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4D Printing for Space Mechanisms: Shape Memory High Performance Polymer-Based Blends and Composites

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“Forse è proprio questa la benedizione più grande che si possa ricevere in una vita: capirlo subito, mentre lo si sta vivendo. Il privilegio di scoprire giovanissimi qual è quella passione, quel sogno che ci brucia dentro come una febbre, che ci tiene svegli la notte, che non ci fa sentire la fatica, la solitudine, lo sconforto, la paura. Un motore nucleare personalissimo che produce speranza, fiducia, ottimismo senza lasciare scorie radioattive. Contro qualsiasi previsione avversa, contro i dubbi di chi resta alla finestra a guardare, perché ci vuole coraggio a dichiarare il proprio amore e a perseguire un sogno fino alle luci dell'alba. Ma la ricompensa è la felicità. Sembra poco? Non lo è. Sì, perché è quel tipo di felicità che non dipende dall'esito della prova, ma deriva dalla prova stessa. La felicità è la sfida”.

Tommaso Ghidini, “Homo Caelestis”

Abstract

The development of lightweight and reliable materials for deployable space structures remains a challenge in aerospace engineering. Such materials must withstand demanding thermal and environmental conditions while providing the mechanical performance and actuation capabilities required for controlled deployment. This PhD research investigates the development of polymer blends and composites for the four-dimensional (4D) printing of space mechanisms, focusing on shape-memory behaviour, resistance to space-relevant environmental conditions, and remote activation.

The first part of the research investigates polyether ether ketone (PEEK)-polyetherimide (PEI) blends for high-temperature additive manufacturing. Four blend compositions were prepared by melt compounding and processed into filaments for Fused Filament Fabrication (FFF). Their rheological, thermal, morphological, mechanical, and thermomechanical properties were evaluated to understand how composition and processing affect the resulting material properties and shape-memory performance. All four blends could be processed successfully and showed shape fixity and recovery upon thermal activation. Of the compositions studied, the blend containing 70 wt.% PEEK and 30 wt.% PEI showed the most promising overall performance, combining good mechanical properties with effective shape-memory behaviour and structural changes during thermal cycling.

The second part examines the suitability of these materials for space applications. Additively manufactured specimens were tested at the European Space Research and Technology Centre of the European Space Agency (ESA-ESTEC) under simulated space-environment conditions. The tests included outgassing measurements, atomic oxygen exposure, and thermal vacuum cycling. The materials showed low outgassing, good resistance to atomic oxygen exposure, and stable dimensions during repeated thermal cycling. Their mechanical properties and shape-memory behaviour were also largely retained after testing. These results indicate that PEEK-PEI blends could be suitable for deployable structures exposed to the conditions encountered in low Earth orbit.

The final part of the research focuses on remote activation by incorporating carbonyl iron particles into the PEEK-PEI matrix. A composite containing 50 wt.% carbonyl iron, 35 wt.% PEEK, and 15 wt.% PEI was prepared by melt compounding and processed using FFF. The addition of carbonyl iron increased the stiffness and tensile strength of the material while maintaining its thermal stability and thermally activated shape-memory behaviour. Microwave irradiation was then used to trigger shape recovery without direct contact. A recovery ratio of

87.77% was achieved after approximately 90 seconds of irradiation at 750 W. This demonstrates the potential of combining mechanical reinforcement and remote actuation in a single 3D-printed composite.

In conclusion, this research investigates the development of PEEK-PEI blends and carbonyl iron-filled composites for 4D-printed space mechanisms. By examining material composition, additive manufacturing, environmental resistance, and remote activation, the work provides insight into the factors that influence their performance in potential aerospace applications. The results highlight the potential of these materials for lightweight deployable structures and contribute to the development of polymer-based systems that can be manufactured into a specific shape and activated when required.

