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Continuous carbon fiber reinforced filaments manufactured by a cost-effective and two-step impregnation approach

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Abstract

Fused filament fabrication (FFF) based 3D printing of continuous carbon fiber-reinforced thermoplastic composites (C-CFRTP) has emerged as a new manufacturing method and offered new avenues for the design and fabrication of complex composite structures. To ensure printing quality and improve mechanical performance of composites, the prevailing approach is producing pre-impregnated filaments before 3D printing. However, current manufacturing methods of filaments still rely on traditional pultrusion approaches, necessitating high facility investment and resulting in elevated prices. Here, we propose a low-cost C-CFRTP filament manufacturing method utilizing a two-step impregnation process. To ensure high filament quality while maintaining compactness, we introduce a liquid-solid two-step impregnation method aimed at flattening carbon fiber bundles during impregnation to achieve thorough and uniform infiltration. We successfully fabricated carbon fiber reinforced polyamide (PA) prepreg filaments and analysed its impregnation and mechanical properties. This study holds significant implications for enhancing impregnation efficiency and reducing the cost of C-CFRTP.

Keywords: Fiber-reinforced composites; 3D printing; prepreg filaments; impregnation process

1. Introduction

In recent years, 3D printing technology has risen to become a cutting-edge manufacturing method of composite materials, especially the printing of continuous carbon fiber reinforced thermoplastic composites (C-CFRTP) based on the fused filament fabrication (FFF) method. This method not only brings a new perspective to the design of complex composite structures, but also provides an efficient and flexible way for their production [1,2]. By combining the versatility of 3D printing with the exceptional strength-to-weight ratio of continuous carbon fibers, enabling the creation of complex geometries with enhanced mechanical properties [3,4]. As a result, 3D printing of C-CFRTP has garnered significant attention across various industries, promising to revolutionize traditional manufacturing processes and unlock new possibilities in lightweight, high-performance structural design.

While it is possible to print directly from dry fibers and polymer matrix [5], inherent challenges like poor interfacial bonding and composite voids due to incomplete impregnation persist [6,7]. To overcome these limitations, the prevailing approach involves the production of pre-impregnated C-CFRTP filaments [8,9]. This method entails impregnating fibers with a molten resin polymer or polymer powder, enhancing the impregnation degree and fiber volume content in

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the printed composite [10-12]. Qing et al. engineered a specialized impregnation machine, conducting continuous carbon reinforced PLA prepreg tests to optimize prepreg quality by controlling impregnation mold temperature, forming mold temperature, and fiber movement speed [13]. Likewise, Nergün et al. [14] employed a melt impregnation-based production line to create C-CFRTPs, achieving improved mechanical properties through enhanced interlaminar bonding facilitated by an infrared heating source during printing. These innovations underscore the critical role of pre-impregnated filaments in ensuring printing quality and elevating mechanical performance in C-CFRTP based 3D printing applications.

However, the above-mentioned pultrusion techniques necessitate high facility investments. And these methods typically utilize a one-step impregnation process [15,16], leading to decreased mechanical strengths [17-20]. To address this issue, we propose a novel and cost-effective process to manufacture C-CFRTP filaments. Our two-step impregnation process is meticulously designed to ensure high filament quality while streamlining production and reducing costs. To achieve thorough and uniform infiltration, a unique multi-column cavity has been employed to flatten carbon fiber bundles during impregnation, ensuring exceptional filament density and quality. By optimizing impregnation efficiency and circumventing the need for costly pultrusion facilities, our study holds implications for the widespread adoption of C-CFRTP filaments.

2. Experimental setup

2.1. Material usage

In the experiments, T300 1K continuous Carbon fiber with a single fiber diameter of 6 μm (Toray composite materials, Inc) was used as reinforcement. Concerning matrix materials, PA12 polyamide emulsion was used as the thermoplastic matrix and PA845H emulsion (Michelman, Inc) was employed as a sizing agent for PA12. The fiber sizing can improve the interfacial bonding strength and the mechanical properties of C-CFRTP filaments. In this study, carbon fiber reinforced polyamide filaments from Markforged and basalt fiber reinforced epoxy filaments from Anisoprint were employed for comparative analysis.

