Study on Forming Technology of Composite Micro-wire Made From AF and PLA

ZOU Ailing1,2,a, SHAN Zhongde1,3,b*, CHEN Yiwei1,2,c, WANG Shaozong3,d, LIU Xiaojun2,e
1. State Key Laboratory of Advanced Forming Technology and Equipment of China Academy of Machinery Science and Technology, Beijing, China
2. Beijing National Innovation Institute of Lightweight ltd. , Beijing, China
3. Nanjing University of Aeronautics and Astronautics, Nanjing, China
aemail:kacainse@163.com, bemail: shanzd@cam.com.cn,
cemail: chenyiwei@hnu.edu.cn, demail: wszbit@163.com, email: liuxj0304@163.com

Abstract. In order to improve the interlaminar shear property of the composites manufactured by the additive of aramid fiber (AF) reinforced with polylactic acid (PLA), the preparation process of AF reinforced thermoplastic resin composite micro-wires has been optimized, which could promote impregnated and toughness. The influence of different water bath temperatures on the interlaminar shear properties of the composites was studied. And the results showed that the largest interlaminar shear strength (ILSS) of AF/PLA composite material was 12.0 MPa, which had confirmed in the water bath temperature of 30℃. As the bath temperature increased, the interlaminar shear performance decreased, and the ILSS of composite micro-wires in 70℃ water bath was 74.67% of that in 30℃ water bath. The composite fiber with high impregnation degree and good toughness has laid a foundation for further research on additive manufacturing of AF/PLA composite.

1. Introduction
The resin matrix composites of AF have beneficial properties such as light weight, high strength, high modulus, high insulation, impact resistance and so on. They are widely used in aerospace, bulletproof protection, military defense and other fields. At present, aramid fiber reinforced thermosetting composites have been widely used, mainly reflected in the aspects of the shell, landing gear door, cargo compartment, interior decoration and seats of Boeing B757 and B767 aircraft, which can achieve a weight reduction of 30% [1]. The United States has applied the composite material of AF to the three-stage engine of the Trident 1 (C4) missile and the shank engine of the Trident D5 missile. Russia has applied the AF composite material to the shell structure material of the three-stage engine of intercontinental solid missile, such as SS-24, SS-25 and Aspen M (SS-27) [2]. Although the AF composites have been effectively used, it is poor of impregnation and cohesiveness, leading to the low shear strength of the composites, which limits its application. At the same time, aramid resin matrix composites are difficult to process, which are prone to defects such as wire drawing and wool drawing, so they cannot meet the requirements of performance and dimensional accuracy. Liu Kuo and Bhattacharyya D studied the process of liquid nitrogen cooling to improve the surface quality and interlayer failure, which was still in the research stage [3-5]. Liu Liangqiang introduced AF into melt
deposition forming process (FDM) to study the tensile and compression properties under different parameters [6-7]. Shan Zhongde had proposed the process of continuous fiber additive manufacturing [8-14]. The preimpregnated composite micro-wires was introduced into the self-developed continuous fiber additive manufacturing equipment to perform composite component forming. This process can achieve near net shape of the thermoplastic resin matrix composites of AF.

In this paper, AF was used as reinforcement and PLA as matrix. The melt impregnation process based on thermoplastic resin of AF was optimized, and a forming device was set up to prepare AF/PLA composite micro-wires. The interlaminar shear properties of AF/PLA composites were studied by continuous fiber additive manufacturing process.

2. Experimental section

2.1. Main reagents and equipment

AF, Tapran®, Yantai Tayho Advanced Materials Co., Ltd.
PLA, 4032D, particle, NatureWorks.
Poly (Butylene Succinate), PBS, TH803S, particle, Xinjiang Blue Ridge Tunhe Chemical Industry Joint Stock Co., Ltd.
Continuous fiber composite micro-wires forming machine, independent research and development.
Continuous fiber additive manufacturing principal prototype, independent research and development.
The related performance indexes of AF are shown in Tab. 1.

| Parameter                  | Value     |
|----------------------------|-----------|
| Fiber optic tube section   | Round     |
| Density/(g/cm³)            | 1.44      |
| Linear density deviation % | ±2        |
| Oil content/%              | 0.8±0.2   |
| Moisture regain/%          | 2.5±1.5   |
| Elongation at break/%      | ≥19.5     |
| Elastic modulus/GPa        | 3.5±1.0   |
| Thermal shrinkage/%        | <0.2      |
| Decomposition temperature/°C | >500  |

In this study, PLA with good biodegradability was selected as the resin matrix, with a density of 1.25g/cm³, a light yellow or transparent material, melting point above 155°C, insoluble in water, ethanol, methanol, etc., and easy to hydrolyze into lactic acid. The toughening agent of the matrix is PBS, the density of 1.20 g/cm³. It’s a white semi-crystalline polymer with a melting point of 115°C and almost insoluble in water. Studies have shown that PLA has certain compatibility with PBS, and the blending of PBS and PLA can improve the toughness of PLA [15-16].

