Warp deformation model of polyetheretherketone composites reinforced with carbon fibers in additive manufacturing

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Keywords: additive manufacturing, fiber reinforced PEEK composites, mechanical properties, crystallinity, warp deformation

Abstract
Fused deposition modeling (FDM) provides a promising technique for the small-batch fabrication of highly customized objects. The required performance of FDM far exceeds the performances of conventional manufacturing methods. However, the temperature difference that occurs during FDM generates internal stress, which causes warp deformation and affects formed sample quality. Hence, identifying the influencing factors of warp deformation is the key to improving the forming quality of FDM samples. In this work, PEEK/short carbon fiber (CF) composites were prepared by using the FDM method, the warp deformation formula was derived, and the warp deformation mechanism was obtained. Results showed that the material linear expansion coefficient, forming chamber temperature, and forming size had considerable effects on warp deformation. Moreover, CF could improve the warp deformation of the PEEK/CF composites because of their low Poisson’s ratio and high thermal conductivity. The addition of CF could reduce the residual stress of the composites and improve warp deformation. In addition, annealing could improve the tensile and bending mechanical properties of the PEEK/CF composites. Specifically, after 3 h of heat treatment at 190 °C, the tensile and bending mechanical properties of the composites reached 10.7% and 11.6%, respectively. Crystallinity analysis revealed that the mechanical properties of the PEEK/CF composites strongly depended on their crystallinity. High cooling temperature rates were associated with low crystallinity, tensile strengths, and elastic moduli. DMA analysis showed that the addition of CF could improve the high-temperature resistance of the PEEK/CF composites as reflected by the higher glass transition temperature of the composites than that of the pure PEEK resin. Porosity analysis showed that the CF content could tailor the pore size and distribution. The study reported here provides a reference for improving the forming quality and mechanical properties of PEEK/CF composites fabricated through FDM.

1. Introduction

Polyether ether ketone (PEEK) is a semicrystalline thermoplastic polymer that is composed of repeating units containing one ketone bond and two ether bonds in its main chain structure. Given its excellent comprehensive properties, such as wear resistance, fatigue resistance, and good biocompatibility, it has myriad applications in the automotive and aerospace industries, medical equipment, and other fields [1–4]. Forming and manufacturing methods for fiber-reinforced PEEK-based composite materials are also attracting attention. PEEK has a glass transition temperature of 143 °C and a melting point of as high as 343 °C. Hence, the commonly used forming methods for this material are injection molding and compression molding. However,
prototypes with complex structures still cannot be obtained through the approaches. This situation has become a crucial problem that restricts the wide application of PEEK-based composites.

Additive manufacturing (three-dimensional [3D] printing) is a recent manufacturing technology through which objects are created from 3D digital CAD models by adding one material layer after another. Compared with traditional subtractive manufacturing, this technology has lower cost and simpler processing, which meets the requirements for the production of small batches and individualized and complex structural parts. Therefore, it has substantial promotion and application value. 3D printing technology can be applied to process all kinds of materials, especially polymer materials based on PEEK, which has a high melting point. Therefore, a large number of scholars have carried out research on residual stress in the forming of composite materials [5–11]. Wang et al [12] systematically studied the influence of short carbon fibers (CF) and orthogonal building orientation on the flexural properties of printed PEEK composites. They found that the addition of CF enhances the uniform nucleation of PEEK during 3D printing, decreases layer-to-layer bonding strength, and greatly changes the fracture mode. Professor Li et al [8] reported the effects of the mechanical properties of PEEK printed through fused deposition modeling (FDM) and its composites on biocompatibility. Their experimental results confirmed that printed CFR-PEEK specimens have significantly improved mechanical properties compared with printed pure PEEK. Laboratory experiments clearly showed that no toxic substances are introduced during the FDM manufacturing of pure PEEK and CFR-PEEK. Arif [13] studied the multifunctional performance of PEEK composites reinforced with carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs). They reported that the Young’s and storage moduli of these materials have increased by 20% and 66% under 3 wt% CNT loading, respectively, and by 23% and 72% under 5 wt% GNP loading, respectively. Moreover, they demonstrated that the crystallization temperature and crystallinity degree of FFF-PEEK increase with the addition of carbon nanostructures.

