Progress in the Preparation Process and Application of Carbon Fiber Reinforced PEEK Composites

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Abstract. Due to their outstanding overall performances, carbon fiber/poly(ether-ether-ketone) (CF/PEEK) composites have attracted a lot of interest recently. High-performance CF/PEEK composites have many advantages such as high strength, good toughness, and high service temperature, which have been widely used in various high-precision fields. This paper reviews the research progress of the CF/PEEK composite molding process and its applications in view of the research hotspots in recent years, laying the foundation for the research on the preparation technology and industrial application of the material. CF/PEEK molding process mainly includes injection molding, press molding, filament winding, 3D Printing, and automated fiber placement (AFP). Different processing methods and material ratios result in CF/PEEK materials with different mechanical properties. Since CF/PEEK has its own unique advantages over traditional metal materials in terms of mechanical properties, corrosion resistance, and density, CF/PEEK materials can be used to replace metal materials in many applications, such as aviation and aerospace, biomedical field and automotive part.

1 Introduction

Thermoplastic polymer Poly(ether-ether-ketone, or PEEK) has a semi-crystalline structure, a lengthy service temperature of 250 °C, and an immediate service temperature of 300 °C. PEEK has a benzene ring in the molecular chain to provide rigidity, with the presence of an ether bond provides flexibility and a carbonyl group enhances intermolecular forces, making PEEK has heat resistance, the molding and processing properties of thermoplastics, electrical insulation property, chemical stability, high flame retardancy, biocompatibility, and thermal stability. Although the history of PEEK is only two decades, its outstanding properties have led to its current widespread use in the nuclear, chemical, electrical, electronic, mechanical instrumentation, automotive, and aerospace industries [1].

As an inert material, PEEK has low surface free energy and its mechanical and frictional properties do not meet the needs of some specific areas. PEEK needs to be modified to produce PEEK composites to improve its overall performance.

Over the past three decades, researchers have invested great effort in the research and development of carbon fiber (CF) reinforced thermoplastic composites [2]. Among these materials, CF/PEEK composites have received great attention for their excellent semi-crystalline PEEK matrix properties.

PEEK chains have a high viscosity and low hydrophilic group adhesion. Because of their non-polar, extremely crystalline graphite substrate structure on the surface, carbon fibers also display remarkable reactive inertness. By enhancing prepreg preparation and composite molding processes as well as carbon fiber surface treatment to enhance fiber-resin penetration and interfacial bonding capabilities, CF/PEEK composites now offer improved mechanical qualities.

The structure of a material determines its properties, and the chemical structure of PEEK makes it chemically inert, biocompatible, and suitably dense for use in the biomedical field as a replacement for all types of human bone. At the same time, CF/PEEK can also be used in aviation and aerospace, and automotive parts due to its good mechanical properties, lightweight, and resistance to corrosion and aging.

CF/PEEK composites have outstanding processing qualities that enable them to be produced using a variety of techniques, have good melting point fluidity, and exhibit thermal stability beyond the melting point. As a result, they are being employed in the industry more and more. [3]. Therefore, it is of great significance to investigate various types of forming methods and forming techniques for CF/PEEK composites. The next part of this paper will introduce the new developments of different kinds of processing methods in recent years, focusing on the mechanical properties of materials after different processing methods.

2 CF/PEEK molding process

2.1 Injection molding

One of the most used techniques for thermoplastic

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molding is injection molding, which developed from the metal die-casting procedure. Because it can create sophisticated, dimensionally correct, or metal-inlaid items in a single operation and can create plastic products that satisfy a wide range of user needs, injection molding is frequently used.

Using injection molding, Fangfang Li et al. investigated the effect of blending systems with different levels of short carbon fibers (SCFs) on the thermal, mechanical, and frictional properties of PEEK with different viscosities, measuring the mechanical resistance to friction by tensile strength, flexural strength, coefficient of friction and wear rate [4]. The improved mechanical properties of PEEK composites were mainly attributed to the excellent properties of SCFs, such as high strength, high modulus, and high-temperature resistance, which played a key role in enhancing the mechanical properties of PEEK composites. The research team used three different sources of PEEK as the matrix material. The results showed that the flexural strength and tensile strength of one of the composites showed maximum values after the addition of 20 wt% SCFs. One of the composites experienced increases in tensile strength and flexural strength of approximately 63 and 107 MPa, respectively. They investigated the material's wear surface using electron microscopy at the same time, making deductions regarding its causes. PEEK with the lowest melt viscosity exhibited the best dispersion of SCFs; however, as PEEK's melt viscosity rose, the dispersion of SCFs within the matrix deteriorated, resulting in lower material characteristics.

