

**Additive Manufacturing of Recycled High-Performance Thermoplastic Composite
Incorporating Extraterrestrial Regolith for In-Situ Resource Utilization**

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Abstract

Additive Manufacturing of Recycled High-Performance Thermoplastic Composite Incorporating Extraterrestrial Regolith for In-Situ Resource Utilization

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Sustainable lunar and Martian missions require materials that can be manufactured, reused, and reinforced directly on planetary surfaces. This thesis develops a comprehensive framework for additive manufacturing (AM) of recycled PEKK and PEKK–regolith composites, unifying crystallization control, recycling science, and extraterrestrial filler incorporation for in-situ resource utilization (ISRU).

First, the thermal and mechanical behavior of PEKK during AM was optimized through a combined “on-the-fly” annealing strategy and a DSC–FEA post-processing method, enabling predictable crystallization, reduced warpage, and significantly improved strength and thermal stability. These principles were extended to architected geometries, showing how raster orientation, lattice topology, and heat treatment govern anisotropy and failure modes in printed structures.

PEKK was then compounded with Martian (10–30 wt%) and lunar regolith simulants (10–60 wt%), in two parallel projects. In lunar project we aimed to maximize the regolith incorporation while in Martian project we focused on maximizing the incorporation from relatively large particles (100 microns) to perforated tube silica particles (less than 20 microns) to study effect of particle morphology beside the maximum incorporation. Mechanical testing across orientations showed that moderate regolith contents maintain printability and flexural performance, while high loadings yield stiff, brittle composites suitable for compressive or sacrificial applications. A predictive tensile model incorporating porosity, filler fraction, and fracture regime was developed and validated.

To enable closed-loop ISRU, PEKK was repeatedly recycled through shredding, pulverization, extrusion, and reprinting. Across multiple cycles, PEKK preserved its chemical, thermal, and mechanical integrity, and annealed recycled material often outperformed virgin PEKK due to reduced porosity. Finally, recycled PEKK was combined with 30 wt% lunar regolith to create a

circular ISRU composite filament used to fabricate functional demonstrators, including gyroid lattices and a ratchet wrench.

Collectively, this work establishes that recycled PEKK and PEKK–regolith composites are viable, high-performance, and circular feedstocks for future extraterrestrial manufacturing, providing a scalable pathway toward sustainable polymer-based ISRU on the Moon and Mars.

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Dedication

To the resilient people of Iran, to those who have stood with courage in the face of hardship, whose voices have echoed in streets and hearts alike, and whose strength under unimaginable pressure has inspired the world. May this work honor your endurance, your courage, and your hope for a just and peaceful future.

I would also like to share the quote that has inspired me the most throughout these years, by Oscar Wilde:

“We are all in the gutter, but some of us are looking at the stars ...”

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List of journal papers and conference presentations

Journal Papers

- [1] F. Malekpour, M. Hojjati; “On-the-Fly Annealing of Polyetherketoneketone PEKK via Fused Deposition Modeling Parameter Optimization Using Taguchi Method”; SAMPE Journal, 2025: <https://doi.org/10.33599/SJ.v61no5.02>
- [2] F. Malekpour, M. Hojjati; “Crystallization Engineering of 3D-Printed PEKK: Rapid Post-Processing Route for Superior Strength and Thermal Stability”; Progress in Additive Manufacturing Journal, 2025: <https://doi.org/10.1007/s40964-025-01305-z>
- [3] F. Malekpour, M. Hojjati; “Tailoring Anisotropy and Mechanical Performance of Additively Manufactured PEKK through Annealing and Architected Design ”; Journal of Science: Advanced Materials and Device, 2025: <https://doi.org/10.1016/j.jsamd.2025.101077>
- [4] F. Malekpour, M. Abdali, M. Hojjati, K. Skonieczny; “Toward Sustainable Additive Manufacturing of PEKK/Martian Regolith Composite for Lightweight Structural Applications on Mars”; Additive Manufacturing Letters, 2025: <https://doi.org/10.1016/j.addlet.2025.100297>
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[2] Malekpour F, Hojjati M. “On-The-Fly Annealing of Polyetherketoneketone PEKK via Fused Deposition Modeling Parameter Optimization Using Taguchi Method”. 78th Society for the Advancement of Material and Process Engineering (SAMPE 2025). Indianapolis, Indiana, USA. 19-22 May 2025.

[3] Malekpour F, Hojjati M. “From Regolith to Rover: Additive Manufacturing and Characterization of PEKK/MRS Composite for Lightweight and Sustainable Mars Rover Wheels”. 74th Canadian Society of Mechanical Engineer (CSME 2025), Montreal, Quebec, Canada, 25-28 May 2025.

[4] Malekpour F, Hojjati M. “Sustainable Additive Manufacturing: Evaluating the Mechanical and Thermal Degradation of Recycled PEKK”. 8th Holistic Innovation in Additive Manufacturing (HI-AM 2025), Waterloo, Ontario, Canada, 23-24 July 2025.

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Chapter 1: “Introduction and Motivations”

“Mankind was born on Earth. It was never meant to die here”

-Interstellar

1. Introduction and Motivations

1.1 Introduction

The cost of space missions remains one of the most significant barriers to sustained human and robotic presence beyond Earth. A large fraction of this cost is directly associated with launching mass from Earth's gravity well, where every kilogram of payload incurs substantial financial, logistical, and energy penalties. As space exploration evolves from short-duration missions toward long-term operations on the Moon and Mars, traditional Earth-supplied manufacturing paradigms become increasingly impractical. Future missions will require not only advanced materials and structures, but also self-reliant, adaptive, and sustainable manufacturing strategies capable of operating in extraterrestrial environments.

Sustainability in space is fundamentally different from sustainability on Earth. While terrestrial sustainability focuses on reducing environmental impact and conserving resources, extraterrestrial sustainability emphasizes resource independence, circularity, and mission resilience. In this context, manufacturing systems must minimize reliance on Earth-based supply chains, reduce waste, and enable reuse of materials already present or delivered to the planetary surface. Achieving such autonomy is essential for lowering mission costs, extending operational lifetimes, and enabling scalable space infrastructure.

This thesis addresses these challenges by developing a comprehensive framework for sustainable polymer-based additive manufacturing in space, with a specific focus on in-situ resource utilization (ISRU) and material recycling as two complementary pathways toward self-reliant extraterrestrial manufacturing.

1.2 Research Objective

The overarching objective of this thesis is to develop and validate a sustainable, circular, and high-performance additive manufacturing framework for future lunar and Martian missions.

Figure 1.1, demonstrated the mission like stages of the thesis and the objectives of each stage is explained as follows:

1. Establish optimized additive manufacturing and post-processing protocols for PEKK to achieve predictable crystallization, mechanical performance, and dimensional stability. (Stage 1: Chapter 2, 3, and 4)
2. Investigate the feasibility of incorporating lunar and Martian regolith simulants into PEKK matrices for ISRU-driven composite manufacturing and evaluate the mechanical, thermal, and structural performance of PEKK–regolith composites across a wide range of filler loadings and particle morphologies. (Stage 2: Chapter 5 and 6)
3. Assess the resistance of PEKK to degradation under multiple recycling cycles and its suitability for closed-loop additive manufacturing. (Stage 3: Chapter 7)
4. Demonstrate the integration of recycling and ISRU through functional printed components and architected structures relevant to extraterrestrial applications. (Stage 4: Chapter 8)

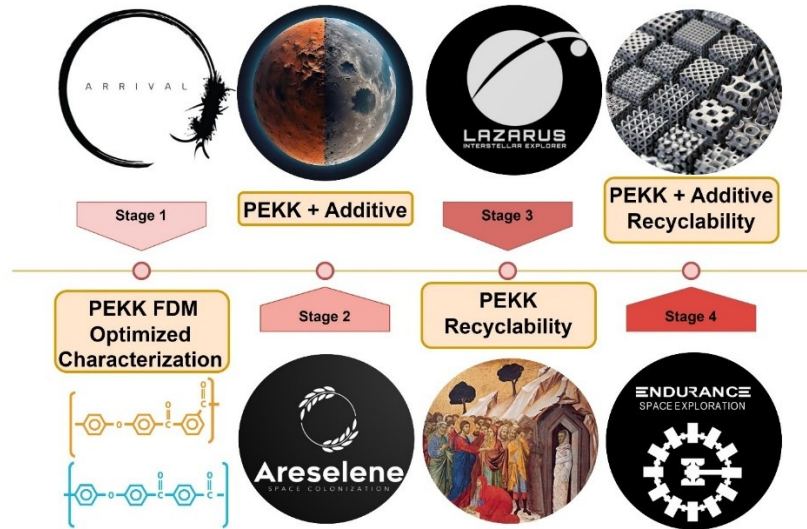


Figure 1.1. Conceptual roadmap of the thesis framework for sustainable extraterrestrial manufacturing; The schematic illustrates the four progressive stages investigated in this work: Stage 1 (Arrival), optimization and characterization of PEKK for FDM-based additive manufacturing; Stage 2 (Areselene), incorporation of extraplanetary regolith additives (Martian (Ares) and lunar (Selene)) into PEKK to enable ISRU-driven composite manufacturing; Stage 3 (Lazarus),

evaluation of PEKK recyclability through multiple additive manufacturing cycles; and Stage 4 (Endurance), integration of recyclability and regolith reinforcement

1.3 Thesis Layout

This thesis is structured according to the Concordia University manuscript-based format and is composed of a sequence of peer-reviewed and publishable research manuscripts addressing sustainable additive manufacturing for extraterrestrial applications.

Chapter 2: Focuses on the optimization of fused deposition modeling (FDM) parameters for amorphous polyetherketoneketone (PEKK) with the objective of achieving enhanced mechanical performance through controlled thermal management during printing. A novel “on-the-fly” annealing strategy is introduced and systematically optimized using a Taguchi design of experiments to quantify the influence of key thermal parameters on crystallinity and tensile behavior. The findings of this chapter have been published in SAMPE Journal (2025).

Chapter 3: Investigates post-processing strategies for additively manufactured PEKK, aiming to establish a rapid and reliable annealing protocol to transition printed parts from an amorphous to a semi-crystalline state without inducing distortion or porosity growth. A combined differential scanning calorimetry (DSC) and finite element analysis (FEA) framework is developed to identify optimal annealing conditions, resulting in significant improvements in mechanical strength and thermal stability. This work has been published in Progress in Additive Manufacturing (2025).

Chapter 4: Examines the role of architected design and raster orientation in tailoring anisotropy in additively manufactured PEKK structures. The objective of this chapter is to correlate printing strategy, crystallization behavior, and failure mechanisms in both solid and lattice geometries, providing design guidelines for load-bearing applications. The results presented in this chapter have been published in Journal of Science: Advanced Materials and Devices (2025).

Chapter 5: addresses Martian in-situ resource utilization (ISRU) by incorporating Martian regolith simulants into PEKK to fabricate composite filaments suitable for additive manufacturing. The

objective is to evaluate the effects of regolith particle size, morphology, and loading fraction on printability, mechanical performance, and fracture behavior, and to develop a predictive tensile strength model accounting for porosity and filler content. Portions of this work have been published in Additive Manufacturing Letters (2025) and Sustainable Materials and Technologies (2025).

Chapter 6: Focuses on lunar ISRU by extending the composite framework to high regolith-loaded PEKK systems using lunar regolith simulants. The primary objective is to maximize regolith incorporation while maintaining structural integrity and manufacturability, enabling the production of stiff, load-bearing, and sacrificial components relevant to lunar infrastructure. The findings of this chapter have been published in Composites Part B: Engineering (2025).

Chapter 7: Investigates the recyclability of PEKK under multiple additive manufacturing cycles, with the objective of evaluating thermal, mechanical, and chemical stability in support of circular manufacturing in space. Repeated shredding, extrusion, and reprinting cycles are analyzed to determine degradation resistance and performance retention, establishing PEKK as a robust candidate for closed-loop additive manufacturing systems. This work is currently under review in Polymer Degradation and Stability (Second round of peer-review is completed).

Chapter 8: Integrates recycling and ISRU by combining recycled PEKK with lunar regolith to demonstrate a circular ISRU manufacturing paradigm. The objective of this chapter is to assess the feasibility of producing functional, reusable, and sacrificial structures from recycled PEKK–regolith composites, including architected lattices and demonstrator components. This manuscript is currently submitted in Composites Part B: Engineering.

Chapter 9: Summarizes the key conclusions drawn from the entire body of work and discusses future research directions toward fully autonomous, scalable, and sustainable polymer-based manufacturing systems for long-duration lunar and Martian missions.

Chapter 2: “3D Printing Parameter Investigation”

“Despite knowing the journey and where it leads, I embrace it”

-Arrival

This work has been published in:

F. Malekpour, M. Hojjati; “On-the-Fly Annealing of Polyetherketoneketone PEKK via Fused Deposition Modeling Parameter Optimization Using Taguchi Method”; SAMPE Journal, 2025:

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2. On-the-Fly Annealing of Polyetherketoneketone PEKK via Fused Deposition Modeling Parameter Optimization Using Taguchi Method

2.1 Abstract

Annealing is a key strengthening mechanism for enhancing the stiffness and strength of semi-crystalline thermoplastics like Polyetherketoneketone (PEKK). It is particularly important in additive manufacturing when Fused Deposition Modeling (FDM) parts are in an amorphous state with low crystallization. However, annealing poses challenges such as material softening, shrinkage, and void deconsolidation before crystallization. To overcome these issues, this study introduces a novel method called on-the-fly annealing. Moreover, FDM additive manufacturing by its nature is a time-consuming process. This intuitive method minimizes the defect and reduces the manufacturing cost in terms of processing time and required facilities. The pathway is to deploy a comprehensive methodology through tuning thermal processing parameters, utilizing the Taguchi optimization method. Primarily, the limits of thermal degradation and crystallization zone temperature were determined through TGA and DSC analyses, respectively. Four thermal parameters including nozzle, bed, tuyere, and chamber temperature were investigated across three levels. Tensile tests and ANOVA analysis were used to assess the impact of these parameters on the mechanical properties of 3D-printed parts. Results indicate that bed temperature is key to on-the-fly annealing, as it controls heat flux and greatly enhances the strengthening and crystallization of the specimen. Nozzle and tuyere temperatures mainly influence the elastic modulus, while chamber temperature affects toughness and elongation. This study reveals that on-the-fly annealing is achievable, and the mechanical properties of 3D-printed parts can also be adjusted by appropriately selecting thermal printing parameters.

2.2 Introduction

Fused Deposition Modeling (FDM) of high-performance thermoplastics from the Polyaryletherketone (PAEK) family is getting more attention thanks to the development of 3D printers with enclosure [1]. However, the additive manufacturing of such polymers is not without challenges, especially in the semi-crystalline phase. In FDM, it takes a few seconds to have the deposition from the melting phase to solidified beads. Meanwhile, if crystallization happens, it

would lead to an extra shrinkage compared to conventional thermoplastics and consequently more residual stress added layer by layer. The extensive residual stress will show up as a warpage causing detachment from the build plate and leading to print failure or dimension instability [2].

One solution to that problem is to utilize high-performance thermoplastic with much slower crystallization kinetics which guarantees almost no crystallization will take place from the molten stated extrusion of material to the solidified state, causing better adhesion to the build plate [3,4]. This would result in the final product being in an amorphous state. As such, one of the candidates for the FDM of high-performance thermoplastic would be Amorphous Polyetherketoneketone (A-PEKK) for various applications from aerospace to biomedical industries due to its high strength, resistance to corrosion, and erosion [5,6].

Focusing on the variance of PEKK, it should be mentioned that the combination ratio of two types of PEKK isomers known as Terephthalic “T” and Isophthalic “I” will result in the production of different grades of PEKK with variable crystallization kinetics. Terephthalic isomers with straight molecular structures contribute to faster crystallization kinetics making Semi-crystalline Polyetherketoneketone grades (SC-PEKK) [7–9]. Meanwhile, Isophthalic isomers with branch-like structures slow down the crystallization kinetics, producing A-PEKK which is preferred for additive manufacturing since they are transient manufacturing processes inheriting residual stress by their nature. Differential scanning calorimetry (DSC) analysis of PEKK with a T/I ratio of 80/20 compared to 60/40 shows higher glass transition temperature (T_g), faster crystallization, and higher degree of crystallinity [3,4,10–16].

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Although FDM of A-PEKK offers easier manufacturability compared to SC-PEKK and other semi-crystalline thermoplastics like Polyetheretherketone, it requires post-processing, specifically annealing, to improve the mechanical strength of the 3D-printed parts by transitioning them from an amorphous to a semi-crystalline state. However, this post-processing step presents its own set of challenges. Since the annealing post-processing relies on cold crystallization, it requires raising the temperature above the glass transition temperature (T_g). At these elevated temperatures, the structural stability of the part becomes critical, as insufficient support can cause the structure to collapse under its own weight [17]. Additionally, during the FDM process of thermoplastics, gaps often form between adjacent beads due to the high viscosity of the material, which limits its ability to flow into these spaces, resulting in organized voids within the structure. If heat diffusion during annealing is not carefully controlled, these voids can expand before crystallization occurs, leading to an increased level of porosity in the final structure. Furthermore, even if the annealing process is executed correctly, shrinkage of the material along the bead direction is inevitable, creating challenges with tolerances and dimensional stability. These issues, including structural collapse, void expansion, porosity, and shrinkage, are illustrated in Figure 2.1.

There are many manufacturing parameters involved in FDM that can have significant contributions to the quality of the final result and can reinforce or weaken the influence of each other in some cases [18]. The categories can be divided into three main groups. The first group is thermal parameters such as nozzle, build plate, and enclosure temperature which directly have been set to a specific number and can vary based on different commercialized printers. The other group with influence the process time of extrusion. Considering conditions in which the amount of extruded materials is the same parameters like layer height and print speed would determine the time required for a part to be printed. Finally, the last group parameters like raster angle, build orientation, and pattern will affect the print quality as a structural parameter by determining of print pathway and prioritizing bead placement adjacently. To overcome these challenges one solution could be the manipulation of thermal heat transfer during the 3D printing process to have both additive manufacturing and annealing at the same time without inquiring post-processing and that is here the concept of on-the-fly annealing is coming from.

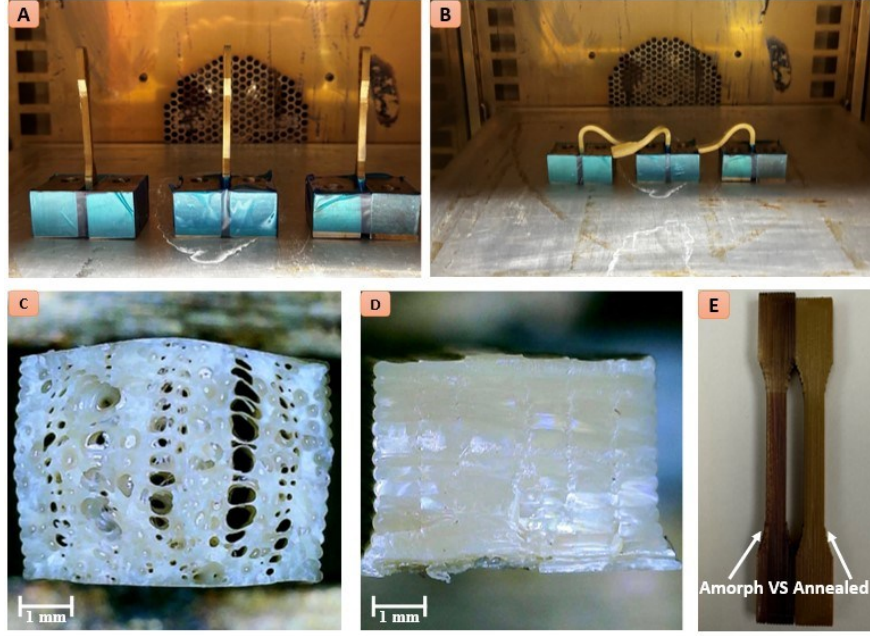


Figure 2.1. Defects through annealing post-process of 3D-printed tensile coupons, A) Placing sample vertically inside the oven, B) Deformation of the samples as a result of material softening and insufficient supports on the overhangs, C) uneven annealing of the part leading to void expansion, D) Even annealing of the part resulting in no void expansion, E) comparison to show the shrinkage of the part in the longitudinal direction due to crystallization.

Since there are plenty of parameters to investigate their effects as a whole, a design of experiments (DOE) is required to figure out which combination of parameters set would result in what mechanical behavior of the final 3D printed part. Taguchi's design of experiment is commonly used in this case as shown in the literature on this topic [19–23]. This study aims to investigate the effect of thermal parameters on the FDM of A-PEKK through Taguchi's DOE. The goal is to find tuned parameter sets for specific mechanical properties by quantifying the effect of each parameter through analysis of variance (ANOVA) focusing on signal-to-ratio values to figure out the importance of each parameter over the targeted mechanical properties.

2.3 Experimentation

2.3.1 Material

A-PEKK filament with a 1.75 ± 0.05 mm diameter, provided by Spool3D (Alberta, Canada) under the product code PEKK175-1000, was utilized in this study. Since PEKK is hygroscopic, the

filament was dried at 125 °C for 5 hours and stored in a drying chamber at 65 °C before 3D printing. It is worth mentioning that the supplier's recommendation for the FDM of this filament was to set nozzle temperature between 360 °C to 400 °C and build a plate (bed) between 90 °C to 130 °C.

2.3.2 Thermal Analysis

Before start designing the experiment for the effect of thermal parameters on tensile mechanical properties of FDM-manufactured A-PEKK, initial thermal analysis like differential scanning calorimetry DSC and thermogravimetry analysis TGA would be beneficial. DSC would help find out properties like T_g, crystallization zone, and the nature and thermal response of the raw material through a controlled heat cycle and TGA would determine the safe zone for increasing the thermal properties. Not only in the initial steps but also after manufacturing and mechanical testing of the parts, these two analyses contribute to assessing the effect of the additive manufacturing process, using a small amount of the processed material.

DSC analysis was performed using a TA Instruments DSC Q200 (TA Instruments, USA) and categorized into two main focus areas. The first category aimed to investigate the thermal behavior of A-PEKK, including its thermal history, crystallization zones, and crystallization kinetics. The DSC testing procedure involved heating the sample at a rate of 10 °C/min from 0 °C to 380 °C, followed by a 5-minute isothermal hold at 380 °C. Subsequently, the sample was cooled at a rate of 5 °C/min back to 0 °C to capture the thermal history and properties of the raw material.

To address this issue, a new parameter, known as relative crystallinity (X_{cRev}), was introduced, as defined in Eq.(2.1). This parameter provides a more consistent basis for assessing crystallinity. For all tests across both categories, sample sizes ranged from 5 to 10 mg and were prepared in aluminum hermetic pans following the TA Instruments DSC guidelines [24] and ASTM D3418 standards [25].

$$X_{cRev}(\%) = \frac{(\Delta H_M - \Delta H_{CC}) - \Delta H_{Ref}}{\Delta H_M^0} \times 100, \quad \Delta H_{Ref} = \text{Min}(\Delta H_M - \Delta H_{CC}) \quad (2.1)$$

In Eq. (2.1), ΔH_{CC} represents the enthalpy of cold crystallization, while ΔH_M denotes the melting enthalpy. The parameter ΔH_{Ref} , determined through DSC calibration and the properties of the raw material, is defined as the minimum net enthalpy for trials using amorphous state PEKK. This value

corresponds to the raw filament form and serves as the reference point for zero crystallization. According to the literature, the theoretical melting enthalpy of fully crystalline PEKK (ΔH_M^0) is standardized at 130 J/g [9,10,26,27].

A TGA test was performed before the parameters' limit determination to ensure no degradation with the parameter value chosen in Taguchi DOE. Also, after 3D printing, the material's thermal stability for each parameter set was assessed three times using a Thermogravimetric Analyzer (TGA Q50, TA Instruments, New Castle, Delaware, USA). Following ASTM E1131 [28], for each sample, 35–40 mg was placed in a ceramic pan and heated from room temperature to 800 °C at a rate of 10 °C/min, leading to weight loss due to material decomposition.

2.3.3 *Design of Experiment (DOE)*

The focus of this study is on thermal parameters that can be directly controlled during the manufacturing process and the rest of the parameters are set as constant values as shown in Figure 2.2. The build plate (often referred to as the bed), and nozzle temperature were manipulated using the open-source software Cura Slicer while tuyere and enclosure temperatures were manually set on the CreatBot PEEK-300 3D printer (CreatBot, China) which bring us up to four thermal parameters in total. Regarding results obtained from the DSC if the initial layer of the printed part has a temperature above T_g , better adhesion to build plate and enough mobility for stress relaxation will be provided. Therefore, it would lower the risk of print failure since the first layer of successful printing is crucial for completing a decent part. On the other hand, the tuyere feature on CreatBot PEEK-300 acts as an active annealing and can manipulate heat transfer on the part to take it closer to a slower temperature drop and extend crystallization time in the open window of the crystallization zone. The temperature for this parameter should be in the crystallization zone to slow down the temperature drop from the melting point to the enclosure temperature around the crystallization temperature zone. TGA result also will determine the upper limit for the nozzle temperature to avoid any possibility of burnt material and clogging.

In terms of characterization method, if each parameter is investigated in three levels, the full factorial of the evaluation would be 81 distinguished parameter sets to fully analysis the effect which multiplying this number by 3 for three repetitions of each set would result in 243 samples for the analysis. Since high-performance thermoplastics are more costly compared to conventional filament besides the large number of samples for full factorial analysis, it is essential to utilize the

design of experiment methods to reduce the cost and time consumption of the investigation. Utilizing Taguchi DOE will reduce the number of parameters sets for 4 parameters at 3 levels (P4L3) from 81 sets in full factorial to only 9 sets (L9 orthogonal array) [29] as shown in Table 2.1.

Table 2.1. Taguchi DOE based on 4 thermal parameters in 3 levels of variation resulting in 9 categories

Taguchi Set Number #	Code	1 st : Build Plate	2 nd : Nozzle	3 rd : Tuyere	4 th : Enclosure
DB#1	AAAA	160	380	Off	60
DB#2	ABBB	160	400	200	90
DB#3	ACCC	160	420	250	120
DB#4	BABC	180	380	200	120
DB#5	BBCA	180	400	250	60
DB#6	BCAB	180	420	Off	90
DB#7	CACB	200	380	250	90
DB#8	CBAC	200	400	Off	120
DB#9	CCBA	200	420	200	60

This study aims to look for target parameters for the enhancement of mechanical properties in five categories including maximum strength, elastic modulus, elongation, toughness, and crystallinity. Since the goal is maximum value in all categories, in the analysis of variance (ANOVA) the goal is to look for levels that have the largest values of signal-to-noise ratio (SNR) and therefore Eq. (2.2) as the “Larger is better” SNR formula is utilized for the optimum parameter set in each category.

$$SNR_L = -10 \log \left(\frac{1}{n} \sum \frac{1}{y^2} \right) \quad (2.2)$$

Where n is the number of trials and y is the value of the target investigation subject like ultimate tensile strength (UTS). Noise refers to uncontrollable factors in the experiment, including variations in filament composition, inconsistencies in material properties, and fluctuations in processing conditions. The SNR which is also known as mean to standard deviation ratio helps minimizes variation and quantifies the ability to meet the goal of every experimental property [23,30]. Mean

of means (Delta-value) and SNR were studied for each target value using Minitab software (Minitab LLC, State College, PA). Finally, the Delta-value for each target category determined the most significant parameter over that particular property.

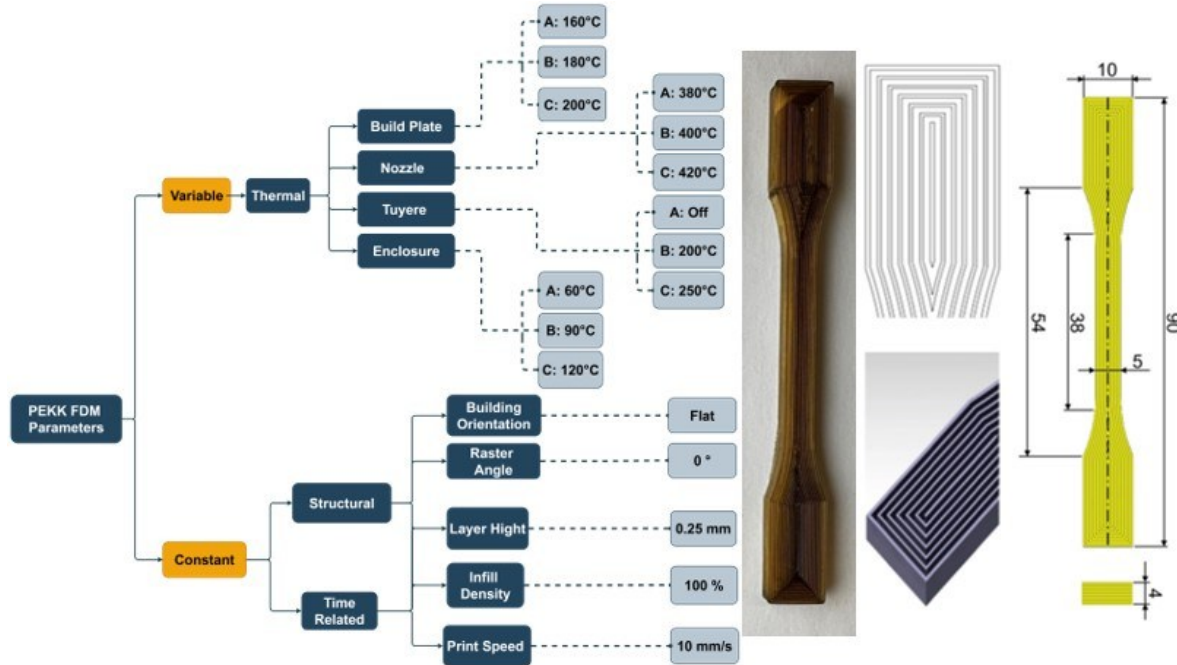


Figure 2.2. FDM parameters are divided into constant (values are constant) and variable (Level defined); the pattern is concentric for all samples and printed flat to have maximum surface contact with the build plate; geometrical dimensions of the dog bone coupons are shown on the yellow schematic

2.3.4 Mechanical Testing

Tensile coupons were manufactured following ISO 527 [30] and 3D printed using the CreatBot PEEK-300 3D printer, as illustrated in Figure 2.2. To minimize the time between the deposition of each layer, each sample was printed individually at the center of the build plate rather than in batches. This approach reduced air exposure for each layer, enhancing layer-to-layer adhesion. The tensile tests were conducted using a Hoskin Scientific universal testing machine (Hoskin Scientific, Canada), equipped with a 5 kN S-type load cell on the upper grip. The machine operated at a displacement rate of 2 mm/min, as shown in Figure 2.4. Each test set consisted of at least three repetitions, and a preload ranging from 10 N to 20 N was applied for the tensile test.

2.4 Results

The first DSC result of the raw filament shows that T_g is more than 150 and the crystallization temperature zone has a peak value between 200 °C and 250 °C as shown in Figure 2.3a. As so, regarding the justification mentioned in the design of the experiment section, the lowest value for the build plate temperature was considered to be 160 °C. CreatBot PEEK-300 will reach a maximum of 200 °C for the build plate temperature, which is considered the upper limit. The average of these two values, 180 °C, was considered the third level. Moreover, based on the crystallization zones whether in crystallization from melt or cold crystallization, the first tuyere temperature level was selected as off which means this option is not active during the process, second as 200 °C for the middle level, and finally 250 °C as the upper level. The reason for such selection on limits of crystallization zone was because the tuyere heat transfer mechanism is through forced air convection. Based on the supplier recommendation on the nozzle temperature it is suggested to keep the nozzle temperature between 360 °C and 400 °C. However, based on the TGA result in Figure 2.3b, degradation of the material starts at temperatures above 480 °C. Higher temperatures would result in lower viscosity and more contact area between adjacent beads. Finally, relying on trials and errors the minimum enclosure temperature is 60 °C set as a lower value and CreatBot PEEK-300's maximum enclosure temperature can reach 120 °C. The mid-level was considered as the average of these two values at 90 °C.

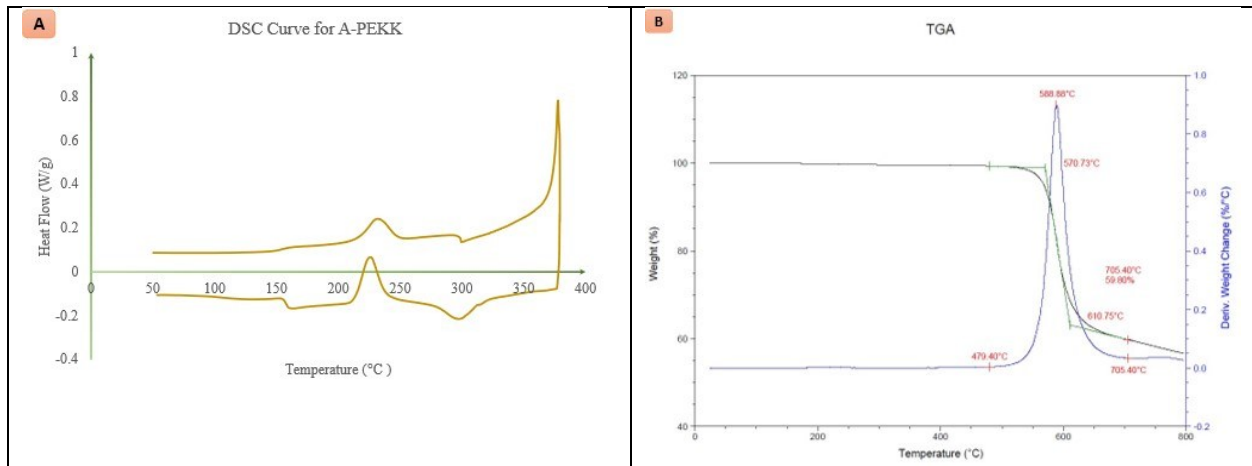


Figure 2.3. Prerequisite thermal analysis for determining the limitation of FDM thermal variables (a) DSC result of A-PEKK as received for detecting crystallization zones; (b) TGA result of A-PEKK as received for determination of upper limits for thermal parameter values

2.4.1 Tensile Properties

As shown in Figure 2.4, different parameter sets have different fracture responses. The stunning phenomenon observed in some sets of 3D-printed A-PEKK is the developing necking. It is known that polymer strength is increased due to chain alignment [31] and in the case of A-PEKK the strengthening mechanism is more than the increase in the amount of stress due to necking cross-section area reduction. Consequently, when the necking happens, it will develop all through the part until it strikes a defect and then the rupture occurs. As it can be seen there is a visible boundary between plastically deformed and undeformed areas.

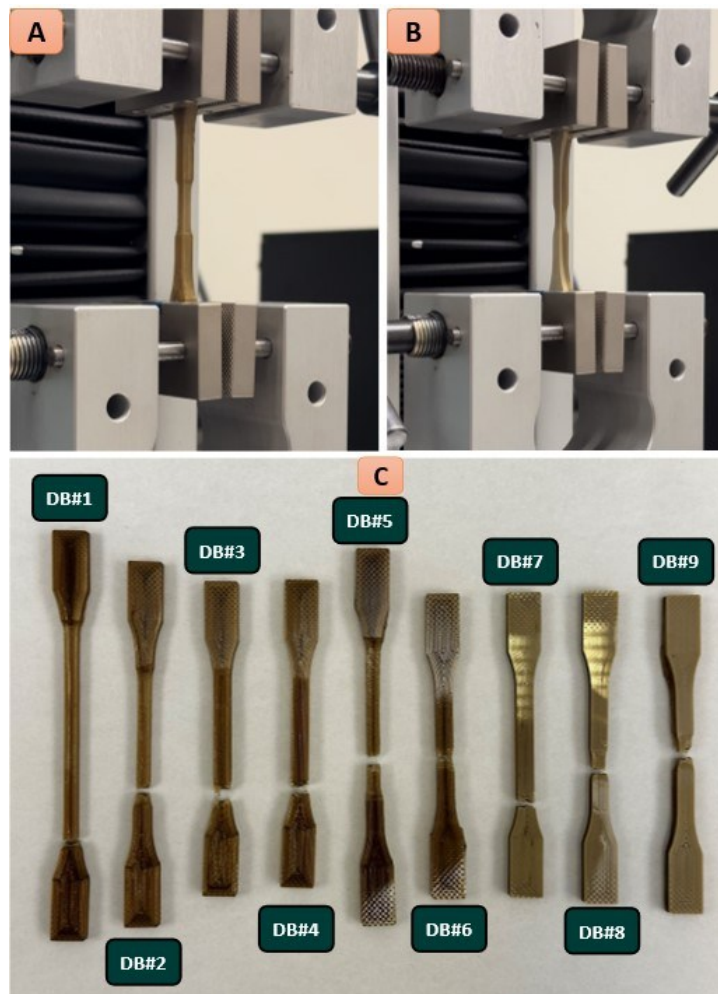


Figure 2.4. Tensile testing of (a) DB#1; (b) DB#9; (c) Different parameter sets would have different fracture behaviors and their necking area development is not the same.

The results of the tensile test are categorized into four sections including ultimate tensile strength (UTS), elastic modulus, strain to failure, and toughness. As demonstrated in Figure 2.5a, the sets that had bed temperature values of 200 °C, show a greater strength compared to other sets. Since this temperature is close to the start point of the cold crystallization zone, on-the-fly annealing starts to occur during the 3D printing process, causing a change in color from translucent amber to opaque tan. The bottom layers start to crystallize upward till they reach a distance that due to the temperature gradient, the temperature of the middle layers reaches a point where crystallization would be so slow and no change in color is observed [3]. Meanwhile in Figure 2.5b, no noticeable change in elastic modulus is observed since none of the sets are fully annealed.

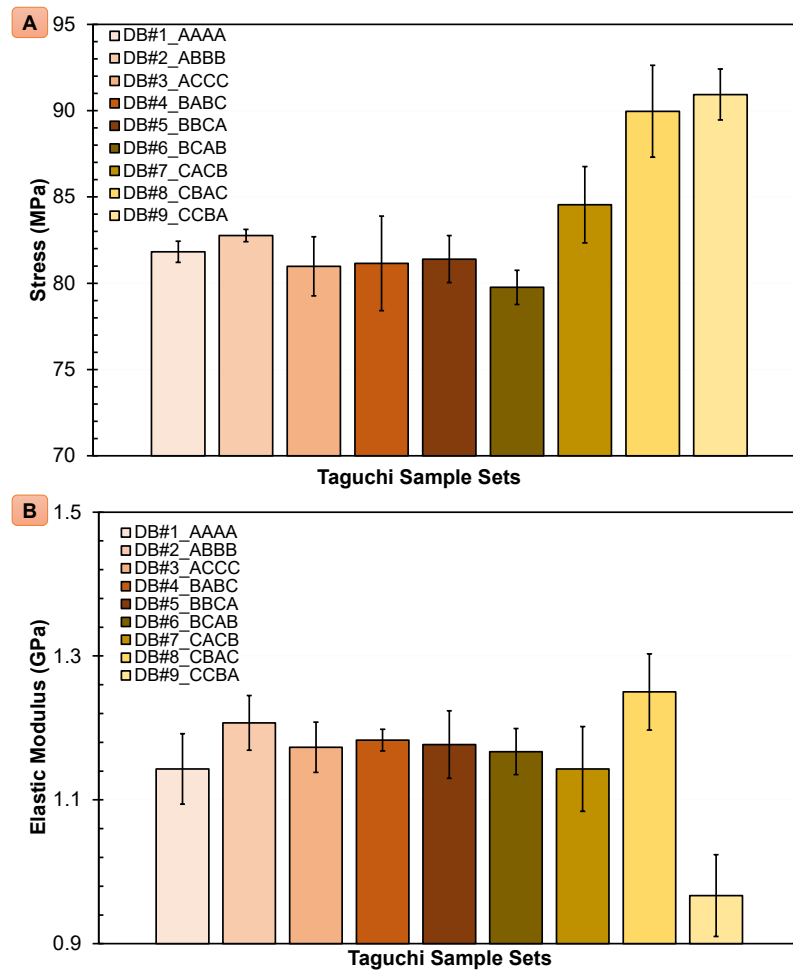


Figure 2.5. (a) Ultimate tensile strength results of Taguchi parameter sets, (b) Elastic modulus results of Taguchi parameter sets Hybridization effect on LVI behavior of composites.

On the other hand, the strain to failure and consequently toughness is diverse for various sets. The huge scatter in the data of some sets can be justified by such explanation that the transition from ductile fracture to brittle fracture can cause such scatter. When the part is ductile its sensitivity to defects is low due to localized plastic deformation and strengthening and strain to failure would happen in large values with low scatter (DB#1). For brittle parts, the sensitivity to defects is high, and after reaching UTS rather than developing necking, a brittle-like rupture will happen and once again data scatter is low (DB#3, DB#4, DB#7, and DB#8). However, some parts developing necking happen for them but they are still sensitive to defects (DB#2, DB#5, DB#6, and DB#9). This would result in large scatter data of their strain to failure and toughness as was observed in the previous study by Paszkiewicz et al. [32].

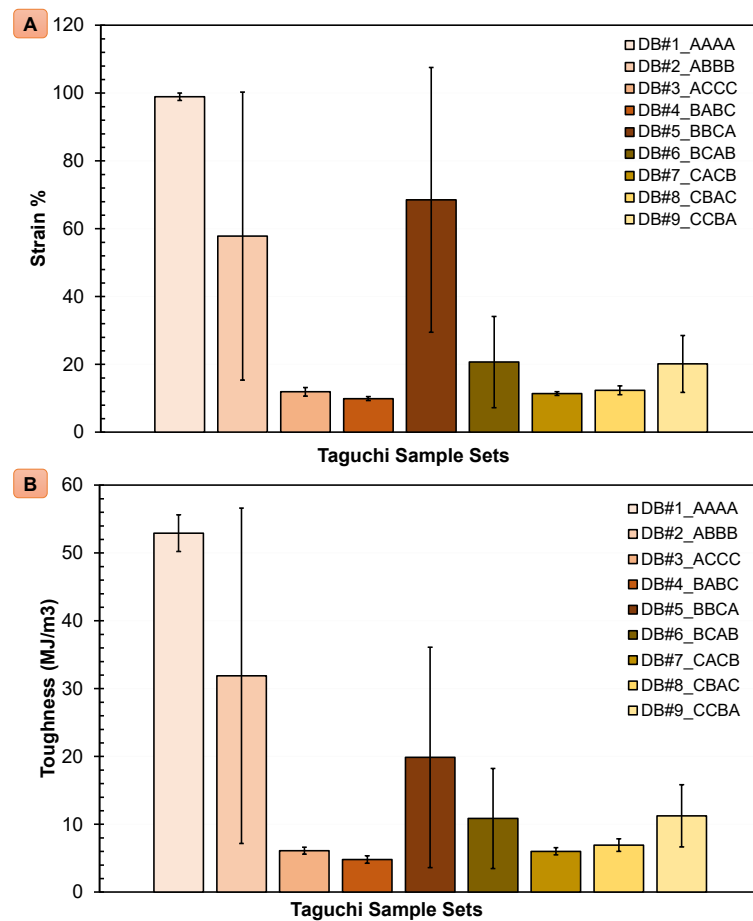


Figure 2.6. (a) Strain to failure results of Taguchi parameter sets, (b) toughness results of Taguchi parameter sets.

2.4.2 Crystallization Evaluation

According to Figure 2.7, In the calculation of crystallization degree net value of crystal melt and formation of raw filament was considered as the baseline to propose more reliable values for the amount of crystal formed during the FDM process. The endothermic energy absorption for melting crystals revealed that the bottom layers of the parts all sets except DB#5 were greater than the top layers. This exception for DB#5 comes from the fact that the tuyere level in this set was at its maximum level (250 °C) while the enclosure level was at its minimum (60 °C). For the sets with the bed temperature of 200 °C, the bottom layers have almost reached to maximum capacity of crystallization while the top layers are still in an amorphous state but still have higher values of crystallization around 10% compared to sets with the lower bed temperature (160 °C and 180 °C). Also, the higher strength of sets with a bed temperature of 200 °C can be justified by having a higher degree of crystallization in the bottom layers.

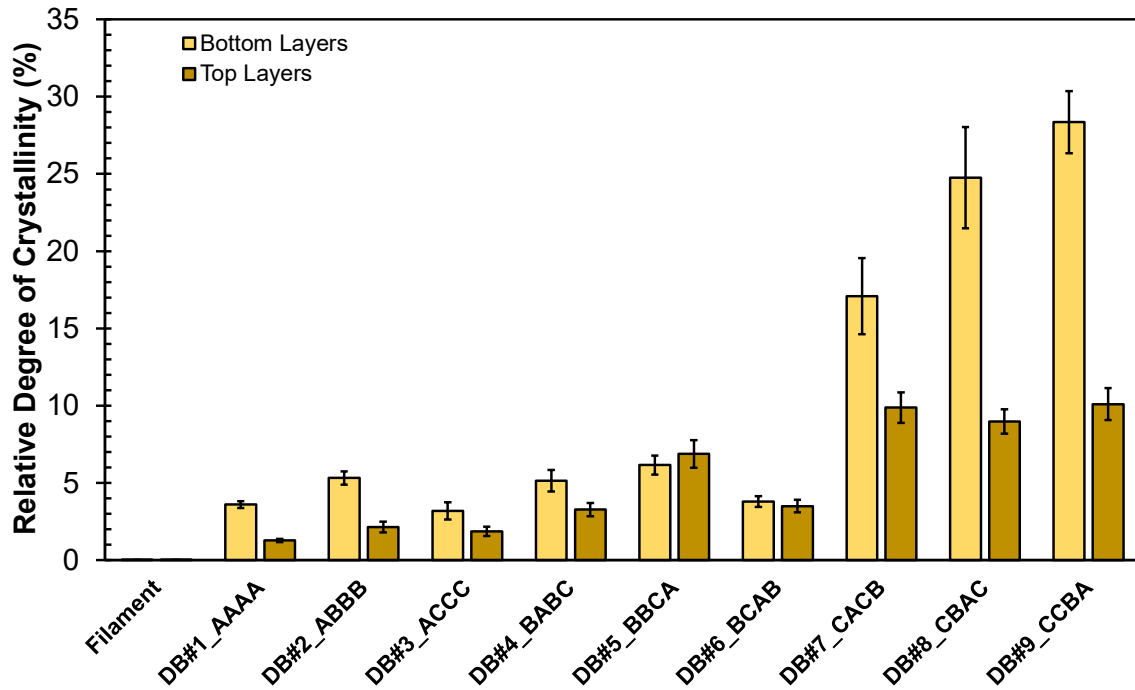


Figure 2.7. Crystallinity evaluation of Taguchi set parameter through sample examination from the bottom and top layer of each set.

2.4.3 Thermal Degradation Evaluation

TGA results as shown in Figure 2.8, show very close results between all sets and the raw filament itself in terms of final mass loss, degradation temperature start, and degradation temperature peak. But from the quality control aspect, there is some kind of degradation happening at the nozzle temperature of 420°C that was not shown in the results. It can be concluded that thermal degradation through TGA is only observable through weight changes, while there might be some sort of degradation that TGA cannot reveal as also pointed out by Croshaw et al. [33].

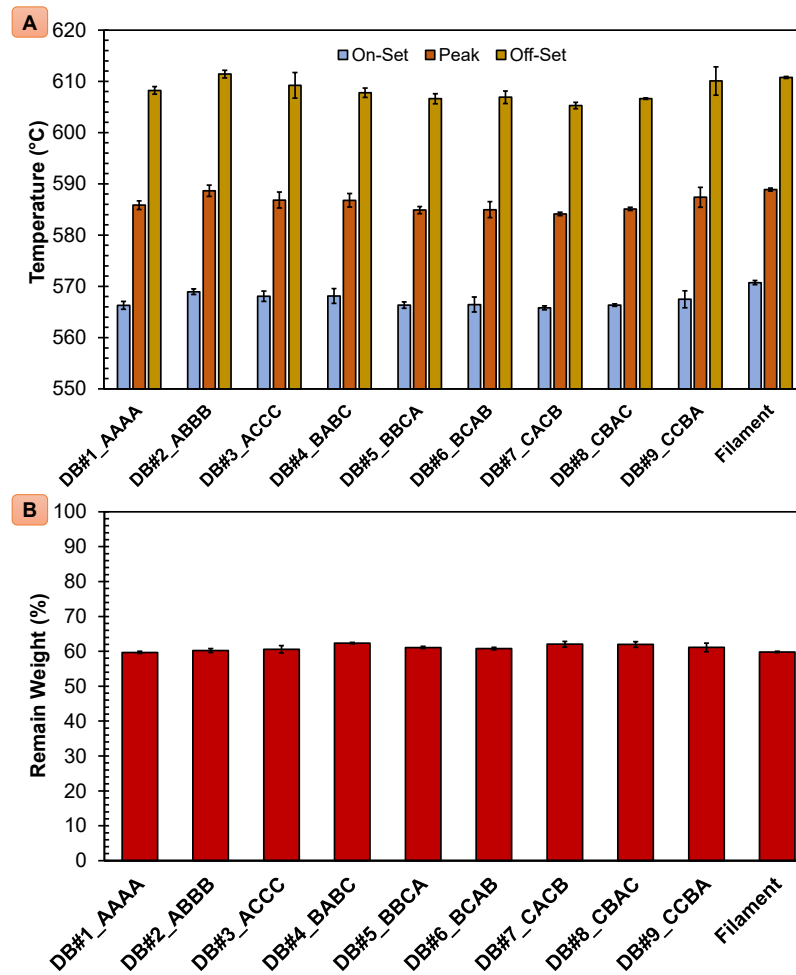


Figure 2.8. TGA result shows no noticeable change in the (a) amount of decomposed material for all Taguchi parameter sets, (b) in terms of temperature for the start, peak, and finishing point.

2.4.4 Analysis of Variation for Parameter Sets Selection

To decide on how to select the combination of thermal parameters to maximize each property individually, the result of SN for each thermal parameter will determine which level should be selected to gain the highest value for the property and the Delta-value shows the share of each parameter's importance to reach this goal.

2.4.4.1 Targeting Strength

Noticing results in Figure 2.9, bed temperature has the most significant role in maximizing the tensile strength by a share of 51.7% as was observed it can have a huge impact on the crystallization of the parts. It must be noted that this might change if the thickness of the sample becomes too large. To reach the maximum strength it is suggested to choose the temperature for the bed as 200 °C, nozzle as 400 °C, tuyere as 200 °C, and enclosure as 60 °C.

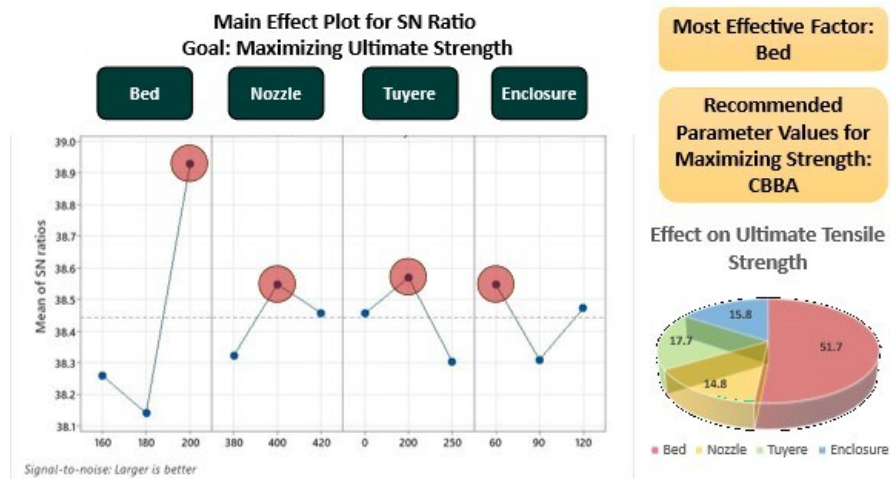


Figure 2.9. Parameter shares based on Delta-value and level selection based on SN ratio for pursuing ultimate tensile strength.

2.4.4.2 Targeting Stiffness

Regarding the result in Figure 2.10, nozzle and enclosure temperature both have the same and highest effect on the stiffness of the part with 31.1% share value. This contribution can be justified as if the nozzle temperature increases more than 400 °C will result in the formation of the bubbles as mentioned earlier while a nozzle with 400 °C results in lower viscosity compared to 380 °C which would cause smaller voids between adjacent beads due to better flow of the material. Also, increasing the enclosure temperature would make the part more brittle and stiffer. The proper level selections for maximizing the value of elastic modulus are the temperature for the bed as 180 °C,

nozzle as 400 °C, tuyere as off, and enclosure as 120 °C.

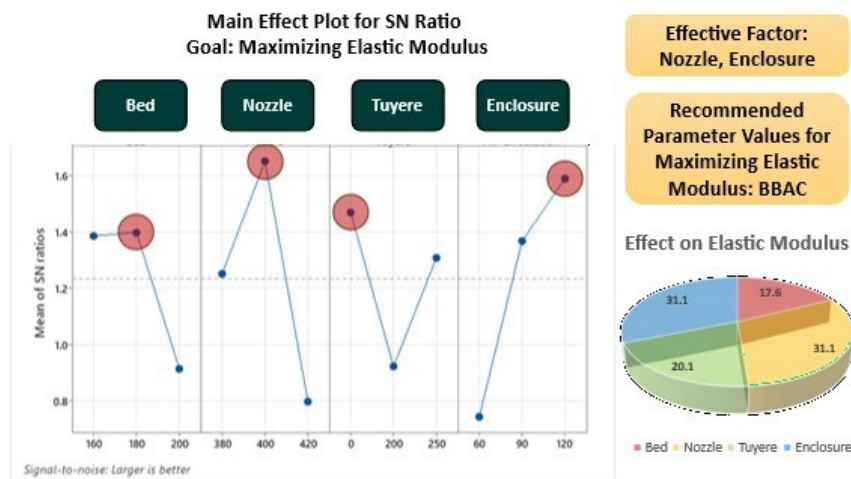


Figure 2.10. Parameter shares based on Delta-value and level selection based on SN ratio for pursuing maximum stiffness.

2.4.4.3 Targeting Strain to Failure

In terms of elongation, as shown in Figure 2.11, enclosure temperature plays the most important role in the determination of brittle or ductile fracture of the specimen by a share value of 42.7%. As mentioned earlier, increasing the enclosure temperature would make the part more brittle and stiffer making it sensitive to defects after passing the ultimate stress point. The level selections for maximizing the value of strain to failure are the temperature for the bed as 160 °C, nozzle as 400 °C, tuyere as off, and enclosure as 60 °C.

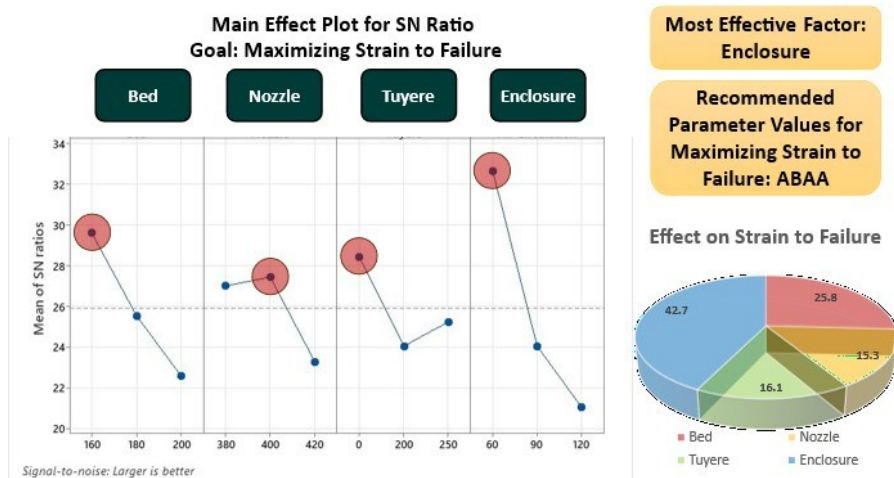


Figure 2.11. Parameter shares based on Delta-value and level selection based on SN ratio for pursuing maximum strain to failure.

2.4.4.4 Targeting Toughness

Similar to strain to failure, it is the enclosure temperature that plays a crucial part for the same reason with a share portion of 36.9% as shown in Figure 2.12. The level selections for maximizing the value of toughness are the temperature for the bed as 160 °C, nozzle as 380 °C, tuyere as off, and enclosure as 60 °C and as was expected the results are much the same as targeting maximum elongation.

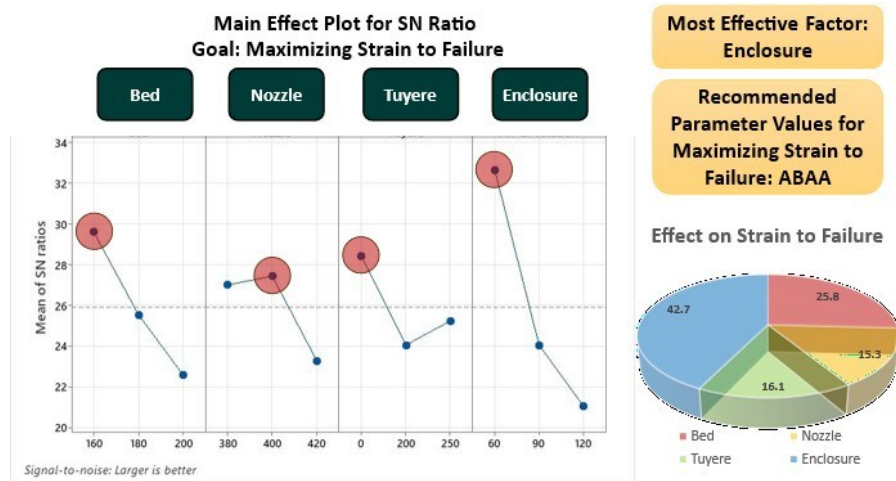


Figure 2.12. Parameter shares based on Delta-value and level selection based on SN ratio for pursuing maximum toughness.

2.4.4.5 Targeting Crystallization

For the average value of crystallinity, the analysis in Figure 2.13 shows that the bed temperature has the most significant and distinguished effect on the crystallization of the part due to diffusion of the heat from bottom layers and causing on-the-fly annealing meanwhile the print is going on. The share value for the bed in this case is 69.1%. The level selections for maximizing the value of toughness are the temperature for the bed as 200 °C, nozzle as 400 °C, tuyere as 200 °C, and enclosure as 60 °C.

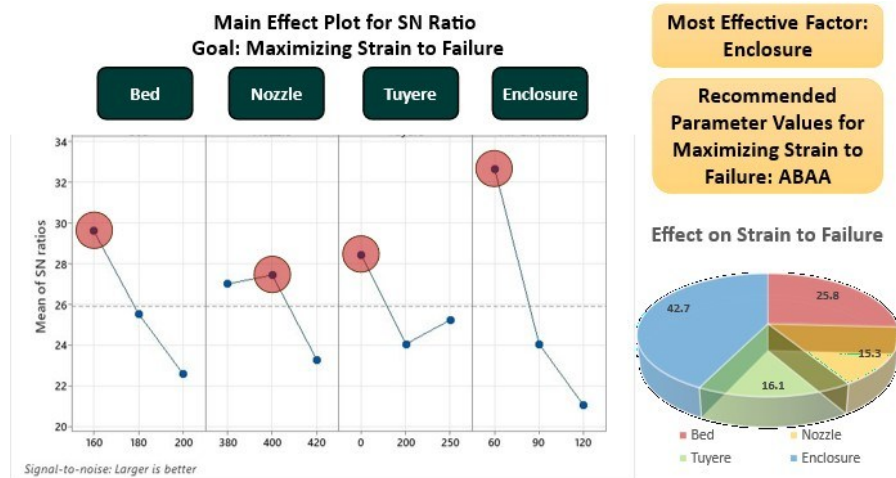


Figure 2.13. Parameter shares based on Delta-value and level selection based on SN ratio for pursuing maximum crystallinity.

2.4.4.6 Delta-Value Integrated Analysis

A summary of the Delta-values is depicted in Figure 2.14, showing the share value of each parameter with a total of 100% on ultimate tensile strength, elastic modulus, strain to failure, toughness, and degree of crystallization. This radar chart prioritizes the importance of each parameter on each subject and will give useful information for parameter selection at just a glance. Crystallinity and strength are two factors collating each other on having built plate the most effective parameter on them while strain to failure and toughness are mostly affected by enclosure temperature. In the case of A-PEKK, nozzle, and tuyere temperature had the least contribution on the determination of part property since their temperature value is transient and A-PEKK crystallization is too slow to have a response on the value of them.

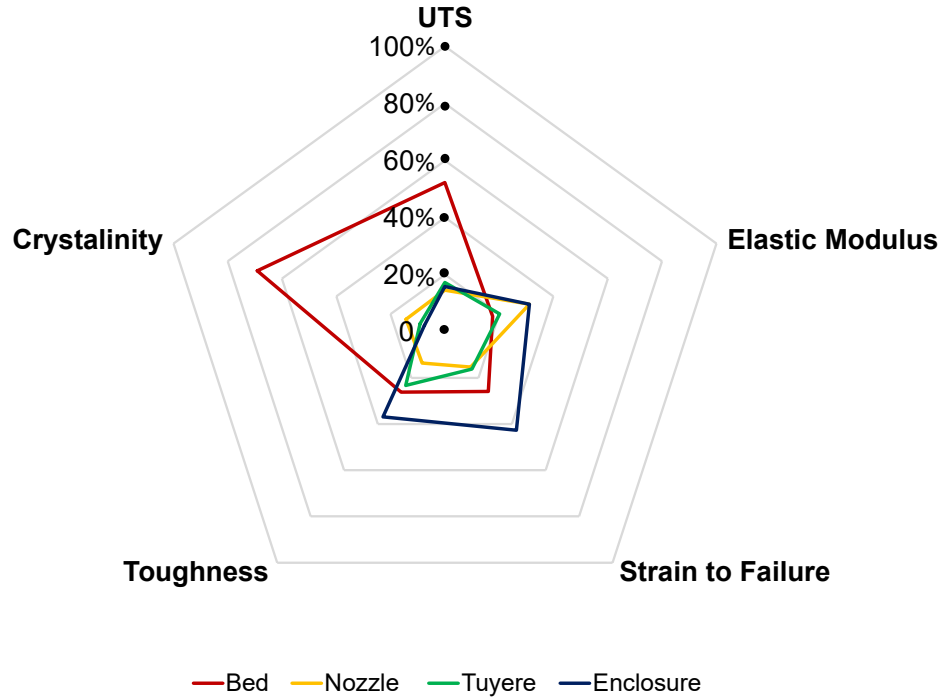


Figure 2.14. Radar chart of Delta-value showing the significance of each parameter on different tensile properties of the 3D printed part.

2.5 Conclusions

High-performance thermoplastic FDM has become popular in the last five years due to the development of commercialized engineering 3D printers. Among those high-performance thermoplastics, A-PEKK has a huge potential to unlock owing to its slow crystallization kinetics inheriting some level of tunability through the selection of additive manufacturing process parameters. Regarding that, through systematic optimization of thermal parameters using Taguchi DOE, this study established the critical relationship between processing conditions and mechanical performance. The aim for evaluating the effect of thermal parameters on the FDM of A-PEKK was successfully achieved by combining four significant thermal parameters and observing their effect as a whole while minimizing the number of required experiments for such characterization through a compatible DOE.

Moreover, as a secondary goal of this study, it can be claimed that on-the-fly annealing is achievable for A-PEKK in case the 3D printer enclosure would be able to reach up to 200 °C. Nowadays there are plenty of commercialized printers that can get to that temperature such as

CreatBot PEEK-250 (CreatBot, China), AON3D Hylo (AON 3D, Canada), and Kumovis R1 (Kumovis, Germany). In this case, the annealing of A-PEKK as a secondary is not required since it is already performed during the additive manufacturing process itself, reducing the cost and manufacturing time significantly.

Chapter 3: “Post-Processing Protocol”

“If there is a better way, find it”

-Thomas Edison

This work has been published in:

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3. Crystallization Engineering of 3D-Printed PEKK: Rapid Post-Processing Route for Superior Strength and Thermal Stability

3.1 Abstract

The limited crystallinity of additively manufactured amorphous polyetherketoneketone (PEKK) parts restricts their mechanical strength and thermal stability, posing a challenge for broader industrial adoption, particularly in high-performance sectors such as aerospace. In this study, we present a rapid and effective annealing protocol specifically designed to enhance the crystallinity of amorphous PEKK parts fabricated via material extrusion (MEX), without compromising structural integrity. A combined framework integrating differential scanning calorimetry (DSC) and finite element analysis (FEA) was employed to systematically define optimal annealing conditions, identifying 210°C for 30 minutes as the most effective treatment. This optimized approach increased relative crystallinity from 1.6% to 28.9%, leading to a 29.5% improvement in tensile strength, a 17.3% increase in flexural strength, and a notable 51.4°C rise in heat deflection temperature. Morphological characterization using scanning electron microscopy (SEM) confirms the transition to a semi-crystalline microstructure with enhanced thermal and dimensional stability. The results establish a scalable, time-efficient pathway for post-processing 3D printed PEKK, bridging the gap between the ease of amorphous processing and the superior performance of semi-crystalline systems. This work significantly advances the potential of additive manufacturing for high-temperature, load-bearing applications, offering a practical solution to a critical challenge in materials engineering.

3.2 Introduction

Polyetherketoneketone (PEKK) is a high-performance thermoplastic in the polyaryletherketone (PAEK) family, renowned for its exceptional mechanical, chemical, and thermal properties. PEKK offers superior strength, stiffness, and heat resistance, making it suitable for applications in extreme environments, such as the aerospace, automotive, and oil and gas industries [1,5,34]. In addition to its thermal stability, PEKK is highly resistant to chemicals, radiation, and wear, providing long-term durability even in harsh conditions [35]. It can be processed through various manufacturing

techniques, including material extrusion additive manufacturing (MEAM), extrusion, and compression molding, which allow for versatile applications. PEKK's unique combination of toughness and low weight makes it ideal for high-performance components where structural integrity and reliability are essential.

MEX is an additive manufacturing technique widely used for creating 3D objects by extruding thermoplastic materials layer by layer. In MEX, a filament of material, typically a polymer, is heated to a semi-liquid state and deposited through a nozzle onto a build platform. The process is controlled by a computer, which directs the movement of the nozzle and the deposition pattern based on the 3D model's design. Each successive layer bonds to the previous one as it cools, gradually forming a solid object. MEX is known for its accessibility, versatility, and ability to produce functional prototypes, custom parts, and complex geometries with reasonable mechanical properties. It's widely used in industries such as aerospace, automotive, medical, and consumer products due to its cost-effectiveness and ease of use.

One critical challenge in 3D printing of high-temperature semi-crystalline thermoplastics such as PEKK is its dimensional stability during sample preparation [36]. Improper parameter settings can lead to bed adhesion failure and eventually print failure. MEX inherently introduces residual stresses as layers are deposited sequentially. These stresses arise from thermal gradients in the manufacturing process, with quenching stress resulting from thermal contraction during solidification, and volume changes due to phase transitions during crystallization [2,36,37]. The crystallization kinetics of 3D-printed semi-crystalline thermoplastics are crucial to successful printing outcomes. A recent study by Lannunziata et al. [27] highlighted bed adhesion challenges in 3D printing of Polyetheretherketone (PEEK). Their solution involved a modified raft under the print and real-time annealing. PEEK's rapid crystallization rate can cause significant warping and distortion in printed samples. In contrast, PEKK's crystallization rate is more adaptable, depending heavily on cooling rates, which vary with different grades of material [3,32]. Furthermore, PEKK's commercial grades boast a higher glass transition temperature and a lower melting point than PEEK [38], making it more suitable for 3D printing applications.

PEKK has two types of isomers: Terephthalic "T" and Isophthalic "I," also referred to as "Para-linkage" and "Meta-linkage," respectively [7]. Commercial grades of PEKK are classified based on the ratio of T/I isomer percentages. The "T" isomer promotes chain packing, leading to increased

crystallization, while the "I" isomer enhances chain flexibility by reducing linearity, resulting in slower crystallization kinetics and a more amorphous structure [7–9]. Differential scanning calorimetry (DSC) analysis of PEKK with a T/I ratio between 80/20 and 60/40 shows its impact on glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), crystallization kinetics, and the degree of crystallinity [3,4,10–16].

Pomatto and Moore [11] found that an 80/20 T/I ratio in PEKK exhibits significantly faster crystallization kinetics, by 1 to 2 orders of magnitude, compared to 70/30 and 60/40 grades. Other studies on crystallization kinetics support this, with Rodzeń et al. [3] measuring peak crystallization time and Rebert et al. [4] examining the half-time crystallization of Arkema PEKK grades. These findings suggest that PEKK's crystallization kinetics can be tailored to suit different manufacturing processes and specific applications. Amorphous PEKK (A-PEKK) has a lower degree of crystallinity, leading to reduced mechanical strength and thermomechanical stability compared to semi-crystalline PEKK (SC-PEKK). However, it offers a key advantage: improved printability due to the higher mobility of its polymer chains. This allows for less residual stress from thermal gradients during fused filament fabrication, resulting in better bed adhesion and higher print quality. After printing, a post-processing heat treatment, known as annealing, is typically required to increase the crystallinity of the printed part, enhancing its mechanical properties and stability [3,18,32,39–41]. Das et al. [42] further demonstrated that parameters like complex viscosity and storage/loss moduli strongly correlate with weld quality and crystallinity evolution in high-performance thermoplastics. These insights suggest that optimized rheological characteristics not only enhance layer bonding but also help promote semi-crystalline phase formation during post-annealing.

While several studies have explored the annealing of 3D-printed PEKK to enhance crystallinity and performance, most have relied on trial-and-error methods without a unified framework to guide optimization. For instance, Ojha et al. [18] and El Magri et al. [39] reported mechanical improvements following thermal treatment but did not systematically justify their choice of annealing parameters based on crystallization kinetics or thermal modeling. This lack of integration limits reproducibility and scalability, especially for high-performance applications. More recent studies have explored the impact of process parameters and post-processing on the mechanical and thermal properties of 3D-printed PEKK. Maloney et al. [43] employed a response surface

methodology to investigate how print speed, layer thickness, and temperature settings affect the flexural behavior and crystallinity of PEKK parts. They reported that increased residence time within the printer's heated chamber enhanced crystallinity and improved flexural modulus. Continued by Maloney et al. [44], they examined the effect of post-printing annealing on PEKK properties, showing that prolonged heat treatment raised crystallinity and thermal stability. While these works focus on either print parameter optimization or extended thermal conditioning, our study offers a complementary perspective by establishing a rapid, practical annealing route using thermal analysis-driven optimization. In contrast to empirically driven or long-duration post-processing, our approach couples DSC-based kinetic understanding with mechanical testing and FEA simulation, resulting in a short, effective annealing protocol validated through crystallinity, mechanical strength, and thermal deflection metrics.

In this study, we present a novel, physics-guided methodology that combines differential scanning calorimetry (DSC) with finite element analysis (FEA) to optimize annealing conditions for amorphous PEKK fabricated via material extrusion additive manufacturing (MEAM). The DSC component characterizes crystallization behavior and defines optimal temperature and time ranges, while the FEA simulates transient heat transfer to ensure uniform annealing throughout complex geometries. This hybrid approach enables the rapid identification of annealing parameters (210°C for 30 minutes), resulting in significantly improved crystallinity, tensile strength, flexural performance, and heat deflection temperature. Our work offers a time-efficient and scalable post-processing protocol, bridging the gap between ease of amorphous printing and the superior performance of semi-crystalline structures. This integrative strategy ensures both process efficiency and enhanced part performance, providing a scalable solution for industrial applications.

3.3 Material & Methods

The approach for this study, outlined in

Figure 3.1. Author-developed schematic illustrating the experimental workflow from manufacturing to characterization.

, focuses on applying an innovative optimization methodology to the 3D printing process of amorphous PEKK samples and validating the improvements through mechanical testing and

thermomechanical analyses. The experiment's repeatability and the consistency of the manufacturing process are carefully evaluated to ensure the reliability and validation of the study.