2.2. Impregnation method of C-CFRTP filament

The C-CFRTP impregnation process, as illustrated in Fig. 1, consists of three essential stages in fiber production: emulsion sizing, pre-heating, and impregnation with PA filaments. Prior to PA filament impregnation, a thermoplastic emulsion is applied to enhance bonding between carbon fibers and PA materials, thereby improving composite interface properties. A motor with rubber-gears has been applied to ensure that the impregnation filaments is pulled out of the chamber continuously. It provides sufficient friction force to maintain stable traction force and consistent traction speed. Following extensive experimentation, a glue dripping device has been implemented to replace the conventional resin bath, offering precise control over the impregnation of dry fibers at a flow rate of 10 ml/min. This flow rate is synchronized with a fiber movement speed of 5 mm/s, while a nearby cooling device rapidly cools and shapes the fibers over short distances. The longitudinal orientation of the enclosed dripping unit not only significantly reduces footprint but also minimizes emulsion evaporation and material wastage. Additionally, three foam rollers play a pivotal role in dry and spread fibers into ribbons. This process effectively expels pores and air bubbles from the carbon fibers, ensuring thorough emulsion penetration without clogging.

A thermocouple is embedded in the impregnation chamber for temperature monitoring and a proportion-integration-differentiation (PID) algorithm is utilized for temperature control. The pre-heating process is carefully controlled at 215 °C to mitigate volatile components within the fibers and diminish the porosity of the final product. During filament impregnation, the temperature is elevated to 275°C, ensuring complete melting of the PA filaments and thorough filling of the impregnation chamber. Central to this process are five 5mm

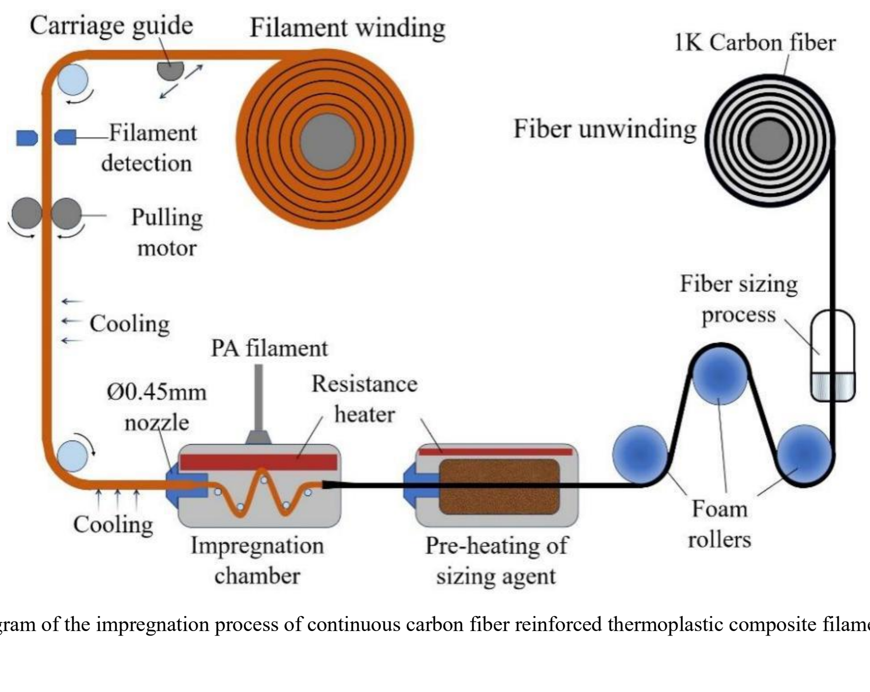

Fig. 1 Schematic diagram of the impregnation process of continuous carbon fiber reinforced thermoplastic composite filaments.

diameters and strategically positioned pins within the chamber, which exert multi-directional traction in the fibers, further enhancing the product's density and reducing porosity. Moreover, within the impregnation chamber, the fiber tape undergoes transformation into dispersed filaments, a crucial step that bolsters the mechanical properties of the resulting filaments. This innovative configuration not only optimizes material utilization but also elevates the overall performance and consistency of the manufactured fibers.