2.2. Sample preparation

According to the relevant research on AF soaked in warm water, the tensile properties almost remain unchanged after soaking in warm water at 21°C for 5 minutes, while the strength after soaking in water at 88 °C is 85% of that in water at 21°C [17]. Then, the constant temperature water bath of 20°C, 30°C, 40°C, 50°C, 60°C and 70°C were used to pretreat the sizing agent of the AF and prepare the AF/PLA composite micro-wires. The preparation parameters of the composite micro-wires are shown in Tab. 2.

| Serial number | Parameter                        | Value     |
|---------------|----------------------------------|-----------|
| 1             | Water bath temperature/°C        | 20, 30, 40, 50, 60, 70 |
| 2             | Coiling speed/(m/min)            | 1.50 [13] |
| 3             | Three-stage temperature of screw extrusion/°C | 210, 230, 230 |
| 4             | Extrusion rate/rpm               | 6 [13]    |
| 5             | Outlet diameter/mm              | 1         |
| 6             | Mass ratio of PBS/%             | 8% [18]   |
| 7             | Temperature of heating fiber spreading/°C | 200      |
| 8             | Temperature of powder melting temperature/°C | 230     |
2.3. Main test instrument
Field Emission Scanning Electron Microscope (SEM), Geminisem 500 Field Emission Scanning Electron Microscope, Carl Zeiss AG.
Universal Material Testing Machine, INSTRON5567 Material Testing Machine, Instrang Corporation, USA.

2.4. Performance test
The shear performance of the composite components was tested according to the JC/T 773-2010 standard. The empirical value of the test speed was 3mm/min, the fillet radius of the loading head was 2mm±0.2mm, and the fillet radius of the support was 2mm±0.2mm. The width of the loading head and support was greater than the thickness of the sample. The loading head acts on the center position of the two supports, and the span was 30mm. According to the above standard to determine the sample size 60mm×30mm×6mm. The model was analyzed and path planning was carried out by Repetier-Host software, which was the open-source slicing software. G code was exported after optimization and verification. The additive manufacturing process parameters are shown in Tab. 3.

Tab. 3 AF/PLA additive manufacturing process parameters

| Parameter                        | Value       | Parameter                        | Value       |
|----------------------------------|-------------|----------------------------------|-------------|
| Printing layer thickness/mm      | 0.33        | Printing speed/(mm/s)            | 8           |
| Printing spacing/mm              | 3           | Printing temperature/℃           | 220         |
| Printing platform temperature/℃  | 20          | nozzle diameters/mm              | 1.5         |

3. Study on forming technology of AF/PLA composites

3.1. Forming technology of composite micro-wires material
The continuous fiber additive manufacturing process proposed by Xi’an Jiaotong University melts the resin wire in the heated printing nozzle to conduct in-situ melt impregnation of the continuous fiber primary wire [19-20]. The impregnation process was short and affected by the additive manufacturing process parameters, such as printing temperature, printing speed, wire feeding speed, etc.. In order to promote the dipping properties of composite materials, the team proposed and developed composite micro-wires preparation device [18], the device including wire feeding mechanism, screw extrusion mechanism and winding mechanism, etc., which could realize continuous fiber in the soaking chamber of screw extrusion mechanism with molten resin impregnation and forming composite micro-wires, forming carbon fiber (CF), AF reinforced thermoplastic resin composite micro-wires. The device schematic diagram is shown in Fig. 1.

![Fig. 1 Schematic diagram of composite micro-wires preparation device](image_url)

1. Fiber unwinding mechanism 2. Aramylon filament 3. Melt impregnation chamber 4. Composite micro-wires 5. Winding mechanism 6. Screw extrusion mechanism 7. Resin particles
In the continuous fiber composite micro-wires forming machine, the AF primary filament was directly composite formed with molten polylactic acid resin, and the resin was impregnated in multiple directions in the screw extrusion infiltrating chamber. The resin flow is shown in Fig. 2. This process was referred to as the original process preparation. In the original process of preparation, the AF filament was subjected to heat around the wire inlet, and the fiber diverged and split into bundles. Small bubbles were irregularly formed inside the formed composite micro-wires, and the resin was unevenly wrapped outside, where were resin knots. Problems existing in the preparation process were shown in Fig. 3.