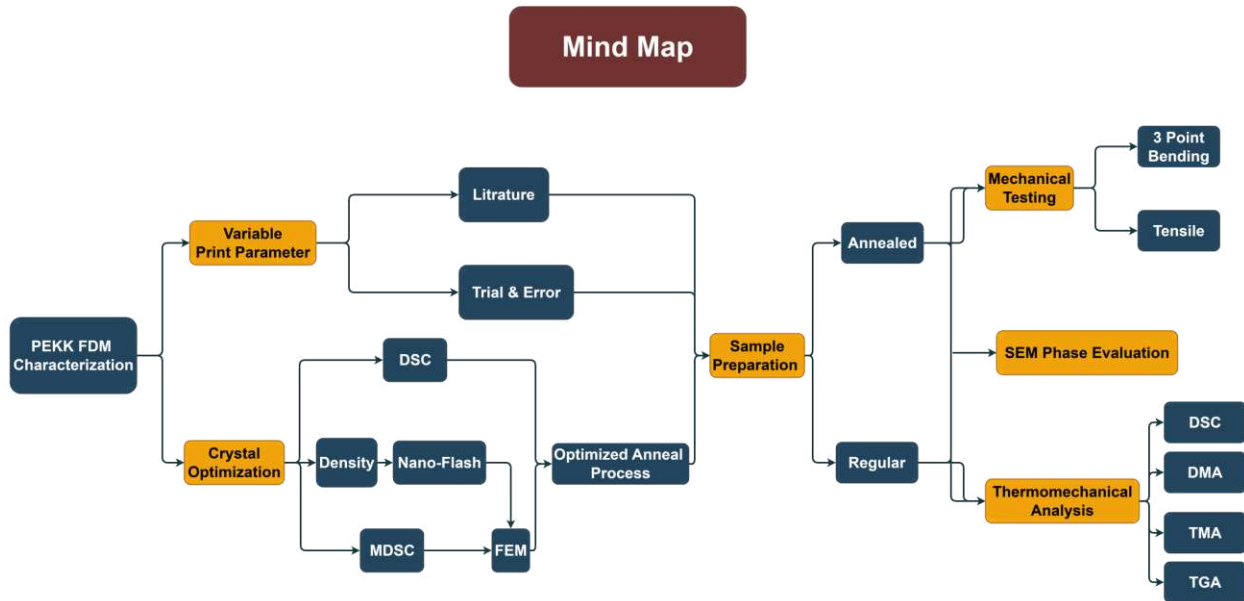


Figure 3.1. Author-developed schematic illustrating the experimental workflow from manufacturing to characterization.

3.3.1 Material

For this study, amorphous PolyEtherEtherKetone (PEKK) filament with a diameter of 1.75 ± 0.05 mm supplied by Spool3D (Alberta, Canada) was used. It is commercially available as PEKK175-1000. The filament was dried and stored in a drying chamber at 65 °C for a minimum of two days prior to printing.

3.3.2 3D Printing

All samples were produced using a CreatBot PEEK-300 3D printer (CreatBot, China) for various analyses, as shown in Figure 3.2b. These analyses include tensile testing, three-point bending, dynamic mechanical analysis (DMA), and thermal diffusivity measurement via the nano-flash (Laser Flash Analyzer (LFA)) technique. The rheological behavior of PEKK plays a pivotal role in the material extrusion process and its subsequent crystallization kinetics. As Mackay [45] highlights, the viscoelastic nature of polymer melts affects flow stability, pressure

development, and layer formation, factors that directly influence the thermal and morphological history of deposited filaments. In particular, rheology controls the time-temperature window available for effective interlayer diffusion and crystallization before the polymer vitrifies. As so, to minimize the time between the deposition of each layer, each sample was printed individually in the center of the build plate, rather than in batches. This approach minimized the exposure time of each newly extruded layer to ambient air before the next layer was deposited, reducing the potential for thermal contraction effects and interfacial cooling, besides lowering the viscosity, thereby improving interlayer adhesion by limiting residual stress development. [3,18–20,26,27,32,39–41,46]. Along with trial and error, a set of optimized parameters was selected (shown in Table 3.1), resulting in high-quality parts with no need for adhesive glue. Visual inspection of the final parts revealed no curling, bubbles, burns, voids, or pores.

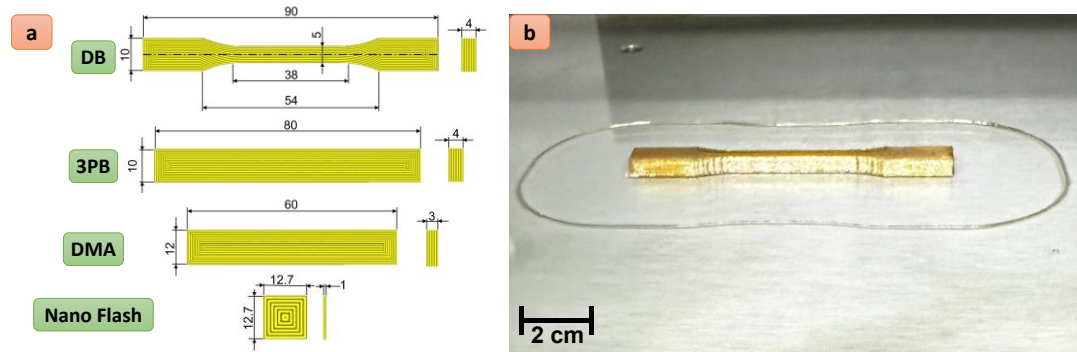


Figure 3.2. 3D printed testing sample; (a) Sample schematics from top to bottom are tensile, three-point bending, DMA, and LFA coupons (all dimensions are in mm), (b) Dog bone coupon with a two-line skirt and no adhesive glue.

Table 3.1. 3D printing set of parameters

Print parameter	Value	Units
Nozzle temperature	380	°C
Bed temperature	160	°C
Chamber temperature	60	°C
Print speed	10	mm/s
Ironing speed	20	mm/s
Infill density	100	%
Layer height	0.25	mm
Extruder diameter	0.4	mm
Build pattern	Concentric	-
Build orientation	Flat	-

3.3.3 *Annealing Optimization*

3.3.3.1 Differential Scanning Calorimetry (DSC)

The optimization approach in this study is based on differential scanning calorimetry (DSC). The tests were conducted in three categories using a TA Instruments DSC Q200 (TA Instruments, USA). The first category focused on evaluating the behavior of A-PEKK, including its thermal history, crystallization zones, and crystallization kinetics, as well as verifying calibration and data accuracy of the instrument. For this, a three-cycle DSC test was performed with a heating rate of 10 °C/min from 0 °C to 380 °C, followed by a 5-minute isothermal hold at 380 °C, and then cooling at a rate of 5 °C/min back to 0 °C to observe the thermal history of the raw material. The use of different heating and cooling rates was based on the observed difference in crystallization behavior between heating (cold crystallization) and cooling (from melt). Initial trials showed that at a cooling rate of 10 °C/min, crystallization from the melt was too slow to be captured in the DSC signal. By reducing the cooling rate to 5 °C/min, crystallization became detectable, confirming that crystallinity development in PEKK during cooling is significantly slower than during heating. This finding aligns with the very low crystallinity observed in as-printed parts and supports the need for post-processing annealing. Next, the DSC's overshoot response to different heating rates was examined by testing the material as received at heating rates of 5 °C/min, 10 °C/min, and 20 °C/min.

The second category simulates the isothermal annealing process of A-PEKK, which will later be carried out in an oven. By using DSC, the required sample size for optimizing crystallinity is significantly reduced. Based on the cold crystallization temperature range, annealing temperatures of 200, 205, 210, 215, 220, 225, and 250 °C were held for 30, 60, and 120 minutes under isothermal conditions. To achieve the isothermal state, the samples were heated at a rate of 20 °C/min from 0 °C to the target annealing temperature. After annealing, a cooling rate of 20 °C/min was applied from the annealing temperature back to 0 °C to complete the cycle. A final heating step at 5 °C/min was included to reassess the formed crystals and observe the melting kinetics of the isothermally generated cold crystals.

The final category aims to assess the degree of crystallinity using a heating rate of 10 °C/min in a semi-quantitative and quantitative manner. The calculation of crystallinity percentage is highly sensitive to the selection of crystallization zone limits and machine calibration, which can introduce significant variability in the results. Therefore, a new parameter is proposed known as relative crystallinity ($X_{C_{Rev}}$), as defined in Eq.(3.1). For all tests across the categories, 5 to 10 mg of material was used, prepared in an aluminum hermetic sample pan according to the TA Instruments DSC guidelines [24] and ASTM D3418 [25].

$$X_{C_{Rev}}(\%) = \frac{(\Delta H_M - \Delta H_{CC}) - \Delta H_{Ref}}{\Delta H_M^0} \times 100, \quad \Delta H_{Ref} = \text{Min}(\Delta H_M - \Delta H_{CC}) \quad (3.1)$$

In Eq. (3.1), ΔH_{CC} represents the enthalpy of cold crystallization, and ΔH_M refers to the enthalpy of melting. Based on the calibration of the DSC and the properties of the raw material, ΔH_{Ref} is defined as the minimum net enthalpy for the trials with A-PEKK, serving as the reference point for zero crystallization. According to the literature, the theoretical melting enthalpy of fully crystalline PEKK (ΔH_M^0) is taken as 130 J/g [7,9,10,20,26,27].

3.3.3.2 Modulated Differential Scanning Calorimetry (MDSC)

To accurately measure the material's heat capacity as a function of temperature, a modulated DSC (MDSC) test was performed using the TA Instruments DSC Q200 (TA Instruments, USA), similar to a standard DSC test but with modifications to the setup. The sample, weighing 5 to 10 mg, was placed in a Tzero aluminum hermetic pan. The test began after maintaining an isothermal condition

for 5 minutes at 0 °C. The temperature was then ramped to 210 °C at a rate of 3 °C/min, with modulation at ± 1.00 °C every 100 seconds, following the TA Instruments MDSC guidelines [47].

3.3.3.3 Density

Another key parameter for heat transfer simulation and analysis is density. Due to the inevitable presence of voids in additive manufacturing, it is essential to measure the density of the 3D-printed parts. Additionally, crystallization can cause changes in the part's density [18]. In this study, the density was measured using the Archimedes method, as outlined in the standard, which is straightforward yet highly accurate. A Sartorius balance density kit (Sartorius, Germany) was used to weigh the part once in air and once submerged in distilled water maintained at a controlled temperature of 23 ± 0.5 °C, in accordance with ASTM D792 [48].

3.3.3.4 Lazer Flash Analyzer (LFA)

A laser flash analyzer, also known as a Nano-flash, is used to measure the thermal diffusivity of materials. This parameter, directly measured by the analyzer, is calculated as shown in Eq. (3.2). The parameters $\alpha(T)$, $\rho(T)$, $C_p(T)$, and $\lambda(T)$ represent thermal diffusivity, density, heat capacity, and thermal conductivity as functions of temperature, respectively. For sample preparation, rectangular samples, as depicted in Figure 3.2a, are 3D printed, and their density is measured. To ensure even heat distribution across the sample surface during testing, a graphite coating is applied three times on each side, with 10-minute intervals between applications to allow each layer to fully dry. The Netzsch-LFA 447 Nano-Flash (Netzsch, Germany) is used to test three samples simultaneously across five temperature stages, ranging from 35 °C to 235 °C in 50 °C increments, with each sample exposed to three laser shots individually. The procedure is performed according to the instructions in the Netzsch-LFA 447 Nano-Flash manual [49].

$$\alpha(T) = \frac{\lambda(T)}{\rho(T) \times C_p(T)} \quad (3.2)$$

3.3.3.5 Finite Element Analysis (FEA)

To ensure dimensional stability and uniform thermal distribution during annealing, samples were placed on a steel plate inside a preheated convection oven. The steel plate served to moderate heat transfer, preventing rapid surface heating and minimizing internal thermal gradients. Thermocouples were used in preliminary trials to measure temperatures at the sample–plate interface, on the coupon surface, and in the ambient oven air. These values were used as boundary conditions in the finite element simulation to determine the time required for the entire part to reach

a crystallization-effective temperature (≥ 205 °C). While the approach was validated for flat coupons, more complex geometries could be annealed using the same setup with additional thermocouple placement or geometry-specific FEA to ensure thermal uniformity.

In addition to the importance of crystallization kinetics for calculating the time required for complete crystal formation, understanding the temperature profile within the annealed part and the time needed to reach isothermal annealing conditions is crucial. For transient heat transfer analysis using Abaqus/CAE software (Dassault Systèmes, France), material properties such as density, heat capacity, and thermal conductivity, which have been previously investigated, are essential.

Due to the complexity of the tensile coupon geometry compared to other 3D-printed parts, the analysis is performed on dog bone-shaped parts using a sweep medial axis with a 0.5 mm hexagonal mesh as the DC3D8 element type. This model simulates the isothermal annealing process of the tensile coupon, thermally tied to a steel plate. The steel plate is subjected to a convection heat source from the oven, with a thermal convection coefficient of $0.05 \text{ mW}/(\text{mm}^2 \times ^\circ\text{C})$ as measured in trial and error, besides the annealing temperature serves as the sink temperature. Data for the boundary conditions of the simulation are gathered using thermocouples placed inside the Blue-M oven (Blue-M, USA), attached to the steel plate, coupons, and their interfaces during the trials.

3.3.4 FE-SEM

To observe the phase change from amorphous state PEKK to semi-crystalline form, SEM analysis was performed using HITACHI Regulus 8230 FE-SEM scanning electron microscope (HITACHI, Japan). Cryofracture methodology was utilized to prepare the fracture surface of samples. The samples were submerged in liquid nitrogen for 15 minutes and then the annealed and the amorphous sample were gold-coated for 45 and 25 seconds, respectively. For proper imaging for the annealed sample observation took place at 5 kV while for amorphous sample it was at 15 kV.

3.3.5 Mechanical Testing

Tensile and flexural (three-point bending) coupons were manufactured according to ISO 527 [50] and ISO 178 [51] standards, respectively. The tests were conducted using a Hoskin Scientific universal testing machine (Hoskin Scientific, Canada) equipped with a 5 kN S-type load cell on the upper grip, operating at a displacement rate of 2 mm/min. The preload applied for the tensile test ranged from 10 N to 20 N, while for the three-point bending test, it ranged from 1 N to 2 N. Tensile testing of the amorphous and annealed PEKK filament was conducted using a same universal testing machine and a crosshead speed of 2 mm/min with gage length of 20 cm. Due to the absence of specialized grips designed for filament testing, a customized fixture was implemented. The gripping zones were reinforced by wrapping the filament around the grip,

inspired by ASTM D638 [52], ensuring firm contact and preventing slippage. This method enabled effective load transmission, and the obtained mechanical properties were in good agreement with manufacturer-reported values for the as-received amorphous filament.

3.3.6 *Thermomechanical Analysis*

3.3.6.1 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was conducted using the TA Instruments DMA Q800 (TA Instruments, USA) following the manufacturer's guidelines [53], ASTM D4065-12 [54], and specifically ASTM D5418-15 [55] for dual cantilever beam testing. The sample geometry is illustrated Figure 3.2a and a strain amplitude of 0.1% was applied to the sample with a frequency of 1 Hz. The temperature profile ranged from 50°C to 180°C for regular coupons and from 50°C to 250°C for annealed ones, both with a heating rate of 2°C/min.

3.3.6.2 Thermomechanical Analyzer (TMA)

To validate the thermomechanical behaviour observed in the DMA, a Thermomechanical Analyzer TMA Q400 (TA Instruments, USA) was used. The experiment was performed over a temperature range of 50°C to 200°C at a heating rate of 5°C/min, following ASTM E831 [56]. A cubic sample, 4 mm in height, was cut from the center of the tensile coupons and placed under the expansion probe to evaluate the variation in the coefficient of thermal expansion (CTE) as a function of temperature.

3.3.6.3 Thermogravimetric Analyzer (TGA)

In the final step, the thermal stability of the material, both before and after the manufacturing processes, was evaluated using a Thermogravimetric Analyzer TGA Q50 (TA Instruments, USA). Following ASTM E1131 [28], 30 mg to 40 mg of the material was placed in a ceramic pan and subjected to a temperature increase from room temperature to 800°C at a rate of 10°C/min, under a nitrogen atmosphere, resulting in weight loss as the material decomposed in the absence of oxidative degradation.

3.4 Results & Discussion

3.4.1 Optimization Parameter

3.4.1.1 Material Crystallization

As an initial step, the DSC cyclic heat flow that is shown in Figure 3.3a indicates that the raw filament exhibits a very low degree of crystallinity, consistent with its amorphous processing history. During the first heating cycle, cold crystallization is observed, with an energy level nearly equivalent to the crystal melting peak, confirming a predominantly amorphous structure with latent potential for crystallization. However, after holding the material in a molten state for 5 minutes at isothermal conditions and then cooling it, crystallization occurs between approximately 200°C and 250°C, establishing a new thermal history for the polymer. In the second heating cycle, no cold crystallization is observed, indicating that the material has fully crystallized at a 10°C/min heating rate, leaving no potential for further crystal formation. This behavior is consistent upon repeating the process for a third cycle, yielding similar results.

It has been shown that an increase in heating rate decreases the degree of cold crystallization [7,57]. In addition, the accuracy of the temperature range for cold crystallization is influenced by the heating rate, which can be observed as an overshoot in the heat flow signal, as illustrated in Figure 3.3b. This overshoot has a minor effect on T_g but significantly impacts the cold crystallization region. Pomatto and Moore [16] also highlighted the limitations of the conventional DSC method in precisely determining the crystallization zone temperature and suggested using Fast Scanning Calorimetry (FSC) as an alternative. Addressing this issue would allow for more accurate selection of the cold crystallization temperature zone and reduce optimization costs. Based on the results at a 5°C/min heating rate, the temperature range for optimization is between 200°C and 250°C, with a crystallization peak at 216°C.

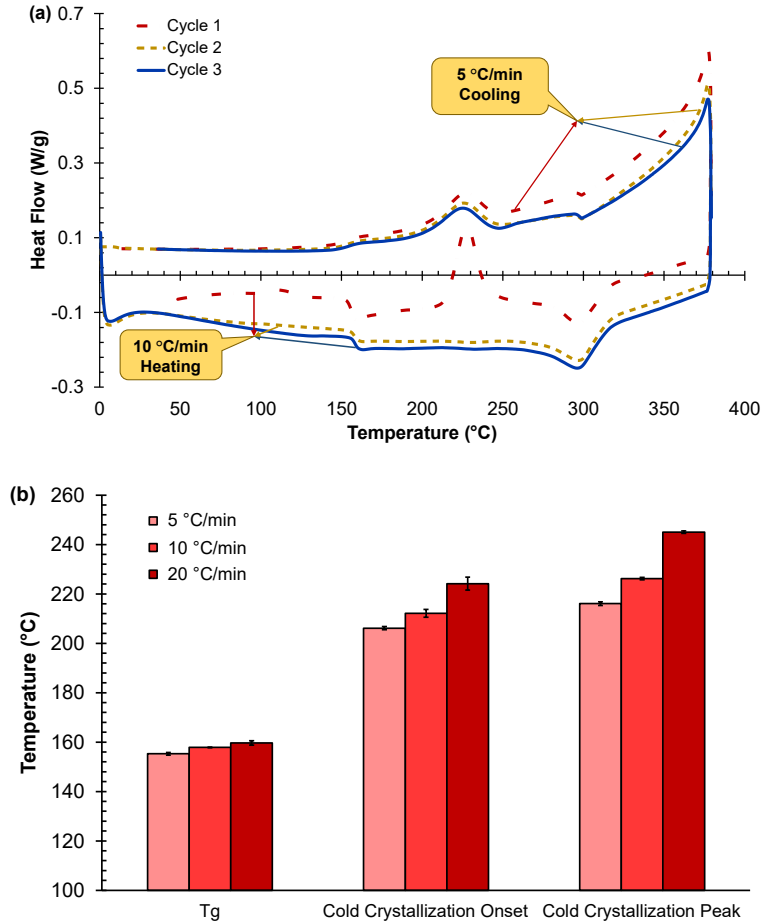


Figure 3.3. Explanation of crystallization kinetics of PEKK as received through DSC; (a) Thermal history of the material and DSC repeatability, (b) Variation in Tg and crystallization set point parameters with heating rate.

3.4.1.2 Optimum Annealing Temperature

The crystallization behavior of PEKK under isothermal annealing conditions was investigated using DSC, as shown in Figure 3.4. As illustrated in Figure 3.4a, crystal formation reaches saturation approximately 15 minutes after the onset of isothermal crystallization for all annealing temperatures. The heat flow peaks represent two types of crystals: primary (high-temperature) and secondary (low-temperature) crystals [7,10]. These peaks converge as annealing temperatures reach 220 °C or higher, eventually forming a single sharp PEKK peak. This interpretation of crystallization kinetics is further supported by the crystal melting peaks shown in Figure 3.4b, which confirms that higher annealing temperatures increase the melting point of the secondary

crystal type. However, extending the annealing time beyond saturation has no further impact on crystallization kinetics.

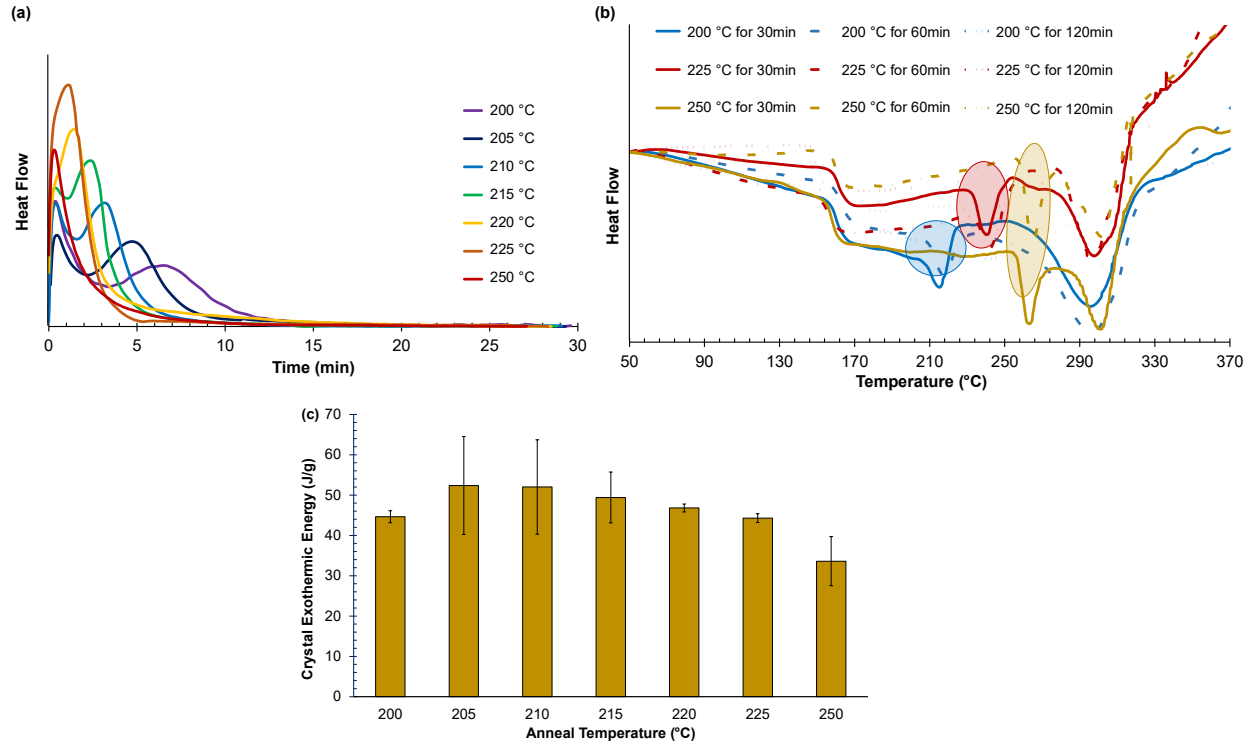


Figure 3.4. Isothermal annealing simulation in DSC; (a) Cold crystallization kinetics of 3D printed PEKK in various temperatures in cold crystallization zone, (b) Crystal type evaluation through melting heat flow response in various annealing time and temperature, (c) Isothermal crystal formation energy after process.

Figure 3.4c illustrates that as the annealing temperature increases from 200 °C to 250 °C, the energy associated with crystal formation follows a rising-then-falling trend, which is critical for optimization. Statistical analysis was performed to validate the crystallinity differences across annealing temperatures. A one-way ANOVA with Tukey's post-hoc test ($n = 3$ per condition) indicated a consistent upward trend in crystallinity with increasing annealing temperature, with the highest values observed at 210 °C ($F(6,14) = 2.37, p = 0.087$). While the differences did not reach the conventional 95% significance level, the results confirm that 210 °C produces the most favorable crystallization behavior. This conclusion is further supported by the tensile, flexural, and DMA results, which demonstrated significant improvements in mechanical and thermal performance at 210 °C.

3.4.1.3 Optimization Annealing Time

After selecting 210°C as the annealing temperature and determining the time required to reach crystallization saturation, the minimum time needed for the coldest point of the sample to reach the optimized annealing temperature range must be calculated. This is where controlling the sample's temperature profile during annealing becomes critical. The temperature profile varies depending on the thickness of the steel plate on which the samples are placed. Through several trials with steel plates of 1 mm, 6 mm, and 12 mm thickness, it was found that the 12 mm thick plate takes too long to reach the oven's set temperature. Conversely, the 1 mm thick plate heats up too quickly, causing a rapid temperature rise in the samples. This leads to a sudden increase in air pressure within the voids of the samples, resulting in bubbling, as shown in Figure 3.5, and ultimately disqualifying the samples.

To address the issues mentioned above, a 6 mm thick steel plate was selected to moderate the heat flow, allowing gradual heat transfer from the surface to the bottom of the samples. After several trials with the 6 mm plate, visually acceptable annealed samples were obtained following the annealing time recommended in the literature [39,40], which exceeds an hour but shows potential for optimization. The optimal processing time was then determined through transient heat transfer finite element analysis, using input data for PEKK derived from the test results.

Figure 3.6a shows that the density of the annealed 3D printed part is 2.6% higher than that of the amorphous 3D printed part, but 2.7% and 0.6% lower than the annealed and raw filament, respectively. Figure 3.6b illustrates the temperature dependence of PEKK's heat capacity. The curve follows a similar pattern for both the regular amorphous 3D printed sample and the annealed 3D printed sample; however, the annealed sample's curve shifts downward due to tighter chain packing from crystallization, resulting in higher density. In Figure 3.6c, the final material property for the FEA is derived from nano-flash analysis, which indicates that PEKK's thermal diffusivity is temperature-dependent but remains unaffected by whether the sample is regular or annealed. Using the temperature-dependent properties of density, heat capacity, and thermal diffusivity, the thermal conductivity is calculated using Eq. (3.2) and directly input into the FEM software.

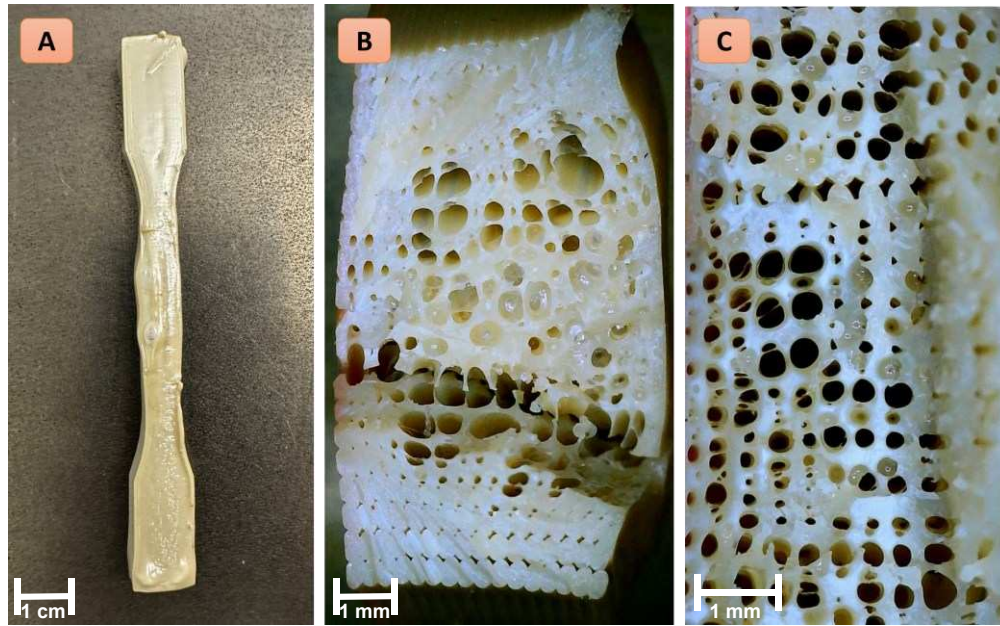


Figure 3.5. Sample disqualification caused by rapid warming up; (a) Tensile sample deformed and bubbled up, (b) Void enlargement in tensile sample, (c) Void enlargement in flexural sample.

For the heat transfer simulation, the temperature-dependent data was used as input properties for the model, and boundary conditions were established based on thermocouple measurements during the trial-and-error phase. As shown in Figure 3.6d, after 15 minutes, no areas on the tensile sample had temperatures below 205°C. This time frame is considered the optimal starting point for crystallization to begin. By adding the 15 minutes from the DSC annealing process to the FEA simulation time, the optimized annealing process is proposed as a 30-minute isothermal hold at 210°C. For further clarification, the transition of temperature through time is shown in Figure 3.7. It is important to note that different thermal conditions were applied in DSC testing and oven-based annealing. In isothermal DSC, heating and cooling rates were tightly controlled (20 °C/min) to characterize isothermal cold crystallization behavior. In contrast, the oven annealing process used a dynamic pre-heating up to an isothermal selected temperature (210 °C), where ramp rates were not precisely controllable due to equipment limitations. The fastest practical ramp to the annealing temperature was approximately 10 °C/min. As such, the DSC tests were used for detailed thermal analysis, while oven annealing conditions were designed to reflect feasible industrial scenarios.

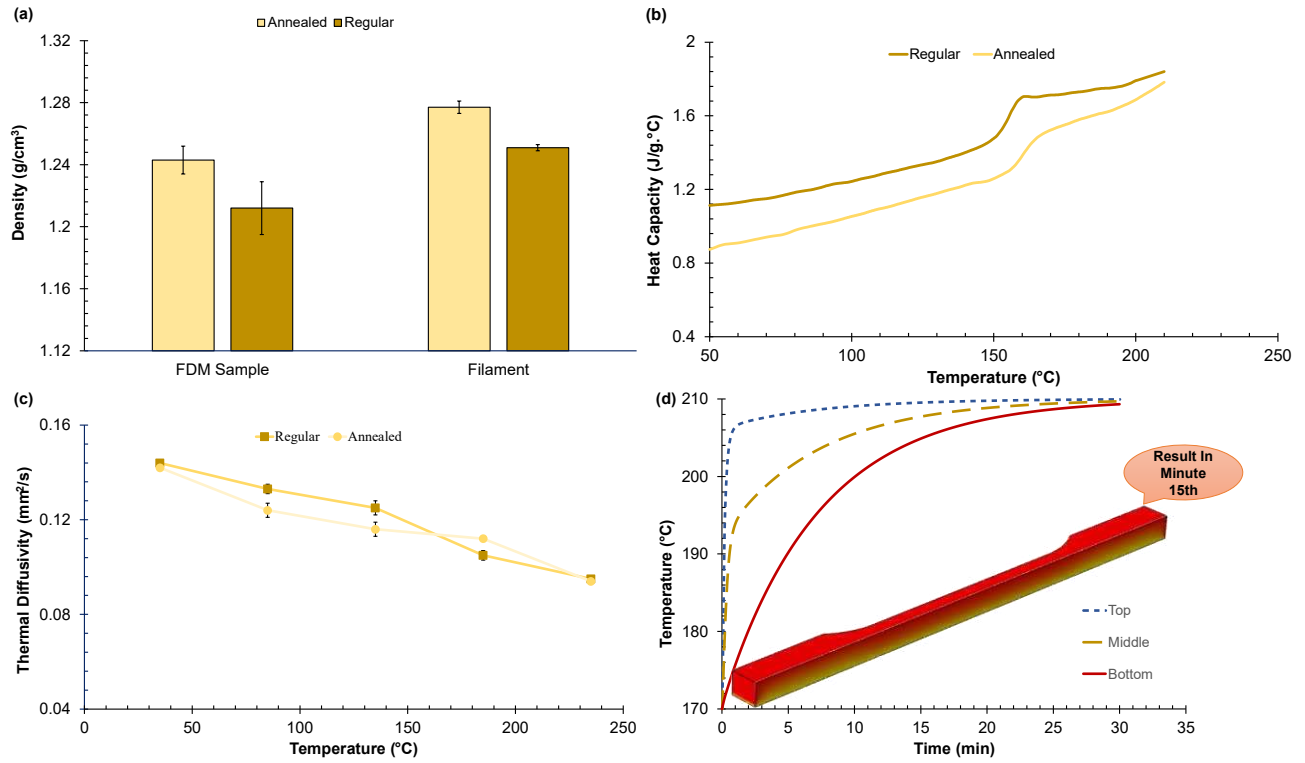


Figure 3.6. FEA input data and result; (a) density data, (b) heat capacity data, (c) thermal diffusivity data, (d) FEA result of the dog bone coupon with the schematic of the temperature profile in the middle section of the specimen at minute 15th.

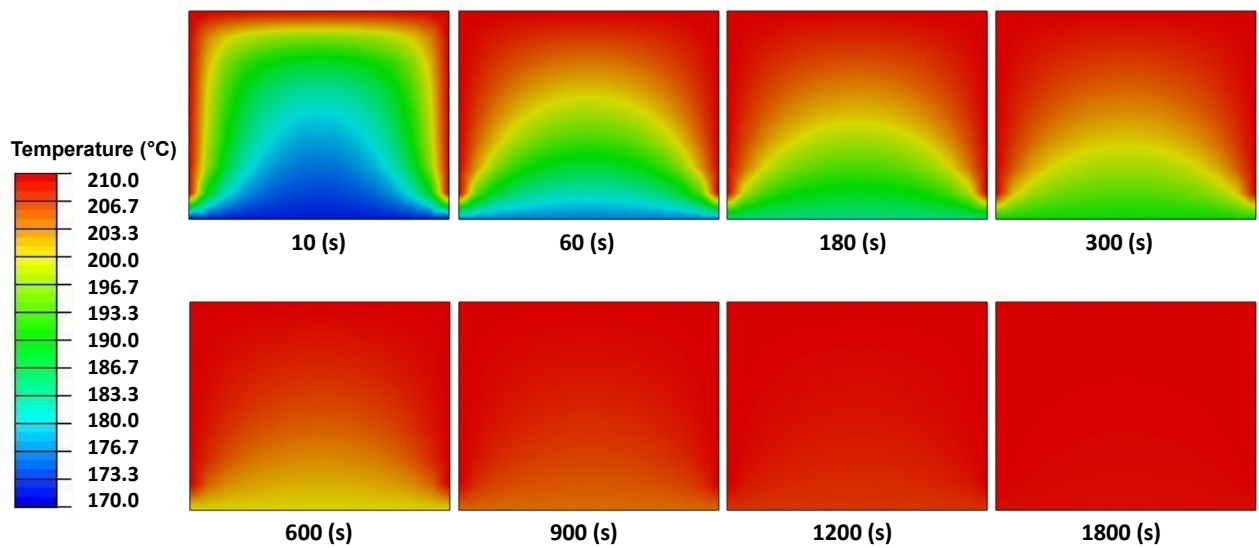


Figure 3.7. FEA transient temperature profile of the middle cross-section of the dog bone coupon through time.

3.4.2 FE-SEM Phase Evaluation

A review of the literature reveals that a few studies have investigated the crystal structure of PEKK. Due to the complex sample preparation process and the expertise required for crystallography imaging, such graphical information is invaluable, especially given the challenges in achieving full crystallization. As shown in Figure 3.8, the structure observed under the FE-SEM for the annealed sample after cryofracture exhibits a textured surface in certain regions. At higher magnifications, crystal formations resembling blossoms are visible, along with the gold coating. These formations, known as spherulitic nucleation, are separated by grain boundaries, highlighted with blue lines, similar to findings in previous studies [7,16]. In contrast, the amorphous regions lack any discernible patterns or boundaries, a characteristic typical of an amorphous fracture surface. These observations further emphasize the importance of crystallinity in determining the material's structural and mechanical properties.

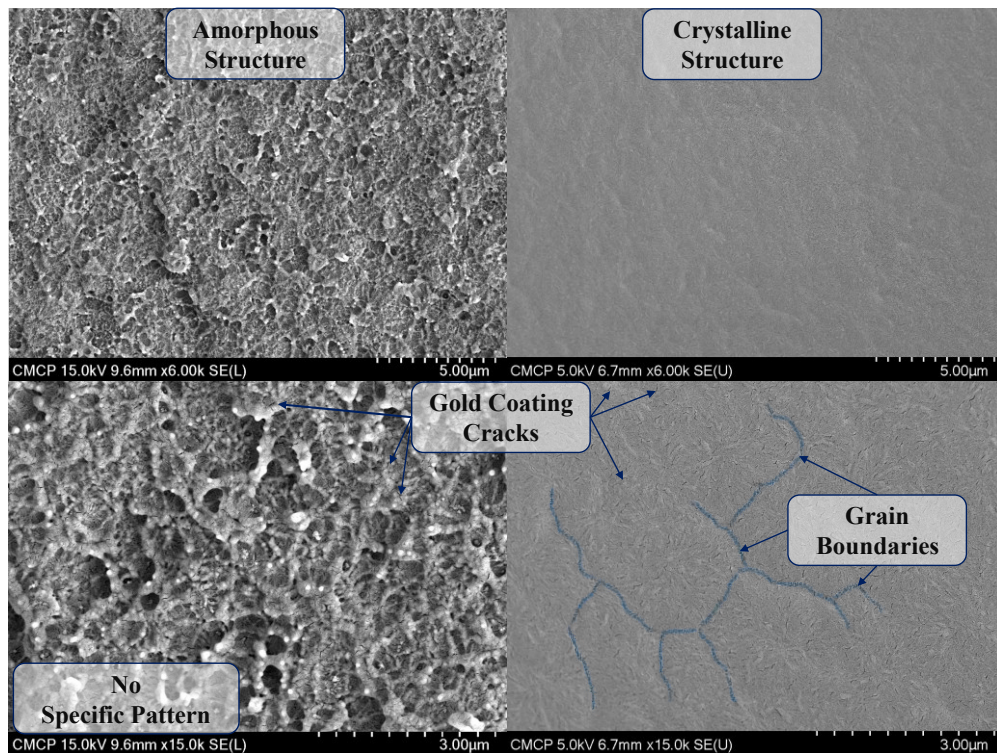


Figure 3.8. FE-SEM phase evaluation for crystal morphology; Left) PEKK amorphous structure without a specific pattern, Right) PEKK crystalline structure with the blossom of crystals, creating grain boundaries adjacent to each other.

3.4.3 Mechanical Testing Results

The tensile mechanical properties of A-PEKK as 3D printed and its filament, before and after annealing, are shown in Figure 3.9. After optimized crystallization, as depicted in Figure 3.9a, the tensile strength of the 3D printed sample and filament increased to 106 MPa and 122 MPa, representing enhancements of 29.5% and 38%, respectively. Following the optimized process, Figure 3.9b shows that the elastic modulus increased from 1.6 GPa to 1.9 GPa for the 3D printed part, and from 2.6 GPa to 3.0 GPa for the filament, reflecting a 15% increase in stiffness for both. However, in terms of ductility, a significant reduction in energy absorption is observed, as shown in Figure 3.9c and Figure 3.9d, due to embrittlement from the high degree of crystallization. The strain at failure dropped from 98.9% to 10.9% for the 3D printed part and from 136.7% to 6.01% for the filament. Additionally, the toughness of the material decreased by 86.3% for the 3D printed part and 95% for the filament.

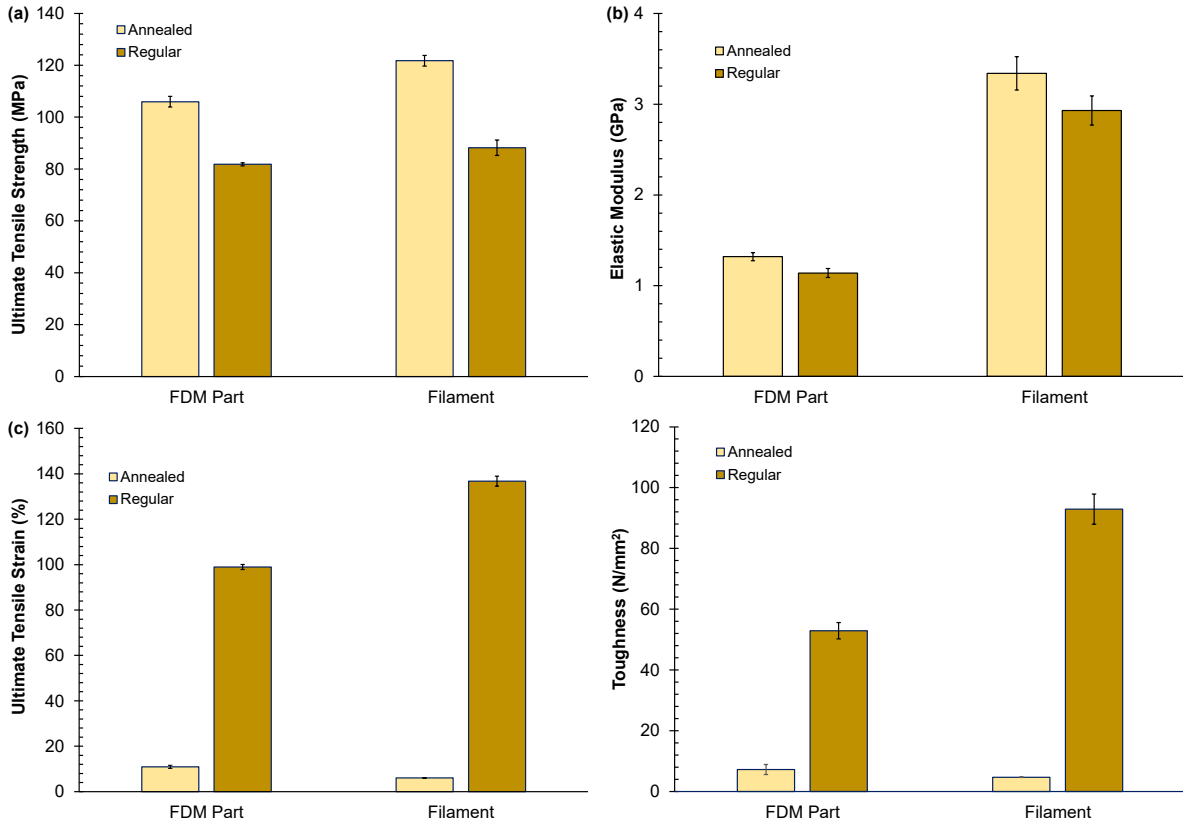


Figure 3.9. Tensile test results are categorized into four sectors; (a) Tensile strength, (b) Elastic modulus, (c) Ultimate tensile strain, (d) Tensile Toughness.

The flexural properties of A-PEKK also change after the optimized annealing process, though not as drastically as the tensile properties. As shown in Figure 3.10, the flexural strength increased from 123.5 MPa to 144.9 MPa, and flexural stiffness improved by 10.7%, reaching 3.1 GPa. Unlike the tensile properties, which saw a reduction in ductility, the strain at failure and flexural toughness showed slight increases after annealing, by 5.1% and 8.2%, respectively.

The observed improvements in tensile and flexural strength following annealing are directly attributable to the increase in crystalline content within the PEKK matrix, which enhances intermolecular packing and promotes more effective load transfer between polymer chains. This aligns with the established understanding that semicrystalline polymers exhibit greater mechanical strength due to the presence of ordered lamellae that resist plastic deformation. The significant rise in elastic modulus for both 3D printed parts and filaments further support this, indicating a stiffer molecular network resulting from denser crystal structures. However, the drastic reduction in strain at failure and toughness reflects a common trade-off in polymer crystallization: while crystallinity improves strength and stiffness, it limits chain mobility, leading to embrittlement and reduced energy absorption. These results highlight the importance of balancing crystallinity and ductility, particularly when designing components that require both high strength and energy absorption.

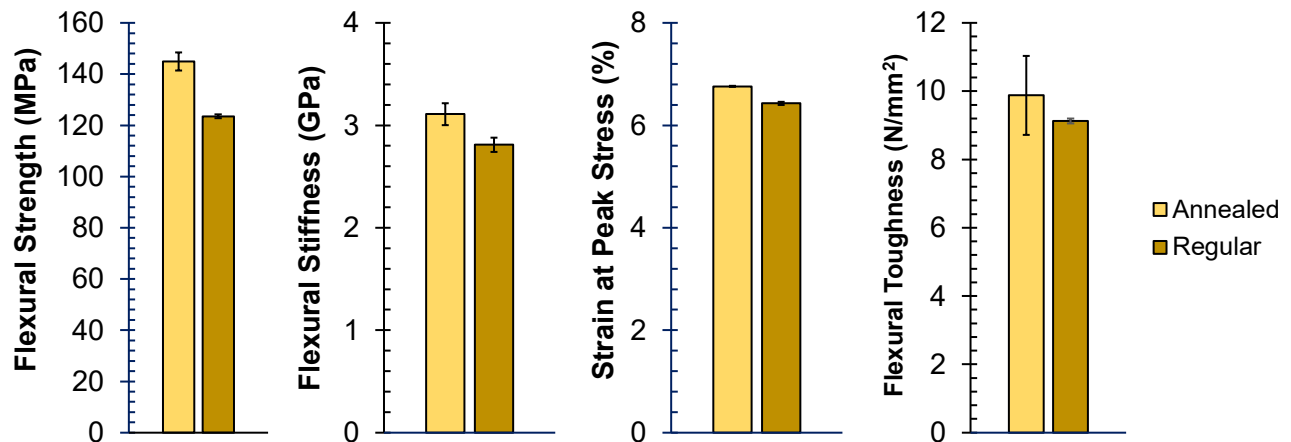


Figure 3.10. Flexural test results in four categories: Flexural Strength, flexural stiffness, strain at maximum stress, and flexural toughness.

3.4.4 Thermomechanical Testing results

The thermomechanical response of the material in DMA is proposed in four different sectors as shown in Figure 3.11. The annealing process on the 3D printed samples causes a slight increase in their z-direction (build orientation) due to upward void expansion in between printed strands as a result of polymer softening when passing through T_g to enter the crystallization zone, as also reported by Yu et al. [17]. The precision of the DMA results for the magnitude of storage and loss modulus of the dual cantilever beam is highly dependent on the thickness measurement.

Although annealing typically enhances stiffness through increased crystallinity, the annealed samples exhibited a slightly lower storage modulus than the regular samples. This variation is primarily attributed to minor thickness differences after annealing, which strongly affect storage modulus values in DMA testing, as well as void expansion during the transition through T_g . However, the thermomechanical trend of both moduli through temperature is decently precise for proposing glass transition parameters, as shown in Figure 3.11a and Figure 3.11b.

Figure 3.11c shows that an optimized annealing process would reduce the damping response of A-PEKK in the glass transition region by five times at the peak point. Not only this but also material stability against permanent deformation at high temperatures, mostly known as heat deflection temperature (HDT), is increased by a significant reduction in permanent middle point displacement beyond HDT, as shown in Figure 3.11d. This behavior is also justified via the TMA result depicted in Figure 3.12c, showing that the normalized z-direction dimension change is reduced by an order of magnitude after optimized annealing in the T_g region.

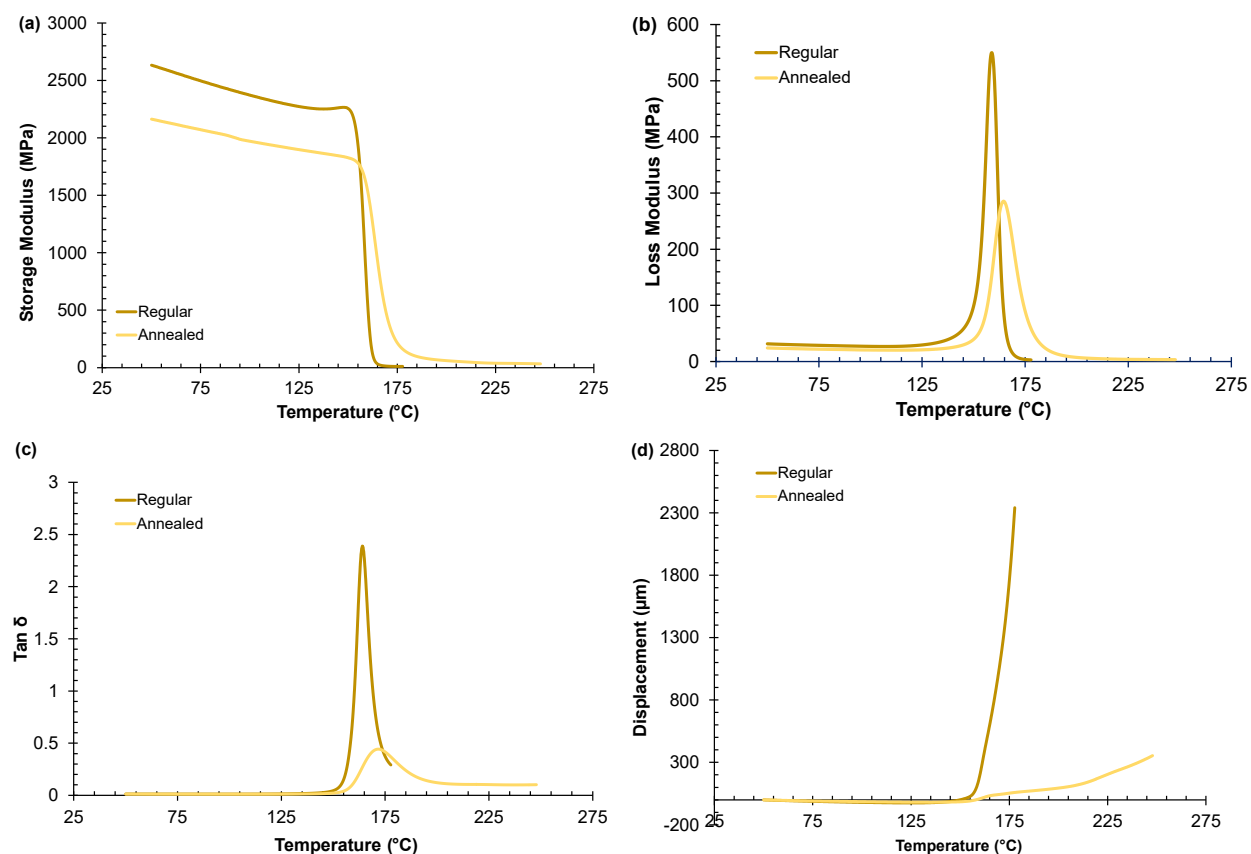


Figure 3.11. DMA results are categorized into four sectors; (a) Storage modulus, (b) loss modulus, (c) Damping response, (d) Permanent displacement of the middle point.

Figure 3.12 is a summary of the four categories of thermoanalytical techniques results. In Figure 3.12a, the relative degree of crystallinity after the 3D printed process increased from 1.6 % to 8.8 % as a consequence of the additive manufacturing process. After applying the optimized crystallization process, it reached a maximum of 28.9 %, almost the same as for the annealed filament. As a consequence of the high crystallization, Tg parameters obtained from DMA based on storage modulus, loss modulus, and tan alpha factor increased by 3.5 °C, 5.9 °C, and 7.6 °C, respectively. Since Tg is a parameter mostly related to the amorphous behavior and not the crystal portion of the polymer, these increases are minuscule, but the effect of the crystal portion of the annealed sample on HDT is remarkable. The HDT parameter jumped from 159 °C to 210.4 °C after optimized annealing, as shown in Figure 3.12b, making it a perfect material to use in high-temperature applications. Finally, as demonstrated in Figure 3.12d, the thermal stability against degradation from TGA results shows that the optimized annealing heat treatment does not degrade the material but also slightly improves its stability against high temperatures.

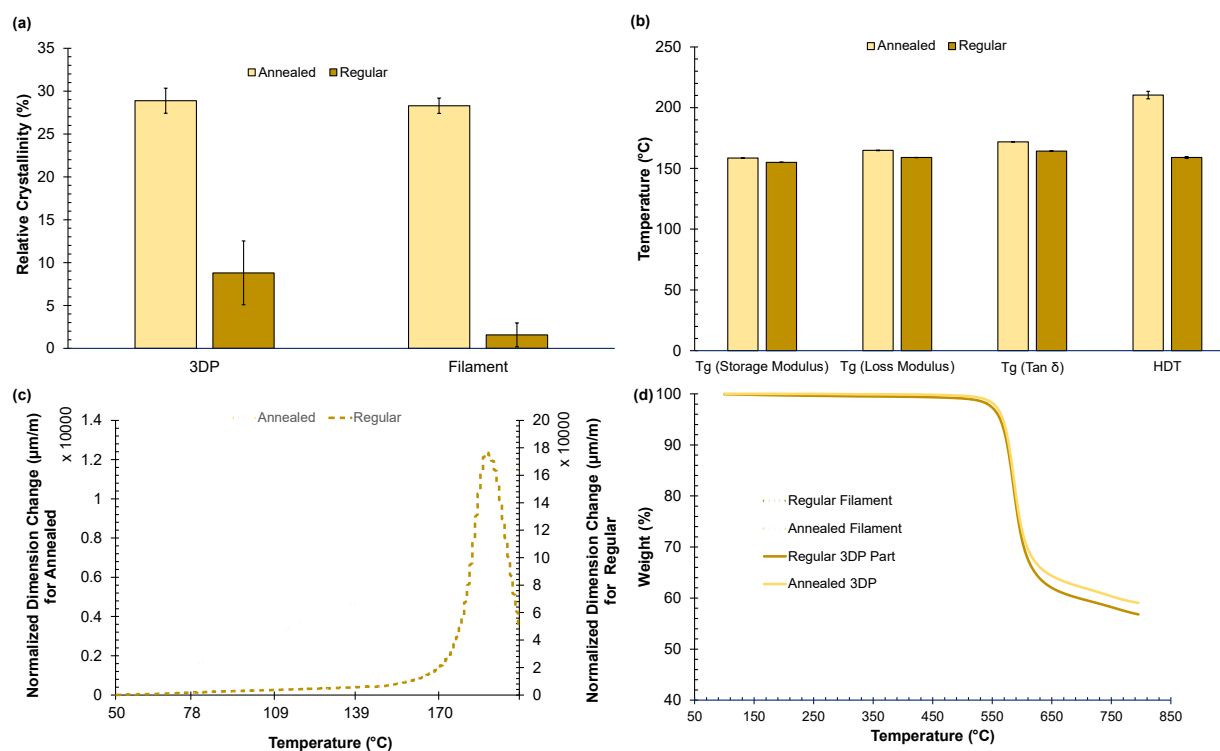


Figure 3.12. Thermoanalytical techniques result; (a) Relative crystallinity percentage, (b) DMA thermal parameter output, (c) TMA comparison result, (d) TGA results for thermal stability comparison.

The enhancements in thermomechanical performance observed through DMA, TMA, and TGA are consistent with the underlying influence of increased crystallinity on thermal stability and chain mobility. In semicrystalline polymers such as PEKK, the crystalline regions act as physical cross-links that restrict amorphous chain movement, especially in the glass transition region. This restriction is evident in the significant drop in damping behavior ($\tan \delta$) and the modest but measurable increases in glass transition temperature indicators derived from DMA. The considerable improvement in HDT following annealing further underscores this phenomenon: a more interconnected crystalline network resists softening and deformation under load at elevated temperatures, which is critical for applications requiring dimensional stability. The minor variation in T_g reflects its sensitivity to the amorphous phase, while the substantial jump in HDT is a direct manifestation of the crystalline phase reinforcing the material above T_g . Additionally, the TMA results confirm that annealed samples exhibit reduced thermal expansion, likely due to the constrained mobility of polymer chains between crystalline lamellae. Importantly, TGA data indicates that the optimized annealing treatment does not induce thermal degradation but may even

enhance oxidative stability by promoting tighter packing and reduced free volume. Collectively, these findings demonstrate that a thermally guided crystallization strategy can significantly improve PEKK's high-temperature performance without compromising its chemical integrity.

3.5 Conclusion

PEKK additive manufacturing has gained significant attention recently due to its outstanding properties and compatibility with 3D printing. As a result, numerous studies have focused on its characterization, additive manufacturing processes, and heat treatment. However, earlier research primarily concentrated on optimizing material extrusion (MEX) manufacturing parameters, with less emphasis on annealing as a post-processing step. This study presents an optimized annealing process aimed at reducing the cost and time of post-processing 3D printed A-PEKK. The effectiveness of the optimization was evaluated through mechanical and thermomechanical characterization techniques.

The optimization method utilized DSC to determine the optimal annealing temperature and an FEA model to establish the minimum processing time. Potential defects during heat treatment were analyzed, and appropriate solutions were proposed. The optimized manufacturing process recommends a 30-minute isothermal annealing at 210°C. Then, the morphology of spherulitic nucleation and cryofracture surface texture of the annealed sample was investigated through a scanning electron microscope. After achieving saturated crystallization, the maximum degree of crystallinity reached 29% compared to the A-PEKK. Mechanical testing following the optimized annealing showed improvements of 29.5% in tensile strength and 17.3% in flexural strength for the 3D printed part. Additionally, DMA and TMA results confirmed a significant increase in thermal stability, enhancing resistance to deformation at high temperatures while no change in degradation pattern would happen due to heat treatment, relaying on TGA results. This makes amorphous PEKK a standout material for high-performance applications after undergoing the optimized annealing process.

Chapter 4: “Tailoring Anisotropy”

“Don't fight so hard against things you can't change

... Learn to change what you can and accept what you can't”

- C.L. Wilson

This work has been published in:

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4. Manufacturing Process Assessment and Comparative Study of Full-Thermoplastic Composite Plates and PET Foam Sandwich Panels

4.1 Abstract

Processing and post-processing parameters critically determine the structural performance of additively manufactured parts. Poly-ether-ketone-ketone (PEKK), a high-performance thermoplastic, offers considerable promise for aerospace applications. However, its mechanical behavior in material extrusion (MEX) remains constrained by pronounced anisotropy and weak interlayer bonding. Addressing these limitations requires understanding how printing architecture and post-processing jointly influence mechanical response. Therefore, the objective of this study is to evaluate the effectiveness of an optimized annealing protocol, established in our previous work (210 °C for 30 minutes), in reducing anisotropic behavior and enhancing mechanical performance across different raster orientations and architected structures. Tensile and flexural coupons were fabricated at raster angles of 0°, ±45°, and 90° using three infill patterns (line, concentric, and mixed) and tested before and after annealing. Additionally, compressive coupons of Schwarz G and Schwarz P lattices with 40% relative density were examined to represent structural architected geometries, tested both parallel and perpendicular to the print-layer direction. Results show that reinforcement by annealing is pattern-dependent. At the maximum reinforcement, concentric infill yielded the greatest tensile strength improvement (29.5%), whereas the 90° raster exhibited the largest flexural strength gain (17.6%). For structural lattices, compressive strength increased by 37.5% in Schwarz G, while a reduction of 18.6% was observed in Schwarz P. While annealing enhanced stiffness, strength, and thermal stability, it also introduced dimensional changes and occasional void-related defects. Overall, this study demonstrates the interplay between anisotropic printing architecture and post-processing, providing pathways to tailor PEKK components for aerospace and structural applications requiring either superior strength (annealed) or enhanced toughness (as-printed).

4.2 Introduction

Poly-ether-ketone-ketone (PEKK), a high-performance member of the poly-aryl-ether-ketone (PAEK) family, has gained increasing attention in advanced sectors such as aerospace, automotive, and biomedical engineering, owing to recent progress in additive manufacturing technologies [1,5,32,58]. PEKK is particularly attractive because of its outstanding chemical resistance, high mechanical strength, and excellent thermal and radiation stability for in-space manufacturing (ISM) even under vacuum condition [26,35,59]. Beyond terrestrial aerospace and biomedical applications, PEKK has also been investigated for in-situ resource utilization (ISRU) in extraterrestrial environments, where its thermal stability and processability enable sustainable fabrication of structural components directly from regolith composites [58]. Among the available additive manufacturing (AM) processes, material extrusion (MEX) offers a cost-effective and flexible route for producing PEKK components with complex geometries and shorter production cycles [1]. Nevertheless, the adoption of PEKK via MEX for load-bearing applications is hindered by inherent limitations, most notably anisotropy in mechanical response and insufficient interlayer bonding, which restrict its structural reliability [60,61].

The processing parameters of AM, such as raster orientation, infill pattern, and build orientation, play a decisive role in determining the final mechanical properties of printed parts [39,41,62–65]. This sensitivity is particularly pronounced in high-temperature thermoplastics such as PEEK and PEKK, where melt viscosity, interlayer diffusion, and thermal gradients strongly influence structural performance. Recent studies on functionally graded and high-temperature MEX-printed PEEK components further highlight how controlled process parameters and thermal environments govern anisotropy, bonding quality, and the resulting mechanical behavior [18,66,67]. A substantial body of research has examined the influence of these geometrical parameters on thermoplastics, including PEKK [5,19,20,40,43,46,68]. Yet, most of these studies have focused on as-printed specimens, overlooking the potential of post-processing strategies to mitigate anisotropy and enhance structural performance.

Post-processing, particularly thermal treatments such as annealing, can modify the degree of crystallinity, relax residual stresses, and improve interlayer diffusion, thereby offering a pathway to tailor the balance between strength, stiffness, and toughness [17,69]. Besides, interfacial

phenomena play a fundamental role in governing material performance across a wide range of systems. Even in inorganic heterostructures, studies have shown that modifying interfacial energy states or diffusion pathways can significantly alter overall functional behavior [70]. Several recent studies have quantitatively demonstrated that annealing can significantly modify the stiffness, strength, and thermal stability of high-performance thermoplastics such as PEKK and PEEK [1,18,35]. For instance, annealed PEEK components exhibit measurable increases in elastic modulus, yield strength, and heat-deflection temperature as crystallite size and lamellar ordering evolve during thermal treatment [27]. Similarly, annealing of PEKK has been shown to increase tensile and flexural moduli through enhanced primary and secondary crystallization and reduced amorphous-phase mobility, resulting in crystallinity increases of 15–30%, elastic modulus improvements of 10–15%, and strength gains of 15–30%, depending on the material grade and printing conditions [3,7,13,44,71,72]. A systematic evaluation of annealing on the anisotropic response of MEX-printed PEKK across different raster orientations and infill patterns is still lacking. Furthermore, while coupon-scale studies provide valuable insights into the role of geometry, they do not fully capture the behavior of architected structures, which are increasingly employed in aerospace and biomedical applications to achieve lightweight yet mechanically robust designs.

In other automated manufacturing processes, such as automated fiber placement (AFP) of thermoplastic composites, understanding crystallization kinetics has proven critical to controlling distortion during fabrication due to residual stresses in the manufacturing process arise from thermal gradients, originating both from quenching stresses caused by thermal contraction during solidification and from volume changes associated with phase transitions as crystallization initiates [36,37,73,74]. In our previous work [71], we developed an optimized annealing protocol (210 °C for 30 min) for MEX-printed PEKK, demonstrating significant improvements in crystallinity, tensile strength, flexural performance, and heat deflection temperature. While these results highlight the potential of annealing, the interplay between post-processing and printing architectures, including raster orientations, infill patterns, and architected lattice structures, remains underexplored.

To address these limitations, this work investigates how optimized annealing influences the anisotropic behavior of PEKK components fabricated by MEX. Rather than focusing solely on

conventional coupon tests, the study integrates both simple geometries and architected lattice structures to capture performance across different length scales. By examining how post-processing interacts with raster orientation, infill pattern, and structural architecture, the study aims to clarify the trade-offs between mechanical reinforcement and dimensional stability. The insights gained provide a framework for tailoring high-performance thermoplastic parts for demanding aerospace and engineering applications, where the choice between superior strength after annealing and greater toughness in the as-printed state must be carefully balanced.

4.3 Material & Methods

The workflow of this study, illustrated in Figure 4.1a, outlines the methodology adopted to characterize 3D-printed PEKK with respect to the anisotropy introduced by MEX parameters and the influence of optimized annealing as a post-processing step. The experimental design was structured to verify performance enhancements through systematic mechanical testing (Figure 4.1e). To ensure reliability and reproducibility, each testing category was conducted on a minimum of three specimens, and data scatter was reported for all cases.

The selection of raster angles and infill patterns, illustrated in Figure 4.1b, was designed to investigate both interlayer adhesion between deposited strands and the longitudinal mechanical response of strands acting as fibers. Raster orientations of 0° , $\pm 45^\circ$, and 90° were chosen to capture the transition from longitudinal (0°) to transverse (90°) loading, with $\pm 45^\circ$ serving as an intermediate configuration. In terms of infill, three patterns of line, concentric and mixed were employed. For consistency, all layup sequences were applied in a symmetric stacking manner across patterns and orientations. To broaden this study toward structural performance, compression tests were also conducted on architected lattices, specifically the Schwarz G (Gyroid) and Schwarz P (Primitive) structures, designed with the geometric parameters shown in Figure 4.1d.

4.3.1 Material

Amorphous PEKK filament (1.75 ± 0.05 mm diameter, grade PEKK175-1000) was supplied by Spool3D (Canada). PEKK is also highly hygroscopic [75], and absorbed moisture can lead to porosity, poor interlayer bonding, and reduced mechanical performance during printing. To mitigate these issues, the filament was dried in a ventilated chamber at 125°C for 8 h prior to use

and subsequently stored in a dry storage unit until printing. This preparation step was essential to ensure consistent extrusion quality and to minimize moisture-related defects in the printed samples.

4.3.2 Fabrication Methodology

4.3.2.1 3D Printer & Settings

All specimens in this study were fabricated using a high-temperature CreatBot PEEK-300 3D printer (CreatBot, China), suitable for processing PAEK-family polymers (Figure 4.1c, d). To minimize the time interval between successive layer depositions, each coupon was printed individually at the center of the build platform rather than in batches. This approach reduced the exposure of deposited layers to ambient air, thereby promoting better interlayer adhesion. According to the supplier's recommendations, the extrusion temperature range for this filament is 360–400 °C, with a build plate temperature of 90–130 °C. However, preliminary trials revealed that higher bed temperatures reduced part warpage, and a setpoint of 160 °C was ultimately adopted. The remaining process parameters were determined through a combination of literature review [19,20,26,32,39,41] and iterative optimization are summarized in Table 4.1. Under these conditions, high-quality parts were consistently obtained without the need for adhesive glues or auxiliary adhesion aids. Visual inspection of the manufactured specimens confirmed the absence of common processing defects such as curling, voids, or surface burns.

All specimens in this study were printed in a flat XY orientation to isolate the effects of raster angle, infill pattern, and lattice topology under a single consistent thermal environment. Although build orientation can also influence anisotropy in high-performance MEX polymers, the TPMS specimens fabricated here possessed a through-thickness dimension of 40 mm, such that the thermal history of upper layers becomes largely independent of bed temperature. Across all TPMS and coupon builds, no warpage, curling, or layer separation was observed, indicating that the selected print parameters were thermally stable and consistent with PEKK processing ranges reported in the literature.

It should be mentioned that the CreatBot PEEK-300 used in this study provides a chamber temperature of approximately 60 °C, which is lower than the 120–160 °C range typically recommended for optimal PEKK interlayer fusion. Although this limitation can reduce interlayer bonding quality in bulk parts, its impact in the present study was mitigated by the flat build

orientation of the coupons and the highly open architecture of the TPMS structures, which reduced thermal gradients and prevented warpage. No distortion or corner lifting was observed during printing, indicating that the selected thermal parameters remained within acceptable ranges.

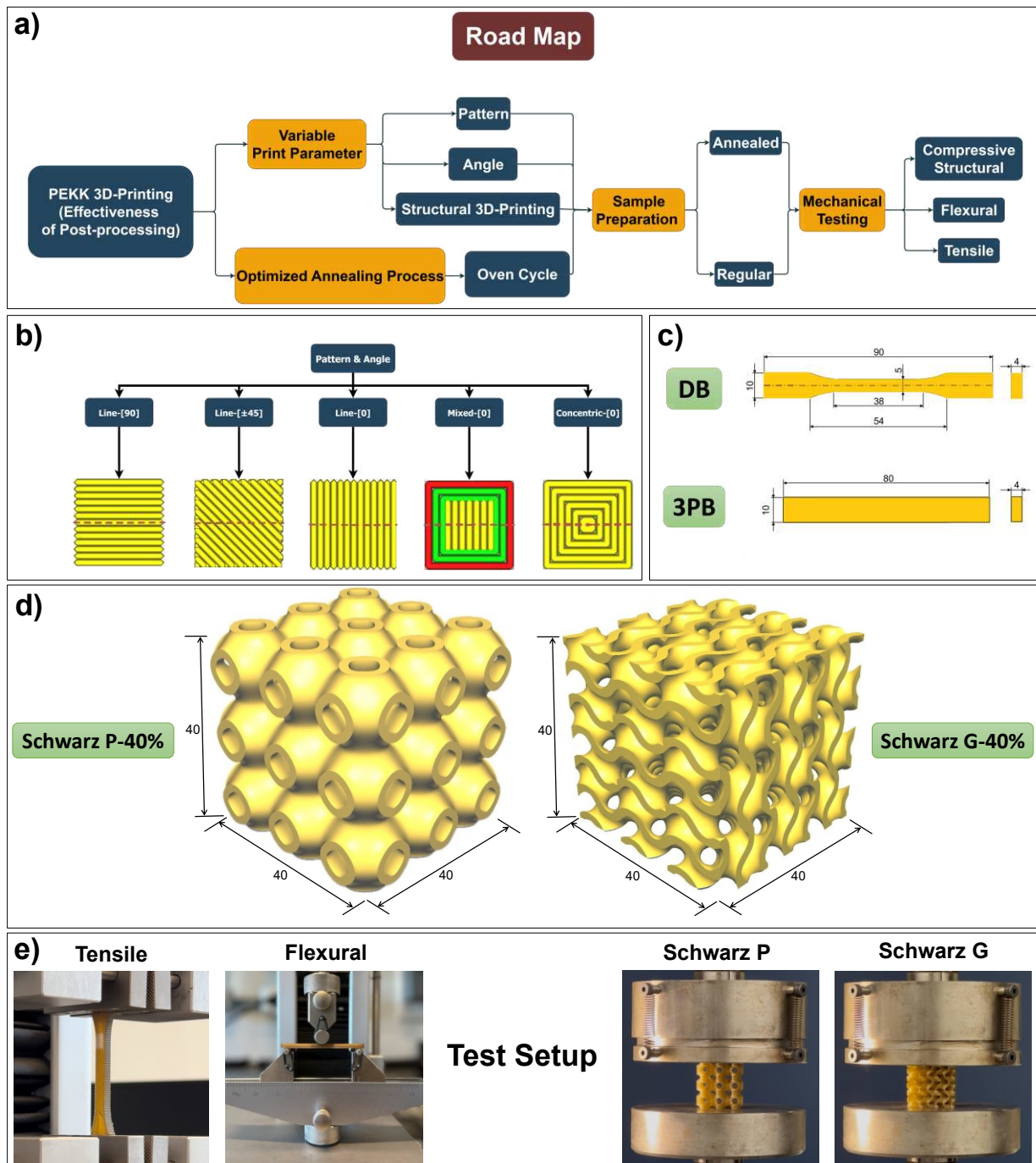


Figure 4.1. Schematic overview of the study: (a) Workflow illustrating the methodology: PEKK filament preparation, 3D printing, annealing post-processing, and mechanical testing of coupons

and architected structures; (b) Raster orientations (0° , $\pm 45^\circ$, 90°) and infill patterns (line, concentric, mixed); (c) Tensile and flexural samples geometry (all dimensions are in mm); (d) Compressive Schwarz P and G samples with relative density of 40% as structural coupons for the study (all dimensions are in mm); (e) Mechanical testing test setups.

Table 4.1. MEX set of parameters and manufactured coupons

Print parameter	Value	Units
Nozzle temperature	380	$^\circ\text{C}$
Bed temperature	160	$^\circ\text{C}$
Chamber temperature	60	$^\circ\text{C}$
Print speed	40	mm/s
Infill density	100	%
Layer height	0.25	mm
Extruder diameter	0.4	mm
Build orientation	Flat	-

4.3.2.2 Coupon Fabrication

For the fabrication of tensile and flexural coupons, five raster/orientation combinations were employed as shown in Figure 4.1b: 90° with line pattern (L-[90°]), $\pm 45^\circ$ with line pattern (L-[$\pm 45^\circ$]), 0° with line pattern (L-[0°]), 0° with concentric pattern (C-[0°]), and 0° with mixed pattern (M-[0°]). The geometrical dimensions of these specimens followed the standards illustrated in Figure 4.1c.

The selection of raster angles and infill patterns was guided by the objective of analyzing strand-level anisotropy under 100% infill conditions. At this density, adjacent extruded strands are intended to make full contact, allowing mechanical behavior to be governed primarily by strand orientation, inter-strand bonding, and the symmetry of the deposition process. Accordingly, two fundamental deposition pathologies exist: (i) placing strands adjacently along a linear toolpath, or (ii) depositing concentric contours to achieve a symmetric layer. A hybrid approach combines these two strategies.

For the line infill, raster angles of 0° , $\pm 45^\circ$, and 90° were selected to span the transition from full longitudinal load bearing (0°) to full interlayer-dominated loading (90°), with $\pm 45^\circ$ representing

intermediate shear-dominated behavior. To retain layup symmetry, $+45^\circ$ and -45° layers were always deposited consecutively.

