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Review

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Molding of polyether ether ketone (PEEK) and its composites: a review

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Abstract: Over the last half-century, polyether ether ketone (PEEK) has emerged as a widely adopted thermoplastic polymer, primarily due to its lower density, exceptional mechanical properties, high-temperature and chemical resistance, and biocompatibility. PEEK and its composites have found extensive applications across various fields, including machinery, aerospace, military equipment, electronics, and biomedicine, positioning themselves as promising substitutes for traditional metal structures. Nevertheless, achieving optimal performance and functional molding of PEEK and its composites presents a formidable challenge, given their inherent characteristics, such as semi-crystallinity, high melting temperature, heightened viscosity, low dielectric coefficient, and hydrophobic properties. In this paper, we present a comprehensive review of the molding methods and processes of PEEK and its composites, including extrusion molding, hot compression molding, injection molding, and 3D printing. We also introduce typical innovative applications within the fields of mechanics, electricity, and biomedicine while elucidating methodologies that leverage the distinctive advantages of PEEK and its composites. Additionally, we summarize research findings related to manipulating the properties of PEEK and its composites through the optimization of machine parameters, process variables, and material structural adjustments. Finally, we contemplate the prevailing development trends and outline prospective avenues for further research in the advancement and molding of PEEK and its composites.

Key words: PEEK; Composites; Extrusion molding; Hot compression molding; Injection molding; 3D printing

1 Introduction

For over five decades, thermoplastic polymers and their composites have emerged as a favored alternative to metals, owing to their low density, impressive toughness, reliable processability, recyclability, and versatile design capabilities. Polyether ether ketone (PEEK) stands as a high-performance polymer at the pinnacle of the thermoplastic performance hierarchy (Fig. 1a). Initially developed in the laboratories of ICI in the UK in 1978, PEEK transitioned to mass production in the 1980s. In 1980, the foundational material data for PEEK was first published by D.J. Blundell and B.N. Osborn, providing key information on the glass transition temperature (Tg) of 144 ℃ and the melting temperature (Tm) of 334 ℃.

It features a continuous conjugated structure with spatially intertwined π-π bonds, diverging from the molecular configuration of typical polymers that rely on linear C-C bonds as the main chain. Consequently, the chemical bonds in PEEK have significantly higher energy, allowing them to withstand high temperatures without fracturing or rupturing. Meanwhile, within the molecular structure of PEEK, the ketone group and ether group on the benzene ring are para-distributed. The forces acting on the main chain of the PEEK molecule are symmetrically distributed on both sides of the

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benzene ring, maximizing the strength advantages of this planar-type group, yielding outstanding mechanical properties (Fig. 1b). Moreover, PEEK has been used as a substitute for traditional metal interbody fusions since the late 1990s (Laubach et al., 2022), owing to its excellent biocompatibility. PEEK has a Young's modulus of 3-4 GPa, similar to that of human cortical bone (6-30 GPa) and significantly lower than that of titanium and titanium alloys (over 100 GPa). This minimizes the risk of bone resorption resulting from stress shielding. In summary, PEEK demonstrates exceptional mechanical properties, remarkable high-temperature resistance, and excellent biocompatibility, positioning it as a high-performance material in various challenging environments. Presently, PEEK finds widespread applications across diverse industries, including aerospace, defense, engineering, and biomedicine, presenting itself as a potential alternative to metals (Guo et al., 2023; Hastie et al., 2022; Hu et al., 2022; Ren et al., 2022; He et al., 2021).

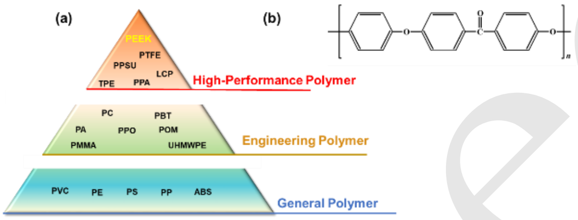

Fig. 1 (a) PEEK is located at the top of the polymer performance pyramid. (b) Molecular structure of PEEK

Like other thermoplastic polymers, PEEK has been developed and molded by various processes, including extrusion molding, hot compression molding, injection molding, and 3D printing, resulting in a diverse array of unique components and profiles. Through these processes, it is possible to achieve additive, blending, and chemical modification of PEEK. The PEEK composite materials prepared in this way are endowed with a wide range of characteristics, including mechanical, electrical, and biocompatibility properties. This is crucial for expanding its application scope. Due to differences in melt molding processing methods and parameters, PEEK and its composites encounter variable shear and temperature fields, resulting in a diverse spectrum of mechanical properties arising from variances in aggregate structure and reinforcement state. An impact on other aspects of service performance is also observed. Consequently, achieving more extensive and enhanced service performance of PEEK and its composites has become a persistent focus of research. However, PEEK requires significantly higher molding temperatures and pressures than general polymers and other engineering polymers. Moreover, variations in processing principles lead to discrepancies in the types of materials available for molding, as well as the mechanical properties and structural complexity of the molded parts. Therefore, selecting appropriate processes and rational parameters becomes essential when the molding objectives differ. Research on the influence of the molding process on the structures and properties of PEEK and its composites holds significant importance in enhancing their applicability and service performance.

In this review, we focus mainly on progress in research on various thermoforming methods for PEEK and its composites, such as extrusion molding, hot compressing molding, injection molding, and 3D printing, as follows:

(1) In Section 2, we introduce the developmental lineage and molding principles of the four main molding processes including extrusion molding, hot compressing molding, injection molding, and 3D printing.

(2) In Section 3, we present the use of the properties of the extrusion molding process based on the excellent characteristics of PEEK materials. This encompasses the development of various types of base profiles and functional composites.

(3) In Section 4, we describe continuous fiber-reinforced PEEK composites and other composites with excellent properties that have been developed through hot compression molding.

(4) In Section 5, we characterize some typical applications of PEEK and its composites in the fields of mechanics, electricity, and biomedicine, which are mass-produced by injection molding.

(5) In Section 6, we propose how to maximize the advantages of 3D printing for molding high-performance PEEK composite materials and their complex structures.

(6) In Section 7, we summarize the current state of the molding of PEEK and its composites and analyze its future directions.

2 Main molding processes of the polymer structure component

To provide a clearer illustration of the outcomes derived from the integration of PEEK with diverse molding techniques and their corresponding research progress, it is imperative to introduce the fundamental molding processes applicable to polymer materials. A comprehensive understanding of the distinct principles governing these processes aids in discerning the merits and drawbacks associated with each method under different circumstances. Such insights significantly benefit producers in making informed choices among different processes to achieve diverse production objectives.

2.1 Extrusion molding

The extrusion molding process is a frequently used technique for processing plastics. In 1930, BASF in Germany pioneered the use of extrusion molding for producing polystyrene, which had until then been used in the manufacture of rubber products. In 1939, the Italian LMP company and the German Troester company developed twin-screw and single-screw extruders for plastics production via extrusion molding. This led to the initiation and gradual refinement of the extrusion molding process for polymer materials (Sakai, 2013).

The principle of extrusion molding is shown in Fig. 2. The extrusion molding process is usually divided into four parts: feeding, kneading, conveying, and cooling (Lewandowski and Wilczynski, 2022). Polymer chips, powders, particles, and their blends with reinforcements enter the screw through a feed hopper. As the screw rotates, these materials are melted by the heat from the screw's temperature field and shear action. As it approaches the extruder die, the grooves on the screw become shallower and the polymer melt is compressed and extruded under high pressure to exhaust the water vapor and achieve complete homogeneous mixing with the reinforcement. The melt is then conveyed to the extruder die. Finally, the high-pressure extruded melt is shaped by the die and cooled to a stable form by a gas or liquid medium (Hyvarinen et al., 2020).

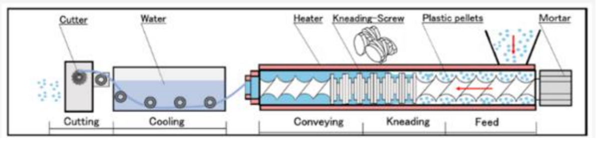

Fig. 2 The principle of extrusion molding (Wen et al., 2022). [Copyright, 2021, MDPI]

Based on their mechanical structure, extruders can be classified as single-screw, twin-screw, or multi-screw extruders (Sakai, 2013). Single-screw extruders feature one screw and come with either smooth or grooved barrels. Twin-screw extruders, have two screws that can rotate in either the same or opposite directions. When rotating together, they are commonly used in the development and processing of composite materials. Conversely, when rotating in opposite directions, high pressure can be generated between the meshing areas, making it suitable for extruding profiles with high mechanical properties. While mechanically more complex, the twin-screw extruder offers superior mixing and melting speeds. In contrast, the single-screw extruder is simpler with lower technical barriers to application.

One notable advantage of extrusion molding is its capability to develop new composite materials, thereby enhancing or adding to the functionality of polymers (Hyvarinen et al. 2020; Lewandowski and Wilczynski, 2022; Sakai, 2013). This process facilitates the creation of conductive polymer composites, a feat typically unattainable with polymer materials alone. Moreover, it allows for the production of composite materials reinforced with short fibers and materials with an adjustable modulus, suitable for bone scaffolds. By modifying the shape or geometry of the extruder die, various basic profiles with features such as rods, tubes, films, fibers, or filaments can be obtained. These basic profiles can undergo further processing through secondary cold processing, 3D printing, and mechanical structure assembly. However, the limitations of the molding method make the extrusion molding impractical for producing continuous fiber-reinforced composites with ultra-high mechanical properties or complex structures. Additionally, the significant pressure drops of the material melt near the extruder die pose challenges in controlling deformation and compromise the mechanical properties of extrusion-molded parts.

2.2 Hot compress molding

Hot compression molding stands out as a pivotal method for shaping polymer materials. The fundamental principle involves placing a certain amount of polymer material into a metal mold. Subjected to controlled temperature and pressure, the molten material undergoes plasticization, flows to fill the cavity, and ultimately solidifies into the specified shape of the product (Fig. 3). The hot compression molding process generally encompasses pre-pressure preheating, feeding, exhausting, pressure holding, cooling and demolding, and product post-treatment (Jaafar et al. 2019).

This method yields diverse products depending on the material used. Beyond polymer pellets and powders, the mold can accommodate homogeneous mixtures of short fibers or other reinforcements and polymers. For instance, it becomes feasible to create a reinforced polymer material with continuous fibers by layering one or multiple sheets of continuous fiber prepreg in the mold and hot pressing them together with the polymer. Additionally, integral molding with the polymer and its composite material is achievable by pre-inserting a metal component of the target part into the mold.

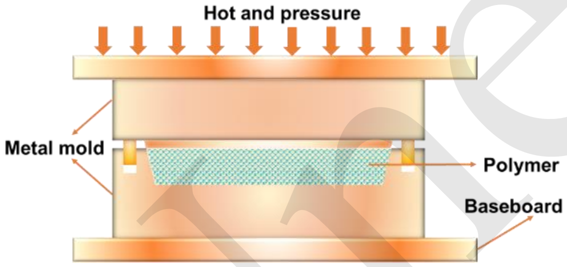

Fig. 3 The principle of hot compression molding.

In addition to its simplicity of operation and high production efficiency, hot compression molding has several advantages based on its molding characteristics. Firstly, all stages of hot compression molding, including material feeding, melting, diffusion, cooling, and forming, are conducted within the mold. This implies a shared thermodynamic process between the material and the mold, set and controlled by the system throughout the entire production cycle. Hot compression molding circumvents the extrusion molding, making it more suitable for molding high-viscosity plastics, such as ultra-high molecular weight polyethylene, certain specialty engineering polymers, and short fiber-reinforced composites with a fiber content exceeding 50% (Santos et al. 2021). Secondly, hot compression molding facilitates the incorporation of continuous fiber products with polymers and advanced designs, enabling the creation of continuous fiber-reinforced thermoplastic composites with variable mechanical properties. This method proves valuable in producing continuous fiber-reinforced thermoplastic composites endowed with exceptional mechanical properties and resistance to crack extension. Finally, hot compression molding exerts a prolonged and uniform pressure on the molded polymer. This contributes to enhanced inter-diffusion among molecular chains, resulting in elevated mechanical properties of hot compression-molded products. Moreover, this pressure molding type reduces warpage susceptibility, improves repeatability, minimizes internal stresses, and ensures stable mechanical properties. However, this molding method has certain limitations. The production of complex structures with concave shapes, side slopes, or small holes poses a significant challenge for hot compression molding. Precise control of temperature and pressure is essential, as the material is susceptible to oxidation and degradation, potentially impacting product quality. Furthermore, machine constraints make molding larger-sized products challenging.

