and small printing diameter of the CFRTP filaments still exist. To solve this problem, other efficient heating solutions should be studied. As shown in Table 1, four different kinds of heating method are compared and discussed. The traditional resistive heating cannot quickly and uniformly heat fiber reinforced filament, which results in small end-use products with extremely low printing speed. Laser bonding process can only heat the surface of the CFRTP and scan the whole area point by point with limited speed. UV or digital light shows a fast printing speed and good surface quality, without introducing continuous fiber reinforcements. A new microwave assisted additive manufacturing process has been innovated by the authors to improve the printing speed, print large diameter CFRTP filaments and save energy consumption, compared to traditional printing processes. The first prototype of a 3D microwave printer named SERPENS (Super Efficient and Rapid Printing by Electromagnetic-heating Necessitated System) has been designed and manufactured, and a printing speed as high as 100 mm/s has be achieved so far with the assistance of a temperature control system [15]. Compared with conventional forming process of composite materials, like autoclave and hot pressing, the microwave additive manufacturing process only needs three steps to fabricate composite parts, as shown in Figure 1.

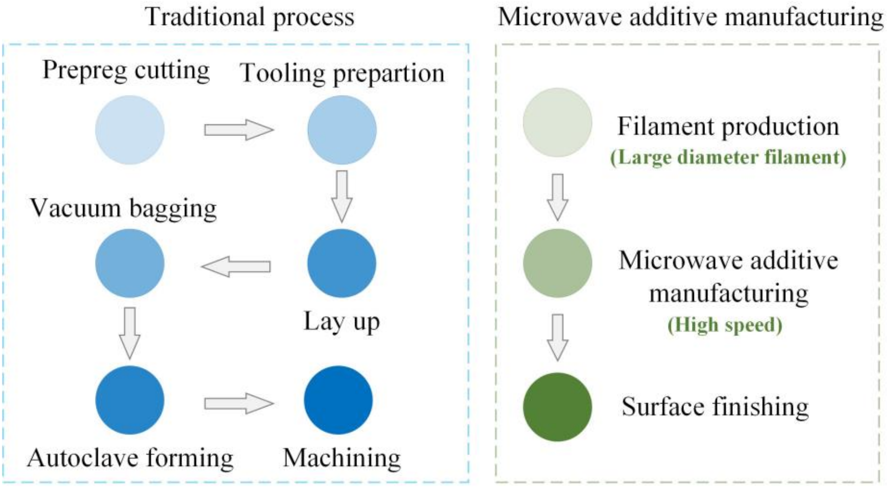

Figure 1. Difference between traditional composite manufacturing and microwave additive manufacturing process

In traditional process, generally, the composite prepreg needs to be cut to different shapes and lay up on a tooling, and then the materials packaged with a vacuum bag will be heated in the autoclave. After the hot-forming process, the composite parts need to be machined, such as drilling and edge cutting. However, for the microwave additive manufacturing, composite parts have been printed to demanded geometries rapidly without tooling and multiple preparation steps. During the printing process, the pre-prepared continuous carbon fiber reinforced thermoplastic filament is heated inside an elaborately designed resonant microwave applicator. The microwave is coupled into the applicator through a coaxial microwave port and heats the filament without contact. Thanks to the advantage of volumetric and selective heating, even the large diameter filaments are quickly heated, while the applicator and the surrounding media remain at room temperature. To improve the mechanical strength and print large diameter filaments during the microwave additive manufacturing process, the production process of large-diameter continuous carbon fiber reinforced polyamide filaments have been introduced. The polyamide sizing agent is applied to improve bonding strength between carbon fiber and matrix resin.