The concentric pattern was included as a representative symmetric deposition strategy, where contours are placed outward-to-inward around the geometry. This approach produces a smooth outer profile and a continuous curvilinear toolpath. The line pattern, in contrast, represents a straight, adjacent-strand deposition strategy with uniform raster spacing. To examine a hybrid deposition approach, a mixed pattern was also considered: concentric contours were used to form the outer shell of each layer, while the interior region was filled using a linear raster. This configuration enables comparison between pure linear deposition, pure concentric deposition, and a combined strategy that incorporates both pathologies. Given these inherent trade-offs, all three patterns were included to systematically quantify their anisotropic mechanical performance before and after annealing.

For the architected structures, Schwarz G (Gyroid) and Schwarz P (Primitive) lattices with a relative density of 40% were selected, as illustrated in Figure 4.1d. These lattices represent widely studied triply periodic minimal surface (TPMS) geometries that are increasingly employed in aerospace and biomedical applications [76]. Schwarz G features a smooth, continuous surface with no sharp edges, providing more isotropic-like load distribution, whereas Schwarz P is strut-dominated and more open, leading to different stress localization and deformation mechanisms [77].

The sheet-based Schwarz structures type G and P are constructed for 3D printing with the size of $40 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$, with $3 \times 3 \times 3$ unit cells as shown in Figure 4.1d, based on the following formulations which are a mathematical construct that comprises a unit cell containing Schwarz Gyroid and Schwarz Primitive surfaces as shown in Eq. (4.1) and Eq. (4.2), respectively.

$$\sin(x)\cos(y) + \sin(y)\cos(z) + \cos(x)\sin(z) = 0 \quad (4.1)$$

$$\cos(x) + \cos(y) + \cos(z) = 0 \quad (4.2)$$

A relative density of 40% was chosen to strike a balance between manufacturability and structural integrity. At low densities ($<20\%$), lattice parts become fragile and dominated by defects,

making it difficult to isolate the effect of annealing. Conversely, at high densities ($>60\%$), the response approaches that of bulk material, reducing the influence of geometry. The intermediate regime at 40% ensures that both geometry and material properties contribute to performance, making it an ideal condition to study anisotropy and post-processing effects. Furthermore, relative densities in the range of $30\text{--}50\%$ are commonly targeted for aerospace components to achieve weight reduction while maintaining mechanical reliability [78,79].

To ensure reproducibility of lattice generation, additional geometric and modeling parameters are reported here. The Schwarz G and Schwarz P structures were modelled as implicit TPMS surfaces in nTopology (nTopology, USA). Because the final specimen dimension was $40 \times 40 \times 40$ mm with $3 \times 3 \times 3$ repeated unit cells, the resulting unit-cell size was approximately 13.3 mm in each direction. The target 40% relative density was achieved by numerically calibrating the TPMS iso-surface threshold. For TPMS geometries, iso-value cannot be analytically derived from relative density. Therefore, the iso-surface parameter was iteratively adjusted in nTopology until the computed solid volume fraction converged to 40% . The corresponding structural thickness of the TPMS sheets was approximately 1.0–1.3 mm after voxelization. All implicit bodies were discretized at a voxel resolution of $100\text{ }\mu\text{m}$ prior to STL export to preserve surface continuity and ensure accurate slicing.

4.3.2.3 Post-Processing (Annealing Protocol)

After fabrication, all specimens were divided into two categories: as-printed (regular) and post-processed (annealed), to evaluate the effect of the established annealing protocol on reinforcement and anisotropic behavior. The thermal treatment followed the procedure developed in our previous work [71]. Isothermal Annealing was performed in a customized Blue-M convection oven (Blue-M, USA) equipped with a programmable temperature-controller interface for precise thermal regulation. Samples were placed on a steel plate to promote uniform heat conduction across the bottom surface. The oven temperature was ramped from room temperature to $210\text{ }^{\circ}\text{C}$ over 15 minutes through forced convection. Specimens were then held isothermally at $210\text{ }^{\circ}\text{C}$ for 30 minutes. Cooling was performed inside the oven with the heating elements turned off while the forced-convection air-circulation system remained active, producing a controlled cooldown to below $100\text{ }^{\circ}\text{C}$ over approximately 15 minutes.

The annealing temperature and time profile as an isothermal hold was selected based on combined DSC evidence and thermal-modeling analyses reported for PEKK. DSC studies consistently place the cold-crystallization maximum near 210 °C, where chain mobility is sufficient to promote crystal growth, interlayer molecular interdiffusion, and relaxation of frozen-in thermal stresses while remaining safely below the melting region. Complementary finite-element simulations further estimate the time required for the coldest region of the printed part to reach and stabilize at this isothermal temperature, supporting the choice of a 30 min dwell to ensure uniform crystallization throughout the component.

Although the gyroid structures had a greater height compared to tensile and flexural coupons, their perforated geometry allowed sufficient heat penetration, and the same protocol ensured full crystallization, as later confirmed by Differential scanning calorimetry (DSC) analysis. For annealing of the lattice structures, the orientation of the bottom surface in contact with the oven's heating plate was selected to match the subsequent loading direction. This ensured consistency between thermal exposure and mechanical testing, as the lattices were later compressed in two configurations: with the load applied perpendicular to the deposited layers (Z direction) or parallel to the deposited layers (T direction). Though no direct temperature monitoring was performed during annealing, the use of open TPMS architectures enabled efficient convective heat penetration throughout the specimens. Consistency in crystallinity across bottom, core, and top locations, verified by DSC measurements performed in triplicate, indicates that the annealing protocol achieved uniform thermal exposure across the sample volume.

4.3.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed using a DSC Q200 instrument (TA Instruments, USA) to replicate the annealing cycle and assess crystallization behavior. Initially, neat PEKK filament was subjected to the simulated oven cycle to demonstrate crystallinity saturation under the applied conditions. The heating profile consisted of ramping from 0 °C to 210 °C at 20 °C/min, maintaining an isothermal hold at 210 °C for 30 min, and cooling back to 0 °C at 20 °C/min.

Subsequently, post-processed specimens were analyzed to evaluate the degree of crystallinity. For this purpose, DSC tests were conducted with a heating rate of 10 °C/min from 50 °C to 350

°C. The crystallinity content was assessed in a semi-quantitative manner using the relative crystallinity parameter, $X_{C_{Rev}}$, as expressed in Eq. (4.3) [71].

$$X_{C_{Rev}}(\%) = \frac{(\Delta H_M - \Delta H_{CC}) - \Delta H_{Ref}}{\Delta H_M^0} \times 100, \quad \Delta H_{Ref} = \text{Min}(\Delta H_M - \Delta H_{CC}) \quad (4.3)$$

The calculation of crystallinity percentage is highly sensitive to the selection of integration limits for the crystallization zone as well as instrument calibration, which can introduce significant scatter in the results. In Eq. (4.3), ΔH_{CC} and ΔH_M represent the enthalpy contributions from cold crystallization and melting, respectively. To account for baseline variability ΔH_{Ref} was defined as the minimum net enthalpy measured from multiple trials of raw amorphous PEKK, serving as a reference corresponding to zero crystallinity [71]. Finally, the theoretical enthalpy of fusion for perfectly crystalline PEKK, ΔH_M^0 , was taken as 130 J/g, consistent with values reported in the literature [7,9,10,26]. DSC samples (8–10 mg) were prepared by cutting small fragments from the fractured regions of specimens using a precision razor blade. Cutting was selected over crushing or grinding to avoid mechanically induced heating or morphological alteration. Each fragment was sealed in an aluminum hermetic pan in accordance with ASTM D3418 [25]. For each specimen category (filament, tensile, flexural, Schwarz G, and Schwarz P), DSC was performed on three independent samples obtained by cutting material from the bottom, middle, and top layers of the printed components to assess both process uniformity and statistical repeatability. The reported crystallinity values represent the mean of these triplicate measurements, with a scatter of $\pm 1.5\%$.

4.3.4 Mechanical Testing

For all tensile, flexural, and compression configurations, at least three specimens were tested to ensure repeatability while managing the material cost associated with aerospace-grade PEKK. Mechanical properties are reported as mean $\pm$ standard deviation. Error bars shown in all plots represent standard deviation. Due to the categorical nature of the experimental parameters and the limited sample size typical of high-temperature PEKK studies, formal ANOVA-based significance testing was not performed. Instead, the focus of this work is on consistent trends and repeatable behavior across replicates, which is appropriate for the preliminary stage of this multi-variable investigation.

4.3.4.1 Tensile Test

Tensile coupons were fabricated according to the ISO 527 [50] standard, as illustrated in Figure 4.1e. Mechanical testing was conducted using a universal testing machine (Hoskin Scientific, Canada) equipped with an S-type 5 kN load cell mounted on the upper grip. The crosshead speed was set to 2 mm/min, and a preload of 10–20 N was applied to ensure proper specimen alignment prior to testing. Tabs or adhesive reinforcements were intentionally avoided to prevent introducing additional thermal or bonding inconsistencies that could bias interlayer-dominated failure modes. To minimize slippage, the grip pressure was adjusted according to ISO 527 [50] recommendations, and all specimens were visually inspected after testing. Samples that fractured inside the gripping jaws were excluded and reprinted

Both amorphous and annealed PEKK filaments were subjected to tensile testing on the same universal testing machine used for coupon characterization, employing a crosshead speed of 4 mm/min and a gauge length of 100 mm. Due to the absence of specialized grips for filament testing, a customized fixture was implemented. The gripping zones were reinforced by wrapping the filament around the grips, inspired by ISO 527 [50] recommendations, to ensure firm contact, prevent slippage, and avoid premature end failure. This method provided stable load transfer, and the measured mechanical properties showed good agreement with the manufacturer-reported values for the as-received amorphous filament.

4.3.4.2 Flexural Test

Flexural specimens were prepared in accordance with the ISO 178 [51] standard, as shown in Figure 4.1e. Three-point bending tests were carried out using a universal testing machine (Hoskin Scientific, Canada) equipped with an S-type 5 kN load cell. The crosshead speed was set to 2 mm/min, and a preload of 1–2 N was applied to ensure stable contact between the specimen and the loading nose prior to testing.

4.3.4.3 Compression Test for Schwarz Lattices

Uniaxial compression tests were performed following the guidelines of ISO 604 [80], as illustrated in Figure 4.1e. Testing was carried out using a universal testing machine (Instron 3382, Instron, USA) equipped with a 50 kN load cell. The crosshead speed was set to 2 mm/min to satisfy quasi-static compression conditions at room temperature up to 50% strain. A preload of 40–50 N was applied to ensure proper contact between the specimen and the compression platens prior to testing.

4.4 Results & Discussion

The following section presents the results of as-printed and annealed PEKK specimens. First, DSC analysis is introduced to validate the effectiveness of the annealing protocol and quantify crystallinity changes. Mechanical performance is then reported by testing category, tensile, flexural, and compressive, followed by an assessment of dimensional accuracy and broader implications. In each case, the observed improvements or limitations are interpreted in the context of anisotropy, interlayer adhesion, crystallinity development, and post-processing effects.

4.4.1 DSC Evaluation

The DSC analysis was conducted to validate the effectiveness of the annealing protocol and quantify crystallinity development in PEKK (Figure 4.2). In Figure 4.2a, DSC test simulates the oven cycle profile consisted of heating to 210 °C, a 30 min isothermal hold, and subsequent cooling. During the isothermal stage, cold crystallization initiated immediately after the ramp, with heat flow stabilizing after approximately 15 min, indicating that crystallization equilibrium had been reached. Although steady state was achieved at this point, the isothermal step was extended for an additional 15 min to ensure saturation throughout the sample volume, particularly at the coldest regions of thicker coupons, consistent with the protocol established in our previous study [71].

Following mechanical testing, fractured specimens from the annealed filament, tensile, flexural, and Schwarz lattice samples were examined by DSC to quantify the degree of crystallinity. A representative thermogram is shown in Figure 4.2b. The results consistently exhibited a glass transition temperature (T_g) near 160 °C and a multi-stage melting response, reflecting the presence of multiple crystal populations. Overall, three crystallization-related melting events were observed. The dominant high-temperature peak between 270–330 °C corresponds to primary lamellar crystals, which originate from nucleation and spherulitic growth and possess greater lamellar thickness and stability. The lower-temperature peak at approximately 210–240 °C is associated

with secondary crystals formed during cold crystallization; these crystals arise from the rearrangement and ordering of amorphous chain segments between pre-existing spherulites and therefore melt at lower temperatures. Additionally, a small intermediate shoulder indicates imperfect or mesophase crystals that undergo partial reorganization during the heating scan. This combination of primary and secondary melting peaks, accompanied by an intermediate transition, is characteristic of PEKK subjected to cold-crystallization-based annealing treatments [7,10].

Using Eq. (4.3), the total enthalpy of both melting events corresponded to an average crystallinity of 28.9%, with a scatter of $\pm 1.5\%$ across all tested samples. These findings confirm that the annealing protocol produced reproducible crystallinity levels in both coupons and architected structures, demonstrating the robustness and consistency of the applied thermal treatment.

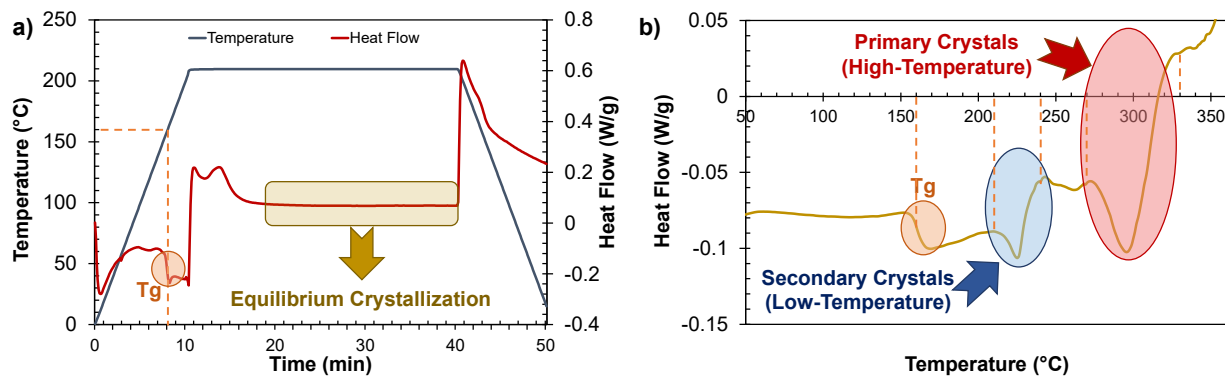


Figure 4.2. DSC evaluation of PEKK annealing protocol. (a) Simulated oven cycle profile; (b) Representative DSC thermogram of annealed specimens, revealing bimodal melting behavior with secondary crystals (210–240 °C) and primary crystals (270–330 °C).

4.4.2 Mechanical Testing

Representative fracture morphologies of tensile, flexural, and compressive specimens in both amorphous (regular) and annealed conditions are shown in Figure 4.3. Distinct fracture modes were observed depending on loading condition, strand orientation, and post-processing state. Amorphous specimens exhibited either ductile tearing or brittle splitting depending on whether the applied stress acted parallel or transverse to the deposited strands. When loading was aligned with the filament direction (e.g., L-[0] tensile and the tensile side of flexural specimens), localized necking and fibrillation were observed, indicating effective load transfer along continuous extruded

roads. Conversely, amorphous samples loaded transverse to the strand direction (e.g., L-[90] or compression in the T-direction) showed interlayer-dominated crack propagation, typically initiating at inter-strand voids or weak interfaces.

Annealed specimens displayed consistently more brittle behavior across all loading modes, attributable to increased crystallinity, reduced amorphous-phase mobility, and higher residual stresses introduced during heat treatment. Cracks propagated rapidly with limited plastic deformation, and in several cases, particularly L-[90] tensile coupons and lattice structures compressed in the Z-direction, failure occurred catastrophically through “cascading fracture”, where stress-wave amplification triggers multiple simultaneous fracture planes within a brittle or quasi-brittle material [81]. The only exception was the flexural L-[0] configuration, which retained noticeable ductility; its continuous longitudinal strands enabled localized plastic bending even after annealing.

Compression results further reinforced these trends in annealed samples. Under Z-direction loading, Schwarz G specimens displayed shear-band formation at $\sim 45^\circ$ followed by abrupt fragmentation in the annealed state, whereas T-direction loading produced interlaminar splitting and vertical crack propagation due to interlayer shear dominance. These fracture paths reflect the competing roles of intralayer strength versus interlayer adhesion. SEM examination (Figure 4.8) supports these interpretations: annealed specimens exhibit thicker interlayer bridges and rougher fracture surfaces, evidence of enhanced chain interdiffusion, whereas amorphous specimens show smoother separations and more ductile tearing features.

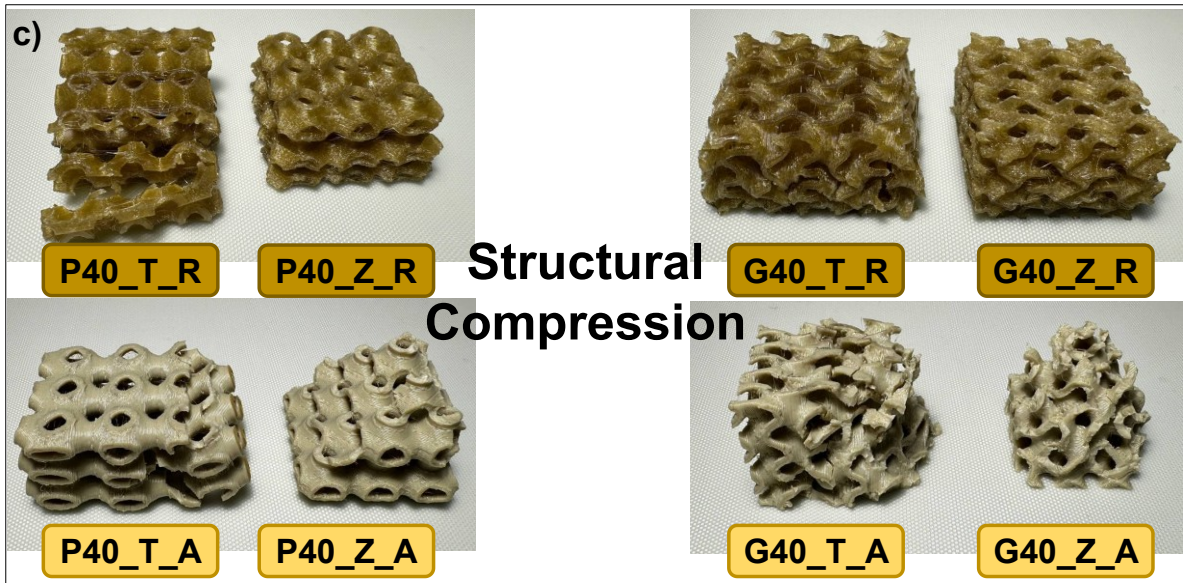
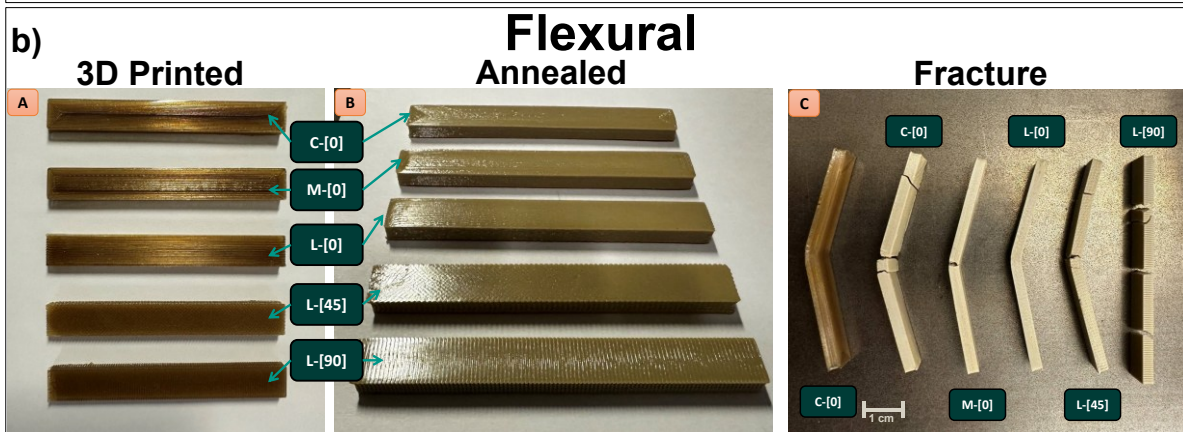
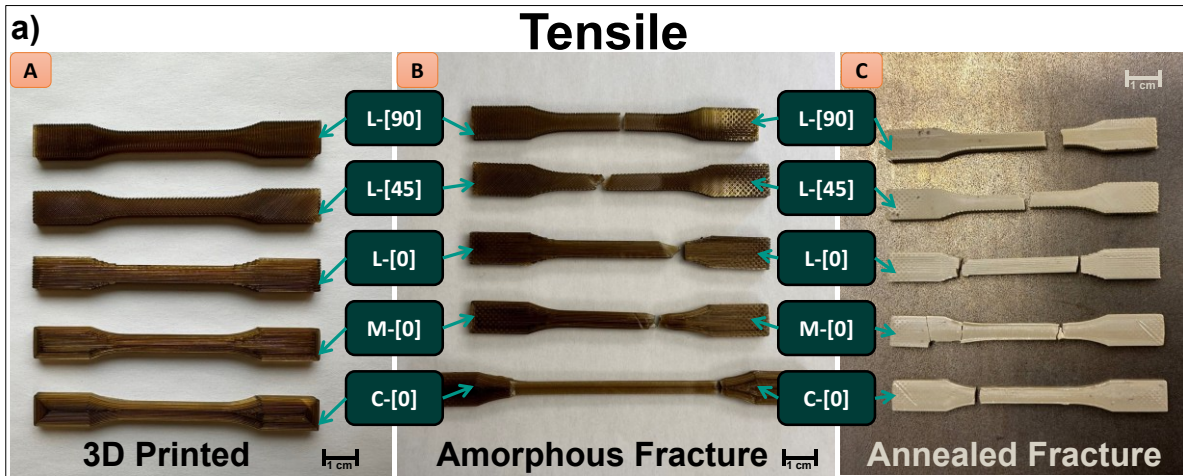


Figure 4.3. Representative fracture morphologies of (a) tensile, (b) flexural, and (c) compressive lattice specimens, demonstrating differences in failure modes depending on loading condition and geometry.

4.4.2.1 Tensile Behavior of Coupons

The tensile performance of PEKK coupons before and after annealing is presented in Figure 4.4. Across all configurations, annealing improved tensile strength, though the extent of reinforcement depended on raster orientation and infill pattern. The most significant gain was observed for concentric infill (C-[0]), which achieved a 29.5% increase relative to the as-printed state. Nevertheless, this improvement was still lower than the reinforcement observed in the filament itself, which exhibited a remarkable 38% increase in strength (from 88.2 MPa to 121.8 MPa) after annealing. This contrast suggests that manufacturing defects such as inter-strand gaps in printed parts diminish the full potential of reinforcement achievable in the bulk filament. The increase range observed here for the patterns lies at the upper end of this range, reflecting the effectiveness of the optimized annealing protocol and the favorable load alignment in the C-[0] configuration [18,20,39,68].

To further examine the microstructural origins of the mechanical trends, representative tensile-fracture SEM images from PEKK printed under identical MEX thermal conditions (concentric C-[0] and transverse L-[90] patterns) are shown in Figure 4.8. These micrographs illustrate the characteristic inter-strand contact morphology governing all raster orientations examined in this study. Amorphous specimens exhibit seamless interlayer fusion, indicating effective selection of thermal printing parameters, accompanied by uniform inter-strand voids and clear neck growth between adjacent deposited roads. Following annealing, strands display thicker interlayer bridges and enhanced interdiffusion driven by increased chain mobility above T_g . At the same time, exposure to temperatures above T_g allows trapped air to expand, producing enlarged inter-strand voids or localized bubble growth within strands. These observations corroborate the mechanical results, where annealing improves strength but may simultaneously introduce void-related defects depending on geometry and stress state.

Elastic modulus values across all orientations and infill patterns were similar in both amorphous and annealed states, indicating that elastic behavior is nearly isotropic. In contrast, ultimate tensile

strength was more sensitive to strand alignment. Strength increased progressively as the print direction transitioned from 90° to 0° , consistent with loading conditions shifting from interlayer bonding to strand-dominated fiber response.

All patterns and orientations except L-[0] exhibited more than 20% reinforcement in tensile strength after annealing. For the L-[0] configuration, sharp transitions at the grip-to-gauge interface introduced stress concentrations that became more pronounced after annealing, leading to premature brittle failure. In the amorphous state, this configuration also failed prematurely, though after limited plastic deformation, with fractures initiating at the grips rather than within the gauge length (Figure 4.3a). It is important to note that these early failures did not occur within the clamped region but rather at the geometric transition between the grip and gauge sections, where the L-[0] line-pattern introduces an abrupt strand count reduction. Since this behavior reflects a true structural limitation of the architecture, and not a gripping artifact, these results were included in the analysis. By contrast, concentric amorphous samples exhibited extensive plastic deformation, with strains exceeding 100%, resembling the behavior of neat PEKK filament.

The key distinction among the three 0° infill patterns was the location and evolution of necking. In line-pattern coupons, necking often initiated near the grips, while the addition of outer concentric contours in mixed and concentric patterns shifted the necking region toward the specimen center. This transition is attributed to smoother thickness gradients introduced by concentric walls, which reduce stress concentrations at the grip interface. From a residual stress perspective, symmetric printing pathways such as concentric infill promote more uniform temperature distributions during cooling, thereby reducing residual stress gradients. This condition increases the likelihood of stable plastic deformation and delayed fracture compared to asymmetric pathways like line infill.

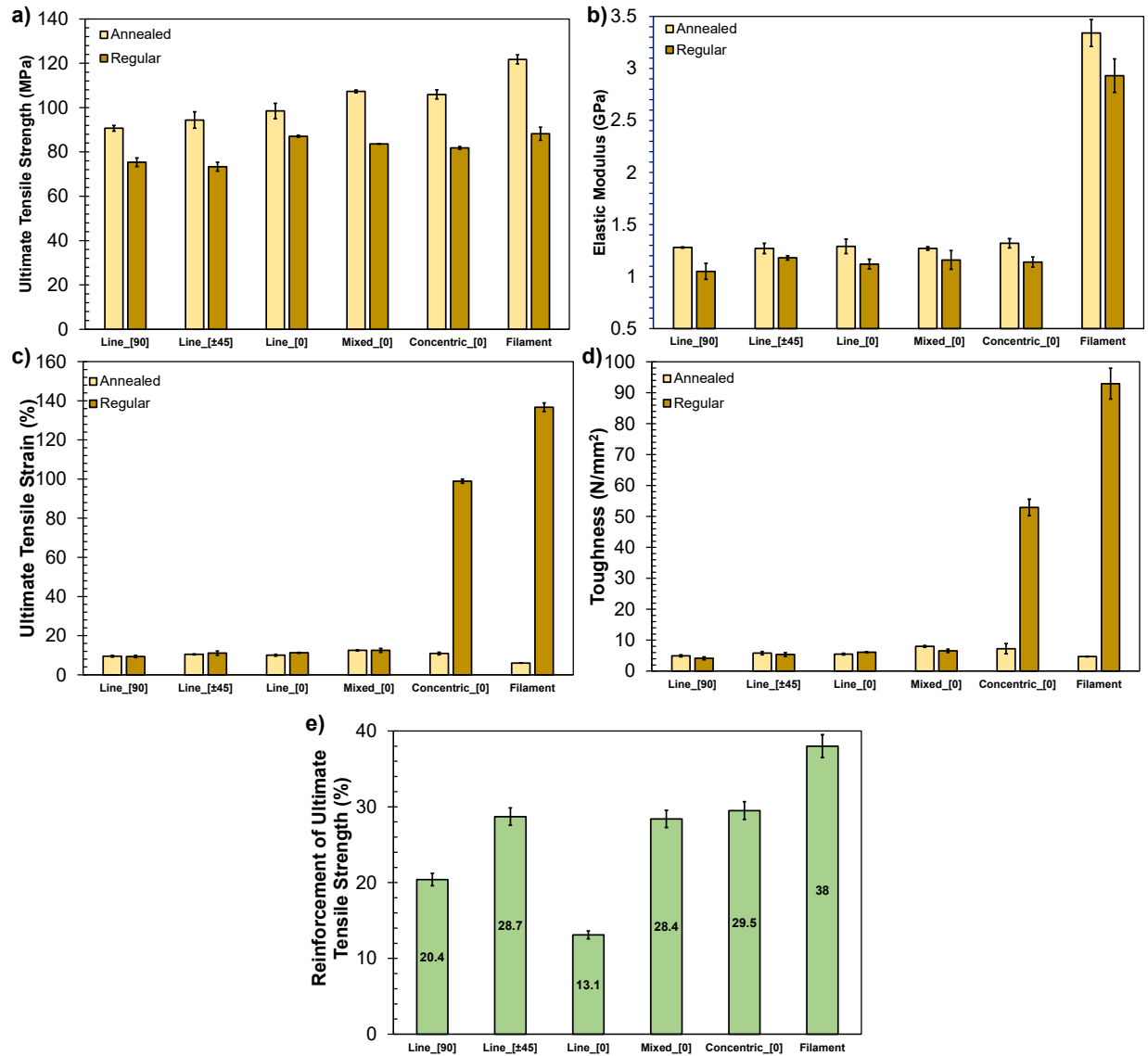


Figure 4.4. Tensile strength of PEKK coupons in amorphous (regular) and annealed conditions for different raster orientations and infill patterns.

4.4.2.2 Flexural Behavior of Coupons

The flexural performance of PEKK coupons in both amorphous and annealed conditions is summarized in Figure 4.5. Similar to the tensile results, annealing enhanced flexural strength across all printing configurations, though the degree of improvement varied with raster orientation and infill pattern. The largest increase was observed for the 90° line-pattern specimens (L-[90]), and (C-[0]) which exhibited a 17.6% and 17.3% gain in flexural strength following annealing, respectively. Specimens printed at $\pm 45^\circ$ (6.9% gain) also benefited from post-processing, but to a

lesser extent. Under bending, the $\pm 45^\circ$ orientation places strands at an oblique angle relative to the primary tensile and compressive stresses. Instead of carrying load directly (like 0°) or relying mainly on interlayer adhesion (like 90°), the $\pm 45^\circ$ strands experience shear stresses along their length. As a result, the relative reinforcement for $\pm 45^\circ$ is smaller compared to 0° or 90° , where strand continuity or interlayer adhesion dominate. These results align with published PEKK and PEEK studies, where post-annealing typically increases flexural strength by 10–25% [43].

This orientation-dependent response reflects the dominant role of interlayer adhesion under bending loads. In flexural testing, tensile stresses develop on the specimen's outer surface, where crack initiation and propagation are strongly influenced by the quality of interlayer bonding. Annealing reduced interfacial defects and improved molecular interdiffusion, particularly in the L-[90] orientation, where strands are deposited transverse to the tensile stress due to flexural loading and interlayer adhesion is critical.

Elastic modulus values in bending showed only minor variation across infill patterns and orientations, indicating that stiffness is less sensitive to post-processing than ultimate strength. Fracture observations (Figure 4.3b) confirmed that annealed flexural specimens generally exhibited more brittle behavior, consistent with increased crystallinity. A notable exception was the L-[0] configuration, which retained full ductility even after annealing. This behavior can be explained by the alignment of strands with the tensile stress direction on the lower surface of the flexural specimen, allowing localized plastic deformation before final failure.

In the line infill pattern, all strands are continuous and aligned longitudinally, enabling the structure to sustain larger deformations without fracture. By contrast, in concentric and mixed patterns, the presence of contour walls introduces 90° changes in strand orientation at the ends of each deposition path. After annealing, thermal shrinkage exacerbates residual stresses in these regions, making them more susceptible to brittle failure compared to the line pattern (Figure 4.3b). Consequently, the flexural toughness of L-[0] coupons was markedly higher than that of the other infill patterns. Overall, these results confirm that annealing enhances bending strength primarily by reinforcing weak interlayer interfaces, with the greatest benefits achieved when layers are oriented transverse to the applied load.

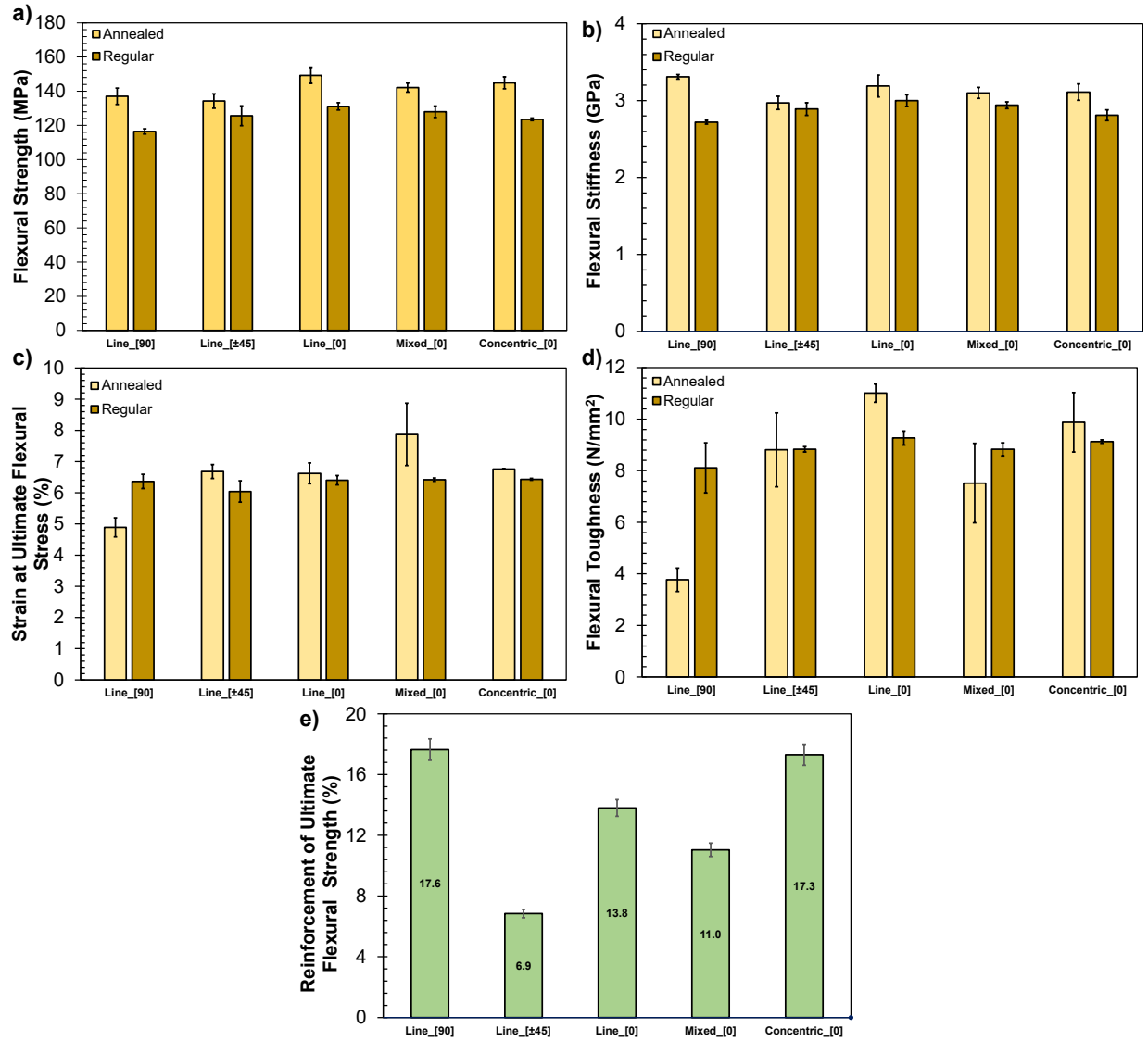


Figure 4.5. Flexural strength of PEKK coupons in as-printed (regular) and annealed conditions across different raster orientations and infill patterns.

4.4.2.3 Compression Behavior of Lattices

The compressive performance of Schwarz G and Schwarz P lattices in both amorphous and annealed conditions is presented in Figure 4.6. Two orientations were tested: Z, where the load was applied perpendicular to the printed layers, promoting interlayer consolidation; and T, where the load was applied parallel to the layers, directly challenging interlayer adhesion and promoting buckling between layers.

Fracture observations revealed that Schwarz G lattices deformed more uniformly, with gradual collapse of unit cells and stable load-bearing behavior. This is consistent with the gyroid's continuous surface geometry, which allows effective redistribution of stresses and better utilization of enhanced interlayer bonding after annealing. By contrast, Schwarz P lattices exhibited localized strut failures and early collapse along junctions, where annealing-induced shrinkage and residual stresses created weak points. As shown in Figure 4.3c, all specimens loaded in the T direction exhibited interlaminar failure, a mode not observed in any of the Z-direction tests. In the Z orientation, annealed samples failed catastrophically, with large fragments expelled as the compressed material suddenly released stored elastic energy. In contrast, T-direction loading primarily resulted in progressive crack propagation along the interlayer bonds. This distinction was also evident in the fracture surfaces: Z-direction failures were characterized by shear planes at approximately 45°, while T-direction failures displayed vertical cracks aligned with the interlayer interfaces.

It is worth noting that annealed lattice specimens tested in the T orientation often exhibited a curved top surface. To ensure uniform load distribution during testing, a rubber layer was placed between the loading platen and the specimen. While this reduced the apparent stiffness of the T-oriented annealed samples, the effect on compressive strength and toughness was negligible, since these lattices were extremely brittle. The origin of the curved surface after annealing will be further explained in the next section. All compressive load–displacement curves were converted to engineering stress–strain to enable direct comparison across lattice types and post-processing conditions. Engineering strain was computed by normalizing the crosshead displacement by the initial specimen height (40 mm). Engineering stress was calculated by dividing the applied load by the effective load-bearing area, taken as 40% of the nominal 40×40 mm footprint, matching the designed relative density shown in Figure 4.6a highlight the distinct deformation mechanisms of the two lattice types. Across all lattice types, peak compressive stress and compressive toughness was used as the principal mechanical metric because annealed structures fail before a stable plateau or densification stage forms.

For amorphous Schwarz G specimens in the Z orientation, the response featured an extended plastic plateau before hardening at higher strains with a average peak stress of approximately 31.3 MPa. In the T orientation, however, although the average peak value remained the same,

amorphous Schwarz G specimens exhibited progressive crack propagation after reaching peak load, producing damping-like spikes in the load curve. Annealed Schwarz G specimens, by contrast, showed no plastic plateau and fractured catastrophically at peak load (43.1 MPa in Z orientation and 36 MPa in T orientation).

In contrast, Schwarz P lattices displayed different behavior (Figure 4.6d). In Z-oriented amorphous specimens, compression proceeded layer by layer, with each of the three cell levels collapsing sequentially starting at the average peak load of 16.8 MPa. In the T orientation, however, amorphous Schwarz P specimens failed through shear-driven fracture of cell layers, producing repeated load drops as each level sheared with a peak at 12.2 MPa. After annealing, both orientations lost any indication of progressive deformation and instead failed suddenly and completely at the maximum load (13.6 MPa in Z orientation and 10.9 MPa in T orientation).

For Schwarz G lattices, annealing increased compressive strength by an average of 37.5%, with the Z orientation benefiting most from improved interlayer consolidation. In contrast, Schwarz P lattices exhibited a reduction of ~18.6% in compressive strength after annealing in the Z orientation. In the T orientation, where the load is applied parallel to the deposited layers, failure was governed by interlayer shear and buckling. Because annealing cannot fundamentally change this failure mode, its effect on compressive strength was comparatively minor for both lattice types. Nevertheless, the same trend (reinforcement in Schwarz G and strength reduction in Schwarz P) was observed though with smaller magnitude (Figure 4.6b, e).

The opposite response of Schwarz G and Schwarz P lattices to annealing originates from their fundamentally different load-bearing mechanisms. Schwarz G is a sheet-based TPMS architecture with smooth, continuously connected surfaces, enabling load distribution across broad areas of the structure. Annealing improves its performance by stiffening the polymer and strengthening interlayer bonding, which together increase resistance to the formation of 45° shear bands during Z-direction compression. In contrast, Schwarz P is a strut-dominated architecture composed of interconnected cylindrical segments. Compressive loads in the Z direction act directly along these slender struts, making performance highly sensitive to local geometry, warpage, and stiffness changes. Annealing increases crystallinity and reduces ductility, causing the struts to lose their ability to redistribute stresses through localized plastic deformation. Instead, the stiffer, more brittle struts fail through premature shear-out or Euler-type instability, resulting in strength reduction.

Importantly, no micro-cracking occurred during annealing; above T_g , the amorphous regions retain sufficient chain mobility to relax local stresses, preventing fracture initiation during the thermal cycle. This geometry-dependent brittle transition explains why annealing enhances Schwarz G but degrades Schwarz P, and why both architectures show only modest changes in the T orientation, where failure is dominated by interlaminar shear rather than intrinsic material stiffening.

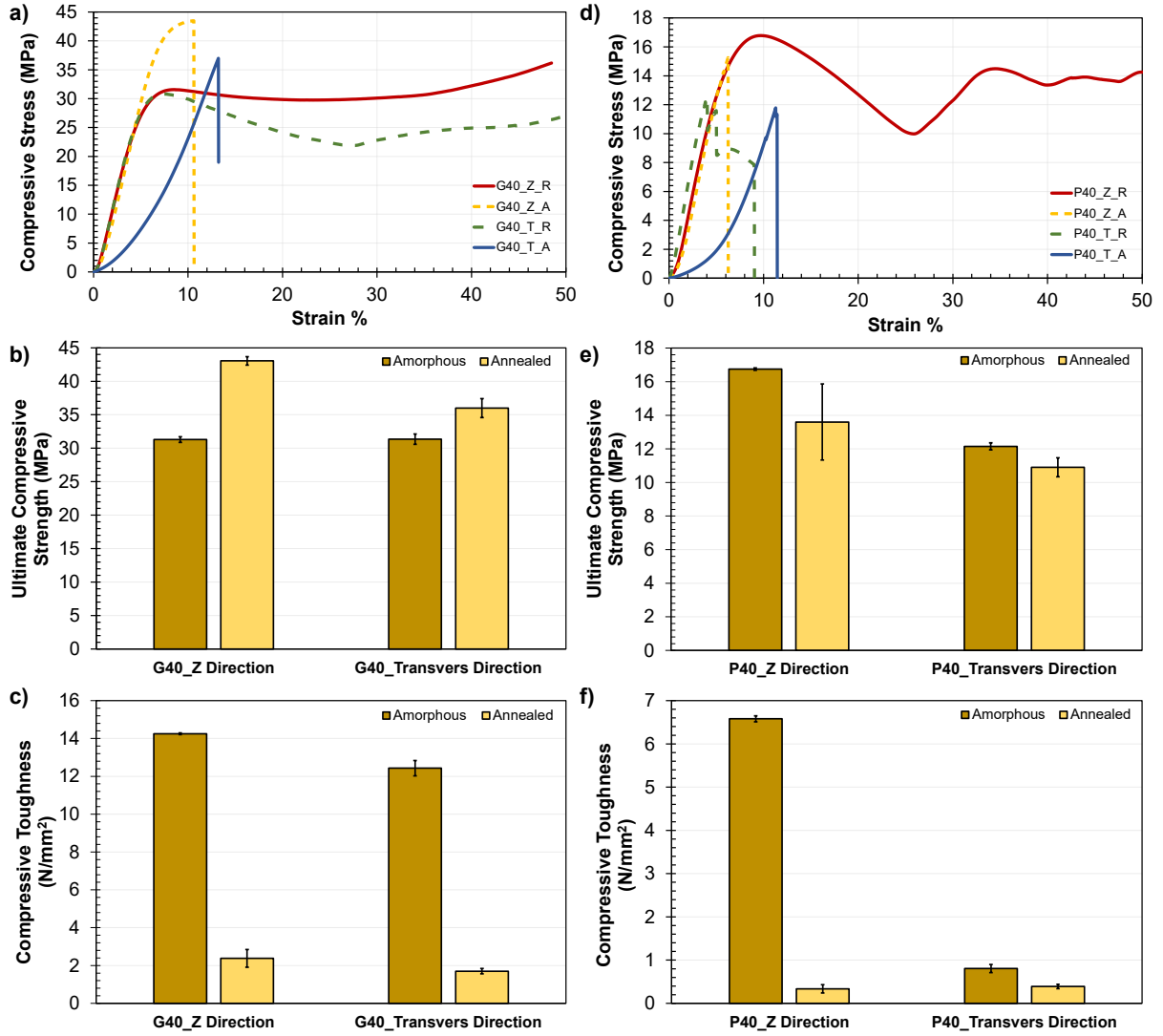


Figure 4.6. Compressive behavior of Schwarz G and Schwarz P lattices in as-printed (amorphous) and annealed conditions. (a,d) Normalized representative stress–strain curves under Z (perpendicular to layers) and T (parallel to layers) orientations; b,e) Compressive strength comparison; (c,d) Compressive toughness comparison

4.4.3 Dimensional Accuracy, Defects, & Challenges

Shrinkage and distortion after annealing were consistently observed across all geometries and represent a critical consideration for post-processing of MEX PEKK. As shown in Figure 4.7a, three representative structures, including rover wheel prototypes and a NASA ratchet wrench, exhibited in-plane shrinkage (XY) (around 17% in surface) and expansion along the build direction (Z) after annealing. To further investigate this behavior, lattice specimens were heat treated in two orientations: Z-oriented samples were placed flat on the oven plate in the same orientation as during 3D printing, while T-oriented samples were rotated 90° about the X-axis before annealing. Dimensional changes in both orientations are summarized in Figure 4.7b. Interestingly, regardless of placement, all specimens consistently expanded in the printed Z direction (around 10%), confirming that thickness swelling is an inherent effect of the annealing process.

The primary driver of this anisotropic distortion is stress relaxation of stretched and compressed filaments. During material extrusion, strands are stretched along the deposition path and simultaneously compressed through the thickness. Rapid cooling freezes this non-equilibrium configuration. Upon reheating above the glass transition temperature (T_g), polymer chains regain mobility and relax toward their natural configuration: in-plane shrinkage occurs, while recoiling along the thickness direction produces expansion [17]. This process is further amplified by void swelling. As the polymer softens above T_g but before crystallization begins, entrapped air within voids expands. Since no open pathways exist for outgassing, the voids enlarge preferentially in the Z direction, contributing to overall thickness expansion [71].

At higher temperatures, approaching the cold-crystallization zone, softening ceases and crystallization begins. Outer layers, exposed first to heat, initiate crystallization earlier and shrink accordingly, compressing the still-soft inner layers. Once the inner layers reach crystallization temperature, they also attempt to shrink. However, by this stage the outer layers have already stiffened, constraining the contraction of the inner layers. This mismatch generates residual stresses: compressive stresses in the outer crystallized shells and tensile stresses in the inner layers. The result is bending of the sample surfaces into a convex profile, as illustrated in Figure 4.7c. While the system is globally balanced, these residual stresses represent a fundamental challenge for dimensional accuracy and may also act as precursors to microcracking or warpage in complex geometries.

Moreover, the SEM images in Figure 4.8 further support the proposed mechanisms of void expansion and stress redistribution during annealing. In the annealed condition, voids located at inter-strand interfaces appear more swollen compared to the amorphous state, consistent with thermal softening above T_g and internal pressure increase within trapped air pockets prior to crystallization onset. This microstructural evidence aligns with the observed macroscopic thickness expansion and surface convexity in annealed parts. Amorphous (as-printed) specimens exhibit seamless interlayer fusion, indicating that the selected thermal printing parameters were effective, while still showing uniform inter-strand voids and measurable neck growth between adjacent extruded roads. On the other hand, annealed specimens show thicker interlayer bridges and improved fusion due to enhanced chain mobility; however, heating above T_g also allows trapped air to expand, producing enlarged inter-strand voids and in-strand bubbles growth (especially bubbles are visible in L-[90] after annealing) in some regions. The fracture surfaces of annealed specimens in the transverse (L-[90]) direction exhibit noticeably rougher and more tortuous crack paths compared to the smoother, more planar failure surfaces of amorphous samples, further indicating enhanced interlayer fusion and stronger inter-strand bonding after annealing.

From a design perspective, these observations emphasize that annealing provides substantial mechanical benefits but at the expense of dimensional precision. For aerospace and high-performance applications, where tight tolerances are often required, such trade-offs must be considered early in the design stage. In practice, annealing is most advantageous for components where strength, stiffness, and thermal stability outweigh minor dimensional distortions, such as structural load-bearing elements. Conversely, when geometric fidelity or toughness is critical, as in assemblies with tight fitting tolerances or parts subjected to impact loading, as-printed specimens may be preferable. These results suggest a dual-pathway design strategy:

- employ annealing for architectures that exploit interlayer reinforcement (e.g., concentric infill or gyroid lattices) to maximize strength, and
- retain the as-printed state for geometries prone to warpage, high residual stress, or requiring superior toughness.

These findings also point toward an important direction for future work. While this study quantified shrinkage and distortion trends, the next step will be to incorporate these dimensional changes into the design stage of the printing process. By anticipating shrinkage and expansion during annealing, models can be printed with intentional compensation so that, after heat treatment,

the final component reaches the targeted dimensional tolerances. Such an approach is particularly critical for aerospace and precision-engineering applications, where both mechanical performance and geometric fidelity must be achieved simultaneously.

4.4.4 Discussion

The mechanical behavior of MEX-printed PEKK is governed by a complex interplay between printing architecture, material crystallinity, interlayer diffusion, and residual stresses. Although the literature on PEKK additive manufacturing has grown in recent years, it remains highly fragmented. Most available studies investigate isolated variables, such as raster orientation, annealing temperature, or crystallinity evolution, without integrating these factors into a unified framework. This limitation is further compounded by the large diversity of commercial PEKK grades, which differ in ketone-to-ether ratio, molecular weight, T/I isomer ratio, flow behavior, and crystallization kinetics. As a result, published mechanical trends vary widely, and direct cross-study comparisons are seldom meaningful.

A major source of inconsistency in the available literature is that post-processing conditions are typically selected empirically, relying on trial-and-error temperature–time combinations rather than physically informed selection [18,44]. Prior to our recent work, no study had provided a systematic justification for annealing temperature based on combined DSC data and finite-element thermal analysis. The optimized annealing protocol used in the present study (210 °C, 30 min) was developed from this prior work [71], ensuring that processing conditions align with the cold-crystallization peak, maximize chain mobility, and achieve through-thickness thermal equilibrium. the present work provides an integrated investigation that combines multiple raster orientations, three infill patterns, and architected TPMS lattices, all evaluated under an annealing window established in our prior DSC-based and thermo-kinetic modelling study.

The present study extends this foundation by delivering one of the most integrated assessments to date of how raster orientation, infill pattern, and TPMS architecture collectively respond to the same thermally optimized post-processing treatment. The observed mechanical trends, reinforcement in concentric and line-based geometries, diminished performance in transverse-oriented lattices, and orientation-dependent brittle or ductile response, are consistent with the governing mechanisms of anisotropic strand alignment, inter-strand bonding heterogeneity, and void expansion during heating. Although internal temperature monitoring or thermal simulation

was not performed in this study, the applied annealing protocol was supported by the architecture and thermal behavior of the printed structures. Both Schwarz G and Schwarz P lattices were designed as open TPMS geometries with continuous internal channels, allowing forced convection to penetrate deeply through the 40 mm thickness during annealing. To the best of our knowledge, no previous study has quantified how annealing differentially reinforces or degrades surface-based (Schwarz G) versus strut-based (Schwarz P) lattices or linked crystallization-driven dimensional changes to their mechanical implications. This positions the present work as one of the most comprehensive assessments of PEKK anisotropy, architecture, and post-processing currently available in the literature.

The directional deformation observed after annealing is directly linked to both strand orientation and the distribution of printing-induced stresses. During MEX deposition, each extruded road experiences longitudinal stretching as it is dragged by the nozzle, while simultaneously being compressed through the thickness as the newly deposited strand is flattened against the previous layer. Because the majority of strands are oriented in the XY plane, this trapped stretching produces an in-plane tensile residual stress field, while the through-thickness compression results in a stored compressive stress field along Z. Upon heating above T_g , chain mobility is restored and these orientation-dependent stresses relax: longitudinal recoil of the stretched strands produces contraction in the XY plane, whereas recovery of the compressed strand cross-section produces expansion in the Z direction. This mechanism remains dominant regardless of how the lattice is placed in the oven, explaining why all architectures consistently exhibited in-plane shrinkage and out-of-plane swelling. Additionally, curved toolpaths (e.g., concentric regions) introduce local variations in strand orientation and constraint, leading to nonuniform shrinkage and convex warpage as outer layers crystallize earlier than inner layers. These effects highlight the strong coupling between deposition path, residual stress distribution, and dimensional stability during annealing.

Moreover, it is important to note that the present study reports only qualitative dimensional trends, as quantitative metrology of shrinkage and swelling was not within the scope of this work. All dimensional observations in Figure 4.7 were made before mechanical testing using manual measurement tools, which were sufficient to detect directional deformation but not to extract statistically meaningful strain magnitudes for each geometry type. This work forms the second

stage of a multi-step research program, and the annealing protocol used here was established in our previous crystallization-engineering study. A more rigorous, quantitative investigation of annealing-induced dimensional evolution, including high-resolution 3D scanning, oven-orientation effects, and correlations with crystallization kinetics, is currently underway as part of our follow-on study. These future measurements will provide compensation guidelines for design of PEKK components intended for post-processed applications regarding geometrical dimensioning and tolerances of annealed 3D-printed PEKK structures.

Finally, a remaining limitation of the present study is that all specimens were fabricated in a flat (XY) build orientation. This choice was intentional and necessary for isolating the effects of raster orientation, infill pattern, and lattice topology under a single, controlled thermal condition. Moreover, the TPMS structures investigated here possess a substantial through-thickness dimension of 40 mm, meaning that the thermal history of the upper layers becomes largely independent of the build-plate temperature. Consistent with this, no warpage, curling, or layer separation was observed across any printed geometry, confirming that the selected parameters effectively stabilized the printing process and fell within recommended ranges for PEKK. Nonetheless, we acknowledge that build orientation remains an important contributor to mechanical anisotropy in high-performance MEX materials, particularly for thicker structural components intended for aerospace or load-bearing applications, where vertical deposition paths may experience different thermal gradients, weld temperatures, and crystallization kinetics [82,83]. As our research program advances toward more structural, higher-thickness PEKK components, a dedicated investigation of build-orientation effects will be performed, integrating thermal modeling, embedded thermocouples, and mechanical characterization of upright (Z-built) geometries to fully quantify orientation-dependent anisotropy. Furthermore, the relationship between crystallinity and modulus in PEKK has been previously established in our earlier study, where annealing schedules produced larger crystallinity variations suitable for correlation analysis. Here, the annealing protocol was intentionally chosen to drive all samples into the near-saturated secondary-crystallization regime, resulting in a narrow crystallinity band that ensures mechanical differences arise primarily from print anisotropy rather than thermal history. A broader crystallinity–modulus mapping is planned for future work using controlled partial-annealing schedules to intentionally generate wider crystallinity gradients.

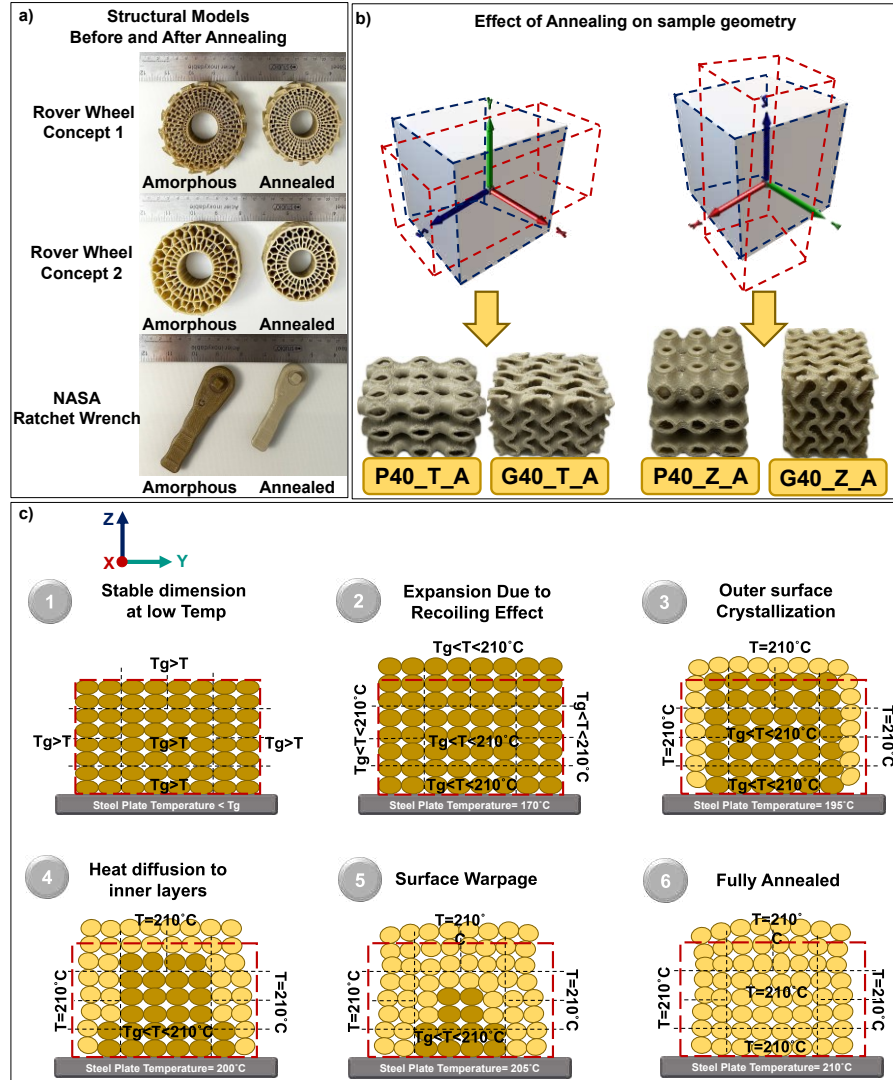


Figure 4.7. Dimensional accuracy and distortion of PEKK parts after annealing; (a) Representative structural models (rover wheel concepts and NASA ratchet wrench) before and after annealing; (b) Dimensional changes of lattice specimens annealed in different orientations (Z and T), demonstrating consistent expansion along the printed Z direction regardless of placement. (c) Schematic illustration of the underlying mechanism: stress relaxation of stretched/compressed strands and void expansion cause Z-direction swelling, while non-uniform crystallization induces residual stresses that bend the outer layers into a convex profile.

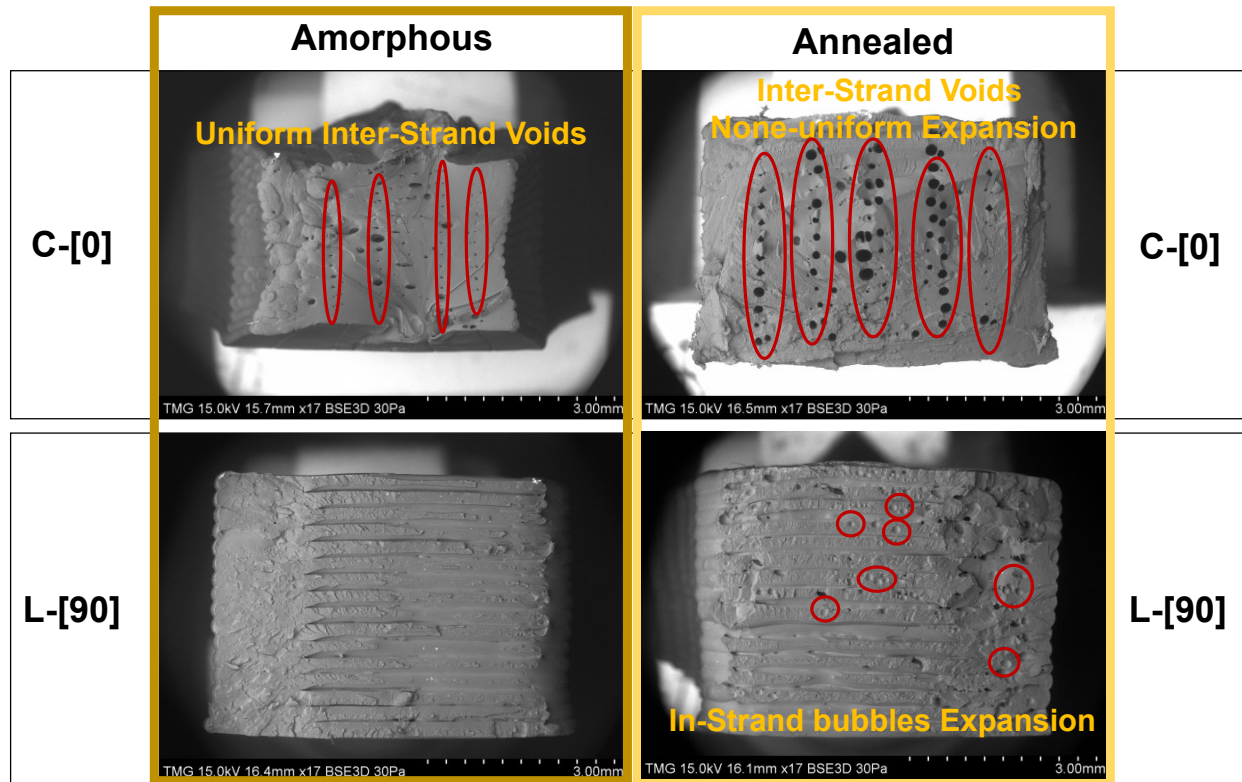


Figure 4.8. SEM fracture surfaces of amorphous and annealed PEKK tensile specimens (concentric pattern), showing inter-strand gaps, void morphology, and enhanced interlayer fusion following annealing according to the rough fracture surface of annealed samples compared to the amorphous ones in transvers direction [72].

4.5 Conclusion

This study investigated the influence of an optimized annealing protocol (210 °C for 30 min) on the anisotropic mechanical behavior of MEX-printed PEKK across multiple printing architectures, including raster orientations, infill patterns, and Schwarz-type TPMS lattices. By applying a consistent post-processing protocol to a broad set of geometries, the work provides an integrated framework for understanding how strand alignment, interlayer diffusion, crystallization, and architected topology collectively govern the structural performance of PEKK.

Annealing produced a measurable and architecture-dependent reinforcement. In tensile loading, the concentric pattern (C-[0]) exhibited the highest improvement (29.5%) due to its symmetrical deposition strand pathway. Flexural specimens showed the largest gains (17.6%) when loaded transverse to the printed strands (90°), confirming that annealing preferentially strengthens inter-

strand interfaces. In compression, Schwarz G lattices benefited substantially (+37.5%), whereas Schwarz P exhibited a reduction in strength (−18.6%) when loaded normal to the layers, highlighting the sensitivity of strut-dominated topologies to annealing-induced shrinkage and stress redistribution.

DSC analysis verified the formation of primary and secondary crystal populations, resulting in a reproducible crystallinity level of ~29%, while dimensional-accuracy measurements revealed systematic XY shrinkage and Z-direction swelling across all geometries. These observations underscore the dual nature of annealing: it enhances mechanical performance but introduces geometric distortions driven by void expansion, stress relaxation, and heterogeneous through-thickness time dependent crystallization.

Overall, this work demonstrates that the mechanical response of PEKK after annealing cannot be attributed to a single factor but arises from multi-scale interactions between thermal history, deposition architecture, and structural topology. The results provide practical guidelines for selecting raster orientations and architected designs based on the desired trade-off between strength (favoring annealed states) and toughness (favoring as-printed configurations). Future work will include a quantitative shrinkage measurement and compensation strategy, besides microstructural mapping of crystallinity and residual stresses to further refine dimensional and mechanical predictability.

Chapter 5: “Ares: God of Mars”

“Mars is the testbed of our ability to live beyond Earth”

- Chris Hadfield

This work has been published in:

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5. Additive Manufacturing of PEKK Composites with Selected Martian Regolith Particles for In-Situ Resource Utilization

5.1 Abstract

Sustainable in-situ resource utilization (ISRU) requires materials and processes that minimize Earth dependency while enabling autonomous construction on Mars. This study investigates the fabrication and characterization of polyetherketoneketone (PEKK)/Martian Regolith Simulant (MRS) composite filaments optimized for additive manufacturing. By systematically reducing MRS particle size ($<100\text{ }\mu\text{m}$, $<50\text{ }\mu\text{m}$, and $<20\text{ }\mu\text{m}$), the achievable filler loading in pulverized PEKK was progressively increased to 30 wt% without phase segregation. Filaments were produced using twin-screw extrusion and comprehensively characterized through rheological, thermal, and microstructural analyses prior to material extrusion (MEX) printing. Mechanical and thermomechanical testing of 3D-printed parts revealed that particle morphology and size distribution significantly influence porosity, interlayer adhesion, and anisotropy. SEM and EDX analyses confirmed uniform MRS dispersion and matrix infiltration into perforated silicate particles, facilitating enhanced strand fusion. At high filler contents, mechanical strength plateaued, indicating a transition in fracture mechanisms rather than continued degradation. Dynamic Mechanical Analysis (DMA) demonstrated consistent elastic behavior between 0° and 90° orientations, while thermal post-processing enhanced thermal stability but introduced porosity, particularly at intermediate filler levels. A tensile strength model incorporating filler volume fraction, porosity, and fracture mode accurately predicted experimental results across compositions. These findings establish high-loading PEKK/MRS composites as a viable material system for sustainable, recyclable ISRU-based additive manufacturing on Mars.

5.2 Introduction

Building on recent advances in space manufacturing, additive manufacturing (AM) has emerged as a practical In-Situ Resource Utilization (ISRU) strategy, enabling the on-site production of infrastructure using Martian regolith and reducing reliance on costly Earth-supplied payloads [84–89]. Early research on Martian regolith simulants (MRS) focused on bulk-molded

cements activated by alkaline or biopolymer binders [90–94]. More recently, the field has shifted toward polymeric and geopolymeric composites compatible with AM, enabling 3D-printed structures directly on the Martian surface [84,85,94,95]. From an operational standpoint, regolith incorporation is also pertinent to radiation mitigation, as mineral fillers can increase attenuation relative to neat thermoplastics; while not measured here, this trend has been demonstrated for related polymer/regolith systems and motivates high-loading composites for habitat and tooling components [96–99]. Among various regolith-based materials, MRS, a basaltic, ceramic-rich particulate, has gained growing attention for its compatibility with AM platforms [34,89,93–95,97,100–105]. In particular, material extrusion (MEX) techniques are increasingly favored due to their simplicity, thermoplastic compatibility, and suitability for reduced-gravity environments [34,84,103,106]. Table 5.1 provides an overview of recent studies, reflecting the rising prominence of AM methods in ISRU due to their processing adaptability and expanding role within the field.

Among AM approaches, MEX is particularly promising for space applications due to its simplicity, thermoplastic compatibility, and adaptability to reduced-gravity conditions [34,86,94,107–109]. However, selecting materials for extraterrestrial MEX must account for challenges such as defect formation in microgravity, vacuum-based sintering limitations, and the need for autonomous, remote-controlled operation. Additionally, Martian infrastructure must withstand radiation, thermal extremes, and mechanical loads over extended durations [90,97]. Compared to laser-based AM, which often requires excessive energy and struggles with densifying high-melting-point regolith, polymer-regolith extrusion offers a more energy-efficient and scalable solution, well-suited to the mass and resource constraints of space missions [87,102,105].

Table 5.1. Literature for additive manufacturing of Martian regolith.

AM Method	Matrix	Regolith Type	Regolith wt%	Novelty	Ref.
FGF	Polypropylene (PP)	MGS-1	40	A comparative analysis of mechanical properties and foaming behavior between AM and injection molding (IM) of highly filled PP/regolith composites revealed that heat release of regolith constituents contributes to surface defects in AM-produced parts.	Matetich and Vold, 2024 [103]
DIW	Water & Sodium Silicate	MRS	60 & 70	Evaluation of geopolymer binder–regolith mixtures under simulated Martian conditions (low pressure and temperature) with full mechanical and porosity analysis; explored layer deposition effects and curing viability.	Hedayati and Stulova, 2023 [95]
DIW	alkaline silicate solution	HIT-MRS-1	Not mentioned	Demonstration of biomimetic pattern-dependent mechanical properties in regolith-based geopolymer composites, achieving high compressive strength (up to 32.2 MPa) and tailored toughness via fiber alignment and pattern control.	Ma et al., 2022 [94]
FDM	Medium-density polyethylene	MRS-Biolit	10	Integrated radiation shielding simulations experimental filament extrusion and additive manufacturing of PE/regolith composites, demonstrating validated mechanical integrity and radiation attenuation performance under simulated Martian exposure conditions.	Zaccardi et al., 2022 [97]
LSD	-	MGS-1C	Up to 80	Demonstrated ISRU-adapted clay-based shaping techniques using stable Martian regolith slurries; achieved 30.8 MPa compressive strength in unfired green parts via LSD with minimal additives, promoting low-energy, binder-free infrastructure construction on Mars	Karl et al., 2020 [104]
DED	Ti64	MMS-1	Up to 100	Demonstrated that small additions of regolith to Ti64 significantly increase microhardness (from 5% up to 100%), while enabling metal–ceramic composites suitable for in-situ structural manufacturing on Mars.	Afrouzian et al., 2022 [105]
FDM	Amorphous PEKK	MGS-1	10	FDM-printed PEKK/Martian regolith composite filament for load-bearing applications	Malekpour et al., 2025 [34]

Despite its advantages, extrusion-based regolith composites face key challenges, including weak interlayer bonding, elevated porosity, and flow instability, especially at higher filler concentrations [110,111]. Achieving reliable mechanical performance requires careful control of matrix–filler interactions, which directly affect adhesion and extrusion consistency [112]. Without this control, part quality remains unpredictable, limiting their application in critical surface infrastructure. Addressing these issues calls for not only improved composite formulations but also a deeper understanding of how processing parameters and particle morphology influence microstructure and performance. In this context, polymer-regolith AM is more than a fabrication method, it is a cornerstone for autonomous, scalable, and sustainable construction beyond Earth.

Amorphous polyetherketoneketone (PEKK), a high-performance thermoplastic in the PAEK family, offers outstanding mechanical strength, thermal stability, and chemical resistance, making it a strong candidate for space-grade composites [1,18,26,71]. Its mechanical properties are tunable through isomer composition, which controls crystallization behavior [3,4,10]. The amorphous grade of PEKK is particularly suitable for MEX due to its naturally slow crystallization rate, low melt viscosity, reduced warpage, and enhanced interlayer bonding [4,113,114]. However, to achieve full crystallinity and improve structural performance, thermal post-processing is required [44,71]. Previous studies have demonstrated that PEKK/MRS composites with up to 10 wt% regolith can be successfully 3D printed, offering good printability and structural integrity [34]. Yet, significant challenges remain in increasing filler content, ensuring uniform particle dispersion, and understanding how regolith loading affects microstructure and anisotropic mechanical properties.

Despite the rapid expansion of polymer–regolith additive manufacturing, a crucial research gap persists. Few studies have demonstrated the ability to process high-loading thermoplastic/regolith composites and precise consideration of particle size through MEX while maintaining homogeneous premix quality and print reliability. Additionally, most reported works rely solely on bulk-density measurements and overlook microstructural defects, such as pore morphology and interlayer bonding. Finally, predictive modeling frameworks that incorporate both porosity and fracture behavior remain largely undeveloped for regolith-reinforced thermoplastics. This study addresses these gaps by:

- Systematically increasing MRS content up to 30 wt% through controlled particle-size reduction ($<100\text{ }\mu\text{m} \rightarrow <50\text{ }\mu\text{m} \rightarrow <20\text{ }\mu\text{m}$) while preserving homogeneous mixing.

- Archimedes density to quantify porosity and pore morphology and image-based pore analysis as a qualitative approach for establishing structure–defect correlations.
- Performing microstructural and fractographic analyses to reveal interlayer failure modes and the effect of particle reinforcement mechanism.
- Developing a porosity-aware tensile strength model that integrates filler volume fraction and fracture regime, validated across thermal-treatment states.

These contributions aim to extend the understanding of high-loading regolith-filled thermoplastics and provide a predictive foundation for scalable, sustainable additive manufacturing within ISRU frameworks.

5.3 Materials & Methods

The methodology, illustrated in Figure 5.1a, follows a structured workflow that begins with the preparation of raw materials, including the drying and mixing of sieved Martian regolith simulant (MRS) and pulverized polyetherketoneketone (PEKK). This is followed by filament extrusion, 3D printing of test specimens, and post-processing. The final stage involves comprehensive testing and characterization of both neat and composite filaments, as well as their printed parts, to evaluate their mechanical, thermomechanical, and rheological properties.