2.3 Injection molding

In 1872, John Wesley Hyatt, an American inventor, designed the world's first recorded injection molding machine. The birth of modern injection molding technology occurred in 1946 when James White invented the first injection molding machine capable of automatic extrusion molding (Zema et al. 2012). The injection molding process involves melting polymer particles or powders into a viscous melt using a plasticizing screw. Typically comprising five stages: feeding, melting, injecting, packing, and cooling (Zhou et al., 2022), the pressurized molten polymer, driven by a plunger or screw at high speed, is injected into a metal mold to maintain pressure and then cooled to the specified shape (Fig. 4). Injection processing and production are applicable to powdered and pelletized thermoplastic polymers and their short fiber-reinforced composites.

Injection molding is the most common and widely used polymer molding process today. Renowned for its ease of automation and consistent production quality, it is also one of the most theoretically developed and computer-simulated polymer molding processes. Advanced metal mold design and processing techniques have significantly enhanced the advantages of injection molding. Firstly, injection molding ensures high productivity even for parts with complex 3D structures, such as impellers, vertebrae, and automotive spoilers, providing an advantage of near-net molding that extrusion molding and hot compression molding lack. Secondly, injection-molded products exhibit higher geometric accuracy. The popularity of injection molded products is also attributed to their excellent mechanical properties. During injection molding, polymers and their composite melts undergo a high-speed injection process, leading to directional arrangement of molecular chain segments and fibers through high-speed shear, thereby improving their mechanical properties. Additionally, the holding pressure process in injection molding plays a crucial role in achieving the high mechanical properties of its products.

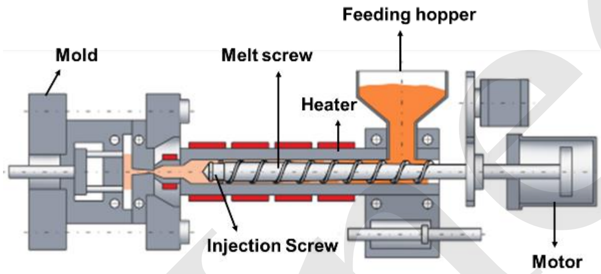

Fig. 4 The structure of a typical basic injection molding machine (Wilczynski et al., 2022). [Copyright, 2022, MDPI]

However, injection molding is an intermittent production process where the polymer melts in the barrel, and the mold undergoes separate thermodynamic processes. The temperature difference between the two and the pressure during molding significantly affects the structure and fiber distribution of the polymer product. Consequently, conventional injection processes, involving up to a dozen control parameters, are intricate. Injection machines and molds are comparatively complex and expensive, and the overall molding cycle time is lengthy. The manipulation of injection molding also requires a certain technical competency. Additionally, the presence of gates and runners decreases material usage, rendering it unsuitable for customized or non-mass-produced products. Due to its molding method, injection molding presents challenges when attempting to mold high-viscosity materials, including composites with high levels of short fibers and continuous fiber-reinforced thermoplastic composites. This limitation also affects the compatibility of injection molding with different types of materials.

2.4 3D printing

In 1986, Charles W. Hull applied ultraviolet technology to the field of rapid prototyping and invented SLA (Stereo lithography) technology, marking the birth of 3D printing technology (Valino et al., 2019). Currently, 3D printing technology can be classified into over ten types based on specific operating principles. For thermoplastic polymers and their composite materials, the most widely used 3D printing technology is fused deposition modeling (FDM), also known as fused filament fabrication (FFF). This methodology was first pioneered by the American scholar Scott Crump in 1988. FDM is a continuous process that involves melting a polymer filament or particle via electric heating, and the melted material is then extruded out of a nozzle in a preset two-dimensional trajectory. The nozzle is lifted layer-by-layer or the platform moves down layer-by-layer, ultimately forming a three-dimensional printed structure (Fig. 5).

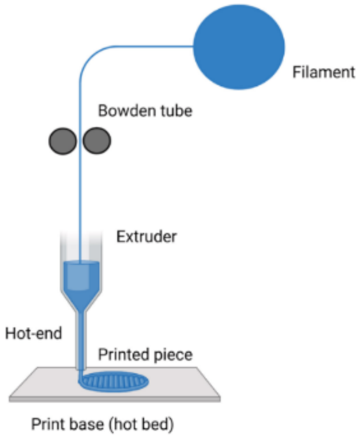

Fig. 5 The principle of injection molding fused deposition modeling (FDM). (Cano-Vicent et al., 2021) [Copyright, 2021, ELSEVIER]

The most important feature of 3D printing is its additive manufacturing process. This revolutionary molding method brings many significant advantages. Firstly, the layer-by-layer molding method makes complex three-dimensional structures two-dimensional. Shaped trusses, porous structures, and three-period minimal surface (TPMS) structures, which are difficult or impossible to form through subtractive manufacturing and isotropic manufacturing, have become possible. It has brought new energy to the advancement of controlled industrial lightweighting. Secondly, 3D printing is an optimal molding method for personalized customization of items like dentures, vertebral cages, and bone scaffolds, as it does not require a mold. This feature is also beneficial for modern industrial design, allowing for convenience in original model verification.

Despite significant strides in 3D printing technology, challenges persist, especially in large-scale applications. The current non-pressure continuous molding process faces difficulties in maintaining the temperature of previously printed interfaces, resulting in low surface activity and inadequate layer-to-layer bonding strength. This creates significant mechanical strength anisotropy in 3D-printed parts, limiting their applicability. Additionally, continuous fiber 3D printing technology has room for improvement, particularly in fully leveraging material advantages for enhanced mechanical properties. Producing 3D-printed continuous fiber-reinforced polymer composites with minimal porosity and ultra-high interfacial strength remains an ongoing challenge. The efficiency and precision of many 3D printing technologies also fall short in producing large batch parts and high-precision components.

3 Extruded PEEK and its composites

3.1 Profiles of extruded PEEK and its composites

Secondary processing of polymer sheets, rods, and tubes manufactured by extrusion molding (Fig. 6) to form specified products is a common process. Although there has been limited academic research on these manufacturing processes, the extrusion of PEEK sheets, tubes, and rods has generated a significant number of patents over the last three decades (Ji, 2021; Nishitani, 1990; Qiao, 2021; Suzuki, 2001; Zhu et al, 2021.). For instance, Ji (2021) invented an extrusion die for PEEK rods which enables the simultaneous production of several rods with smooth surfaces and dense interiors, and Suzuki (2001) designed an extrusion device suitable for the continuous production of high-performance, thin PEEK tubes. The extrusion machine equipped with an enhanced die, body, and heating method can better adapt to the high temperature and high-pressure demands necessary for PEEK molding. Moreover, it can enhance the quality of PEEK and result in a denser internal structure for the profile and higher production efficiency.

Fig. 6 Profiles molded by extrusion molding.

With the rise of 3D printing technology during the past decade, the preparation of PEEK standard filaments with uniform diameter and excellent performance has become a hot topic. Using extrusion molding, PEEK composite filaments are crafted by blending with various reinforcements such as nano-hydroxyapatite (nHA), nano-strontium, nano-zinc, nano-graphite, and carbon nanotubes (CNT). This innovative technique brings substantial advantages, enhancing the biocompatibility, heat resistance, mechanical properties, thermal conductivity, and electrical conductivity of 3D-printed components. A particularly challenging aspect of this study revolves around reducing the internal porosity of CF/PEEK composite filaments. Naganaboyina et al. (2023) achieved uniform blends of CF and PEEK through a ball milling process, delving into the correlation between extrusion molding parameters and filament formation. Their work showcased the positive relationship between temperature gradients in the barrel, high screw speeds, and pressures in ensuring filament diameter uniformity. Additionally, it shed light on filament brittleness due to the elevated fiber content, emphasizing the impact of cooling rate and ambient temperature on filament quality. Experimental findings underscored that porosity resulting from inadequate bonding of internal CF to the PEEK matrix significantly contributes to the deterioration of tensile properties. Diouf-Lewis et al. (2022) successfully obtained 0.6-mm diameter CF/PEEK filaments with a fiber mass fraction of up to 30% through extrusion molding. Their in-depth investigation into porosity and fiber distribution within the filaments, aided by micro-CT scans, revealed fibers mostly exceeding 890 μm in length. Void sizes ranged from about 1-28 μm, with smaller voids near the outer surfaces and larger voids in the center. SEM experiments suggested that the sizing agent on the surface of the carbon fibers played a role in forming a robust interface. Kuba et al. (2022) demonstrated creativity in using extrusion molding to develop continuous CF/PEEK filaments for 3D printing. They explored the impact of different viscosities of PEEK on internal porosity and found that ultra-low viscosity PEEK reduced voids within the filaments by 45% compared to standard PEEK. This supports the idea that reducing material viscosity and enhancing its flow on the carbon fiber's surface is an effective strategy to minimize filament porosity. This collective body of research highlights the intricate dynamics between material properties, processing parameters, and the production of high-quality PEEK composite filaments for advanced 3D printing applications.

3.2 Functional PEEK composites developed by extrusion molding

The exceptional reprocessing ability of thermoplastic polymers contributes significantly to their widespread popularity. Researchers aim to amplify the versatility of thermoplastic polymers by compounding them with materials that confer specific functionalities, thereby expanding their applications. PEEK, with its intrinsic low dielectric constant and natural insulating properties, has limitations in electrical applications. Recent endeavors have focused on enhancing the electrical conductivity of PEEK by incorporating highly conductive fillers through the extrusion molding process.

Various conductive fillers, such as nano-silver (Riviere et al., 2016), graphite (Goyal, 2013; Mokhtari et al., 2021), fly ash (Parvaiz et al., 2011), and carbon nanotubes (CNT) (Bangarusampath et al., 2009; Gao et al., 2015; Lin et al., 2017; Wen et al., 2022; Zhang et al., 2012), have been explored in the formulation of functional PEEK composites. Extrusion molding has emerged as a pivotal technique, showcasing unique advantages in developing these composites. Carbonaceous materials, renowned for their exceptional electrical, mechanical, and thermal properties, have garnered significant attention in this context. In the early stages of exploration, Bangarusampath et al. (2009) produced multi-walled carbon nanotube (MWCNT) reinforced PEEK composites, enhancing composite conductivity by nearly 10 orders of magnitude with a mere 2% Wt addition of MWNTs. Gao et al. (2015) demonstrated ingenuity in preparing carbon black (CB) reinforced PEEK/thermoplastic polyimide (TPI) alloys, applying the difference in affinity between TPI and PEEK for selective carbon black localization. This transformation from an island structure to a continuous structure resulted in a notable reduction of the electroosmotic flow threshold to 5 Wt%. Continuing this line of investigation, Gao and colleagues extended their study to the electrical conductivity of MWCNTs/PEEK/TPI ternary composites, achieving low electrical leakage thresholds with a mass fraction of MWCNT as low as 0.8 Wt%. However, the compatibility issue between CNT and PEEK led to CNT agglomeration, impacting the formation of the thermal conductive network. Recent research efforts have concentrated on improving the dispersion of MWCNTs in PEEK. Zhang et al. (2012) enhanced dispersion by incorporating polyether sulfone (PES)-encapsulated MWCNTs in the PEEK matrix, resulting in improvements in dielectric, mechanical, and thermal properties. Lin et al. (2017) used a liquid crystalline copolymer of poly (aryl ether ketone) (FPEDEKKLCP) as a processing aid to reduce the melt viscosity of MWCNTs/PEEK composites, concurrently enhancing the dispersion of MWCNTs in the PEKK matrix. In a novel approach, Wen et al. (2022) prepared hydroxyphenolphthalein-type polyether ketone-grafted carbon nanotubes (PEK-C-OH-g-MWCNTs-COOH) composites through an esterification reaction. This innovative method significantly improved the distribution of CNTs and enhanced the electrical conductivity from 1.3 S/m to 3.0 S/m. These advancements provided methods for refining the electrical properties of PEEK through formulations and processing techniques.