Abstract

Lo sviluppo di materiali leggeri e affidabili per strutture spaziali dispiegabili rappresenta ancora una sfida nell'ambito dell'ingegneria aerospaziale. Tali materiali devono essere in grado di resistere a condizioni termiche e ambientali particolarmente severe, garantendo al contempo le prestazioni meccaniche e le capacità di attuazione necessarie per un dispiegamento controllato. Questa ricerca di dottorato si concentra sullo sviluppo di miscele polimeriche e materiali compositi destinati alla stampa 4D di meccanismi spaziali, con particolare attenzione al comportamento a memoria di forma, alla resistenza alle condizioni ambientali tipiche dello spazio e all'attivazione a distanza.

La prima parte della ricerca riguarda lo studio di miscele di poli(eter eter chetone) (PEEK) e poli(eterimmide) (PEI) per la produzione additiva ad alta temperatura. Sono state preparate quattro composizioni mediante miscelazione allo stato fuso (melt compounding) e successivamente trasformate in filamenti per la fabbricazione a filamento fuso (Fused Filament Fabrication, FFF). Le proprietà reologiche, termiche, morfologiche, meccaniche e termomeccaniche dei materiali sono state valutate al fine di comprendere come la composizione e le condizioni di processo influenzino le proprietà finali e le prestazioni a memoria di forma. Tutte e quattro le miscele sono risultate processabili con successo e hanno mostrato capacità di fissaggio e recupero della forma mediante attivazione termica. Tra le composizioni esaminate, la miscela contenente il 70% in peso di PEEK e il 30% in peso di PEI ha evidenziato le prestazioni complessive più promettenti, combinando buone proprietà meccaniche con un efficace comportamento a memoria di forma e variazioni strutturali durante i cicli termici.

La seconda parte esamina l'idoneità di questi materiali per applicazioni spaziali. I provini realizzati mediante produzione additiva sono stati sottoposti a test presso il Centro europeo di ricerca e tecnologia spaziale dell'Agenzia spaziale europea (ESA-ESTEC), in condizioni che simulano l'ambiente spaziale. Le prove hanno incluso misure di degassamento, esposizione all'ossigeno atomico e cicli termici in vuoto. I materiali hanno mostrato bassi livelli di degassamento, una buona resistenza all'esposizione all'ossigeno atomico e una stabilità dimensionale durante cicli termici ripetuti. Anche le proprietà meccaniche e il comportamento a memoria di forma sono stati in larga misura preservati dopo le prove. Questi risultati indicano

che le miscele PEEK-PEI potrebbero essere adatte alla realizzazione di strutture dispiegabili esposte alle condizioni ambientali tipiche dell'orbita terrestre bassa (Low Earth Orbit, LEO).

La parte finale della ricerca si concentra sull'attivazione a distanza attraverso l'incorporazione di particelle di ferro carbonilico nella matrice PEEK-PEI. Un materiale composito contenente il 50% in peso di ferro carbonilico, il 35% in peso di PEEK e il 15% in peso di PEI è stato preparato mediante miscelazione allo stato fuso e successivamente processato tramite FFF. L'aggiunta di ferro carbonilico ha incrementato la rigidità e la resistenza a trazione del materiale, mantenendone al contempo la stabilità termica e il comportamento a memoria di forma attivato termicamente. È stata quindi utilizzata l'irradiazione a microonde per innescare il recupero della forma senza contatto diretto. Dopo circa 90 secondi di irradiazione a una potenza di 750 W, è stato raggiunto un rapporto di recupero della forma pari all'87,77%. Questo risultato dimostra il potenziale della combinazione tra rinforzo meccanico e attuazione a distanza in un unico materiale composito stampato in 3D.

In conclusione, questa ricerca esamina lo sviluppo di miscele PEEK-PEI e materiali compositi caricati con ferro carbonilico per la realizzazione di meccanismi spaziali mediante stampa 4D. Attraverso lo studio della composizione dei materiali, della produzione additiva, della resistenza ambientale e dell'attivazione a distanza, il lavoro fornisce indicazioni sui fattori che ne influenzano le prestazioni in potenziali applicazioni aerospaziali. I risultati evidenziano il potenziale di questi materiali per la realizzazione di strutture dispiegabili leggere e contribuiscono allo sviluppo di sistemi a base polimerica che possono essere fabbricati secondo una geometria specifica e attivati al momento del bisogno.