5.3.1 Materials

An amorphous PEKK filament (1.75 ± 0.05 mm diameter) was sourced from Spool3D (Alberta, Canada; product code PEKK175-1000). The supplier recommends FDM processing with a nozzle temperature of 360–400 °C and a build plate temperature of 90–130 °C. However, a higher build plate temperature of 160 °C was adopted after calibration to reduce warping. The filament was pelletized and pulverized using an AF LAB Pulverizer (Orenda, Canada), with three successive cycles reducing the particle size to below 500 μm . The MRS used was the MGS-1 grade [115], obtained from Space Resource Technologies (Exolith Lab, UCF, USA), and mechanically sieved into three fractions: <100 μm , <50 μm , and <20 μm (Figure 5.1a). Due to their hygroscopic nature [75,115], both pulverized PEKK and MRS powders were dried at 125 °C for 5 hours prior to compounding. Mixing was performed at 50 RPM for 10 minutes at PEKK/MRS weight ratios of 90/10, 80/20, and 70/30, corresponding to the particle sizes of <100 μm , <50 μm , and <20 μm , respectively. These ratios were determined based on saturation limits: <100 μm particles reached

saturation at 10 wt%, <50 μm enabled 20 wt%, and <20 μm supported 30 wt% without visible agglomeration or sedimentation. To establish a baseline, a 0 wt% MRS (pure PEKK) control was also prepared and extruded in-house, enabling direct comparison with the commercial filament to isolate extrusion-induced effects. All blends achieved uniform dispersion and were stored in a drying chamber at ambient temperature (25% RH) for no more than 24 hours before processing.

5.3.2 *Filament Fabrication*

Previous research by McGlasson et al. [116] highlighted that filler dispersion quality in elastomeric composites is closely related to accumulated shear strain during processing. Twin-screw extrusion remains the most effective method for integrating particulate fillers into polymer matrices due to its high shear, efficient mixing, and excellent dispersion uniformity [117]. In this study, PEKK/MRS blends were processed using a Process 11 twin-screw extruder (Thermo Fisher Scientific, Germany), equipped with a high-performance screw sequence optimized for engineering thermoplastics [118]. The screw configuration included two-stage mixing zones (Figure 5.1b) and was operated at 50 RPM. The extrusion profile was controlled through eight heating zones, also shown in Figure 5.1b.

- **Zone 1 (Z1)** served as the powder feeding section with fixed parameters and no user temperature control.
- **Zone 2 (Z2)** was set to 260 °C to prevent overheating of Z1 and the hopper.
- **Zones 3–7 (Z3–Z7)** were maintained at 315 °C, based on PEKK's cold crystallization temperature [71,119].
- **Zone 8 (Z8)** was elevated to 330 °C (15 °C higher than previous zones) to reduce melt viscosity and die pressure near the exit, minimizing nozzle clogging.

A vacuum degassing system was employed after the primary mixing zone to remove entrapped air or volatiles. The molten composite was then extruded through a 2 mm die nozzle. Filament diameter was controlled (target: 1.75 ± 0.15 mm) by applying tension during drawing. Air cooling, rather than water quenching, was used to avoid moisture uptake, and final filaments were stored in a dry chamber at 10% relative humidity.

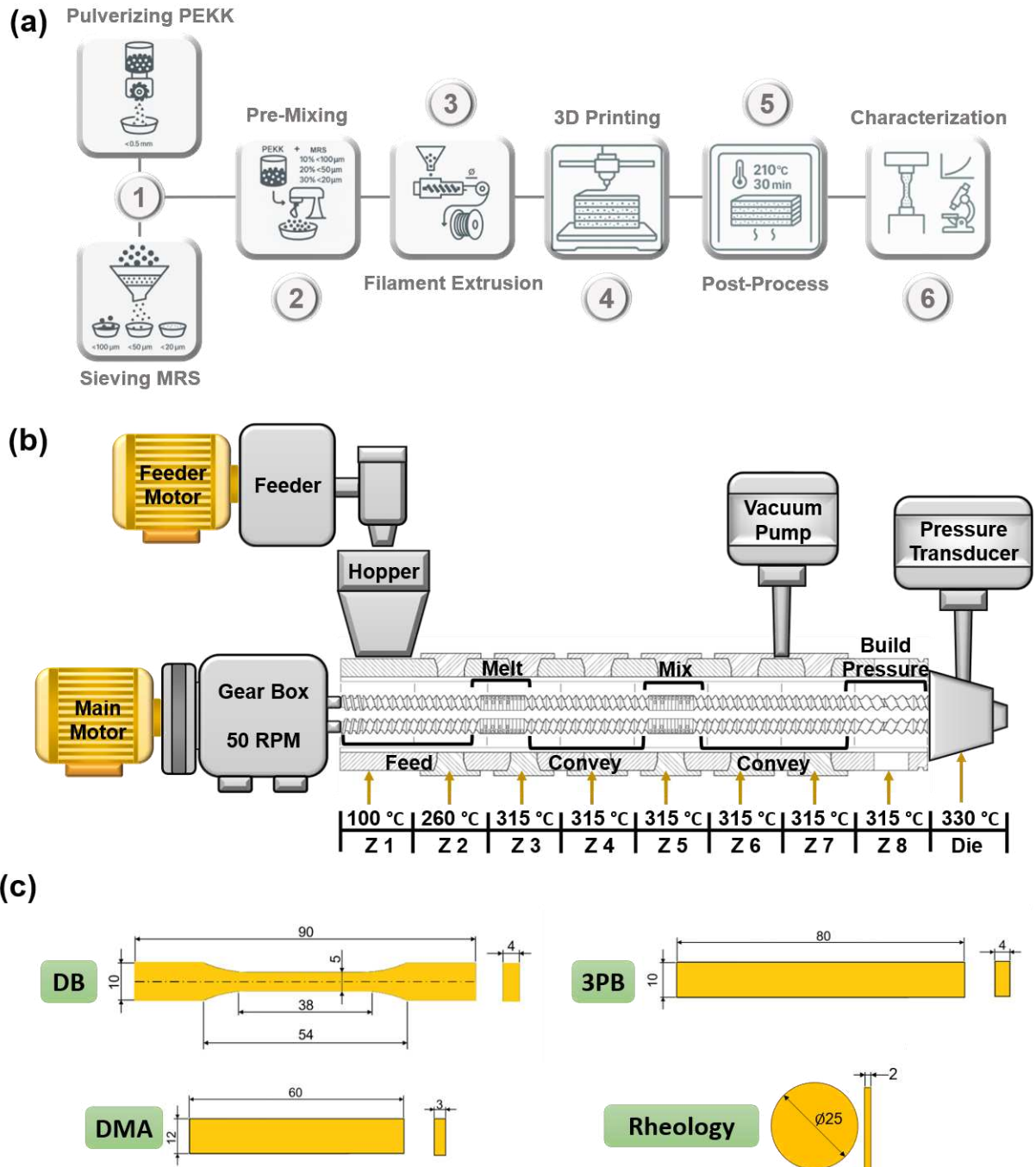


Figure 5.1. Overview of the manufacturing process: **a)** Sequential workflow of the complete fabrication process, **b)** Micro-extruder setup and screw configuration, detailing key stages of the extrusion procedure, **c)** Geometrical specifications of the 3D-printed test samples (dimensions in mm).

5.3.3 3D-Printing

To ensure optimal print quality, the filament was redried at 125 °C for 5 hours under proper ventilation prior to each 3D printing session. The material extrusion (MEX) process for fabricating test specimens was prepared using Ultimaker Cura for slicing, with printing parameters summarized in Table 5.2. This parameter selection was informed by our previous study on the influence of thermal conditions in MEX of amorphous PEKK, aiming to optimize the processing parameters for maximum ductility in the fabricated samples [69]. All prints were performed using a CreatBot F160-PEEK 3D printer (CreatBot, China). To improve build plate adhesion and reduce the risk of warping, a thin layer of nano adhesive glue (Vision Miner, USA) was applied to the glass surface before each print.

Table 5.2. MEX set of parameters

Print parameter	Value	Units
Nozzle temperature	380	°C
Bed temperature	160	°C
Chamber temperature	60	°C
Print speed	40	mm/s
Infill density	100	%
Layer height	0.25	mm
Extruder diameter	0.8	mm
Raster Angle	0 and 90	°
Build orientation	Flat	-

5.3.4 Post-Processing

The annealing treatment after processing used the same method described in our earlier research [71]. The thermal procedure started with heating the samples to 210 °C in a 15-minute period. The temperature was then maintained at 210 °C for 30 minutes. Following this, the samples underwent controlled cooling back to ambient temperature during the final 15 minutes. The complete annealing cycle took one hour from start to finish.

5.3.5 Characterization Techniques

5.3.5.1 Thermogravimetric Analysis (TGA)

To evaluate the dispersion quality of MRS within the PEKK matrix, thermogravimetric analysis (TGA) was conducted to quantify the volumetric filler distribution. Thermal stability assessments were performed on both neat PEKK and PEKK/MRS composites using a TGA Q50 instrument

(TA Instruments, USA), in accordance with ASTM E1131 [28]. For each material system, at least three samples were analyzed from both the extruded filaments and their corresponding 3D-printed parts. Specimens weighing between 30 mg and 40 mg were placed in ceramic crucibles and heated from room temperature to 800 °C at a ramp rate of 10 °C/min under a nitrogen atmosphere. Given that MRS consists entirely of thermally stable ceramic constituents, it does not degrade within this temperature range. Therefore, the residual mass difference between neat PEKK and PEKK/MRS samples reflects the MRS content by weight (W_{MRS} (%)), providing an indirect measure of filler dispersion. The relative thermal degradation profiles also enable quantification of the inorganic phase through the measured weight loss (W_{TL} (%)), as expressed in Eq. (5.1):

$$W_{MRS}(\%) = \left(1 - \frac{WT_{L_{PEKK/MRS}}(\%)}{WT_{L_{PEKK}}(\%)} \right) \times 100 \quad (5.1)$$

5.3.5.2 Rheology

The rheological properties of the 3D-printed composite components were evaluated using an MCR 302 parallel-plate rheometer (Anton Paar, Austria). The testing protocol involved two phases: first, a frequency sweep analysis was conducted on neat PEKK at standard extrusion temperatures to identify an appropriate fixed frequency for the subsequent thermal analysis. In the second phase, composite filaments with Martian regolith concentrations ranging from 0% to 30% by weight underwent temperature sweep testing across 250 °C to 390 °C. This temperature range was selected to capture both the cold crystallization behavior and the operational nozzle temperatures employed in 3D printing.

5.3.5.3 Density

Density measurements were performed in two categories:

- (I) True density of MRS, using gas pycnometry, and
- (II) Bulk density of polymer-based samples, using the Archimedes principle.

Accurately determining the true density of MRS was critical to computing the theoretical volume fraction of regolith in each composite formulation, given the varying MRS weight fractions.

True Density of MRS:

To obtain the grain density of MRS, a helium gas pycnometer (Ultrapyc 5000, Anton Paar, Austria) was used. Each measurement was repeated at least three times according to the standard operating procedures. Helium was chosen for its high diffusivity, allowing penetration into micropores between fine regolith particles, enabling precise solid volume determination.

Bulk Density of Polymer-Based Samples:

The bulk density of the filaments and printed specimens was determined using a Sartorius density determination kit (Germany) based on the Archimedes method, in accordance with ASTM D792 [48]. Samples were weighed in air and then submerged in distilled water at 23 ± 0.5 °C. This immersion-based method does not allow water to enter internal voids, enabling estimation of porosity by comparing measured and theoretical densities.

Porosity Estimation:

Due to inevitable voids formed during additive manufacturing and the effect of crystallization on polymer density [36], measuring the actual density of the 3D-printed samples was necessary. The Archimedes-measured density, combined with known densities and weight fractions of PEKK and MRS, enabled estimation of total porosity in both filaments and printed components. The theoretical volume fraction of MRS was calculated using Eq. (5.2), based on the measured weight fractions and true densities of each component. Using this volume fraction, the theoretical composite density was calculated via the rule of mixtures, as shown in Eq. (5.3):

$$V_{MRS} = \frac{\frac{\omega_{MRS}}{\rho_{MRS}}}{\frac{\omega_{MRS}}{\rho_{MRS}} + \frac{\omega_{PEKK}}{\rho_{PEKK}}} \quad (5.2)$$

$$\rho_c = (1 - V_{MRS}) \cdot \rho_{PEKK} + V_{MRS} \cdot \rho_{LRS} \quad (5.3)$$

where:

- V_{MRS} is the theoretical volume fraction of MRS
- ω_{MRS} is the weight fraction of MRS
- ω_{PEKK} is the weight fraction of PEKK (note: $\omega_{PEKK} = 1 - \omega_{MRS}$)
- ρ_{MRS} is the density of MRS
- ρ_{PEKK} is the density of PEKK
- ρ_c is the theoretical density of composite filament

The approximation serves as a benchmark for quantifying porosity, representing the internal void content within the fabricated filaments and 3D-printed components, by comparing the theoretical density with the experimentally measured values. The porosity (P) was calculated using Eq. (5.4):

$$P(\%) = \left(1 - \frac{\rho_{exp}}{\rho_c}\right) \quad (5.4)$$

Here, ρ_{exp} represents the experimentally measured density obtained using the Archimedes method, while ρ_c denotes the theoretical composite density calculated from the volume fractions of the individual constituents, as previously described. This method allows for the quantification of the void fraction introduced during filament extrusion, 3D printing, and post-processing as a key factor that significantly impacts the mechanical and thermal performance of the final printed parts.

5.3.5.4 Scanning Electron Microscopy (SEM)

To investigate the MRS particle characteristics and composite microstructure, scanning electron microscopy (SEM) was performed on both the sieved Martian regolith powders and the cross-sections of PEKK/MRS composite filaments. The analysis aimed to assess the effectiveness of particle size separation, the quality of filler dispersion within the PEKK matrix, the presence of microstructural defects, and the apparent volume fraction of MRS in each formulation. Imaging was conducted using a HITACHI Regulus 8230 Field Emission SEM (FE-SEM) operated at 15 kV, and all specimens were gold-coated to ensure adequate surface conductivity. SEM micrographs were captured at 50X, 100X, 200X, 500X, and 1000X magnifications, and image analysis was performed to estimate the MRS content based on visible particle distribution. To complement the morphological evaluation, Energy Dispersive X-ray (EDX) spectroscopy was used to identify the elemental composition, particle type, and assess the spatial distribution and uniformity of MRS within the polymer matrix. Both the powder and composite samples underwent EDX mapping to confirm the presence and dispersion quality of the ceramic phase.

Moreover, fracture surface characterization on tensile coupons was conducted using a HITACHI S-3400N scanning electron microscope (HITACHI, Japan) operated at an accelerating voltage of 15 kV. Additionally, grayscale thresholding was applied to SEM images captured at 17X and 50X magnifications to qualitatively evaluate and compare pore size and distribution among the samples, considering their composition, thermal processing history, and printing orientation.

5.3.5.5 Mechanical Testing

Tensile and flexural test specimens were fabricated in accordance with ISO 527 [50] and ISO 178 [51], respectively, as depicted in Figure 5.1c. Mechanical testing was conducted using a universal testing machine (Hoskin Scientific, Canada) equipped with a 5 kN S-type load cell mounted on the upper grip. The tests were carried out at a constant displacement rate of 2 mm/min. A preload of 1–10 N was applied for the tensile tests, while a preload of 1–2 N was used for the three-point

bending tests to ensure proper sample alignment and contact prior to loading. Each test was repeated at least five times according to the standard procedures.

5.3.5.6 Dynamic Mechanical Analysis (DMA)

DMA was carried out using a DMA Q800 (TA Instruments, USA) in accordance with ASTM D4065-12 [54] and ASTM D5418 [55] for dual cantilever beam testing. Specimens were tested under a strain amplitude of 0.1% at a fixed frequency of 1 Hz. The thermal scan was conducted over a temperature range of 140 °C to 220 °C, with a heating rate of 2 °C/min, to evaluate the viscoelastic behavior of the materials under dynamic loading conditions.

5.3.6 Mechanical Property Modeling Approach

To predict the tensile strength of PEKK/MRS composites, the classical rule of mixtures was initially considered, where the composite strength is calculated as a weighted average of the matrix and filler strengths based on their respective volume fractions [120]. However, additive manufacturing introduces porosity, which degrades mechanical performance, especially in parts printed at 90°, where interlayer bonding is weak. To address this, a modified rule of mixtures was used, incorporating porosity (P) as a correction factor. The tensile strength of the composite (σ_c) is given by:

$$\sigma_c = (\sigma_m(1 - \phi_f) + \sigma_f\phi_f)(1 - P) \quad (5.5)$$

where σ_m is the tensile strength of the fully dense PEKK matrix, σ_f is the tensile strength of the filler particles (MRS), ϕ_f is the filler volume fraction, and P is the porosity fraction. Given the negligible contribution of MRS to tensile strength compared to the matrix, the model was simplified by assuming $\sigma_f \approx 0$, leading to:

$$\sigma_c = \sigma_m(1 - \phi_f)(1 - P) \quad (5.6)$$

This linear correction is valid in ductile regimes, typically at low filler contents, where the polymer matrix dominates failure behavior. However, as filler content increases or after post-processing, the composite becomes more brittle, and porosity acts as a stress concentrator rather than just reducing load-bearing area. To capture this, an exponential porosity sensitivity model was adopted:

$$\sigma_c = \sigma_m(1 - \phi_f)(e^{-nP}) \quad (5.7)$$

Here, n is the porosity sensitivity coefficient, representing how strongly porosity accelerates mechanical failure. This coefficient was determined by fitting the experimental tensile strength data ($\sigma_{c,exp}$) using the logarithmic form of Eq. (5.7):

$$\ln\left(\frac{\sigma_{c,exp}}{\sigma_m(1 - \phi_f)}\right) = -nP \quad (5.8)$$

By distinguishing between ductile and brittle failure regimes, this two-tiered model enables accurate prediction of tensile strength degradation due to both filler volume and porosity, providing a robust foundation for optimizing composite performance in extraterrestrial applications.

5.4 Results & Discussion

5.4.1 Quality Control

Quality assurance measures were applied throughout each stage of the manufacturing workflow to detect defects and implement corrective strategies as needed. As a result, the following results reflect not only the quality and consistency of sieved particles and the extruded filament but also evaluate the challenges of 3D printing parameters and post-processing conditions, all of which were systematically controlled to ensure reproducibility and reliability of the final components. In the following figures, the name for different composition is labeled as P_MRS%* in which P represent the PEKK matrix and MRS%* determine the weight percentage of MRS in that composition.

5.4.1.1 Martian Regolith Simulant (MRS) Particle Study

Figure 5.2 and Figure 5.3 provide an in-depth characterization of the MRS particles employed in this study.

Figure 5.2a presents particle size distribution curves for the MGS-1 grade, adapted from the supplier's datasheet [121], confirming the polydisperse nature and fine granularity of the sieved batches. After sieving, the true grain densities of each particle size fraction were determined using gas pycnometry, a technique that provides accurate measurements by eliminating pore volume effects. This density data is essential for calculating the theoretical density and volume fraction of

composites, both of which are key to porosity estimation and formulation design. As shown in Figure 2b, the true density exhibited a systematic decrease with reducing particle size: from 3.4 g/cm³ for the <100 μ m fraction to 3.2 g/cm³ for <50 μ m, and down to 2.9 g/cm³ for the <20 μ m batch. This trend indicates that finer particles possess lower intrinsic densities, likely due to increasing proportions of lower-density phases or more porous particle morphologies. SEM images at 200X, 300X, and 1000X magnifications (Figure 3a) validate the effectiveness of the sieving process, confirming controlled particle separation. The MRS particles display heterogeneous morphologies, comprising angular, rough-surfaced grains and rounded, perforated tubular structures. The size distribution spans from the nanometer to micrometer scale, consistent with vendor specifications. Interestingly, the proportion of perforated tubular particles increases in finer fractions, whereas coarser batches (<100 μ m) are dominated by sharp-edged, irregular particles. This morphological evolution with decreasing particle size helps explain the observed reduction in bulk density. While angular particles may interfere with extrusion and compromise mechanical interlocking with the matrix, perforated structures offer the potential for mechanical “hooking” if the polymer matrix infiltrates their internal voids, potentially improving load transfer. To elucidate the chemical nature of these particles, Figure 3b presents EDS elemental mapping of the <20 μ m fraction. The results reveal that most fine particles are silicon-rich and exhibit perforated geometries, while coarser particles predominantly consist of aluminum-based compounds. A smaller population of iron-rich particles is also observed, adding to the mineralogical diversity of the regolith simulant.

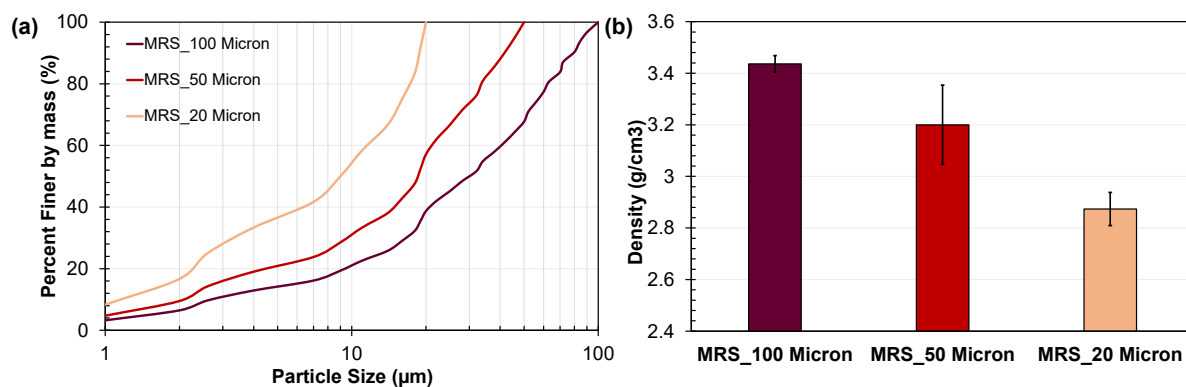


Figure 5.2. Characterization of Martian Regolith Simulant (MRS) particles: (a) Particle size distribution curve of MGS-1 grade as MRS, adapted from [121], (b) Comparison of MRS particle densities measured via gas pycnometry.

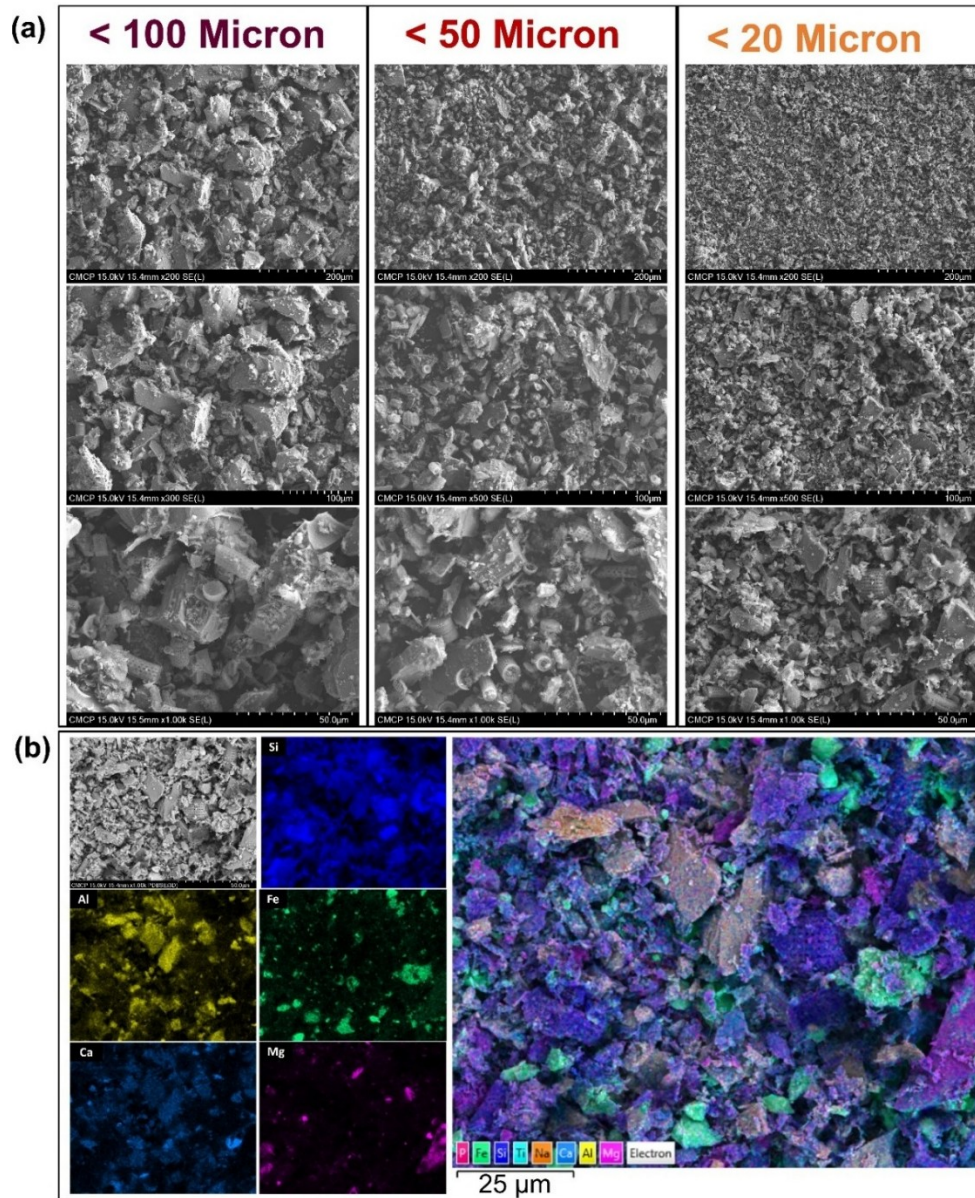


Figure 5.3. Characterization of MRS particles via SEM imaging: a) SEM micrographs of each MRS batch captured at three magnification levels, confirming the targeted particle size ranges post-sieving, with a noticeable increase in perforated tubular particles at finer sizes, b) EDS elemental mapping of the <20 µm MRS batch, illustrating that the majority of fine particles consist of perforated silicon-based structures.

5.4.1.2 Filament, 3D Printing, and Post-Process Manufacturing Challenges

During filament production across all three MRS compositions, no nozzle clogging was encountered, and continuous, uniform filaments were successfully wound onto spools for

subsequent 3D printing. However, a noticeable increase in the torque required to operate the twin-screw extruder was observed when transitioning from the 20 wt% to the 30 wt% MRS formulations. Interestingly, despite the higher filler content, the surface finish of the extruded filaments became progressively smoother as finer MRS particles were incorporated.

During the 3D printing process, no nozzle blockage occurred, largely due to the use of a 0.8 mm nozzle across all compositions, which effectively accommodated both the coarser, low-content MRS blends and the finer, high-content formulations. Furthermore, no warping or dimensional distortion was observed in any of the printed specimens.

A key challenge emerged during post-processing: the expansion of air voids between deposited filament strands, a known characteristic of material extrusion-based additive manufacturing. This void expansion behavior differed between low and high MRS loadings and was influenced by whether continuous flow channels existed between the strands. For annealing to initiate cold crystallization in semi-crystalline thermoplastics, the material must be heated beyond its glass transition temperature (T_g) [2,17]. In regions lacking open pathways, trapped air expands upon heating, generating larger voids as the polymer softens past T_g . Conversely, open-channel configurations allow for outgassing, promoting more stable interlayer fusion. While crystallization inherently leads to material shrinkage [36], this dimensional reduction predominantly occurred in the longitudinal and transverse directions. However, the expansion of inter-strand voids during annealing had a more pronounced effect on overall thickness, often resulting in a net increase in sample thickness. Notably, the extent of these dimensional changes varied among compositions due to differences in MRS content, porosity, and the rheological softening behavior of the composite.

Overall, these findings highlight the critical importance of optimizing regolith loading, extrusion conditions, and post-processing strategies to reduce structural defects, achieve dimensional precision, and improve the mechanical performance of PEKK/MRS composite components.

5.4.1.3 Filler Weight Content Evaluation

TGA was performed to assess the thermal degradation behavior of the composite filaments and to verify the actual MRS content in each formulation. As illustrated in Figure 5.4a, neat PEKK

displayed a single-phase degradation pattern, characterized by high thermal stability with degradation onset above 550 °C. In contrast, pure MRS remained stable throughout the tested temperature range, owing to its composition of inert mineral oxides. The PEKK/MRS composite filaments exhibited a two-step degradation profile: the first weight loss phase corresponded to the decomposition of the PEKK matrix, while the subsequent residual weight, which became more pronounced at higher filler contents, was attributed to the thermally stable MRS fraction.

To validate the formulation accuracy, the residual mass measured at 800 °C was used to estimate the effective MRS content in each sample using Eq. (5.1), as shown in Figure 5.4b. The experimental residue values aligned closely with the intended filler loadings, confirming the successful and uniform integration of MRS into the PEKK matrix during extrusion. Given the typical TGA measurement margin of error ($\pm 1\%$), the calculated MRS content should be considered approximate but nonetheless provides a reliable check that the formulations remained within the expected target range. Notably, as the MRS content increased and particle size decreased, the measurement error further diminished, indicating improved homogeneity within the composite system. Minor discrepancies may arise from factors such as residual MRS particles adhering inside the extruder barrel, inherent TGA precision limits, or local variations in filler distribution affecting homogeneity and measurement.

Overall, the TGA findings demonstrate that the composite filaments retain adequate thermal stability for extrusion processing and effectively achieve the desired filler incorporation across all tested compositions.

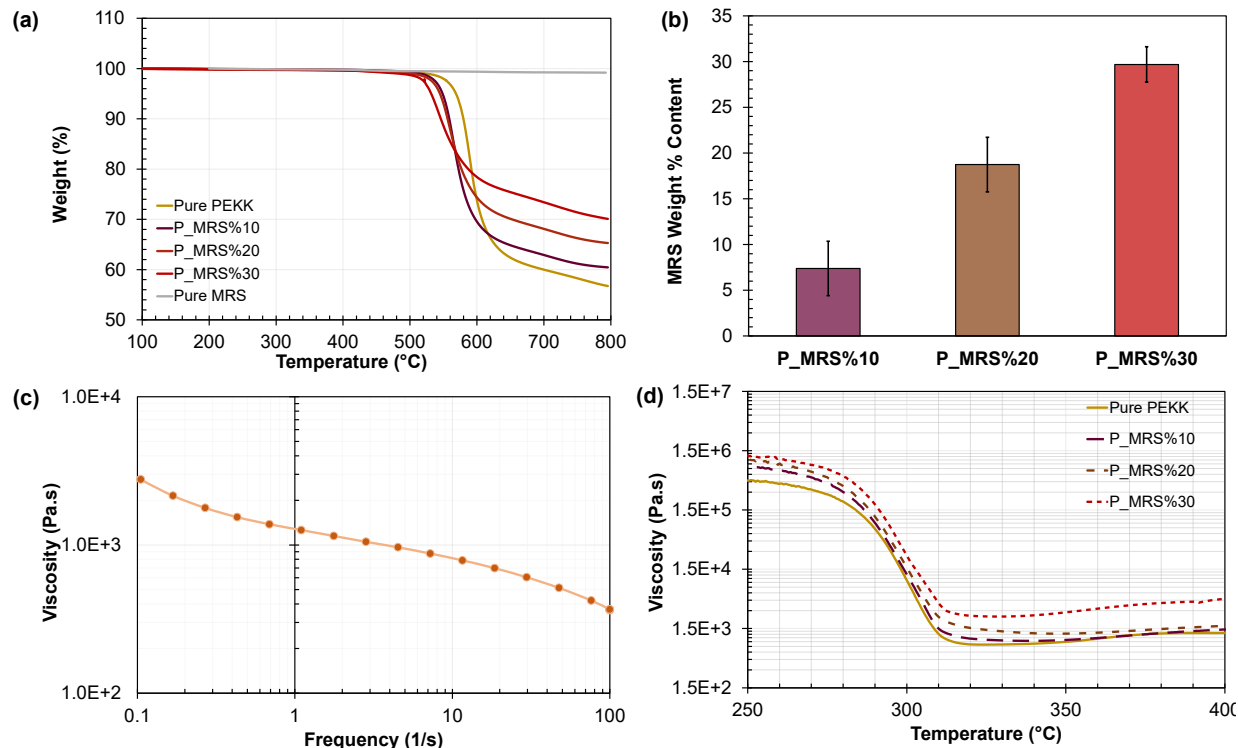


Figure 5.4. Filament manufacturing quality assessment through TGA analysis and rheological characterization of PEKK/MRS composite: a) TGA curves of neat PEKK, pure MRS, and PEKK/MRS composite filaments, confirming the thermal stability of the composite system across different formulations, b) Estimated MRS weight fractions in the composite filaments based on residual mass analysis, c) Frequency sweep of neat PEKK at 330 °C, revealing a region of minimal frequency sensitivity near 1 Hz, d) Temperature sweep of composite filaments containing 0 to 30 wt% MRS at a fixed frequency of 1 Hz, showing a pronounced increase in viscosity for formulations with ≥ 20 wt% MRS beyond the crystal–melt transition (~ 300 °C).

5.4.1.4 Rheological Assessment

Rheological analysis of the PEKK/MRS composites was carried out to evaluate their processability during filament extrusion and 3D printing. As shown in Figure 5.4c, a frequency sweep test was first conducted on neat PEKK at 330 °C, corresponding to the melt temperature at the die exit of the micro-extruder. The resulting viscosity profile exhibited a plateau region near 1 Hz, where the slope of the curve approached zero, indicating minimal sensitivity to shear rate and a stable flow regime. Based on this observation, 1 Hz was selected as the reference frequency for subsequent temperature sweep measurements to ensure consistent and meaningful comparisons across all composite formulations.

Figure 5.4d illustrates the temperature-dependent viscosity behavior of composite filaments with MRS loadings ranging from 0 to 30 wt%. As the temperature increased from 250 °C to 390 °C, all formulations showed a gradual decrease in viscosity up to the crystal-melt transition temperature (~300 °C). However, composites containing 30 wt% MRS displayed a pronounced “viscosity jump” beyond the cold crystallization and melting peak, with viscosity values rising to two to three times those of lower-filled systems. This abrupt increase is likely attributed to the structural interactions and rearrangements of the ceramic filler at elevated temperatures, which hinder polymer chain mobility and elevate melt resistance. These rheological findings are consistent with the observed rise in extrusion torque during filament production at higher MRS concentrations and provide a clear explanation for the processing difficulties encountered when manufacturing highly filled PEKK/MRS composites.

5.4.1.5 Microstructural Analysis and Particle Dispersion

To evaluate the microstructural distribution of MRS particles and the development of porosity within the PEKK/MRS composite filaments, cross-sectional SEM imaging was conducted on samples with varying MRS loadings, as shown in Figure 5.5. The analysis revealed a uniform dispersion of MRS particles throughout the PEKK matrix, with no signs of agglomeration or phase separation, even at elevated filler contents. Micro-porosity was observed only in the 30 wt% formulation, as demonstrated in Figure 5.7a, suggesting that higher filler concentrations may begin to challenge the packing and flow behavior of the composite. These results highlight the effectiveness of the twin-screw extrusion process in producing well-dispersed, structurally consistent filaments, reinforcing its potential for scalable manufacturing of regolith-based composites.

In addition to qualitative assessments, quantitative image analysis was performed to determine the volume fraction of MRS in each formulation. A grayscale thresholding method was applied to the SEM micrographs, allowing the ceramic filler phase to be distinguished from the surrounding polymer matrix. The analysis was conducted across several magnification levels and averaged to obtain representative values. The calculated volume fractions closely matched theoretical predictions derived from the relationship between mass fractions and material densities (as defined in Eq. (5.2)), which supports the conclusion that the composites achieved accurate and homogeneous filler incorporation. This agreement is illustrated in Figure 5.5b, and further supported by physical density measurements of the filaments and corresponding 3D-printed

samples, as shown in Figure 5.5c. Porosity levels, calculated from the discrepancy between theoretical and measured densities, are presented in Figure 5.5d and corroborate the structural observations made through SEM.

To further validate the composition and distribution of MRS particles within the matrix, EDX mapping was conducted (Figure 5.6). The EDX spectra confirmed the presence of silicon, aluminum, iron, magnesium, calcium, and sodium, all appearing as oxides embedded in a carbon-rich matrix associated with PEKK. EDX maps generated for 10%, 20%, and 30% MRS composites revealed an increase in elemental signal intensity proportional to filler content, with consistent spatial dispersion and no signs of clustering or particle accumulation. The dominant carbon signal from the matrix decreased progressively with increasing MRS content, from 77.8 wt% in the 10 wt% sample to 68.6 wt% in the 30 wt% sample, reflecting the increasing replacement of polymer with mineral filler. Silicon and aluminum were found to be the most prevalent elements by both weight and spatial coverage, indicating their prominence in the MRS composition. Additionally, co-localization of silicon and calcium signals suggests the likely presence of calcium silicate phases, which are commonly associated with Martian regolith.

The analysis also explored the interaction between PEKK and the perforated tubular particles found within the fine MRS fraction. Figure 5.7b presents a cluster of these particles in their raw state, absent of matrix, displaying longitudinal and circumferential perforations at the nanoscale. Figure 5.7c provides visual evidence that PEKK infiltrates these porous interiors during processing, suggesting a mechanical interlocking or “hooking” mechanism that may enhance interfacial bonding and improve mechanical performance. The elemental composition of these particles was confirmed via EDX mapping in Figure 5.7d, showing exclusive signals of silicon and oxygen, consistent with pure silicon oxide structures.

Together, these findings confirm the success of the extrusion and printing processes in producing composites with controlled filler distribution and morphology. The combined SEM and EDX analyses provide strong evidence of uniform dispersion, effective matrix-filler integration, and potential microstructural reinforcement via perforated particles, which collectively contribute to the reliability and performance of the PEKK/MRS composite system.

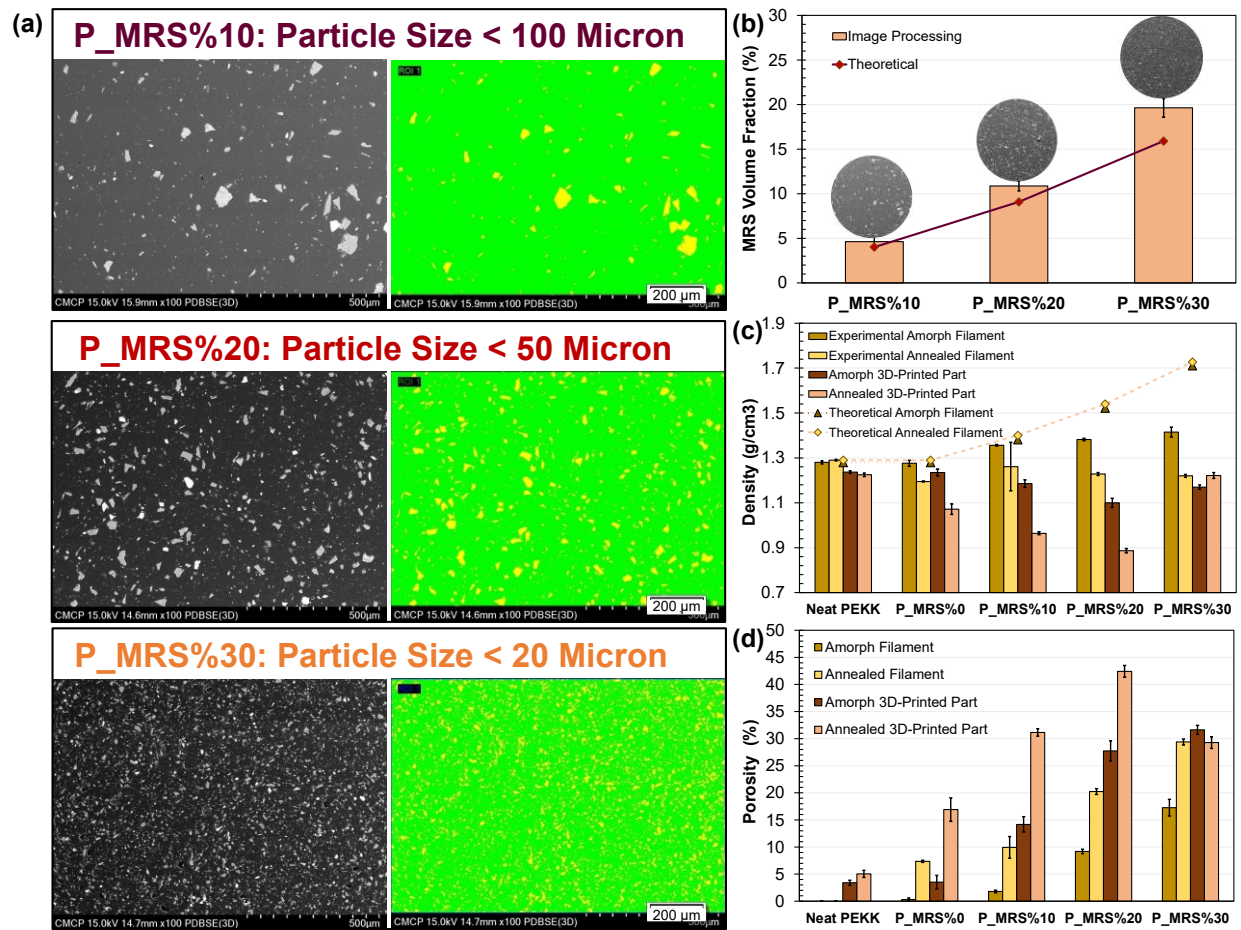


Figure 5.5. Microstructural and physical characterization of PEKK/MRS composite filaments and 3D-printed parts: a) Cross-sectional SEM images showing MRS particle dispersion in PEKK/MRS composite filaments with increasing MRS content; the right column presents representative image processing overlays used for MRS phase detection; b) Comparison between theoretical and SEM image-based estimations of MRS volume fraction across all filament compositions; c) Measured

densities of filaments and 3D-printed samples compared with theoretical density values; d) Calculated porosity for each filament and printed part.

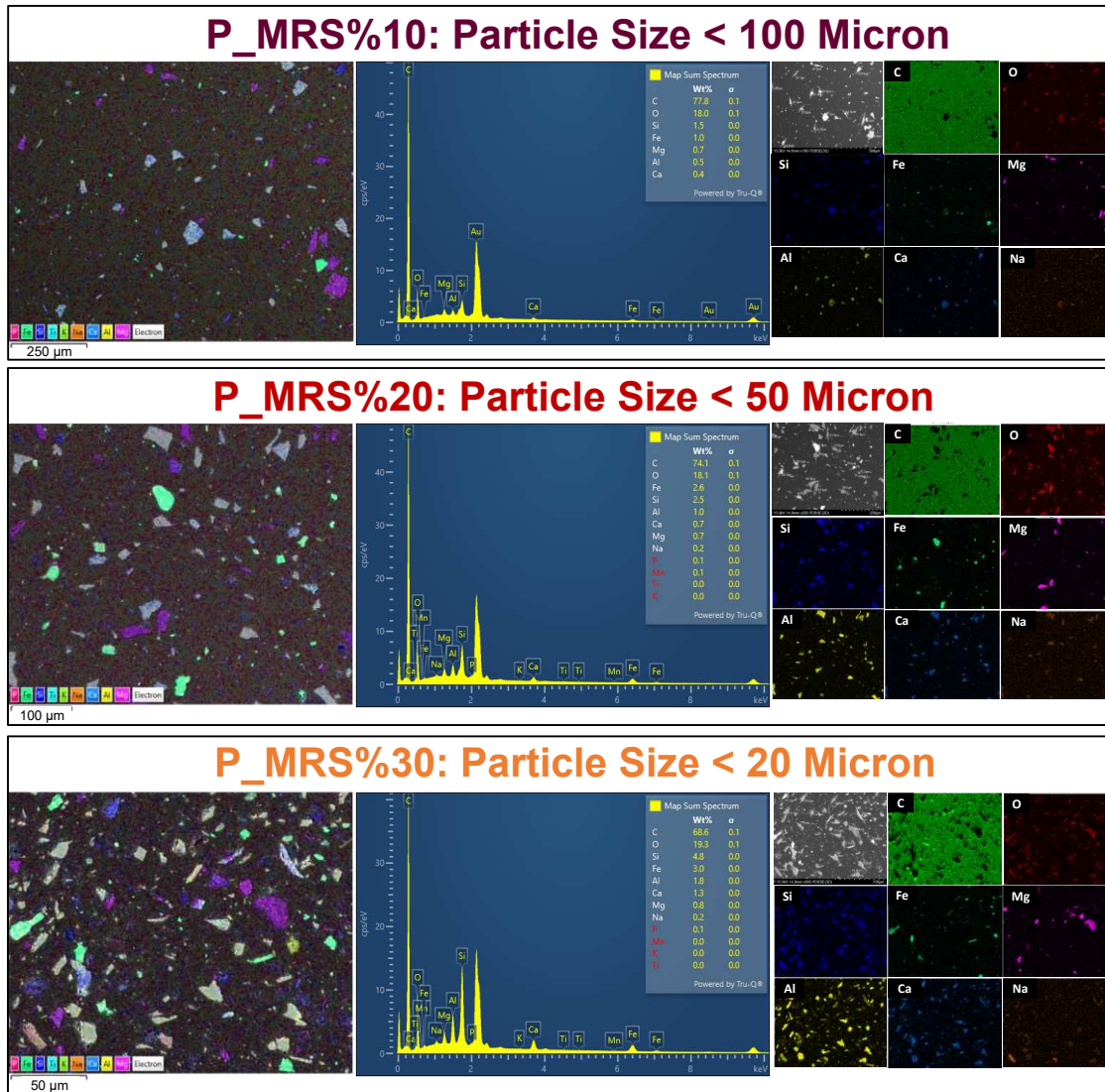


Figure 5.6. EDS analysis of PEKK/MRS composite filaments: EDS spectra and elemental mapping confirm the presence of key mineral oxides within the MRS phase; silicon and aluminum signals intensify with decreasing particle size and increasing MRS content, indicating a higher concentration of silicon-rich phases in finer particles.

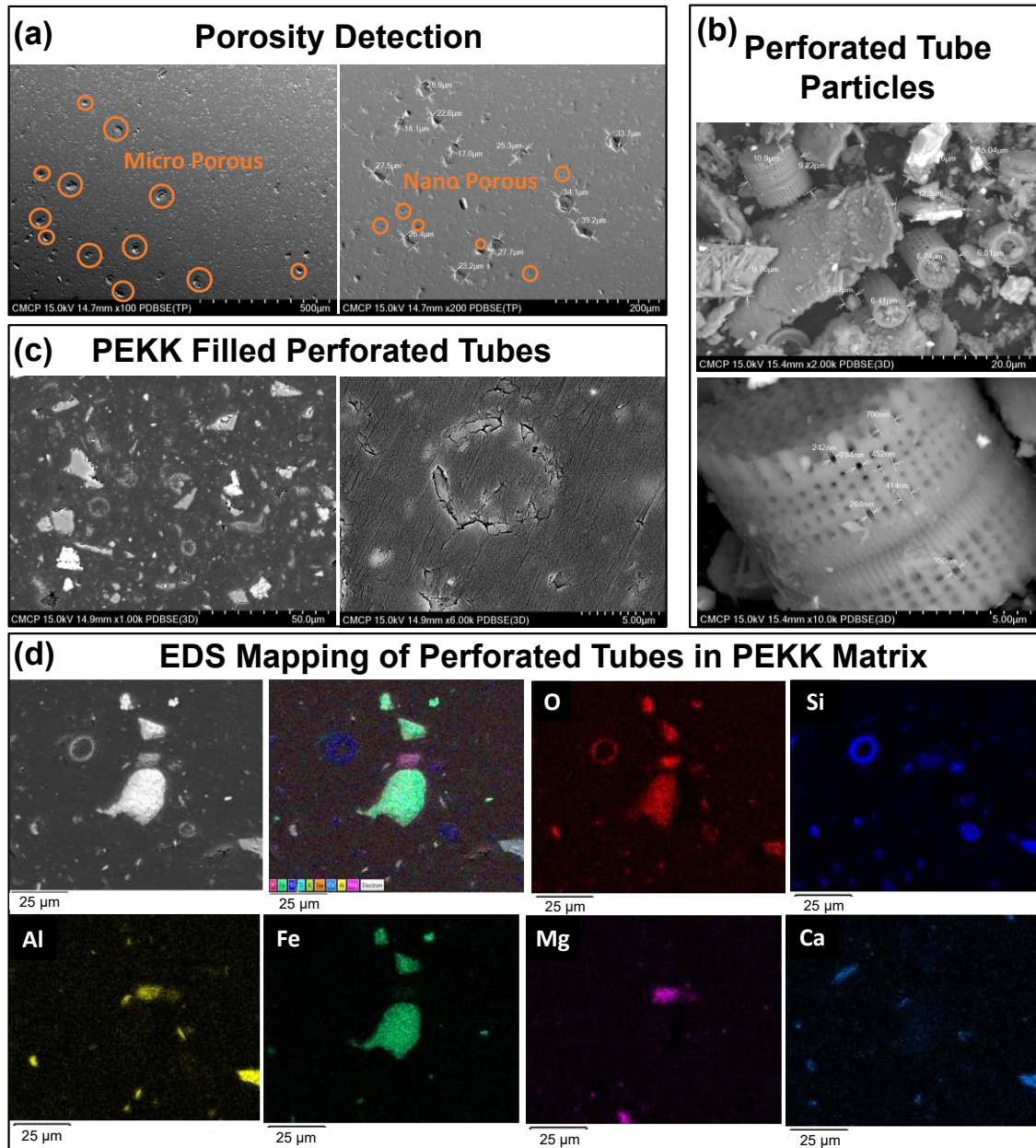


Figure 5.7. Microstructural observations of PEKK/MRS composite filaments highlighting interactions between the matrix and perforated MRS particles: a) Manufacturing defects observed in composite filaments with 30 wt% MRS with more pronounced microporosity; b) SEM images of perforated silicon-rich particles with hollow cylindrical morphologies with nano-scale perforations along both the circumferential and axial directions; c) Evidence of PEKK matrix infiltration into the hollow interiors of the perforated particles; d) Phase identification confirming that the PEKK-filled perforated structures are composed of silicon oxide.

5.4.2 Density & Porosity

To assess the volume fraction of MRS in each composite formulation, high-magnification SEM micrographs were analyzed through image processing, and the resulting experimental values were compared against theoretical predictions calculated using Eq. (5.2). These theoretical values were derived from the weight fractions of individual components and the solid-phase densities obtained via gas pycnometry, offering highly accurate measurements of material density. As depicted in Figure 5.5b, the comparison between the SEM-based estimations and the rule-of-mixtures calculations confirmed strong agreement across all compositions. This validation underscores the accuracy of both the image analysis approach and the theoretical model. Interestingly, a nonlinear rise in volume fraction was observed in the 30 wt% MRS composition, reaching 19.6%, a shift attributed to differences in the mean density of the MRS batches used across formulations. This deviation also explains the sudden increase in viscosity observed earlier (Figure 5.4d), suggesting that a critical concentration threshold governs flow behavior in these composites. Measured densities of the extruded filaments and the 3D-printed parts, both in amorphous and annealed states, are presented in Figure 5.5c. As expected, annealing caused a modest increase in density due to crystallization-induced densification. However, the density trends also reflected the combined effects of MRS loading, void formation during extrusion, and the presence of inter-strand gaps in the printed structures. To quantify these effects, porosity was calculated using the measured volume fraction data and theoretical void-free densities, with the results shown in Figure 5.5d. A general increase in porosity was evident with rising MRS content in the filament samples, largely due to the elevated melt viscosity of highly filled composites, which impairs vacuum-assisted degassing during extrusion and results in more trapped voids. The additive manufacturing process introduced further porosity, especially between adjacent extruded strands, a known limitation of MEX methods. Additionally, intra-strand porosity increased in the printed parts due to the relatively lower extrusion pressures and shear rates at the printer nozzle compared to those in the twin-screw micro-extruder, allowing entrapped air to expand and new voids to form during deposition. Thermal post-processing via annealing further affected porosity behavior.

To provide a clearer quantitative comparison, the calculated porosity values for all compositions are summarized as follows. For filaments, the porosity increased from 0 % for neat PEKK to 0.3 %, 1.8 %, 9.2 %, and 17.3 % for amorphous P_MRS%0, P_MRS%10, P_MRS%20, and P_MRS%30, respectively. After annealing, the corresponding porosities rose to 0 %, 7.4 %, 9.9 %, and 17.3 %, respectively.

20.2 %, and 29.4 %, reflecting the effect of thermal expansion on entrapped voids. For 3D-printed parts, amorphous specimens exhibited porosity values of 3.4 %, 3.5 %, 14.2 %, 27.7 %, and 31.6 %, while annealed samples showed 5.1 %, 16.9 %, 31.2 %, 42.4 %, and 29.3 %, respectively.

In composites with up to 20 wt% MRS, porosity increased after annealing, primarily due to the expansion of trapped voids within the softened PEKK matrix. However, this trend reversed for the 30 wt% MRS formulation, where porosity decreased after annealing. In these highly filled systems, the increased stiffness and viscosity appeared to restrict pore expansion, while crystallization enhanced matrix densification. Consequently, annealing served as an effective densification mechanism at high filler loadings, reducing porosity and potentially enhancing mechanical integrity. These results collectively demonstrate the complex interplay between filler concentration, processing conditions, and thermal treatment in determining the final density, porosity, and structural quality of PEKK/MRS composites. The numerical data align well with the qualitative observations from SEM fracture-surface imaging and the porosity trends presented in Figure 5.14a.

5.4.3 *Mechanical, Thermomechanical Properties*

In the 0° orientation, tensile testing of amorphous samples revealed a transition from ductile to brittle behavior with increasing MRS content. As shown in Figure 5.8a, neat PEKK demonstrated the highest tensile strength at 86.9 MPa, which decreased sharply to 67.5 MPa and 48.5 MPa for 10 wt% and 20 wt% MRS, respectively. Beyond 20 wt%, the decline in strength plateaued, with 30 wt% MRS samples maintaining a similar tensile strength of 46.3 MPa. Simultaneously, elongation at break and toughness decreased consistently due to the presence of rigid MRS particles, which acted as stress concentrators and impaired plastic deformation.

Annealing had a significant effect on the tensile properties. For neat PEKK, it enhanced tensile strength, while for composites containing up to 20 wt% MRS, strength decreased following annealing, correlating with the increased porosity observed in earlier analysis (Figure 5.5d). Interestingly, the 30 wt% MRS composite showed improved tensile strength after annealing, attributed to reduced porosity for this composition. Regardless of filler content, annealing reduced toughness and increased brittleness, confirming the embrittling effects of both filler addition and thermal post-processing.

For samples printed at 90°, all amorphous specimens fractured in a brittle manner, but differences in stress–strain behavior were noted between neat PEKK and MRS-filled composites (Figure 5.8b). Pure PEKK fractured abruptly with no stabilization phase, while MRS-containing samples exhibited a near-horizontal plateau prior to failure. This suggests that MRS particles delayed interlayer failure, likely by bridging adjacent strands and postponing delamination. Despite creating local stress concentrations, these particles appeared to improve interlayer cohesion.

Post-annealing, all 90°-oriented samples showed sudden brittle failure at the end of their stress–strain curves, with tensile strengths ranging between 40–50 MPa. The annealed P_MRS 0% sample had the lowest strength, which was linked to filament diameter variations from in-house fabrication. In the 90° orientation, even minimal under-extrusion can critically weaken a part, as load-bearing depends heavily on the weakest layer. Polymer shrinkage during annealing further undermines interlayer adhesion at these points. Although flow rate adjustments could mitigate this issue, all specimens in this study were produced under identical processing conditions for consistency.

Toughness trends in 90° orientation revealed that the addition of MRS slightly delayed fracture and improved energy absorption, suggesting a modest toughening effect despite the ceramic inclusions. These findings were further supported by flexural tests performed on 0° printed samples, as shown in Figure 5.9a. In the amorphous state, composites up to 20 wt% MRS demonstrated good ductility under bending, enduring strains up to 10% without fracturing. At 30 wt%, however, brittle failure occurred before reaching that threshold.

Annealing made all compositions stiffer and more brittle. Only neat PEKK and 0% MRS composites retained some plastic deformation. After annealing, flexural strength for neat PEKK increased from 126.9 MPa to 150.3 MPa (18.4% gain), and for the 10 wt% MRS composite, from 93.6 MPa to 110.9 MPa (18.5% gain). Higher MRS loadings (20–30 wt%) showed minimal improvements, under 3%, indicating diminishing reinforcement returns at elevated regolith content. Flexural toughness decreased sharply with increasing MRS content and was further reduced after annealing, reinforcing the embrittling effects of both ceramic fillers and thermal processing.

In the 90° orientation, flexural results (Figure 5.9b) mirrored tensile findings. MRS particles delayed failure and slightly improved toughness by transforming the fracture profile from abrupt to more gradual. However, at higher filler content, both strength and toughness declined due to the rigid ceramic phase. The P_MRS%0 sample again showed lower strength, linked to under-extrusion during filament production. Unlike tensile tests, flexural tests are less affected by single weak strands due to the mixed tension–compression loading, which explains why annealing improved flexural strength in this specific case.

A closer examination of Figure 5.9b shows that flexural strength increased from 68.9 MPa for neat PEKK to 76 MPa for the 10 wt% MRS composite in the amorphous state, but declined to 62 MPa and 58.9 MPa at 20 wt% and 30 wt% MRS, respectively. This trend coincides with the sharp rise in volume fraction from 20% to 30 wt%, nearly doubling the ceramic content. While this increase would typically degrade performance, the choice of finer, perforated MRS particles appears to provide some mechanical interlocking benefits that mitigate the loss.

Post-annealing, all compositions showed decreased toughness. Flexural strength increased across most formulations, except for P_MRS%20, which had the highest porosity and thus failed to benefit from the added crystallinity. This result highlights the delicate balance between reinforcement and processing-induced defects in determining final mechanical properties.

To further examine thermomechanical performance, DMA was performed on both amorphous and annealed samples printed at 0° and 90°, as shown in Figure 5.10 and Figure 5.11. Across all samples and orientations, storage modulus, loss modulus, and tan delta trends were remarkably consistent, indicating that the PEKK/MRS composites behave nearly isotropically within the elastic region. In the amorphous state, storage modulus dropped sharply near the glass transition (~150–160 °C), consistent with softening. This transition was accompanied by distinct peaks in tan delta, confirming a highly viscoelastic behavior. All compositions exhibited similar tan delta peaks, suggesting that damping is primarily dictated by the polymer matrix, not the filler content.

The most prominent differences appeared between amorphous and annealed samples. After annealing, the tan delta peak dropped from ~2.5 to ~0.5, indicating reduced segmental mobility and increased stiffness from crystallization. Amorphous samples showed two tan delta peaks, one

for the glass transition and another for cold crystallization ($\sim 200\text{--}250\text{ }^{\circ}\text{C}$). In contrast, annealed samples displayed only a single peak at T_g , confirming complete crystallization.

Despite variability in porosity among the samples, general trends in storage and loss modulus aligned with filler content and void volume. Higher MRS content led to a rightward shift in all thermal transition temperatures, reflecting improved thermal resistance due to the ceramic phase limiting chain mobility. Finally, all annealed samples and amorphous specimens with 30 wt% MRS showed excellent dimensional stability after DMA testing, with no visible deformation even at high temperatures. This highlights the combined effectiveness of thermal post-processing and filler incorporation in enhancing the high-temperature performance of PEKK composites.

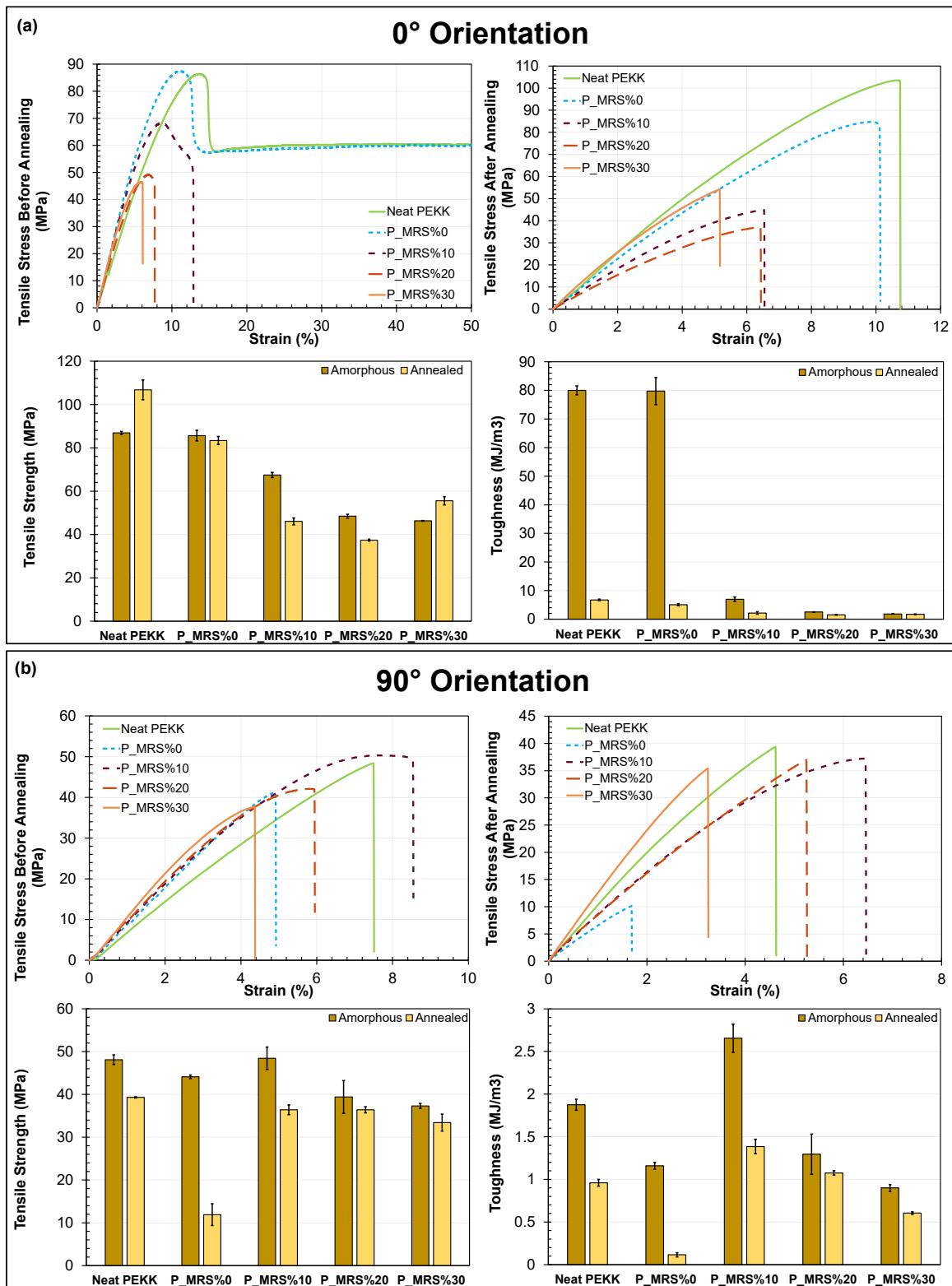


Figure 5.8. Tensile properties of 3D-printed pure PEKK and PEKK/MRS composites before and after annealing, printed at a) 0° orientation, b) 90° orientation. Standard deviation calculated upon 5 replications.

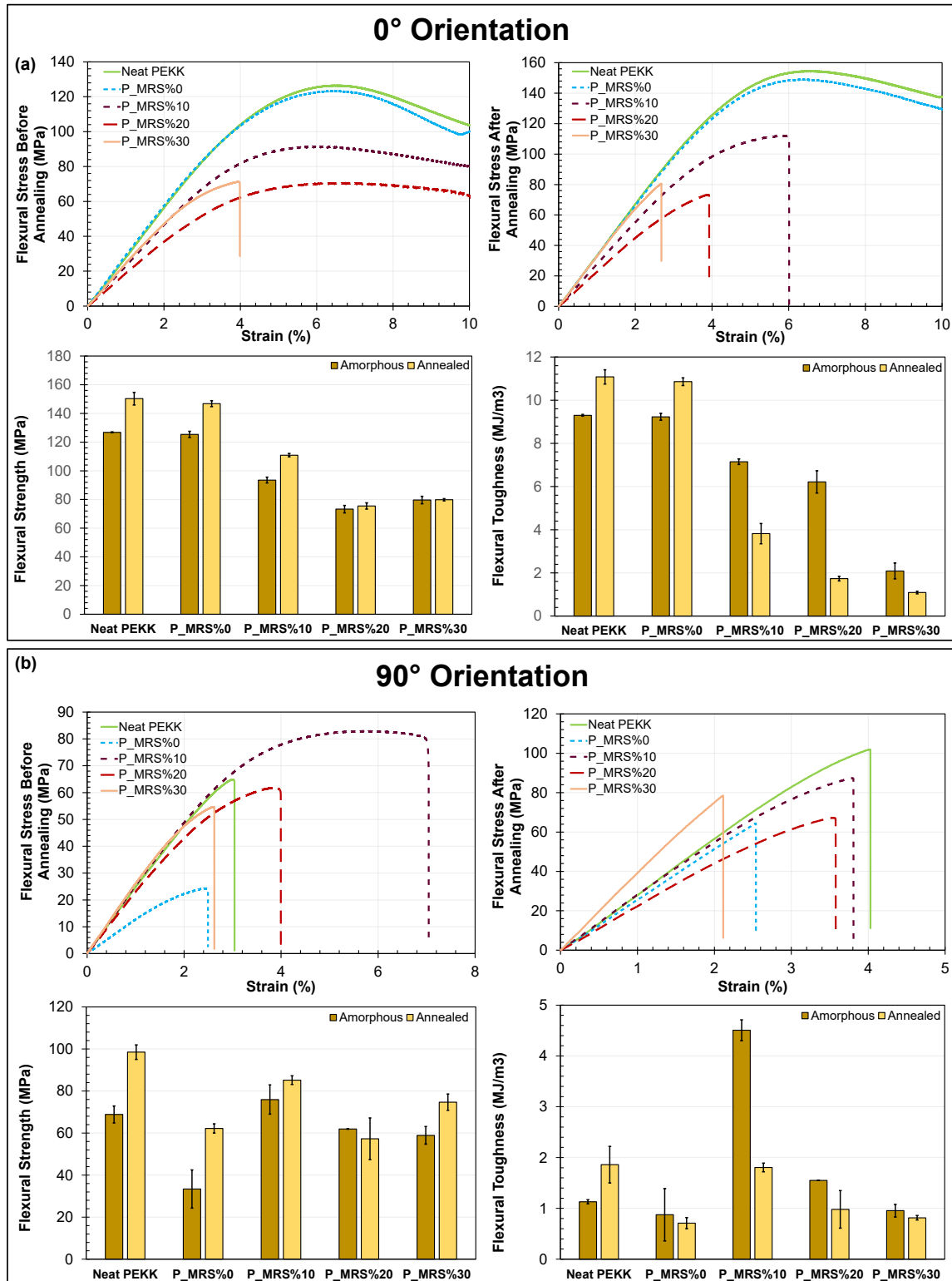


Figure 5.9. Flexural performance of 3D-printed pure PEKK and PEKK/MRS composites before and after annealing, printed at: a) 0° orientation, b) 90° orientation. Standard deviation calculated upon 5 replications

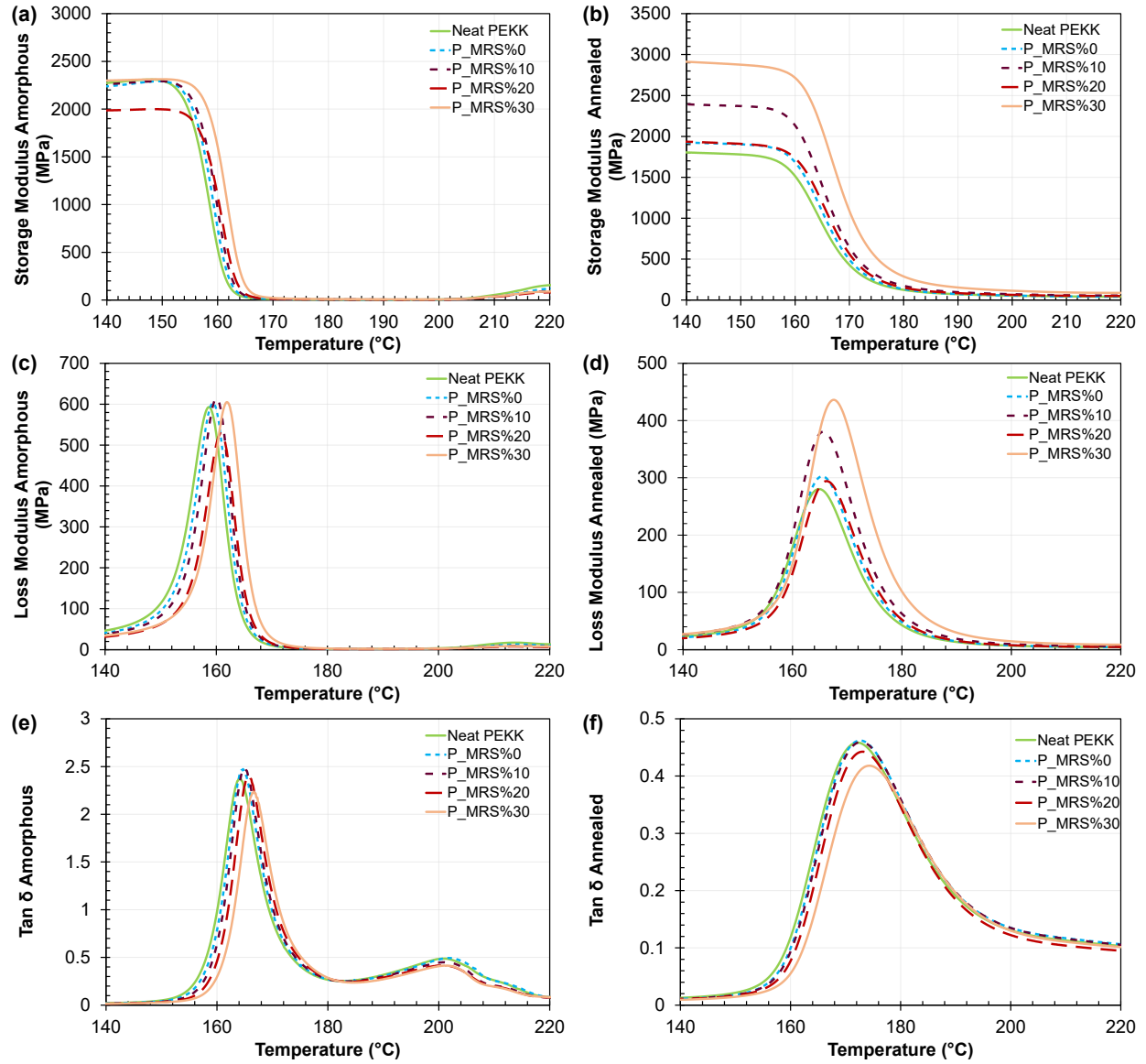


Figure 5.10. DMA results of PEKK/MRS composites printed at 0° orientation, comparing different compositions in the amorphous (left) and annealed (right) states: (a, b) Storage modulus (E') of amorphous and annealed samples, respectively; (c, d) Loss modulus (E'') of amorphous and annealed samples; (e, f) Loss tangent ($\tan \delta$) of amorphous and annealed samples.