2. EXPERIMENTATION

2.1 Production of CFRTP filaments

The polyacrylonitrile-based continuous carbon fibers (HTA40 1K 67tex and HTS40 6K 400tex) were used and the matrix resin was a 910 polyamide (PA) filament (1.75mm diameter, melting temperature: 190°C-255°C) from Taulman3D. The PA845 nylon sizing agent (Michelman company) was applied to treat the carbon fiber surface and enhance the interfacial strength between fiber and matrix. The process schematic for the production of continuous carbon fiber reinforced polyamide filaments is shown in Figure 2. Firstly, the as received carbon fibers have to go through a hot end to complete a desizing process, which is to heat the fiber in atmosphere at 420°C. Before the fibers enter into a sizing pool, a fan has been used to cool them to room temperature. Then the fibers are guided through a sizing pool filled with PA845 to be infiltrated. Because the sizing agent contains solvents and affects the polyamide resin, a dry hot end should be applied to pre-heat the fiber and volatilize the solvents. Finally, a hot impregnation die mixes the carbon fiber and the molten PA and compresses the filament into a uniform diameter. The compressed filament has a circular cross-section and two pultrusion rollers provide sufficient pulling force for the continuous production of filaments, which then have been winded on a spool, as shown in Figure 2. The diagram production system for filament impregnation is shown in Figure 3. About 2 mm/s production speed is applied during the production process of the 1K and 6K carbon fibers. In these experiments, four different diameters have been produced and tested, i.e. 0.35 mm, 0.45 mm, 0.85 mm and 1.05 mm.

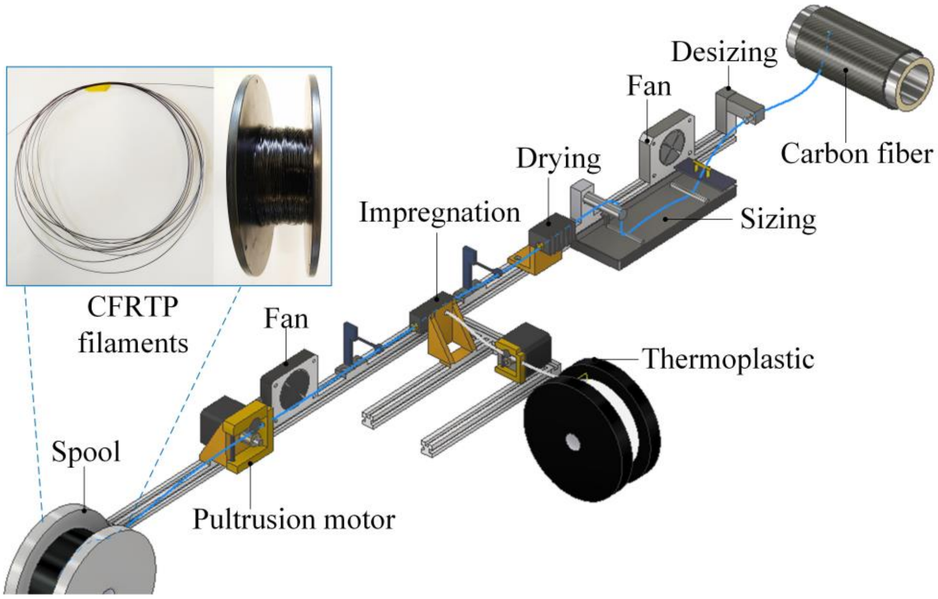

Figure 2. Design concept of the CFRTP filament production system.