AF/PLA composite micro-wires prepared by the original process shown in Fig. 3 (a), was observed in Geminisem500, which was the type field emission scanning electron microscope, as shown in Fig. 3 (b). The radiation voltage was 3kV and the magnification was 95-2500. The SEM scanning electron microscope images are shown in Fig. 4.

According to the SEM test figure of AF/PLA composite micro-wires in Fig. 4, it could be seen that the internal fiber of the composite micro-wires had poor bonding effect with the resin matrix. As shown in the figure, there were non-bond zone and inconsistent in fiber length in the composite micro-wires. Because of AF surface sizing agent, narrow fiber width and heated divergence problem etc., the impregnation of AF composite micro-wires was affected, while the preparation process of AF thermoplastic resin composite micro-wires was optimized.
3.2. Optimization of process and device for AF composite micro-wires

Based on the existing problems above all, the preparation process and equipment of the AF reinforced resin matrix composite micro-wires were optimized.

Due to the short melt impregnation chamber length of continuous fiber composite micro-wires forming machine, which is only 140mm, the bonding time between fiber and resin is limited. At the same time, due to the lack of fiber pretreatment mechanism, dissolved organic oil solutions on the fiber surface could not be removed, and the fiber width could not be expanded, which restricts the improvement of impregnation effect of AF thermoplastic resin composite micro-wires. Based on the original process, two times of impregnation could be realized after optimization. There were three pretreatments before impregnation, such as constant temperature water bath to pulp, heating spread fiber and powder melt impregnation. The impregnation effect of composite micro-wires was effectively improved through four processes of desizing, fiber spreading, presoaking and impregnation.

For the continuous fiber composite micro-wires forming machine, the pretreatment of AF was optimized and upgraded. Thermostatic water bath, multistage heating fiber spreading, vibrating powder were projected. The schematic diagram of the overall design scheme is shown in Fig. 5, and the physical device of the upgraded part is shown in Fig. 6. The whole preparation process is described as follows.

1. The AF was removed by means of constant temperature water bath, where the AF was transported by multi-stage silk material, in order to maximize the dissolution of the dissolved organic oil solutions.
2. The wet AF was extruded to reduce the absorbed water content, which was expanded by multi-stage heating and then dried. The fiber bundles were widened to complete the pretreatment.
3. The thermoplastic resin powder was added to the pretreated fiber surface by vibrating sieve, which was fully contacted with the fiber by extrusion roller. The fiber and the thermoplastic resin powder were heated in a high-temperature chamber to make the resin impregnate the fiber for the first time.
4. The thermoplastic resin particles were melted to impregnate the AF for the second time to form the AF reinforced thermoplastic resin matrix composite micro-wires, and then to wind it up.

Fig. 5 The schematic diagram of the overall design scheme

Fig. 6 Schematic diagram of the optimized composite micro-wires forming equipment
1. Water bath pulping mechanism 2. Heating spread fiber mechanism 3. Vibration pulping mechanism 4. Heating melting mechanism 5. Melt screw extrusion mechanism 6. Control panel 7. Vibration pulverizing mechanism
AF could be spreading by heating spread fiber mechanism, which was one part of the optimized composite micro-wires forming equipment as shown in Fig. 6. The width of the fiber is increased by two times after the multi-stage extension. The AF impregnating by the thermoplastic resin powder, which was molten state, entered the heating melting mechanism. Then, with the traction of the winding mechanism, the AF became composite micro-wires with a circular cross section after passing through the wire outlet. Using the optimized preparation technology and device, to preparation of AF/PLA composite micro-wires, the surface of composite micro-wires was smooth. After the process optimization, the composite micro-wires had uniform diameter, no bubble inside the wire and no resin junction on the surface. The toughness of the composite micro-wires had been improved, which was convenient for additive manufacturing. The comparison of appearance effect is shown in Fig. 7. The terminal face of the optimized composite micro-wires was observed, as shown in Fig. 8. The cross section of the composite micro-wires was regular and nearly round, and the fiber bundle was located in the middle of the composite micro-wires, while the thermoplastic resin was clearly visible in the fiber bundle. By comparing the SEM observation figure of the original process shown in Fig. 4, the result proved that the impregnation effect was improved.

3.3. Characteristics of AF/PLA composite micro-wires at different water bath temperatures

In the experiment, thermoplastic composite with different linear densities had been prepared by adjusting the ratios of AF and the thermoplastic resin. According to the cross-section structure of
composite micro-wires, the volume content of AF could be characterized. In the process of composite micro-wires preparation, vernier calipers were used to measure the diameter of the formed wire at the temperature of 20°C-70°C. There were 10 groups of data recorded respectively. The average value was taken as the diameter of the composite micro-wires under the process parameters. The composite micro-wires prepared was shown in Fig. 9.