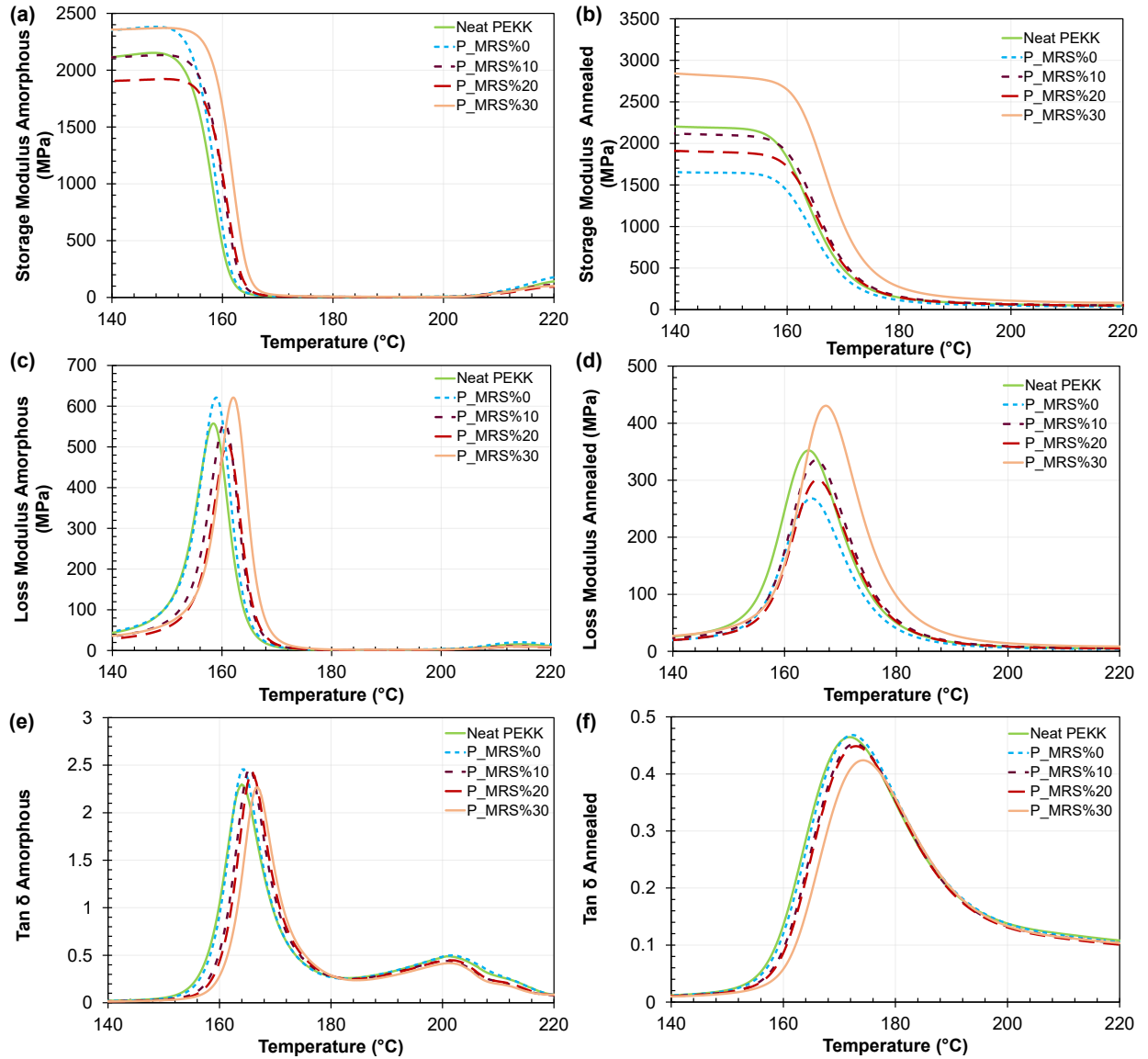


Figure 5.11. DMA results of PEKK/MRS composites printed at 90° orientation, comparing different compositions in the amorphous (left) and annealed (right) states: (a, b) Storage modulus (E') of amorphous and annealed samples, respectively; (c, d) Loss modulus (E'') of amorphous and annealed samples; (e, f) Loss tangent ($\tan \delta$) of amorphous and annealed samples.

5.4.4 Fractography and Failure Mechanisms

It should be noted that cross-sectional SEM imaging of the 3D-printed parts was not feasible because of their high porosity and the abrasive nature of MRS particles, which complicates surface preparation. The absence of resin infiltration into closed pores results in insufficient material support during polishing, while the removal of hard regolith particles can distort the surrounding

void geometry. Consequently, fracture-surface SEM imaging was adopted to qualitatively compare porosity and interlayer morphology between compositions and thermal conditions. This approach, combined with Archimedes density measurements, provided reliable insight into the evolution of porosity.

Fractographic analysis was conducted on tensile specimens printed at both 0° and 90° orientations for all compositions in amorphous and annealed states to investigate the failure mechanisms and validate the proposed interlayer reinforcement behavior. Across all annealed samples, a predominantly brittle fracture mode was observed, consistent with the stiffness increase induced by post-crystallization.

In the 0° orientation (Figure 5.12), SEM imaging revealed that the incorporation of Martian Regolith Simulant (MRS) particles promoted fusion and diffusion between adjacent extruded strands, to the extent that the boundary lines between printed roads became indistinguishable. This effect intensified as particle size decreased and MRS content increased, resulting in more homogeneous inter-strand bonding. Notably, at high filler loadings, the fracture surfaces of amorphous and annealed samples appeared morphologically similar, suggesting that failure mode was governed primarily by MRS content rather than thermal history.

For the 90° orientation (Figure 5.13), fracture surfaces of neat PEKK showed a typical pull-out pattern and clean separation along inter-layer interfaces, whereas the composites exhibited a progressive disappearance of this feature. In MRS-containing samples, particles were observed bridging adjacent layers, indicating improved heat conduction and interlayer fusion. However, as the MRS content increased, the rise in viscosity during extrusion led to small dimensional variations in filament diameter. In 90° prints, these variations manifested locally as under-extrusion regions, not due to poor adhesion but to flow sensitivity at high viscosity, while the overall fusion quality visibly improved through particle-mediated bonding.

The evolution of porosity with MRS content and annealing, shown in Figure 5.14a, further supports this interpretation. Increasing filler content and decreasing particle size produced a more uniform and thermally stable pore structure, where pore geometry remained unchanged after annealing, reflecting the higher viscosity and resistance to softening above T_g. Conversely, low-

filler composites exhibited pronounced pore expansion and rounding, consistent with void growth during annealing.

Finally, high-magnification SEM images in Figure 5.14b confirmed that the perforated tubular silica particles were filled with PEKK matrix material, validating the proposed hooking mechanism. These particles acted as mechanical anchors, improving stress transfer and interfacial adhesion relative to irregular, non-perforated regolith particles. Collectively, these observations provide direct evidence that the incorporation of fine, perforated MRS particles enhances inter-layer bonding, mitigates delamination, and stabilizes the porosity structure through both mechanical interlocking and thermal-viscous effects.

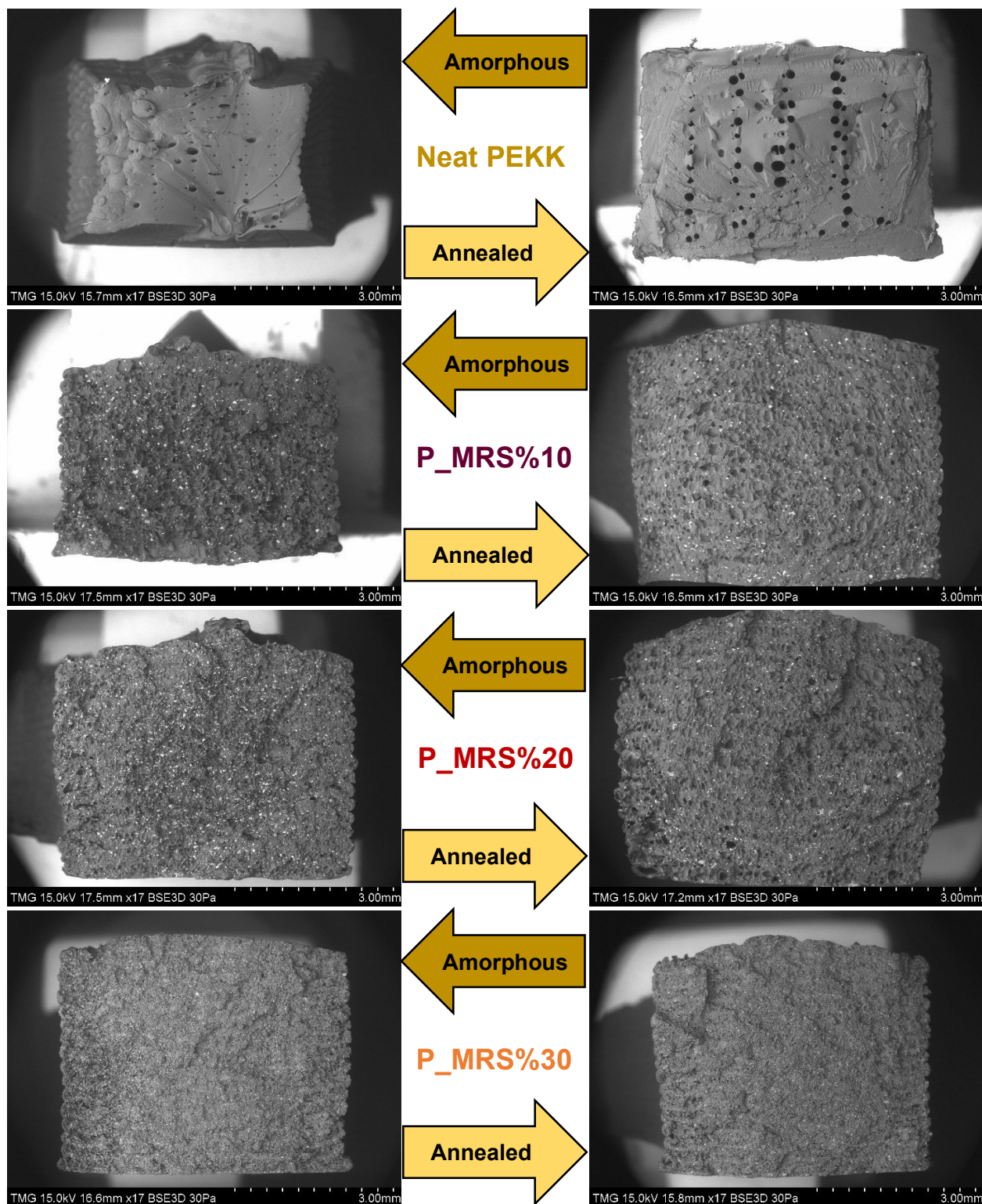


Figure 5.12. Fractography of tensile specimens printed at 0° orientation.

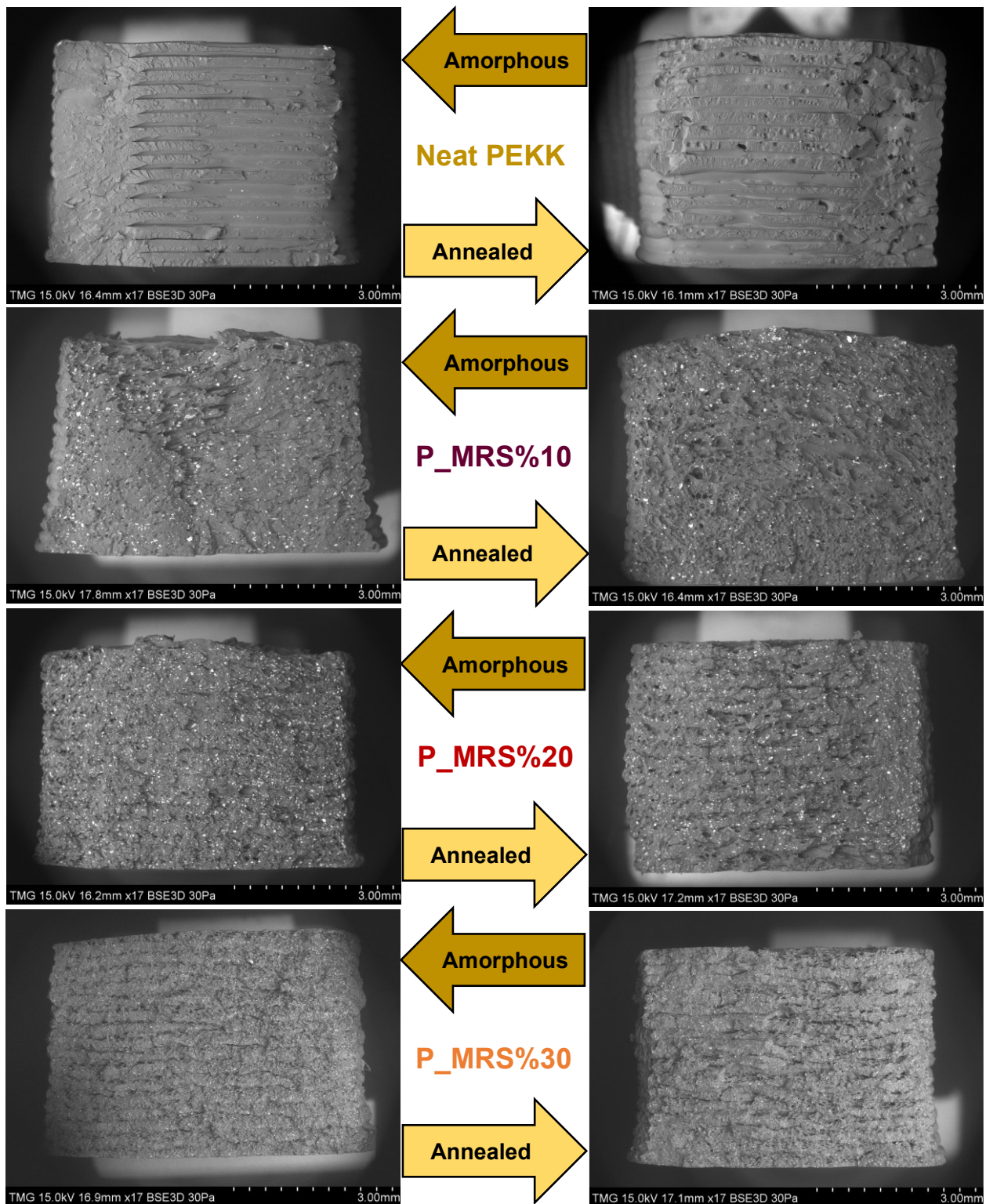


Figure 5.13. Fractography of tensile specimens printed at 90° orientation.

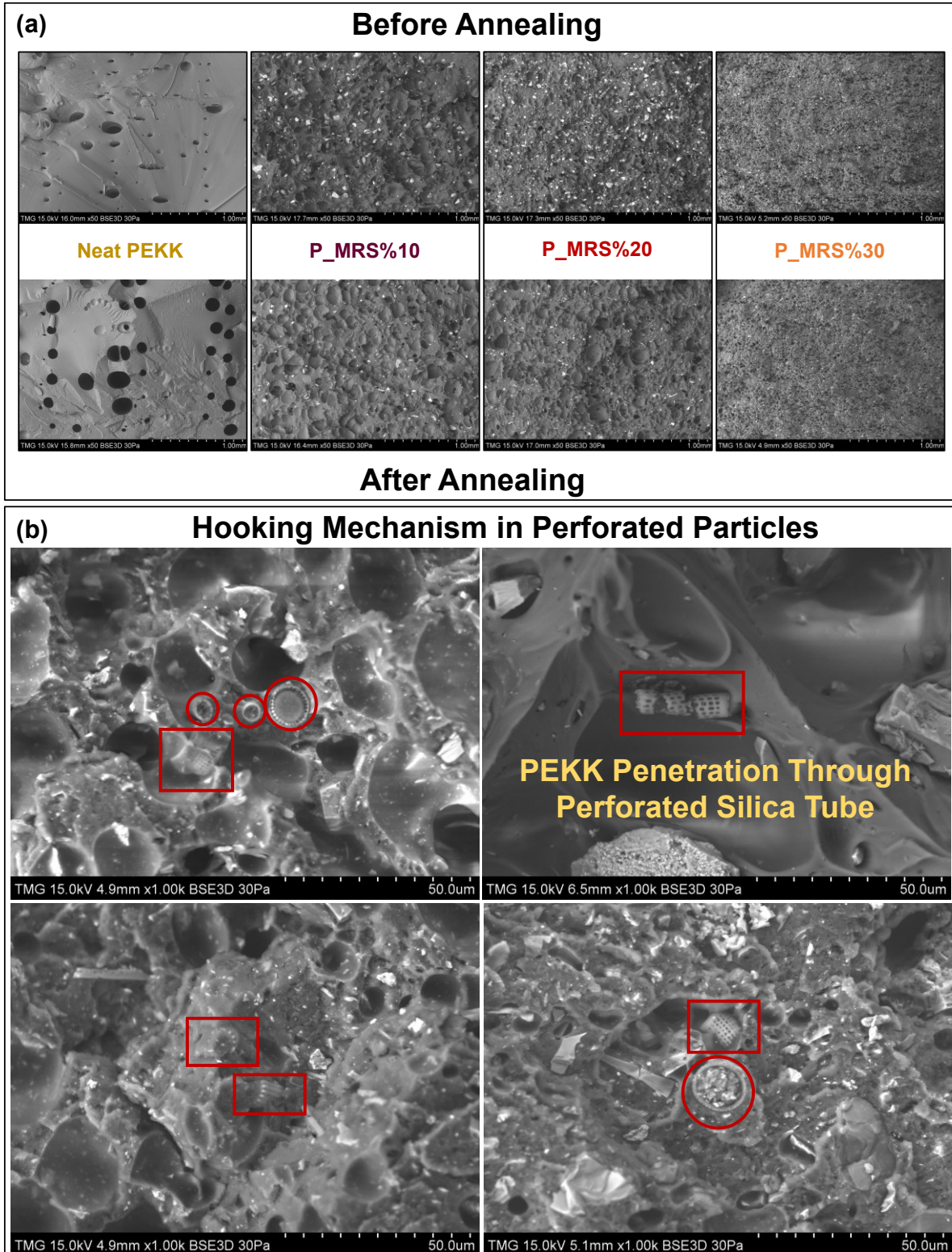


Figure 5.14. High-magnification SEM images for: (a) Comparison of porosity evolution before and after annealing for all PEKK/MRS compositions, (b) confirming the hooking mechanism: perforated tubular silica particles are infiltrated by the PEKK matrix

5.4.5 Mathematical Model Validation

To evaluate the predictive accuracy of the developed mathematical model for tensile strength in PEKK/MRS composites printed at 0° orientation, experimental data from the 3D-printed specimens were compared to the model outputs, as shown in Figure 5.12. The model integrates three main factors influencing tensile performance: the theoretical MRS volume fraction (Figure 5.5b), the experimentally determined porosity levels (Figure 5.5d), and the fracture behavior (ductile or brittle), inferred from the tensile stress–strain curves in Figure 5.8a.

Figure 5.15a presents the comparison for the amorphous samples. A close match was observed between predicted and measured tensile strength at low MRS loadings (0–10 wt%). At 20 wt% MRS, the material exhibited a transition from ductile to semi-brittle fracture, as reflected in the model outputs. At even higher filler contents (≥ 20 wt%), the exponential model maintained reasonable predictive accuracy, although it slightly underestimated the tensile strength at 30 wt% MRS, likely because the reinforcing effect of the perforated filler particles was not explicitly incorporated. Despite this, the model effectively captured the overall declining trend in tensile strength, supporting its validity for systems predominantly governed by brittle failure mechanisms.

Under annealed conditions (Figure 5.15b), the model continued to show strong agreement with the experimental data for the neat PEKK and P_MRS%0 samples, particularly regarding the impact of porosity. However, in intermediate MRS compositions (10–20 wt%), discrepancies emerged, attributed to the combined effects of void expansion, their geometry, and the presence of larger regolith particles. While crystallization generally enhances strength, this benefit was offset by the rise in porosity for these compositions. Notably, at 30 wt% MRS, the model's predictions aligned well with the experimental results, consistent with the observed reduction in porosity following thermal treatment (Figure 5.5d). Overall, the comparison demonstrates that the proposed model serves as a reliable framework for estimating tensile strength in 0°-oriented PEKK/MRS composites and provides a tool for guiding future optimization of filler content and porosity management in polymer-regolith systems intended for AM.

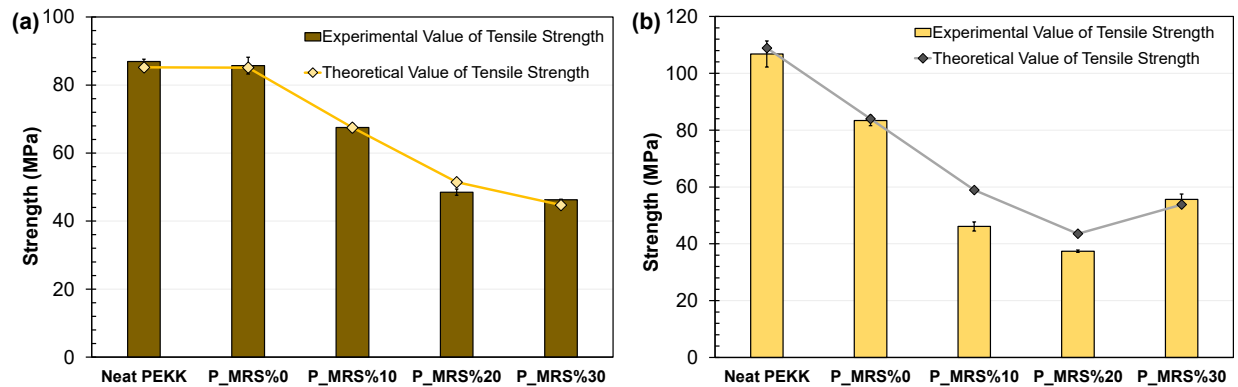


Figure 5.15. Comparison between experimental tensile strength and model predictions for PEKK/MRS 3D-printed composites at 0° orientation, incorporating the effects of filler content, measured porosity, and fracture behavior. The model demonstrates strong agreement with experimental data under both thermal conditions: (a) Amorphous samples, (b) annealed samples.

5.4.6 Operational relevance for Martian ISRU

Several process steps adapt directly to Martian constraints. Sieving is inherently dry and can be performed in a sealed, inert-purged enclosure to control dust. Our use of air cooling already aligns with water-limited operations. The build-plate adhesive employed in the laboratory can be replaced in practice by non-liquid adhesion strategies (textured PEI/PEEK build plates for example), eliminating adhesives altogether.

Regarding dust abrasion, silica-rich MRS is abrasive; higher filler loadings and fine particles can increase wear of hoppers, screws, and nozzles [122–124]. Mitigations compatible with ISRU include hardened or replaceable nozzle tips, sacrificial liners, and scheduled maintenance/replacement. Finally, although radiation shielding was not measured here, prior studies on polymer/regolith systems indicate increased attenuation with filler loading; our high-loading PEKK/MRS path is therefore consistent with dual-use components where mechanical utility and shielding are both desirable.

5.5 Conclusion & Future Work

This study demonstrates the successful fabrication of high-loading Martian Regolith Simulant (MRS)/PEKK composites tailored for additive manufacturing (AM) under in-situ resource utilization (ISRU) frameworks. By systematically decreasing regolith particle size (<100 μm , <50 μm , <20 μm) while maintaining a constant PEKK powder size, homogeneous mixing was achieved

up to 30 wt% MRS without phase separation or sedimentation. Contrary to conventional expectations, the mechanical performance did not continuously decline with higher filler content; instead, a strength plateau emerged at 30 wt%, attributed to enhanced stress transfer through matrix infiltration into perforated silicate particles. SEM and image-based analyses confirmed uniform particle dispersion and revealed the critical influence of particle morphology on porosity and interfacial bonding.

Mechanical testing across 0° and 90° print orientations demonstrated anisotropic strength and toughness behavior typical of extrusion-based composites, while DMA revealed near-isotropic viscoelastic performance in the elastic regime. Thermal post-processing improved crystallinity and thermal stability, with porosity evolution found to depend strongly on filler content, expanding at moderate loadings but stabilizing at higher MRS concentrations. The predictive tensile-strength model, integrating measured porosity and filler volume fraction, exhibited strong agreement with experiments, providing a quantitative framework for optimizing regolith–polymer composites.

This study establishes the foundational step toward sustainable ISRU-based additive manufacturing by demonstrating the feasibility of PEKK/MRS composites for Martian infrastructure. Building on this foundation, future work will include a comprehensive life-cycle assessment (LCA) to evaluate energy use, recyclability, and long-term performance under simulated Martian conditions. System-level modeling will also assess the scalability of filament reuse and energy requirements, bridging material-level insights with operational sustainability to enable autonomous, resource-efficient additive manufacturing on Mars.

Chapter 6: “Selene: Goddess of Luna”

“That’s one small step for man, one giant leap for mankind.”

- Neil Armstrong

This work has been published in:

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6. Sustainable Lunar Additive Manufacturing of High Regolith-Loaded PEKK Composites for Space Infrastructure

6.1 Abstract

Minimizing the cost and complexity of space missions requires sustainable strategies for in-situ manufacturing using local resources. Additive manufacturing, particularly material extrusion (MEX), offers a practical route for fabricating lunar infrastructure components from regolith-reinforced thermoplastics. This work presents the development and characterization of Polyether-Ketone-Ketone (PEKK)/Lunar Regolith Simulant (LRS) composites with loadings up to 60 wt%, fabricated via twin-screw extrusion. Thermal, rheological, and microstructural analyses revealed uniform LRS dispersion and identified a critical viscosity threshold above 30 wt% that coincides with a ductile-to-brittle fracture transition. Density and porosity measurements showed that annealing increased porosity at low filler contents but reduced it at high loadings through matrix densification. Mechanical testing confirmed the interplay between filler fraction, fracture mode, and post-processing, with annealed 60 wt% composites achieving a 13.7% tensile strength improvement compared to their as-printed counterparts. A novel adapted tensile strength model was proposed, explicitly integrating volume fraction, porosity, and fracture regime, and demonstrated strong agreement with experimental results across both amorphous and annealed states. Demonstration prints of complex lunar rover wheel prototypes validated printability at high regolith contents and highlighted superior dimensional stability after annealing. These findings establish a material–process–property framework for defect-controlled additive manufacturing of high-regolith composites, supporting the design of resilient, resource-efficient structures for long-term lunar infrastructure under extreme thermal cycling, radiation, and vacuum conditions to support sustainable in-situ aerospace additive manufacturing development for future space missions.

6.2 Introduction

Cost and complexity of space missions remain a central challenge for future lunar and planetary exploration, a challenge rooted in the legacy of past missions like Apollo and Luna that laid the

foundation for modern science, and now reemerging with renewed momentum through upcoming crewed and robotic missions aimed at sustainable in-situ resource utilization on the Moon [125–127]. While past lunar missions, from the Soviet Luna program to the Apollo landings, marked the dawn of humanity's direct engagement with extraterrestrial surfaces, the next era of lunar exploration is shaped by the imperative of sustainability [125,128,129]. In-situ resource utilization (ISRU) has emerged as a critical strategy to reduce mission costs and logistical complexity by leveraging lunar regolith as a primary material for infrastructure and consumables, paving the way for long-term habitation and reduced Earth-dependence [84,88,130,131]. In terms of extracting and collecting in-situ regolith samples, researchers are designing and developing systems to not only explore the Moon's core structure but also propose solutions to facilitate collecting samples through magnetic transport to deal with the low gravity and vacuum conditions on the Moon's surface. [132,133].

As the technology continues to evolve, Additive manufacturing (AM)-based ISRU offers a transformative path toward self-sufficient lunar and Martian outposts, reducing Earth dependency and enabling infrastructure development on demand which emerged as a cornerstone of extraterrestrial construction strategies, offering a scalable and flexible approach to fabricating structures directly from locally available regolith [84,85,128]. Particularly under the constraints of limited payload capacity and high launch costs, in-situ additive fabrication using lunar and Martian soil simulants represents a pragmatic solution to the challenges of long-duration space habitation [90,134]. Numerous studies have categorized lunar regolith simulant composites based on their intended manufacturing applications and performance demands. While early efforts primarily focused on civil engineering uses, such as bulk-molded cement formed through alkali activation with NaOH and sodium silicate binders [107,135–140], recent advancements have increasingly integrated polymer and geopolymer systems with 3D-printing technologies for lunar construction. These developments highlight the growing relevance of extrusion-based fabrication methods [84,130,141]. Additionally, thermoplastics are gaining traction as binders due to their recyclability, aligning with the goals of sustainable manufacturing. A summary of recent research is provided in Table 6.1, emphasizing the rise of polymer-based additive manufacturing techniques. These methods are attracting increasing interest due to their manufacturing simplicity and are becoming a prominent focus within the field of in-situ resource utilization (ISRU).

Table 6.1. Literature for Polymer-based additive manufacturing of extraterrestrial regolith

AM Method	Polymeric Matrix	Regolith Type	Regolith wt%	Novelty	Ref.
Stereolithography (SLA)	Shape Memory Vitrimer (SMV)	Lunar regolith simulant (LRS)	Up to 40%	Recyclable, self-healing, 4D-printable vitrimer-regolith composites for space use, with shape memory effect and healing efficiency after impact	Gyabaah et al. [23], 2024
SLA	photocurable diacrylate-based resin and dispersants for stereolithography	Lunar Highland (LHS)-1	70%	Optimized DLP AM process for regolith, achieving successful printing of complex parts like nuts and bolts. Analyzed sintering behavior, porosity, roughness, and microstructure.	Aiyeki et al. [24], 2025
Direct ink writing (DIW)	Epoxy resin matrix	SC80 Lunar	73%	Correlation between rheological properties and printability; excellent temperature resistance and structural integrity after freeze-thaw cycles, simulating lunar conditions.	Bao et al. [25], 2025
DIW	Geopolymer matrix with 1% short fiber	HIT-LRS-1	30%	Bio-inspired sandwich architectures enhance anisotropic damage tolerance and compressive strength	Ma et al. [26], 2025
Fused granulate fabrication (FGF)	Polypropylene (PP)	Mars global simulant (MGS)-1	40%	Comparison of mechanical performance and foaming behavior between AM and IM processes for highly loaded PP/regolith composites; identified thermal release from regolith constituents as a cause for surface defects in AM	Matetich and Vold[27], 2024
Fused filament fabrication (FFF)	Thermoplastic Polyurethane (TPU)	EAC-1A	Up to 30%	Flexible lunar components (e.g., tubes, grids) made by APF using TPU/regolith blends with in-depth mechanical, thermal, and porosity analysis.	Fateri et al. [28], 2025
FFF	Medium-density polyethylene (MDPE)	Mars regolith simulant (MRS)-Biolit	10%	Combined radiation shielding simulation (OLTARIS) with experimental filament extrusion and 3D-printing of PE/regolith composites; validated the mechanical and shielding performance under Martian radiation conditions.	Zaccardi et al. [29], 2022
FFF	Polyether-ether-ketone (PEEK)	LMS-1D	30%	extrude and 3D-print PEEK/regolith composite filament at 30 wt%, showing reduced tensile strength but improved layer bonding and Young's modulus; also analyzed microstructure, porosity, and mechanical implications under lunar ISRU conditions.	Azami et al. [30], 2025
FFF	Polylactic Acid (PLA) and Polypropylene (PP) as binders	BP-1 and LHS-1	Up to 85%	Structural regolith-polymer composites 3D-printed in lunar thermal vacuum conditions, validating feasibility for lunar shelter infrastructure (LINA) using 80:20 LHS-1: PLA	Gelino et al. [31], 2024
FFF	PLA-based filaments with pine wood fiber	Inorganic clay fillers	60%	Vacuum FFF printing of highly filled polymer composites is feasible and does not significantly alter mechanical, thermal, or chemical properties; showed changes in dimensional accuracy due to increased surface tension under vacuum	Slejko et al. [32], 2023
FFF	Amorphous Polyether-ketone (PEKK)	MGS-1	30%	3D-printing of PEKK/Martian regolith composite filaments, focusing on the effect of particle size for maximizing the amount of incorporation while maintaining high strength	Malekpour et al. [33], 2025

Among the AM techniques, material extrusion (MEX) methods such as fused filament fabrication (FFF) or direct ink writing (DIW) are especially promising due to their operational simplicity, compatibility with thermoplastics, and adaptability to low-gravity environments [85,86,94,107–109,142]. Recent research demonstrates the successful use of regolith simulants in the production of complex parts, ranging from radiation shielding panels to load-bearing structures, by blending simulants with polymers like PLA, PEEK, and epoxy resins [34,107,143–146]. These innovations are not only expanding the material design space but are also addressing critical issues such as microgravity-induced defects, vacuum sintering conditions, and the need for autonomous construction technologies [89]. Unlike laser-based AM methods, which suffer from high energy consumption and limited densification when applied to high-melting-point regolith particles, polymer-regolith composites processed via extrusion offer an energy-efficient alternative that aligns with the mass and resource constraints of space missions [87,102,130,133,147–149]. However, these systems face critical challenges including poor interlayer adhesion, high porosity, and regolith-induced flow instability, especially at elevated filler contents [110,111].

Despite progress in lunar-based manufacturing and construction (LBMC), key challenges remain in achieving high regolith loadings without compromising mechanical strength, minimizing porosity in extrusion-printed parts, and establishing predictive models that capture ductile-to-brittle transitions. These gaps limit the reliability of regolith–polymer composites for structural applications. These limitations result in unpredictable mechanical performance, severely constraining the structural reliability of printed components intended for surface infrastructure. Addressing this gap requires not only material innovation but also a deeper understanding of the coupled interactions between processing conditions, particle dispersion, and final part properties. In this context, polymer-regolith composite additive manufacturing is more than a fabrication method. It is a gateway to enabling autonomous, scalable, and sustainable off-world construction.

To ensure adequate interlayer adhesion and consistent extrusion behavior in polymer-regolith filaments, compatibility between the polymer matrix and any additives or fillers must be carefully managed [112]. In addition to material-process compatibility, the extreme lunar environment imposes stringent performance requirements. Lunar surface conditions involve thermal cycling between approximately -180°C during the lunar night and $+120^{\circ}\text{C}$ during the lunar day, exposure to vacuum, and high levels of cosmic radiation [150]. These harsh conditions can exacerbate

porosity-driven weaknesses and accelerate fracture in polymer-based composites. Selection of amorphous Polyether-ketone-ketone (PEKK) over other high-performance polymers is supported by its inherently slower crystallization rate, isomer-tunable thermal behavior, and superior interlayer adhesion [113]. This space-grade high-performance thermoplastic offers an exceptional opportunity for long-term sustainability and economical solution due to its MEX printability and recyclability ensuring structural integrity when printing regolith-loaded filaments under low-atmosphere or vacuum conditions [26,151,152]. PEKK is a high-performance thermoplastic known for its tunable mechanical properties, which are largely influenced by the crystallization kinetics of its various grades [3,4,10]. This crystallization behavior depends on the ratio of its isomeric forms, specifically, the proportion of straight-chain (“Terephthalic”) versus branched-chain (“Isophthalic”) isomers [7]. Grades containing 40% or more Isophthalic content (usually considered as amorphous PEKK), exhibit lower melt viscosity, reduced processing temperatures, minimized warpage, and improved suitability for MEX [3,4]. However, their inherently slower crystallization kinetics necessitate post-processing heat treatment to achieve desired material properties, which in turn increases both manufacturing time and overall production costs.

This work presents the first comprehensive demonstration of high regolith-loaded PEKK composites (up to 60 wt%) processed via MEX, linking rheology, porosity, and fracture mechanics through a novel tensile strength model. The term “high regolith-loaded” refers to PEKK composites containing 30–60 wt% lunar regolith simulant (LRS), which is substantially higher than the typical 5–20 wt% filler levels reported for thermoplastic additive manufacturing. To the best of the authors’ knowledge, this work is the first to develop a printable PEKK-based composite filament containing up to 60 wt% LRS, marking the highest reported regolith fraction successfully processed through material-extrusion additive manufacturing. Given the critical importance of leveraging local resources to reduce Earth-dependency in future lunar missions, this research investigates a comprehensive framework for developing and characterizing regolith-based composite materials tailored for additive manufacturing. Key focus areas include the fabrication of highly LRS-loaded PEKK composite filaments, rigorous assessment of filament quality and print consistency, mechanical and thermal evaluation of 3D-printed components. Moreover This work presents a novel tensile strength model integrating volume fraction, porosity, and fracture mode, validated experimentally on high-regolith PEKK composites. A central theme of this work lies in the interconnected effects of rheological behavior, fracture mode transition, and thermal post-

processing on the performance of PEKK/LRS composites. The observed viscosity threshold above 30 wt% LRS not only marked a shift in extrusion stability but also coincided with a transition from ductile to brittle fracture behavior, highlighting the critical role of filler content in governing deformation mechanisms. Finally, functional printability through the fabrication of a structurally complex lunar rover wheel prototype using rich-regolith loaded filaments was demonstrated.

By addressing both material behavior and process integration, the study aims to identify practical pathways for producing high-strength, load-bearing components under the constraints of lunar manufacturing. Ultimately, this work contributes to the growing body of research supporting In-Situ Resource Utilization (ISRU) and highlights the potential of polymer-regolith composites in enabling long-term, self-sufficient extraterrestrial infrastructure.

6.3 Materials & Methods

6.3.1 Materials

An amorphous PEKK filament with a nominal diameter of 1.75 ± 0.05 mm, supplied by Spool3D (Alberta, Canada) under the product code PEKK175-1000, was used in this study. According to the manufacturer, the recommended MEX processing parameters for this filament include a nozzle temperature between 360 °C and 400 °C and a build plate temperature between 90 °C and 130 °C. However, through iterative testing, a build plate temperature of 160 °C was ultimately selected to effectively minimize warpage during printing. The filament was pelletized and subsequently pulverized using an AF LAB Pulverizer/Micronizer (Orenda, Canada), with three consecutive passes to achieve a particle size below 500 μm . For LRS, Lunar Mare Simulant (LMS)-1D was procured from Space Resource Technologies (Exolith Lab, University of Central Florida, USA) [153]. This simulant features a particle size distribution ranging from 0.04 to 35 μm , with a mean particle size of 6 μm . The full particle size distribution is illustrated in Figure 6.2b, and has been shown to align well with the finest portions of key Apollo lunar samples [154]. The fine particle size of this simulant facilitates uniform mixing with the polymer matrix, making it a particularly suitable choice for this study.

Given that both PEKK and LRS are hygroscopic materials [155,156], the pulverized PEKK and LRS powders were dried at 125 °C for 5 hours prior to processing. Sibille et al. [157] provide foundational guidelines for the development and standardization of lunar regolith simulants,

highlighting the critical importance of mineralogical fidelity, and importance of having dehydrated particles to mimic the same particle morphology. Their work underscores the necessity of using low-hygroscopic and well-characterized simulants to ensure accurate and reliable results in ISRU-oriented additive manufacturing of regolith–polymer composites. Following the dehydration process, the materials were blended at varying LRS weight fractions (wt%) ranging from 0% to 60%, in 10% increments, to produce individual composite formulations. The inclusion of the 0 wt% LRS (pure PEKK) sample serves as a baseline to evaluate the reliability of the in-house manufacturing process and to identify any potential defects introduced during fabrication, as compared to the commercially produced neat filament. Each batch was mixed for 10 minutes at 50 rpm, as illustrated in Figure 6.1b, and subsequently stored in a drying chamber maintained at room temperature and 25% relative humidity. Filament extrusion was carried out within 24 hours to minimize moisture reabsorption.

6.3.2 *Filament Fabrication*

Among the various polymer mixing techniques, twin-screw extrusion is widely regarded as the most effective for incorporating particulate additives into a polymer matrix, offering superior dispersion and homogeneity [158]. The PEKK/LRS mixture was continuously fed into a Process 11 twin-screw extruder (Thermo Fisher Scientific, Germany) with a high-performance polymer screw configuration recommended by Thermo Fisher Scientific [118] (Shown in Figure 6.1a screw configuration) with two-stage mixing screws at 50 rpm, following a predefined temperature profile distributed across eight heating zones, as illustrated in Figure 6.1a. In the screw configuration, the first mixing stage was positioned at the entrance of the melting zone, while the second was placed immediately after the initial conveying stage to ensure thorough mixing of the regolith particles within the PEKK matrix. McGlasson et al. [116] demonstrated that filler dispersion quality in elastomer composites is strongly dependent on accumulated strain for achieving superior nanoscale homogeneity, a finding that supports the use of high-shear continuous extrusion, as that produced by this specific combination of screws in the twin-screw micro-extruder in this study, thus ensures uniform regolith distribution within the PEKK matrix.

Zone 1 (Z1), designated solely for powder feeding, does not allow user-defined input. To prevent overheating in this initial zone, the temperature of Zone 2 (Z2) was set to 260 °C. The subsequent zones (Z3 to Z7) were maintained at 315 °C, a temperature selected based on the cold

crystallization melting point determined in our previous study [71], as well as recommendations from the literature on PEKK extrusion processes [119]. The temperature in Zone 8 was set at 15 °C higher to reduce melt viscosity at the die exit, thereby lowering die pressure and minimizing the risk of nozzle clogging. Moreover, a vacuum pump was used just after mixing the segment of the micro-extruder to reduce air bubbles that might have formed in previous stages. A die nozzle with a 2 mm orifice was installed, and with appropriate pulling tension, a high-quality composite filament with a uniform diameter of 1.75 ± 0.15 mm was produced. To summarize, the manufacturing process began with material preparation, including dehydration and mixing, followed by extrusion and air cooling of the fabricated filament. The cooled filament was then wound to create an inventory spool for eventual 3D-printing. This sequence is illustrated in Figure 6.1b. To prevent moisture absorption, the filament was cooled using blown air rather than a water bath and subsequently stored in a dry box maintained at 10% relative humidity. Prior to each printing session, the filament was further dried at 125 °C for 5 hours to ensure optimal print quality.

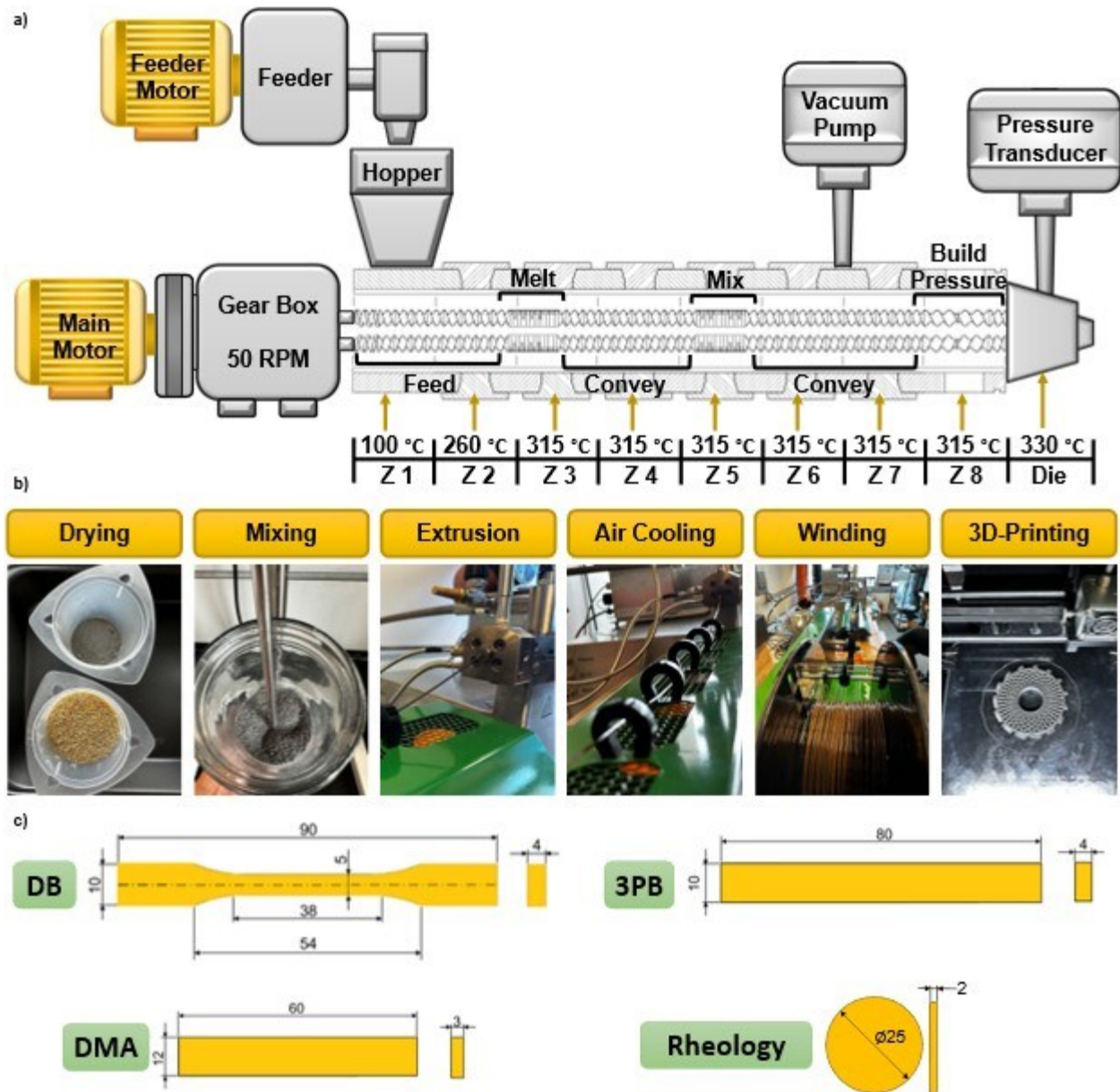


Figure 6.1. Manufacturing process: (a) Micro-extruder parameter set up and screw configuration, illustrating each stage of the extrusion [159], (b) process sequence for whole manufacturing process, (c) 3D-printed sample geometry (all dimensions are in mm).

6.3.3 3D-Printing

For MEX of test specimens as well as a conceptual wheel design, slicing was performed using Ultimaker Cura with the parameters detailed in Table 6.2. The thermal parameters for 3D-printing were established based on our earlier study, which optimized processing conditions to maximize the ductility of printed samples [69,160]. The prints were performed using a CreatBot F160-PEEK

3D-printer (CreatBot, China). To enhance adhesion and minimize warpage during printing, a layer of nano adhesive glue (Vision Miner, USA) was applied to the surface of the glass build plate prior to each print.

Table 6.2. MEX set of parameters

Print parameter	Value	Units
Nozzle temperature	380	°C
Bed temperature	160	°C
Chamber temperature	60	°C
Print speed	40	mm/s
Infill density	100	%
Layer height	0.25	mm
Extruder diameter	0.8	mm
Raster Angle	0	°
Build pattern (Tensile, Rheology)	Concentric	-
Build pattern (Flexural, DMA)	Line	
Build orientation	Flat	-

6.3.4 Post-Processing

At this stage, the samples were divided into two groups: those subjected to post-processing annealing and those left in the amorphous state without heat treatment (as-printed), to distinguish the effects of post-processing on the specimens. The post-processing annealing procedure followed the protocol established in our previous study [71]. The heat treatment began by ramping the temperature to 210 °C for 15 minutes. This was followed by an isothermal holding phase at 210 °C for 30 minutes. Subsequently, the samples were allowed to cool to room temperature over the next 15 minutes. In total, the entire annealing process was completed within one hour.

6.3.5 Characterization Techniques

6.3.5.1 Thermogravimetric Analysis (TGA)

TGA was utilized to evaluate the volumetric dispersion of LRS filler in the PEKK matrix. For the analysis, the thermal stability of the pure PEKK, pure LRS, and PEKK/LRS in all compositions were assessed, using a Thermogravimetric Analyzer TGA Q50 (TA Instruments, USA), at least three times each for the filament and 3D-printed parts, following ASTM E1131 [28]. Each sample was prepared with a mass between 30 mg to 40 mg, placed in a ceramic pan, and subjected to a

temperature increase from 100 °C to 800 °C at a rate of 10 °C/min in a Nitrogen atmosphere. As LRS consists of only ceramics and thus no thermal degradation would happen to them at these temperatures, the difference between pure PEKK and PEKK/LRS TGA results show the weight percentage content of LRS in composition over a volume. To measure the content of LRS in the composite filament and 3D-printed composite parts, the weight loss of the pure PEKK samples from pure filament and pure 3D-printed parts was used as a reference. The difference between the thermal stability response of pure PEKK against PEKK/LRS composite enables the calculation of LRS weight fraction ($W_{LRS}(\%)$) in the composition following Eq. (6.1), where $WT_L(\%)$ is weight loss percentage.

$$W_{LRS}(\%) = \left(1 - \frac{WT_{LPEKK/LRS}(\%)}{WT_{LPEKK}(\%)} \right) \times 100 \quad (6.1)$$

6.3.5.2 Rheology

Rheological characterization of the composite 3D-printed parts was conducted using an MCR 302 parallel-plate rheometer (Anton Paar, Austria). Initially, a frequency sweep test was performed on pure PEKK at the typical extrusion temperature to determine a suitable constant frequency for subsequent temperature sweep measurements. In the second stage, composite filaments containing 0% to 60% wt regolith were subjected to a temperature sweep ranging from 250 °C to 390 °C; this range encompasses both the cold crystallization peak and the typical nozzle temperatures used during MEX processing.

6.3.5.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was conducted using a TA Instruments DSC Q200 (TA Instruments, USA) to evaluate crystal thermal history, cold crystallization zone, and kinetics with regard to LRS percent content. All samples involved at least three replicates, with 8 to 10 mg of material for each replicate, prepared in an aluminum hermetic sample pan according to the TA Instruments DSC guidelines [24] and ASTM D3418 [25]. All amorphous filament samples were tested, with a heating rate of 10 °C/min from 0 °C to 380 °C, followed by a 5-minute isothermal hold at 380 °C, and then cooling at a rate of 5 °C/min back to 0 °C. For the crystallinity saturation evaluation of post-processed samples, only the samples from annealed and amorphous 3D-printed parts of (regular) pure PEKK (most amount of PEKK matrix) and PEKK/LRS 60% (least amount of PEKK matrix) were assessed, with a heating rate of 10 °C/min from 140 °C to 360 °C.

6.3.5.4 Density & Porosity Measurements

Density measurements were carried out in two distinct categories: one focused on LRS itself using multiple methodologies, and the other on polymer-based samples. As the composite filaments vary based on the LRS weight percentage, accurately determining the density of the LRS was essential for calculating the theoretical volume fraction of LRS within each formulation

To determine the bulk densities of LRS, several techniques were employed. First, the uncompacted powder was poured into a precision 25 ml stainless steel cylinder. Manual compaction was performed using a hand-held hammer, applied three times at each stage, with additional powder added after each cycle until the cylinder was completely filled. In a more controlled setup, a GranuPack Impact system was used to assess the tapped density. This method involved subjecting the powder to 5,000 controlled vertical impacts over a five-minute period, continuing until a minimal change in the powder column height was observed, indicating saturation of this particular compaction process. Lastly, to determine the true (grain) density, a gas pycnometer (Ultrapyc 5000, Anton Paar, Austria) was used. This method involved filling the pycnometer's vacuum chamber with helium to precisely measure the volume of the powder, enabling highly accurate density calculation.

Given the inherent presence of voids in additively manufactured parts and the effect of crystallization on material density [18], it was necessary to measure the actual density of filaments and 3D-printed samples for porosity calculation. By combining this data with the known densities and volume fractions of the composite constituents, porosity levels in the filaments and printed parts were estimated using Archimedes' principle, following ASTM D792 [48], a method known for its simplicity and reliability. For this purpose, a Sartorius density determination kit (Sartorius, Germany) was employed to weigh each sample in air and submerged in temperature-controlled water.

Using Eq. (6.2), the theoretical volume fraction of the LRS in a composite filament can be calculated from the weight fractions and densities of the components. Moreover, the theoretical density of each composite filament was calculated using the rule of mixtures, based on the theoretical volume fractions and individual densities of PEKK and LRS, as expressed by Eq. (6.3):

$$V_{LRS} = \frac{\frac{\omega_{LRS}}{\rho_{LRS}}}{\frac{\omega_{LRS}}{\rho_{LRS}} + \frac{\omega_{PEKK}}{\rho_{PEKK}}} \quad (6.2)$$

$$\rho_c = (1 - V_{LRS}) \cdot \rho_{PEKK} + V_{LRS} \cdot \rho_{LRS} \quad (6.3)$$

Where:

- V_{LRS} is the theoretical volume fraction of LRS
- ω_{LRS} is the weight fraction of LRS
- ω_{PEKK} is the weight fraction of PEKK (note: $\omega_{PEKK} = 1 - \omega_{LRS}$)
- ρ_{LRS} is the density of LRS
- ρ_{PEKK} is the density of PEKK
- ρ_c is the theoretical density of composite filament

This estimation provides a reference point for evaluating the amount of porosity as the internal void content in the manufactured filaments and 3D-printed parts when compared with experimentally measured densities. The porosity (P) was determined using Eq. (6.4):

$$P(\%) = \left(1 - \frac{\rho_{exp}}{\rho_c}\right) \quad (6.4)$$

where ρ_{exp} is the density determined via the Archimedes method, and ρ_c is the theoretical density calculated based on the component volume fractions as mentioned earlier. This approach enables quantification of the void fraction introduced during filament extrusion, 3D-printing, and post-processing. Void fraction is a critical parameter influencing the mechanical and thermal performance of the final parts.

6.3.5.5 Scanning Electron Microscopy (SEM)

To evaluate the quality of LRS particle dispersion, observe microstructural defects, and calculate the volume fraction of LRS in each composition, scanning electron microscopy (SEM) was performed on both filaments and 3D-printed samples. Cross-sectional dispersion at longitudinal and transversal directions was assessed using the HITACHI S-3400N scanning electron microscope (HITACHI, Japan) at 15 kV. Moreover, image processing (grayscale thresholding) was performed on microscopic images at magnifications of 50X, 100X, 200X, 500X, and 1000X to measure the volume fraction of LRS in the composite filament. Finally, to compare the void content in 3D-printed parts, the fracture surfaces of tensile samples containing 10% and 20% LRS were

examined. Point energy dispersive spectroscopy (EDS) analysis was specifically performed on the 10% LRS sample, targeting the bonding interface between a ceramic particle and the surrounding polymer matrix to evaluate elemental composition and interfacial characteristics.

6.3.5.6 Energy Dispersive X-ray Analysis (EDX)

Energy dispersive X-ray (EDX) mapping analysis was performed on both the LRS powder and the cross-sections of the composite filaments with 10%, 30%, and 60% LRS using a HITACHI Regulus 8230 Field Emission Scanning Electron Microscope (FE-SEM) (HITACHI, Japan) operated at 15 kV with a gold coating applied to the samples. The primary objectives of this analysis were to measure the particle size of the LRS, identify the elemental composition, and evaluate the distribution and dispersion of LRS particles within the polymer matrix across the filament cross-sections.

6.3.5.7 Mechanical Testing

Tensile and flexural (three-point bending) test specimens were fabricated following ISO 527 [50] and ISO 178 [51] standards, respectively, as illustrated in Figure 6.1c. The experiments were performed using a Hoskin Scientific universal testing machine (Hoskin Scientific, Canada) with a 5 kN S-type load cell mounted on the upper grip. The machine operated at a displacement rate of 2 mm/min. For the tensile tests a preload of 1–10 N was applied, while for the three-point bending tests the preload ranged from 1–2 N.

6.3.5.8 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was performed using a TA Instruments DMA Q800 (TA Instruments, USA) following ASTM D4065-12 [54] and ASTM D5418 [55] for dual cantilever beam testing. The samples were subjected to a strain amplitude of 0.1% at a frequency of 1 Hz. The temperature range spanned from 140 °C to 220 °C, with a heating rate of 2 °C/min.

6.3.6 Tensile Strength Modeling

The mechanical properties of particulate composites are traditionally estimated using the rule of mixtures, which assumes that the overall strength of the composite is a linear combination of the strengths of the matrix and filler, weighted by their volume fractions [120]. However, in real processing scenarios, especially in 3D-printed parts, additional porosity must be accounted for, as voids significantly reduce load-bearing capacity.

Accordingly, a modified rule of mixtures including porosity effects was considered for predicting the tensile strength (σ_c) of the PEKK/LRS composites as shown in Eq. (6.5):

$$\sigma_c = (\sigma_m(1 - \phi_f) + \sigma_f\phi_f)(1 - P) \quad (6.5)$$

where:

- σ_m is the tensile strength of the fully dense PEKK matrix,
- σ_f is the tensile strength of the filler particles (LRS),
- ϕ_f is the filler volume fraction,
- P is the porosity.

Given that the LRS particles have negligible tensile strength compared to PEKK, the model can be reasonably simplified by assuming $\sigma_f \approx 0$, leading to Eq. (6.6):

$$\sigma_c = \sigma_m(1 - \phi_f)(1 - P) \quad (6.6)$$

In ductile-dominated regimes (typically at lower filler loadings), the matrix continues to carry the majority of the load and failure occurs through plastic deformation. In such cases, porosity primarily reduces the effective load-bearing area and a linear porosity correction factor $(1 - P)$ is typically sufficient. However, at higher regolith filler loadings or after post-processing, the mechanical response of the composite transitions from ductile to brittle fracture behavior, which significantly influences its sensitivity to porosity. In brittle fracture regimes, the presence of pores doesn't contribute to cross-sectional reduction but instead causes localized stress concentration and early crack initiation. To account for the amplified degradation in mechanical performance under such conditions, an exponential porosity sensitivity model is more appropriate, as shown in Eq. (6.7):

$$\sigma_c = \sigma_m(1 - \phi_f)(e^{-nP}) \quad (6.7)$$

where n is a porosity sensitivity coefficient that reflects the degree to which porosity accelerates failure in brittle regimes. The coefficient n was determined by fitting experimental tensile strength data ($\sigma_{c,exp}$) across different porosity levels, following the relation in Eq. (6.8):

$$\ln\left(\frac{\sigma_{c,exp}}{\sigma_m(1 - \phi_f)}\right) = -nP \quad (6.8)$$

This dual-regime modeling framework distinguishes between ductile and brittle fracture behavior. It would enable a more appropriate prediction of tensile strength degradation in composites with varying degrees of filler content and porosity.

6.4 Results & Discussion

6.4.1 Manufacturing Quality Assessment

Quality control was implemented at every stage of the manufacturing process to monitor defects and identify solutions for their mitigation. Accordingly, the following results reflect not only the quality of the fabricated filament but also assess the influence of 3D-printing parameters and post-processing conditions, all of which were closely monitored to ensure consistency and reliability.

6.4.1.1 LRS Particle Study

Figure 6.2 presents a comprehensive characterization of the Lunar Regolith Simulant (LRS) particles used in this study. SEM images at four magnification levels (Figure 6.2a) reveal the highly irregular morphology of the particles, characterized by angular edges and rough surfaces. Such morphology can deteriorate mechanical interlocking with the polymer matrix and may also affect flowability during extrusion. The observed size distribution ranges from the nanoscale up to several tens of microns, consistent with the broad particle size distribution reported by the supplier. This LMS-1D particle size distribution, adapted from the supplier in Figure 6.2b, highlights its polydispersity and fine granularity, with a significant fraction of particles below 10 μm .

Figure 6.2c compares the LRS density values obtained via three different measurement techniques: bulk density of uncompacted and compacted powder in stainless-steel cylinder, compacted bulk density using the GranuPack Impact method, and true (grain) density measured by helium gas pycnometer. The uncompacted bulk density of the LRS was measured at 1.2 g/cm^3 , which increased to 1.9 g/cm^3 after manual compression, reflecting the reduction of interparticle voids under applied force. When compaction was performed using the GranuPack Impact method, the resulting tapped density was 1.5 g/cm^3 . This lower value, compared to manual compression, is attributed to the interlocking nature of the fine angular particles, which can trap air and hinder efficient packing during vibrational tapping. The gas pycnometer provided a true grain density

value of 3.9 g/cm^3 by directly measuring the volume of the solid phase, excluding pore space. This true density is critical for the accurate calculation of the composite's theoretical density and volume fraction. The clear variance among the methods underscores the importance of selecting a density measurement technique appropriate to the level of precision required, especially for composite design and porosity evaluation.

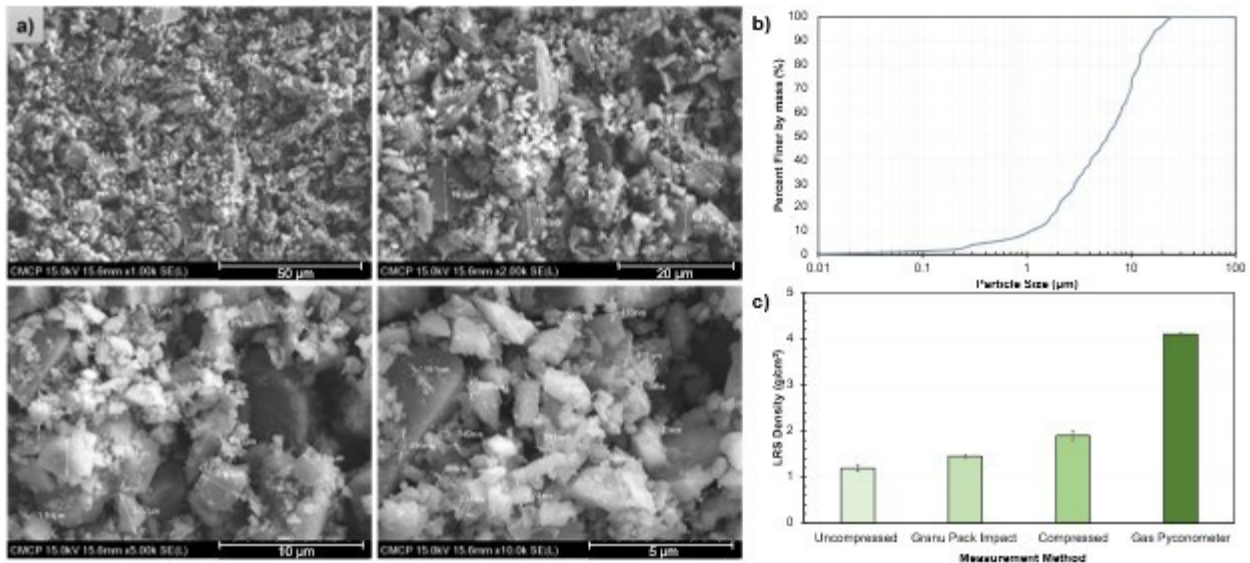


Figure 6.2. Characterization of Lunar Regolith Simulant (LRS) particles: (a) SEM images of LRS particles captured at four magnification levels, revealing their irregular morphology and confirming a broad particle size distribution spanning from the micro- to nanoscale, (b) Particle size distribution curve of LMS-1D grade LRS, adapted from [153], highlighting the fine granularity and polydispersity of the simulant, (c) Comparison of LRS particle density values obtained through three different measurement methods: uncompacted bulk, compacted via impact (GranuPack), and true (grain) density measured by gas pycnometer.

6.4.1.2 Manufacturing challenges

Figure 6.3 highlights key manufacturing challenges encountered during the fabrication and processing of PEKK/LRS composite filaments and 3D-printed parts. One of the primary issues observed during extrusion was lump formation (Figure 6.3a) at higher regolith loadings (e.g., 60 wt%). This phenomenon indicates inhomogeneous material flow, likely resulting from localized agglomeration of LRS particles close to the nozzle inner orifice wall at the exit. Such inhomogeneity not only compromises filament diameter uniformity but can also lead to nozzle clogging and surface defects during printing.

Filament diameter measurements further confirm the influence of LRS content on extrusion stability. As shown in Figure 6.3b, filaments containing 50 wt% LRS maintained consistent diameters within the target range, suggesting stable extrusion. In contrast, the 60 wt% LRS filament (Figure 6.3c) exhibited intermittent diameter spikes outside the acceptable tolerance, indicating flow instability and poor rheological behavior at this high filler concentration. It was also observed that filament manufacturing became significantly more challenging at LRS contents of 40% and above, with increased instances of nozzle clogging, higher torque, and melting pressure

Post-processing and part quality were also affected by the material's microstructure. Imaging of the fracture surface of a tensile sample (Figure 6.3d and e) reveals two types of voids: primary voids located within the extruded strands (magnified in SEM images), and secondary voids found between adjacent strands. These voids are characteristic of 3D-printed structures and are further influenced by print path, bonding quality, and regolith interference at the interlayer boundaries. Further examination (Figure 6.3e) demonstrated that secondary void expansion is influenced by the presence or absence of open channels between strands. To get into the cold crystallization temperature zone of any semi-crystalline thermoplastic for annealing, we must exceed the glass transition temperature (T_g) [2,17]. In configurations lacking open flow paths (left), trapped air expanded under heat, forming large voids due to polymer softening after passing T_g , whereas open-channel configurations (middle) enabled outgassing and resulted in more stable interlayer bonding. A schematic (right) summarizes the observed defect types, highlighting the internal strand porosity, inter-strand voids, and random distribution of LRS particles throughout the matrix.

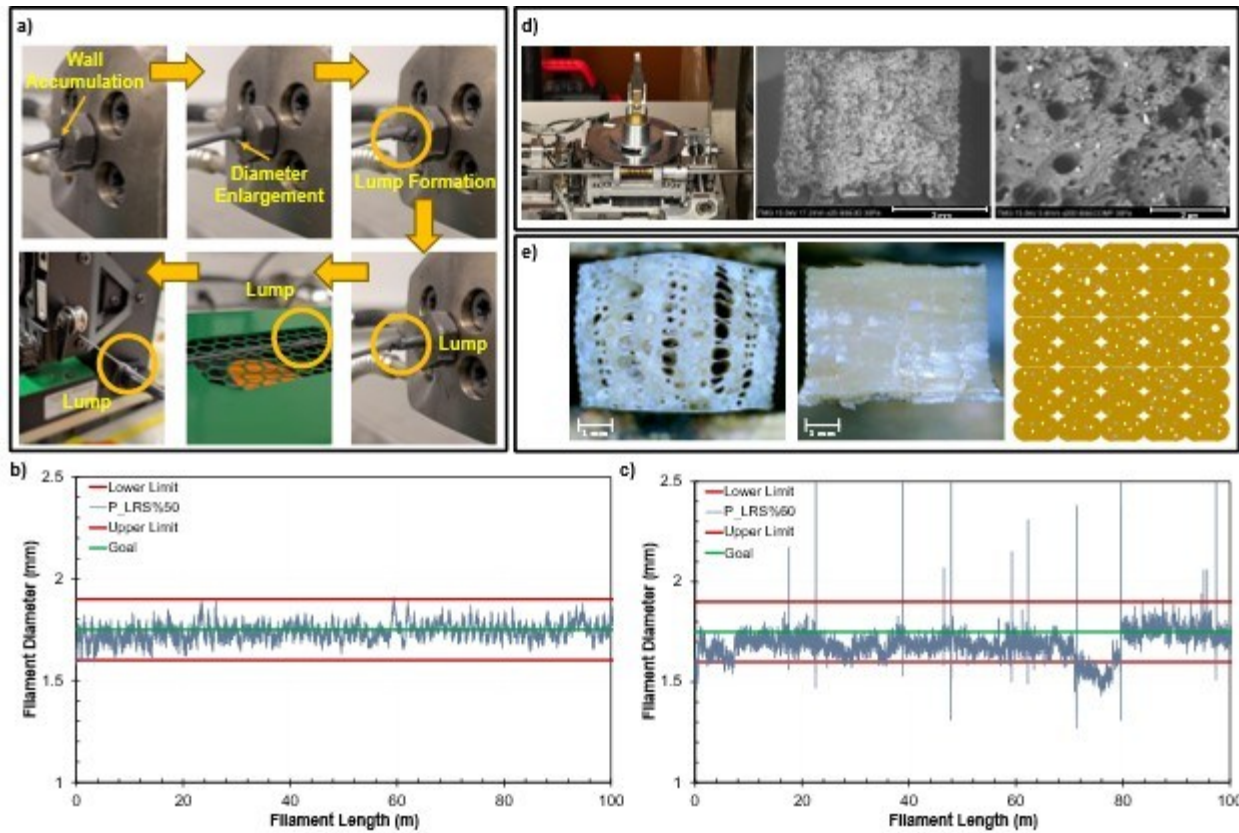


Figure 6.3. Manufacturing defects observed in PEKK/LRS composite filaments and printed parts; (a) lump formation during extrusion, indicating inhomogeneous material flow or filament with 60% regolith, (b) filament diameter profile for 50 wt% LRS, showing consistent measurements within the target range and no significant spikes, (c) filament diameter profile for 60 wt% LRS, displaying intermittent spikes outside the target range, demonstrating instability at high regolith content (d) SEM image of the fracture surface of a tensile sample with 10 wt% LRS, illustrating primary voids within extruded strands (at X200 magnification) and secondary voids between adjacent strands (at X25 magnification), (e) left: secondary void expansion in the absence of open channels; Middle: stable bonding with no secondary void expansion under open channel conditions; Right: schematic representation of void types: primary voids within strands, secondary voids between strands, and randomly distributed LRS particles (grey) throughout the matrix.

6.4.1.3 Assessment of LRS Weight Fraction in Composite Filaments

TGA was conducted to evaluate the thermal degradation behavior of the composite filaments and to verify the actual LRS weight fraction in each formulation. As shown in Figure 6.4a, pure PEKK exhibited a single-stage thermal degradation profile with high thermal stability, initiating

degradation above 550 °C. In contrast, pure LRS remained thermally stable over the entire temperature range, as it is composed primarily of inert mineral oxides. The composite filaments demonstrated dual-phase degradation behavior, with the initial weight loss corresponding to the decomposition of the PEKK matrix, followed by a more gradual weight drop as LRS content increases associated with the thermally stable LRS residue.

To assess the accuracy of the composite formulation, the residual weight at 800 °C was used to estimate the actual LRS content in each sample, as shown in Figure 6.4b. The measured residue percentages calculation using Eq. (6.1), were in good agreement with the targeted LRS weight fraction, confirming the effective homogenous incorporation of LRS into the PEKK matrix during the extrusion process. Minor discrepancies between theoretical and experimental values are attributed to processing losses and experimental errors during filament preparation. Overall, the TGA results confirm that the composite maintains sufficient thermal stability for MEX processing while validating the intended filler content across all compositions.

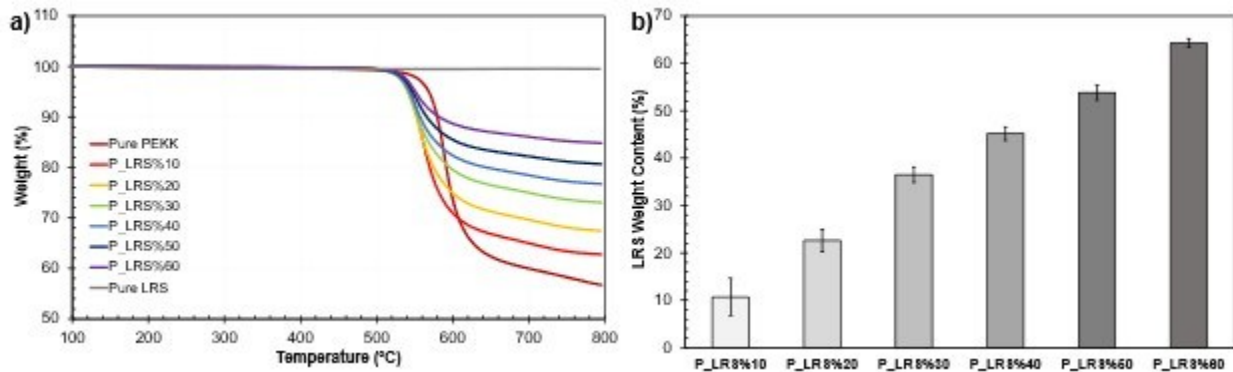


Figure 6.4. TGA results for evaluating the thermal stability and filler content of PEKK/LRS composites; (a) TGA curves of pure PEKK, pure LRS, and PEKK/LRS composite filaments, showing thermal degradation behavior across compositions and confirming the thermal stability of the hybrid material system, (b) estimated LRS weight fraction in the composite filaments based on residue analysis, highlighting the correlation between target and measured LRS concentrations.

6.4.1.4 Rheological Assessment

Rheological characterization of the PEKK/LRS composites was conducted to assess their processability during filament extrusion and 3D-printing. As shown in Figure 6.5a, a frequency sweep test was performed on pure PEKK at 330 °C, corresponding to the melt temperature at the

micro-extruder die exit. The viscosity curve revealed a region of minimal sensitivity to shear frequency near 1 Hz, where the slope of the curve approached zero, indicating a stable flow regime. Based on this observation, 1 Hz was selected as the reference frequency for the subsequent temperature sweep measurements to enable consistent comparison across all composite formulations.

Figure 6.5b presents the temperature-dependent viscosity behavior of composite filaments containing 0 to 60 wt% LRS. As the temperature increased from 250 °C to 390 °C, a gradual decrease in viscosity was observed for all compositions up to the crystal-melt transition (~300 °C) followed by a minimum viscosity at cold crystallization and melting peaks. However, an abrupt difference in that minimum (and post-peak) viscosity, referred to as a "viscosity jump", was observed in samples with LRS content of 40 wt% and above. This phenomenon is likely due to the agglomeration or structural rearrangement of the ceramic filler at elevated temperatures, which disrupts the polymer flow and increases melt resistance. These results align with the observed difficulties in filament extrusion and dimensional control at higher LRS weight fractions and offer a clear rheological justification for the processing challenges encountered during both filament manufacturing and 3D-printing of highly LRS loaded composites.

The abrupt rise in viscosity observed above 30 wt% LRS (Figure 6.5b) corresponds to a critical percolation threshold at which regolith particles begin to form continuous contact networks within the melt. This particle crowding creates frictional resistance to flow and locally restricts polymer-chain relaxation, leading to a sharp increase in effective viscosity and reduced molecular mobility. As the average inter-particle spacing approaches the radius of gyration of PEKK chains, the polymer segments become topologically confined, decreasing chain diffusion and entanglement dynamics (compare Figure 6.7c and d). This confinement, combined with interfacial stress accumulation around rigid particles, initiates micro-cracks under loading and manifests as a ductile-to-brittle transition in mechanical response (Figure 6.11a and b). Such behavior aligns with the particle-jamming and chain-mobility restriction mechanisms reported in other high-filler thermoplastic systems [161–164].