Table 1 Extrusion molding of various PEEK composite materials

Filler	Ratio	Electro-osmotic flow threshold	Conductivity（S/m）	Ref.
AgNP	10.8% (vol)	10.8% (vol)	6.7×10^{4}	(Riviere et al., 2016)
AgNWs	0.55% (vol)	0.55% (vol)	1.45×10^{5}	
EG	11.7% (wt)	8.5% (wt)	2.4×10^{-3}	(Mokhtari et al., 2021)
EG	10% (wt)	1.5% (wt)	1.23×10^{2}	(Goyal, 2013)
MWCNT	17% (wt)	1.5% (wt)	10^{2}	(Bangarusampath et al., 2009)
TPI/CB	12.5% (wt)	5% (wt)	0.533	(Gao et al., 2015)
MWCNTs/ FPEDEKKLCP	0.4% (wt)		8.4×10^{-2}	(Lin et al., 2017)
MWCNTs-COOH	26.1% (wt)	4.5% (wt)	1.3	(Wilczynski et al., 2022)
PEK-C-OH-g-MWCNTs-COOH	30% (wt)	5% (wt)	3.0	

* AgNP denotes a spherical silver nanoparticle and AgNW a silver nanowire. EG stands for expanded graphene

Developing new composites through extrusion molding to enhance the biocompatibility advantages of PEEK is a current focus among researchers. Numerous studies have demonstrated that co-extrusion with hydroxyapatite (HA) effectively improves the bioactivity of PEEK, with bioactivity positively correlated with HA content (Abu Bakar et al., 2003a; Abu Bakar, 2003b; Abu Bakar, 2003c; Ma and Tang, 2014; Tang et al., 2004; Bathala et al., 2019). Traditional biomaterials, including strontium HA (Ma and Tang, 2014), calcium silicate (CS) (Zheng et al., 2021), and glass fibers (GF) (Song et al., 2017), have shown similar effects. However, enhancing bioactivity is not the sole consideration for extruded PEEK materials in biomedical applications like bone implantation. Achieving mechanical properties comparable to human bone and high fatigue strength are equally crucial and more challenging. Khor et al. (Abu Bakar et al., 2003a; Abu Bakar, 2003b; Abu Bakar, 2003c; Tang et al., 2004) conducted comprehensive mechanical characterization using co-extrusion to mold HA/PEEK composites ranging from 5 to 40%. Mechanical behavior analysis revealed excellent tensile fatigue resistance, with a high estimated fatigue strength at 50% of ultimate tensile strength for 1 million cycles. Additionally, the tensile modulus of the composites increased while the tensile strength decreased, resulting in a significant enhancement of brittleness. Notably, the tensile modulus of HA/PEEK approached that of human cortical bone when the volume fraction of HA was 30%. Khor's group observed that blending PEEK with micron-sized HA led to matrix debonding, causing poor interfacial adhesion and triggering crack initiation and expansion, ultimately resulting in material failure. This raised concerns about long-term loading. The use of nano-bioactive materials with superior mechanical characteristics became more desirable. For instance, Marcomini (2017) et al. co-extruded nHA treated with a silane coupling agent with PEEK and systematically compared the micro- and meso-structures and mechanical property performance of the composites before and after silane treatment. Silane-treated nanocomposites exhibited higher stress, six times higher fracture deformation, and higher impact strength than untreated nanocomposites. The cycles to failure for silane coupling agent-treated nanocomposites were nearly 200% higher than those for untreated samples. This enhancement was attributed to the strengthened interfacial bond of PEEK/HA with the addition of the silane coupling agent, resulting in better dispersion of nHA in the PEEK matrix.

PEEK and its composites stand out as ideal alternatives to metals today, thanks to their exceptional mechanical properties. Extruded short carbon fiber (SCF) and short glass fiber (SGF) reinforced PEEK have been standardized and mass-produced by major raw material manufacturers, finding applications in various processes such as thermoforming, injection molding, and 3D printing. Parts crafted from these materials have garnered widespread validation from researchers. Moreover, researchers have delved into expanding the applications of PEEK composites by focusing on their favorable friction properties through extrusion molding. Puértolas et al. (2019) engineered graphene nanoparticle-reinforced PEEK composites using a twin-screw extruder and extensively studied their friction characteristics. The inclusion of nanographene sheets (GNPs) as fillers in PEEK-based materials, without any chemical functionalization, led to significant enhancements: a notable (34%) increase in hardness, a substantial reduction (-60%) in the coefficient of friction (COF), and a remarkable decrease (-38%) in the wear coefficient on the material surface. Zhong et al. (2011) developed hybrids of zirconium dioxide (ZnO_2) filled CF/PEEK, demonstrating their outstanding wear performance in high-pressure underwater environments, attributed to the synergistic effects of ZnO_2 particles and CF. Additionally, Gladson et al. (2019) extrusion-molded AgNWs/PEEK/polytetrafluoroethylene (PTFE) ternary composites, achieving superior anti-friction materials with coefficients of friction as low as 0.2.

3.3 Discussion

Extrusion molding is widely used in preparing materials, including basic PEEK profiles like rods, tubes, and plates. It also blends PEEK with fillers to enhance properties like biocompatibility and electrical conductivity, usable in 3D printing and injection molding. Despite its advantages, challenges persist. Basic research on PEEK and its profiles is lacking. Achieving effective melt blending with fibrous or powdered fillers remains difficult, often causing interface degradation. Additionally, research on extrusion foam molding for PEEK is limited but holds potential for lightweighting. Addressing these challenges is crucial for advancing PEEK and its composites via extrusion molding.

4 Hot compression molded PEEK and its composites

4.1 Hot compression molding of continuous fiber-reinforced PEEK composite

Hot compression molding is a pivotal method for fabricating continuous fiber-reinforced PEEK composites, allowing for a substantial increase in fiber mass fraction and resulting in exceptional mechanical properties. Numerous scholars have delved into the effects of hot compression molding process parameters, such as molding pressure, temperature, and holding time, on the mechanical properties of molded continuous fiber-reinforced PEEK (CFRP) composites (Lessard et al. 2015; Li et al. 2018; Machado et al. 2016; Mayer et al. 1998; McCool et al. 2012; Patel et al. 2010; Sala et al. 2002). Dai (2021) produced laminates comprising multilayer unidirectional prepreg tapes with 67% Wt of continuous carbon fiber (CCF) via the molding process. The most influential molding parameters affecting tensile strength were identified as molding temperature, holding time, and molding pressure. The optimal molding process was determined to be 400 °C, 3 MPa, 30 min, resulting in a remarkable tensile strength of about 500 MPa. In a more detailed and systematic study, Ma (2023) molded 16 layers of CCF/PEEK prepreg tape with a mass fraction of 54% into a single laminate. Their findings highlighted the interplay between molding temperature, pressure, and holding time in promoting matrix infiltration and reducing voids. However, prolonged exposure to high pressure and temperature led to PEEK degradation, resulting in embrittlement and lower impact strength. Moreover, the study emphasized the differential roles of molding temperature, pressure, and holding time in influencing crystallization behavior. While the crystallinity of the composites remained constant under different molding temperatures, higher temperatures prompted the PEEK matrix to spread to the surface of the fibers, fostering the growth of spherical crystals. This phenomenon resulted in more and larger crystals, increased composite toughness, and elevated Tm at the macroscopic level. The rise in molding pressure enhanced the density of crystalline domains, boosting mechanical strength. Increased holding time promoted matrix/fiber contact and the growth of transverse crystalline layers, improving bending strength. The experimentally determined optimal molding parameters for continuous CF/PEEK composites, ensuring both transverse bending properties and type I interlaminar fracture toughness, were identified as 405 ℃, 1.5 MPa, and 30 min, closely aligning with those derived by Dai et al. Notably, molding parameters are not the sole determinants of the final mechanical properties, with the laying method of unidirectional prepreg tape also playing a crucial role. Dai et al. (2022) demonstrated the efficacy of preparing unidirectional prepreg tape laminates laid in the [0°/90°] direction, achieving outstanding tensile strength (810 ±10 MPa) and bending strength (521 ± 12 MPa). The strong anisotropy of unidirectional prepreg tapes, characterized by extremely high tensile strength in the fiber alignment direction, underlines their potential. However, their brittleness in other directions limits their applications, prompting the exploration of braided prepreg tapes for scenarios requiring more deformation and bending. Hu et al. (2022) investigated the influence of process parameters on CF-reinforced PEEK composite materials, emphasizing that excessively low and high molding temperatures resulted in increased melt viscosity. Elevated temperatures caused thermal degradation and embrittlement of PEEK, while insufficient molding pressure led to reduced melt infiltration into the fibers, and excessive pressure resulted in resin loss, fiber misalignment, and deformation. The optimized molding parameters were determined to be a molding temperature of 390 ℃, molding pressure of 2.5-3.5 MPa, and a holding time of 20-30 min. This study corroborated the findings of Zheng (2019), who conducted a similar investigation over a broader range of molding temperatures and pressures, highlighting the importance of balancing molding parameters to achieve optimal mechanical properties. The complexity of factors affecting the mechanical properties and molding accuracy of CF/PEEK thermoformed laminates extends to the specific working environment and the state of continuous fiber reinforcement. Systematic research by various scholars has addressed interfacial strength, fiber deformation during the molding process, and moisture-heat aging, yielding valuable insights. For instance, Batista et al. (2021) investigated the effect of the crystallinity of CF/PEEK plain fabric laminates on their weathering resistance. Their experiments, conducted according to ASTM standards, revealed that UV/condensation treatment induced secondary crystallization, enhancing interlayer shear strength and material hot compression strength. Humid-heat treatment increased crystallinity, improving Young's modulus and hot compression strength. Moisture entering the composites in salt spray experiments led to increased crystallinity, reduced water absorption, and demonstrated CF/PEEK's excellent weathering resistance. Almudaihesh et al. (2020) explored the influence of water immersion on the mechanical strength of different types of CF/PEEK composites, finding variable strength losses after 40 days of immersion. This research provided a basis for setting safety factors and selecting suitable types for CF/PEEK service in underwater environments. Bismarck et al. (2007) studied the deformation behavior of CF/PEEK laminates exposed to boiling water under end-loaded hot compression bending conditions. The duration of deformation failure was found to be closely related to the matrix, fiber, and interface states of the laminate. The study suggested that thermoplastic composites leading to compression bending or large planar deformations are "safe" only if the maximum service temperature of the finished part is well below the Tg of the polymer matrix. Otherwise, severe material failure cannot be ruled out, even at low-bending radii.

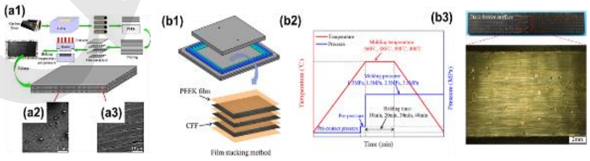

Fig. 7 (a1) The preparation of the composites and SEM morphologies of as-prepared composites in (a2) vertical and (a3) horizontal views. (Dai et al., 2022) [Copyright, 2022, ELSEVIER] (b1) Fabrication process; (b2) hot-pressing process parameters of weave CFF/PEEK; (b3) The surface morphology of weave CFF/PEEK composite fabricated with 400 ℃ molding temperatures. (Hu et al., 2022) [Copyright, 2022, WILEY]

Improving the interfacial strength between CF and PEEK has emerged as a key factor in enhancing the overall mechanical properties of hot compression-molded CF/PEEK laminates. Various modifiers, such as HA (Zhao et al., 2022), aminated polyphenylene sulphide (PPS-NH2) (Ren et al., 2022), PEEK derivatives (Ren et al., 2023), CNT (Lyu et al., 2021), have been explored to chemically modify CF or introduce new functional groups, experimentally verifying their capacity to enhance the interfacial strength of CF/PEEK. For instance, Yapici (2014) investigated the introduction of oxygen functional groups on the surface of CF with piranha solution and chromate solution to improve the bond strength of laminates. Lyu et al. (2021) modified CF with hydroxylated PEEK grafted MWCNT, resulting in increased interlaminar shear strength, flexural strength, and flexural modulus of the modified CF/PEEK composites. The results showed that the interlaminar shear strength increased by 73.0% (84.7 MPa), flexural strength by 163.2% (906.2 MPa), and flexural modulus by 84.8% (58.4 GPa). In summary, the comprehensive exploration of hot compression molding parameters, the laying method of unidirectional prepreg tape, and the broader considerations of working environment and fiber reinforcement state have collectively contributed to the development of high-performance continuous fiber-reinforced PEEK composites.