Assuming that the number of single fibers in the fiber bundle was constant, and the AF was not damaged in the forming process. While the cross section of the formed composite micro-wires was round, and the fiber volume fraction of the composite micro-wires was expressed as follows.

\[
V_f = \frac{N \cdot S_f \cdot L}{S_F \cdot L}
\]  

Where, \( N \) is the number of AF monofilaments in the AF bundle. \( S_f \) is the cross-sectional area of AF monofilament. \( L \) is the length of composite micro-wires material. \( S_F \) is sectional area of composite micro-wires.

\[
S_f = \pi \cdot \left(\frac{d_f}{2}\right)^2
\]

\[
S_F = \pi \cdot \left(\frac{d_F}{2}\right)^2
\]

Where, \( d_f \) is the diameter of a single AF. \( d_F \) is the cross section diameter of the composite micro-wires.

According to the diameter of the composite micro-wires prepared at different temperatures measured, the fiber volume fraction was calculated based on the above formula. The results are shown in Tab. 4.

Tab. 4 Diameter and fiber volume fraction of composite micro-wires prepared

| Parameter         | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
|-------------------|------|------|------|------|------|------|
| Diameter/mm       | 1.04 | 1.04 | 1.05 | 1.03 | 1.04 | 1.05 |
| Fiber volume fraction/% | 7.63 | 7.63 | 7.49 | 7.49 | 7.49 | 7.49 |

As be seen from Tab. 4, the diameter of composite micro-wires prepared at 20°C-70°C had little difference, the maximum difference was 0.02mm, and the fiber volume fraction ranges from 7.49% to 7.63%, which had negligible impact on continuous fiber additive manufacturing.

3.4. Interlaminar shear properties of AF/PLA

The continuous fiber reinforced composite additive manufacturing process was adopted. AF/PLA composite micro-wires prepared at different water bath temperatures was formed into test samples. The
forming process parameters were shown in Tab. 3, and the interlaminar shear properties of the formed test samples were tested.

The 0°/90° path was adopted in combination with the set process parameters to design the fiber structure of the interlaminar shear composite sample. According to the printing process parameters, the test samples were divided into 15 layers. Repetier-Host software was used to plan the structure path of each layer to avoid the existence of diagonal lines, broken lines and repeated paths. After the G code was derived, the prototype of continuous fiber additive manufacturing principle was imported. The composite micro-wires materials prepared at different water bath temperatures were introduced into the printing nozzle through the wire feeding wheel, as shown in Fig. 10. The programmed program was run, and when the printing nozzle and printing platform were heated up to the temperature described in Tab. 3, the interlaminar shear samples of composite materials were prepared. The interlaminar shear samples of composite materials formed by composite micro-wires prepared at different water bath temperatures are shown in Fig. 11.

According to the test results of interlaminar shear performance, the ILSS at 30°C was the largest such as 12.0MPa, while the smallest such as 8.96MPa at 70°C. In the whole experiment, the ILSS had increased with the water bath temperature increasing, and had reached the maximum at 30°C, while gradually had decreased. The performance was 74.67% of the ILSS at 30°C. When the water temperature was 30°C, the surface sizing agent of AF was effectively removed, and the ILSS was the highest.
However, when the water temperature had been more than 30℃, not only the surface size agent was removed, but also the AF was damaged. In the end, the bonding strength between the fiber and the matrix was reduced, and the interlaminar properties of the composites are finally affected.

4. Conclusion
In this research, the technology of AF composite micro-wires was optimized and the composite material was prepared. Through testing mechanical properties, the following conclusions were drawn.

(1) Based on the original process, the forming process of thermoplastic resin matrix composite filament was optimized. A three-stage pretreatment process was proposed, which included constant temperature water bath for desizing, heating fiber expansion, and powder melt impregnation to improve the impregnation effect of AF.

(2) It was studied that the AF/PLA composite filaments was formed at 20℃-70℃ water bath temperature. Compared with the composite micro-wires prepared by the original process, it had smooth surface and uniform diameter, without resin bond and bubble. Then the fiber volume fraction was from 7.49% to 7.63%.

(3) The ILSS of the composites prepared by continuous fiber additive manufacturing process were studied. The results showed that the ILSS of the composites prepared was the highest at water bath temperature of 30℃, which was 12.0MPa. The ILSS at water bath temperature of 20℃ was lower than that at water bath temperature of 30℃. When the water bath temperature exceeds 30℃, the ILSS had decreased gradually with the increase of water bath temperature. Therefore, the water bath temperature of 30℃ was used to prepare the composite filament, which could lay a foundation for further research on AF/PLA additive manufacturing.