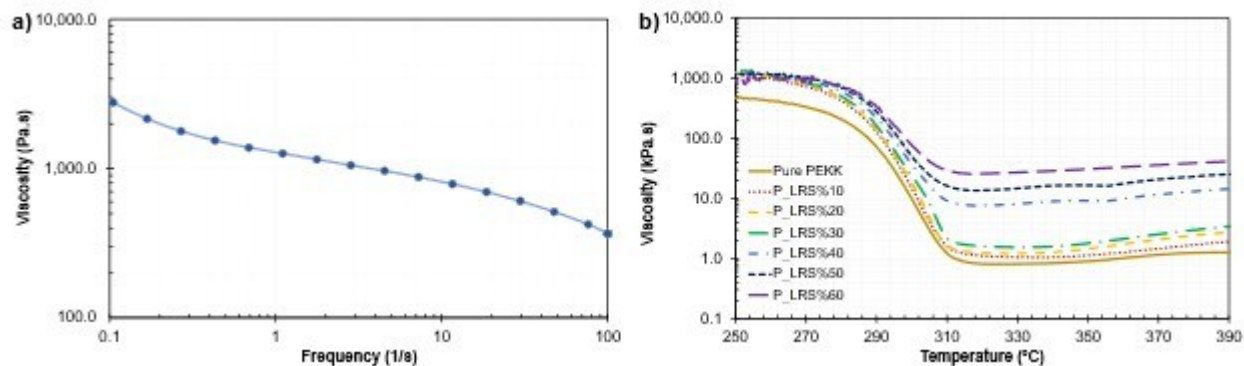


Figure 6.5. Rheological behavior of PEKK/LRS composite as-printed parts evaluated using parallel-plate rheometry, (a) frequency sweep of pure PEKK at 330 °C, identifying a region of minimal sensitivity to frequency variation around 1 Hz, (b) Temperature sweep profiles of composite filaments with 0–60 wt% LRS at a fixed frequency of 1 Hz, showing significantly higher viscosity for formulations with ≥ 40 wt% LRS above the crystal-melt transition (~ 300 °C), consistent with processing challenges during extrusion and 3D-printing.

6.4.1.5 LRS Dispersion

To assess the microstructural distribution of regolith particles as well as the evolution of porosity in PEKK/LRS composite filaments, SEM imaging was conducted on cross-sections of samples with LRS weight fraction ranging from 10 wt% to 60 wt%, as shown in Figure 6.6. The term macrovoids refers to pores with diameters greater than approximately 50 μm , typically visible to the naked eye and originating from air entrapment during filament extrusion. These larger voids are mostly distributed within the bulk of the extruded strands. Conversely, the term microvoids denotes submicron to tens-of-micron pores that form primarily at the interface between irregularly shaped LRS particles and the PEKK matrix. Due to the angular morphology of LRS particles and imperfect wetting at their surfaces, small interfacial gaps can persist even after consolidation. Many of the orange-circled regions in Figure 6.6 (a-d) therefore represent interfacial microvoids partially encompassing an adjacent LRS particle, rather than isolated pores. The images reveal an excellent dispersion of LRS particles throughout the polymer matrix, with no signs of agglomeration or phase segregation, even at higher LRS weight fractions. This homogeneity indicates successful mixing and extrusion performance and supports the reliability of the twin-screw extrusion method for regolith-based composites. In addition to qualitative evaluation, image processing was applied to high-resolution SEM micrographs to quantify the LRS volume fraction. A grayscale thresholding

approach was used to isolate ceramic particles from the polymer background (shown in the right-side column). In this method, micro- and macro-voids grouped with the matrix may slightly affect the calculated volume fraction. However, since their presence is minimal in the filament cross-sectional images, they were neglected in the calculation. This procedure was applied across multiple magnification levels, and the results were averaged to calculate the volume fraction of LRS in each sample. The measured values showed a strong correlation with theoretical predictions, as will be discussed in Section 3.3, confirming consistent filler incorporation (Figure 6.10a).

Porosities were also spotted, both at the micro and macro levels observed within the filament cross-section. As LRS content increased, the frequency and size of these voids showed noticeable variation. These observations provide critical insight into how filler content affects not only dispersion but also internal void formation, which can impact the mechanical performance of the printed parts.

EDX mapping was conducted to verify the elemental composition and spatial distribution of LRS particles in the PEKK matrix, as shown in Figure 6.7. The analysis of pure LRS powder (**Error! Reference source not found.**a) identified characteristic peaks for silica (Si), alumina (Al), iron oxide (Fe), magnesium (Mg), calcium (Ca), sodium (Na), titanium (Ti), and oxygen (O), confirming the complex mineral composition typical of lunar regolith simulants.

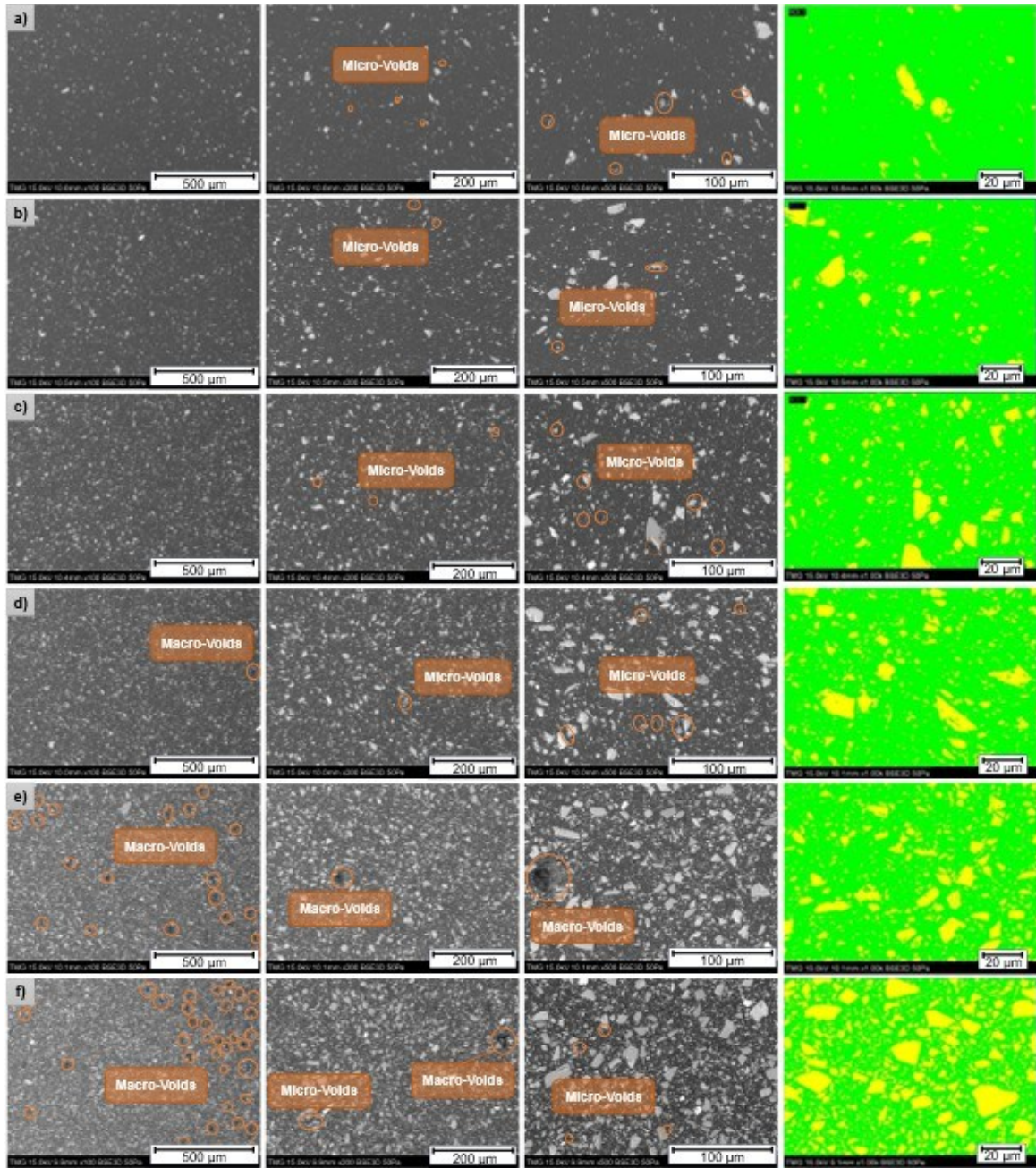


Figure 6.6. SEM analysis of LRS dispersion and porosity in PEKK/LRS composite filaments: (a–f) Cross-sectional SEM images of filaments with increasing LRS content from 10 wt% to 60 wt%, demonstrating uniform particle dispersion at all loading levels and void categories (macro-voids ($>50\ \mu\text{m}$, extrusion-originated) and “micro-voids” (interfacial, morphology-induced)); last column representative an example of high-magnification SEM image with image processing overlay for LRS phase detection, used for quantifying volume fraction through grayscale thresholding.

Subsequent EDX analysis of composite filaments with 10%, 30%, and 60% LRS (Figure 6.7 (b-d)) revealed a progressive increase in elemental intensity corresponding to the increasing LRS weight fraction. The elemental maps showed a uniform spatial distribution of inorganic elements throughout the cross-sections of the filaments, indicating excellent dispersion and no significant agglomeration of LRS particles, even at high LRS weight fractions. The carbon (C) signal, dominant in the background, represents the PEKK matrix. As the regolith content increases, the relative carbon intensity decreases, from 80.4 wt% at 10 wt% LRS to 54.7 wt% at 60 wt% LRS, reflecting the progressive replacement of polymer by mineral filler. The measured carbon weight fraction does not exactly match the polymer matrix content, as carbon is not the sole element in PEKK. Moreover, EDS mapping is primarily qualitative rather than quantitative, and the reported weight percentages therefore lack high accuracy. The contrast between carbon and inorganic elemental signals in the EDS maps provides clear visual confirmation of the composite structure and its evolving composition. Among the detected metal elements, Si, Al, and Mg were the most prominent in terms of spatial coverage and volume fraction, suggesting they constitute the primary mineral components of the LRS. Furthermore, the layered elemental mapping revealed overlapping regions of Si and Mg, which may indicate the presence of magnesium silicate phases within the regolith particles, consistent with the known mineralogy of lunar simulants.

This analysis not only validates the successful incorporation of LRS into the PEKK matrix but also supports the earlier SEM findings regarding uniform particle dispersion. The correlation between the target and observed elemental intensity further confirms the consistency and reliability of the composite filament fabrication process.

To further investigate the composition and elemental distribution of the composite after 3D-printing, EDS point analysis was conducted on the fracture surface of the PEKK/LRS 10% tensile sample (Figure 6.8a). It is important to note that the pores observed on the tensile-fracture surfaces in Figure 6.8a are not newly generated during mechanical loading but are manifestations of pre-existing voids within the composite. Carbon was attributed to the PEKK polymer, while localized intensities of metallic oxides indicated the heterogeneous dispersion of LRS particles. Notably, in all selected spectrums, the persistence of carbon as plastic residues on dense ceramic particles even after fracture suggests good interfacial adhesion, as portions of the polymer remained bonded to

the regolith particles. These findings support the structural integrity of the composite and confirm effective particle–matrix bonding during the printing process.

However, pore volume fraction was significantly increased after 3D-printing. Previously, it was observed that the number of pores increased with rising LRS weight fraction during filament manufacturing, likely due to trapped air during extrusion at higher viscosity. The problem was exacerbated during printing as both extrusion pressure and shear flow were lower, allowing trapped bubbles to expand. This trend is illustrated in Figure 6.8b and c, which compare the fracture surfaces of amorphous printed samples containing 10 wt% and 20 wt% LRS, respectively. Although the size of the primary pores remains similar between the two samples, a noticeable increase in the number of pores is evident in the 20 wt% LRS sample, indicating higher overall porosity at increased filler content. These findings emphasize the need for careful control of processing parameters such as better vacuum and more control on viscosity to minimize void formation in highly filled PEKK/regolith composites for future studies.

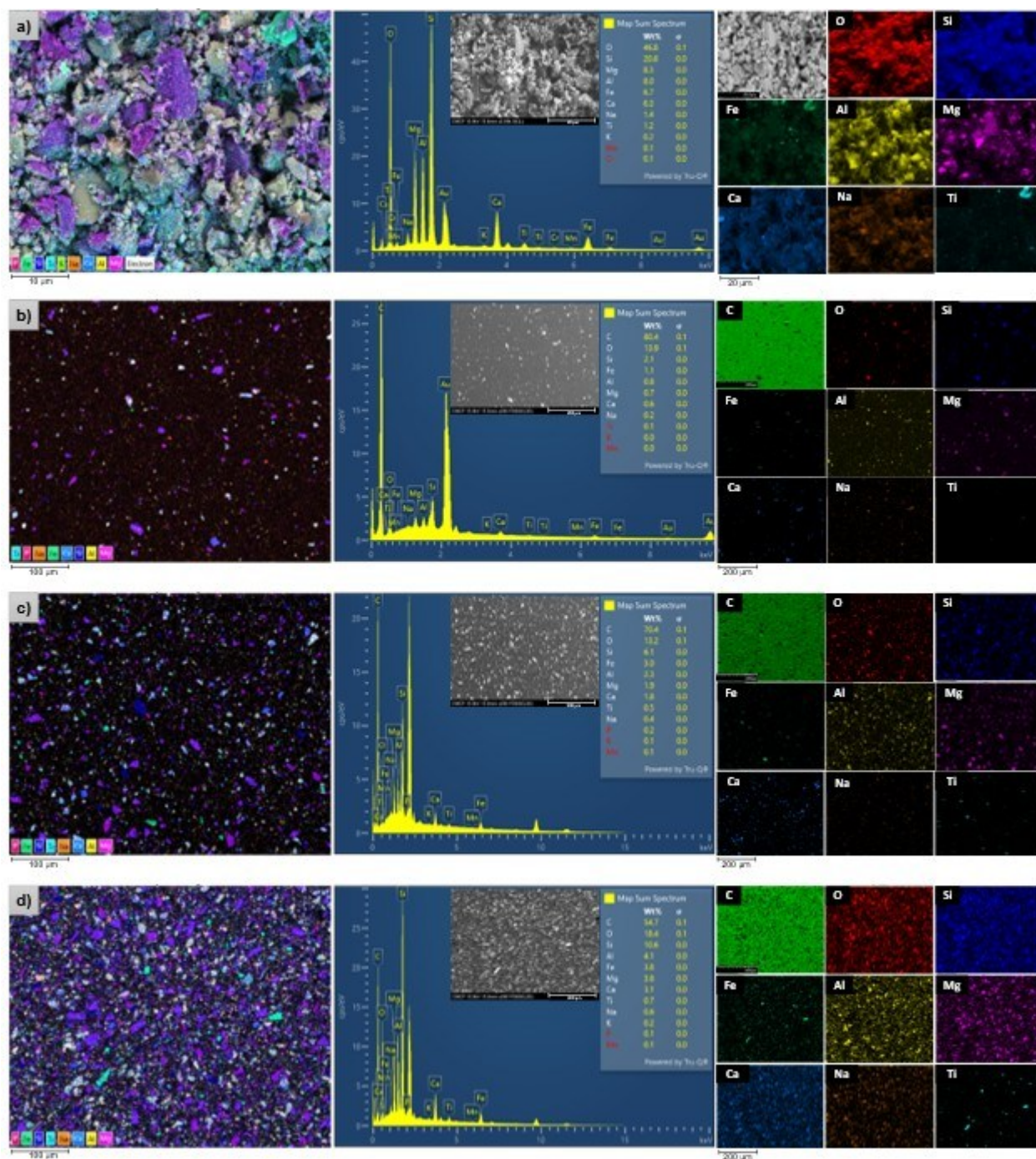


Figure 6.7. EDX analysis of LRS powder and PEKK/LRS composite filaments: (a) EDS spectrum and elemental mapping of pure LRS powder, confirming the presence of key mineral oxides (Si, Al, Fe, Mg, Ca, Na, Ti, O), (b–d) Elemental mapping and spectra for PEKK/LRS composite filaments with 10%, 30%, and 60% LRS weight fraction, respectively.

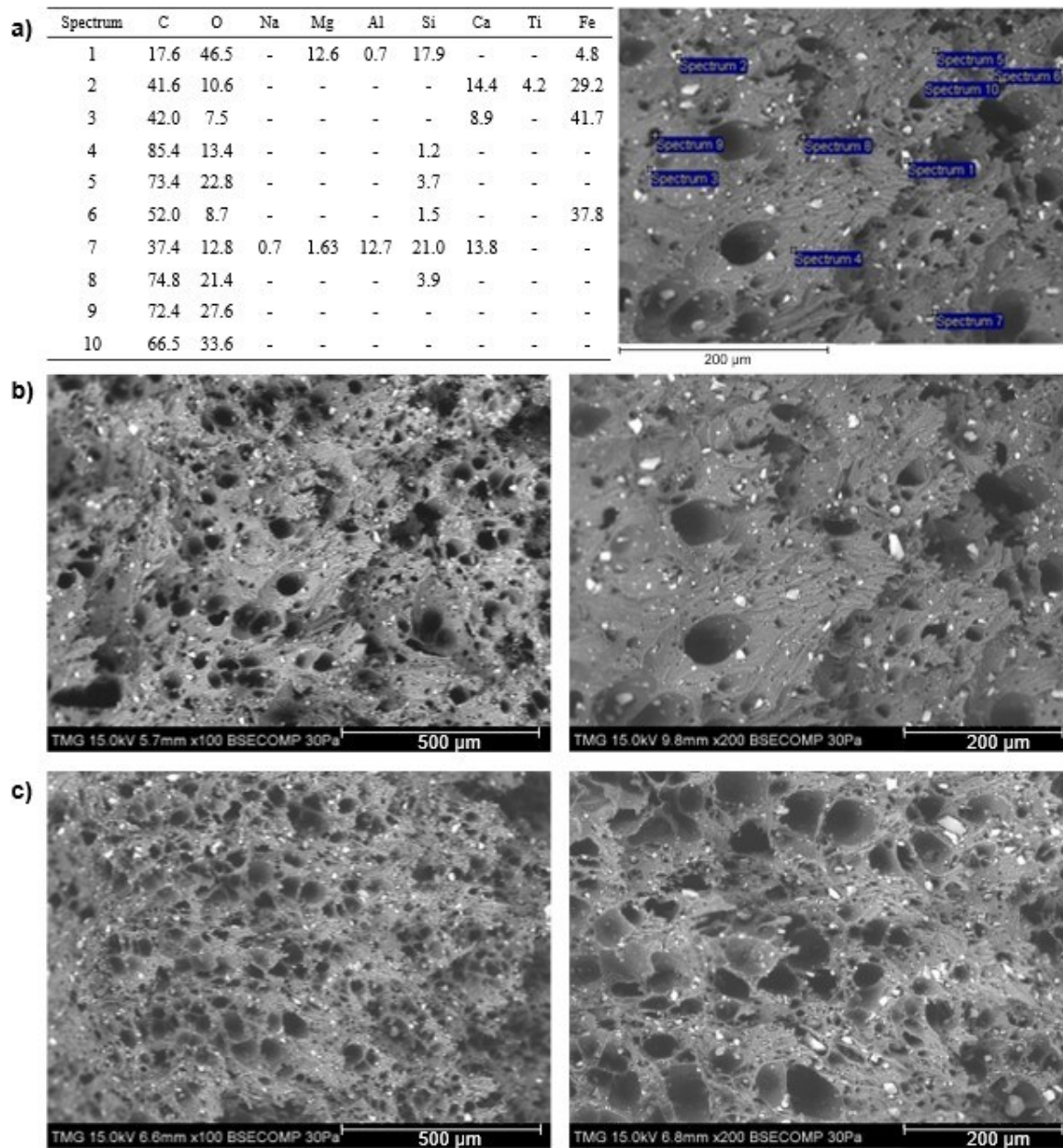


Figure 6.8. Fracture surface analysis of 3D-printed PEKK/LRS composites: (a) EDS point analysis conducted on the fracture surface of a tensile sample with 10 wt% LRS, confirming elemental composition and adhesion at the matrix–particle interface, (b) SEM image of the fracture surface of a 3D-printed amorphous part with 10 wt% LRS, showing primary pores within the strands, (c) SEM image of the fracture surface of a 3D-printed amorphous part with 20 wt% LRS, revealing a similar pore size but increased pore count, indicating higher porosity with increased regolith content.

6.4.2 *Crystallization Behavior*

The crystallization behavior of PEKK/LRS composite filaments was investigated using DSC, with results shown in Figure 6.9. Analysis of the as-fabricated composite filaments (Figure 6.9a) revealed that increasing the LRS content led to a noticeable shift in the cold crystallization peak toward lower temperatures, likely due to better heat distribution. This trend is favorable from a processing perspective, as it enables the annealing process to occur at reduced temperatures. Moreover, the DSC curves confirmed that crystallization had not already occurred during filament extrusion, likely due to the rapid cooling rate outpacing the kinetic requirements for crystal formation. Interestingly, an increase–decrease pattern in the crystallization peak temperature was observed across compositions during cooling from the molten state. However, given that the focus of this study lies in isothermal cold crystallization as a post-processing treatment, this melt-crystallization behavior holds limited relevance for our application. It should also be noted that the degree of crystallinity calculated from DSC heat flow is highly sensitive to sample weight, making absolute crystallinity values less reliable for quantitative comparison. Nevertheless, the temperature zones indicating crystallization activity remain consistent and meaningful for understanding the thermal response of the composites.

To validate that the annealing process effectively saturated the crystallization in all compositions, pure PEKK and the highly filled PEKK/LRS 60% samples were subjected to post-annealing DSC analysis (Figure 6.9b). Prior to annealing, both samples showed minimal or no crystallization, confirming that 3D-printing alone does not facilitate significant crystalline structure formation. After annealing, both samples exhibited pronounced crystallization peaks, confirming that the chosen annealing protocol was sufficient to induce full crystallization across the compositional range. These findings support the use of a standardized post-processing heat treatment for achieving consistent material properties in printed parts regardless of LRS weight fraction.

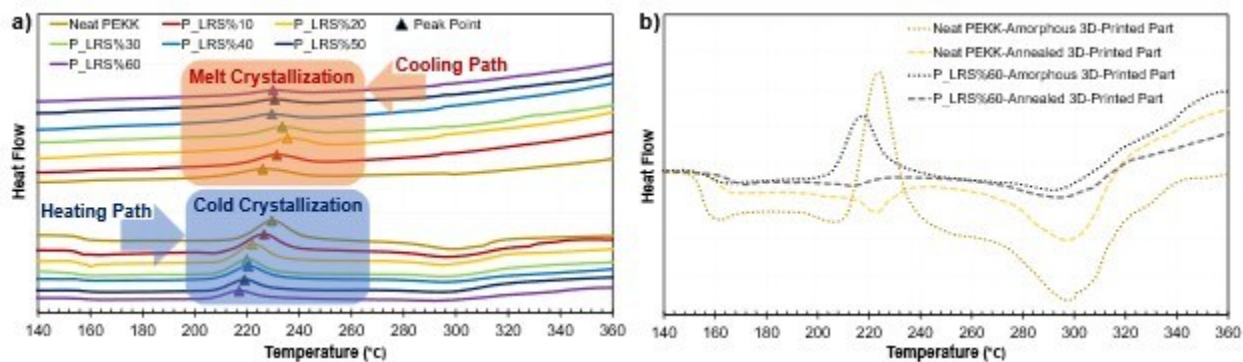


Figure 6.9. DSC analysis of crystallization behavior in PEKK/LRS composite filaments and 3D-printed parts: (a) DSC curves of composite filaments with 0–60 wt% LRS content, revealing a shift in cold crystallization peak to lower temperatures as LRS content increases, and confirming the absence of crystalline structures during filament fabrication due to rapid cooling, (b) Comparison of cold crystallization behavior before and after annealing in 3D-printed amorphous parts for pure PEKK and PEKK/LRS 60%, demonstrating that both compositions reached crystallization saturation through identical annealing conditions.

6.4.3 Density & Porosity

To quantify the volume fraction of LRS within each composite formulation, image processing was performed on high-magnification SEM micrographs as described in Section 3.1.5, and the results were compared to theoretical volume fractions calculated using Eq. (2.2). These calculations incorporated the weight fraction of each component along with density values obtained from gas pycnometry. As shown in Figure 6.10a, representing SEM images of each filament cross-section besides its volume fraction, a close agreement was observed between theoretical and image-derived values, validating both the mixing protocol and the image analysis methodology. LRS volume fraction is a nonlinear function of its weight fraction (Eq. (6.2)), rising more rapidly with increasing weight fraction, and reaching 32.2% at 60 wt% loading. This increasingly large step in volume fraction may explain the abrupt rise in viscosity previously observed in Figure 6.5b, indicating a possible threshold in flow behavior driven by particle concentration.

Figure 6.10b displays the measured density of filaments and 3D-printed parts in both amorphous and annealed states across all compositions. It is expected that the density increases slightly with annealing due to crystallization-induced densification, but the influence of LRS weight fraction and structural voids also affects the final value. Using the volume fraction and theoretical density

of an ideal void-free composite, porosity was calculated for each condition (Figure 6.10c). The results reveal an overall increase in porosity with higher LRS weight fraction. This is primarily attributed to the elevated viscosity of regolith-rich composites, which reduces the effectiveness of vacuum-assisted air removal during extrusion, allowing more voids to be trapped. Besides the fact that MEX additive manufacturing makes secondary voids between adjacent strands, the 3D-printing process itself introduced additional porosity due to the lower extrusion pressure and the shear rate at the printer nozzle compared to the micro-extruder. These conditions allowed existing voids to expand and new ones to form, contributing to higher overall porosity in amorphous printed parts.

Additionally, the annealing process contributed to further porosity evolution. For filaments and parts with LRS content up to 30 wt%, porosity increased after annealing due to void expansion in the softened, low-viscosity matrix. However, in composites with 40 wt% LRS and above, this trend began to reverse. The higher viscosity and modulus of these compositions appeared to limit pore expansion, while crystallization during annealing contributed to matrix densification. Consequently, the 60 wt% LRS annealed samples exhibited lower porosity than their amorphous counterparts, an indication that thermal post-processing can serve as a densification mechanism at high filler loadings. This comprehensive analysis underscores the complex interplay between filler content, processing parameters, and post-treatment effects in determining the final structural quality of PEKK/LRS composites.

Matrix densification through crystallization occurs in all annealed composites; however, its net influence on porosity depends on the balance between void expansion and structural confinement in 3D printed samples. At lower LRS contents (≤ 30 wt%), the softened matrix above T_g permits expansion of pre-existing voids, and the subsequent crystal growth cannot fully compensate for this increase in free volume, resulting in a net rise in porosity. At higher loadings (≥ 40 wt%), the matrix is mechanically constrained by a dense particle network that suppresses thermal dilation while crystallization between adjacent particles compresses residual voids, producing an overall reduction in porosity. The dual role of LRS, both constraining matrix flow and promoting interfacial crystallization, governs this contrasting behavior across the filler-loading spectrum.

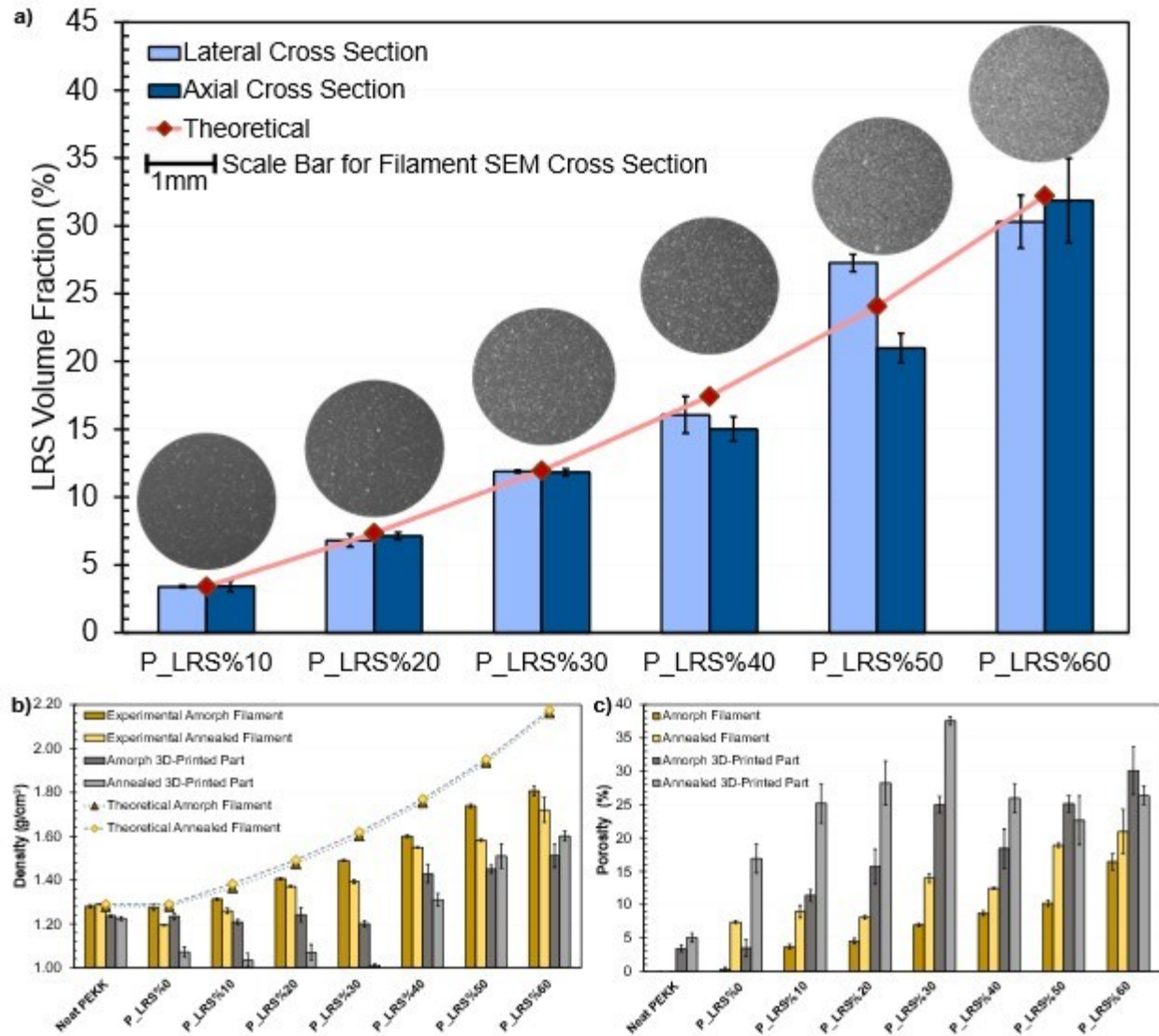


Figure 6.10. LRS volume fraction estimation, density measurement, and porosity evaluation of PEKK/LRS composites: (a) comparison between theoretically calculated and SEM image-based volume fractions of LRS across all filament compositions, (b) measured densities of filaments and 3D-printed parts in both amorphous and annealed states, (c) calculated porosity for each filament and printed part (amorphous and annealed), derived by comparing measured densities to theoretical values.

6.4.4 Mechanical & Thermomechanical Properties

Fracture type and post-test deformation analyses were performed on PEKK/LRS composite samples following tensile, flexural, and Dynamic Mechanical Analysis (DMA) testing, as summarized in Figure 6.11. Tensile fracture observations (Figure 6.11a) revealed a clear transition from ductile to brittle failure with increasing LRS content. Amorphous (R) samples containing up to 20 wt% regolith exhibited ductile fracture characteristics, including elongation and necking, while those with 30 wt% or more LRS failed in a brittle manner with minimal deformation. This behavior indicates a critical filler content beyond which the polymer matrix loses its ability to absorb strain energy effectively.

Flexural test results (Figure 6.11b) showed a similar trend. Amorphous samples with up to 20 wt% LRS displayed significant plastic deformation and did not fracture during testing. At 30 wt%, signs of plastic deformation were still evident, but failure occurred before the test was finished (reaching 10% flexural strain). Samples with 40 wt% or more LRS fractured in a brittle manner, showing little to no plasticity. In annealed (A) specimens, the effect of post-crystallization was more pronounced. Only pure PEKK retained its capacity for plastic deformation, while all regolith-filled composites failed in a brittle fashion, suggesting that increased crystallinity reduced the matrix's ductility and enhanced stiffness, making it less tolerant to strain.

Post-DMA deformation analysis (Figure 6.11c) further supported these findings. Amorphous samples exhibited increasing resistance to deformation as LRS content rose, implying higher structural rigidity with increased filler content. Notably, annealed samples showed no observable deformation after DMA testing across all compositions, indicating enhanced thermal stability and dimensional retention due to crystallization. These results collectively demonstrate that both LRS weight fraction and thermal post-processing significantly influence fracture mechanics and increase the thermomechanical stability of PEKK.

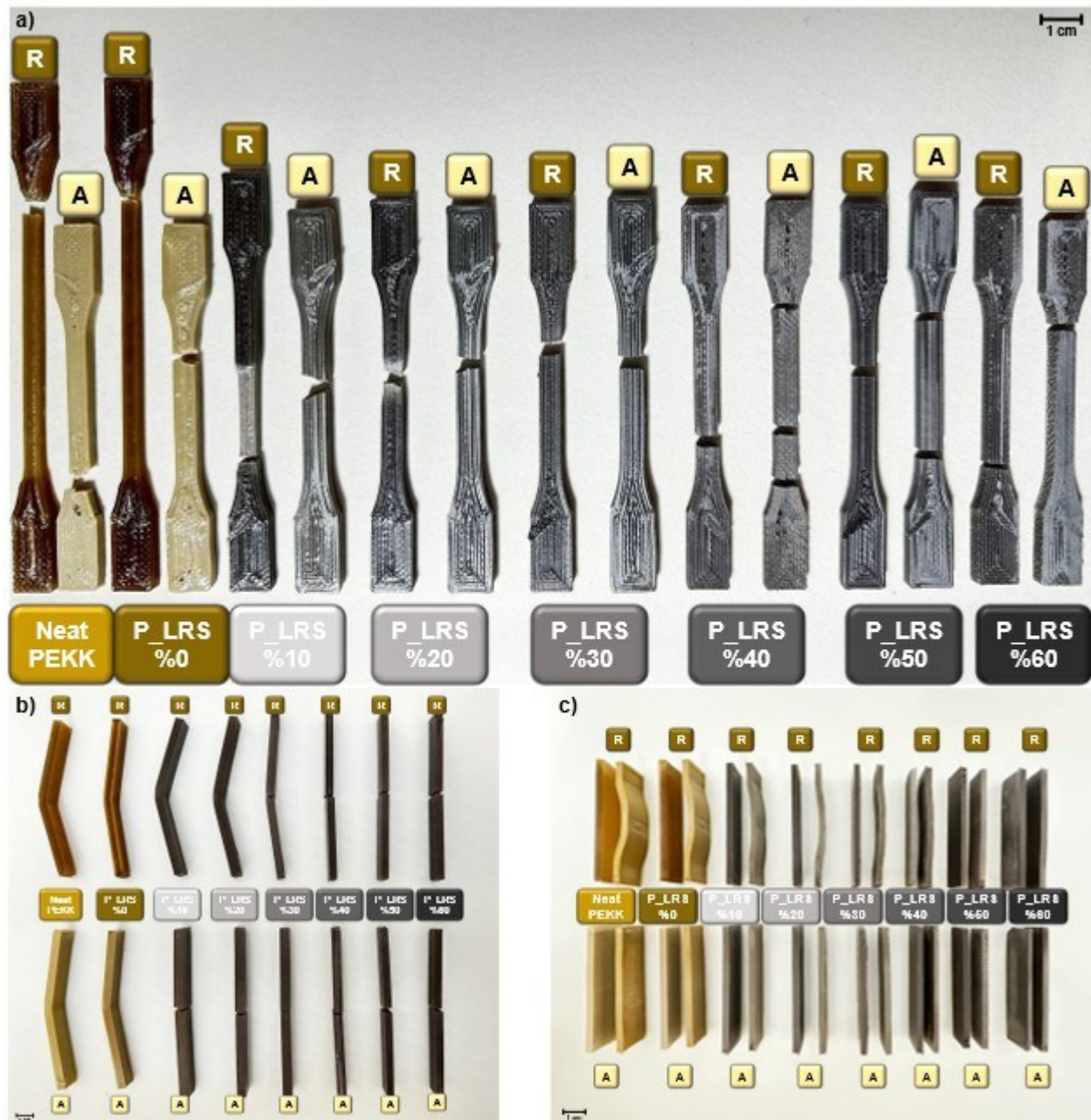


Figure 6.11. Fracture behavior and deformation analysis of PEKK/LRS composites after mechanical and thermomechanical testing: (a) tensile fracture surfaces of amorphous (R) and annealed (A) samples, showing a transition from ductile to brittle failure with increasing LRS content, (b) flexural fracture profiles samples, (c) DMA sample deformation, in pairs showing before (left side) and after (right side).

6.4.4.1 Tensile Testing

As shown in Figure 6.12a, amorphous samples exhibited relatively ductile behavior at low LRS contents (≤ 20 wt%), with a gradual transition to more brittle fracture characteristics at higher LRS weight fractions. This shift resulted in a convergence of tensile strength values across higher LRS weight fractions. The increase in LRS weight fraction consistently led to reduced elongation and toughness, as the rigid ceramic particles acted as stress concentrators, limiting plastic deformation. Annealing significantly altered the tensile response, as observed in Figure 6.12b. Notably, Figure 6.12c shows that while tensile strength increased for neat PEKK (fabricated from commercial filament), most annealed composite samples exhibited lower tensile strength compared to their amorphous counterparts, particularly up to 30 wt% LRS. This reduction is attributed to increased porosity introduced during annealing, as previously discussed in Figure 6.10c. However, at 40 wt% LRS, this trend began to stabilize, and for 50% and 60% LRS, tensile strength increased again, consistent with the reduced porosity observed in those samples after annealing.

The trend in elastic modulus (Figure 6.12b) reflects a competing effect between the stiffening influence of ceramic particles and increased crystallinity, versus the softening effect caused by porosity. Elongation at break (Figure 6.12e) declined sharply with both increasing LRS content and post-processing, confirming a clear transition toward brittle mechanical behavior. This decline was also reflected in the toughness values (Figure 6.12f), which dropped significantly in annealed samples, particularly at higher LRS concentrations, due to reduced energy absorption capacity under tensile loading.

Summarizing at the two extremes of LRS weight fraction, the tensile strength of neat PEKK increased from 86.9 MPa in the amorphous state to 103.2 MPa after annealing, marking an 18.7% improvement. For the composite containing 60 wt% LRS, tensile strength increased from 40.1 MPa to 45.6 MPa after annealing, representing a 13.7% improvement. These results highlight the complex interplay between filler content, porosity, and thermal treatment in shaping the tensile behavior of PEKK/LRS composites.

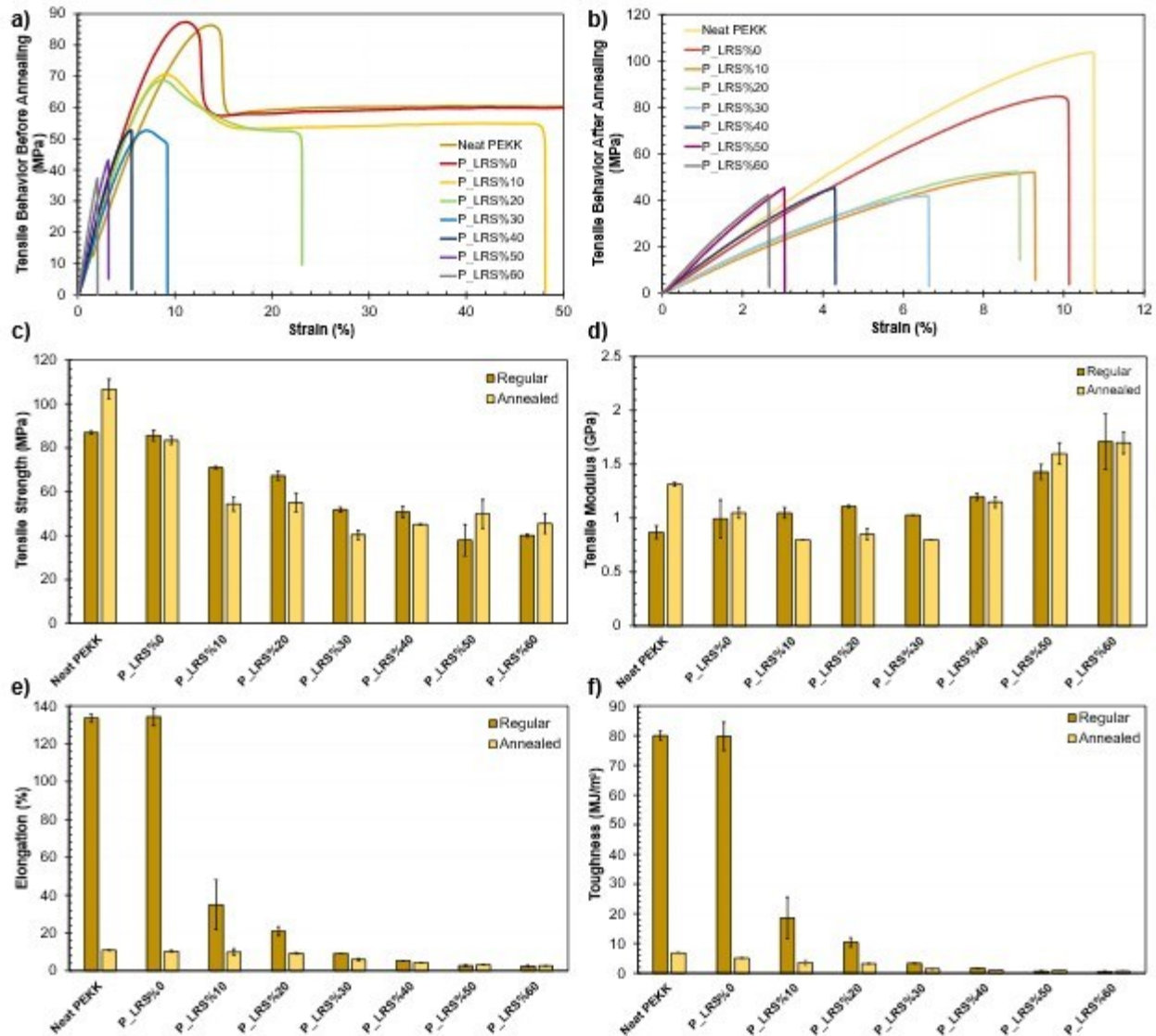


Figure 6.12. Tensile properties of 3D-printed PEKK/LRS composites in regular (amorphous) and annealed conditions: (a) stress-strain curves before annealing, (b) stress-strain curves after annealing, (c) tensile strength comparison across compositions, (d) tensile modulus values, (e) elongation at break, (f) toughness values before and after annealing.

6.4.4.2 Flexural Testing

Flexural testing of PEKK/LRS composites was conducted to evaluate their resistance to bending-induced failure and to understand the impact of LRS weight fraction and post-processing on structural behavior. As shown in Figure 6.13a, amorphous samples with up to 20 wt% LRS exhibited considerable plastic deformation, sustaining bending without fracture up to 10% strain. However, with 30 wt% LRS, early signs of brittle behavior emerged, and samples fractured before

reaching 10% flexural strain. All amorphous samples with 40 wt% LRS and above fractured in a brittle manner, consistent with the loss of matrix ductility due to high ceramic particle loading. After annealing, the flexural response became noticeably stiffer and more brittle across all compositions (Figure 6.13b). Only pure PEKK (neat PEKK and 0% LRS) retained any plastic deformation, while all other annealed composites fractured without appreciable strain. This behavior aligns with the crystallization-induced stiffening and reduced ductility post-annealing, which is further exacerbated by the regolith content.

Figure 6.13c illustrates the flexural strength trends across all compositions. For neat PEKK and 0 wt% LRS, a similar behavior was observed and annealing improved the flexural strength from 126.9 MPa in the amorphous state to 150.3 MPa after annealing, representing an 18.4% increase. However, for all other composite formulations, flexural strength declined following annealing, likely due to the high sensitivity of flexural performance to internal porosity. For instance, in the highly filled PEKK/LRS 60% composite, strength decreased from 72.6 MPa to 69.5 MPa after annealing, a reduction of approximately 4.5%. This suggests that the benefits of increased crystallinity may be offset by porosity-related weakening in composites with elevated regolith content.

Strain at ultimate strength (Figure 6.13d) declined rapidly with increasing LRS content and was further decreased by annealing. This indicates the reduced ability of the material to undergo bending deformation, especially in rigid, crystallized composites. The flexural modulus (Figure 6.13e) increased steadily with LRS loading and annealing, reflecting the combined stiffening effects of ceramic reinforcement and crystalline matrix development. In particular, annealed samples with ≥ 40 wt% LRS showed the highest stiffness, suitable for applications requiring dimensional stability under load. Flexural toughness (Figure 6.13f), defined as the energy absorbed before fracture, decreased significantly with increasing LRS content and post-processing, reaching a plateau at ≥ 40 wt% LRS, where differences in energy absorption became negligible across compositions.

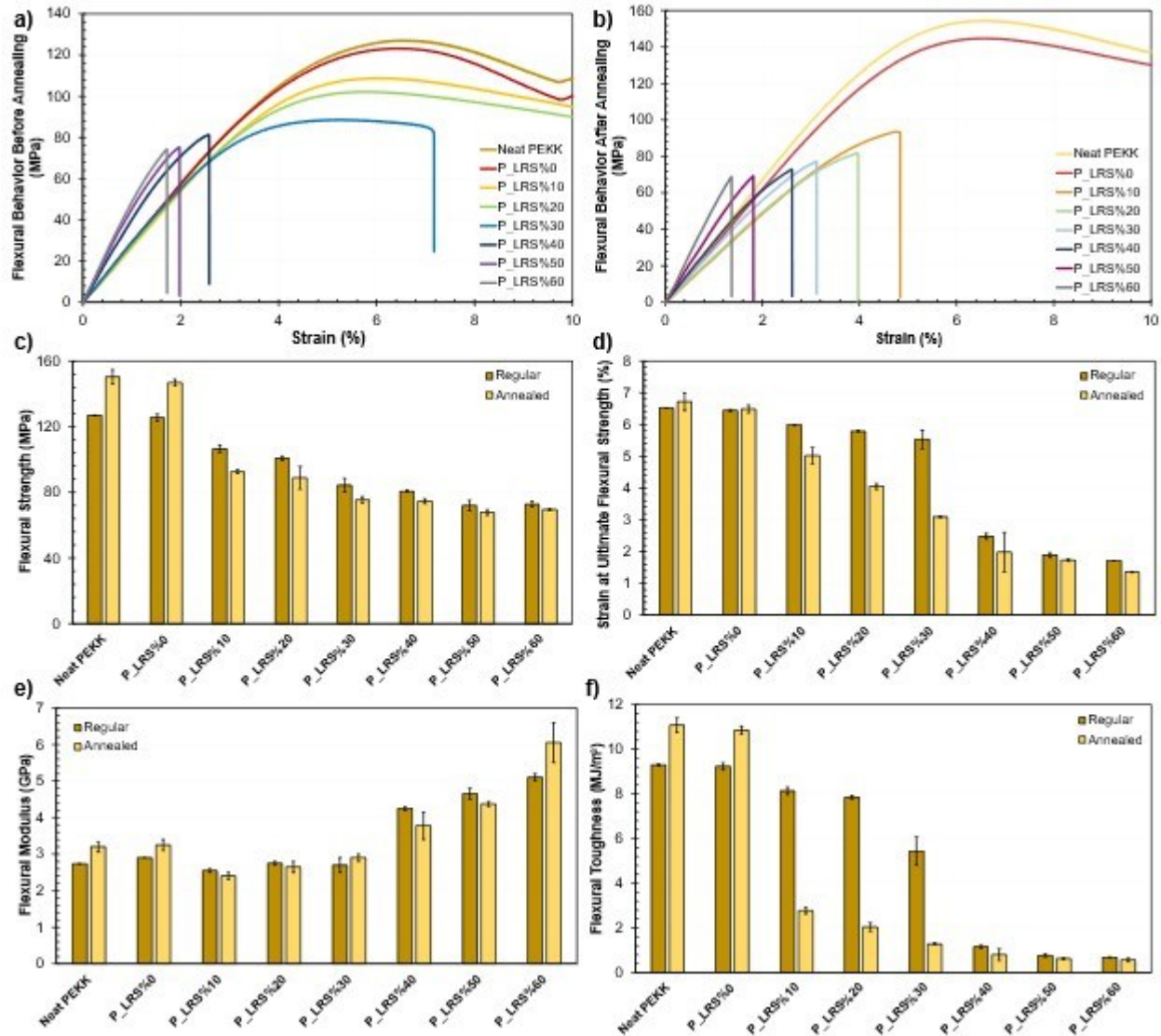


Figure 6.13. Flexural properties of 3D-printed PEKK/LRS composites in regular (amorphous) and annealed conditions: (a) stress-strain curves before annealing, (b) stress-strain curves after annealing, (c) flexural strength, (d) strain at ultimate flexural strength, (e) flexural modulus, (f) flexural toughness of amorphous and annealed samples.

6.4.4.3 DMA Testing

DMA was performed to assess the thermomechanical behavior and viscoelastic response of PEKK/LRS composites under varying filler content for amorphous and annealed 3D-printed samples, enabling direct comparison of how LRS content and post-processing influence the softening behavior and dimensional stability of the materials as shown in Figure 6.14. In the amorphous condition (left column of Figure 6.14), all samples exhibited a sharp decline in storage modulus (Figure 6.14a) as the temperature approached the glass transition region (~150–160 °C),

indicative of significant softening. This transition was accompanied by pronounced tan delta peaks, reflecting a highly viscoelastic response. Notably, increasing the LRS content mitigated the magnitude of loss modulus and its peak to a higher temperature, likely due to the reinforcing effect of the ceramic particles and their restriction on polymer chain mobility (Figure 6.14b). Despite this, all amorphous samples experienced permanent deformation at elevated temperatures, with the amount of deformation decreasing progressively with increasing LRS content, signaling improved thermal rigidity with higher filler loading (Figure 6.14d).

In contrast, the annealed samples (right column of Figure 6.14) demonstrated significantly enhanced thermal stability. The storage modulus was consistently higher across the temperature range, and the decline in modulus near T_g was more gradual and less severe compared to amorphous counterparts. Tan delta peaks were broader and reduced in intensity, suggesting decreased segmental mobility and a more constrained viscoelastic response due to the development of crystalline regions during annealing. Additionally, post- T_g dimensional stability improved markedly in all annealed samples, with no visible deformation recorded, even in high-temperature zones. This outcome underscores the beneficial role of thermal post-processing in stabilizing the polymer structure and limiting creep or flow at elevated service temperatures.

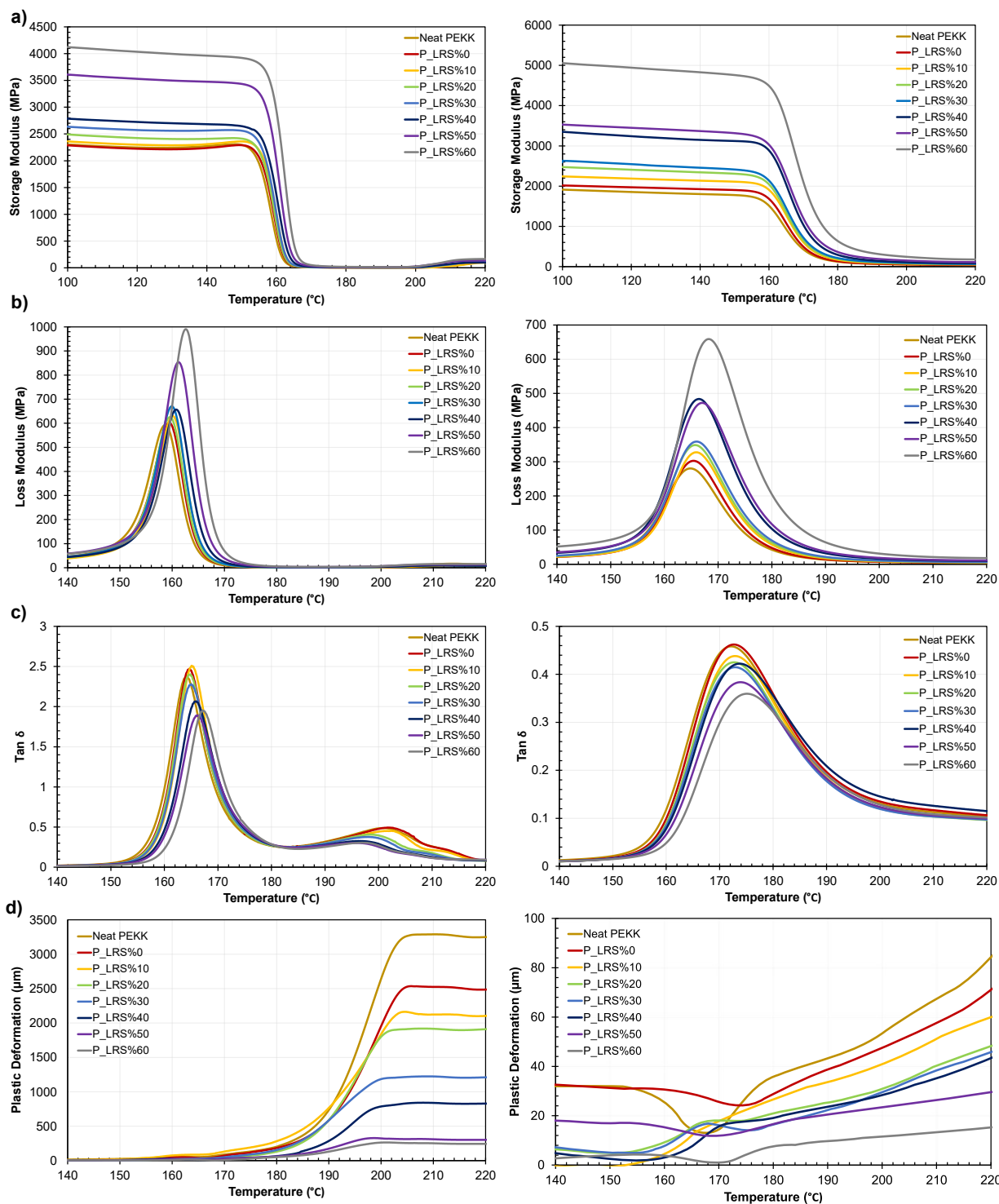


Figure 6.14. DMA results of PEKK/LRS composites across different compositions at regular (amorphous) (left) and annealed (right) state: (a) storage modulus (b) loss modulus, (c) loss tangent, (d) plastic deformation at elevated temperature.

6.4.5 Tensile Strength Model Validation

To assess the accuracy of the mathematical model developed in Section 2.6 for predicting the tensile strength of PEKK/LRS composites, experimental results from 3D-printed parts were compared with model predictions, as presented in Figure 6.15. The model incorporates three key variables affecting tensile strength: the LRS theoretical volume fraction (ϕ_f) (Figure 6.10a), the experimentally measured porosity (P) (Figure 6.10a), and the fracture mode (ductile/linear or brittle/exponential), which was qualitatively assessed based on the fracture surface observations (Figure 6.11).

Figure 6.15a illustrates the comparison for amorphous samples. A strong correlation between the predicted and measured tensile strength values was observed for low to moderate LRS contents (0–30 wt%), where the fracture behavior transitions from ductile to semi-brittle. However, at higher LRS contents (≥ 40 wt%), the deviation slightly increases due to the compounding effect of porosity and interfacial debonding, which may not be fully captured by the model's empirical assumptions. Nevertheless, the model accurately tracks the declining trend in tensile strength, reinforcing its validity for materials dominated by brittle fracture mechanisms.

In the annealed condition (Figure 6.15b), the model continued to show excellent predictive capability, particularly for samples with ≤ 30 wt% LRS. While crystallization tends to enhance strength, this benefit is offset by increased porosity in many compositions, which the model effectively integrates. For high LRS composites (50–60 wt%), the model's predictions closely matched the experimental values, aided by the reduced porosity observed after annealing in these formulations (Figure 6.10c). The strong alignment between theoretical and experimental results across both thermal states highlights the model's robustness in capturing the interplay between material composition, microstructural defects, and fracture behavior.

Overall, this comparison validates the use of the proposed model as a reliable tool for predicting tensile strength in 3D-printed PEKK/LRS composites and offers a valuable framework for future optimization of filler content and processing parameters in regolith-reinforced polymer systems.

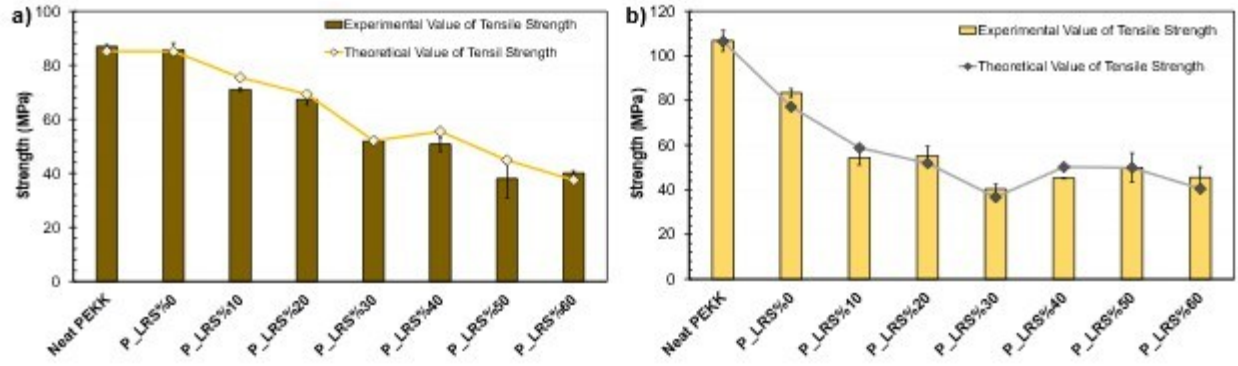


Figure 6.15. Comparison between experimental tensile strength and mathematical model predictions for PEKK/LRS 3D-printed composites, accounts for the influence of filler content, measured porosity, and the fracture type, demonstrating a high correlation with experimental trends in both thermal conditions: a) Amorphous and (b) annealed samples.

6.4.6 Printability and Structural Stability

To demonstrate the printability and post-processing performance of PEKK/LRS composites at high regolith loadings, two functional lunar rover wheel concepts were fabricated using both neat PEKK and regolith-reinforced composites (Figure 6.16a). The designs were based on auxetic graded lattice structures inspired by the work of Sidhu and El-Sayegh [165] on non-pneumatic tire architecture. The first concept, a re-entrant auxetic graded wheel concept, was fully printed with neat PEKK and partially printed with PEKK/LRS-50% (Figure 6.16b). The second concept, a diamond auxetic graded wheel concept, was also fully printed with neat PEKK and partially fabricated using PEKK/LRS-60% (Figure 6.16c). Due to limited availability of composite filament, only partial sections were printed with PEKK/LRS, with the objective of validating printability at these extreme filler contents.

All models were successfully printed using the process parameters listed in Table 6.2, confirming the extrusion stability and geometrical fidelity of the PEKK/LRS filaments, even at 50–60 wt% LRS. Following fabrication, the printed wheels were subjected to post-processing annealing to assess their structural and dimensional stability. Post-annealing observations revealed that wheels made from neat PEKK exhibited sidewall shrinkage and height expansion, attributed to crystallization shrinkage and inter-strand void expansion along the build direction, respectively. In contrast, both composite-based wheel segments, PEKK/LRS-50% and PEKK/LRS-60%, retained their original dimensions in all directions, showing no signs of shrinkage or warping

(Figure 6.16d). This dimensional stability can be attributed to the reinforcing effect of LRS particles at elevated temperatures, which inhibit thermal deformation by providing structural rigidity during crystallization and preventing void expansion.

These results not only demonstrate the printability of regolith-reinforced PEKK composites at high loadings but also highlight their superior structural integrity under post-processing conditions, an essential requirement for functional components in extraterrestrial environments.

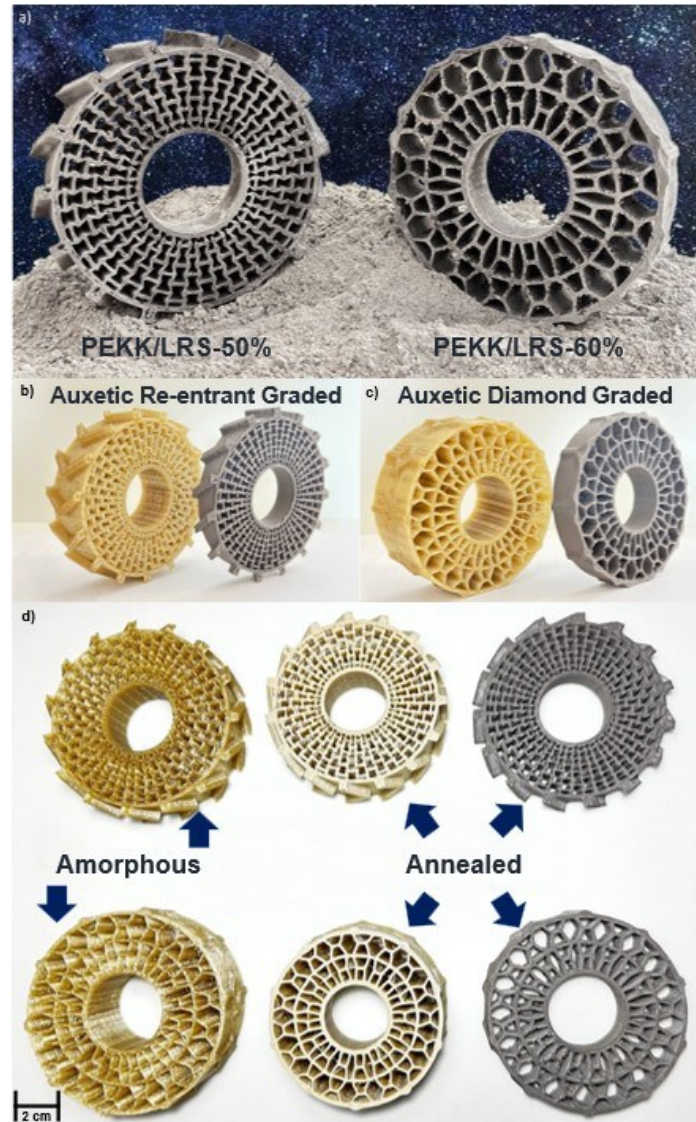


Figure 6.16. Printability and structural stability assessment of 3D-printed lunar rover wheel: (a) overview of the printed wheel models based on auxetic graded structures, (b) Auxetic re-entrant graded structure, fully printed with neat PEKK and partially printed with PEKK/LRS-50% (c) Auxetic diamond graded structure, fully printed with neat PEKK and partially printed with

6.4.7 Operational Implications for Lunar Additive Manufacturing

Although the primary objective of this study was to evaluate the printability and mechanical performance of PEKK/LRS composites under terrestrial conditions, the findings have direct implications for ISRU and AM in lunar environments. A consistent processing route was intentionally applied to all compositions to isolate the material-level influence of LRS concentration without introducing variability from process optimization. Future investigations will refine parameters such as extrusion-zone vacuum power, 3D printing nozzle temperature, and ambient annealing pressure to further control porosity and enhance interlayer fusion.

The vacuum environment of the Moon offers several inherent advantages for composite fabrication. The absence of atmospheric gases enables efficient degassing and prevents oxidation during extrusion and printing, provided that the polymer feedstock (PEKK) is adequately dried and conditioned prior to deployment. Similarly, the high vacuum can act as an inherent *autoclave substitute*, promoting interlayer consolidation and reducing the likelihood of void expansion during post-processing.

Moreover, MEX technology is intrinsically robust to microgravity effects. Commercial polymer-extrusion 3D printers have demonstrated reliable performance even when printing in inverted orientations, indicating that extrusion is governed primarily by pressure-driven flow rather than gravity. Under microgravity, the absence of gravitational sagging or overhang collapse may further enhance geometric fidelity and reduce the need for support structures when producing complex components. Collectively, these factors suggest that space-based manufacturing of PEKK/LRS composites could achieve higher part density and lower porosity than terrestrial processing, advancing the practicality of sustainable, low-cost lunar infrastructure fabrication.

The lunar surface experiences extreme temperature fluctuations ($-180\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$) capable of inducing dimensional and interfacial stresses in structural materials. Although such conditions are difficult to replicate experimentally, the low thermal conductivity of both PEKK and LRS helps moderate temperature gradients and limit internal stress development. At cryogenic temperatures, PEKK transitions into a rigid, glassy state yet maintains dimensional stability due to its aromatic backbone and semi-crystalline architecture, while dispersed LRS particles constrain thermal contraction and distribute internal stresses more uniformly. Together with PEKK's high glass-transition temperature, its crystallinity stabilization, and the ability of LRS particles to delay matrix

softening at elevated temperatures, these characteristics are expected to improve tolerance to both cryogenic contraction and thermal expansion. In addition, PEKK and the silicate-based regolith filler are known radiation-shielding materials, capable of attenuating ultraviolet and ionizing radiation, a further benefit for long-term exposure on the lunar surface. The present work therefore represents a foundational step within a broader research initiative on sustainable lunar manufacturing; future phases will address thermal-cycling durability through coupled simulation, cryothermal testing, and radiation-exposure assessment under vacuum conditions.

The 3D-printed lunar wheel prototype fabricated in this study serves as a proof of concept demonstrating the printability and geometric scalability of the developed PEKK/LRS composite. While functional performance evaluation was beyond the current scope, the successful fabrication of a coherent structure confirms the feasibility of processing high-regolith-content thermoplastic composites into complex ISRU components. Subsequent work will focus on mechanical and thermal validation, including topology optimization of the wheel geometry based on mission-specific loading requirements and its interaction with simulated lunar regolith, to achieve optimized weight-to-strength and traction characteristics. Moreover, the next phase of this research will employ micro-XCT analysis to quantify closed pore populations and evaluate their evolution during large-scale structural 3D printing of the developed composite in functional lunar rover wheel prototypes.

A further operational advantage of thermoplastic-based ISRU composites lies in their inherent recyclability. The PEKK/LRS system can be reprocessed through mechanical size reduction and re-extrusion, enabling defective or end-of-life parts to be reused as new feedstock. Although the presence of LRS particles increases melt viscosity and slightly limits flowability, PEKK's exceptional thermal stability and chemical resistance permit multiple recycling cycles with minimal degradation. This recyclability supports a closed-loop material economy for lunar manufacturing, reducing dependence on Earth-supplied polymers. Future research will quantify the property retention of recycled PEKK/LRS composites and optimize reprocessing parameters for in-situ applications.

PEKK/LRS-60%, (d) dimensional comparison of neat PEKK and composite wheels after annealing.

6.5 Conclusion

As space agencies and private enterprises turn their focus toward sustainable extraterrestrial presence, the development of structurally reliable, resource-efficient materials for lunar infrastructure becomes essential. This study demonstrated the feasibility and material-process integration of PEKK/LRS composite filaments for sustainable lunar additive manufacturing. Composite filaments containing up to 60 wt% Lunar Mare Simulant (LMS-1D) were successfully fabricated via twin-screw extrusion and 3D-printed using MEX method. Despite challenges in extrusion stability and porosity at high filler loadings, rheological analysis and manufacturing trials confirmed the printability of filaments at 50% and 60% regolith content.

Thermal and mechanical characterization revealed critical thresholds: above 30 wt% LRS, viscosity, and void content sharply increased, influencing process stability and tensile performance. Nonetheless, annealing proved effective in enhancing crystallinity, reducing porosity for highly filled composites, and stabilizing thermal and dimensional properties. The printed wheel prototypes validated the structural integrity and dimensional resilience of these composites in functional designs. Furthermore, the incorporation of a physics-informed mathematical model provided strong predictive agreement with experimental tensile performance. The rheological shift across the increase of LRS weight fraction influenced porosity development, with low regolith loadings exhibiting increased void expansion after annealing (37.6% porosity at 30 wt% LRS), while higher loadings demonstrated a reversal of this trend due to matrix densification and enhanced rigidity (26.4% porosity at 60 wt% LRS). The tensile strength model developed herein integrates these interdependent phenomena, volume fraction, porosity, and fracture mode, providing a comprehensive framework that links material processing to mechanical performance. By explicitly connecting rheological, microstructural, and mechanical responses, this study establishes a cohesive pathway for understanding and optimizing the design of regolith-reinforced thermoplastics for sustainable lunar manufacturing.

Overall, this work contributes a robust foundation for in-situ lunar manufacturing by advancing the understanding of high-performance-thermoplastic-regolith (HPTR) composite behavior across processing, structural evolution, and functional performance domains. A key novelty lies in the experimental validation of not only the printability but also the dimensional stability and mechanical viability of highly filled composites in complex, load-relevant structures such as

auxetic lunar rover wheels. The findings bridge a critical gap between material development and functional deployment, laying the groundwork for the next stage of ISRU-driven infrastructure offers both a scalable approach and a compelling proof-of-concept for future lunar construction systems, advancing the vision of self-sufficient off-Earth manufacturing. This framework can be extended to optimize regolith–thermoplastic systems for other ISRU structures such as shielding panels and habitat elements.

Chapter 7: “Lazarus: Resurrect”

“Lazarus, Come out”

- John 11:43

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7. On the Resistance of PEKK to the Degradation during Multiple Recycling Cycles for Additive Manufacturing

7.1 Abstract

The recyclability of high-performance poly(ether ketone ketone) (PEKK) is critical for sustainable additive manufacturing and future in-space resource utilization. This study systematically evaluates the thermal, mechanical, and chemical stability of PEKK subjected to multiple recycling loops to elucidate potential degradation mechanisms. Thermogravimetric analysis revealed negligible (<1%) mass loss after 5 h of isothermal exposure below 450 °C, confirming the polymer's excellent thermal resistance under extrusion and printing conditions. Cyclic differential scanning calorimetry (DSC) demonstrated stable melting and cold-crystallization behavior across six thermal cycles, indicating preserved crystallization kinetics. Tensile testing showed that the amorphous strength remained within 83–91 MPa across all cycles, while annealed samples maintained strengths of 102–116 MPa. Flexural strength similarly remained consistent, ranging from 112–127 MPa (amorphous) and 147–160 MPa (annealed), and dynamic mechanical analysis (DMA) results indicated minimal changes in viscoelastic properties. Together, these mechanical and thermomechanical analyses confirm that PEKK retains its structural integrity after three complete recycling sequences involving shredding, pulverization, extrusion, and reprinting. Fourier transform infrared spectroscopy detected no new carbonyl or hydroxyl bands, excluding oxidative chain scission, while X-ray fluorescence (XRF) revealed only trace (<0.5 wt%) metallic contamination. Scanning electron microscopy (SEM) of fracture surfaces further confirmed well-fused interlayer morphology and minimal porosity evolution. Collectively, these results demonstrate that PEKK maintains its molecular and microstructural integrity during repeated thermal–mechanical cycles, highlighting its exceptional thermal-oxidative stability and its suitability for circular, high-performance, and extended-lifetime polymer applications.

7.2 Introduction

As additive manufacturing (AM) advances toward sustainable production and in-space manufacturing (ISM), the ability to recycle and reprocess high-performance polymers has become

essential for extending material lifetimes, conserving resources, and enabling closed-loop manufacturing cycles [26]. Poly(ether-ketone-ketone) (PEKK), a high-performance member of the poly(aryl-ether-ketone) (PAEK) family, has attracted increasing attention in aerospace, automotive, and biomedical sectors due to its excellent mechanical strength, chemical resistance, and thermal stability, as well as its compatibility with modern AM technologies [1,5,32,58]. PEKK's intrinsic flame retardancy, radiation resistance, and performance retention under vacuum further enhance its suitability for ISM applications [26,35,59,166,167]. In contrast to biodegradable thermoplastics such as polylactic acid (PLA), which undergo significant chain scission, crystallinity loss, and strength reduction under repeated thermal or radiation exposure, PEKK retains its thermal stability and interfacial performance through multiple processing cycles [168–171]. These characteristics make PEKK a strong candidate for fabricating composite components using in-situ resources available on extraterrestrial surfaces [61,72].

The recycling of polymer-based composite materials generally involves end-of-life collection, mechanical grinding, and reprocessing into powder or scrap for reuse in additive manufacturing. Major degradation mechanisms such as fiber–matrix decoupling, chain scission, and increased crystallinity can reduce interfacial strength over successive cycles, highlighting the need for controlled processing [172]. Comprehensive reviews of thermoplastic composite recycling methods have identified mechanical recycling as the most sustainable and industrially viable approach for high-performance polymers such as PEEK and PEKK, since it preserves molecular integrity, minimizes energy consumption, and avoids the chemical waste associated with solvent- or pyrolysis-based methods [173–176]. The PAEK family represents a rare class of polymers that combine exceptional durability with recyclability, unifying thermal endurance, mechanical robustness, and emerging circularity concepts, although their chemical resistance also makes recycling more challenging [177].