However, most of the aforementioned studies focused on the printing and forming mechanical properties of 3D-printed composites utilizing filaments, and few have reported on the warp deformation and formed quality of PEEK-based composites fabricated through 3D printing. During FDM, a temperature difference occurs in the thermoplastic material because the melting temperature is rapidly transitioned to the chamber temperature. This large temperature difference promotes stress concentration in the composite material system and facilitates microcrack formation, interface delamination, and warp deformation, which all seriously affect the quality and performance of FDM-formed parts [14, 15]. Therefore, this study aimed to evaluate the formed quality of PEEK-based composites to improve the performances of FDM-printed samples. We investigated the effect of carbon fiber (CF) content (0 wt%, 5 wt%, 10 wt%, and 15 wt%) on residual stress in PEEK/CF composites, derived the warp deformation formula, and identified the warp deformation mechanism to provide an important reference for reducing and eliminating internal stress. Specific attention was paid to the question of whether FDM printing resulted in different crystalline states and the influence of tensile strength.

2. Experimental materials and test methods

2.1. Experimental materials

PEEK (450 G) was supplied by VICTREX Company (England). Chopped CF (WD-100AW) with an average fiber length of 100 μm were purchased from Nanjing Weida Composite Material Co., Ltd. Prior to use, the PEEK and CF were dried for at least 3 h at 150 °C.

PEEK and CF/PEEK composite filaments were supplied by Shanxi Jugao AM Co., Ltd. The CF contents of the CF/PEEK composites were approximately 5 wt%, 10 wt%, and 15 wt%. The diameters of the filaments for 3D printing were controlled to 1.75 ± 0.05 mm.

2.2. Test equipment and test conditions

(1) Differential scanning calorimetry

Instrument: DSC/500/578, Mettler Toledo, Switzerland.

Test conditions: the sample mass was 1.5 mg. The temperature was raised from room temperature to 300 °C, lowered to −100 °C after 5 min of holding, and elevated to 120 °C after 5 min of holding. The heating rate was 10 K min

−1. The whole process was performed under nitrogen protection at the flow rate of 40 ml min

−1.

(2) Shear strength test

Instrument: WDW-1 universal material testing machine, Beijing University of Chemical Technology Testing and Analysis Center.

Test conditions: interlayer shear strength analysis was performed in reference to the standard ISO 14130:1998 (fiber-reinforced plastic composite material–short beam method to determine the interlayer
shear strength. The sample size was 20 mm × 10 mm × 3 mm, and the loading speed was 5 mm·min⁻¹. The span was 10 mm, the upper support radius was 5 mm, and the lower support radius was 2 mm. The formula used to calculate the interlaminar shear strength \( \tau_M \) (MPa) is

\[
\tau_M = \frac{3}{4} \times \frac{F}{b \times h}
\]

where \( F \) is the maximum load (N), \( b \) is the sample width (mm), and \( h \) is the sample thickness (mm).

(3) Tensile strength test

Instrument: WDW-10E universal material testing machine, Beijing University of Chemical Technology Testing Machine Technology Co., Ltd.
Test conditions: in accordance with the standard ISO 527:1997 (plastics—tensile performance test) for tensile strength analysis, the sample size was 180 mm × 15 mm × 2 mm, and the loading speed was 5 mm·min⁻¹.

The formula for calculating the tensile strength \( \sigma_M \) (MPa) is

\[
\sigma_M = \frac{F}{A}
\]

where \( F \) is the maximum load (N), and \( A \) is the cross-sectional area of the sample (m²).

(4) Bending strength test

Instrument: WDW-1 universal material testing machine, Beijing University of Chemical Technology Testing and Analysis Center.
Test conditions: in reference to the standard ISO 14130:1998 (reinforced plastic composite material—short beam method to determine interlaminar shear strength), the sample size was 100 mm × 10 mm × 4 mm, the loading speed was 5 mm·min⁻¹, the span was 64 mm, the upper support radius was 5 mm, and the radius of the lower support was 2 mm.

(5) CT scan test

Instrument: x-ray computed tomography reconstruction with nanoVoxel-3000 (Sanying Precision Instruments Co., Ltd, Tianjin, China) was performed to identify the geometrical parameters of PEEK/CF composites.
Test conditions: test voltage of 100 kV, current of 100 \( \mu \)A, test frame number of 1440, resolution of 12 \( \mu \)m, and single frame combination of 3 sheets.