To mitigate potential damage and breakage of carbon fibers due to uneven tension, the device incorporates fiber unwinding and filament winding mechanisms synchronized with the traction speed. These components are strategically positioned on pulleys above the impregnation and heating units, transforming the apparatus from a flat, linear configuration to a compact, three-dimensional setup.

Incorporation of filament detection based on a laser sensor ensures continuous monitoring of filament movement, enabling uninterrupted and stable operation even in unattended scenarios. Ultimately, the device successfully produces C-CFRTP filaments with a typical diameter of 0.4 ± 0.05mm, good surface quality, and excellent hardness and elasticity.

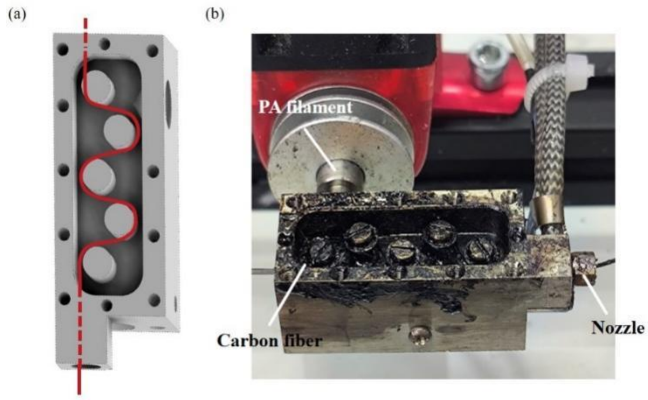

Fig. 2 (a) Schematic 3D model of the impregnation chamber; (b) Physical diagram of the impregnation chamber.

2.3. Design of the impregnation chamber

A steel block was used as the shell of impregnation cavity chamber with a 35mm length and 12mm width, for the benefit of heating up to the impregnation temperature with a micro thermocouple fixed inside the chamber to monitor temperature. Five pins are regularly distributed inside the impregnation cavity, as shown in Fig. 2(a). The pins can increase impregnation permeability and improve impregnation quality by guiding the fibers to contact the pins and spread the fibers and enhance their cohesion. Solid black PA filament was pushed into the impregnation cavity with the help of an extruder, where it was fused, as shown in Fig. 2(b). Using five pins ensured that the friction did not become excessive, avoiding making traction difficult, maintaining fiber impregnation speed, and improving filament production efficiency.

2.4. Design of the impregnation system

The setup operates under program control and is illustrated in Fig. 3. The carriage guide lead screw should be calibrated first to initialize the system. Subsequently, the heating block starts to heat up, and a micro thermocouple was fixed on the chamber to monitor the temperature. Upon reaching setpoint temperature, the code starts running to control the stepper motors. While the carbon fiber spool rotated by the unwind motor, the pulling motor then draws the filament through the two impregnation chambers and then uniformly winds it on the winding spool driven by the winding motor. At the same time, the peristaltic pump starts to work and pumps the sizing agent into the pipe at an even rate. In this process, a laser sensor is mounted before the guiding device to detect if the device is functioning properly. If it detects that the filament is moving normally, the program continues, otherwise there may be a malfunction somewhere in the middle and the program can be paused automatically.

3. Results and discussions

3.1. Distribution of carbon fibers and the D_f of filament

For continuous carbon fiber filaments that are intact, the die diameter of the composite prepreg is negatively correlated with the volume content of the continuous fiber. The relationship between continuous fiber volume fraction V_f and composite prepreg diameter D_d can be described by the following formula:

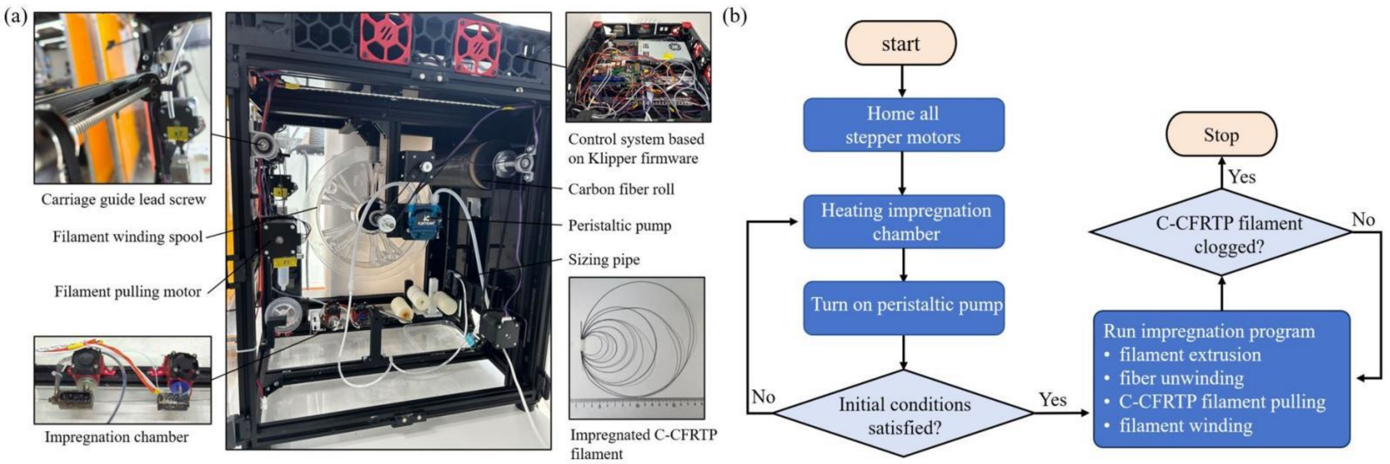

Fig. 3 (a) Production equipment for the C-CFRTP filaments; (b) flow chart of the manufacturing procedure.

$$V_f = N\left(\frac{D_f}{D_d}\right)^2 \quad (1)$$

N represents the single carbon fiber number and the diameter of a single carbon fiber filament is represented by D_f.By utilizing printheads of different diameters, it is possible to extrude products of different D_d , so prepregs with different volume fractions can be made. According to the carbon fiber number N of 1000 in the fiber bundle, the diameter of single carbon fiber of D_f =6 μm, and the diameter of the pre-immersion mold of D_d=0.4 mm, the theoretical fiber volume content is 22.5%.

The single composite strand fabricated in FFF is a unidirectionally reinforced composite. The permeability of the unidirectional composite can be predicted by the Gebart formula [5,21,22]. Thus, the permeability along the radial direction of fiber bundle K_r, can be expressed by:

$$K_r = C_1\left(\sqrt{\frac{V_{fm}}{V_f}} - 1\right)^{\frac{5}{2}} R^2 \quad (2)$$

where, C_1 and V_{fm} are the characteristic coefficients of fiber arrangement.

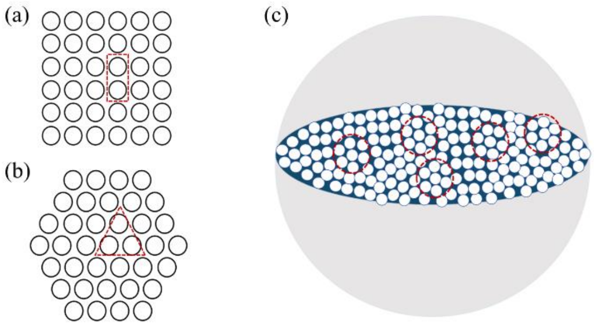

Fig. 4 The fiber arrangement for continuous carbon fiber reinforced thermoplastic composites. (a) A quadratic array, (b) a hexagonal array, and (c)schematic representation of the fiber arrangement of single stranded composites made by FFF.