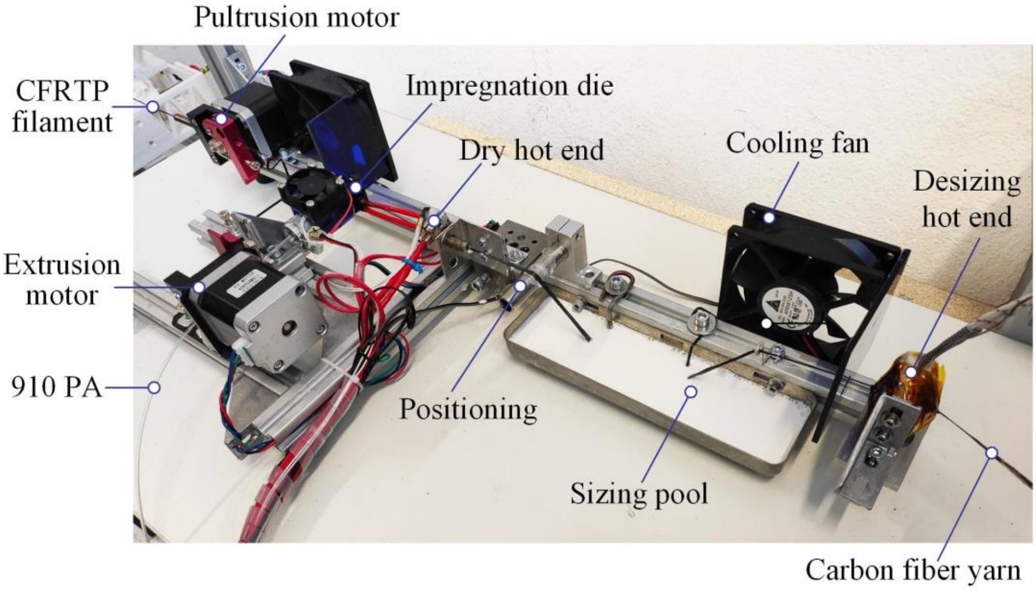

Figure 3. Diagram of CFRTP filament production system.

2.2 Design of the impregnation die

As shown in Figure 4(a), the impregnation die has a slender heating chamber and a resistive heater has been installed near the chamber. The treated carbon fibers go inside the chamber continuously due to the pull force from two pultrusion rollers. The polyamide filaments have been pushed into the heating chamber with the help of a filament extruder (used for a FDM printing process). A copper-based jet nozzle has been installed on an aluminum die, as shown in Figure

4(b). The diameter of the produced filaments can be easily modified by changing the copper jet nozzle to different diameters.

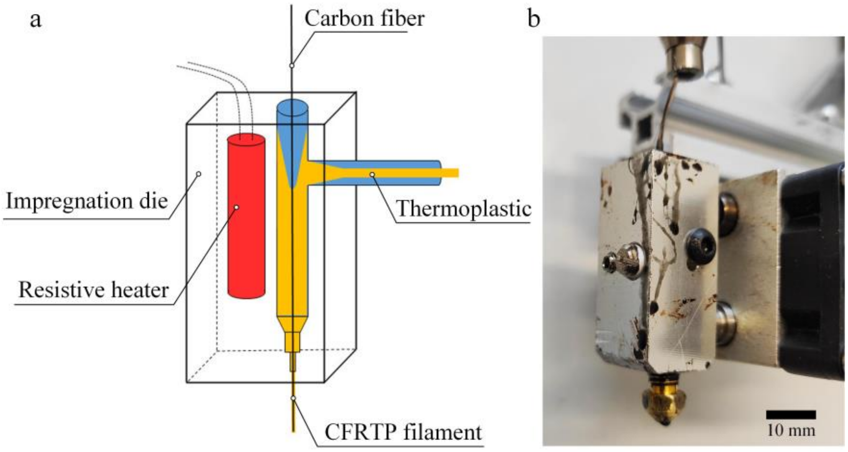

Figure 4. (a) Schematic of the impregnation die, (b) impregnation die made of aluminum.