Solution-based degradation routes developed for PAEK composites require harsh catalytic conditions and elevated temperatures, underscoring the inefficiency of solvent-assisted recycling compared to direct mechanical reprocessing [178]. Industrial-scale studies have begun exploring mechanical recycling of PEKK/carbon-fiber demonstrators. Grinding and electrodynamic fragmentation (EDF) were found to produce recyclable feedstock, yet compression-molded parts exhibited up to 60 % loss in tensile and shear strength, indicating that current composite recycling

strategies remain limited to down-cycled, lower-performance applications [179]. Similar trends were reported for recycled CF/PEKK laminates, where property reductions were primarily attributed to fiber fragmentation and poor interfacial adhesion, even though the PEKK matrix itself retained physicochemical stability [180,181].

Pedoto et al. [182,183] examined the thermo-mechanical and aging behavior of neat and carbon-fiber-reinforced PEKK above its glass transition temperature, identifying oxidation and chain branching as dominant mechanisms during long-term exposure at elevated temperatures. Under 5 bar O₂ for up to 1000 h, only superficial color changes were observed with negligible influence on crystallinity or mechanical performance. Complementary long-term studies by Yang et al. [184] on PAEK and CF/PAEK composites confirmed that secondary crystallization between 200 °C and 250 °C can initially improve strength, while prolonged exposure induces oxidative scission of amorphous regions and formation of oxygenated surface groups. Roland et al. [185] further demonstrated that thermo-oxidative aging of PEKK at 280 °C is dominated by crosslinking rather than chain scission, resulting in limited embrittlement and outstanding structural stability.

Croshaw et al. and Choupin et al. [186,187] revealed that under melt-state conditions, PEKK primarily experiences homolytic ether-bond cleavage followed by radical coupling, generating long-chain branching. This mechanism increases viscosity and slightly lowers crystallinity without producing oxidation or mass loss. Dolo et al. [188] modelled thermal degradation of carbon-fiber-filled PEEK during laser-assisted tape (LATP) placement, showing that oxidation-related fluorenone (1711 cm⁻¹) and ester (1739 cm⁻¹) bands form only beyond a critical degradation index, confirming that short heating cycles below 400 °C do not trigger molecular breakdown. Likewise, Al Lafi et al. [189] used 2D-Fourier Transform Infrared Spectroscopy (FTIR) to identify oxidation-induced carbonyl species in irradiated PEEK, demonstrating that color darkening arises from superficial oxidation rather than bulk degradation. Together, these findings establish oxidation as the principal degradation mechanism in PAEK systems and justify monitoring such signatures in recycled PEKK; in this work, FTIR and XRF are employed to determine whether the observed color change originates from surface oxidation or external contamination.

Recycling studies on conventional AM polymers generally report cumulative degradation across repeated processing cycles. Polyethylene terephthalate glycol (PETG), for example, shows progressive tensile strength loss and increased brittleness after 3–5 recycling loops due to glycol

chain scission and reduced molecular weight [190]. Polyamide 12 (PA12), another widely used AM polymer, experiences diminished ductility and rising porosity after each reprocessing step, primarily attributed to oxidative degradation and changes in crystallinity [191]. High-density polyethylene (HDPE) likewise exhibits decreasing elongation at break and melt flow instability with repeated extrusion–printing cycles [192] or for the case of polypropylene (PP), it suffers viscosity reduction and embrittlement after multiple melt histories [193]. The motivation behind this study stems from the increasing demand for sustainable processing routes for high-performance polymers in additive manufacturing. Unlike commodity polymers, which often suffer measurable chain scission, oxidation, or viscosity loss after limited reprocessing, PEKK possesses an aromatic and highly stable backbone that suggests superior recyclability [194], yet this behavior has not been rigorously quantified. Establishing the extent to which PEKK retains its mechanical, thermal, and molecular integrity through repeated melt-extrusion cycles is therefore essential for industries seeking long-lifetime, reprocessable materials for aerospace, medical, and energy applications. The outcomes of this work provide a scientific basis for adopting recycled PEKK in high-value components, offering potential reductions in material waste, production costs, and environmental impact while enabling long-term circular use in conventional and in-space manufacturing environments.

The present study addresses this gap by systematically evaluating the thermal, crystallization, mechanical, and chemical stability of PEKK subjected to multiple recycling loops involving shredding, pulverization, filament extrusion, and reprinting. A multi-modal characterization approach was employed, including thermogravimetric analysis (TGA) to assess long-term isothermal stability, cyclic differential scanning calorimetry (DSC) to monitor potential changes in crystallization kinetics, and tensile, flexural, and dynamic mechanical analysis (DMA) to quantify the evolution of mechanical and viscoelastic properties. Complementary Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF) were used to evaluate potential oxidative pathways or elemental contamination, while scanning electron microscopy (SEM) provided direct insight into fracture morphology and porosity evolution. Unlike previous recycling studies on commercial polymers discussed earlier, which frequently report substantial reductions in ductility, toughness, or thermal stability after multiple reprocessing steps, this work demonstrates that PEKK retains its properties to a far greater extent, consistent with the robust molecular architecture of high-performance PAEK polymers. Collectively, the results reveal that PEKK undergoes minimal

degradation across repeated thermal–mechanical cycles, maintaining its structural, chemical, and functional integrity. These findings hold direct relevance for industries that depend on PEKK for its exceptional mechanical strength, thermal resistance, and chemical durability. Applications such as aerospace brackets, sacrificial space structures, satellite components, high-temperature tooling, oil-and-gas connectors, and medical-grade devices routinely utilize PAEK-family polymers but face cost and sustainability challenges due to their high material price and energy-intensive processing.

7.3 Material & Methods

7.3.1 *Material*

Amorphous PEKK filament (1.75 ± 0.05 mm diameter) was supplied by Spool3D (Canada). The manufacturer specifies that the PEKK filament be stored in a resealable plastic bag in the presence of the supplied desiccant pack, with drying performed prior to and during printing. Although PEKK exhibits lower moisture uptake compared to polymers such as PET and PA12, it remains sensitive to residual moisture during high-temperature melt processing; therefore, drying was performed prior to extrusion and additive manufacturing [75,195,196]. PEKK readily absorbs moisture, which can lead to porosity, weakened interlayer bonding, and reduced mechanical performance during printing. To mitigate these effects, the filament was dried in a ventilated chamber at 125 °C for 8 h prior to use and subsequently stored in a dehumidifying chamber after each printing session. This preparation step was essential to ensure consistent extrusion quality and to minimize moisture-induced defects in the printed specimens. For each recycling cycle, only the material obtained from the previous stage was reused, without adding any virgin PEKK, to isolate and evaluate the intrinsic degradation behavior of the polymer.

It should be noted that the commercial amorphous PEKK filament used in this study is supplied without detailed disclosure of its precise copolymer composition (T/I isomer ratio, molecular weight distribution, and possible stabilizing additives). Because the objective of this work is to evaluate the relative degradation behavior of the same material across repeated recycling cycles, the absence of full compositional disclosure does not affect the internal validity of the study. However, the results should be interpreted as representative of this specific commercial-grade PEKK rather than universally applicable to all PEKK formulations.

7.3.2 *Manufacturing Processes*

7.3.2.1 Recycling Process

The recycling workflow consisted of multiple additive manufacturing and reprocessing cycles designed to evaluate the intrinsic recyclability of PEKK (Figure 7.1a). Initially, standard test specimens were 3D-printed from neat PEKK filament and subjected to mechanical testing. The scrap parts were then sorted based on their thermal history (heat-treated or non-heat-treated) before being shredded using a Felfil Shredder 750 (Felfil, Italy). Each batch underwent five consecutive shredding cycles, reducing the granule size to below 3 mm in diameter. The shredded material was subsequently pulverized using an AF LAB Pulverizer (Orenda, Canada) through three successive milling passes, yielding a uniform powder with particle size below 500 μm , suitable for feeding into the twin-screw micro-extruder. Achieving consistent powder fineness was critical for maintaining filament-diameter stability during extrusion.

Prior to extrusion, both amorphous and annealed PEKK powders were dried at 125 °C for 8 h to remove residual moisture. The resulting recycled filament was used to print the first-generation recycled specimens (Recycled #1). Samples printed from filaments derived from annealed scrap were annealed again after printing, whereas those produced from amorphous scrap were left untreated. This separation allowed a more precise evaluation of any degradation associated with the annealing process. The same protocol was repeated for two additional recycling loops, producing Recycled #2 and Recycled #3 batches.

Because DMA testing involves an additional controlled thermal exposure, the corresponding post-test specimens were discarded to ensure that all recycled materials in subsequent batches experienced an identical thermal history. To assess the influence of the in-house extrusion process itself, the as-received neat PEKK filament was pelletized ($< 500 \mu\text{m}$) and re-extruded once, generating a Recycled #0 batch. This control group represented a reused, but not truly recycled material, allowing the impact of extrusion alone to be distinguished from that of complete recycling. For consistency, no further recycling was performed on Recycled #0 specimens, as the first genuine recycling cycle (Recycled #1) was defined to originate exclusively from scrap of 3D-printed parts fabricated using the virgin filament.

7.3.2.2 Filament Manufacturing

Recycled PEKK filaments were processed using a twin-screw extruder (Process 11, Thermo Fisher Scientific, Germany) equipped with a high-performance screw configuration optimized for engineering thermoplastics [118]. The screw design included two-stage mixing elements (Figure 7.1c) and operated at 50 rpm. The extrusion parameters were determined through a combination of the manufacturer's recommended processing window for PEKK, existing literature on PAEK melt behavior, and iterative optimization performed during preliminary printing trials [61,72,119]. For filament extrusion, the eight-zone temperature profile was selected to ensure sufficient melt homogenization while avoiding polymer overheating, consistent with melt-processing temperatures reported for PEKK and PEEK. The extrusion temperature profile was divided into eight zones, as illustrated in Figure 7.1c:

- Zone 1 (Z1) – powder feeding section (low temperature, no heat element is involved in this zone, and the temperature of this zone increases due to thermal conduction from the adjacent zone)
- Zone 2 (Z2) – maintained at 260 °C to prevent heat conduction toward the hopper³
- Zones 3–7 (Z3–Z7) – held at 315 °C, consistent with the melt-crystallization temperature range of PEKK [71,119].
- Zone 8 (Z8) – elevated to 330 °C (15 °C higher) to reduce melt viscosity and minimize die pressure at the exit.

A vacuum degassing system positioned after the first mixing stage was used to remove entrapped air and volatiles. The molten polymer was extruded through a 2 mm die nozzle, and filament diameter (target = 1.75 ± 0.15 mm) was regulated by tension control using a Filabot spooler (Filabot, USA) equipped with a Mitutoyo Fila Measure sensor (Mitutoyo, Japan) for inline dimensional monitoring. Filaments were air-cooled through a Filabot air path (Filabot, USA) instead of water quenching to prevent moisture uptake and subsequently stored in a dry chamber at 10 % relative humidity until printing.

7.3.2.3 Additive Manufacturing

All specimens were fabricated using a high-temperature CreatBot F160-PEEK 3D printer (CreatBot, China), capable of processing high-performance thermoplastics within the PAEK family (Figure 7.1b). To minimize the time interval between successive layer depositions, each specimen was printed individually at the center of the build platform rather than in batches. This strategy reduced interlayer cooling time and exposure to ambient air, thereby improving layer adhesion and overall part integrity.

According to the supplier's specifications, the recommended extrusion temperature range for PEKK is 360–400 °C with a build plate temperature of 90–130 °C. However, preliminary printing trials demonstrated that increasing the bed temperature effectively mitigated warpage; therefore, a build plate temperature of 160 °C, slightly above the glass transition temperature (T_g) of PEKK [197], was selected for all subsequent prints. The remaining printing parameters were optimized through a combination of literature guidelines [19,20,32,39,41,69,197] and iterative experimental adjustment and are summarized in **Error! Reference source not found..** Under these conditions, specimens exhibited excellent surface quality and dimensional consistency without the need for adhesives or auxiliary adhesion aids. Visual inspection confirmed the absence of common printing defects such as warping.

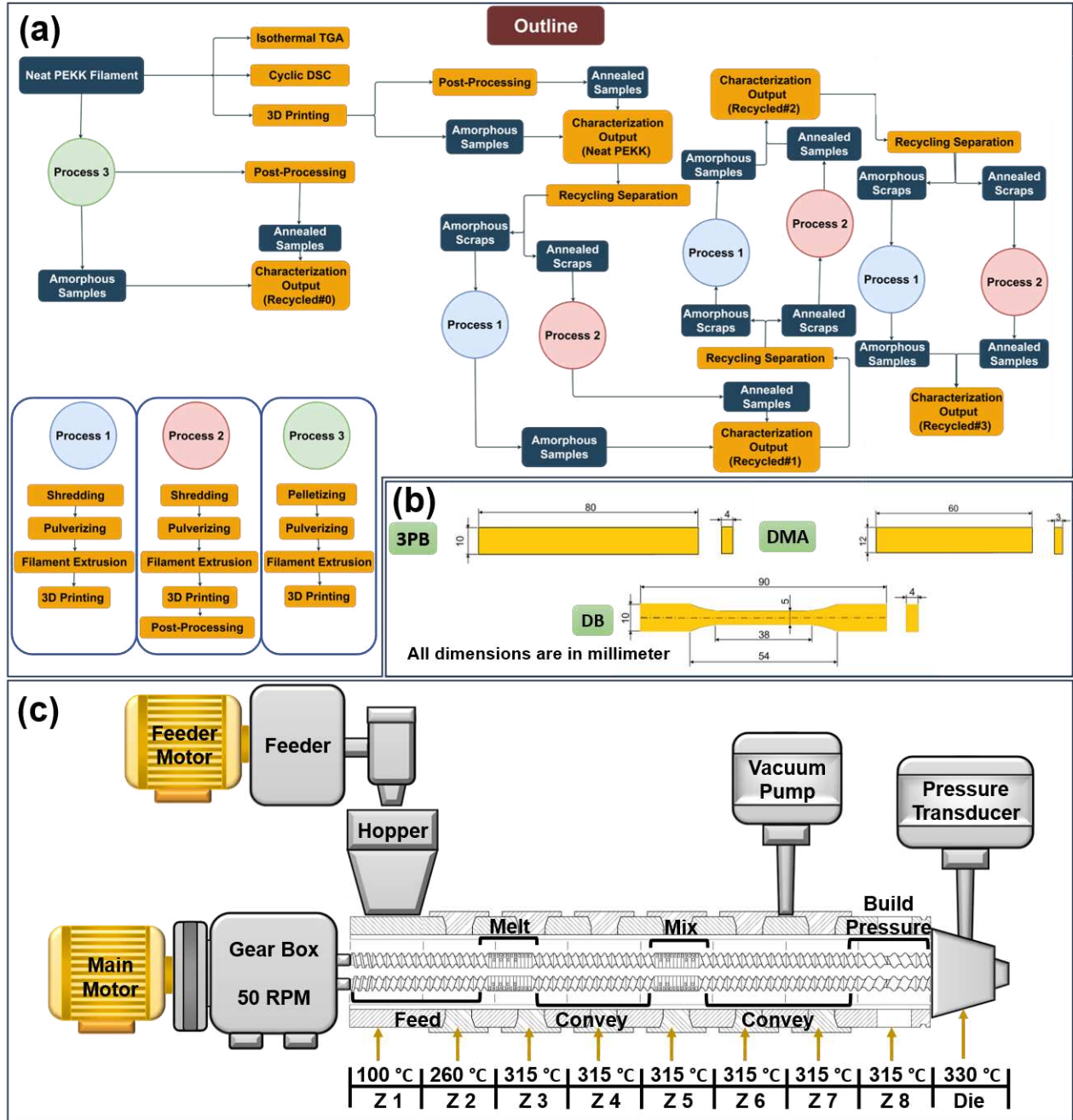


Figure 7.1. Manufacturing process: (a) Micro-extruder parameter set up and screw configuration, illustrating each stage of the extrusion [159], (b) process sequence for whole manufacturing process, (c) 3D-printed sample geometry (all dimensions are in mm).

Table 7.1. MEX set of parameters and manufactured coupons

Print parameter	Value	Units
Nozzle temperature	380	°C
Bed temperature	160	°C
Chamber temperature	60	°C
Print speed	40	mm/s
Infill density	100	%
Layer height	0.25	mm
Extruder diameter	0.8	mm
Build orientation	Flat	-

7.3.2.4 Annealing Protocol

After 3D printing, all specimens were classified into two categories, as printed and annealed, to assess the impact of thermal post-treatment on both the material's properties and its potential degradation behavior. The annealing schedule, adapted from previously optimized conditions [71], involved heating the samples to 210 °C over 15 min, holding this temperature for 30 min, and subsequently cooling to ambient temperature within 15 min, resulting in a total cycle duration of roughly 1 h.

7.3.3 Characterization Techniques

7.3.3.1 Thermal Characterization

- **TGA:**

To evaluate the isothermal thermal stability of PEKK, thermogravimetric analysis was performed on the neat PEKK filament using a TGA Q50 instrument (TA Instruments, USA), in accordance with ASTM E1131 [28]. The test was designed to assess long-term thermal degradation under controlled conditions. Isothermal measurements were conducted at 300 °C to 550 °C, in 50 °C intervals, where each specimen was held for 5 h after reaching the target temperature at a heating rate of 10 °C/min under a nitrogen atmosphere. For each condition, a minimum of three replicates were tested to ensure reproducibility. Samples weighing between 30 mg and 40 mg were placed in ceramic crucibles and heated from ambient temperature to the designated setpoint before the isothermal hold.

TGA was also conducted on the neat and recycled PEKK batches (Recycled #1–#3). The complete test specifications and full set of degradation curves are provided in the Supplementary Information, which confirm that all recycled cycles exhibit identical thermal behavior to neat PEKK.

- **DSC:**

DSC was carried out using a DSC Q200 instrument (TA Instruments, USA) to examine potential variations in the crystallization behavior of PEKK under repeated thermal cycling. Since each recycling iteration involves two melting events (one during filament extrusion and another during 3D printing) the test was designed to simulate three complete recycling loops, corresponding to six thermal cycles in total.

The samples were heated from 0 °C to 380 °C at a rate of 10 °C/min, held isothermally at 380 °C for 5 min, and then cooled to 0 °C at 5 °C/min. This temperature range and cycling scheme were selected to replicate the highest thermal exposure encountered during processing, considering that extrusion typically occurs at ~330 °C and printing at ~380 °C.

Different heating and cooling rates were adopted to account for the asymmetry between cold crystallization (during heating) and melt crystallization (during cooling). Preliminary trials revealed that a cooling rate of 10 °C/min was too rapid for detectable crystallization, while reducing it to 5 °C/min enabled clear identification of exothermic peaks. This confirmed that PEKK crystallizes much more slowly during cooling than heating, explaining the low crystallinity commonly observed in as-printed specimens and justifying the implementation of a controlled annealing step in the process [71].

It is worth mentioning that the measured crystallinity percentage is highly dependent on how the crystallization region is defined and on the instrument's calibration, both of which can introduce considerable variability. To quantitatively assess changes in crystallization behavior across thermal cycles, the first heating run of the as-received amorphous PEKK filament was used as the baseline reference. The relative crystallinity for subsequent cycles, (X_{cRev}), was calculated using Eq. (7.1), which normalizes the net crystallization enthalpy of each cycle to the first-cycle value. All DSC

tests were conducted on 5–10 mg specimens sealed in aluminum hermetic pans, following TA Instruments guidelines [24] and ASTM D3418 [25].

$$X_{C_{Rev}}(\%) = \frac{(\Delta H_M - \Delta H_{CC}) - \Delta H_{Ref}}{\Delta H_M^0} \times 100, \quad \Delta H_{Ref} = 1st \text{ Cycle } (\Delta H_M - \Delta H_{CC}) \quad (7.1)$$

In Eq. (7.1), ΔH_{CC} represents the enthalpy of cold crystallization, and ΔH_M refers to the enthalpy of melting. Based on the calibration of the DSC and the properties of the raw material, ΔH_{Ref} represents the net enthalpy change of the first heating cycle, which is treated as the zero-crystallinity reference. Although this net value may be negative, it does not imply negative crystallinity; rather, it reflects instrument calibration and serves solely as a reference point, posing no conceptual inconsistency. According to the literature, the theoretical melting enthalpy of fully crystalline PEKK (ΔH_M^0) is taken as 130 J/g [7,9,10,20,26,27]. Using Eq. (7.1), for the evaluation of crystallinity, DSC was performed on both neat and recycled PEKK batches. The complete test conditions and the full set of thermograms are provided in the Supplementary Information, confirming that all recycled cycles exhibit crystallization kinetics identical to that of neat PEKK.

7.3.3.2 Mechanical Testing

- **Tensile test**

Tensile specimens were prepared following the ISO 527 standard [50], as shown in Figure 7.1b. Tests were performed using a universal testing machine (Hoskin Scientific, Canada) equipped with a 5 kN S-type load cell mounted on the upper grip. A crosshead speed of 2 mm/min was applied under displacement control, with a preload of 10–20 N to ensure accurate specimen alignment and eliminate slack prior to loading.

- **Flexural Test**

Flexural testing specimens were prepared as standard ISO 178 coupons [51] (Figure 7.1b). Three-point bending was performed on a universal testing machine (Hoskin Scientific, Canada) utilizing an S-type 5 kN load cell. The test was conducted at a crosshead speed of 2 mm/min. A 1–2 N preload was applied prior to testing to ensure stable contact between the specimen and the loading nose.

- **DMA**

DMA was carried out using a DMA Q800 (TA Instruments, USA), referencing ASTM D4065-12 [54] and ASTM D5418 [55] for dual cantilever beam testing (as shown in Figure 7.1b). Specimens were tested under a constant strain amplitude of 0.1% at a fixed frequency of 1 Hz. The thermal scan, ranging from 100 °C to 240 °C with a heating rate of 2 °C/min, was conducted to evaluate the viscoelastic behavior of the materials under dynamic loading conditions.

7.3.3.3 Chemical Composition Analysis

- **FTIR**

FTIR analyses were conducted using a PerkinElmer Spectrum 100 spectrometer (PerkinElmer, USA) equipped with a Universal ATR accessory, following a scanning range of 4000–650 cm^{-1} and a resolution of 2 cm^{-1} . Spectra were collected for neat PEKK filament and for the amorphous and annealed samples across three recycling cycles. The obtained spectra were processed using Euclidean correlation to confirm characteristic absorption bands corresponding to aromatic and ketone linkages in the PAEK backbone. Major peaks were identified at 3060 cm^{-1} (aromatic C–H stretching), 1650 cm^{-1} (C=O stretching of ketone groups), 1580–1490 cm^{-1} (aromatic C=C skeletal vibrations), 1305 cm^{-1} (ether C–O–C stretching), and 1010–920 cm^{-1} (aromatic C–H bending)

- **XRF**

Elemental analysis was performed using a Bruker S8 Tiger wavelength-dispersive X-ray fluorescence spectrometer (Bruker, Germany). Measurements were conducted under a helium atmosphere using the QE-Organics-28 mm setup to ensure optimized detection of low atomic number elements. Solid samples of neat and recycled PEKK were analyzed. Each spectrum was processed through semi-quantitative SpectraPlus analysis software (Bruker, Germany) for elemental identification and comparative evaluation across neat filament and recycling cycles.

- **SEM**

Fracture surface analyses of the tensile specimens were performed using a HITACHI S-3400N scanning electron microscope (HITACHI, Japan) operated at an accelerating voltage of 15 kV. The primary objective of this examination was to evaluate the fracture morphology, identify the

presence of contaminant particles, and assess the evolution of porosity and interlayer bonding quality through successive recycling cycles. All samples were sputter-coated with a thin layer of gold to prevent surface charging prior to imaging.

7.4 Results & Discussion

7.4.1 Thermal Characteristics

7.4.1.1 Thermal Stability

The isothermal thermogravimetric behavior of neat PEKK is presented in Figure 7.2a. For consistency, all curves were recorded starting from 300 °C, with a heating rate of 10 °C/min until reaching the target isothermal temperature. This approach allowed for a direct comparison of the degradation onset between conditions, as some specimens exhibited minor mass loss prior to reaching the isothermal stage.

Below 450 °C, PEKK exhibited outstanding thermal resistance, with a total mass loss of less than 1 % after 5 h. This result indicates minimal volatilization or chain scission within this temperature range, although at temperatures above 380 °C, prolonged isothermal exposure could gradually alter the ether-to-ketone ratio even in the absence of measurable weight loss [186]. However, a pronounced weight reduction was observed once the temperature exceeded 450 °C, marking the onset of thermally induced degradation. After 5 h of exposure, the weight loss reached approximately 7.5% at 450 °C, 32.1% at 500 °C, and 38.3% at 550 °C. At temperatures above 450 °C, mass loss occurred rapidly during the initial stage of exposure and then gradually approached a steady state, signifying stabilization of the residue mass. Notably, the curve at 450 °C did not completely level off, suggesting that degradation reactions were still ongoing but very slowly at the end of the test period.

These results confirm that PEKK demonstrates exceptional resistance to thermal degradation below 450 °C, consistent with previous findings for PAEK-family polymers [188]. The onset of significant decomposition corresponds to the cleavage of ether and ketone linkages, accompanied by the evolution of volatile products such as CO₂ and aromatic fragments. At temperatures exceeding 500 °C, the formation of a carbonaceous char becomes dominant, producing a stable residue typical of aromatic ketone-based thermoplastics. This char layer not only inhibits further volatilization but also contributes to enhanced thermal stability and intrinsic flame retardancy at

elevated temperatures. Additional TGA curves for all recycling cycles (Recycled #1–#3) are presented in Supplementary Information, Figure. S7.1. No differences in degradation onset or mass-loss rate were observed, confirming that thermal stability is maintained throughout the recycling process.

7.4.1.2 Crystallization Kinetics (DSC)

The cyclic DSC thermograms of neat PEKK are presented in Figure 7.2b, showing the evolution of melting and crystallization behavior under repeated thermal exposure. Each cycle represents sequential heating and cooling between 0 °C and 380 °C, simulating the worst-case cumulative thermal exposure that could occur during multiple extrusion and printing stages in the recycling process.

Apart from the first cycle, which reflects the initial thermal history of the neat filament, all subsequent cycles exhibit nearly overlapping trends, indicating consistent thermal response across repeated heating and cooling. Quantitative crystallinity values extracted from the DSC data (Figure 7.2b) show minimal variation across cycles (23% to 28%), confirming that repeated melting does not measurably alter the degree of crystallinity. As described in the methodology section, crystallinity values depend strongly on the chosen limits of the crystallization region, so some scatter in the calculations is normal. These values have also been demonstrated in Table 7.2 for clarity. Throughout all six cycles, the melting temperature (T_m) and cold-crystallization temperature (T_{cc}) remained largely unchanged, indicating that crystallization kinetics remain stable across cycles. However, during the cooling phase, the crystallization peak progressively shifted toward lower temperatures, accompanied by a gradual decrease in exothermic enthalpy. This behavior suggests that PEKK's ability to crystallize upon cooling diminishes slightly with increasing thermal history, reflecting a kinetic constraint on crystal nucleation and growth. Such asymmetry between crystallization during heating and cooling is characteristic of high-performance aromatic thermoplastics, where rigid molecular backbones hinder chain mobility [3,8,198–201]. Consequently, rapidly cooled as-printed parts tend to exhibit low initial crystallinity, underscoring the importance of a controlled annealing step to enhance crystalline ordering and mechanical integrity [71]. Moreover, annealing led to a consistent increase in crystallinity for all PEKK samples, independent of recycling cycle. Across all samples and recycling stages, the crystallinity increased by an average of 28.5%, with a standard deviation of

$\pm 2.2\%$, relative to the amorphous condition. The consistency of the crystallization behavior and melting characteristics, including the preservation of the multi-stage melting response associated with primary and secondary crystal populations, is further illustrated in the Supplementary Information (Figure. S7.2).

However, DSC cannot resolve changes in molecular weight, and therefore the absence of chain scission cannot be concluded without supplementary techniques such as gel permeation chromatography (GPC) or intrinsic viscosity measurements. The preservation of enthalpy across cycles further confirms that PEKK sustains a stable degree of crystallinity, implying that its chain architecture and crystallization kinetics remain unaffected by repeated high-temperature exposures typical of additive manufacturing.

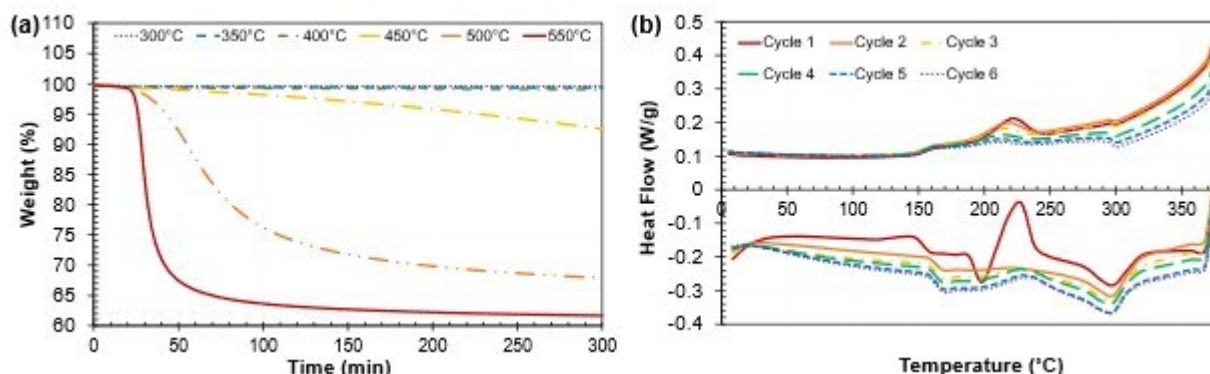


Figure 7.2. Thermal characterization of neat PEKK: (a) Isothermal TGA curves at 300–550 °C showing $< 1\%$ weight loss below 450 °C (TGA curves for all recycling cycles are provided in the Supplementary Information (Figure. S7.1) due to complete overlap with the neat PEKK profile); (b) Cyclic DSC profiles (0–380 °C) demonstrating stable melting/crystallization with slight cooling shift due to slower crystallization.

Table 7.2. Relative crystallinity evolution across repeated DSC cycles.

DSC Cycle	Crystal Melt Enthalpy (ΔH_{cc}) (J/g)	Cold Crystal Enthalpy (ΔH_M) (J/g)	Relative Crystallinity ($X_{C_{rev}}$) (%)
1	21.8	15.9	0
2	0.0	31.0	28.4
3	1.8	26.1	23.2
4	1.9	30.6	26.6
5	3.1	29.8	25.1
6	3.3	31.7	26.4

7.4.2 Mechanical Characteristics

7.4.2.1 Tensile Test

Representative stress–strain curves and corresponding comparisons of tensile strength and toughness for all PEKK batches are presented in Figure 7.3. Across all recycling stages, the amorphous specimens exhibited consistent mechanical behavior, with tensile strength values ranging from 83–90 MPa (Figure 7.3c), indicating that repeated reprocessing had negligible influence on load-bearing capacity.

For annealed specimens, a distinct improvement in strength was generally observed compared to the amorphous counterparts, consistent with enhanced crystallinity and interlayer consolidation following thermal treatment. The only exception occurred in the Recycled #0 batch, which exhibited a noticeable drop in strength (83.4 MPa) relative to both the neat and subsequent recycled samples. This reduction was attributed to a manufacturing irregularity, where the extruded filament diameter exceeded the upper tolerance limit ($1.75 + 0.15$ mm). The resulting over-extrusion restricted air venting between deposited strands, leading to bubble entrapment and localized porosity expansion during annealing, thereby lowering the effective strength.

The increase in tensile strength for annealed samples observed after the first recycling cycle is attributed to manufacturing-related effects rather than chemical enhancement. In the neat and Recycled #0 batches, mild over-extrusion restricted inter-strand venting, leading to localized porosity expansion during annealing. In contrast, recycled filaments exhibited diameter variations within ± 0.15 mm, enabling alternating under-/over-extrusion that formed micro-vent pathways. These channels allowed trapped air to escape during printing and annealing, suppressing void growth and improving interlayer fusion. Re-extrusion also homogenizes melt viscosity, further contributing to more consistent strand bonding. As supported before by TGA and further by FTIR and XRF results, these mechanical changes arise from processing-induced porosity differences rather than chain scission or chemical degradation. The same porosity-governed mechanism explains the flexural and DMA trends, where reduced void content in Recycled #1 leads to increased stiffness and strength, while later cycles remain stable due to consistent venting behavior. A gradual reduction in strain-at-failure was observed after the first recycling round, particularly in amorphous samples. Since FTIR, DSC, and TGA analyses confirmed the absence of chain scission or oxidative degradation, and preservation of crystallization kinetics the reduction in ductility is

attributed to processing-related mechanisms rather than chemical changes. Specifically, trace inorganic contaminants (<0.5 wt%) identified by XRF may act as local stress concentrators, while reprocessing alters the porosity distribution and ligament geometry within the gauge section, limiting stable neck propagation. In contrast, annealed samples, being inherently semi-brittle due to higher crystallinity, exhibited minimal change in strain-at-failure, consistent with a fracture mechanism dominated by interlayer voids rather than molecular degradation.

In later batches (Recycled #1–#3), optimization of filament manufacturing ensured balanced dimensional control within the ± 0.15 mm tolerance range. This adjustment allowed limited inter-strand venting, reducing pore pressure during annealing and consequently improving density and interlayer bonding. As a result, annealed recycled specimens reached peak strengths of 115.9 MPa (Recycled #1) and 112 MPa (Recycled #2), surpassing even the neat annealed sample (106.7 MPa). The consistent mechanical performance across three recycling cycles demonstrates that PEKK retains its structural integrity and recyclability, confirming its suitability for circular additive manufacturing processes.

Beyond strength, the tensile toughness of PEKK specimens exhibited a clear dependence on the recycling stage (Figure 7.3d). The neat, Recycled #0, and Recycled #1 batches demonstrated high ductility, sustaining strains exceeding 100% before fracture, indicative of substantial plastic deformation and effective chain mobility. However, after the first recycling round, a notable decrease in strain at break was observed, suggesting an accumulation of contaminants or oxidative species during reprocessing. These defects likely act as localized stress concentrators, reducing chain entanglement and making the polymer more prone to premature failure.

In amorphous samples, the necking phenomenon propagated progressively along the gauge section once the material surpassed its yield point, until fracture occurred at the weakest cross-section. A reduction in strain-at-failure was observed after the first recycling round. While such behavior can be consistent with early-stage chain scission or oxidative stiffening [184], these mechanisms cannot be confirmed without direct molecular-weight quantification (e.g., GPC). Thus, the observed embrittlement is attributed to a combination of morphological factors (e.g., interlayer porosity, contaminant particles) and possible chemical effects that remain below the detection limit of DSC.

For annealed samples, the overall deformation remained limited due to their inherently higher crystallinity and stiffness, which promote brittle fracture. Nevertheless, recycled annealed specimens exhibited slightly improved toughness compared to the neat annealed batch. This enhancement is linked to reduced porosity in the reprocessed filaments, as the optimized extrusion conditions created open venting channels between deposited strands, enabling trapped air to escape during annealing. Consequently, the recycled annealed samples displayed greater resistance to crack initiation and marginally higher strain at break, confirming the beneficial effect of mitigating fracture sensitivity.

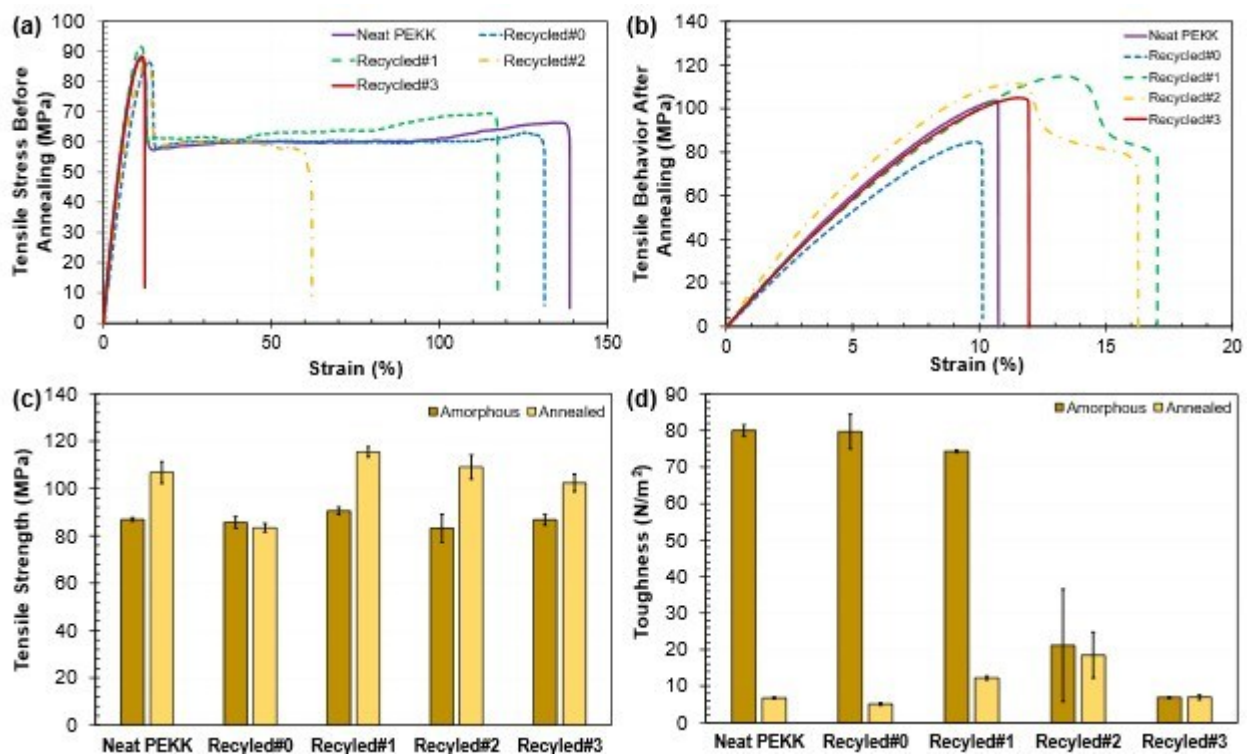


Figure 7.3. Tensile strength of PEKK coupons in amorphous (regular) and annealed conditions across recycling rounds

7.4.2.2 Flexural Test

The flexural response of PEKK through successive recycling cycles is shown in Figure 7.4. Consistent with the tensile results, the Recycled #0 batch exhibited slightly lower flexural strength than the neat annealed PEKK, attributed to over-extrusion during filament fabrication, which trapped air between deposited strands and led to porosity expansion upon heat treatment. In contrast, subsequent recycled batches (Recycled #1–#3) displayed improved filament dimensional

control and better inter-strand venting, effectively minimizing porosity and enhancing interlayer adhesion. As a result, both amorphous and annealed recycled samples maintained or even slightly surpassed the mechanical performance of the virgin material.

The amorphous specimens showed only minor reductions in flexural strength across three recycling loops 126.9 MPa (neat) to 114.4 MPa (Recycled #3), with a gradual decrease in the area under the stress–strain curve, indicating a modest reduction in flexural toughness but no sign of embrittlement. For annealed specimens, the trend was even more favorable: flexural strength increased from 150.3 MPa (neat) to a maximum of 160.4 MPa (Recycled #1), followed by a stable plateau around 151–153 MPa in later cycles (Figure 7.4c). This improvement arises from reduced porosity and enhanced interlayer consolidation resulting from balanced extrusion tolerances and efficient gas release during annealing. The combination of high crystallinity and low defect density provided superior stiffness and consistent flexural resistance. All amorphous and annealed samples withstood the full 10 % flexural strain limit of the test without fracture, confirming sustained ductility and energy-absorption capacity. Although all flexural specimens withstood 10% strain without fracture, the reduced modulus and energy absorption in later cycles for amorphous samples are consistent with the slight embrittlement observed in tension and primarily relate to porosity evolution rather than changes in polymer chemistry. While this approach is not as sensitive as micro-CT for detecting internal void evolution, such advanced equipment was not available; therefore, flexural response, together with tensile data and microstructural imaging, was used to qualitatively assess structural integrity during recycling.

Overall, after three complete recycling cycles, PEKK retained its structural integrity and exhibited no evidence of mechanical degradation under bending. These results reinforce PEKK's exceptional thermal–mechanical resilience and its strong potential for closed-loop additive manufacturing and reuse in high-performance applications.

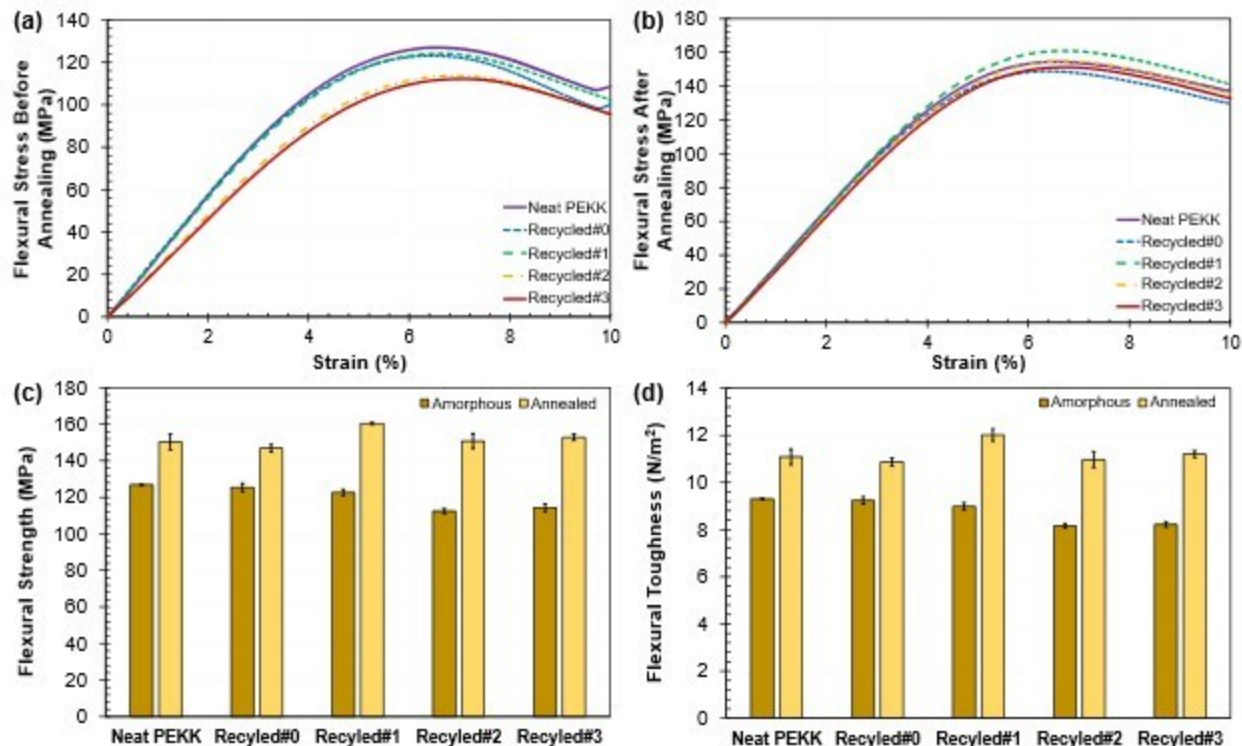


Figure 7.4. Flexural strength of PEKK coupons in as-printed (regular) and annealed across recycling rounds

7.4.2.3 DMA

The storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) of neat and recycled PEKK in both amorphous and annealed conditions are shown in Figure 7.5. Across all recycling cycles, the temperature-dependent profiles of E' and E'' exhibited similar shapes, though slight variations in magnitude were observed. For the amorphous specimens, the storage modulus decreased moderately from approximately 2300 MPa (neat) to 2100 MPa (Recycled #3), indicating a minor reduction in stiffness after multiple reprocessing loops. In contrast, the annealed samples followed a different trend: both the neat and Recycled #0 specimens displayed lower moduli (~ 2000 MPa) due to closed inter-strand porosity, whereas Recycled #1 reached a peak modulus of about 2800 MPa, followed by gradual declines to 2500 MPa (Recycled #2) and 2300 MPa (Recycled #3). This evolution reflects the influence of filament dimensional control and open-vent channel formation on reducing porosity rather than any intrinsic polymer degradation.

The $\tan \delta$ profiles further confirm this interpretation. In both amorphous and annealed groups, the loss-factor curves nearly overlapped, and the peak positions remained unchanged,

demonstrating that repeated thermal cycling did not affect the glass-transition behavior or viscoelastic relaxation of PEKK. For the amorphous samples, two peaks were observed: one near 160 °C, corresponding to the glass transition, and a secondary peak around 205 °C, associated with cold crystallization of the amorphous matrix at elevated temperature. The annealed specimens, already containing a well-developed crystalline phase, exhibited a single, narrower $\tan \delta$ peak at ~175 °C, approximately five times lower in magnitude than that of the amorphous samples. This reduction in damping capacity confirms the higher crystallinity, reduced chain mobility, and superior thermal stability of the annealed state.

Overall, DMA results verify that no thermomechanical degradation occurred through three recycling cycles. PEKK preserved its stiffness, transition temperature, and viscoelastic response, underscoring its reliability for long-term reuse in high-temperature additive-manufacturing applications.

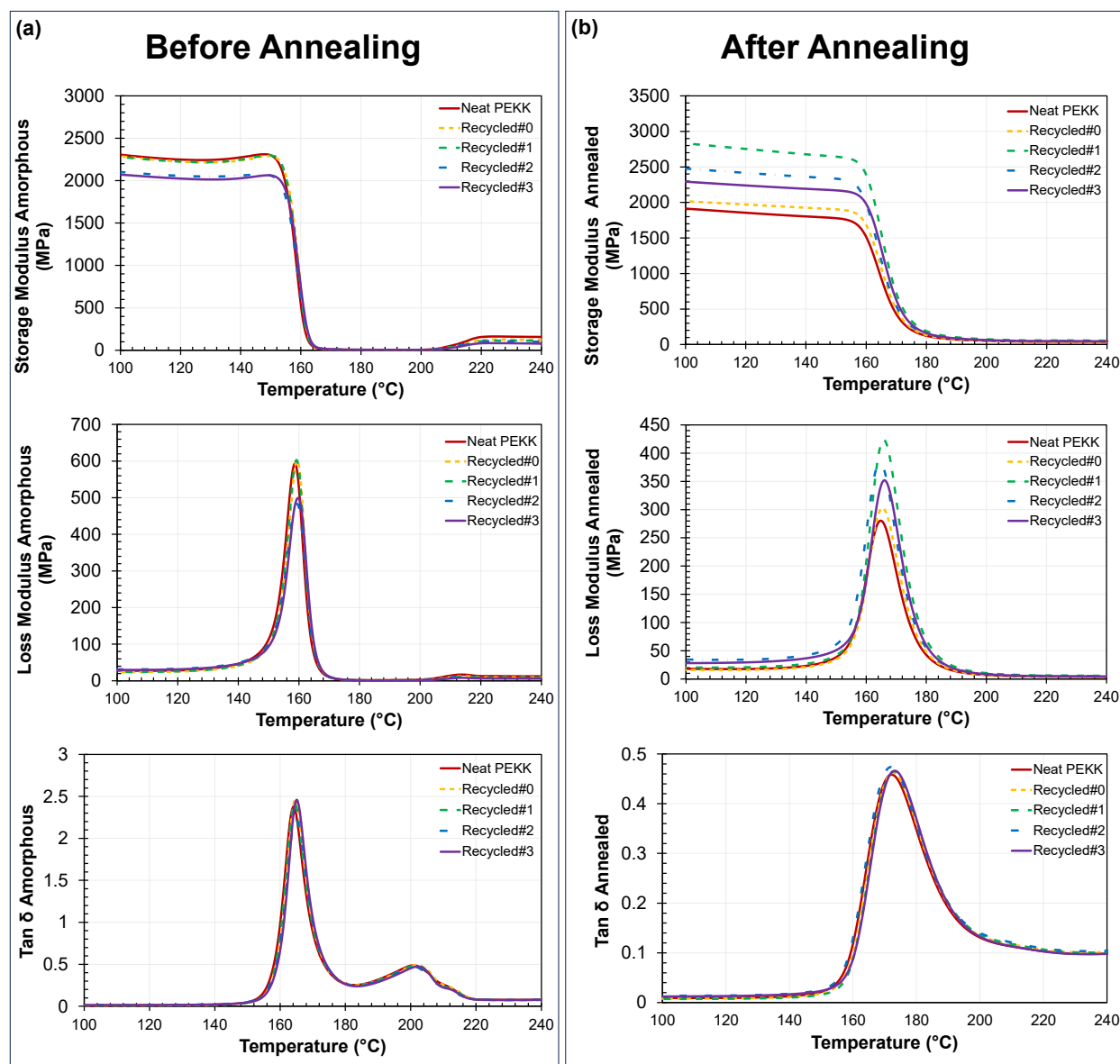


Figure 7.5. DMA results of PEKK coupons in: (a) as-printed (regular) and (b) annealed across recycling rounds.

7.4.3 Chemical Characteristics

7.4.3.1 FTIR Spectra

FTIR spectra of neat and recycled PEKK samples (amorphous and annealed) are presented in Figure 7.6. All spectra exhibit the characteristic absorption bands of the PAEK backbone: aromatic C–H stretching at 3060 cm^{-1} , aliphatic C–H stretching between $2850\text{--}2920\text{ cm}^{-1}$, the carbonyl C=O stretching of ketone groups at 1650 cm^{-1} , aromatic skeletal vibrations at $1580\text{--}1490\text{ cm}^{-1}$, and the ether linkage C–O–C stretching near 1305 cm^{-1} [33,68].

Across all recycling cycles, the FTIR spectral profiles exhibited nearly identical trends, with no appearance of new oxidation-related carbonyl bands in the 1700–1600 cm^{-1} region. A gradual increase in the intensity of the characteristic C=O and C–O–C absorption bands was observed with each recycling round, which may suggest minor oxidative or chain rearrangement effects associated with repeated thermal exposure. Subtle variations detected in the 2800–3100 cm^{-1} region, corresponding to C–H stretching vibrations, could be linked to the slight darkening of the material surface after successive recycling. These spectral differences are more plausibly attributed to physical or morphological changes, such as alterations in crystallinity or interchain packing, rather than to chemical degradation [30]. Overall, the preservation of all major functional groups confirms that the molecular backbone of PEKK remains chemically stable after three recycling loops, fully consistent with the thermal and mechanical findings that demonstrate its outstanding recyclability.

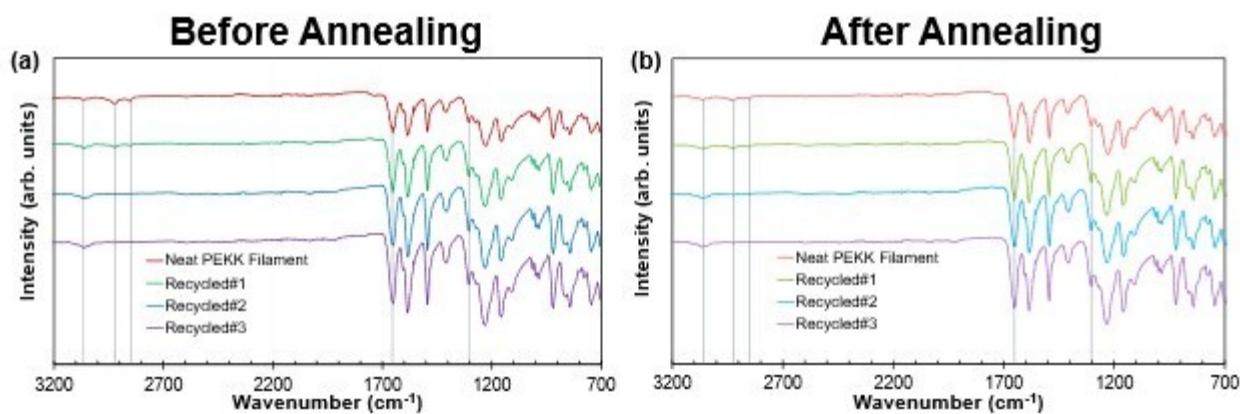


Figure 7.6. FTIR spectra of neat and recycled PEKK in (a) amorphous and (b) annealed conditions.

7.4.3.2 XRF

The semi-quantitative XRF analysis of neat and recycled PEKK samples is summarized in Table 7.3. The elemental composition of neat PEKK corresponded precisely to its nominal molecular formula ($\text{C}_{13}\text{H}_8\text{O}_3$), with negligible metallic or inorganic impurities. After successive recycling cycles, minor traces of Al, Si, Fe, and P were detected, with total contaminant content increasing slightly from 0.10 wt % in Recycled #1 to 0.40 wt % in Recycled #3.

These elements likely originate from contact with metallic components of the shredding, pulverizing, or extrusion equipment and possible environmental dust exposure during material handling. Despite this slight increase, the total impurity level remained below 0.5 wt %, which is insufficient to alter the polymer's bulk properties or induce chemical degradation. The preservation

of the dominant C–O–C and C=O bands in the FTIR spectra supports this interpretation, indicating that the contaminants are extrinsic and physically introduced, rather than products of molecular decomposition.

Table 7.3. Elemental composition of neat and recycled PEKK determined by XRF

Batch	C ₁₃ H ₈ O ₃ (%)	Contaminant (%)				
		Al	Si	Fe	P	Other Contaminant
Neat PEKK	100	0.00	0.00	0.00	0.00	0.00
Recycled#1	99.9	0.04	0.02	0.00	0.04	0.00
Recycled#2	99.8	0.06	0.03	0.02	0.05	0.04
Recycled#3	99.6	0.17	0.05	0.04	0.05	0.09

7.4.3.3 SEM

Fractographic examination of neat and recycled PEKK samples (Figure 7.7) provides insight into microstructural integrity and contamination evolution following repeated recycling. Figure 7.7 compares the tensile fracture surfaces of neat PEKK and Recycled #3 at two magnification levels (17× and 50×), with the higher-magnification images enabling clearer visualization of void morphology, strand fusion, and the distribution of inorganic particles. The finer-scale assessment shows that, even after three recycling loops, the fracture morphology remains largely comparable to that of the virgin material, with no observable transition toward brittle behavior. Recycled amorphous specimens display elongated fibrillar structures and ductile tearing modes consistent with micro-void coalescence, confirming that the dominant deformation mechanisms remain ductile and that interlayer fusion is preserved. In contrast, the annealed recycled specimens exhibit a semi-brittle response, where dendritic rough fracture patterns indicate localized stiffening associated with increased crystallinity, yet still do not suggest polymer degradation-induced embrittlement.

After three recycling cycles, the overall porosity level very slightly increased across recycling cycles for amorphous samples due to recycling process defects, confirming the mechanical results that demonstrated stable tensile and flexural responses. In contrast, annealed specimens displayed a noticeable reduction in pore size and density, consistent with improved venting between deposited strands during reprocessing. This observation supports the earlier interpretation that the

open vent channels formed during extrusion and printing mitigate internal pressure buildup during annealing, thereby reducing trapped voids.

A few bright, micron-sized particles, circled in red in Figure 7.7, were detected on the fracture surface of the Recycled #3 samples. These features correspond to minor inorganic inclusions consistent with the trace metallic elements (total Al, Si, Fe, P < 0.5 wt %) identified by XRF analysis. Their sparse presence confirms that contamination introduced during recycling is minimal and does not compromise interlayer adhesion or fracture behavior. While these isolated particles may act as local stress concentrators and assist crack initiation after the specimen reaches its ultimate strength, they do not alter the global fracture mode or mechanical behavior trends. Importantly, no increase in void density or crack-plane roughness was detected at higher magnification, further indicating that repeated processing did not induce microstructural embrittlement. Collectively, the higher-magnification SEM evidence supports the conclusion that PEKK maintains its fracture morphology integrity throughout the recycling process.

These SEM observations are consistent with tensile and flexural measurements, which show preserved ductility after three recycling cycles for amorphous samples, supporting the conclusion that PEKK retains its microstructural integrity and remains resistant to embrittlement during repeated reprocessing. Overall, SEM observations confirm that repeated recycling does not cause morphological degradation in PEKK. The polymer retains dense, well-fused layers with limited porosity and negligible contamination, reinforcing its suitability for closed-loop additive manufacturing.

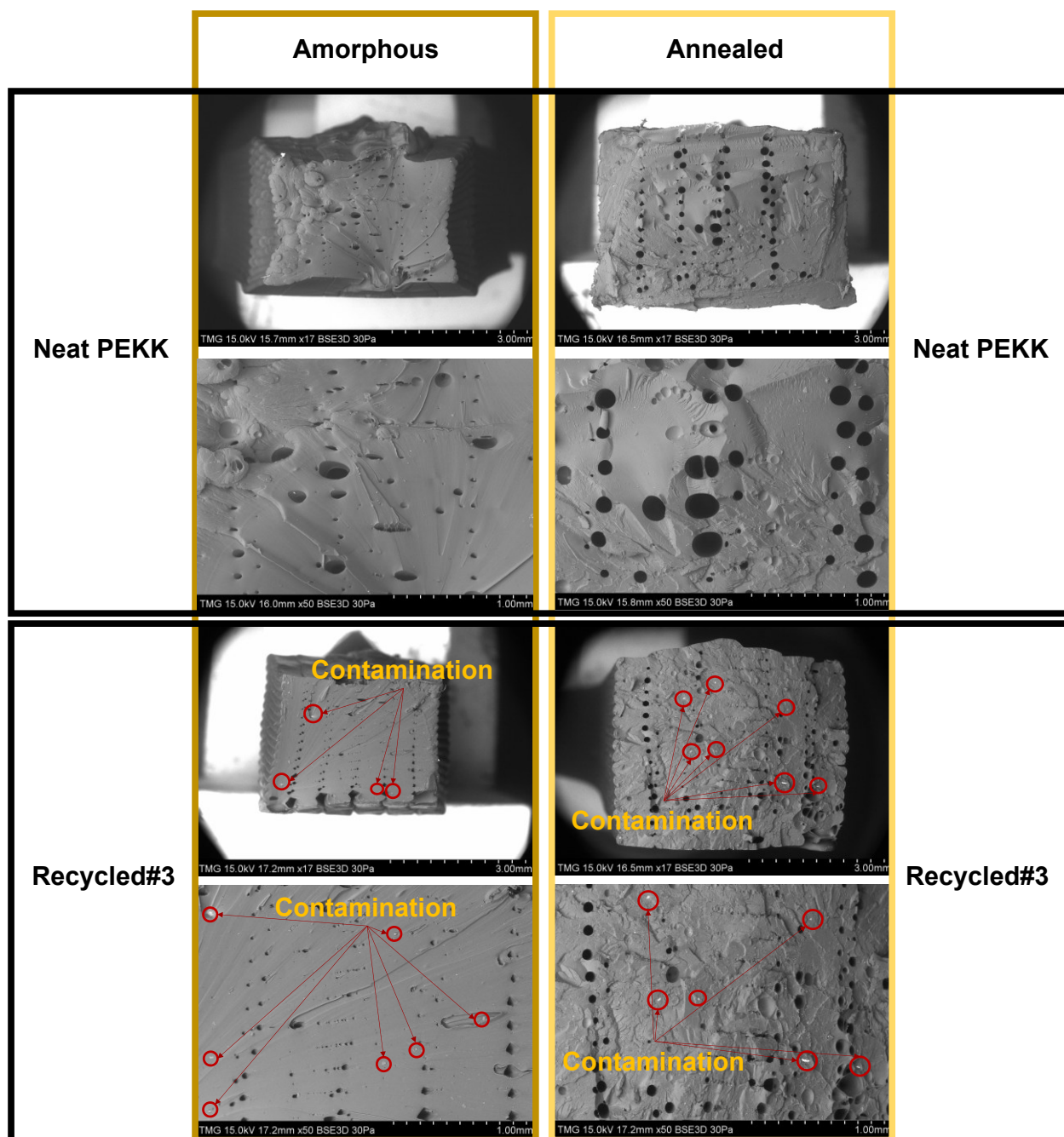


Figure 7.7. Scanning electron micrographs of tensile fracture surfaces in 17x and 50x magnification for neat and Recycled #3 PEKK samples under amorphous and annealed conditions. Bright circled regions indicate minor inorganic inclusions (< 0.5 wt %) consistent with XRF results

7.4.4 Discussion

The experimental results collectively indicate that PEKK displays an atypically high resistance to degradation during repeated melt-reprocessing, yet several mechanistic aspects

require deeper consideration. In contrast to commodity polymers such as PETG, PA12, PP, and HDPE [34–37], where multiple reprocessing cycles often yield notable reductions in molecular weight, crystallinity, and ductility after only a few loops, PEKK retained its structural and functional performance across all recycling rounds. This behavior reflects the intrinsic thermal robustness of the PAEK backbone, which is characterized by high aromatic content and strong ether–ketone linkages.

7.4.4.1 Thermal and chemical stability

TGA confirmed that significant mass loss does not occur below ~ 450 °C, well above extrusion and 3D-printing temperatures, suggesting that conventional thermally driven scission pathways are significantly slow during recycling processing. Cyclic DSC likewise showed stable melting and cold-crystallization temperatures across six cycles, indicating that the length and mobility of crystallizable segments remain unchanged. FTIR spectra revealed no emergence of oxidative carbonyls or hydroxyls, further ruling out bulk oxidative degradation. Minor intensity variations in C=O and C–O–C bands likely reflect changes in morphology or chain packing rather than chemical transformation. XRF detected only trace (<0.5 wt %) elemental contaminants, insufficient to promote catalytic degradation mechanisms.

7.4.4.2 Mechanical behavior and microstructural effects

The mechanical results demonstrate that tensile and flexural strength remained largely constant with recycling, while strain-at-failure decreased in the amorphous state. This divergence is particularly informative: strength retention suggests that the load-bearing molecular framework is intact, whereas reduced ductility indicates sensitivity to microstructural features rather than chemical degradation. SEM images support this interpretation. Amorphous samples showed consistent porosity levels, whereas annealed samples displayed reduced void size in recycled batches due to improved vent pathways during heat treatment. Small inorganic inclusions and subtle geometric irregularities introduced during shredding and pulverization may act as local stress concentrators, reducing strain-at-failure without affecting stiffness or strength.

This pattern differs from the classical ductility loss seen in PETG or PA12 recycling, where chain scission is the primary driver. Literature studies employing GPC analysis on PAEK-family polymers consistently report that chemical degradation via chain scission is unlikely under short residence times and processing temperatures well below the onset of thermal degradation [31]. In

the present work, PEKK was exposed only briefly to temperatures within the established processing window, making chemical degradation improbable. This interpretation is further supported by the absence of new FTIR absorption bands and the unchanged onset degradation temperature observed by TGA.

In PEKK, the reduction in ductility appears to be governed by processing-induced defect evolution rather than molecular weight decline. It is important to distinguish between chain scission arising from chemical degradation and that induced by mechanical grinding. Mechanical size-reduction processes can physically shorten polymer chains without generating new chemical functionalities, rendering such changes undetectable by FTIR analysis. Literature on closely related PAEK polymers supports this distinction. McLauchlin et al. reported a progressive reduction in elongation at break for repeatedly reprocessed PEEK on the third round of recycling process, while tensile strength and crystallinity remained largely unchanged. Based on DSC, XRD [69].

In the present work, PEKK was similarly exposed only briefly to temperatures within its established processing protocol. The reduction in strain-at-failure observed in amorphous specimens is therefore attributed to a combination of mechanically induced chain shortening during grinding and microstructural stress concentrators, including minor inorganic inclusions and processing-related porosity. Owing to the higher sensitivity of tensile testing to damage and defect-driven deformation mechanisms, these effects are more pronounced in tensile strain-at-failure measurements than in flexural testing [45], which is less sensitive to early-stage chain scission.

7.4.4.3 Crystallinity, viscoelasticity, and structure–property links

DMA results showed only minor variations in storage modulus across recycling cycles, changes that were predominantly attributed to manufacturing-induced defects rather than intrinsic polymer degradation. The $\tan \delta$ peaks remained closely aligned for all batches, indicating preserved segmental mobility and stable crystallinity. Because crystallinity strongly governs stiffness and thermal resistance in PAEK polymers, its consistency across cycles further supports the conclusion that repeated melt-processing does not meaningfully alter the molecular architecture of PEKK.

7.4.4.4 Alignment with broader recycling literature and remaining questions

Relative to existing polymer-recycling studies, PEKK demonstrates substantially higher retention of mechanical and thermal properties than conventional engineering thermoplastics, underscoring

its suitability for circular-use scenarios involving repeated thermal exposure. Nevertheless, two important limitations remain due to equipment constraints. First, molecular-weight evolution could not be directly quantified in the absence of GPC or intrinsic viscosity measurements. Moreover, potential oxidative contributions during melt processing in ambient conditions could not be conclusively resolved. Future investigations should include controlled-atmosphere extrusion experiments, alongside advanced chemical characterization techniques such as GPC for molecular-weight tracking and X-ray photoelectron spectroscopy (XPS) for surface oxidation analysis, to more precisely elucidate early-stage degradation pathways.

7.5 Conclusion

This study systematically investigated the resistance of PEKK to degradation during multiple recycling loops involving shredding, pulverization, extrusion, and reprinting. Comprehensive thermal, mechanical, and chemical analyses collectively confirmed that PEKK maintains exceptional structural and chemical integrity after three complete recycling cycles.

Thermogravimetric analysis demonstrated negligible mass loss below 450 °C, confirming excellent thermal stability under typical additive manufacturing conditions. Cyclic DSC revealed negligible changes in melting or cold crystallization behavior through six consecutive thermal cycles, indicating preserved molecular architecture and crystallization kinetics. Mechanical testing (tensile, flexural, and DMA) further verified the absence of mechanical deterioration, with recycled samples exhibiting comparable or even superior strength relative to neat PEKK. FTIR spectra showed no evidence of oxidation or chain scission, as the characteristic ether (C–O–C) and carbonyl (C=O) bands remained unchanged after repeated reprocessing. XRF analysis detected only trace metallic impurities (≤ 0.5 wt %), originating from equipment contact, with no impact on polymer chemistry or performance. SEM analyses further corroborated these findings by revealing dense, well-fused interlayer structures with minimal porosity and isolated inorganic inclusions consistent with the XRF results.

In summary, the results confirm that PEKK is highly resistant to both thermal and mechanical degradation under repeated recycling. Its chemical stability, structural robustness, and negligible property loss highlight its potential for circular additive manufacturing, in-space resource utilization, and sustainable high-performance applications where material reuse and long-term

reliability are essential. Because the PEKK formulation used in this study is commercially proprietary, the findings reflect the behavior of this specific grade. Nonetheless, the strong stability observed across multiple recycling cycles aligns with the known robustness of the PAEK family and provides a benchmark for future comparisons across different PEKK grades. The stability demonstrated across thermal, mechanical, and chemical evaluations indicates that recycled PEKK can reliably serve in high-value applications where reprocessable, long-lifetime materials are critical. These results provide a foundation for industrial implementation of circular PEKK feedstock in aerospace, medical, and high-performance engineering sectors, where material reuse offers significant cost, sustainability, and supply-chain benefits.

Chapter 8: “Endurance: Continue to Survive”

“Newton’s 3rd Law-

The only way humans have ever figured out of getting somewhere
is to leave something behind.”

-Interstellar

This work has been under-Reviewed in:

F. Malekpour, M. Hojjati; “Circular Additive Manufacturing of Recycled PEKK–Regolith Composites for Sacrificial Structures in Lunar In-Situ Resource Utilization”; Submitted to: Composites Part B: Engineering

Status: Under-Review

8. Circular Additive Manufacturing of Recycled PEKK–Regolith Composites for Sacrificial Structures in Lunar In-Situ Resource Utilization

8.1 Abstract

Circular additive manufacturing enabled by in-situ resource utilization (ISRU) offers a promising pathway for fabricating sacrificial structures required in long-duration lunar missions while minimizing material payload and waste. In this study, recycled Poly(EtherKetoneKetone) (PEKK), recovered from end-of-life sacrificial components after completion of their functional duty, was compounded with 30 wt% lunar regolith simulant (LRS) to develop a recyclable composite filament for material extrusion (MEX) additive manufacturing. The recycled composite was processed via twin-screw extrusion and used to fabricate standardized mechanical specimens, Schwarz-G gyroid lattices, and a functional demonstrator. Thermal analyses confirmed that recycling and regolith incorporation did not compromise the thermal stability or crystallization behavior of PEKK, while a reduction in cold-crystallization temperature indicated improved annealing efficiency due to enhanced thermal transport from the ceramic phase. DMA showed preserved viscoelastic response and segmental mobility across amorphous and annealed conditions. Mechanical testing revealed orientation-dependent tensile and flexural behavior governed primarily by porosity and interlayer bonding rather than polymer degradation. Compression of gyroid lattices demonstrated progressive plastic densification and high energy absorption in the amorphous state, confirming their suitability as sacrificial architectures, while annealing increased stiffness at the expense of ductility. A NASA-style ratchet wrench fabricated from the recycled PEKK/regolith composite further illustrated material reusability and adaptive design capability, with regolith addition significantly reducing annealing-induced shrinkage and improving dimensional stability. Overall, the results show that recycled PEKK reclaimed from sacrificial structures and reinforced with lunar regolith enables closed-loop additive manufacturing of sacrificial components, supporting sustainable ISRU-based construction strategies for future lunar exploration.

8.2 Introduction

The increasing ambition of long-duration space missions, including the establishment of permanent lunar habitats, has placed renewed emphasis on in-situ resource utilization (ISRU) and circular manufacturing strategies [1–6]. Transporting construction and repair materials from Earth remains one of the major logistical and economic barriers to sustainable lunar operations, where each kilogram of payload incurs significant launch costs and energy expenditure [5,7]. In this context, in-space manufacturing (ISM) and additive manufacturing (AM) technologies have emerged as enablers of autonomy, on-demand production, and material reuse in extraterrestrial environments [8–10]. Developing materials that combine high mechanical performance, processability, and recyclability is therefore critical for enabling closed-loop AM systems capable of supporting construction, maintenance, and repair on the Moon.

High-performance thermoplastics from the Poly(ArylEtherKetone) (PAEK) family, particularly Poly(EtherKetoneKetone) (PEKK), offer a unique combination of strength, toughness, radiation resistance, and thermal stability suitable for extreme environments [11–15]. Unlike thermosets or metallic systems traditionally considered for space structures, PEKK is fully reprocessable and can be recycled through mechanical and thermal routes with minimal loss of performance [16–21]. Recent studies have demonstrated that PEKK retains its molecular and mechanical integrity after multiple recycling cycles, with negligible oxidation or chain scission, thus providing a robust platform for material circularity under AM conditions [22]. These characteristics make PEKK an attractive candidate for ISRU scenarios, where recyclability and resource efficiency are paramount.

In parallel, the utilization of locally available extraterrestrial materials such as lunar regolith has gained traction as an ISRU feedstock for structural composites [23–25]. Lunar regolith simulants (LRS) have been explored as fillers or reinforcements in polymer matrices to reduce polymer content, enhance stiffness, and leverage in-situ materials for additive manufacturing [26–30]. Several investigations have reported on the mechanical, thermal, and morphological behavior of polymer–regolith composites fabricated by extrusion or powder-bed fusion methods, indicating promising potential for load bearing or shielding applications [6,31–34]. However, the integration of recycled high-performance polymers with lunar regolith remains underexplored, particularly in

the context of maintaining circularity while producing structural components with predictable deformation and energy absorption characteristics.

A relevant reference from NASA’s Jet Propulsion Laboratory (JPL) is the “Mars Sample Return (MSR)” project, which employs metallic lattice structures as sacrificial impact absorbers for re-entry and landing protection [35,36]. While effective, such metallic systems are difficult to recycle or repurpose in-situ due to their high melting temperatures and energy-intensive reprocessing. By contrast, a polymer-based sacrificial structure fabricated from recycled PEKK reinforced with lunar regolith could be reprocessed on the lunar surface using moderate energy input, offering a practical and sustainable alternative. The inherent toughness of amorphous PEKK and the stiffness of its semi-crystalline counterpart provide an adaptable performance window that can be tailored through processing and thermal treatment. These attributes make recycled PEKK–regolith composites strong candidates for impact-mitigating “sacrificial” lattices or reusable components within lunar manufacturing ecosystems.

Building on prior research demonstrating the thermal-mechanical stability of recycled PEKK [22], the present study extends the concept toward circular additive manufacturing for ISRU. Recycled PEKK from previous processing loops was compounded with 30 wt% LMS-1D lunar regolith simulant and extruded into filament suitable for material extrusion (MEX) additive manufacturing. The composite filament was used to 3D print tensile, flexural, and dynamic mechanical specimens, as well as Schwarz-G gyroid structures to evaluate deformation and energy absorption under compression. Additionally, a NASA-style ratchet wrench was printed from both neat PEKK and the recycled PEKK/LMS composite as a functional demonstrator of reusability and design adaptability in lunar-like environments. The objective of this work is to evaluate the mechanical and structural performance of recycled PEKK–regolith composites fabricated through AM and to assess their feasibility as sacrificial and functional structures for lunar ISRU applications. The results aim to establish a pathway for closed-loop material utilization in space, where polymers can be recycled, reinforced with local resources, and re-manufactured into new components with minimal waste and resource dependence.