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Table of Acronyms

Acronym	Definition
ABS	Acrylonitrile Butadiene Styrene
AM	Additive Manufacturing
ATOX	Atomic Oxygen
ATR	Attenuated Total Reflectance
BCC	Body-Centred Cubic
BJ	Binder Jetting
CAD	Computer-Aided Design
CCD	Charge-Coupled Device
CNC	Computer Numerical Control
CNT	Carbon Nanotube
CVCM	Collected Volatile Condensable Material
DBS	Retractable Directional Backscattered Detector
DLP	Digital Light Processing
DMA	Dynamic Mechanical Analysis
DMLS	Direct Metal Laser Sintering
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetry
EDS	Energy-Dispersive X-ray Spectroscopy
EBSD	Electron Backscatter Diffraction
ECSS	European Cooperation for Space Standardization
EDX	Energy-Dispersive X-ray
ESA	European Space Agency
ESTEC	European Space Research and Technology Centre
ETD	Everhart-Thornley Detector
FEG	Field Emission Gun
FFF	Fused Filament Fabrication
FTIR	Fourier-Transform Infrared Spectroscopy
HPP	High-Performance Polymer
IR	Infrared
LCD	Liquid Crystal Display
LEO	Low Earth Orbit
LENS	Laser Engineered Net Shaping
LPIB	Laser Pulse Induced Breakdown
ME	Material Extrusion
MFI	Melt Flow Index
MJ	Material Jetting
NASA	National Aeronautics and Space Administration
PA11	Polyamide 11

Acronym	Definition
PA12	Polyamide 12
PAEK	Poly-Aryl-Ether-Ketone
PEEK	Poly(Ether Ether Ketone)
PEI	Polyetherimide
PID	Proportional-Integral-Derivative
PLA	Polylactic Acid
PTFE	Polytetrafluoroethylene
RH	Relative Humidity
RGA	Residual Gas Analyzer
RML	Recovered Mass Loss
RT	Room Temperature
SED	Secondary Electron Detector
SEM	Scanning Electron Microscopy
SLM	Selective Laser Melting
SMP	Shape Memory Polymer
SLS	Selective Laser Sintering
TGA	Thermogravimetric Analysis
T _g	Glass Transition Temperature
T _m	Melting Temperature
TML	Total Mass Loss
TVAC	Thermal Vacuum
UV	Ultraviolet
VUV	Vacuum Ultraviolet
WVR	Water Vapor Regained
XRD	X-ray Diffraction

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Chapter 1. Introduction

Throughout history, humanity has repeatedly been confronted with new challenges arising from the relentless advancement of technology. Each technological breakthrough, while offering new opportunities, continually requires a rethinking of methods, materials, and strategies in order to meet increasingly complex demands. Within this framework, engineering plays a crucial role in research, where the demand for innovative solutions intersects with the need for adaptability, sustainability, and performance.

In recent years, the advent of additive manufacturing has marked a turning point in production technologies, introducing the concept of three-dimensional printing, or 3D printing [1]. However, technological progress has not halted at this stage: a further evolution, known as 4D printing, is transforming the way materials and manufacturing processes are conceived. Unlike conventional 3D printing, which produces so-called “static” objects, 4D printing incorporates smart materials capable of changing their shape over time in response to external stimuli such as temperature, humidity, light, or electric fields [2], thereby introducing dynamic behaviour. The inclusion of time as an additional variable alongside the three spatial dimensions gives rise to the fourth dimension.

Among these materials are shape memory materials, which are capable of “remembering” a predefined configuration and returning to it when appropriately stimulated. Temperature is one of the most effective stimuli for triggering this configurational change, whether applied directly or indirectly, enabling precise and localized control of the transformation.