(6) Dynamic mechanical properties

Instrument: DMA/SDTA861e, Mettler Toledo Co., Ltd, Thailand.
Test conditions: sample size of 55 mm × 10 mm × 3 mm, tensile mode, vibration frequency of 1 Hz, temperature range of 30 °C–300 °C, and heating rate of 3 °C·min⁻¹.

(7) Porosity test (mercury intrusion method)

Instrument: POREMASTER GT60 mercury porosimeter. Test data were obtained by the Beijing Center for Physical and Chemical Analysis.
Test conditions: normal temperature, pressure range of 0.20–30 000 psi, and mercury injection time of 70 min.

(8) Residual stress test (blind hole method)

Instrument: MTS3000 blind hole method automatic residual stress analyzer, Italy SINT Company.
Test conditions: test standard ASTME837-2013a, room temperature, humidity of 60%, high-speed motor speed of 50 000 rpm, and drilling step accuracy of 10 \( \mu \)m.

2.3. Fabrication of 3D-printed specimens

Five samples of each geometry were created by using PEEK/CF material to investigate the relationships among printing factors, mechanical properties, and porosity. The printing process is shown in figure 1. The specifications of the geometric models of tensile stress, bending stress, shear stress, and porosity were similar to those in GB/T 16421-1996, GB/T 9341-2008, GB/T1450.1-2005, and GB/T 21650.1-2008, respectively. The test sample models conforming to the relevant test standards were designed in Solidwork software, and the geometric models were exported as files in stereolithography format for importation by the FDM software. The geometric models are presented in figure 2, and the main FDM process parameters used to print the PEEK/CF composite samples are provided in table 1.
3. Analysis and discussion of experimental results

3.1. Analysis of the porosity of PEEK/CF composites

The forming quality and mechanical properties of a composite material are affected by the material’s porosity. PEEK/CF samples with fiber contents of 0%, 5%, 10%, and 15%, which were denoted as PEEK, PEEK/CF-5, PEEK/CF-10, PEEK/CF-15, respectively, were prepared, and their porosities were tested via CT scanning and mercury intrusion test to investigate the influence of fiber content on porosity. The test results are shown in figure 3.

The CT scan pictures of the PEEK/CF composite materials are presented in figure 3. Pictures with a depth of 0.5 mm in the CT scan were selected for the convenience of observation. The images demonstrate that as the CF content was increased, the pores in the PEEK/CF composite materials shrunk and their distribution became
dense because the CF added to the PEEK resin filled and shrank the pores that formed in the PEEK/CF composite materials. Comparing the PEEK and PEEK/CF-5 samples revealed structures with uniform pore sizes and distributions. From the perspective of pore state, the pore distribution and size of the PEEK/CF-5 sample were significantly higher than those of the pure PEEK sample. Each CT scan slice showed the same situation for the PEEK/CF-10 and PEEK/CF-15 samples. In contrast to those of the PEEK and PEEK/CF-5 samples, the pore structure and size of the PEEK/CF composite material did not undergo obvious gradient changes.

As shown in figure 4, the Mercury intrusion method was performed to quantify the porosity of PEEK/CF composites with different CF contents accurately. These figures shows that with the increase in CF content, the porosity of the PEEK/CF composites gradually increased because at the same melting temperature, the CF content increased hindrance to the movement of the PEEK molecular chain strengthened, viscosity was enhanced, and the overall melt fluidity of the composite material worsened. Meanwhile, the thermal expansion performance of the PEEK/CF composites reduced with the increase in the CF content. This result shows that CF could tailor the pore size and distribution by FDM in future research.