Yan Liu et al. used 20% short carbon fiber reinforced PEEK resin as the main raw material and also used injection molding to prepare the air intakes and test pieces [5]. The injection molding method replaced the original hand-glued wet molding method used for air intakes and improved the material utilization and dimensional accuracy. The tensile strength, tensile modulus, and punch-type shear strength of PEEK/CF 20wt% composites with fiber lengths of 2-4 mm were 158 MPa, 10.2 GPa, and 75 MPa, respectively, while the tensile strength, tensile modulus, and punch-type shear strength of PEEK/CF 20wt% composites with fiber lengths of 4-6 mm were 209 MPa, 16.8 GPa, and 100 MPa, respectively. The three mechanical properties of the PEEK/CF 20wt% composites with fiber lengths of 4-6 mm were superior. The CF/PEEK material is also one of the best material choices for air intakes due to its tunable tensile strength and modulus of elasticity, excellent creep resistance, resistance to moisture and heat, aging, and impact resistance.

However, the fibers in injection molding usually use short fibers, which are not ideal for mechanical property enhancement due to fiber length limitations, and the strength of the molded product is low and does not meet the requirements of high-precision applications [6]. To improve this, also using injection molding, Tao Wang et al. investigated PEEK/SCF composites prepared using PI (polyimide) as the sizing agent. This was achieved by dipping short carbon fibers into a polyamic acid (PAA) solution to coat the PAA layer, followed by thermal oxidization to obtain PI-modified SCF, and finally by using injection molding to prepare SCF-reinforced PEEK materials with different PI concentrations of 16.8% and 8.2%, respectively. Additionally, tests on a single fiber were performed, and CF/PEEK composites treated with 1.0 wt% showed improved interfacial shear strength (IFSS). The interfacial adhesion between CF and PEEK was improved while PI sizing increased by 24.8%, from 70.6 to 88.1 MPa.

2.2 Press molding process

Hot press molding and laminate molding are both forms of compression molding. Hot press molding, in which a certain amount of molding powder is placed into a metal counterpart and the product is molded under a certain temperature and pressure, is a relatively old method and the technology is relatively mature.

Recent research has tended to explore more methods of adding small amounts of their materials for modification during the molding process. Zhenguang Li et al. used hot pressing to produce PEEK/graphene oxide (GO)-zinc oxide (ZnO)/carbon fiber (CF) (PEEK/GO-ZnO/CF) composites by first heating the modified graphene with PEEK, then blending it with PEEK, and finally hot pressing it with CF woven fabrics, resulting in a more wear-resistant composite [7]. The frictional wear rate was 13×10^{-6} mm^3/Nm at 25 °C, and the tensile strength reached 265 MPa and the bending strength 262.7 MPa.

2.3 Filament winding

One of the crucial shaping steps in the creation of high-performance composite materials is filament winding, especially in the preparation of various high-pressure vessels, storage tanks, corrosion-resistant pipes, high-pressure pipes, etc. It is characterized by high production efficiency, low manufacturing costs, designability, and highly repeatable quality.

However, the presence of residual stresses after winding is a cause for concern, which can affect the subsequent mechanical performance of the pipe. Haibo et al. investigated ways of adjusting tape tension during the molding of CF/PEEK materials to control residual stresses in thermoplastic composite fiber windings, while, from a practical point of view, such an operation could easily be achieved even on an industrial scale [8].

The high energy density of laser heating, the fast response time, the precision of temperature control, and the speed of processing are favored by researchers. Cheng Ye et al. prepared winding samples from carbon fiber-reinforced PEEK (AS4D/PEEK) high-performance thermoplastic composite prepreg and analyzed three process parameters, namely heating zone temperature, winding speed, and fiber tension, and examined the interlaminar shear strength (ILSS) and selected it as a judgment parameter [9]. The research team found that the response values showed an increasing and then decreasing pattern with increasing values of each parameter, and that the heating zone temperature and winding speed had a significant effect on ILSS. A set of enhanced process parameters, including the heating zone temperature of 436.6 °C, the winding speed of 81.3 mm/s, and the tension of the fiber at 201.9 N, were also derived. Under the optimum combination of process parameters, the winding product had the best quality, and the interlaminar shear strength is 52.8 MPa.