Fig. 4(a) and (b) illustrate two different states of fiber arrangement following the secondary and hexagonal arrays, respectively. As shown in Fig. 4(c), the cross-sectional morphology of a single C-CFRTP indicates that the actual fiber arrangement is more consistent with the hexagonal array. Therefore, the characteristic coefficients of the fiber arrangement were determined as:

$$\begin{cases} C_1 = \dfrac{16}{9\pi\sqrt{6}} \\ V_{fm} = \dfrac{\pi}{2\sqrt{3}} \end{cases}$$

$$K_r = \frac{16}{9\pi\sqrt{6}}\left(\sqrt{\frac{\pi/2\sqrt{3}}{V_f}} - 1\right)^{\frac{5}{2}} R^2 \quad (3)$$

In this paper, the single carbon fiber number is 1000. By using a nozzle with a diameter of 0.40 mm, changing the base speed and extrusion temperature, filaments with different carbon fiber mass content and fiber volume content have been prepared successfully. Thus, the cross-section of the impregnated filament is shown in Fig. 4(c). The volume fraction and the permeability along the radial direction of fiber bundle are 23.7% and 7.43 μm^2, respectively.

3.2. Analysis and comparison of DSC results

DSC characterization was performed in a protective N_2 environment with a heating speed of 10K/min. PA12 and CF/PA12 samples weighed 7.13 mg and 9.30 mg, respectively. In order to compare the properties of the composite filament produced under the same heat treatment conditions with those of PA itself, the PA was subjected to heat treatment at 275°C for heating and cooling to room temperature. The crystallinity of PA12 is 46.92%, and the endothermic peaks have an area of 89.14 J/g, as can be seen in Fig. 5. Continuous carbon fiber reinforced PA12 has a significantly different endothermic peak and a lower crystallinity of 5.64% when compared to PA12 matrix.

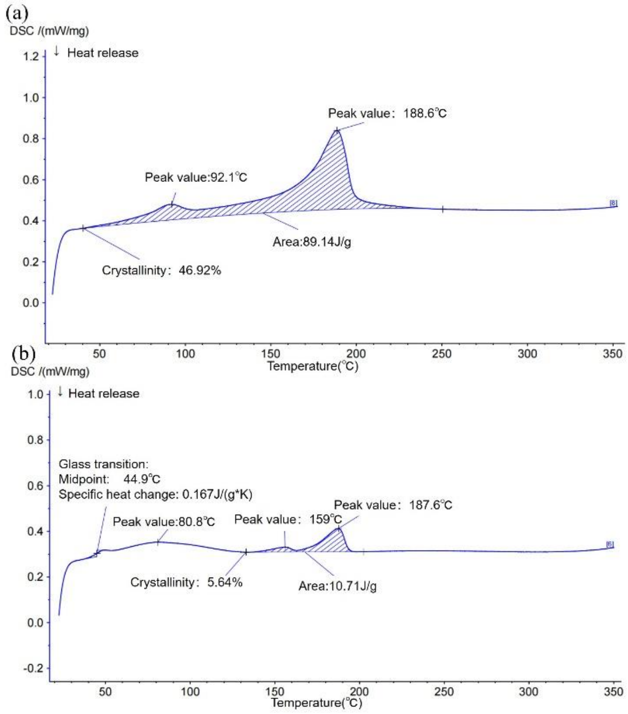

Fig. 5 (a) DSC analysis of PA; (b) DSC analysis of CCF/PA.

3.3. Microstructure analysis

To assess the production quality of C-CFRTP fibers, microstructural characterization was conducted and depicted in Fig. 6 (a) to (d). The carbon fiber reinforced polyamide (CCF/PA) filament exhibited an average diameter of approximately 0.4 mm, slightly lower than the 0.45 mm diameter of the extrusion head, which is attributed to the high viscosity of the thermoplastics.

Fig.6 (a) and (b) illustrate the cross-sectional distribution of carbon fibers within the PA-based C-CFRTP filament, showing a dispersed pattern with minimal porosity. This dispersion results from the unique design of the impregnation chamber, which incorporates strategically positioned pins that generate sufficient friction between the fibers, facilitating the complete unfolding of the carbon fiber tow. This process not only expels air but also ensures uniform encapsulation of carbon fibers by the thermoplastic material. Pre-impregnation with thermoplastic emulsion further enhances interfacial bonding, significantly reducing the risk of fiber debonding and filament damage. Fig. 6 (c) and (d) present longitudinal sections of the CCF/PA filament, revealing orderly fiber alignment with few interruptions or crossovers, indicative of stable quality and strong interconnectivity.