3.2. Static mechanical properties of PEEK/CF composite materials

3.2.1. Analysis of the mechanical properties of the PEEK/CF composites

The PEEK/CF composites were prepared without fan cooling (cooling rate of 0) during FDM and treated at 190 °C for 3 h. The effect of heat treatment on the tensile, bending, and shear properties of the PEEK/CF composites is presented in figure 5. The figure shows that the tensile strength and flexural strength of the heat-treated PEEK/CF composites had significantly improved. When the CF content was 15% (PEEK/CF-15), the tensile strength increased from 85.15 MPa to 94.26 MPa and the bending strength increased from 125.28 MPa to
139.87 MPa. Therefore, the tensile strength and bending strength of the composites had increased by 10.7% and 11.6%, respectively. These results demonstrated that the tensile and bending properties of the PEEK/CF composite materials could be improved through heat treatment likely because the PEEK/CF composite wire melted rapidly during the transition from a high temperature (400 °C) to the chamber temperature (100 °C) over a short period of time. The drastic change in the temperature difference caused the molecular chains of the PEEK resin to freeze below the glass transition temperature rapidly and generated residual stress in the composite material. Stress concentration points, which were easily subjected to external loads, formed. Fracture points then formed. After heat treatment (190 °C/3 h), the temperature was much higher than the glass transition temperature of PEEK (143 °C), and the molecular segments of the PEEK resin were in a highly elastic state that could not only release the residual stress in the system but also improve the movement of molecular segments of PEEK. The amorphous area decreased, and the crystallinity of the PEEK/CF composite material and the amount of regular PEEK formed in the system increased [16]. The highly crystalline PEEK helped share the

Figure 5. Mechanical properties of PEEK/CF composites under different CF contents.

Figure 6. Tensile strengths and elastic moduli of the PEEK/CF samples at different cooling rates.
applied load force. Therefore, the tensile strength and impact strength of the PEEK/CF composite material also increased.

In addition, as inferred from this figure, the shear strength of the sample decreased after heat treatment because heat treatment softened the PEEK/CF composites. This effect, in turn led to a reduction in layer-to-layer adhesion.

3.2.2. Effect of cooling rates on the tensile properties of the PEEK/CF composites

The PEEK/CF composites underwent high-temperature melting during FDM to form a solid phase, and the cooling rates affected the mechanical properties of the composite materials. As discussed in this section, PEEK/CF-5 was taken as an example to study the influence of different air cooling rates (0%, 25%, 50%, 75%, and 100%) on the tensile mechanical properties of the PEEK/CF composites.

Figure 6 shows the tensile strengths and elastic moduli of the PEEK/CF-10 composites at different cooling rates. As the cooling rate was increased, the tensile strengths and elastic moduli of the samples gradually decreased because PEEK was a semicrystalline thermoplastic material and the temperature difference affected the crystallinities of the PEEK/CF molded samples during FDM. When the cooling rate was slow, the temperature difference was small, the PEEK molecular chain could be fully extended, and a regular

**Figure 7.** Analysis of the crystallinity of the PEEK/CF composites.
microcrystalline structure easily formed in the system. The tensile strengths and elastic moduli of the samples increased because the crystallinity of the PEEK/CF composites increased, the binding molecules that transmitted stress between the crystallites enlarged, and the maximum yield stress increased. When the cooling rate was fast, the outer PEEK molecular chains lacked sufficient time to form an ordered microcrystalline structure. Thus, an amorphous structure formed in the PEEK/CF samples during FDM. Hence, the tensile strengths and elastic moduli of the printed PEEK/CF samples decreased with the increase in air-cooling rates.

The PEEK/CF composites were subjected to thermal analysis to study the effect of cooling rates (10, 20, 40, 60 K, and 80 K min⁻¹) on crystallization properties to further prove the above conjecture. As shown in figure 7, as the cooling rate was increased, the exothermic enthalpies of the PEEK/CF samples gradually decreased, and crystallinity also decreased. The thermal analysis of the PEEK/CF composites proved the conjecture regarding the effect of crystallization on mechanical properties.

Figure 8 shows the tensile fracture curve of the PEEK/CF composite with 5% CF content. The maximum yield strength was observed in the tensile fracture curve obtained at the cooling rate of 10 K min⁻¹. The yield strength then dropped rapidly. This behavior was indicative of a typical brittle fracture mode. As inferred from the tensile section of the sample, the fracture surface was neat, and the sample showed a typical brittle fracture mode. When the cooling rate was 80 K min⁻¹, the sample underwent necking during stretching and exhibited ductile fracture because the cooling rate was low, and the inner and outer layers of the composite material easily formed a uniform aggregated microcrystalline structure [16]. However, when the cooling rate was high, the temperature difference of the PEEK/CF composites during melt extrusion was large, the temperature dropped below the glass transition temperature of PEEK over a short period of time, and the chain segment regularity of PEEK was deteriorated. These conditions resulted in the formation of an amorphous structure in the inner and outer layers of the PEEK/CF composites. Therefore, when the cooling rate was exceeded 80 K min⁻¹, the tensile fracture mode of the PEEK/CF composites changed from brittle fracture to ductile fracture. The consistency of this result with the result of the previous DSC analysis further verified the influence of the cooling rate on the mechanical properties of the PEEK/CF composites. Furthermore, this result provides guidance for the preparation of materials with different application fields.