The present work aims to explore the potential and challenges associated with the integration of shape memory materials within the 4D printing paradigm, with particular emphasis on their direct activation through temperature as an external stimulus. Furthermore, given the challenges of controlling this type of stimulus from the ground, indirect activation methods, such as using a heater or microwave actuation are also explored to improve control and reliability. The primary objective of this research is to understand how these technologies can be optimized to develop innovative solutions capable of addressing the growing demands of the aerospace sector, particularly in the deployment of critical components for orbital missions, such as solar panels, antennas, and sensor systems, while also providing a more practical, efficient, and cost-effective alternative to currently employed components.

Specifically, a polymer matrix material was developed in several formulations in order to investigate possible variations in chemical and physical properties as a function of the different

material percentages. The materials used were polyether ether ketone (PEEK), present in the highest proportion, and polyetherimide (PEI). The selection of these polymers, classified as high-performance engineering polymers, is primarily motivated by their compliance with space qualification requirements according to the European Cooperation for Space Standardization (ECSS) regulations. Furthermore, they represent excellent candidates due to their glass transition temperatures (T_g), which lie outside the typical operational temperature range encountered in space applications. It should be noted that during the launch phase, temperature ranges can reach values between $-100\text{ }^{\circ}\text{C}$ and $+100\text{ }^{\circ}\text{C}$ [5] [6] [7].

These materials not only promise to revolutionize traditional applications but also open new horizons in fields such as aerospace, robotics, biomedicine, and advanced design [3].

Chapter 2 introduces Additive Manufacturing, outlining its main techniques and key characteristics, with a particular focus on 4D printing. It provides an in depth discussion of 4D printing principles and activation strategies, while also reviewing Fused Filament Fabrication (FFF), especially in relation to part quality challenges and material limitations.

Chapter 3 presents the experimental investigation of the PEEK and PEI blends developed in this study. Each chapter is structured to include an initial section providing the research background and contextualisation, followed by a detailed description of the experimental methodology, subsequent presentation and discussion of the results, and final conclusions.

Chapters 4 and 5 are dedicated to evaluating the behaviour of the developed materials under simulated space environments, conducted at the European Space Agency facilities in the Netherlands. This is followed by comprehensive post-exposure characterisation to assess material performance degradation and property evolution.

Chapter 6 focuses on the development of PEEK/PEI-based composites incorporating carbonyl iron as a functional filler. The materials were processed into filaments via melt extrusion and subsequently fabricated into test specimens through FFF 3D printing. The 4D printing response was systematically investigated under indirect microwave actuation, complemented by extensive mechanical and thermal characterisations of both filament and printed structures.

Finally, Chapter 7 provides a consolidated conclusion of the thesis, summarising the principal findings and outcomes of the research.

The experimental campaigns relative to Chapter 3, 5, and 6 have been performed in the Material Science and Technology research group of the University of Rome Tor Vergata, Department of Enterprise Engineering, under the supervision of Prof. Francesca Nanni.

The work presented in Chapter 4 has been conducted during a three months stay at the European Space Research and Technology Centre (ESTEC, Noordwijk, the Netherlands) of the European Space Agency (ESA), in the Materials & Electrical Components Laboratory of the Materials, Environment and Contamination Section (TEC-MSE) (*ESA Cooperative Agreement No. 4000149110/25/NL/GLC, OSIP reference I-2024-11177*)

Chapter 2. State of the Art

In this chapter, the background on additive manufacturing and shape-memory materials is presented. Particular focus is given to PEEK-based materials and 4D printing, presenting an overview of the state of the art.

2.1. Additive Manufacturing

Additive Manufacturing (AM), also known as additive production, represents a branch of industrial manufacturing processes that has attracted significant attention from industry in recent years [1]. As shown in Figure 1, the additive technology is part of the manufacturing process. With substantial investments driven by its numerous advantages over more conventional techniques [2], such as, for example, the ability to manufacture complex geometries that require frequent design modifications, the feasibility of operating with low production volumes, and the consequent reduction in costs [3]. Nevertheless, its applications remain limited due to lower precision and longer build times when compared to Computer Numerical Control (CNC) machines [8].