Table 2 Mechanical properties of hot compression PEEK laminates

Materials	Weight Ratio (%)	Tensile Strength (MPa)		Flexural Strength (MPa)	Remark	Ref.
PEEK	/	112		191		(Li et al., 2023).
CCF/PEEK	67	≈500		≈800		(Hu et al., 2022)
Plain CCF/PEEK	68-70			934	ILSS: 69 MPa	(Zheng et al., 2019)
CCF/PEEK	60	889		974	indoor temperature	(Plagianakos et al., 2020)
CCF/PEEK	60	701		877	hot and wet	
UD CF/PEEK	33		108.12			(Almudaihesh et al., 2020).
Plain CF/PEEK	40		36.27			
Twill woven CF/PEEK	40		33.70			
SiO_2/PEEK	0.5% vol	111				(Zhang et al., 2008)
nHA/MWCNT/PEEK	nHA:30 MWCNT:5	Elastic Modulus 7.6077 GPa				(Kumar et al., 2021)
MWCNT/PEEK	5	Elastic Modulus 6.7152 GPa				

4.2 Hot compression of other PEEK composites and materials

The production of sheet-like profiles from PEEK through hot compression molding represents a significant molding approach. Talbott et al. (1987) produced PEEK sheets through hot compression molding, where they controlled the cooling rate to achieve sheets with variable crystallinity. Subsequent experiments explored mechanical properties, including tensile, compression, and shear properties, and fracture toughness, revealing a relationship between these properties and crystallinity. Li et al. (2023) investigated the effect of molding parameters on the mechanical properties of PEEK hot compression laminates, determining optimal parameters as a molding temperature of 400 ℃, molding pressure of 2.5 MPa, and hot compression time of 30 min. Samples produced under these conditions exhibited impressive tensile strength (112 MPa) and bending strength (191 MPa). Additionally, Zalaznik (2016) studied the frictional performance of PEEK sheets produced at different molding temperatures, observing a decrease in the friction coefficient with increasing molding temperature. Lower temperatures were associated with reduced hardness, favoring the formation of a PEEK-PEEK friction film and subsequently decreasing the wear rate. Tian et al. (2021) explored the influence of crystallinity on the interaction between laser beams and PEEK sheets produced with high, medium, or low crystallinity. Experimental and simulation results indicated that light reflectance at 1070 nm wavelength increased with crystallinity, while transmittance decreased. Goyal et al. (2006) investigated the linear expansion of hot compression-molded PEEK sheets, revealing anisotropic behavior influenced by compressive forces during molding. Evans et al. (2015) ingeniously blended PEEK powder with sodium chloride, using a method of hot-press molding to create cylindrical extruded profiles. Subsequently, immersing these profiles in water facilitated the removal of sodium chloride, resulting in PEEK porous structures with a consistent porosity. Both mechanical performance tests and in vivo implantation experiments in rats yielded promising results. The introduction of surface porosity led to samples exhibiting elevated tensile strength, fatigue resistance, and interfacial shear strength, while simultaneously providing accessible porosity for inward bone growth. Preliminary in vivo findings offered compelling evidence of bone ingrowth into the porous network, suggesting potential enhancements in implant stability. A similar and ingenious approach for producing PEEK microcellular foam products involves blending PEEK with a mixture of water-soluble salts, followed by hot-press molding and subsequent boiling water immersion (Ling et al., 2023).

Incorporating continuous fiber composite materials into hot compression molding of PEEK is an intriguing avenue of research. By blending fibers with different properties to create woven fabrics and subsequently stacking these fabrics into laminates through hot compression molding, PEEK composite laminates with various performance characteristics can be achieved. Gupta et al. (2002), C. Lu et al. (2019), Shekar (2010a, 2010b, 2011), and Trzepiecinski et al. (2021) explored the reinforcement of PEEK with fibers such as CF, GF, and PEEK fibers. Lu et al. (2019) prepared CF/PEEK blended woven fabrics and optimized molding parameters, finding that higher mass fractions of PEEK in the weave led to higher interfacial strength. However, excessive PEEK resin content dispersed the CF, causing defects in the laminates. The optimum resin content was determined as 59.07%, resulting in a tensile strength of 738.36 ± 14.49 MPa and a flexural strength of 659.68 ± 57.53 MPa. Shekar et al. (2010, 2011) blended and weaved GF with PEEK fibers, obtaining GF/PEEK laminates with excellent mechanical properties through hot compression molding. These laminates showed higher values of interlaminar shear strength, flexural strength, and tensile strength compared to unidirectional GF/epoxy composites with similar resin content and thickness. The dielectric properties of the GF/PEEK composites were less dependent on frequency and temperature, showcasing their potential for aerospace applications.

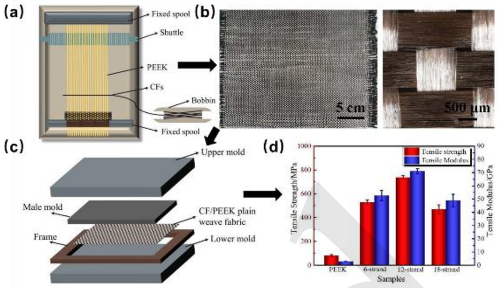

Fig. 8 (a) Carbon fiber and PEEK fiber blended and woven; (b) CF/PEEK woven fabric; (c) Hot-compression CF/PEEK laminate; (d) Tensile properties of CF/PEEK laminates with different number of strands. (Lu et al, 2019) [Copyright, 2019, MDPI]

The use of nanomaterials, such as silica nanoparticles (SiO_2), in PEEK through hot compression molding allows for the development of composite sheets with specific functions. Zhang et al. (2008) used SiO_2 to enhance PEEK's tensile strength and wear resistance. Lai et al. (2007) treated the surface of nano silica with stearic acid before adding it to PEEK, resulting in improved dispersion in the PEEK matrix and enhanced high-temperature mechanical properties.

In the biomedical field, PEEK-based nanocomposites have been explored for orthopedic and prosthetic applications. For example, El-Fattah (2021) demonstrated that hydrophobic SiO_2-filled PEEK can be used in orthopedics when the mass fraction is below 10%. Additionally, hot compression-molded MWCNT/nHA/PEEK (Kumar et al., 2021) and nano Ag-TiO_2/PEEK (Ru et al., 2023) have shown promise in orthopedics, dentistry, and other biomedical applications.

4.3 Discussion

Hot compression molding effectively combines the PEEK matrix with continuous fibers, resulting in exceptional mechanical properties, weather resistance, and abrasion resistance in various laminates and composites. Additionally, it enables the development of nanomaterial-reinforced PEEK composites with enhanced biocompatibility. Despite advances, research gaps remain, including understanding fiber behavior and enhancing interfacial strength. Another promising area requiring further exploration is bonding PEEK composites with metals for lighter metal parts (Lu et al., 2022; Mitschang et al., 2013). Addressing these gaps will advance hot compression molding applications in PEEK and its composites.

5 Injection molded PEEK and its composites

5.1 Molding process of PEEK and its microcellular injection foams

In the injection molding process, various parameters, spanning from raw material to final product molding, intricately impact the service performance of the end product. Chivers and Moore (1994) conducted early research on the impact of annealing on the injection molding of PEEK with different molecular weights. Their experiments revealed that annealing increased the crystallinity of PEEK samples, and the upper limit depended on the molecular weight of the raw material. Higher molecular weights corresponded to smaller upper limits of crystallinity. While the tensile modulus and yield strength increased with crystallinity, molecular weight showed no significant effect. The toughness of PEEK samples was notably affected by both molecular weight and crystallinity size, with toughness increasing with molecular weight and decreasing with crystallinity. Hsiung et al. (1990) maintained the injection melt temperature at 400 ℃, exploring the effects of mold temperature and injection speed on the mechanical properties of injection-molded PEEK samples. Their research indicated a significant effect of mold temperature on the crystallinity of PEEK samples, with higher mold temperatures leading to more fully crystallized samples and increased crystallinity under specific holding times. The optimal impact strength for PEEK samples was achieved at room temperature and 140-160 ℃ with a low injection rate. The modulus and yield stress increased with rising mold temperature, while tensile strength and elongation at break decreased. Park and Kim (2009) investigated the effect of mold temperature on the mechanical properties of thin-walled flexible wheel parts for harmonic gearing, illustrating the negative impact of local crystallinity on part strength. These studies collectively underscore the substantial influence of crystallinity on the mechanical properties of the final molded PEEK samples. Regulating process parameters and controlling the motion state of molecular chains are crucial for producing high-quality injection-molded PEEK samples that meet the toughness and strength requirements. Among these parameters, the size of crystallinity is closely linked to the cooling process of the PEEK melt. Controlling the difference between melt temperature and mold temperature holds significant importance for crystallinity. Generally, when PEEK is melted in the cylinder, its molecular chains exhibit vigorous movement and remain in an amorphous state. The hot PEEK melt enters the mold far below its temperature, leading to rapid cooling. A larger temperature difference results in a faster cooling rate. If the cooling rate is too fast, crystallization of the PEEK melt cannot occur before complete cooling, leading to reduced crystallinity. Setting the mold temperature above the T_g of PEEK, along with a sufficiently long holding time, allows ample growth time for crystallization, ensuring periodic crystallinity. Therefore, the use of an appropriate melt temperature, mold temperature, and holding time is crucial for achieving final molding quality.

The exploration of PEEK microcellular foam products, boasting high foaming expansion ratios and robust performance, stands as a pivotal research avenue (Qi et al., 2022; Wu et al., 2023; Liang et al., 2021). However, conventional injection molding processes often prove unreliable for effectively foaming high-performance polymers (Verdejo et al., 2009). Verdejo et al. (2009) emerged as a trailblazer in addressing this challenge, pioneering the blending of CNT/PEEK composite materials with a foaming agent. Through injection molding, they achieved PEEK foam with exceptional mechanical properties. In recent years, there has been a notable shift towards leveraging supercritical fluid technology for crafting PEEK foamed products. In this innovative process, a high-pressure supercritical fluid such as carbon dioxide or nitrogen is intricately mixed with molten PEEK within a mold. Subsequently, during the demolding phase, a rapid drop in pressure ensues, facilitating the release of carbon dioxide or nitrogen. The result is the formation of PEEK microcellular foam endowed with a distinctive porous structure. These advanced PEEK foams find practical applications in diverse fields such as biomedicine (Ling et al., 2023) and lightweight design. Compared to conventional hot-press molding, microcellular injection molding (MIM) using supercritical fluids has emerged as a more prevalent technique to produce foamed PEEK products. Feng et al. (2022) pioneered the study of MIM PEEK, establishing process parameters based on simulation analysis. Microcellular PEEK with an average cell size of 30 μm and a weight reduction of about 10% was achieved. Their study also analyzed the tensile properties of PEEK before and after foaming, revealing a negative impact of the internal vesicle structure on tensile properties. Ma (2022) used MIM to prepare microcellular PEEK with a maximum weight reduction of 22%, investigating the effect of crystallization on PEEK foaming. The results indicated enhanced tensile strength with increased crystallinity, accompanied by a reduction in the dielectric constant and density of internal vesicles. Zhao Peng's research group (Yang et al., 2022, Guo et al., 2023) conducted a comprehensive study on the injection foam molding of PEEK. They introduced the micro-open mold process and induction heating technology, obtaining PEEK foam with superior weight reduction, surface quality, and mechanical properties, paving the way for MIM PEEK development. The group prepared PEEK foams by MIM with a typical skin-core structure, studying the effects of melt temperature, injection speed, injection volume, and gas content on weight loss ratio, cell structure, and tensile properties of PEEK foams. The thermal properties of PEEK before and after injection foaming remained comparable, indicating minimal impact on thermal properties. The weight loss ratio of microporous PEEK correlated positively with melt temperature, injection speed, and gas concentration, and negatively with injection volume. The injection volume had the most significant effect on weight loss, reaching a maximum experimental weight loss ratio of 17.29%. Cell structure sparsity correlated with nucleation force and cell growth resistance. The cell density was about 6×10^7 cells/cm^3 and the size about 12 μm. Tensile properties positively correlated with injection rate, injection volume, and gas concentration, and negatively with melt temperature. Injection volume had the most significant effect on tensile properties, with maximum tensile strength and modulus reaching 74.13 MPa and 2783.72 MPa, respectively.

However, the MIM technique posed challenges, as the melts adjacent to the cavity sides cooled drastically, leading to a fountain phenomenon when the PEEK melt with supercritical fluid entered the metal cavity at lower temperatures. This resulted in gas overflow, surface quality deterioration, and severe internal porosity deformation. Subsequent research introduced the micro-open mold process into MIM, developing mold-opening microcellular injection molding (MOMIM). In MOMIM, the PEEK melt and supercritical fluid mixture enters the cavity, is held under pressure, and undergoes remixing of supercritical nitrogen gas with the PEEK melt to form a homogeneous structure. The mold is slightly opened along the sample thickness after the holding pressure phase, causing a sudden pressure drop, allowing N_2 dissolution to escape during the holding phase and leading to secondary nucleation. This prevents N_2 escape from the sample surface, improving surface quality and internal cell structure. Experimental investigation of holding time, holding pressure, and mold opening distance revealed excellent PEEK foamed samples with bending properties surpassing those of solid samples, achieving a maximum weight reduction ratio of up to 28%. MOMIM demonstrated significant potential in enhancing PEEK foam properties. In recent work, Guo et al. (2023) introduced induction heating into the injection foam molding of PEEK to address the inefficiencies of oil heater heating. Comparison of oil heater, electric, and induction heating demonstrated that induction heating provides a stable and efficient mold temperature of up to 180 ℃ for PEEK injection molding. Induction heating efficiency was about 158% of electric heating, reducing the cooling time of a single production by 15 s. Surface roughness of PEEK products produced by MIM and MOMIM was reduced by 9.8~61.2%, tensile property improved by more than 18%, and tensile and bending properties improved by more than 18% and 23%, respectively, with induction heating compared to oil heater heating.