3. RESULTS

3.1 Desizing and surface treatment process

Since mechanical properties of carbon fiber reinforced polymer composites have a strong relationship with interfacial strength between the fiber and matrix resin, the sizing agent of the carbon fiber should be selected appropriately to increase interfacial strength. Generally, commercial carbon fibers have an epoxy sizing agent (6K 400tex is EP sizing for epoxy resin, sizing level is 1.3%) and can hardly bond to the thermoplastic. Therefore the original thermoset based sizing of the carbon fibers should be removed and then coated with thermoplastic sizing agent. Usually solvents like acetone or ethanol are used for desizing the carbon fibers, but the long processing time and required solvent temperature of at least 50°C are not advantageous for a continuous production line. In this paper, a thermal pre-treatment by heating carbon fibers to 420°C in atmosphere is applied based on the research results of Ahmed et al. [16]. By measuring the weight loss reveals that the sizing agent begins to decompose at 400ºC and strong weight loss appears at temperatures higher than 500ºC. Temperatures of more than 420°C could lead to surface damages of the carbon fibers. Hence, our processing temperature was set up to 420°C. After the desizing process, the carbon fibers cool down quickly with a fan and then go through a sizing pool that is filled with PA845. The carbon fibers after desizing process is shown in Figure 5(a). The surface of carbon fiber becomes rough and fibers separate to each other. The carbon fibers coated with polyamide sizing are shown in Figure 5(b). It is obvious that the fibers gather together due to the surface tension of the solvent and the low viscosity (maximum 100 cps) of the sizing ensures a homogenous coating of carbon fibers.

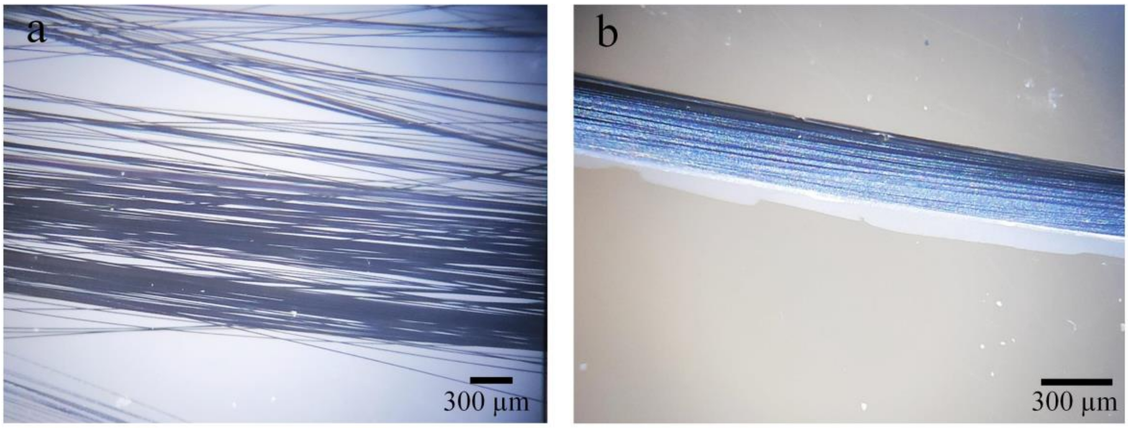

Figure 5. (a) Carbon fibers after desizing, (b) carbon fibers with polyamide sizing.

3.2 Characterization of the produced filaments

The manufactured CFRTP filaments with different diameters are shown in Figure 6(a). It is seen that the filaments have smooth surface and uniform diameters. In this experiment, the 1K carbon fibers are applied as reinforcements in the 0.35 mm, 0.45 mm, and 0.85 mm diameter filaments, and the 6K carbon fibers are used in the 1.05 mm diameter filament. The surface quality of the filament with1.05mm diameter is shown in Figure 6(b). Because of different diameters and fiber volume contents, the produced filaments show different stiffness.