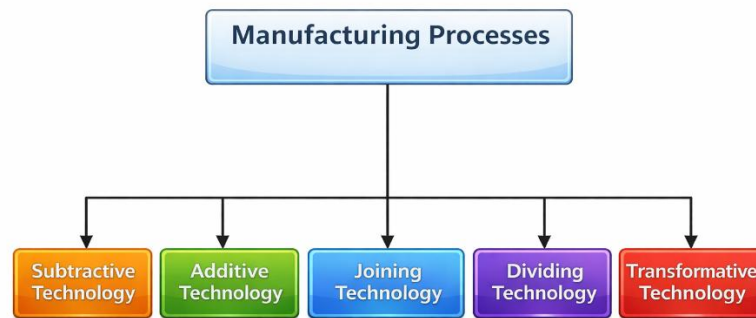


Figure 1: Manufacturing process

The defining characteristic of this manufacturing technique is the fabrication of parts through the deposition of material in a “layer-by-layer” manner. The starting material may be in liquid form, such as resins, or in powder form, as in extrusion-based printing processes [8]. An AM process primarily involves three main phases: the design phase, the processing phase, and the testing phase, which together follow the sequence illustrated in Figure 2 [9].

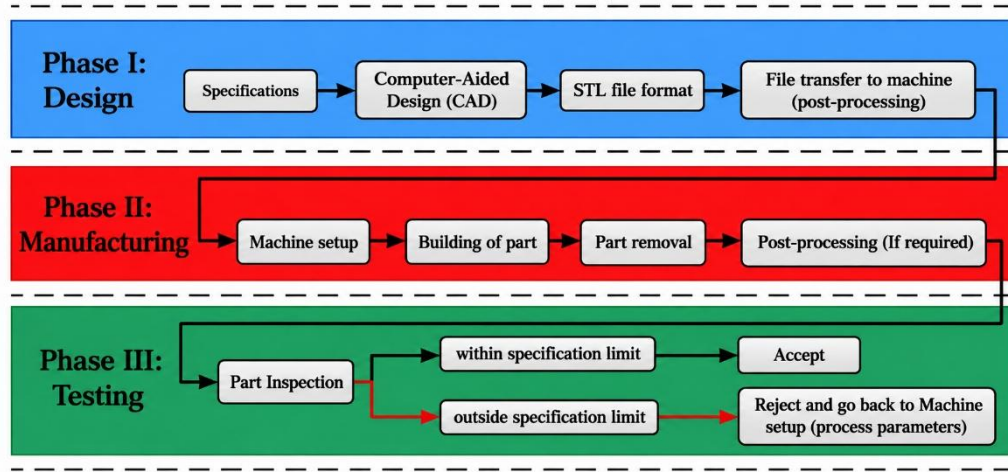


Figure 2: Phases of Additive Manufacturing process [4]

More specifically, the aforementioned phases can be summarized as follows:

- Creation of the 3D model using dedicated CAD (Computer-Aided Design and Drawing) software, which defines and graphically represents the geometry of the part to be manufactured;
- Conversion of the model into STL format, which represents the standard and most widely used file format in the 3D printing sector;
- Importation of the previously generated file into dedicated slicing software, along with the adjustment of parameters required for the final product. During this stage, the final file, ready for printing, is converted into G-code format (a programming language specifically developed for 3D printing machines);
- Transfer of the file directly to the printing machine, followed by the final parameter setup to ensure proper part fabrication;
- Printing of the finished product, fully automated by the machine;
- Optional inspections or post-processing treatments in cases where the printed part does not fully meet the initially imposed requirements.

Different types of AM processes exist and are employed depending on the material preparation method, the layer generation technique, the type of material, or the application requirements (Figure 3).