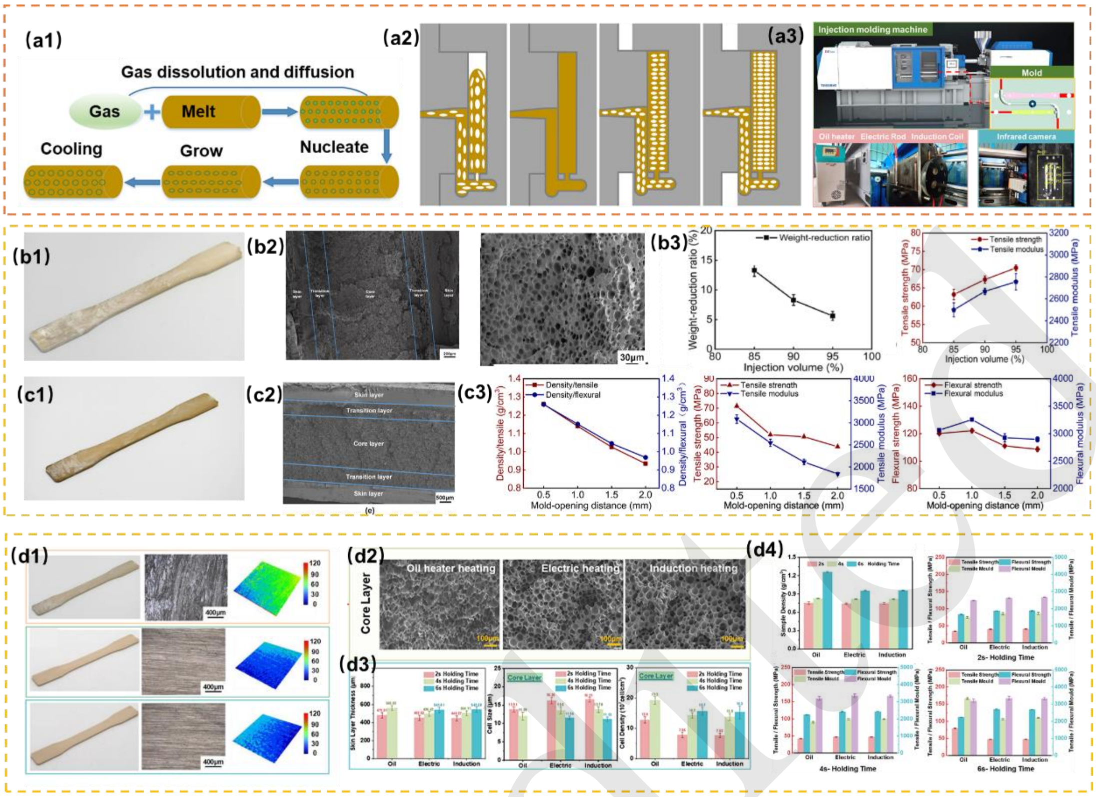

Fig. 9 (a1) The principle of microcellular injection molding technology (MIM) (Yang et al., 2022a); (a2) the principle of micro-open microcellular injection molding technology (MOMIM) (Yang et al., 2022b); [Copyright, 2022, ELSEVIER]; (a3) injection machine equipped with oil heater heating, electric heating, induction heating and an infrared camera (Guo et al., 2023). (b1) A sample molded by MIM; [Copyright, 2023, ELSEVIER]; (b2) typical skin-core structure of MIM PEEK sample and its cell under SEM view; (b3) weight reduction ratio and tensile properties of MIM mold PEEK (Yang et al., 2022a).[Copyright, 2022, ELSEVIER] (c1) A sample molded by MOMIM PEEK; (c2) typical skin-core structure of MIM PEEK sample; (c3) density, tensile properties and flexural properties of MOMIM PEEK sample (Yang et al., 2022b). The difference between oil heating, electric heating, and induction heating for the production of MIM PEEK of (d1) surface roughness; (d2) cell structure ; (d3) density and mechanical properties when holding time was 2, 4, or 6 s (Guo et al., 2023).

5.2 Service performance research on injection molded PEEK composites and its components

Injection molding has irreplaceable advantages because of its efficient and stable method for producing complex structures that require mass production. Therefore, research on the service performance of injection- molded PEEK composites has been the focus of scholars.

PEEK composites have emerged as pivotal materials in the realm of mechanical structures, owing to their exceptional attributes in mechanical properties, crack resistance, and frictional characteristics. The outstanding mechanical prowess of short fiber-reinforced PEEK composites has been substantiated by studies conducted over the years (Bozarth et al., 1987; Kargerkocsis, 1991; Sarasua et al., 1995; Wu and Schultz, 1990). In a groundbreaking study by Berthet et al. (2017), the tensile properties of injection-molded SCF/PEEK reached an impressive 330 MPa, surpassing the specific strength of aerospace aluminum alloys and even rivaling some titanium alloys. Exploring the impact of temperature and fiber orientation on the tensile behavior of SCF/PEEK, Chang et al. (2021) conducted a comprehensive investigation, measuring the tensile mechanical properties at various temperatures (23, 80, 140, and 200 ℃). Their intrinsic model accurately predicted stress-strain curves across a broad temperature range. The results indicated a decline in tensile strength and modulus of elasticity of the injection-molded CF/PEEK samples with rising temperature, coupled with an increase in strain at break. The anisotropy of the samples primarily hinged on fiber orientation, with its temperature dependency dictated by the matrix. The study of crack extension resistance under cyclic loading has attracted significant attention in the realm of short fiber-reinforced PEEK. Factors such as the volume fraction of fibers, fiber orientation, fiber length, and loading direction have been shown to be associated with fatigue crack generation and extension (Evans et al., 1996). Tanaka et al. (2014) delved into the crack extension rate of injection-molded short fiber-reinforced PEEK, establishing a functional relationship with the stress intensity factor. Their study highlighted the directional path dependence of crack expansion, emphasizing the accelerating effect of the core layer on crack expansion parallel to the direction of melt flow and its inhibition in the perpendicular direction. The synergy of PEEK's exceptional properties and the unique advantages of injection molding for mass-producing intricate structures has led to the development of numerous complex components. Notably, Kurokawa et al. (1999) pioneered high-performance CF/PEEK gears using an injection molding process that remained unaffected by operating conditions. Kurkin and Sadykova (2016) devised an injection-molded aerospace structural component with holes, and conducted hydrodynamic calculations to predict its design behavior under static loading using the advanced Moldex 3D program. Czechowicz et al. (2021) introduced the first mass-producible satellite structure, leveraging the design flexibility offered by injection molding with the high-performance polymer PEEK, ensuring swift integration and substantial cost savings.

The biomedical field stands out as a significant application area for injection-molded PEEK and its composites. Li et al. (2022) undertook the sulfonation of injection-molded CF/PEEK samples, coating the surface with a graphene oxide (GO) coating. In vitro cytotoxicity tests and in vivo animal research experiments demonstrated that the prepared GO-SCF/PEEK materials were non-toxic and exhibited a favorable osseointegration effect, indicating promising applications as implant materials for repairing bone defects. Similarly, injection-molded graphene-reinforced PEEK composites, developed by He et al. (2019), showcased commendable performance in in vitro research trials. These materials proved to be biocompatible, facilitating the adhesion and spread of bone marrow stromal stem cells. Several injection-molded composites have demonstrated the ability to inhibit bacterial growth, such as GO/PEEK (Jiang et al., 2021), MWCNT/PEEK (Cao et al., 2018), n-HA/PEEK (Ma et al., 2014), and TiO_2/SiO_2/PEEK (Thanigachalam and Subramanian, 2022). In particular, TiO_2/SiO_2/PEEK exhibited excellent biocompatibility, as shown by direct and indirect cytotoxicity studies in vitro using the MG-63 cell line, with a cell viability of 94.30% and cytotoxicity of 5.70%. Moreover, it showed substantial inhibition zone diameters against *Escherichia coli* and *Bacillus subtilis*, making it a promising candidate for biomedical applications. Fig. 10 illustrates the work of Feng et al. (2022) who developed injection-molded ZnO_2/SCF/PEEK composite materials. These materials demonstrated excellent antibacterial activity against *E. coli* and *Staphylococcus aureus*, confirming their robust biocompatibility. The injection molding process, with its unique industrial advantages facilitating rapid and large-scale production of complex structures, has been effectively harnessed in the biomedical manufacturing sector. In a different avenue, Yuan et al. (2022) pioneered the development of intervertebral fusion cages using injection-molded CS/porous tantalum (pTa)/PEEK and CS/PEEK composite materials. Implanted into live goats for experimental evaluation, the study revealed that both a non-grafted CS/pTa PEEK cage and an autologous bone graft CS/PEEK cage exhibited similar bone fusion performance. The release of calcium and silicon from the cages demonstrated excellent biocompatibility in vivo, offering a novel non-grafted intervertebral fusion solution for patients with degenerative disc diseases, potentially avoiding complications associated with donor site harvesting. Subramanian and Thanigachalam (2022) used injection molding technology to fabricate implants made of PEEK and its composite materials reinforced with titanium dioxide and silicon dioxide. They evaluated the mechanical properties and in vitro antibacterial performance of these implants, obtaining optimal material compositions and implant thread shapes. Based on maximum compressive properties and hardness values, the best combinations were selected, such as 16%wt TiO_2/PEEK, 12%wt SiO_2/PEEK, and 16%wt TiO_2/SiO_2/PEEK in all three groups. Furthermore, the in-vitro antibacterial activity of selected polymer composites was assessed and found to be effective against *E. coli* and *B. subtilis*. The maximum zone of inhibition was found in the 16%wt TiO_2/SiO_2/PEEK sample compared to TiO_2/PEEK and SiO_2/PEEK. Mohammed (2020) evaluated the mechanical properties and bioactivity of three PEEK composite materials. Fourier Transform infrared spectroscopy (FTIR) indicated that strong organisational bonds were established between the PEEK and the bioactive ingredients. X-ray diffraction (XRD) pattern analysis showed the formation of crystalline PEEK and HA in the XRD spectra. The bioactive composites created in this study exhibited improved biocompatibility and bioactivity, encouraging cellular attachment and mineralised matrix deposition. Among the bioactive composites, samples made up of 20%wt nHA and 25%wt nHA:25%wt Ti-6Al-4V showed the highest mechanical strength for use as dental implants.

In the realm of electrical engineering, extensive research has been conducted on injection-molded PEEK composite materials and their intricate structures. Carbon-based materials are commonly used as fillers to impart electrical conductivity to PEEK in large-scale production of electrical components through injection molding. King et al. (2018) conducted injection molding of conductive PEEK composite materials modified with carbon-based fillers, providing a comprehensive comparison of their electrical conductivity, thermal conductivity, and tensile properties. This comprehensive data serves as a reliable guide for developing conductive materials based on PEEK, expanding the range of applications for PEEK and its composite materials. Fischer et al. (2020) showcased the utility of PEEK as a disc-shaped wafer substrate for giant magnetoresistance (GMR) spin valve sensors. The large-scale production of this component, coupled with the direct molding of intricate cavities for subsequent sputter deposition through injection molding, replaced and simplified traditional photolithography and masking processes, almost rendering cleanroom facilities

unnecessary. This study convincingly demonstrated the significant advantages of injection-molded PEEK materials in terms of precision molding and integrated manufacturing, opening up new possibilities for their application. In the domain of nuclear power, injection-molded PEEK has demonstrated strong applicability. Pagé et al. (2002) exposed injection-molded PEEK samples to irradiation in the pool of the SLOWPOKE-2 nuclear research reactor, studying the mixed radiation field effects on PEEK. The specimens, subjected to a gamma, electron, proton, and neutron radiation with exposure doses ranging from 0.15 to 15 MGy, showcased the radiation resistance of PEEK crystals. As the dose increased, molecular scission occurred between the amorphous and crystalline phases of the polymer, resulting in cross-linking within the amorphous phase and a reduction in sample molecular weight. This study highlights the potential applications of injection-molded PEEK in the nuclear industry.