The above analysis indicated that the mechanical properties of the PEEK/CF composites formed through FDM were strongly dependent on the crystallization of the materials. The cooling rate during FDM affected the tensile strengths and elastic moduli of the PEEK/CF composites. The cooling rate of the fused deposition process should be minimized to improve sample crystallinity and increase tensile strength.

3.3. Dynamic mechanical properties of the PEEK/CF composite materials

DMA was selected to characterize the dynamic mechanical properties of the PEEK/CF composites produced via FDM because DMA is sensitive to molecular motions and transitions. The influence of different CF contents on the storage moduli and loss factors of the PEEK/CF composites, as shown in figure 9, is discussed in this section.

Figure 9(a) shows the effect of CF content on the storage moduli of the PEEK/CF composites. As the CF contents were increased, the storage moduli of the PEEK/CF composites gradually increased. CF could strengthen the PEEK resin and improve the rigidity of the PEEK/CF composite materials because of their high
strength and moduli. High fiber content was associated with strong rigidity. Therefore, the storage moduli of the PEEK/CF composites increased with the increase in fiber content.

The damping factor (tanδ) of the samples as a function of temperature is provided in figure 9(b). The temperature located at the peak value could be regarded as the glass transition temperature (Tg) of PEEK/CF composites due to the α relaxation corresponding to the glass transition of the polymer composite materials. As shown in this figure, at approximately 143 °C, the PEEK/CF composite produced the α relaxation peak, which was defined as the Tg of PEEK/CF composites. As expected, the Tg of the PEEK/CF composites increased with the increase in CF percentage, and the height of the transition peak decreased. This finding implied that the volume percentage of the constrained region in the composites had increased and PEEK molecular chain mobility became restricted; thus, the energy needed to reach the highly elastic state increased. Therefore, the PEEK/CF composites demonstrated the following behavior: Tg moved to high temperatures, and the tanδ value decreased. Hence, by increasing the CF content, the high-temperature resistance of the PEEK/CF composites fabricated through FDM improved, and the temperature application range of the PEEK/CF composites broadened.

3.4. Analysis of the warp deformation of the PEEK/CF composites

3.4.1. Influence of CF content on the warp deformation of PEEK/CF

Figure 10 shows the warp deformation of the PEEK/CF composites with different CF contents. It shows that the pure PEEK resin had severe warp deformation at both ends, whereas the warp deformation of PEEK/CF was not obvious. These results might be attributed to two reasons: first, compared with the PEEK/CF composite materials, pure PEEK resin had a lower thermal conductivity coefficient and thus easily formed uneven gradients, which increased internal stress between layers during high-temperature melting molding. In addition, PEEK resin had a high melting crystallization performance and a relatively high volume shrinkage rate [17]. Therefore, the PEEK sample was prone to warping deformation under thermal deformation. Given that the thermal conductivity of CF was considerably higher than that of PEEK resin, heat could be uniformly transferred
to the whole samples through CF during the forming of the PEEK/CF composite materials. This phenomenon reduced the temperature difference in throughout the entirety of the samples. Thus, the samples had low internal stress. Second, during FDM, the fibers could evenly disperse residual stress. This effect could reduce the local residual stress and the volume shrinkage experienced by the PEEK/CF composites. Therefore, the warp deformation of the PEEK/CF had improved.

3.4.2. Warp deformation model of PEEK/CF composites

The warp deformation model of PEEK was established in accordance with the literature [18] as figure 11:

Model assumptions:

1. The number of printing layers is far greater than 1.
2. The internal stress of the composite material after forming is mainly composed of three parts [19]:
   1. Internal stress \( \sigma_1 \) caused by the shrinkage of the new accumulation layer. 2. Bending stress \( \sigma_2 \) caused by the warp deformation of the formed part. 3. Tensile stress \( \sigma_3 \) between the forming surface and the formed part.

The derivation of the warping deformation formula is discussed below.