Figure 3: Types of Additive Manufacturing Techniques

Powder-based additive manufacturing processes are founded on the layer-wise deposition of particulate material, which is selectively consolidated through the application of a high-energy heat source, such as a laser or an electron beam [5], [6]. Owing to their thermal nature, these techniques are compatible with a broad spectrum of materials, including polymers, metals, and ceramics. Although components fabricated via Powder Bed Fusion typically exhibit limited surface quality and dimensional resolution, the high degree of densification achieved during processing results in mechanical properties that are often comparable to those of conventionally manufactured bulk materials [7]. Selective Laser Sintering (SLS) is primarily employed for the processing of polymeric powders, particularly semi-crystalline systems, as well as polymer-based composites [8]. The consolidation mechanisms involved are complex and may include solid-state sintering, viscous flow, liquid-phase sintering, and partial melting phenomena [9]. In the case of composite systems, additional post-processing steps are generally required to eliminate the polymeric binder and promote full densification through sintering or infiltration. Commonly utilized materials in SLS include polyamides (PA11 and PA12), polycarbonate, and polystyrene.

Selective Laser Melting (SLM), also referred to as Direct Metal Laser Sintering (DMLS), is characterized by the complete melting of metallic powders using a high-power laser source [9], [10], [11]. This approach enables the fabrication of fully dense components without the need for subsequent sintering operations. A wide range of engineering alloys, including stainless steels, aluminium alloys, titanium, cobalt-chromium systems, and nickel-based superalloys, can be processed using this technique, yielding components with excellent mechanical and

thermal performance. However, the elevated energy input required for full melting introduces significant challenges in process control and parameter optimization, often resulting in defects such as residual stresses, geometrical distortion, and melt pool instabilities [12]. Electron Beam Melting (EBM) represents a variant of powder bed fusion in which an electron beam is employed as the energy source [13], [14]. This necessitates operation under vacuum conditions and restricts material selection to electrically conductive systems. Nevertheless, EBM offers distinct advantages, including high processing temperatures and rapid scanning capabilities, rendering it particularly suitable for high-melting-point alloys such as nickel-based superalloys [15]. Collectively, powder bed fusion technologies are highly suited for the fabrication of geometrically complex and highly customized components, particularly in high-performance metallic applications. Despite these advantages, their widespread industrial adoption is constrained by high capital costs, process complexity, and stringent requirements for parameter control.

Material Extrusion (ME) processes, in contrast, are based on the controlled deposition of molten material through a heated nozzle, with subsequent solidification upon cooling [16]. The most prevalent implementation, Fused Filament Fabrication (FFF), utilizes thermoplastic filaments as feedstock, although alternative forms such as pellets or powders may also be employed [17], [18]. Due to limitations in achievable processing temperatures and the rheological requirements of the feedstock, ME techniques are predominantly restricted to polymers, waxes, and low-melting-point alloys. Nonetheless, the relative simplicity, accessibility, and low cost of FFF systems have led to their widespread adoption across both industrial and non-industrial contexts [19].

Vat polymerization techniques, commonly referred to as stereolithography (SLA), rely on the selective photopolymerization of liquid resin systems upon exposure to electromagnetic radiation, typically in the ultraviolet spectrum [20], [21], [22]. In vector-scan SLA systems, a focused laser beam selectively traces and cures each layer. Alternatively, mask-projection approaches enable the simultaneous curing of entire layers through spatially modulated light exposure. This modulation is achieved using either digital micromirror devices, as in Direct Light Processing (DLP), or liquid crystal displays in LCD-based systems. These projection-based techniques generally provide enhanced spatial resolution and increased build rates relative to laser-scanning approaches [23].

In addition to the aforementioned methods, several other additive manufacturing technologies exist, albeit with more limited industrial diffusion. Binder Jetting (BJ) involves the selective deposition of a liquid binding agent onto a powder bed to form consolidated layers [24]. Direct

Metal Deposition (DMD), also known as Laser Engineered Net Shaping (LENS) or laser cladding, employs a focused energy source to melt and deposit material directly onto a substrate [25], [26], [27]. Material Jetting (MJ), by contrast, operates through the controlled deposition of droplets of build material, analogous to inkjet printing, followed by solidification to form the final geometry [28], [29].

The feature that makes 3D printing particularly advantageous and innovative compared to traditional manufacturing techniques is the ability to produce a wide variety of components without requiring specific modifications to the 3D printing machine itself. This decouples the machine from being limited to niche products and makes it a highly versatile manufacturing system [10]. Furthermore, the capability to fabricate final geometries without the need for post-processing modifications results in significant economic savings and reduced material waste, making 3D printing a highly cost-effective manufacturing practice. This advantage is also reflected in terms of time efficiency, as the production workflow is independent of additional machinery, rendering the overall process relatively rapid [10].