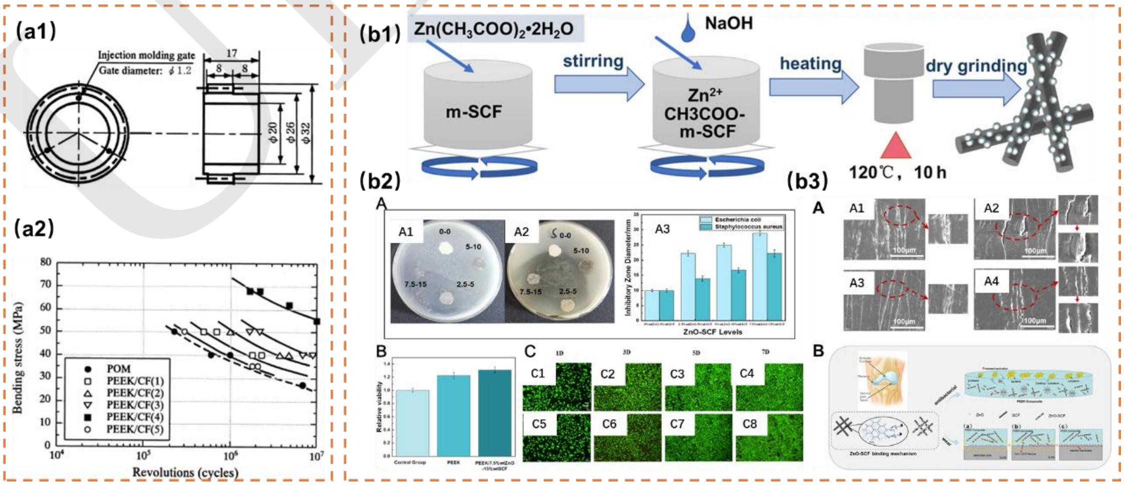

Fig. 10 (a1) Design drawing of a CF/PEEK gear; (a2) bending strain of CF/PEEK gear under cyclic loading, compared to POM gear. (Kurokawa et al., 1999) [Copyright, 2000, ELSEVIER]. (b1) Preparation of the ZnO-SCF material which filled the inject molded PEEK composites; (b2) (A) PEEK/ZnO-SCF composites with different contents were cultured with (A1)

E. coli and (A2) S. aureus for 24 h and (A3) diameter of the inhibition zone; (B) relative survival rates of the pure PEEK and PEEK composites by CCK-8 detection. (C) Live/dead staining diagram: (C1–C4) PEEK composite material and (C5–C8) pure PEEK. (b3) (A) SEM images after XLPE wear: (A1) pure PEEK and (A3–A4) PEEK/ZnO-SCF; (B) wear mechanism diagram of the PEEK/Zno-SCF composite. (Feng et al., 2022) [Copyright, 2022, AMER CHEMICAL SOC]

5.3 Discussion

Injection molding is widely recognized for its industrial advantages, from experimental validation to large-scale production. It plays a vital role in producing complex parts in industries like mechanics, medicine, and electronics. Despite its success, challenges persist for PEEK and its composites. Recycling and reproducing PEEK pose limitations, hindering broader utilization (Sarasua and Pouyet, 1997; McLauchlin et al., 2014). Moreover, research on injection foam molding of PEEK composites lacks data accumulation, and understanding the formation mechanism of internal cells remains incomplete. Ensuring accuracy in large-scale production, especially for PEEK-based composite materials, is another research gap. Integrating computer-based methods for analysis and quality control holds promise for advancing injection molding processes further.

6 3D-printed PEEK and its composites

6.1 3D Printing processes for PEEK and its composites

6.1.1 3D Printing and post-treatment of PEEK and its short fiber composites

In recent years, researchers have concentrated on enhancing the mechanical performance of 3D-printed PEEK products by using more rational parameters and designing effective post-processing techniques. Factors such as nozzle temperature, chamber temperature, print-bed (build platform) temperature, printing speed, layer height, raster width and thickness, raster orientation, and infill percentage have been extensively studied for their impact on the mechanical properties and dimensional accuracy of the final printed components, leading to significant advancements in this field. The foundation of these research efforts lies in the FDM of pure PEEK. Gao et al. (2021) used single-factor experiments and determined that PEEK samples produced via FDM exhibited optimal overall performance in terms of warping deformation, tensile strength, and specific strength when using a raster angle of 0 °/90 ° and a 50% infill density. Further analysis of printing speed, nozzle temperature, build platform temperature, raster width, and layer height through orthogonal experiments revealed that the build platform temperature was the most critical parameter affecting warping deformation. However, both printing speed and nozzle temperature had a more pronounced impact on tensile strength. Through optimization, the warping deformation of the samples was significantly reduced to nearly zero, and tensile strength was improved by 19.6%. In the FDM process, PEEK melt is extruded from the nozzle and undergoes cooling and deposition on the print platform. Printing speed and nozzle temperature jointly affect the energy transfer process of the PEEK material. Additionally, the printer's platform temperature and chamber temperature affect the crystallization and orientation behavior of the extruded PEEK melt. These thermodynamic processes ultimately determine the aggregated structural state and surface energy state of each layer of PEEK samples produced by FDM. Consequently, they have a significant impact on interlayer strength, overall mechanical properties, and warping tendencies. In essence, FDM represents a complex interplay of multiple factors, where speed and temperature fields control the interactions with PEEK material. This viewpoint was corroborated by other scholars in the field (Al Alaween et al., 2023; Li and Lou, 2020). Molecular weight is another factor affecting the mechanical properties and microstructure of 3D-printed PEEK products. Xu et al. (2021) showed that reducing the molecular weight of PEEK can effectively improve its flowability, reduce internal defects, and enhance the mechanical performance of 3D-printed PEEK. FDM has unique characteristics such as layer-by-layer and low speed manufacturing, and is non-pressure forming compared to other manufacturing methods such as injection molding and hot compressing molding. This leads to difficulties in molecular diffusion between different layers, resulting in reduced interlayer bonding strength. Therefore, improving interlayer adhesion is crucial for enhancing the mechanical strength of FDM-printed PEEK samples. Basgul et al. (2021) developed a one-dimensional heat transfer model and combined it with a non-isothermal curing model to successfully predict the interlayer strength of FDM-printed PEEK parts (Fig. 11 (a1), (a2), (a3)). According to this model, the temperature of each layer gradually increased from the bottom layer near the build platform to the top layer, with a temperature difference of up to 30 ℃ between the 1st and the 41st layer by the end of printing. The degree of interface curing also increased with the number of layers. Properly increasing key temperatures such as chamber temperature, build platform temperature, and nozzle temperature was an effective means to enhance the interlayer bonding strength of FDM-printed PEEK samples. Liaw et al. (2021) designed orthogonal experiments to investigate the impact of various parameters on interlayer strength in FDM-printed PEEK specimens. The results indicated that the thermodynamic processes during the printing process determined interlayer strength, with nozzle temperature having the most significant effect. To improve interlayer bonding strength in fiber-reinforced PEEK composites, Qu et al. (2023) integrated ultrasound-assisted additive manufacturing technology into PEEK's FDM process (Fig. 11 (b1), (b2)). They applied high-frequency vibrations (greater than 16 kHz) to concentrate energy into the material, softening it, and applied positive pressure to create a dense structure. This technique significantly reduced sample defects and increased tensile modulus by a factor of three, providing a novel approach to overcoming the limitations of non-pressure forming in FDM.

CF, GF, and CNT-reinforced PEEK samples manufactured using FDM exhibit a wider range of performance characteristics than pure PEEK, reflecting the diversity of research in this area. Rabinowitz et al. (2023) designed orthogonal experiments to investigate the bending performance of SCF/PEEK. The experiments demonstrated that the raster angle and layer height had the greatest impact on the flexural strength of FDM-printed SCF/PEEK samples. Wang et al. (2021) studied the effect of nozzle temperature, build platform temperature, printing speed, and layer height on the mechanical properties of SCF/PEEK and SGF/PEEK. The experiments showed that SCF/PEEK had higher tensile strength, but SGF/PEEK had better bending performance. However, both exhibited reduced toughness compared to pure PEEK, as the presence of fibers resulted in increased porosity and molecular chain breakage. Their tensile strength and bending strength increased with higher nozzle and build platform temperatures. Increasing printing speed and layer height had a negative impact on all mechanical properties of printed fiber-reinforced PEEK composites. These trends are similar to those observed in the FDM process of pure PEEK. Matschinski et al. (2021) researched the impact of nozzle angles on the fibers in FDM-printed SCF/PEEK with a high CF volume fraction of up to 30%. The experiments showed that using smaller nozzle angles reduced damage to the fibers during the printing process. Understanding the fracture behavior of SCF/PEEK samples under high-temperature conditions during FDM printing is of significant importance to enhance their practical applications. Yavas et al. (2023) investigated the effects of temperature on the mechanical and fracture properties of SCF/PEEK with different layer heights under three conditions: room temperature, 75 ℃, and 125 ℃. The experiments revealed significant anisotropy in FDM-printed SCF/PEEK. The resistance to crack propagation in the composite material was correlated with its operating temperature and layer height. The study also examined the reduction in fracture properties of the composite material under high-temperature conditions and the tensile fracture behavior. It revealed that layer height significantly affected the defect size and density of FDM-printed SCF/PEEK composite materials, with larger and more defects occurring with increased layer height. Interlayer bonding strength also significantly influenced the mechanical properties of short fiber-reinforced PEEK composite materials. Moreover, the addition of fibers exacerbated this issue. Li et al. (2019) confirmed this point, showing that the addition of SCFs improved the uniform nucleation process of PEEK during 3D printing, negatively affecting interlayer bonding strength. To overcome this challenge, Han et al. (2020) developed a new process for laser-assisted FDM printing in PEEK (Fig. 11 (c1)), enhancing interlayer interface thermal relaxation and bonding. They used a 2.13-W laser to preheat the deposited portion, resulting in a 350.9% increase in tensile strength along the build direction (Fig.11 (c2), (c3)).

Post-processing plays a crucial role in improving the service performance of FDM-printed PEEK products in addition to adjusting process parameters and using laser-assisted manufacturing to enhance interlayer bonding strength. For example, high-temperature annealing can significantly increase the crystallinity of FDM-printed PEEK products, thereby improving their mechanical properties. Yang et al. (2017) were pioneers in investigating the relationship between crystallinity and mechanical properties of FDM-printed PEEK samples. They first prepared PEEK samples with different crystallinities under various chamber and nozzle temperatures, demonstrating the significant impact of crystallinity (Fig. 11 (d1)) on their tensile strength and tensile modulus (Fig.11 (d2)). Subsequently, they conducted air cooling, furnace cooling, quenching, annealing, and tempering experiments on these PEEK samples, further enhancing their crystallinity and mechanical performance. Furnace cooling and annealing were proven to be superior and more effective for achieving higher crystallinity and better mechanical properties than other methods. This research indicated the enormous potential of their temperature-controlled 3D printing method for designing, controlling, and achieving different crystallinities and mechanical properties of various PEEK components, even within different regions of the same PEEK part (Fig. 11 (d3)). This is of significance in mitigating the mechanical performance limitations of FDM-printed PEEK components. Annealing processes significantly enhance the crystallinity of FDM-printed CF/PEEK, reduce residual stresses, and consequently improve its mechanical properties to be similar to those of pure PEEK. However, the optimal annealing temperature for FDM-printed CF/PEEK is slightly higher than that for pure PEEK. This is because annealing FDM-printed CF/PEEK significantly enhances its interfacial strength (Li et al., 2023; Liaw et al., 2021; Wang and Zou, 2022). This may be attributed to the role of fibers in heterogeneous nucleation during the annealing process, promoting interlayer bonding in the PEEK matrix, and thereby enhancing interlayer adhesion strength. Note that the use of annealing processes may not be suitable for conductive materials. Ye et al. (2022) found that although annealing improved the tensile properties of CNT/PEEK, the aggregation of CNTs caused by the crystallization of the PEEK matrix disrupted the original conductive network in the composite material, resulting in reduced electrical conductivity and electromagnetic interference shielding performance.