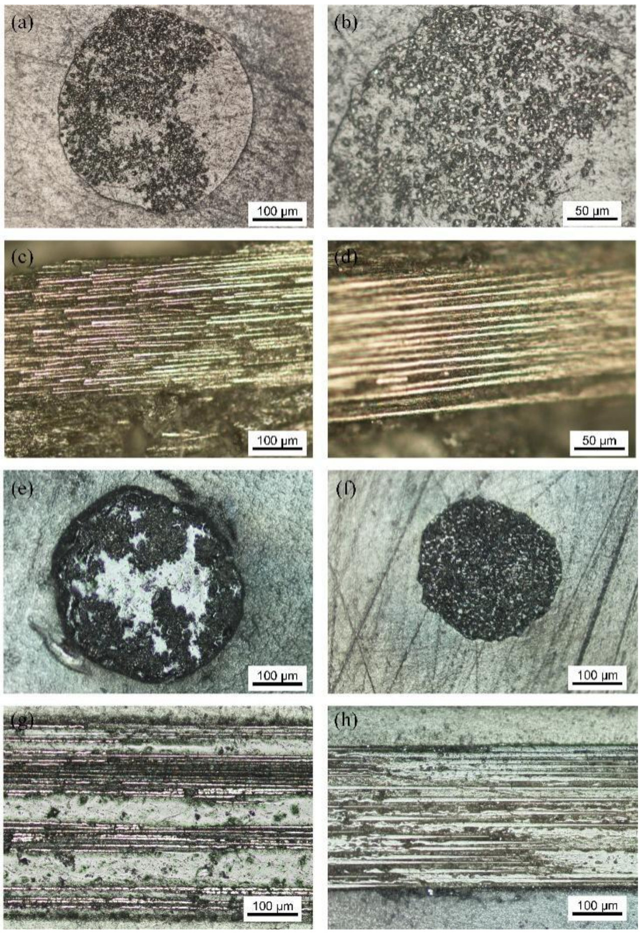

Fig. 6 Microstructure characterization of continuous-carbon fiber reinforced thermoplastic composites filament: (a) and (b) cross-section of the home-made CCF/PA, (c) and (d) longitudinal section of CCF/PA, (e) and (f) cross-section of Markforged and Anisoprint filaments, (g) and (h) longitudinal section of Markforged and Anisoprint filaments.

Additionally, two commercially available industrial C-CFRTP filaments, Markforged (diameter 0.35 mm) and Anisoprint (diameter 0.28 mm), were analyzed. Fig. 6 (e) and (g) depict the transverse and longitudinal sections of the Markforged filaments, highlighting carbon fibers primarily concentrated at the filament periphery, which adversely affects longitudinal fiber alignment. Fig. 6 (f) and (h) illustrate similar sections for the Anisoprint filament, demonstrating a high fiber volume fraction, small diameter, and minimal porosity owing to a thermosetting resin matrix. Comparatively, the carbon fibers of the home-made C-CFRTP filament are dispersed, but fiber distribution lacks uniformity, and the filament cross-section is irregularly shaped rather than consistently round. Consequently, internal carbon fiber forces vary axially under tension, resulting in mechanical properties that lag behind those of industrial filaments.

Nevertheless, the versatility of the home-made CCF/PA filament is evident as adjustments to experimental parameters can alter carbon fiber distribution and surface characteristics, catering to diverse application requirements. These findings underscore opportunities for enhancing filament quality through refined manufacturing processes, thereby addressing specific performance demands across various industrial sectors.

3.4. Tensile strength of fabricated C-CFRTP filaments

Tensile strength and tensile modulus are the main mechanical properties of composite filaments, and five specimens of each material were tested according to the ASTM D4018 standard with a testing speed of 20 mm per minute, as shown in Fig. 7 (b). Since the strength and stiffness of filaments are mainly determined by the carbon fiber content, usually the higher the fiber content, the higher the strength and stiffness. The carbon fibers utilized in the three filaments maybe different, but all of them are classified as T300 grade. The influence of fiber type is comparatively less significant than that of carbon fiber content. Therefore, the conclusion drawn from an analysis focused solely on fiber volume fraction remains valid. We specifically analyzed the ratio of tensile strength and modulus of filaments to the fiber volume fraction to compare the mechanical properties of filaments. The results indicated significant variations across the different materials: CCF/PA exhibited a tensile strength/V_f of 4793.1 MPa with a modulus/V_f of 268.95 GPa, while Anisoprint's filament showed notably lower values at 3395.0 MPa and 96.26 GPa, respectively. Markforged filaments demonstrated a similar tensile strength/V_f of 4568.9 MPa but with a lower modulus/V_f of 227.83 GPa. Upon comparison, the CCF/PA filament