Despite these advantages, which are currently decisive for the use of 3D printing in the fabrication of complex geometries, its application remains confined to a limited range of products due to the restricted number of available printable materials, such as polymers or low-melting-point metal alloys. Moreover, this technology is still affected by several challenges, including poor interlayer adhesion, potentially inferior mechanical properties compared to bulk materials, defects and undesired void formation, and residual stresses in the final component [11]. It should be noted that these issues are not solely attributable to the printing equipment but also to material selection, which may present challenges such as contamination, poor homogeneity, unsuitable viscosity, and other characteristics that can significantly affect print quality and part integrity [11].

The AM technology examined in the following section is Fused Filament Fabrication (FFF), which is the most widely used technique and is particularly suited for the printing of thermoplastic polymers.

2.1.1. Fused Filament Fabrication (FFF)

As previously discussed, the fabrication of components by means of 3D printing is achieved through the deposition of two-dimensional layers along the vertical axis, thereby forming a three-dimensional structure. To understand the operation of this process, it is essential to focus on the core of the 3D printer, namely the extrusion system [10]. This system consists of four

sequential components, all of which are fundamental to the successful extrusion of the part. Specifically, these components are:

- Filament extrusion motor;
- Cylinder or tube with a significantly reduced cross-section, through which the filament passes without melting;
- Heating block, in which filament melting occurs;
- Nozzle, through which the molten filament is extruded.

These components are illustrated in Figure 4 and Figure 5.

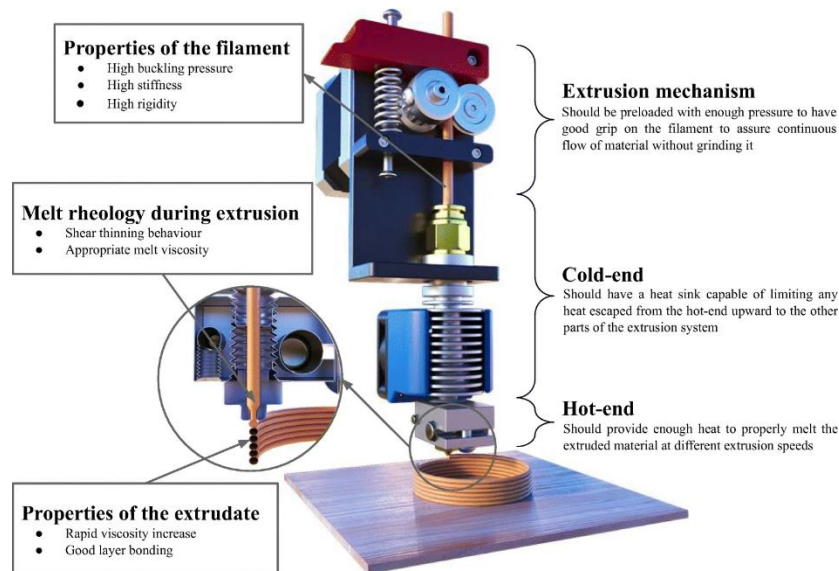


Figure 4: System schematic of a 3D printing facility [10]

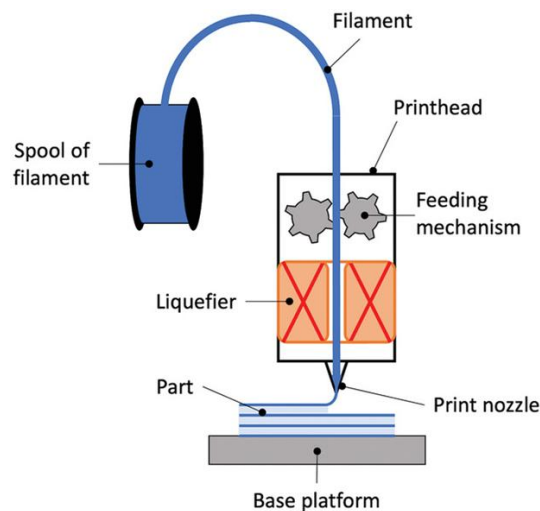


Figure 5: Simplified system schematic of a 3D Printer [30]