Acknowledgments
This work was supported by National Defense Science and Technology Foundation Strengthening Program, Technology Development Fund of China Academy of Machinery Science and Technology Group Co., Ltd (312005Q9), The State Key Laboratory of Advanced Forming Technology and Equipment (SKL2019003).

References
[1] ZHAO, H. (2019) Application and development of aramid resin matrix composites. Advanced Materials Industry, 01:13-15.
[2] LI, Y. MO, J. WANG, X. et al. (2020)Progress of Composite for Solid Rocket Motor Case[J]. Aerospace Manufacturing Technology, 222(04):69-73.
[3] WANG, J. LIU, H. LIU, K. et al. (2020) Experiment of liquid nitrogen cooling drilling test of aramid fiber-reinforced polymer composites. Acta Materiace Compositae Sinica, 37(1):89-95.
[4] BHATTACHARYYA, D. ALLEN, M. MANDER, S. (1993) Cryogenic machining of Kevlar composites. Materials and Manufacturing Processes, 8(6): 631-651.
[5] Wang, F. Wang, Y. Hou, B. et al. (2016) Effect of cryogenic conditions on the milling performance of aramid fiber. The International Journal of Advanced Manufacturing Technology, 83(1-4):429-439.
[6] LIU, L. XIAO, X. DONG, K. et al. (2020) Compression Properties of 3D Printed Continuous Kevlar Fiber /PLA Corrugated Sandwich Composites. China Plastics Industry, 48(01):91-95.
[7] LIU, L. XIAO, X. DONG, K. et al. (2019) Tensile Properties of 3D Printed Continuous Kevlar Fiber Reinforced PLA Composites[J]. China Plastics Industry, 47(12):27-30.
[8] SHAN, Z. FAN, C. ZHAN, L. et al. (2019) Composite Wire Rod Preparing Device. China, 20181100597. 1.
[9] SHAN, Z. FAN, C, SUN, Q. et al. (2020) Research on Additive Manufacturing Technology and Equipment for Fiber Reinforced Resin Composites. China Mechanical Engineering, 31(02):221-226.
[10] Fan, C. Shan, Z. Zou, G. et al. (2021) Interfacial Bonding Mechanism and Mechanical
Performance of Continuous Fiber Reinforced Composites in Additive Manufacturing. Chinese Journal of Mechanical Engineering, 34(1):131-141.

[11] Fan, C. Shan, Z. Zou, G. et al. (2020) Performance of Short Fiber Interlayered Reinforcement Thermoplastic Resin in Additive Manufacturing. Materials, 13(12):2868.

[12] YAN, D. SHAN, Z. ZHAN, L. et al. (2020) Influences Law of Mechanics Properties of 3D Printing Composite Open-hole Plates. China Mechanical Engineering, 31(10):1240-1245.

[13] FAN, C. SHAN, Z. ZOU, G. et al. (2020) Forming Laws of Continuous Fiber Composite Filaments in 3D Printing. China Mechanical Engineering, 31(09):1089-1097.

[14] ZHANG, X. SHAN, Z. FAN, C. et al. (2019) Mechanical Properties of PLA/Continuous Carbon Fiber Composites by Additive Manufacturing. Engineering Plastics Application, 47(08):91-95.

[15] Bhatia, A. Gupta, R. Bhattacharya, S. et al. (2007) Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) blends for packaging application. Korea-Australia rheology journal, 19(3):125-131

[16] YE, D. LU, J. QIAN, T. et al. (2012) Research on Poly (lactic acid)/Poly (butylenes succinate) Blends. China plastics, 26(03):23-27.

[17] HU, Ba. NIU, J. (2013) Advanced composites. 2nd Ed, National Defense Industry Press, Beijing.

[18] XU, W. YANG, Z. YIN, X. et al. (2016) Study on Mechanical Properties of PLA/PBS Toughening Blends Under Tensile Deformation. China Plastics, 30(01):34-38.

[19] Luo, M. Tian, X. Shang, J. et al. (2019) Impregnation and interlayer bonding behaviours of 3D-printed continuous carbon-fiber-reinforced poly-ether-ether-ketone composites. Composites Part A: Applied Science and Manufacturing, 121:130-138.

[20] Liu, T. Tian, X. Zhang, M. et al. (2018) Interfacial performance and fracture patterns of 3D printed continuous carbon fiber with sizing reinforced PA6 composites. Composites Part A: Applied Science and Manufacturing, 114:368-376.