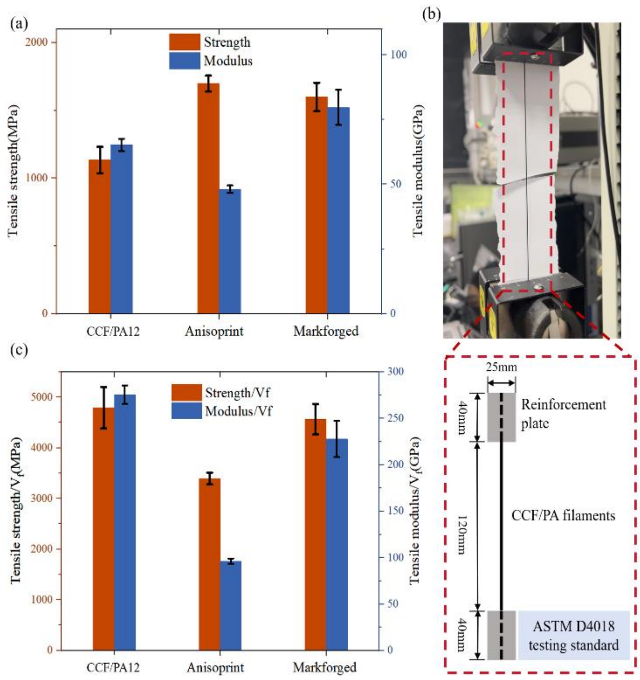

Fig. 7 Comparison of tensile test results of continuous carbon fiber composite prepreg filaments, (a) tensile strength and modulus of the filaments, and (c) strength and V_f ratio of different filaments, (b) experimental demonstration of tensile test.

emerged with the highest modulus/V_f of elasticity and tensile strength/V_f among the tested materials, signifying superior stiffness. Due to the large diameter of the home-made filaments, the tensile strength and modulus of the home-made filaments are lower than others. This issue can be solved by decreasing the diameter of the filaments.

4. Conclusion

In this paper, a new liquid-solid two-step impregnation method is designed for the fabrication of continuous carbon fibers. The method produces prepreg filaments suitable for printing on FDM stand-alone extrusion 3D printers. A fully automated production-collection machine with an overall size of no more than 1 cubic meter has been innovatively developed, and our current research has made it possible for the machine to independently and stably produce C-CFRTP filaments with a diameter of 0.4 mm and a length of more than 900 meters. The study investigates the effects of impregnation on the mechanical properties of continuous carbon fiber reinforced PA filament. Through an analysis of the relationship between the microstructure of the filaments and their macroscopic properties, insights were gained into the behavior and performance of the filaments. Unlike the thermoset materials utilized by Anisoprint, the home-made filaments are composed of thermoplastic materials, which is more suitable for 3D printing. Thermosets feature a matrix with poor compatibility, allowing for coating of printing materials rather than bonding, which limits their suitability for 3D printing. In contrast, thermoplastic materials offer a more compatible matrix and exhibit significant advantages of re-melting printed layers and form a uniform and solid structures with much less porosities. In terms of stability of material properties and fiber distribution, the home-made filaments with two-step impregnation are more stable than single-impregnated Markforged filaments, with a more concentrated distribution of filaments, which meets the need for printing with specific strength distribution.

As industries increasingly seek lightweight, high-performance materials for diverse applications, our research stands poised to catalyze innovation and transformation in the field of advanced composite materials. Additionally, the feasibility of continuous printing using the developed filaments was explored, providing valuable information for future advancements in composite 3D printing technology.

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