Figure 11 shows the deformation of the accumulation layer from the glass transition temperature \( T_g \) to the printing chamber temperature \( T_e \). The theoretical linear shrinkage is \( \varepsilon = \alpha (T_g - T_e) \), where \( \alpha \) is the thermal expansion coefficient of the wire. However, the formed part of the lower layer pulls the material back to its original length. At this time, the interlayer internal stress \( \sigma = E \alpha (T_g - T_e) \) is generated. In this formula, \( E \) is the elastic modulus in the thermal deformation stage, and the part warps upward.

\[
\sigma_1 = E \alpha \Delta T \quad (1)
\]
\[
\sigma_2 = \frac{E(z - d)}{\rho} \quad (2)
\]

In this formula, \( \alpha \) is the thermal expansion coefficient of the wire; \( E \) is the elastic modulus in the thermal deformation stage; \( \Delta T \) is \( T_g - T_e \); \( t \) is the height of the formed part; \( h - t \) is the thickness of each layer of the accumulation layer; \( \rho \) is the warping deformation radius; and \( d \) is the distance from the neutral layer of bending deformation to the printing nozzle.

The formula for total internal stress \( \sigma \) is

\[
\sigma = \sigma_0 + E \alpha \Delta T + \frac{E(z - d)}{\rho} \quad (3)
\]

The sum of the internal stress of the formed part is 0, and the resultant moment of the internal stress to point \( o \) is also 0. Hence, two independent equations were obtained:

\[
\int_0^L \left[ -E \alpha \Delta T + \frac{E(z - d)}{\rho} + \sigma_0 \right] dz = 0 \quad (4)
\]
\[
\int_0^t \left[ -E_0 \Delta T + \frac{E(z - d)}{\rho} + \sigma_0 \right] dz = 0
\] (5)

Let,
\[
\sigma' = \sigma_0 - \frac{E(z - d)}{\rho}
\]

And, (4) and (5) can be simplified to
\[
\int_0^t \left[ -E_0 \Delta T + \frac{Ez}{\rho} + \sigma' \right] dz = 0
\] (6)
\[
\int_0^t \left[ -E_0 \Delta T + \frac{Ez}{\rho} + \sigma' \right] dz = 0.
\] (7)

When the above formula is integrated, \(0 \leq z \leq t\) is the formed part and its temperature is always room temperature. Then, \(\Delta T = 0\), and (6) and (7) are solved simultaneously.

\[
\frac{1}{\rho} = \frac{6E_0 \Delta T}{h} \left( t + h \right) \left( 1 - \frac{t}{h} \right).
\] (8)

For the accumulation layer with a certain number of layers,
\[
\Delta h = h - t = \frac{t}{h} \frac{t}{h} = \frac{n - 1}{n}.
\] (9)

Introducing (9) into (8), the radius of curvature is
\[
\rho = \frac{n^2 \Delta h}{6E_0 \Delta T(n - 1)}.\] (10)

In accordance with the geometric relationship in figure 9 and with the help of Taylor’s formula, (10) is derived as
\[
\kappa = \rho \left( 1 - \cos \frac{L}{2\rho} \right) \approx \frac{L^2}{8\rho}.
\] (11)

Introducing (10) into (11), we can obtain (12) as
\[
\kappa = \frac{3\alpha L^2 \Delta T(n - 1)}{4n^2 \Delta h}.
\] (12)

Given the printing layers, \(n \gg 1\), and \(\Delta h = h/n\), (12) then becomes
\[
\kappa = \frac{3\alpha L^2 \Delta T}{4nh}.
\] (13)
As can be seen from (13), the thermal expansion coefficients of the composite materials, the temperature of the forming chamber, and the forming size of the PEEK/CF sample affected warp deformation. The details of this effect are given below as follows:

1. Thermal expansion coefficient of composite materials. A high expansion coefficient is associated with the considerable deformation of the PEEK/CF composites.

2. Temperature of the printing forming chamber. Low forming chamber temperature is associated with the great temperature difference \( \Delta T (\Delta T = T_c - T_e) \) and the substantial warp deformation of PEEK/CF composites. Therefore, the temperature difference in the forming process should be reduced to attenuate warping deformation.

3. Forming size. Large composite material size is associated with the appreciable internal stress and warping deformation of the formed sample.