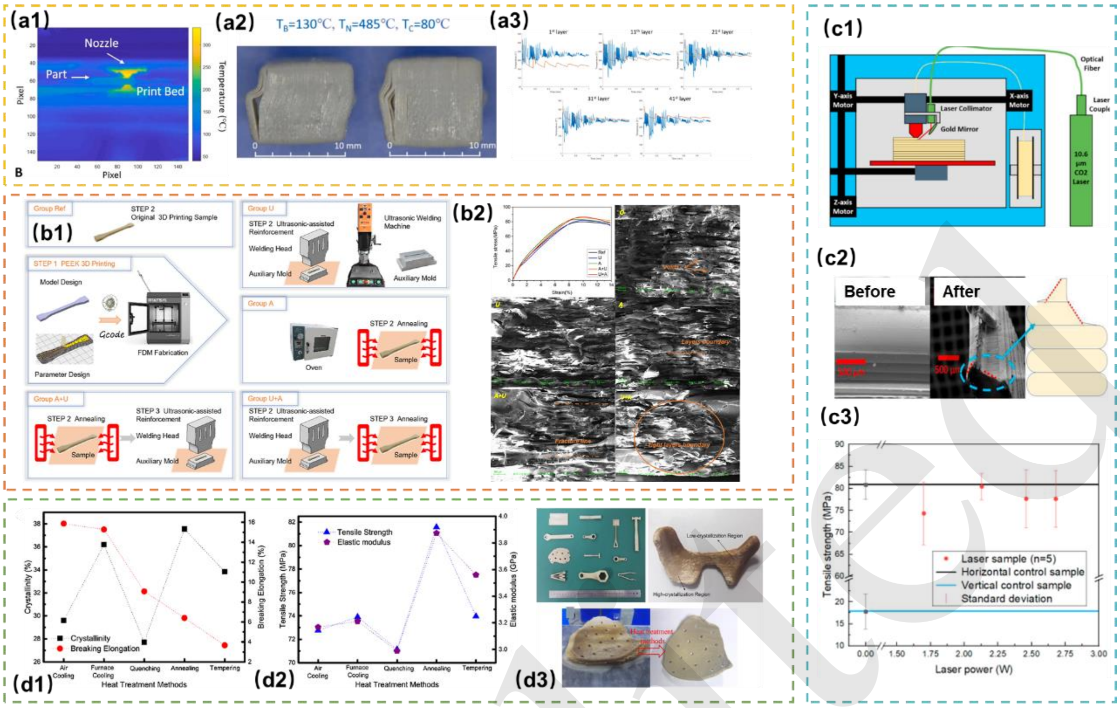

Fig. 11 (a1) Thermal image of each layer of an FDM-molded PEEK sample; (a2) The delamination of the sample is more obvious closer to the printing bed; (a3) temperature predicted by the model (orange) and actual measured temperature (blue) of FDM PEEK samples at different layers (Basgul et al., 2021) [Copyright, 2021, ELSEVIER]. (b1) FDM process combining different methods of ultrasonic assisted molding (U) and annealing treatment (A); (b2) after ultrasound-assisted molding followed by annealing, the interlayer of the FDM PEEK sample changes, the voids decrease, and the tensile strength increases, indicating ultrasound-assisted molding alone also had the effect of reducing voids (Qu et al., 2022) [Copyright, 2022, WILEY]. (c1) Laser-assisted FDM molding enhances interlayer bonding; (c2) SEM of tensile test failure surface for vertical control sample and 2.13-W laser sample, and a schematic (side view) of fracture surface progression; (c3) tensile strength of laser pre-deposition heating PEEK tensile bar and control samples (Han et al., 2020) [Copyright, 2020, ELSEVIER]. After various post-treatment methods, the (d1) crystallinity and (d2) tensile properties of the FDM PEEK sample change. (d3) Some demonstrations of the controllable process: some parts with different degrees of crystallinity under different thermal processing conditions in 3D printing, an implantable bone that has different crystallinity regions, and a piece of PEEK cranium implant (Yang et al., 2017) [Copyright, 2017, ELSEVIER].

6.1.2 3D printing of continuous fiber-reinforced PEEK composites

Continuous fiber 3D printing technology is a relatively recent development in the field. In less than a decade since their inception, continuous fiber-reinforced PEEK composite materials have attracted significant attention for their exceptional performance. Vatandaş et al. (2023) developed a production process for manufacturing high-strength CCF/PEEK 3D-printed samples. Initially, CCF/PEEK filaments were produced using a melt impregnation method, and these filaments were then modified into cylindrical shapes suitable for FDM printing and wound onto spools. The modified CCF/PEEK filaments were printed using an FDM printer capable of cutting CF. Infrared heating was applied to preheat the printing area to temperatures up to 350 ℃. In this groundbreaking research, 3D-printed CCF/PEEK achieved an impressive fiber volume fraction of 60%, with a maximum tensile strength of 859.82 MPa and an elastic modulus of 33.06 GPa. Li et al. (2022) developed a production process for 3D printing continuous glass fiber-reinforced PEEK (CGF/PEEK) composite materials. They initially impregnated glass fiber yarn using a twin-screw extruder. Subsequently, the impregnated continuous CF were printed using a modified continuous fiber 3D printer equipped with two independent heating systems for preheating and printing of CGF/PEEK. The study investigated the influence of preheating temperature, printing speed, yarn drawing speed, strand spacing, and fiber content on the composite material's strength. The results indicated that lower drawing speeds improved fiber dispersion within the strands, as well as strand roundness and strength. Preheating also enhanced the tensile and flexural strength of the composite samples, with the maximum strength achieved at a preheating temperature of 405 ℃ and a printing speed of 1.5 mm/s. Both studies highlighted the detrimental effect of cells near the fibers on the mechanical strength of continuous fiber-reinforced PEEK composite materials. Therefore, developing new processing methods to reduce porosity is crucial for further enhancing their mechanical properties. Werken et al. (2021) used a post-processing technique called hot isostatic pressing (HIP) to treat 3D-printed CCF/PEEK. By considering the effects of crystallinity and porosity, they determined the optimal post-HIP temperature and time, resulting in 3D-printed CCF/PEEK composite materials with an unprecedented tensile strength of up to 1300 MPa and a modulus of 92 GPa. Additionally, Kuba et al. (2022) demonstrated that using a lower viscosity PEEK resin as the matrix can reduce porosity in 3D-printed CCF/PEEK, thereby improving its mechanical performance. The porosity of both 3D-printed filaments and final molded specimens was reduced by 50% by using low-viscosity PEEK resin as the matrix under the same conditions. Interlayer tensile fracture tests revealed a remarkable improvement of 116.8% in the ultimate tensile strength of the final molded low-viscosity PEEK composite material, offering new possibilities for developing 3D printed continuous fiber-reinforced PEEK composites with higher mechanical performance.

Laser automated fiber placement (LAFP) stands out as a more mature 3D printing production process for continuous fiber-reinforced composite materials compared to the previously mentioned technologies (Fig. 12). The fundamental principle of LAFP involves using external lasers to heat the already printed matrix, followed by laying down continuous fibers or prepreg tapes layer by layer, resulting in continuous printing. Zhang et al. (2022) used near-infrared diode laser heating for CF/PEEK in LAFP and studied the effects of processing temperatures, laying speeds, consolidation forces, and prepreg tape tensions on the peel strength of the final laminated plates. Çelik et al. (2021) investigated the influence of different heating lengths and times on the microstructure and macrostructure of CGF/PEEK prepreg tapes during LAFP. The research revealed that the non-uniform temperature field induced by surface peaks and valleys during laser heating had an impact on deconsolidation phenomena and cell formation. This qualitative insight pointed out the synergistic effects of placement speed, heating length, laser power, and consolidation pressure on the temperature field during LAFP, providing valuable information for achieving high-performance CCF/PEEK laminated plates. Enhancing interlayer bonding has emerged as an effective approach to improving the interlaminar shear strength of LAFP-formed CCF/PEEK laminated plates. Chen et al. (2022) highlighted the necessity of preheating in LAFP. Their results demonstrated that laser preheating facilitated the penetration of PEEK molecular chain ends between adjacent layers, enhancing flowability and inter-strand bonding. Luo et al. (2020) used a plasma-laser-assisted process to improve dual-scale interfacial bonding. Analysis indicated that the laser primarily heated the interlayer bonding points during printing to enhance macroscopic interlayer bonding, while the plasma changed the polarity of the CF surface, improving the interface bonding between the PEEK matrix and CF.

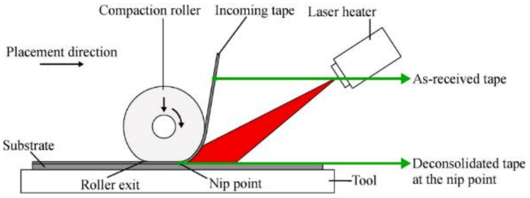

Fig. 12 Typical LAFP process (Celik et al., 2021) [Copyright, 2021, ELSEVIER]

Table 3 Mechanical strength of 3D printed fiber reinforced composites

Materials	Weight Ratio (%)	Tensile strength (MPa)	Flexural Strength (MPa)	ILSS (MPa)	Remark	Ref.
PEEK	/	48.50				(Gao et al., 2021)

PEEK	/	87.34	159.2			(Li and Lou, 2020)
PEEK	/	96	115			(Xu et al., 2021)
PEEK	/	86.5			Ultrasonic-assisted (yield strength)	(Qu et al., 2023)
PEEK	/	80.4			laser interface heating	(Han et al., 2020)
PEEK	/	82			Annealing (73 to 82 MPa)	(Yang et al., 2017)
CF/PEEK	5	95	163			(Wang et al., 2021)
GF/PEEK	5	89	165			
CF/PEEK	5		146			(Li et al., 2019)
CF/PEEK	5			24		(Wang et al., 2022)
()GF/PEEK	5			22.5		
SCF/PEEK	5	99.43		22.94	Annealing	(Liu et al., 2023)
CCF/PEEK	60	859.82				(Liu et al., 2022)
CGF/PEEK	/	523.33	598.57	46.28		(Werken et al., 2021)
CCF/PEEK	42%vol	1300			HIP treatment	(Kuba et al., 2022)

6.2 Complex structures of 3D-printed PEEK and its composites

The innate advantages of additive manufacturing make the application of 3D printing to the molding of complex structures based on PEEK and its composite materials a natural choice. This section introduces typical 3D-printed molded complex structures of PEEK and its composites, including PEEK porous structures, along with their typical applications.

Functionally graded materials (FGMs) are structures whose composition and structure change gradually, resulting in graded changes in material properties to meet specific functional requirements for various applications. Wang et al. (2022) designed a single-nozzle 3D printer capable of multi-material printing, accompanied by a detectable PEEK, CF/PEEK, and GF/PEEK filament length slicing system (Fig. 13 (a1)). Experiments involved the use of 5 Wt% CF/GF-PEEK and 15 Wt% CF/GF-PEEK as reinforcing phases, combined with PEEK to prepare reinforced PEEK FGMs (Fig. 13 (a2)). Two gradient interfacial design methods were used to enhance the interlaminar bonding of the FGMs prepared from 15 Wt% CF/GF PEEK and PEEK. Research showed that implementing a transition interface design with slight changes in gradient composition can enhance the mechanical properties of FGMs by about 12% compared to FGMs without a transition structure. Similarly, Ritter et al. (2023) and McNiffe et al. (2023) developed a 3D printing system that enables a gradual increase in the crystallinity of PEEK layer by layer.

The use of PEEK and its composite honeycomb structures, developed in conjunction with 3D printing technology, shows great potential for novel structural applications, such as energy absorption and smart sensing. Jiang et al. (2023) printed CF/PEEK and HA/PEEK square and triangular core-shell honeycomb structures using FDM. They investigated the effects of crossed paths and non-crossed paths on the compressive strength of the honeycomb. The results showed that the compressive strengths of square and triangular honeycomb core specimens and their composite counterparts increased up to 18.4% when using non-crossed printing paths. Han et al. (2023) developed a honeycomb structure made of CF/PEEK with a zero Poisson ratio. The material exhibited low porosity of only 2.15%. Andrew et al. (2021) conducted research on the mechanical behavior of the material under tensile and compressive cyclic loading. They developed three kinds of 3D print-molded CF/PEEK and PEEK honeycomb structures, with a fixed porosity of 30% (Fig. 13 (b1)). The authors then investigated the energy absorption and self-sensing properties of these structures under quasi-static compression and impact loading. CF/PEEK honeycomb structures exhibited significant piezoresistive behavior under both in-plane and out-of-plane compression (Fig. 13 (b2)), providing a new approach for the development of smart structural systems that can sense in-situ the strain and damage induced by operational or accidental loading. Xiong et al. (2023) reported a multiscale structurally coordinated black PEEK-based wave-absorbing material for star sensors. The honeycomb 3D PEEK-based wave-absorbing material prepared had a high surface absorptivity of about 96.89% and exhibited wide-angle high absorption performance. Additionally, it maintained excellent photoinhibition performance even after undergoing high and low-temperature cycling tests.