Also using laser-assisted winding, Shan Hao et al. used a self-made high-power infrared-heated thermoplastic composite winding machine to investigate the winding process [10]. Again ILSS was chosen as the judging parameter and the effects of key process parameters such as feed tension, lower press roll pressure, winding rate, heating temperature, preheating time, and cooling rate on the performance of PEEK/CF ring products were investigated separately during the winding and forming process, and a series of optimum forming parameters were derived. The outcomes of the trial revealed that the optimum performance of the wound products was achieved with a forming temperature of 410 °C, a preheating time of 40 min, a feeding tension of 8 kg, a cylinder pressure of 0.30 MPa for the lower press roll, a core mold speed of 6 r/min and slow cooling, and an interlaminar shear strength of (82. 29±1. 27) MPa.

2.4 3D printing

Fused deposition modeling (FDM) is a rapidly developing 3D printing technology with promising applications in the medical field. This emerging molding method is now also being used by scholars in the preparation of PEEK/CF composites.

Han Xingting et al. successfully prepared FDM-printed pure PEEK and PEEK/CF composites and characterized them by mechanical tests [11]. The strength of the PEEK samples with reinforced carbon fibers was significantly better than that of bare PEEK in both tensile and flexural tests. The tensile strength of the material increased from 95.21 ± 1.86 MPa to 101.41 ± 4.23 MPa and the tensile modulus increased from 3.79 ± 0.27 GPa to 7.37 ± 1.22 GPa.

Dong Yang et al. experimented with 3D printing to try to break the deficiencies in composite properties caused by short carbon fibers and found that changes in the crystallinity of the composite had a considerable impact on the shrinkage deformation properties and mechanical properties of parts made by 3D printing using PEEK/CF composites [12]. The team first crystallized the print at normal room temperature, then recrystallized and studied the mechanical properties of the material, and finally compared and analyzed the results obtained with those of injection molded materials of the same type and found similar mechanical properties. The following characteristics of the PEEK/CF composite samples were attained under ideal conditions: 50.8-135.0 MPa in tensile strength, 3.5-9.2 GPa in tensile elastic modulus, 86.4-234.2 MPa in flexural strength, 3.7-9.5 GPa in flexural elastic modulus, and 124-2.56% in breaking elongation. The application of 3D-printed PEEK composite materials in the realm of orthopedic implants and aircraft is positively impacted by this study work.

Daisuke Kuba et al. proposed a composite 3D printing method for ultra-low melt viscosity polymers when pure PEEK cannot even be polymerized, to take advantage of the low viscosity and ease of processing to prepare composites with higher strength than standard PEEK/CF composites [13]. After 3D printing with PEEK/CF filaments manufactured at different melt viscosities, the void fraction in the printed product decreases as the polymer melt viscosity decreases. In comparison to the conventional polymer (CF/PEEK 450 G), the ultralow-viscosity polymer (CF/PEEK 90 G) reduced the voids in the filaments by 92%. When compared to CF/PEEK 450 G, the interlaminar tensile strengths of CF/PEEK 90 G were increased by 116.8%. Ultra-low viscosity polymers can be used to create low-void, high-strength products, as evidenced by the finding that specimens manufactured from low-melt viscosity polymers contain small voids and substantial interlayer bonding regions.

2.5 Automated fiber placement (AFP)

Automated fiber placement is one of the most promising processes for the in-situ consolidation of composite materials and is now used in the production of unidirectional prepreg wire bundles or prepreg tapes.

Enhancing the interlaminar bond strength of thermoplastic composites requires the consolidation step in AFP. Arash Khodaei et al. introduced an experimental technique based on tape surface topography as a measure of the degree of intimate contact, and they theoretically investigated two mechanisms that contribute to the development of interlaminar bond strength at the interface between the afferent filament bundle and the substrate [14]. PEEK/CF unidirectional strips were placed on polished steel tools at different placement rates, compression forces, hot gas torch (HGT) temperatures, and tool temperatures. Based on the proposed experimental method, the degree of intimate contact was calculated and compared with predictive models from the literature. The team found in the end that torch and tool temperature had a significant effect on the intimate contact of the material.

Numerous teams have looked into the use of carbon nanotubes in AFP PEEK/CF materials. Chengping Zhang et al. successfully dispersed multi-walled carbon nanotube (MWCNT) nanofillers on the surface of PEEK/CF prepreg by a simple solution, while the AFP in-situ consolidation technique was used to prepare MWCNT/CF/PEEK multi-scale composites and tempered using an autoclave technique to improve the bonding strength of MWCNT to the substrate [15]. The MWCNT/CF/PEEK multiscale composite achieved an ILSS of 91.49 MPa, i.e. an increase of 25.21%, compared to the CF/PEEK composite. The authors discovered electronic pathways developed between the nanoparticles and the material's fibers based on the nanomaterials' outstanding electrical conductivity. This research offers a straightforward, highly automated way of fabricating intricate thermoplastic composite parts with superior mechanical and electrical conductivity.