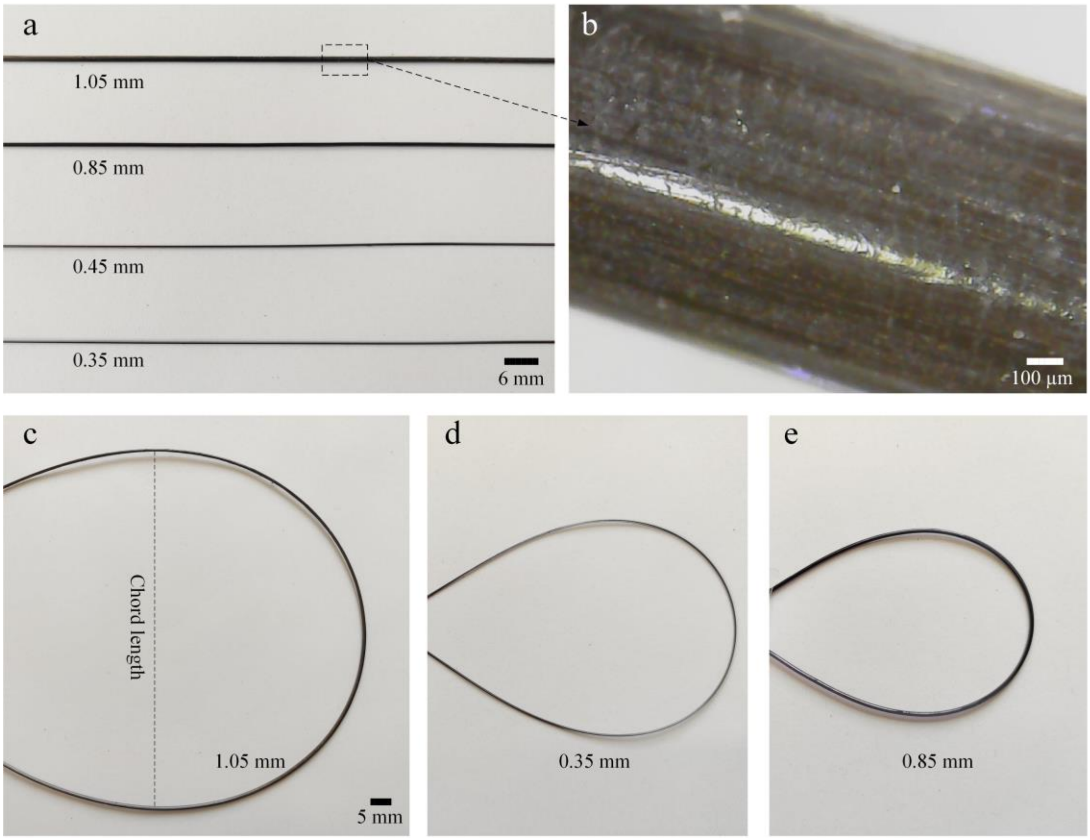

Figure 6. (a) Comparison of the fabricated CFRTP filaments with different diameters and fiber volume contents, (b) magnified 1.05 mm filament, (c), (d) and (e) curved 1.05 mm, 0.35 mm, and 0.85 mm filaments.

Figure 6(c) and (d) show a measurement of chord length of different filaments. All of the three illustrations have the same scale mark. The filaments have been bended to the maximum position until them break and the chord length is measured when it verticals to the tangent of the maximum curvature. The measurement results exhibited that the 1.05 mm filament has the highest stiffness and the chord length is about 85 mm. The 0.85 mm filament has the lowest stiffness and the measured chord length is about 43 mm, because of its low fiber volume content. According to the single carbon fiber diameter and the number of 1K and 6K types, the approximate carbon fiber volume content can be calculated. The 0.35 mm, 0.45mm, 0.85mm, and 1.05 mm diameter filaments have carbon fiber volume content of 40%, 24%, 7% and 27%, respectively. Cross-sectional optical images of the produced filaments are shown in Figure 7. Due to that carbon fibers are very thin (7µm diameter) and have semi-conductive properties (electric resistivity: $1.6\times10^{-3}\Omega\cdot\text{cm}$), the arcing of the carbon fibers appears under the electromagnetic radiation may happen. Thus, each fiber needs to be coated with the polyamide resin. Because the carbon fibers in our work are treated with polyamide sizing before the impregnation process, they are aggregated together inside the filaments and covered around by the polymer resin. There are only few voids in the 1K fiber reinforced filaments, for different diameters of 0.35 mm, 0.45 mm, and 0.85 mm, as shown in Figure 7. The zoomed-in cross-section image of a 0.45 mm filament is shown in Figure 7(c). No obvious voids can be seen inside the carbon fibers. However, compare to the 1K fibers, the 6K fiber reinforced filament has more voids. As shown in Figure 7(f), a void has been marked with yellow lines. The reason may because that the carbon fibers gathered together after infiltrated by the sizing agent, and the drying process cannot remove all of the volatilizing solvent.