A triply periodic minimal surface (TPMS) is a bionic structure that exhibits periodic changes in the X, Y, and Z-axis directions (Han and Che, 2018). Zhang et al. (2023) used PEEK and CF/PEEK as base materials to prepare Schwarz, Diamond, and Gyroid TPMSs using the FDM process (Fig. 13 (c1)). They comprehensively and systematically investigated the load-bearing and energy-absorbing capacities of the three TPMSs under quasi-static compression (Fig. 13 (c2), (c3)). The quasi-static compression behavior of the Gyroid was investigated, resulting in different load-bearing directions. The results indicated that the Diamond and Gyroid structures had superior load-bearing and energy-absorbing capacities. Additionally, the mechanical properties of the structures were significantly improved through post-treatment annealing. Similar studies have been conducted by Du et al. (2023) and Spece et al. (2022) demonstrating the potential of 3D-printed PEEK TPMS with optimized mechanical properties for various applications, including energy absorption, cushioning, shock resistance, and medical implantation. Jia et al. (2023) investigated the osseointegration properties of 3D-printed and molded PEEK/Ta Gyroid gradient structures. The 3D-printed PEEK/Ta Gyroid cages, created by incorporating Ta particles into PEEK, facilitated customized design, improved mechanical properties, and provided microstructures for surface properties, endocytobiological responses, and rapid osseointegration. This technique has the potential to greatly enhance intervertebral osseointegration in spinal fusion procedures.

The 3D printing of PEEK and its composites offers numerous possibilities for producing and applying high-performance bionic structures. Zhang et al. (2020) created a rib cartilage prosthesis using PEEK as the base material through 3D printing. The mechanical properties of the prosthesis can be adjusted by altering the amplitude, wavelength, and thickness of the wave-shaped structure. The prosthesis exhibited mechanical properties similar to those of natural rib cartilage and has the potential to serve as its replacement. The porous structure of pomelo peel is thought to protect the fruit from damage when it falls from the tree. Yang et al. (2022) studied the deformation behavior of three pomelo peel cultivars (Fig. 13 (d1)) to quantitatively characterize their pore structure. An FDM molded PEEK porous structure was created with low porosity on both sides and high porosity in the middle, resulting in a Poisson's ratio close to 0 (Fig. 13 (d2) and (d4)). The study confirmed that optimizing the structure through the natural evolution of pomelo peel could effectively absorb energy (Fig. 13 (d3)).

3D printing enables the production of highly tailored implants to meet individual patient needs, potentially enhancing treatment outcomes and satisfaction (Kennedy et al., 2024). In recent years, there have been significant strides in the application of 3D printed PEEK and its composite materials across various fields, including dentistry, orthopedics, and cardiovascular medicine. PEEK-based dental components, such as prosthetic frameworks, clasps and orthodontic devices (Alevizakos et al., 2020; Celik et. al, 2023; Herford et al., 2017; Ghomi et al., 2021; Prechtel et al., 2020; Reddy et al., 2023), offer patients a broader range of material choices beyond traditional metals, proving particularly beneficial for individuals with metal allergies. These PEEK-based solutions are characterized by their lightweight nature, elasticity, and flexibility, effectively minimizing post-fracture swelling. With the ongoing advancements in 3D printing technology, PEEK-based orthopedic implants are becoming increasingly precise, providing innovative solutions for patients with orthopedic conditions. In cranial and facial reconstruction surgeries, 3D printed PEEK implants offer precise shaping capabilities, restoring both aesthetics and functionality (Papathanasiou et al., 2020; Kim et al., 2009). PEEK's exceptional wear resistance makes it a preferred material for manufacturing surgical instruments, including retractors, trial components, and cutting guides (Zhang, et al., 2023; Kurtz and Nevelos, 2019). Orthopedic procedures often use PEEK-based screws and plates to stabilize fractures, especially in weight-bearing bones (Krätzig et al., 2021; Müller et al., 2020). The radiolucency of these implants proves invaluable for postoperative monitoring. In cardiovascular interventions, 3D printed PEEK scaffolds find applications due to their radiolucency, enabling clear imaging during and after implantation (Oveissi et al., 2020). Furthermore, the customization of heart valve components using 3D printed PEEK allows for adjustments to fit the patient's anatomical structure, reducing the risk of complications and enhancing long-term functionality (Yuerek et al., 2023). Undoubtedly, the outlook for the application of 3D printed PEEK implants in healthcare and patient well-being is promising.

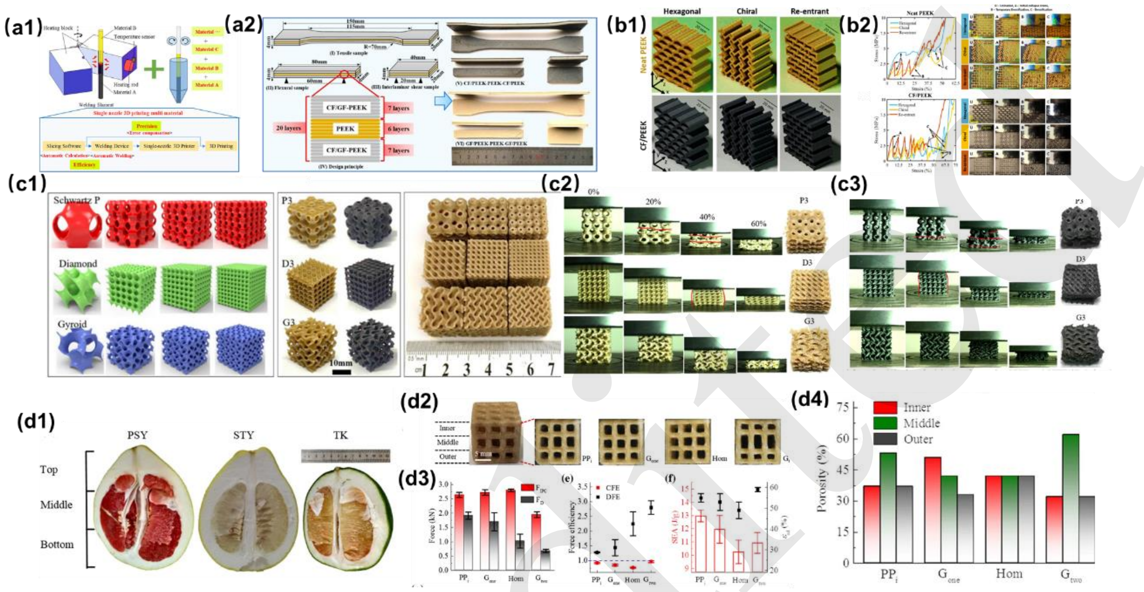

Fig. 13 (a1) Single-nozzle 3D printing multi-material; (a2) shape and dimension of 3D printed functionally graded materials (FGMs) samples for mechanical test (Wang et al., 2022) [Copyright, 2022, ELSEVIER]. (b1) Three types of honeycombs molded by FDM PEEK and CF/PEEK: hexagonal, chiral, re-entrant; (b2) in-plane quasi-static compression behavior of different 2D lattices: characteristic stress–strain curves of PEEK and CF/PEEK lattices with hexagonal, chiral and re-entrant unit-cell geometry (Andrew et al., 2021) [Copyright, 2021, ELSEVIER]. (c1) The design drawings of three kinds of TPMS: Schwarz P (P), Diamond (D) and Gyroid (G) printed by FDM process based on PEEK and CF/PEEK; (c2) the deformation behavior of FDM PEEK and (c3) CF/PEEK TPMS (Zhang et al., 2023) [Copyright, 2023, ELSEVIER]. (d1) Morphology of longitudinal sections of Pingshan Yu (PSY), Shatian Yu (STY) and Ta-Koi (TK). Every fruit is divided equally into three parts: top, middle and bottom parts; (d2) pomelo peel-inspired gradient cube (PPi), one end gradient cube (Gone), homogeneous cube (Hom) and two ends gradient cube (Gtwo); (d3) crush force efficiency (CFE) and dropping force efficiency (DFE) (e), critical strain (εcd) and specific energy absorption (SEA); (d4) porosity (b) of four kinds of cubes (Yang et al., 2022) [Copyright, 2022, SPRINGER].

6.3 Discussion

As the most recent among manufacturing processes, 3D printing has seen rapid development. Optimizing process parameters and incorporating innovative post-treatments like ultrasound and laser have enabled the creation of PEEK and composite structures with exceptional functionality. 3D-printing excels in shaping intricate structures, from FGMs to medical implants, offering new possibilities. However, challenges persist in real large-scale applications. Ensuring consistent mechanical properties in the Z-axis and interlayer bonding strength remains a significant challenge. Controllable molding accuracy and minimizing pore defects are also crucial. Systematic investigation into crystallization behavior and orientation throughout the printing process is needed. Moreover, there's a lack of research on smart structures with 3D-printed PEEK. Interdisciplinary research is necessary to enhance the intelligence of these parts. Addressing these challenges will advance the adoption of 3D-printed PEEK in diverse industrial applications.

7 Summary and outlook

This article centers on the four primary processes used for molding structural parts using PEEK and its composites. We comprehensively review studies on static mechanical properties, specialized mechanical behaviors under variable conditions (such as high temperature, high pressure, water immersion, salt spray, and crack extension), frictional properties, electrical properties, and biocompatibility of these materials or samples. Furthermore, we discuss the development and production of mechanical, structural, electrical, and biomedical products crafted from PEEK and its composites, exploring the synergies of each process's unique advantages in the manufacturing of these products.

In summary, ongoing research into the development and molding processes for PEEK and its composites has harnessed the distinct strengths of each technique. Basic profiles and functional PEEK composites have been innovatively created for extrusion molding. These PEEK-based composite basic profiles, 3D printing filaments, and particles undergo secondary processes such as machining, hot pressing, injection molding, and 3D printing, significantly expanding the application scope of PEEK. Hot compression molding efficiently mass-produces continuous fiber-reinforced PEEK composite laminates with ultra-high mechanical properties. Injection molding industrializes the production of most PEEK structures, fostering widespread application. 3D printing enables personalized customization and, when coupled with advanced computer-aided design (CAD) and computer-aided engineering (CAE) technology, facilitates the creation of intricate PEEK composite porous structures for lightweight applications.

Over the past 50 years, scholars have conducted extensive research on the development of PEEK and its composite materials, as well as molding processes, resulting in fruitful outcomes and high expectations. However, with the future trajectory leaning towards industrial intelligence and systematization, there is a need for process innovation. For specific products, combining the advantages of several processes to achieve rapid prototyping and near-net forming has emerged as a developmental trend. Recently explored process lines, such as hot compression injection (Deng et al., 2021) and 3D printing injection hybrid molding (Boros et al., 2019; Tosello et al., 2019; Yan et al., 2020), demand further research in areas like process analysis, interface bonding, and predicting the overall properties of PEEK matrix composite products. The next phase in this field entails designing innovative processes to mold PEEK-based composites for a broader range of applications and high-performance products.

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Author contributions

Zhengchuan GUO and Junjie HE wrote the first draft of the manuscript, Jianzhong FU, and Peng ZHAO helped to organize the manuscript, Chengqian ZHANG, Ruoxiang GAO, Yifeng PAN checked the manuscript, Zhengchuan GUO Chengqian ZHANG, and Peng ZHAO revised and edited the final version.

Conflict of interest

Zhengchuan GUO, Junjie HE, Ruoxiang GAO, Yifeng PAN, Chengqian ZHANG, Jianzhong FU, and Peng ZHAO declare that they have no conflict of interest.

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中文概要

题　目：聚醚醚酮及其复合材料成型研究进展与展望

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概　要：聚醚醚酮（PEEK）及其复合材料由于其低密度、强力学性能、耐高温、耐腐蚀、以及优良生物相容性的材料优势，在机械、航空航天、军事装备、电子、生物医学等领域都获得了广泛的应用，成为了传统金属材料的理想替代品。然而，聚醚醚酮及其复合材料的半结晶、高熔点、高粘度、低介电系数和疏水性的固有特性限制了其高性能化、功能化成型。本文对聚醚醚酮及其复合材料的成型工艺与方法进行了综述：阐述了结合挤出成型、热压成型、注射成型和3D打印成型的工艺特点与聚醚醚酮的材料特性开发出的各类功能性复合材料与结构；总结、分析了聚醚醚酮及其复合材料在机械、电学和生物医学领域的典型、创新应用；归纳了通过优化成型参数、工艺变量和材料结构实现聚醚醚酮及其复合材料服役性能调控的创新研究结果；展望了聚醚醚酮及其复合材料的成型方法发展趋势，探讨了其进一步的研究方向。

关键词：聚醚醚酮；复合材料；挤出成型；热压成型；注射成型；3D打印