3 Application of CF/PEEK material

3.1 Aviation and aerospace

Since 1995, polyetherimide (PEI), polyphenylene sulfide (PPS), PEEK, and a series of other high-performance thermoplastic composites with a similar structure have been used in aviation components, revolutionizing aircraft manufacturing. With their good chemical resistance and plasticity, polymer materials overcome the disadvantages of traditional metal materials such as easy corrosion damage, complex processing, and large overall mass, and are widely used in aircraft flaps, ribs, and frame load-bearing components to achieve lightweight design goals.

Non-structural external components such as fuel tank covers were developed for the Airbus A380 aircraft using the lightweight, chemical, and oil-resistant properties of PEEK [16]. A high-modulus carbon fiber-reinforced PEEK material is used for the door fittings of the Airbus A350 to A900 aircraft. The material is easy to drill and can reduce weight by up to 40% and cost by up to 40%. The material is also moisture resistant and resists the accumulation of water vapor at the hatch, increasing the strength and stiffness of the product by 20%. The European Space Agency has launched the additively manufactured PEEK material CubeSat three-dimensional small satellite project, which has entered its first test run [17]. NASA has supported a SpiderFab robotic program to additively manufacture support structures for large solar arrays in orbit using PEEK/CF materials, with test trials already underway on the ground.

3.2 Biomedical field

PEEK is one of the candidates to replace stainless steel, titanium, and ultra-high molecular weight polyethylene in the study of the application of orthopedic implants due to its many benefits, including excellent mechanical properties, wear resistance, chemical resistance, good biocompatibility, elastic modulus close to that of human bone, radiation permeability, easy processing, and reproducible sterilization.

Under a simulated body temperature of 37 °C and simulated body fluid (SBF) lubrication conditions, Xue Chenglong et al. concluded that the prepared PEEK/CF also had better mechanical properties compared to titanium alloy (Ti_6Al_4V) [18]. It had a tensile strength of 880 MPa, which was only 15 MPa lower than that of titanium alloy, but its density was much lower than that of the metal material, satisfying the implant's fundamental mechanical requirements, and could replace titanium alloy in the preparation of orthopedic internal fixation materials. Solvay synthesizes 30% CF-reinforced PEEK with excellent creep resistance and long-lasting fatigue stress resistance for use as a structural, load-bearing, implantable medical material for spine, hip, and knee replacements [19].

3.3 Automotive industry

In the automotive industry, PEEK/CF composites have the potential to be used as a plastic alternative to metal. Solvay announces the launch of a new grade of KetaSpire PEEK KT-850 SCF 30, designed for precision braking systems and electronic pump components for electric vehicles. The product was developed to provide better sealing performance than the standard 30% carbon fiber-filled PEEK grade [20]. Robert Bosch UmbH et al. used PEEK/CF instead of metal as a functional part in ABS. The lighter composite part reduced the rotational inertia, thus minimising the reaction time and greatly enhancing the reaction performance of the whole system at a reduced cost compared to the metal parts previously used [21].

4 Conclusion

CF/PEEK composites have good overall properties, and with in-depth research into their mechanical properties, biocompatibility, and molding processes, CF/PEEK composites are bound to be more widely recognized and used in a number of areas and fields such as marine, aerospace, and biomedicine. Injection molding, press molding, and filament winding have only been used in the molding process for this composite for a short time, and there are still many parameters and substances to be added to the production of CF/PEEK composites that need to be explored, as well as many experiments and investigations into how to carry out large-scale production in factories in the future. Fiber agglomeration is easy to occur during CF/PEEK molding, which increases the difficulty of the production process. At the same time, due to the limitation of the molding process, the mechanical properties of the material are often not satisfactory because the length of the carbon fiber is not long enough, especially when it is used in some high-precision fields.

In the meantime, this paper also reviews the application of 3D printing and automated lay-up molding as two relatively new molding technologies in the production of CF/PEEK composites, with the former promising for the preparation of low-viscosity, high-strength materials and the latter perhaps having the opportunity to be used in mass production in the future. In terms of applications, CF/PEEK composites are still primarily used in aerospace materials, but in recent years, based on their plasticity and not inconsiderable mechanical strength, future applications in biomedical and automotive components are worth exploring.

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