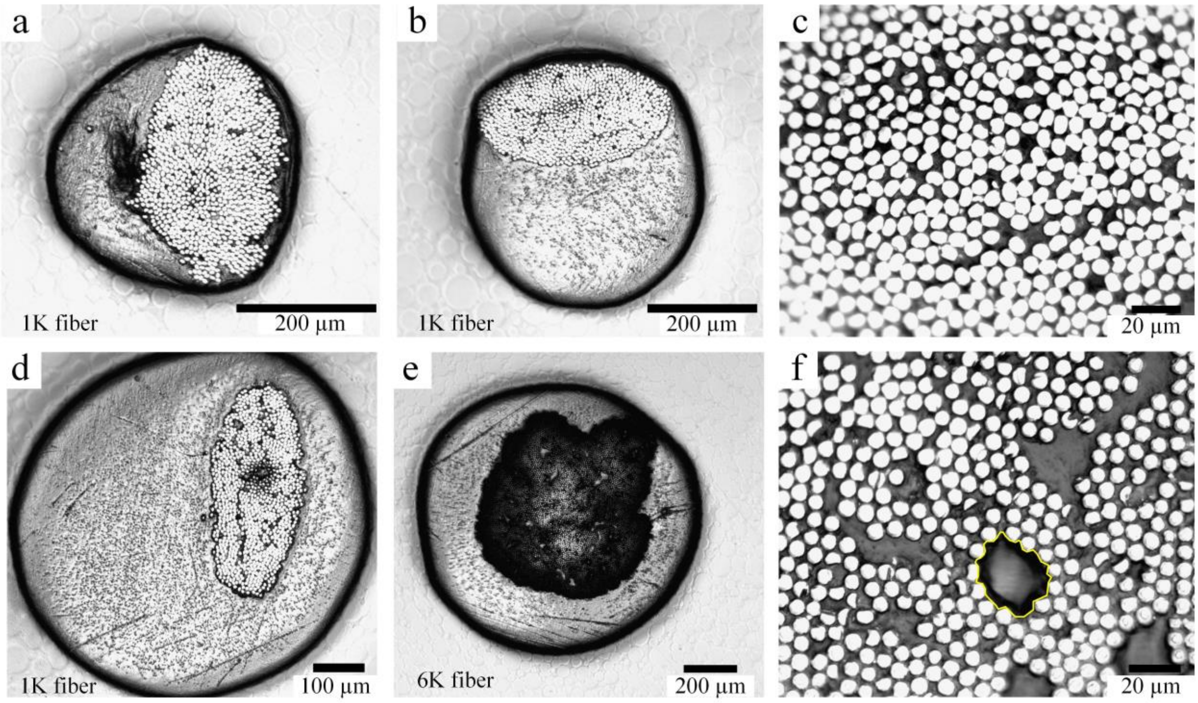

Figure 7. Cross-sectional optical images of the produced filaments, (a) 0.35 mm filament, (b) 0.45 mm filament, (c) zoomed-in 0.45 mm filament, (d) 0.85 mm filament, (e) 1.05 mm filament, (f) zoomed-in 1.05 mm filament.

4. SUMMARY

In this paper, CFRTP filaments have been fabricated continuously with different fiber volume content and diameters. In order to decrease the voids and improve interfacial strength, the surface treatment by using sizing and an impregnation chamber with changeable nozzle jet have been applied. The produced filaments have uniform dimensions and few voids, which can satisfy the requirements of microwave additive manufacturing. In future, three key procedures will be improved; 1) treated fibers should be flattened before drying to decrease voids; 2) distribution of carbon fibers can be optimized; 3) process parameters will be researched to increase production speed.

5. REFERENCES

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