3.4.3. Effect of heat treatment on the residual stress of the PEEK/CF composites

The blind hole method was used to test the PEEK/CF composite material samples and EVAL software was used to calculate the residual stress value of PEEK/CF composites and the elastic performance constants of CF [17] and PEEK. These analyses were conducted to study the influence of the residual stress on the warp deformation of the PEEK/CF composites in detail. The results are provided in figure 12.

Figure 12 shows that as the content of CF content was increased, the residual stress of the PEEK/CF samples gradually decreased. This decrement might be attributed to the lower Poisson’s ratio and higher thermal conductivity of CF than that of PEEK. These differences resulted in the uneven temperature distribution in the PEEK/CF composites and subsequently accounted for the reduction in shrinkage and residual stress during FDM. Therefore, high CF content resulted in the low warp deformation of the PEEK/CF composites. These results also provided direct evidence showing that the warp deformation of the PEEK/CF composites was improved by CF because of the reduction in the residual stress level of the PEEK/CF composites. This change trend was basically consistent with that reported in the literature [20].

Furthermore, the residual stress of the PEEK/CF composite materials dropped significantly after heat treatment (190 °C/3 h) because the heat treatment temperature was higher than the glass transition temperature of the PEEK thermoplastic materials. The materials were in a highly elastic state, and molecular chains were highly mobile, which could effectively release the residual stress that was originally fixed in the matrix [21]. This result showed that heat treatment could reduce the maximum residual stress value of the sample formed through FDM and that subjecting the PEEK/CF composite material to heat treatment was crucial.

4. Conclusion

PEEK/CF composites were prepared through the additive manufacturing method, and the mechanical, crystallization, and dynamic mechanical properties and porosity warp deformation of the PEEK/CF composites were studied. The following conclusions were obtained through comparative analysis and experimental testing.

1. CF could tailor the pore size and distribution by FDM. The porosity of the PEEK/CF composite material gradually increased with the increase in CF content. The highest porosity of approximately 19.2% was obtained with the CF content of 15%. The slice structures of PEEK/CF-10 and PEEK/CF-15 showed poorer pore distribution and pore size uniformity than those of PEEK and PEEK/CF-5.

2. Heat treatment (190 °C/3 h) could significantly improve the tensile and bending mechanical properties of the PEEK/CF composites but would reduce shear strength. When the CF content reached 15%, tensile strength increased by 10.7% from 85.15 MPa to 94.26 MPa and bending strength increased from 125.28 MPa to 139.87 MPa by 11.6%.

3. The mechanics of the PEEK/CF composite materials produced through FDM strongly depended on the crystallization performance of the materials. High cooling rates were associated with the low crystallinity, tensile strengths, and elastic moduli of the PEEK/CF composites. When the cooling rate reached 80 K min\(^{-1}\), the tensile fracture mode of the PEEK/CF composites changed from brittle fracture to ductile fracture.

4. DMA demonstrated that for the PEEK/CF composites produced through FDM, storage moduli gradually increased, damping factor gradually decreased, \( T_g \) moved to high temperatures, and high-temperature resistance improved with the increase in CF content.
(5) With the increase in CF content, the residual stress of the PEEK/CF composites gradually reduced, and CF could improve the warp deformation of the PEEK-based composites. The model of the warp deformation of PEEK produced through FDM was established, and the warp deformation formula was derived. The formula indicated that warp deformation was related to the thermal expansion coefficient, chamber temperature, and forming size and other factors. These results could be used as an index for evaluating and improving the FDM-formed samples of PEEK-based composites for future research.

Acknowledgments

We wish to express sincere appreciation to all those who have offered us invaluable help for this work. And we also gratefully acknowledge the help of language polishing, Dr Tian Ma, who has helped us modify the language in this work.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Author contributions

Conceptualization, Q S; Data curation, Q S; Formal analysis, Q S; Funding acquisition, Z S; Investigation, X L and S W; Methodology, Q S; Project administration, L Z; Resources, Q S; Software, S W; Supervision, Z S; Writing-original draft, Q S; Writing-review & editing, Z S and ZL; All authors have read and agreed to the published version of the manuscript.

Funding

This research was funded by the National Key R&D Program of China (No. 2017YFB1103400), the State Key Laboratory of Advanced Forming Technology and Equipment (SKL2019003), the China Postdoctoral Science Foundation Project (2019M650612), Technology Development Fund of China Academy of Machinery Science and Technology Group Co., Ltd (312005Q9).

Conflicts of interest

The authors declare no conflict of interest.

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