8.3 Materials & Methods

8.3.1 *Materials*

An amorphous PEKK filament (1.75 ± 0.05 mm diameter, grade PEKK175-1000) supplied by Spool3D (Alberta, Canada) was used in this study. The manufacturer recommends a nozzle temperature of 360–400 °C and a build-plate temperature of 90–130 °C for material extrusion processing; however, iterative optimization showed that a higher bed temperature of 160 °C effectively minimized warpage and improved layer adhesion.

The recycled PEKK employed in this work originated from the same neat filament batch used in our previous study [22]. Scrap parts from that work were collected irrespective of their prior thermal history, ensuring that none had exceeded two previous recycling cycles. Because earlier results demonstrated that up to three cycles cause no measurable deterioration in mechanical or thermomechanical properties, the material was considered safe for one additional reprocessing round.

Lunar Mare Simulant (LMS-1D) was obtained from Space Resource Technologies (Exolith Lab, University of Central Florida, USA) [37]. The simulant exhibits a particle size distribution of 0.04–35 μm , with a mean diameter of 6 μm and grain density of 3.9 g/cm³, closely matching the finer fractions of Apollo lunar samples [38]. Its fine particle size enables uniform dispersion within the polymer matrix, making LMS-1D a suitable regolith analog for composite fabrication.

8.3.2 *ISRU Recycling Process*

The outline for the sustainable additive manufacturing of recycled PEKK/LRS composite is demonstrated in Figure 8.1a. The recycling workflow began with the collection of scrap coupons from previous mechanical testing of standard specimens printed from neat PEKK filament. All samples were fabricated under identical MEX thermal parameters, and only those that had undergone no more than two prior recycling cycles were selected. As established in our earlier study [22], PEKK can safely endure up to three recycling loops (same recycling procedure as this study) without significant deterioration in its mechanical or thermomechanical properties; therefore, the selected material was deemed suitable for an additional processing round.

The collected specimens, including both amorphous and annealed types, were combined and shredded using a Felfil Shredder 750 (Felfil, Italy). Each batch underwent five successive shredding passes, reducing the granule size to below 3 mm in diameter. The shredded material was then pulverized with an AF LAB Pulverizer (Orenda, Canada) through three consecutive milling cycles, producing a fine and uniform powder with particle size below 500 μm , appropriate for twin-screw micro-extrusion. Achieving this level of fineness was critical to ensuring filament-diameter stability during extrusion and for homogeneous dispersion of the 30 wt% lunar regolith simulant (LRS) incorporated into the PEKK matrix. The 30 wt% loading was selected based on prior findings that regolith contents above 40 wt% sharply increase melt viscosity and induce brittle fracture behavior, whereas 30 wt% maintains manageable viscosity, sufficient ductility, and safe torque levels during extrusion while minimizing barrel abrasion [23].

Before compounding, both PEKK and LRS powders were dried at 125 °C for 8 h to eliminate residual moisture, as both materials exhibit hygroscopic tendencies [39,40]. According to Sibille et al. [41], proper dehydration and mineralogical fidelity of lunar regolith simulants are essential for accurate ISRU research, as they prevent morphology alteration and ensure consistent processing behavior. Following drying, the powders were manually premixed for 10 min at 50 rpm, producing the ISRU recycled PEKK–LRS compound, which was stored in a drying chamber at 25 % relative humidity until extrusion. Filament extrusion was performed within 24 h of blending to minimize moisture reabsorption and ensure consistent processability.

8.3.3 *Recycled Composite Filament Manufacturing*

The recycled PEKK/LRS composite filament was extruded using a Process 11 twin-screw extruder (Thermo Fisher Scientific, Germany) equipped with a high-performance screw configuration tailored for engineering thermoplastics [42]. The screw assembly incorporated two-stage mixing elements (Figure 8.1b) and was operated at a constant screw speed of 100 rpm. The extrusion process was thermally divided into eight heating zones, as schematically illustrated in Figure 8.1b. Zone 1 (Z1): powder feeding section without active heating; temperature increases slightly through thermal conduction from adjacent zones. Zone 2 (Z2): maintained at 220 °C to limit back conduction of heat toward the hopper. Zones 3–7 (Z3–Z7): stabilized at 315 °C, corresponding to the melt–crystallization range of PEKK [12,43]. Zone 8 (Z8): elevated to 325 °C to lower melt

viscosity and alleviate die pressure near the extrusion exit. (Reading die pressure 25 to 30 bar while the alarm was set on 70 bar, torque at 53% of full capacity)

A vacuum degassing system was installed immediately after the first mixing stage to extract entrapped air and volatile species. The molten composite was extruded through a 2 mm die nozzle, with filament diameter (target: 1.75 ± 0.15 mm) regulated via tension control using a *Filabot* spooler (Filabot, USA) coupled with a Mitutoyo Fila Measure sensor (Mitutoyo, Japan) for inline dimensional feedback. The extruded filaments were air-cooled through a Filabot Air Path instead of water quenching to prevent moisture absorption and subsequently stored in a dry chamber at 10 % relative humidity until printing.

8.3.4 Additive Manufacturing

All samples were fabricated using a high-temperature CreatBot F160-PEEK 3D printer (CreatBot, China), designed for processing both neat and composite high-performance thermoplastics (**Error! Reference source not found.**c). To minimize variations in thermal history and ensure consistent interlayer fusion, each specimen was printed individually at the center of the build platform rather than in batches. This approach effectively reduced cooling time between deposited layers and minimized exposure to ambient conditions, promoting improved bonding and dimensional precision.

The manufacturer specifies a recommended nozzle temperature range of 360–400 °C and a build-plate temperature of 90–130 °C for PEKK. However, preliminary optimization indicated that elevating the bed temperature mitigates warpage and enhances first-layer adhesion. Consequently, a build-plate temperature of 160 °C, slightly above the glass transition temperature (T_g) of PEKK [44], was adopted for all prints. Other printing parameters, including raster orientation, layer height, and infill density, were refined through literature guidance [15,44–49] and iterative testing. The optimized parameters are summarized in **Error! Reference source not found.** . Under these conditions, printed parts displayed smooth surfaces and excellent dimensional fidelity without requiring auxiliary adhesives. Visual inspections confirmed negligible warping or delamination, confirming the suitability of these conditions for both neat and composite PEKK materials.

For the compressive sacrificial architecture, a Schwarz G (gyroid) lattice with a relative density of 40% was selected, as shown in Figure 8.1c. This geometry belongs to the class of triply periodic

minimal surface (TPMS) structures, which have been extensively investigated and increasingly adopted in aerospace and biomedical applications due to their favorable mechanical efficiency and damage tolerance [50]. The Schwarz G lattice is characterized by a smooth, continuous surface without sharp edges, enabling a more uniform and quasi-isotropic distribution of applied loads [51].

The sheet-based Schwarz G architecture was designed for additive manufacturing with overall dimensions of 30 mm $\times$ 30 mm $\times$ 30 mm, comprising a periodic arrangement of 3 $\times$ 3 $\times$ 3 unit cells, as illustrated in Figure 8.1c. A relative density of 40% was chosen to balance manufacturability and mechanical performance. Lattices with lower relative densities (<20%) tend to be highly defect-sensitive and mechanically fragile, complicating the isolation of annealing effects. In contrast, higher relative densities (>60%) exhibit mechanical responses increasingly dominated by bulk material behavior, diminishing the influence of architectural features. The intermediate relative density of 40% ensures that both lattice geometry and material properties contribute significantly to the overall response, making it particularly suitable for evaluating anisotropy and post-processing effects. Moreover, relative densities in the range of 30–50% are commonly targeted in aerospace structural applications to achieve substantial weight reduction while maintaining adequate mechanical reliability [52,53].

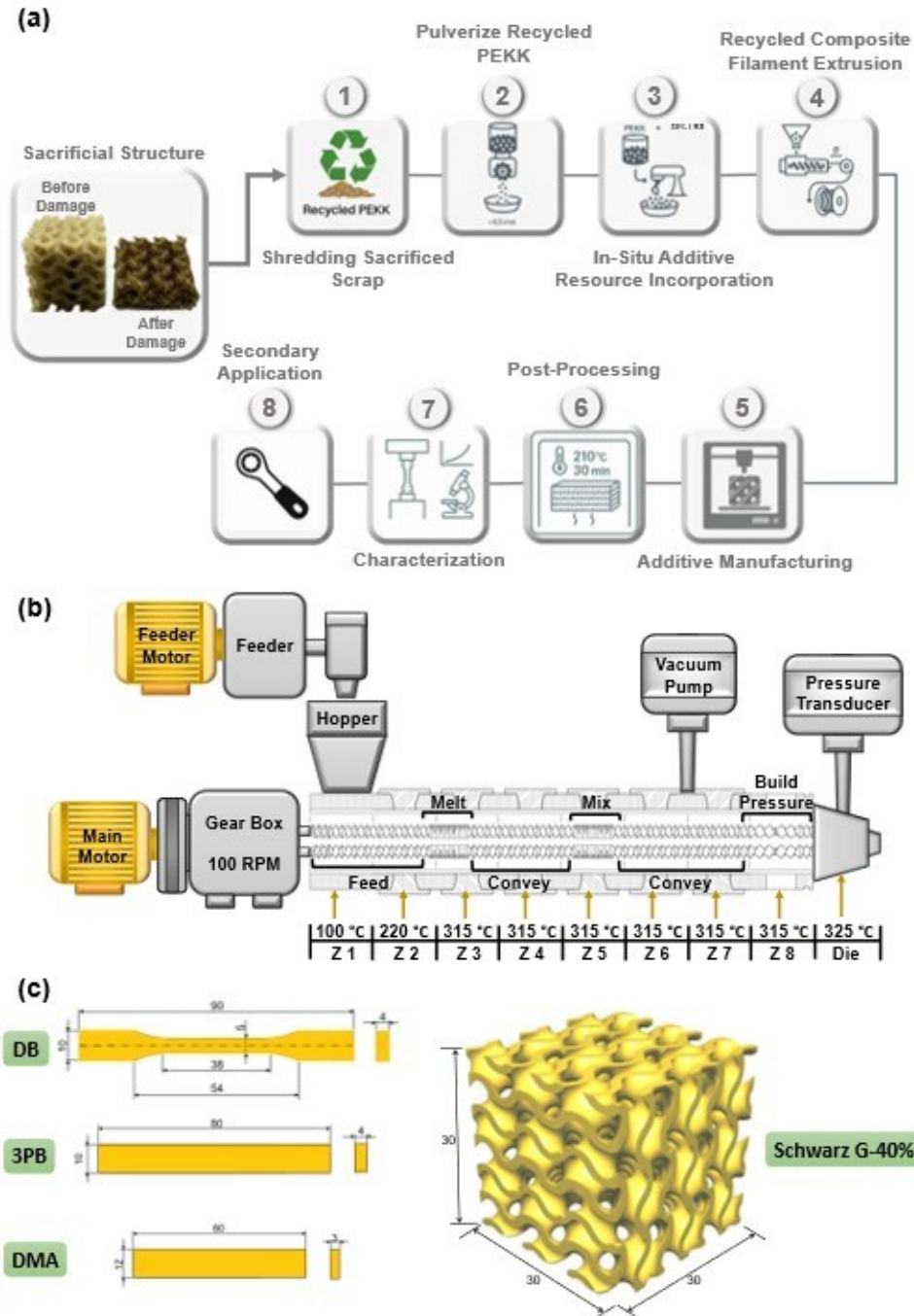


Figure 8.1. Overview of key process parameters: (a) Outline for the sustainable additive manufacturing of recycled PEKK/LRS composite, (b) Schematic representation of the twin-screw extrusion setup, showing the eight-zone temperature configuration and screw design used for filament fabrication [6], (c) Dimensional specifications of the standardized mechanical test specimens (all dimensions in millimetres).

Table 8.1. MEX set of 3D printing parameters

Print parameter	Value	Units
Nozzle temperature	380	°C
Bed temperature	160	°C
Chamber temperature	60	°C
Print speed	40	mm/s
Infill density	100	%
Layer height	0.25	mm
Extruder diameter	0.8	mm
Build orientation	Flat	-

8.3.5 Annealing

Following fabrication, the printed specimens were divided into two processing conditions, as printed (amorphous) and thermally annealed, to evaluate how post-processing influences both mechanical response and possible thermal degradation. The annealing procedure, derived from previously established optimization studies [12], consisted of a controlled temperature ramp to 210 °C within 15 min, an isothermal dwell of 30 min, and a subsequent cooling phase back to room temperature over 15 min, resulting in a total treatment time of approximately one hour.

8.3.6 Characterization

- **SEM**

SEM analysis of the recycled PEKK/LRS composite filaments was performed using a HITACHI S-3400N scanning electron microscope (HITACHI, Japan) operated at an accelerating voltage of 15 kV. Micrographs acquired at 50× and 200× magnifications were processed through grayscale thresholding to qualitatively assess the uniformity of regolith particle dispersion within the polymer matrix.

- **TGA**

Thermogravimetric analysis (TGA) was employed to quantify the incorporation and dispersion of lunar regolith simulant (LRS) within the PEKK matrix. Thermal responses of neat PEKK, standalone LRS powder, and recycled PEKK/LRS composites were examined using a TGA Q50 system (TA Instruments, USA). For each material system, a minimum of three specimens extracted from filament and additively manufactured components were analyzed, following procedures

adapted from ASTM E1131 [54]. Samples with masses between 30 and 40 mg were placed in ceramic pan and heated from 100 °C to 800 °C at a constant rate of 10 °C/min under a nitrogen atmosphere. Because the regolith simulant is composed of thermally stable ceramic phases and exhibits negligible mass loss over this temperature range, deviations between the mass-loss profiles of neat PEKK and recycled PEKK/LRS composite directly reflect the regolith content within the polymer matrix. It should be noted that, based on our previous findings, PEKK does not exhibit measurable thermal degradation after up to three recycling cycles that would alter its thermogravimetric response relative to the virgin material. Accordingly, any differences observed between the TGA profiles of neat PEKK and recycled PEKK/LRS composite can be attributed to the presence of LRS rather than to the recycling history of the polymer itself [22]. The mass-loss behavior of neat PEKK filaments and printed parts was therefore used as a baseline reference. By comparing the residual mass fractions of the composite samples to this reference, the effective LRS weight fraction ($W_{LRS}(\%)$) in both filaments and printed specimens was determined using Eq. (8.1), where $WT_L(\%)$ represents the total weight loss percentage.

$$W_{LRS}(\%) = \left(1 - \frac{WT_{L_{PEKK/LRS}}(\%)}{WT_{L_{PEKK}}(\%)} \right) \times 100 \quad (8.1)$$

- **DSC**

Differential scanning calorimetry (DSC) was performed using a DSC Q200 instrument (TA Instruments, USA) to examine the influence of LRS incorporation on the cold-crystallization behavior and crystallization kinetics of the PEKK matrix. To evaluate crystallinity development and saturation following thermal post-processing, DSC measurements were conducted on fractured specimens from both amorphous and annealed conditions for neat PEKK and recycled PEKK/LRS composite parts. The thermal scans were carried out at a heating rate of 10 °C/min over a temperature range of 130 °C to 330 °C. For each material condition, a minimum of three replicates was analyzed, with sample masses between 8 and 10 mg. Specimens were sealed in aluminum hermetic pans in accordance with ASTM D3418 standard [55].

- **Density & Porosity**

Since additively manufactured components inherently contain internal voids and because crystallization induces density variations in semi-crystalline polymers [12,56], direct measurement

of the bulk density of both filaments and printed specimens was required to accurately quantify porosity. The experimentally measured densities were subsequently combined with the known constituent densities and volume fractions to estimate porosity in the composite filaments and printed parts. Density measurements were performed using Archimedes' method in accordance with ASTM D792 [57], which is widely regarded as a robust and practical approach for polymer–composite systems. A Sartorius density determination kit (Sartorius, Germany) was used to record the mass of each specimen in air and while immersed in temperature-controlled water.

Based on these measurements and relying on previous study [6,23], the theoretical volume fraction of lunar regolith LRS in the composite filament was calculated from the corresponding weight fractions and constituent densities using Eq. (8.2). In addition, the theoretical density of each composite filament was determined using the rule of mixtures, incorporating the calculated volume fractions and the intrinsic densities of PEKK and LRS, as expressed in Eq. (8.3):

$$V_{LRS} = \frac{\frac{\omega_{LRS}}{\rho_{LRS}}}{\frac{\omega_{LRS}}{\rho_{LRS}} + \frac{\omega_{PEKK}}{\rho_{PEKK}}} \quad (8.2)$$

$$\rho_c = (1 - V_{LRS}) \cdot \rho_{PEKK} + V_{LRS} \cdot \rho_{LRS} \quad (8.3)$$

Where:

- V_{LRS} is the theoretical volume fraction of LRS
- ω_{LRS} is the weight fraction of LRS
- ω_{PEKK} is the weight fraction of PEKK (note: $\omega_{PEKK} = 1 - \omega_{LRS}$)
- ρ_{LRS} is the grain density of LRS
- ρ_{PEKK} is the density of PEKK
- ρ_c is the theoretical density of composite filament

This analytical estimation served as a baseline for assessing internal void content in both extruded filaments and additively manufactured specimens by comparison with the experimentally measured densities. The porosity fraction (P) was subsequently calculated using Eq. (8.4):

$$P(\%) = \left(1 - \frac{\rho_{exp}}{\rho_c}\right) \quad (8.4)$$

where ρ_{exp} represents the experimentally measured density obtained using the Archimedes method, and ρ_c denotes the theoretical composite density calculated from the constituent volume fractions. This formulation allows the internal void content introduced during filament extrusion, additive manufacturing, and subsequent post-processing to be quantified. Porosity is a key structural parameter that directly affects the mechanical and thermal performance of printed components. The adopted approach provides a practical and reliable means of porosity evaluation and has been successfully employed in previous studies for quality control of additively manufactured polymer composites [6,23].

- **Tensile test**

Tensile tests were conducted on dog-bone specimens prepared in accordance with the ISO 527 standard [58], as illustrated in Figure 8.1c. Testing was carried out using a universal testing machine (Hoskin Scientific, Canada) fitted with a 5 kN S-type load cell positioned on the upper grip. The experiments were performed under displacement control at a crosshead speed of 2 mm/min, with an initial preload of 10–20 N applied to remove any slack and ensure proper specimen alignment before loading. The samples for this test were fabricated in two separate categories of 0° concentric pattern and 90° line pattern [44].

- **Flexural Test**

Flexural tests were carried out on rectangular coupons fabricated in accordance with the ISO 178 standard [59], as depicted in Figure 8.1c. The experiments were performed using a universal testing machine (Hoskin Scientific, Canada) equipped with a 5 kN S-type load cell under a three-point bending configuration. The crosshead displacement rate was maintained at 2 mm/min, and a small preload of 1–2 N was applied to establish stable contact between the specimen and the loading nose prior to testing. To further evaluate anisotropy, the samples for this test were fabricated in two separate categories of 0° line pattern and 90° line pattern [44].

- **DMA**

DMA was performed using a DMA Q800 instrument (TA Instruments, USA) following the procedures outlined in ASTM D4065-12 [60] and ASTM D5418 [61] for dual-cantilever beam mode testing (Figure 8.1c). The samples were analyzed at a constant strain amplitude of 0.1% and a frequency of 1 Hz. A temperature sweep from 100 °C to 240 °C was applied at a heating rate of 2 °C/min to characterize the viscoelastic response of the materials under dynamic thermal loading. To further evaluate anisotropy, the samples for this test were fabricated in two separate categories of 0° line pattern and 90° line pattern [44].

- **Compression Test**

Uniaxial compression tests on gyroid sacrificial structure (Figure 8.1c). were conducted in accordance with ISO 604 [62]. Experiments were performed using a universal testing machine

(NextGen, Canada) fitted with a 20 kN load cell. All tests were carried out under quasi-static conditions at room temperature, with a constant crosshead displacement rate of 2 mm/min and compressive strains applied up to 50%. Prior to loading, a preload of 40–50 N was applied to ensure full contact between the specimen surfaces and the compression platens. To further evaluate anisotropy, although the samples for this test were fabricated in only one category of line pattern but tested in compressive direction categories of perpendicular (z) and parallel (T) to the deposited layers [44].

8.4 Results & Discussion

8.4.1 *Composite Manufacturing Quality Control*

8.4.1.1 Morphology and Particle Dispersion

Representative SEM micrographs of the recycled PEKK/LRS composite filament are shown in Figure 8.2a at magnifications of 50× and 200×. The images reveal a dense polymer matrix with uniformly distributed LRS particles embedded throughout the cross-section, indicating effective dispersion during twin-screw compounding and subsequent filament extrusion. No evidence of large-scale particle agglomeration or sedimentation was observed, despite the relatively high filler loading of 30 wt%, confirming that the selected screw configuration and processing conditions provided sufficient distributive and dispersive mixing.

At lower magnification (50×), the composite exhibits a homogeneous microstructure with consistent particle spacing and no visible clustering zones. The filament cross-section remains geometrically stable and nearly perfectly circular, indicating uniform melt flow and well-balanced viscosity during extrusion. Consequently, the filament diameter was consistently maintained within the target range of 1.75 ± 0.15 mm throughout the entire recycled composite filament manufacturing process (Figure 8.2b). At higher magnification (200×), individual LRS particles appear well wetted by the PEKK matrix, with clean particle–matrix interfaces and no observable interfacial debonding or pull-out features. This intimate interfacial contact indicates adequate melt infiltration of the polymer into the fine regolith particle network, which is essential for effective load transfer under mechanical loading.

The fine particle size distribution of LMS-1D (mean diameter ≈ 6 μm) plays a critical role in promoting uniform dispersion within the high-viscosity PEKK melt. Unlike coarser regolith

fractions reported to induce stress concentrations and premature failure [6], the present morphology suggests that particle size and surface characteristics of LMS-1D are well matched to the processing window of PEKK, even after recycling. Importantly, no morphological differences were observed between filaments produced from recycled PEKK and those previously reported for virgin PEKK-based regolith composites [23], indicating that the additional recycling step did not impair dispersion quality or matrix continuity.

Overall, the SEM analysis confirms that recycled PEKK can effectively host a high fraction of lunar regolith simulant without compromising morphological uniformity. The absence of particle agglomeration, combined with strong interfacial wetting, provides a microstructural foundation for the retained stiffness, predictable deformation behavior, and progressive energy absorption observed in subsequent mechanical and gyroid compression tests. These results validate the suitability of recycled PEKK/LRS composites for structurally reliable, circular additive manufacturing within lunar ISRU frameworks.

8.4.1.2 Thermal Stability & LRS Content Validation

TGA was employed as a tool to assess both the thermal stability of the recycled PEKK/LRS composite and the effective LRS content within the extruded filament and printed specimens. Representative TGA curves are presented in Figure 8.2c for neat PEKK, standalone LRS powder, and the recycled PEKK/LRS composite.

Neat PEKK exhibited a single-step thermal degradation behavior, with negligible mass loss below 450 °C and a rapid decomposition onset at higher temperatures, consistent with the intrinsic thermal stability of PAEK-family polymers. In contrast, the LRS powder displayed virtually no mass loss over the entire temperature range up to 800 °C, confirming its ceramic and thermally inert nature. The recycled PEKK/LRS composite followed the characteristic degradation profile of the polymer matrix, while retaining a substantial residual mass corresponding to the regolith fraction.

Based on the residual mass at 800 °C, the effective LRS content in the composite was determined to be 33 wt%, with a standard deviation of $\pm 1.3\%$ across all analyzed samples. This value is in close agreement with the nominal 30 wt% target composition and reflects a high level of compositional fidelity during powder blending, twin-screw compounding, and filament extrusion. The low standard deviation further indicates excellent batch-to-batch consistency and homogeneous filler distribution throughout the entire recycled composite filament manufacturing. Importantly, no additional mass-loss features or premature degradation steps were detected in the composite relative to neat PEKK, indicating that the incorporation of LRS and the additional

recycling cycle did not compromise the thermal stability of the polymer matrix. This observation corroborates previous findings that PEKK maintains its thermal integrity through multiple reprocessing loops and confirms that the observed TGA response is governed by filler content rather than polymer degradation [22].

Overall, the TGA results validate both the thermal robustness of the recycled PEKK/LRS system and the reliability of the ISRU recycling workflow in achieving controlled regolith incorporation. This compositional consistency provides a critical foundation for reproducible mechanical behavior and predictable structural performance in additively manufactured components, as discussed in subsequent sections.

8.4.1.3 Crystallization Kinetics (DSC)

The crystallization behavior of neat PEKK and recycled PEKK/LRS composites was investigated by DSC, with representative thermograms presented in Figure 8.2d. The analysis was conducted for both as-printed (amorphous) and annealed specimens to evaluate the influence of LRS incorporation and recycling on crystallization kinetics and thermal phase stability.

For amorphous samples, which inherently exhibit a low degree of crystallinity due to rapid cooling during material extrusion, the addition of 30 wt% LRS resulted in a clear shift of the cold crystallization region toward lower temperatures. Specifically, the cold crystallization peak temperature (T_{cc}) decreased from approximately 225 °C for neat PEKK to 220 °C for the recycled PEKK/LRS composite. This shift indicates that the presence of LRS facilitates earlier crystallization upon reheating. Such behavior is advantageous from a processing perspective, as a lower cold crystallization temperature directly translates into a reduced isothermal temperature requirement during post-processing annealing. This effect can be attributed to the higher thermal conductivity of ceramic-based regolith particles relative to the polymer matrix, which promotes more efficient heat transfer within the composite. Enhanced thermal transport accelerates molecular mobility and nucleation during heating, thereby lowering the temperature threshold required for crystallization. Importantly, this shift is beneficial rather than detrimental, as it improves annealing efficiency without altering the fundamental crystallization mechanism of PEKK.

Despite the observed change in cold crystallization behavior, the melting crystallization peak remained unchanged for both neat PEKK and recycled PEKK/LRS composites. In all amorphous samples, the crystal melting peak upon heating was consistently observed at approximately 295

°C, confirming that neither recycling nor LRS incorporation affected the stability or perfection of the crystalline phase formed upon heating. This result provides assurance that the intrinsic crystallization kinetics of PEKK are preserved under the processing conditions employed in this study.

With this confirmation, the effectiveness of the established annealing protocol was evaluated using DSC data from annealed specimens. The applied isothermal heat treatment resulted in the formation of two distinct crystalline populations in both material systems. The primary, high-temperature crystalline phase exhibited a melting peak at ~295 °C, identical for neat PEKK and recycled PEKK/LRS composites, indicating comparable crystal stability and lamellar thickness. In addition, a secondary, lower-temperature crystalline phase was observed, corresponding to less perfect or thinner lamellae formed during annealing. For annealed neat PEKK, the secondary crystal melting peak appeared at approximately 225 °C, whereas for the recycled PEKK/LRS composite this peak shifted downward to ~215 °C, following the same trend observed in the amorphous samples. This consistent shift confirms that LRS influences crystallization temperature without disrupting crystal formation, while recycling itself does not introduce kinetic limitations or degradation-related effects [22].

Overall, the DSC results demonstrate that recycling and LRS incorporation do not compromise the crystallization behavior of PEKK. Instead, the presence of LRS provides a processing advantage by lowering the cold crystallization temperature, thereby enabling more energy-efficient annealing. The preservation of the primary melting peak across all conditions confirms the robustness of the polymer's crystalline architecture, supporting the reliability of the selected annealing protocol for recycled PEKK/LRS composites in circular additive manufacturing workflows.

8.4.1.4 Porosity Quality Control

Figure 8.2e presents the experimentally measured densities of extruded filaments and additively manufactured specimens for neat PEKK and recycled PEKK/LRS composites in both amorphous and annealed conditions. In general, annealing generally promotes a slight increase in density due to crystallization-induced matrix densification. However, the final density values are governed by the competing effects of crystallization, filler incorporation, and internal void content.

To quantitatively assess internal voids, porosity was calculated using the theoretical density of an ideal, void-free composite derived from constituent volume fractions, as shown in Figure 8.2f. The results reveal a clear increase in porosity with the incorporation of LRS, consistent with trends reported in our previous work on regolith-filled PEKK composites [23]. This behavior is primarily attributed to the elevated melt viscosity associated with high regolith loading, which limits the efficiency of vacuum-assisted air removal during twin-screw extrusion and increases the likelihood of void entrapment. As a baseline, neat PEKK from the manufacturer was considered to have negligible porosity in both amorphous and annealed states (0%). Relying on this baseline, the recycled PEKK/LRS composite exhibited a porosity of approximately 7% in the amorphous filament, which increased to 14% after annealing. This rise reflects the expansion of pre-existing voids during thermal softening of the matrix above the glass transition temperature (T_g), where local structural confinement is limited in filament form.

Moreover, the amorphous neat PEKK printed specimens exhibited a porosity of 3.4%, increasing modestly to 5.1% after annealing. This increase is attributed to the formation of secondary voids between adjacent deposited strands inherent to MEX processing, as well as limited void expansion during annealing. In contrast, the recycled PEKK/LRS printed parts exhibited substantially higher porosity levels, reaching 25% in the amorphous state and increasing to 37.6% after annealing. Several mechanisms contribute to this behavior. First, the extrusion pressure and shear rate at the printer nozzle are significantly lower than those in the micro-extruder used for filament fabrication [6,10,23]. These conditions reduce melt compaction, allowing pre-existing voids to expand and new voids to form during deposition.

Annealing further amplified porosity in LRS-containing samples. Although crystallization promotes matrix densification in all annealed specimens, its net influence on porosity depends on the balance between void expansion and structural confinement. For both neat PEKK and recycled PEKK/LRS composites, heating above T_g softens the matrix and enables expansion of trapped voids. In regolith-filled systems, this expansion dominates over crystallization-induced densification, resulting in a net increase in porosity after annealing. The effect is particularly pronounced in 3D-printed parts, where geometric confinement is limited and voids can expand more freely.

This porosity analysis highlights the strong coupling between filler content, processing conditions, and post-processing thermal history. While LRS incorporation increases porosity due to viscosity-driven limitations in air removal and melt consolidation, the observed trends are consistent and predictable. These findings provide essential context for interpreting the mechanical and energy-absorption behavior of recycled PEKK/LRS structures discussed in subsequent sections.

8.4.2 *Mechanical Properties*

8.4.2.1 Tensile Properties

The tensile behavior of neat PEKK and recycled PEKK/LRS composite specimens was evaluated in both amorphous and annealed conditions for printing orientations of 0° and 90°, with representative stress–strain curves and quantitative comparisons shown in Figure 8.3a–b.

Among all tested configurations, only the amorphous neat PEKK specimens printed in the 0° orientation exhibited extremely large plastic deformation (Figure 8.3a), characterized by the development of stable necking that propagated along the gauge length. This behavior is attributed to the very low level of defects and porosity in these samples, which allows uninterrupted polymer drawing once yielding occurs [12,44]. During necking, molecular chains progressively align along the loading direction, resulting in strain hardening that compensates for the local reduction in cross-sectional area. As a result, the neck continued to propagate through the entire gauge section until reaching the grip tabs, producing exceptionally high tensile toughness.

In contrast, this necking phenomenon was absent in all other configurations, including neat PEKK printed in the 90° orientation and all recycled PEKK/LRS composite specimens. The development of stable necking is highly sensitive to the presence of imperfections along the deformation path. Even minor defects or local porosity act as stress concentrators that interrupt uniform drawing and prematurely arrest neck propagation [22]. Consequently, the tensile toughness of amorphous neat PEKK printed at 0° was more than two orders of magnitude higher than that of all other samples (Figure 8.3b).

Printing orientation played a dominant role in determining tensile toughness. Specimens printed in the 90° orientation exhibited markedly lower toughness regardless of material system or thermal condition. In this orientation, tensile strength and deformation are governed primarily by inter-strand bonding rather than by the intrinsic strength of the extruded filaments. Since interlayer interfaces are more sensitive to voids, filament diameter fluctuations, and local under- or over-extrusion, the capacity for plastic deformation is severely limited, suppressing necking and leading to early failure.

The tensile strength results further reflect these mechanisms. For specimens printed in the 0° orientation, neat PEKK exhibited strengths of 87 MPa (amorphous) and 107 MPa (annealed), consistent with effective load transfer along continuous strands and crystallinity-induced strengthening after annealing. In comparison, the recycled PEKK/LRS composite showed reduced strengths of 52 MPa (amorphous) and 41 MPa (annealed). The reduction is primarily attributed to increased porosity and stress concentration introduced by the regolith particles, as well as reduced chain mobility in the composite system [23]. For specimens printed in the 90° orientation, strength values were uniformly lower and more sensitive to processing inconsistencies. Neat PEKK exhibited strengths of 48 MPa (amorphous) and 39 MPa (annealed), while the recycled PEKK/LRS composite reached 42 MPa (amorphous) and 29 MPa (annealed). The more pronounced strength degradation observed in recycled composite specimens is linked to filament diameter variability introduced during recycling, which increases the likelihood of under- or over-extrusion during printing [6]. Such dimensional inconsistencies directly impair inter-strand contact and bonding, making the 90° orientation particularly sensitive to recycled filament quality.

Overall, the tensile results highlight a strong coupling between material system, printing orientation, and filament dimensional control. While the intrinsic strength of PEKK strands governs the response in the 0° orientation, interlayer adhesion dominates in the 90° orientation, amplifying the effects of recycling-induced filament variability. These findings emphasize the importance of tight filament diameter control in recycled composite systems, especially for load cases dominated by inter-strand bonding.

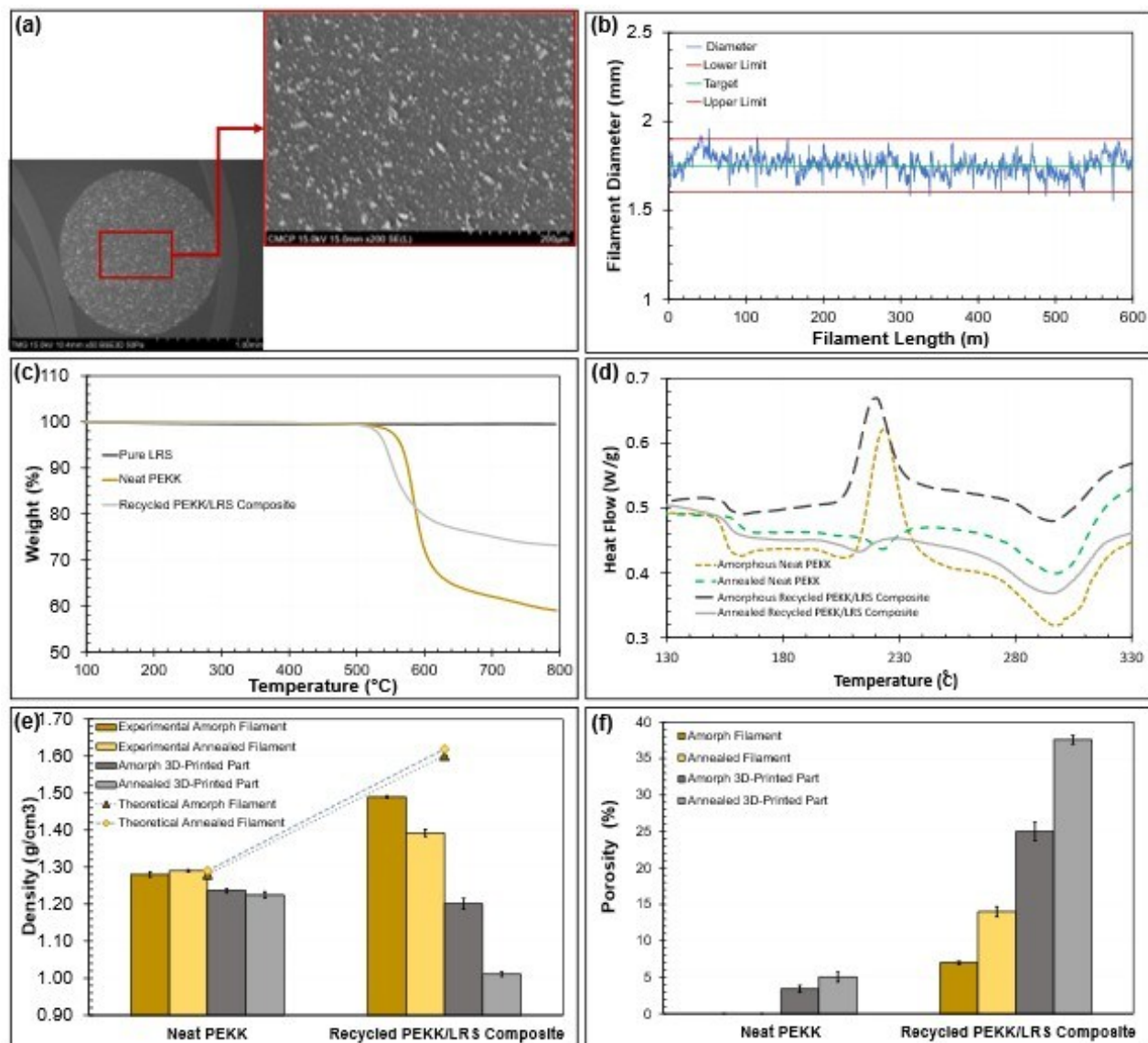


Figure 8.2. Composite manufacturing quality control of recycled PEKK/LRS system; (a) SEM micrographs of the recycled PEKK/LRS composite filament, (b) Filament diameter quality control, (c) TGA curves of neat PEKK, standalone LRS, and recycled PEKK/LRS composite, (d) DSC thermograms illustrating cold-crystallization and melting behavior of neat PEKK and recycled PEKK/LRS composite, (e) Measured density of extruded filaments and 3D-printed specimens before and after annealing, (f) Calculated porosity of filaments and printed parts based on theoretical void-free density.

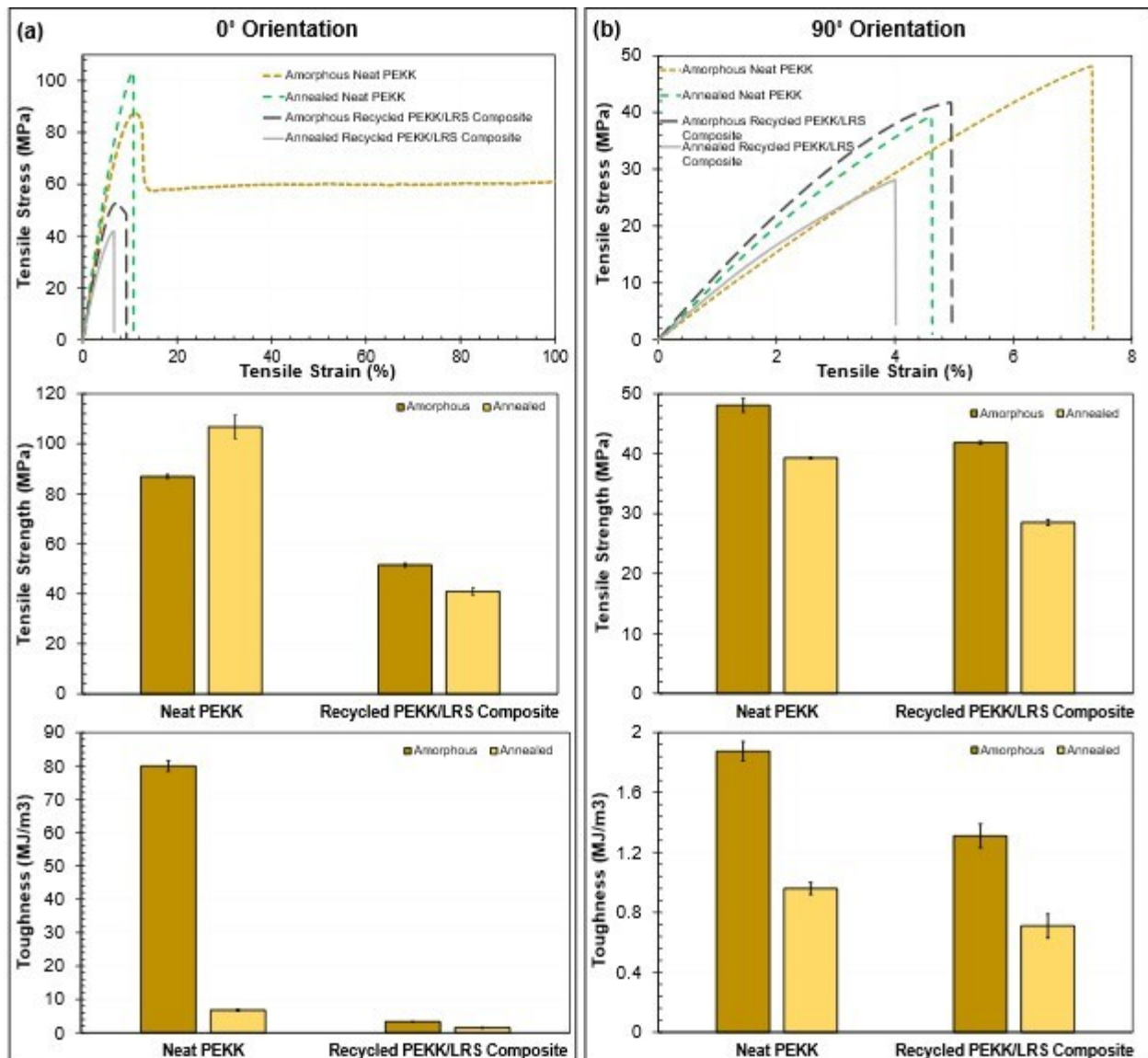


Figure 8.3. Tensile properties of coupons with categories of amorphous (as printed) and annealed conditions in: (a) 0° orientation, (b) 90° orientation.

8.4.2.2 Flexural Properties

The flexural response of neat PEKK and recycled PEKK/LRS composite specimens was evaluated in both amorphous and annealed conditions for printing orientations of 0° and 90°. Representative stress–strain curves and failure modes are shown in Figure 8.4a–b.

For specimens printed in the 0° orientation (Figure 8.4a), neat PEKK exhibited highly ductile behavior in both amorphous and annealed states. Neither condition fractured before reaching the 10% flexural strain limit imposed by the testing standard, indicating substantial bending tolerance

and effective load transfer along continuous strands. Annealing further enhanced the flexural strength, increasing it from 127 MPa (amorphous) to 150 MPa (annealed) as a result of crystallization-induced stiffening and improved strength. In contrast, recycled PEKK/LRS composite specimens printed at 0° fractured prior to reaching the 10% strain limit. The amorphous composite exhibited reduced flexural strength (84 MPa) and failed earlier due to the combined influence of internal porosity and particle-induced stress concentrations. The annealed composite displayed a more abrupt and brittle flexural fracture, with strength decreasing further to 75 MPa. This brittle response is attributed to the restricted plastic deformation capacity of the semi-crystalline matrix, where crystallinity limits chain mobility and suppresses local yielding mechanisms that could otherwise blunt crack propagation.

For specimens printed in the 90° orientation (Figure 8.4b), brittle fracture was observed in all material systems and processing conditions. In this orientation, failure consistently initiated at the inter-strand interfaces beneath the mid-span of the specimen, where tensile stress reaches its maximum during bending. The dominance of interlayer bonding in this configuration renders the specimens highly sensitive to defects and voids at strand interfaces.

Interestingly, annealing exerted an opposite effect in flexure compared to tensile loading for neat PEKK printed at 90°. While annealing reduced tensile strength in the 90° orientation due to increased porosity sensitivity, it enhanced flexural strength, increasing from 69 MPa (amorphous) to 98 MPa (annealed). This difference arises from the distinct stress distributions in tensile and flexural loading. In tensile tests, the entire cross-section is uniformly stressed, meaning that a critical defect anywhere in the gauge can trigger failure. In flexure, however, maximum tensile stress is localized at the outermost bottom layer, reducing the statistical likelihood of encountering a critical defect within that specific region. As a result, the benefits of crystallization-induced stiffening outweigh the detrimental effects of annealing-induced porosity under bending conditions.

For recycled PEKK/LRS composite specimens printed at 90°, annealing produced the opposite trend. The amorphous composite exhibited a flexural strength of 65 MPa, whereas annealing reduced strength to 41 MPa. This degradation reflects the cumulative influence of two additional defect mechanisms. First, recycling-induced filament diameter variability increases the likelihood of under-extruded strands, leading to non-uniform layer strength and compromised inter-strand

bonding. Second, the presence of rigid LRS particles introduces stress concentration sites that promote crack initiation. While amorphous samples can locally accommodate stress through plastic deformation, this mechanism is largely suppressed in the annealed composite due to reduced chain mobility, resulting in earlier brittle failure.

Overall, the flexural results demonstrate that the mechanical response is governed by a complex interplay between printing orientation, thermal history, and defect sensitivity. While annealing generally enhances flexural performance in neat PEKK by increasing stiffness and load-bearing efficiency, its effect becomes detrimental in regolith-filled recycled composites, where porosity, filament inconsistency, and particle-induced stress concentrations dominate the failure response.

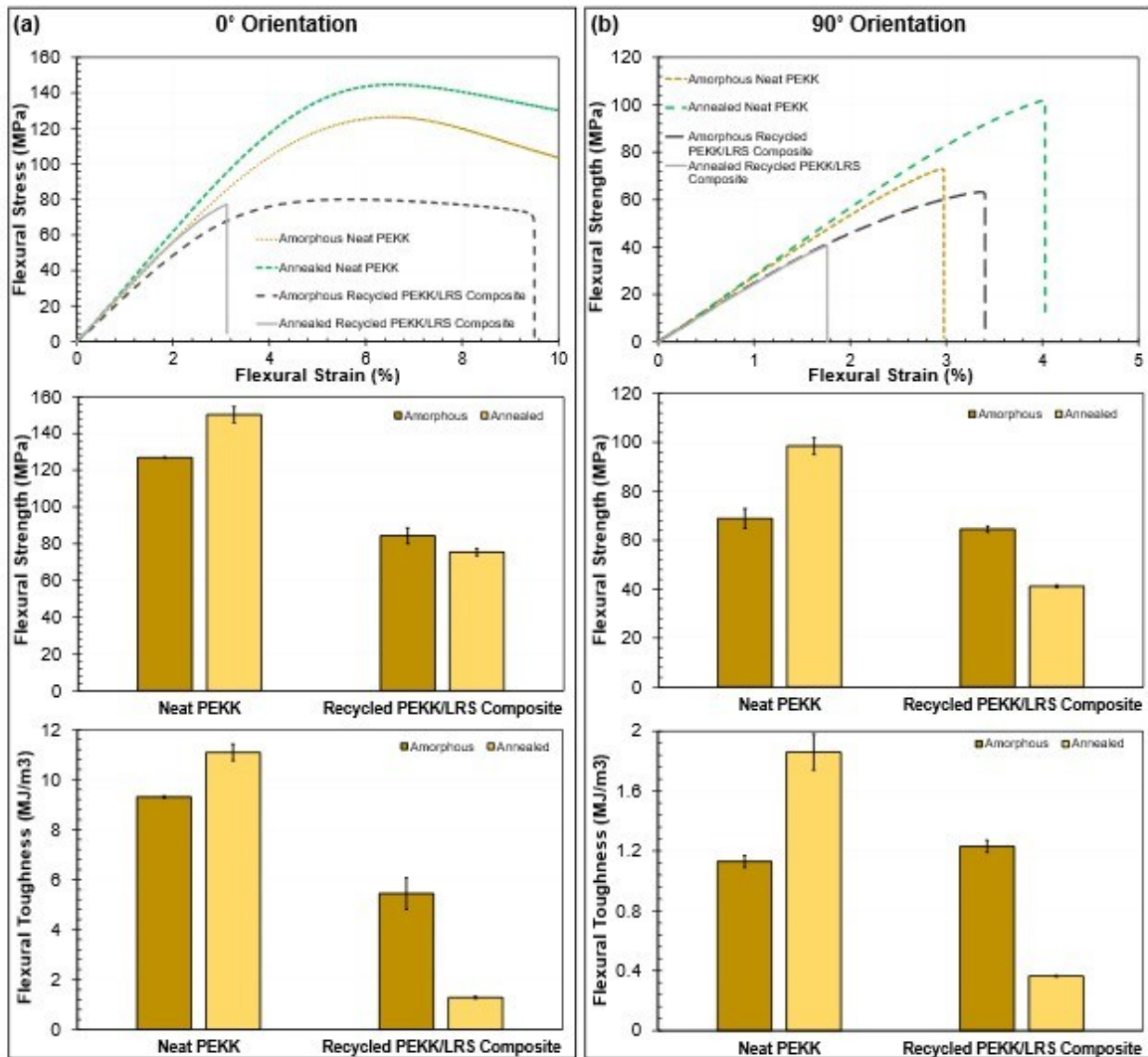


Figure 8.4. Flexural properties of coupons with categories of amorphous (as printed) and annealed conditions in: (a) 0° orientation, (b) 90° orientation

8.4.2.3 DMA

The viscoelastic behavior of neat PEKK and recycled PEKK/LRS composites was evaluated by dynamic mechanical analysis, with storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) presented in Figure 8.5a–b for both amorphous and annealed specimens. Although additively manufactured parts inherently exhibit anisotropy between 0° and 90° printing orientations, the discussion here focuses on material-level trends that are independent of geometric effects.

At first glance, the overall similarity between Figure 8.5a and Figure 8.5b indicates that recycling and LRS incorporation do not fundamentally alter the viscoelastic response of PEKK. Across all material conditions, the addition of 30 wt% LRS resulted in a slight shift of the glass transition temperature (T_g) toward higher temperatures, consistently observed in the storage modulus, loss modulus, and $\tan \delta$ curves. This shift reflects restricted chain mobility caused by the presence of rigid ceramic particles and confirms enhanced thermal stability without disruption of the polymer relaxation mechanisms.

A clear distinction is observed between amorphous and annealed specimens. In amorphous samples, the storage modulus exhibits a noticeable increase upon entering the cold crystallization temperature range. This rise is associated with the formation of new crystalline regions during heating, which increases stiffness as molecular chains reorganize into ordered structures. In contrast, annealed specimens show a stable storage modulus throughout this temperature range, as crystallization has already reached saturation during post-processing and no additional crystal growth occurs during the DMA scan.

The absolute magnitude of the initial storage modulus does not follow a strict monotonic trend across samples, ranging approximately from 2000 to 2500 MPa. This scatter is expected and can be attributed to variations in defect content, filament dimensional accuracy, and specimen geometry, which can influence clamp alignment and effective load transfer during testing. Such variability is commonly reported for additively manufactured polymers and does not detract from the interpretation of temperature-dependent trends. Consequently, the relative evolution of viscoelastic properties with temperature, rather than absolute modulus values, is the primary indicator of material behavior.

In this regard, the $\tan \delta$ curves provide the most reliable insight into intrinsic viscoelastic response, as they are less sensitive to geometric imperfections and defect-induced stiffness variations. As shown in Figure 8.5, the $\tan \delta$ profiles of neat PEKK and recycled PEKK/LRS composites overlap closely within each processing category (amorphous or annealed). This overlap demonstrates that neither the recycling process nor the incorporation of 30 wt% LRS significantly affects the segmental mobility, relaxation dynamics, or damping behavior of PEKK. The position and shape of the $\tan \delta$ peaks remain consistent, confirming preservation of the polymer's molecular architecture.

Overall, DMA results confirm that recycled PEKK retains its viscoelastic integrity after regolith incorporation, and that the observed mechanical changes in tensile and flexural tests are governed primarily by porosity, inter-strand bonding, and stress concentration effects rather than by alterations in polymer chain dynamics. These findings reinforce the suitability of recycled PEKK/LRS composites for high-temperature, cyclic, and long-term structural applications within circular additive manufacturing and ISRU frameworks.

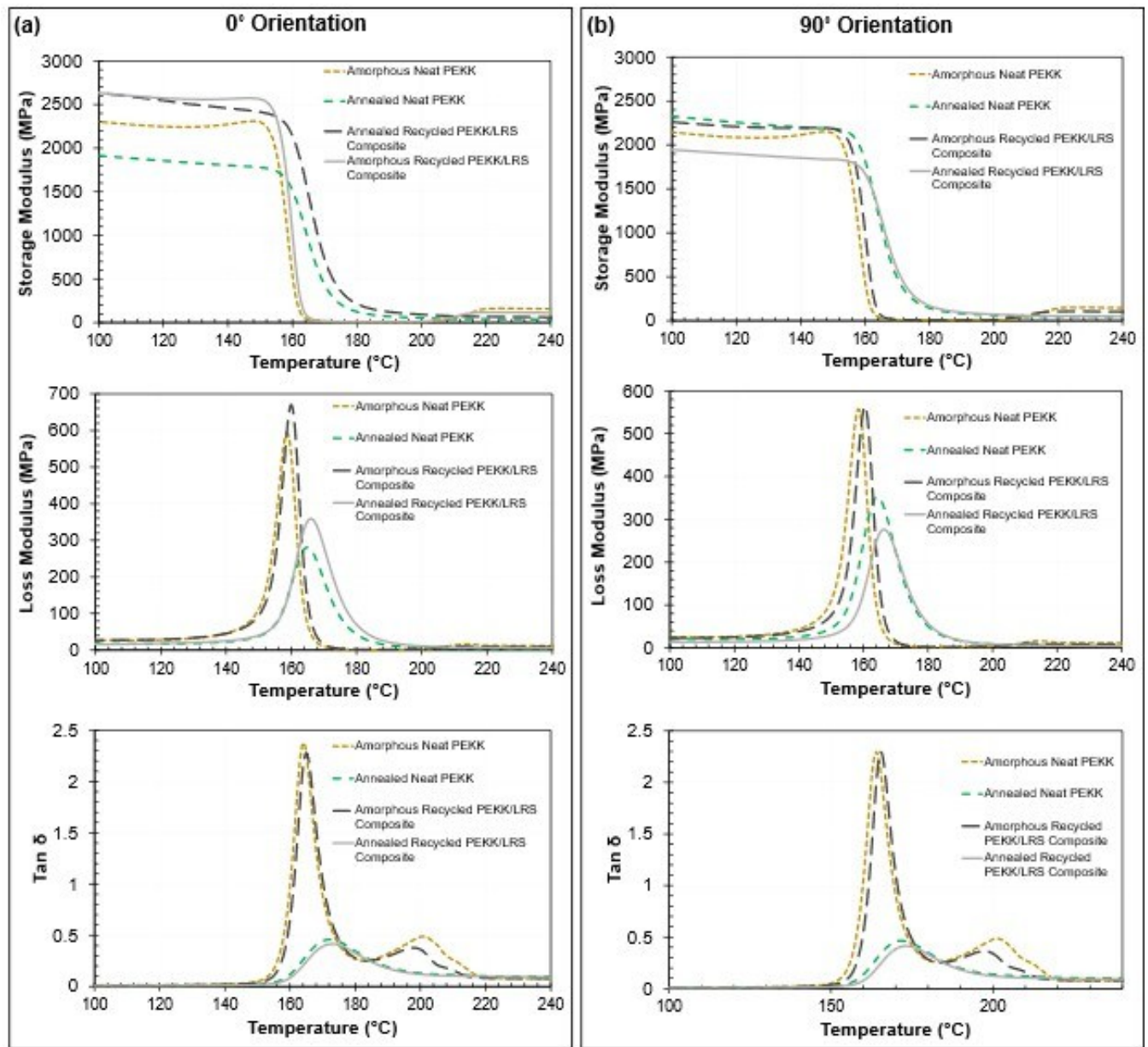


Figure 8.5. Flexural strength of PEKK coupons in as-printed (regular) and annealed across recycling rounds.

8.4.2.4 Gyroid Compression

The compressive response of Schwarz-G gyroid lattices fabricated from neat PEKK and recycled PEKK/LRS composites, as a representative of sacrificial structure, was evaluated under loading applied both perpendicular (Z orientation) and parallel (T orientation) to the deposited layer sequence. Representative stress–strain responses and deformation modes are shown in Figure 8.6a–b.

- **Compression perpendicular to the deposited layers (Z orientation)**

For amorphous gyroid specimens compressed in the Z orientation (Figure 8.6a), neat PEKK exhibited fully ductile behavior characterized by a well-defined elastic regime followed by yielding and an extended plastic densification plateau. After reaching the ultimate compressive strength (30.2 MPa), the lattice continued to sustain nearly constant load over a wide strain range through progressive plastic deformation of the unit cells. Near 50% compressive strain, the load began to increase again as a result of geometric densification, marking the practical end of the test as the gyroid architecture became fully collapsed.

Recycled PEKK/LRS composite gyroids in the amorphous state followed the same deformation sequence, demonstrating stable plastic densification and progressive collapse without catastrophic failure. Although a modest reduction in strength (29 MPa) and toughness was observed relative to neat PEKK, the overall deformation mode remained ductile. This behavior indicates that despite the incorporation of in-situ regolith and the recycled nature of the matrix, the architected composite structure retains promising compressive strength and energy-absorption capability in this loading direction.

In contrast, annealed gyroid specimens compressed in the Z orientation exhibited brittle fracture behavior. Neat PEKK showed an increase in compressive strength to 44 MPa, reflecting crystallization-induced stiffening, but failed abruptly after reaching peak load. The recycled PEKK/LRS composite displayed a similar brittle response with a reduced strength of 23.8 MPa. Despite this reduction, the relative decrease in both strength and toughness after recycling and LRS incorporation remained moderate, suggesting that brittleness is primarily governed by crystallinity rather than filler addition alone.

- **Compression parallel to the deposited layers (T orientation)**

When compressed parallel to the deposited layer sequence (T orientation), distinct deformation mechanisms emerged (Figure 8.6b). For amorphous neat PEKK gyroids, the ultimate compressive strength (32.6 MPa) was comparable to that measured in the Z orientation. However, after reaching peak stress, crack initiation occurred preferentially along interlayer interfaces due to shear stresses acting between adjacent layers. This resulted in a load plateau at stress levels lower than the ultimate strength, associated with interlaminar delamination and slow crack propagation. Despite

this damage mechanism, the structure continued to deform in a ductile manner and ultimately entered a densification regime, where the load increased again as the unit cells collapsed.

This interlayer-dominated failure mode was more pronounced in the amorphous recycled PEKK/LRS composite, which exhibited a significantly reduced compressive strength of 17.3 MPa. The presence of irregular LRS particles, combined with recycling-induced filament variability, weakens interlayer adhesion and promotes sharper crack initiation and propagation under shear-dominated loading. Although the composite followed the same general deformation sequence as neat PEKK, the reduced load-carrying capacity resulted in substantially lower energy absorption in this orientation.

For annealed gyroid specimens tested in the T orientation, the response resembled that observed in the Z orientation in terms of brittleness. Neat PEKK exhibited a compressive strength of 40.4 MPa, while the recycled PEKK/LRS composite reached 24.3 MPa. Annealing promotes interlayer diffusion and reduces anisotropy, leading to more isotropic stiffness; however, the increased crystallinity also suppresses plastic deformation. Once a crack initiated in this configuration, it propagated rapidly along the layer interfaces, resulting in abrupt failure. Although the compressive strengths remained comparable to those measured in the Z direction, the failure mode differed substantially, shifting from progressive densification to rapid brittle collapse.

Overall, the gyroid compression results highlight the strong coupling between loading direction, thermal history, and material architecture. Amorphous lattices favor ductile collapse and high energy absorption through progressive densification, particularly when loaded perpendicular to the layer sequence. Annealing enhances compressive strength but introduces brittleness that limits post-yield deformation. While incorporation of recycled PEKK and LRS moderately reduces strength and toughness, the composite gyroids retain structurally meaningful compressive performance, confirming their suitability as sacrificial, energy-absorbing structures in ISRU-driven circular additive manufacturing applications.

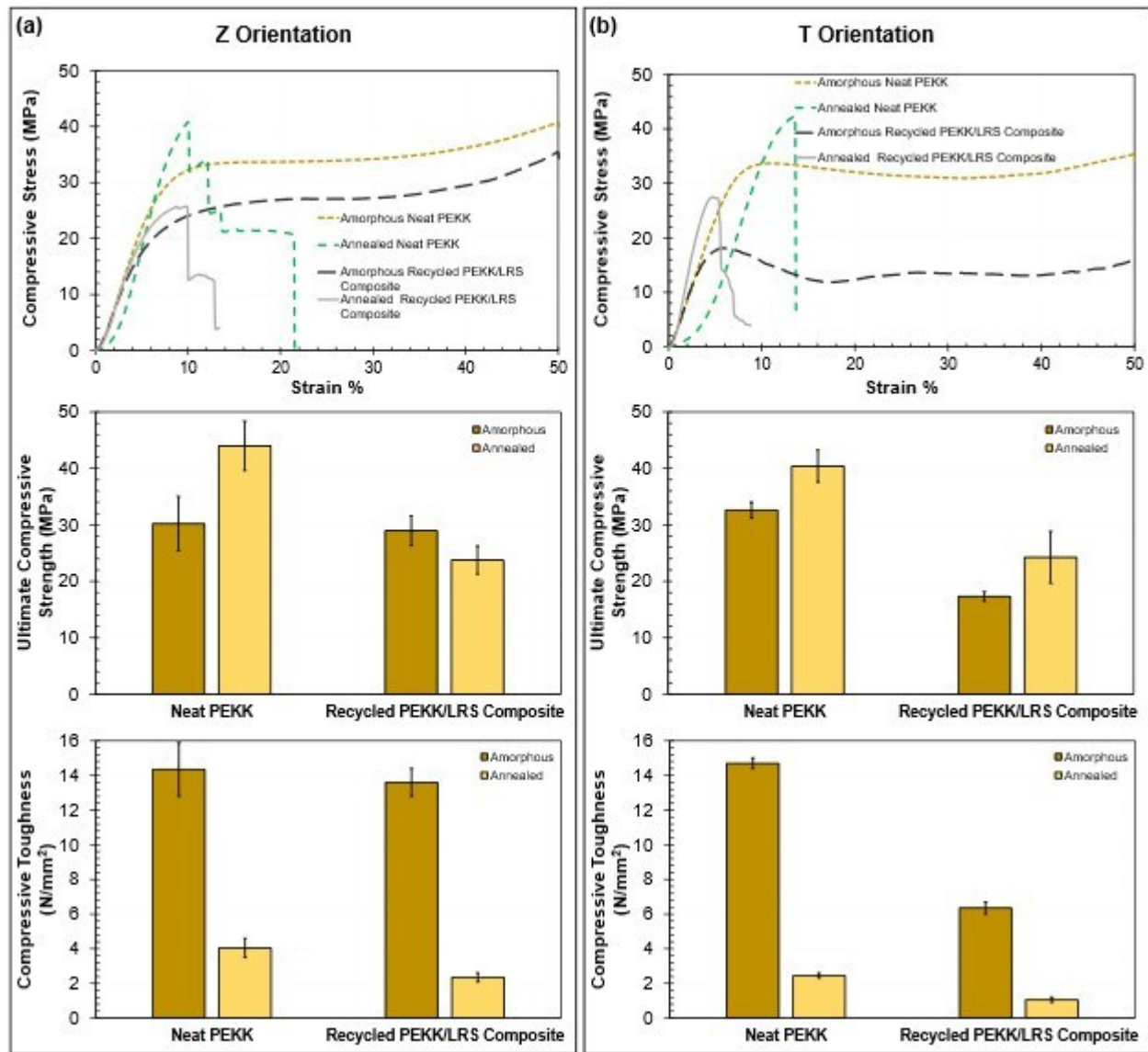


Figure 8.6. Gyroid sacrificial structure compression test results with categories of amorphous (as printed) and annealed conditions in: (a) Perpendicular (Z) orientation, (b) Transvers (T) orientation.

8.4.3 Circularity and ISRU Integration

The results presented in the preceding sections provide insight into how recycled high-performance thermoplastics can be combined with in-situ lunar resources to support a circular additive manufacturing strategy under ISRU constraints. Rather than viewing the recycled PEKK/LRS composite solely through the lens of absolute mechanical performance, its behavior must be interpreted in terms of functional suitability, process adaptability, and resource efficiency in extraterrestrial environments.

From a materials perspective, the thermal and viscoelastic analyses indicate that the fundamental molecular response of PEKK remains largely unchanged after recycling and regolith incorporation. The DSC and DMA results show that crystallization kinetics, glass transition behavior, and segmental mobility are preserved, suggesting that the polymer backbone is not degraded by either recycling or the addition of 30 wt% LRS. Consequently, the mechanical differences observed in tensile, flexural, and compressive loading arise primarily from microstructural factors, such as porosity, interlayer bonding, and particle-induced stress concentrations, rather than intrinsic changes in polymer chemistry. This distinction is particularly relevant for ISRU applications, where predictable material behavior across multiple processing cycles is essential for reliability.

The architected gyroid structures further illustrate how recycled PEKK/LRS composites can be leveraged in a functional manner despite these microstructural trade-offs. In the amorphous state, both neat PEKK and recycled PEKK/LRS gyroids exhibited progressive plastic densification under compression, enabling sustained load bearing and energy absorption. Such behavior is well aligned with the intended role of sacrificial structures, where controlled deformation and damage tolerance are more critical than peak strength. While annealing increased compressive stiffness, it also promoted brittle failure, highlighting the importance of tailoring thermal history to the intended structural function. Within this context, the recycled PEKK/LRS system offers a tunable balance between strength and toughness through a combination of architecture, orientation, and post-processing while being manufactured from scrap parts and in-situ resources, minimizing cost at its lowest value.

Beyond structural lattices, Figure 8.7 illustrates the broader implications of material circularity through the fabrication of a NASA-style ratchet wrench from both neat PEKK and recycled PEKK/LRS composite. This demonstrator serves as a practical example of how recycled materials can be reintroduced into the manufacturing loop to produce functional tools using the same additive manufacturing infrastructure when it reaches its end-of-life cycle. A notable observation is the improved dimensional stability of the recycled PEKK/LRS wrench after annealing, where the incorporation of regolith significantly reduced shrinkage and warpage compared to neat PEKK. The rigid ceramic phase constrains polymer chain relaxation during thermal treatment, mitigating crystallization-induced dimensional changes. This effect is particularly advantageous in lunar

environments, where thermal cycling and limited post-processing capabilities demand tight dimensional control.

When considered together, these findings suggest that the value of recycled PEKK/LRS composites in ISRU scenarios lies not in maximizing bulk mechanical properties, but in enabling resource-efficient manufacturing with predictable, tunable performance. The use of regolith as an additive reduces polymer demand, improves dimensional stability, and supports the fabrication of both sacrificial and functional components. At the same time, recycling maintains material availability within a closed-loop system, reducing waste and reliance on Earth-supplied feedstock.

Several directions naturally emerge from this work. Quantitative life cycle assessment (LCA) will be necessary to evaluate the environmental and energetic benefits of recycling-based ISRU manufacturing relative to conventional supply chains. In addition, systematic measurement and control of shrinkage through additive incorporation and processing optimization warrant further investigation. Finally, the integration of digital image correlation or color-encoded sacrificial architectures could enable real-time monitoring of damage evolution and crack propagation, opening pathways toward smart, damage-aware structures for lunar infrastructure.



Figure 8.7. FTIR spectra of neat and recycled PEKK in (a) amorphous and (b) annealed conditions.

8.5 Conclusion

This study explored recycled PEKK combined with lunar regolith simulant as a filler phase to enable circular additive manufacturing of sacrificial and functional components under ISRU-relevant conditions. Importantly, the recycled polymer used in this work was recovered from end-of-life sacrificial structures after completion of their mechanical duty, directly demonstrating a closed-loop manufacturing pathway applicable to lunar infrastructure.

Rather than being limited by polymer degradation, the performance of the recycled PEKK/LRS system was controlled predominantly by process-induced microstructural features, including porosity, interlayer bonding quality, and particle-related stress concentrations. This indicates that the recycling step itself does not represent a limiting factor for repeated use of PEKK in ISRU-driven additive manufacturing, and that structural performance can instead be tuned through processing control, architectural design, and thermal history.

For architected sacrificial structures, Schwarz-G gyroid lattices fabricated from the recycled PEKK/LRS composite retained a substantial fraction of the compressive load-bearing capability of neat PEKK. In the amorphous condition, the reduction in peak compressive strength was limited to approximately 4% when loaded perpendicular to the deposited layers, while still exhibiting progressive plastic densification and high energy-absorption capacity. In loading parallel to the layer sequence, larger reductions in compressive strength (40–47%) were observed, reflecting the increased sensitivity of sacrificial architectures to interlayer shear and filler-induced stress concentrations. Annealing increased compressive stiffness but introduced brittle failure, leading to strength reductions of up to 46% relative to annealed neat PEKK gyroids. These trends are consistent with the intended sacrificial role of the structures, where controlled deformation and predictable collapse are prioritized over maximum strength.

Beyond sacrificial architectures, the fabrication of a functional demonstrator illustrated the reusability of material recovered from spent structures. The incorporation of regolith as a filler significantly improved dimensional stability during annealing by reducing shrinkage and warpage, an important advantage for precision manufacturing in extraterrestrial environments where post-processing capabilities are limited. Overall, the results show that recycled PEKK filled with lunar regolith can be effectively reprocessed into new sacrificial and functional components, supporting

circular additive manufacturing strategies that reduce polymer demand, material waste, and reliance on Earth-supplied resources for future lunar missions.

Chapter 9: “Conclusions and Future Work”

“Keep Moving Forward”

-Walt Disney

9. Conclusions and Future Work

9.1 Conclusions

This thesis established a comprehensive and unified framework for sustainable polymer-based additive manufacturing in extraterrestrial environments, addressing the intertwined challenges of space mission cost, manufacturing autonomy, and material sustainability. By integrating crystallization engineering, additive manufacturing process optimization, in-situ resource utilization (ISRU), and polymer recycling, this work demonstrated that high-performance thermoplastics, specifically PEKK, can serve as viable, circular feedstocks for future lunar and Martian missions.

Systematic optimization of FDM processing parameters enabled predictable crystallization behavior and mechanical performance in additively manufactured PEKK, while tailored post-processing protocols further enhanced strength and thermal stability without compromising dimensional integrity. The introduction of architected geometries and anisotropy control provided insight into the structure–property relationships governing failure mechanisms in printed components. Building upon this foundation, PEKK was successfully compounded with lunar and Martian regolith simulants, demonstrating that extraplanetary resources can be transformed into mechanically functional composite materials suitable for additive manufacturing. The development and validation of predictive mechanical models further strengthened the engineering relevance of these materials.

In parallel, the resistance of PEKK to thermal, mechanical, and chemical degradation under multiple recycling cycles confirmed its suitability for closed-loop manufacturing. The integration of recycling with ISRU culminated in circular PEKK–regolith composite systems capable of producing functional demonstrators and sacrificial structures, directly addressing the need for material reuse and waste minimization in space. Collectively, this work advances the state of the art in sustainable space manufacturing and provides a scalable pathway toward self-reliant polymer-based ISRU on the Moon and Mars.

9.2 Future Work

While this thesis establishes a strong foundation for sustainable additive manufacturing in space, several critical research directions remain to be explored to transition these concepts from laboratory-scale validation to operational deployment.

Future work should focus on testing under realistic extraterrestrial operational conditions, including vacuum, reduced gravity, extreme thermal cycling, and radiation exposure. Such experiments are essential to validate crystallization behavior, interlayer bonding, and long-term mechanical performance of PEKK and PEKK–regolith composites beyond Earth-like environments. In parallel, dimensional stability and shrinkage evolution during both in-process and post-process crystallization should be examined in greater detail, particularly for large-scale and architected components where thermal gradients and residual stresses may become more pronounced.

From a structural mechanics perspective, further investigation into fracture mechanics and damage tolerance of additively manufactured PEKK-based systems is warranted. This includes mode I and mixed-mode fracture behavior, crack initiation and propagation in regolith-filled composites, and the influence of recycling-induced microstructural changes on fracture resistance. Such studies would enable more reliable design of load-bearing and safety-critical components for space infrastructure.

Application-driven research represents another key direction. The development of functional planetary hardware, such as lunar and Martian rover wheels, mobility components, and deployable structural elements, should be pursued using the material systems developed in this thesis. These demonstrators would allow evaluation of wear resistance, impact performance, energy absorption, and long-term durability under mission-relevant loading scenarios. Integration of topology optimization and lattice-based energy-absorbing architectures could further enhance performance while minimizing material usage.

At the system level, future work should aim to integrate automation, sensing, and adaptive process control into additive manufacturing platforms. Real-time monitoring of temperature, crystallinity evolution, and porosity during printing and recycling could enable closed-loop control

strategies, improving reliability and reducing defect sensitivity, an essential requirement for autonomous space manufacturing.

Finally, a comprehensive life cycle assessment (LCA) tailored to space missions should be conducted to quantitatively evaluate the environmental and logistical benefits of ISRU and recycling-based additive manufacturing. Such an analysis would compare Earth-supplied manufacturing, single-use components, and circular ISRU systems in terms of launch mass savings, energy consumption, mission cost reduction, and sustainability metrics. This systems-level evaluation would provide a critical decision-making tool for future mission planners and technology developers.

Together, these future research directions will further advance the vision of fully autonomous, circular, and sustainable manufacturing ecosystems on the Moon and Mars, enabling long-duration human presence and scalable space infrastructure.

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