To ensure effective and efficient operation of the entire manufacturing process, the filament extrusion stage must guarantee a continuous and stable material flow. To this end, a stepper motor coupled to a drive gear assembly, typically consisting of two counter-rotating wheels

[12] is employed. This assembly is in direct contact with the filament, and careful regulation of the applied pressure is crucial in order to prevent filament grinding or slippage, which would otherwise result in inconsistent material flow [10]. Subsequently, the filament is fed into a tube with a suitable cross-section to allow its transport to the heating block and, ultimately, to the nozzle. Within the heating block, sometimes integrated directly into the nozzle, the material undergoes melting. The design of this component is therefore of paramount importance, as polymers generally exhibit low thermal conductivity, making it necessary to ensure sufficient heating to achieve the required melting state. One effective approach to accomplishing this is to increase the length of the heating block, thereby extending the residence time of the material during extrusion [10]. Inside this component, the material is heated and progressively softens with increasing temperature until it is able to flow under the force exerted by the colder and more rigid filament upstream, which effectively acts as a piston pushing the molten material through the nozzle [12]. The final element of the extrusion system is the nozzle, which is directly connected to the heating block and maintained at the same temperature. Within the nozzle, the cross-sectional area of the material is reduced. Filaments are typically manufactured with diameters ranging from 1.75 mm to 2.85 mm; consequently, the inlet diameter remains similar until a gradual reduction leads to the outlet diameter, which generally lies between 0.15 mm and 1 mm. This reduction in diameter has a direct impact on the surface finish and dimensional accuracy of the final component, as smaller nozzle diameters enable higher levels of precision [10].

Simultaneously with the extrusion process, the motion responsible for forming the desired structure takes place. The print head moves within the X-Y plane, parallel to the build platform onto which the material is deposited. This motion is controlled by a computer, which directs the print head along a predefined path in order to produce the desired geometry. Once the first layer has been deposited, either the print head or the build platform, depending on the printer configuration, moves upward or downward, respectively, to enable the deposition of the subsequent layer. In this manner, movement along the Z-axis occurs according to the predefined number of layers, resulting in the formation of the final geometry [12]. For clarity, this concept is illustrated in Figure 6.

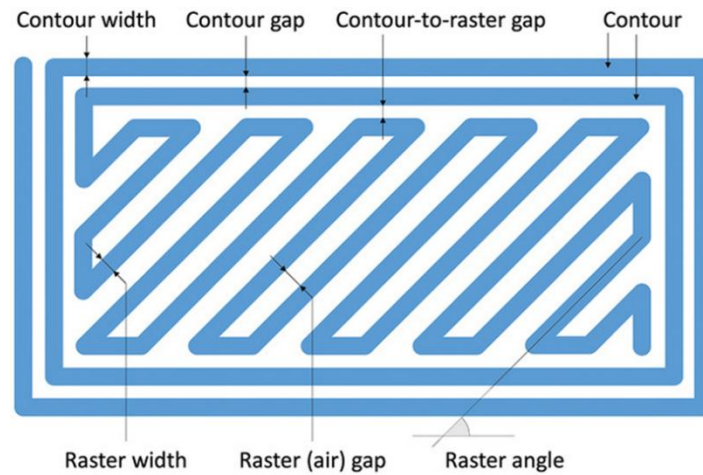


Figure 6: Geometry of a single 3D printed layer (commonly referred to as a *layer*) [30]

Particular attention must be paid to the temperatures involved in the manufacturing process. Specifically, the nozzle temperature, which enables the filament to transition from a rigid/glassy state to a soft/viscous one, must exceed the melting temperature in the case of semicrystalline polymers. For this reason, only a limited range of machines is suitable for each polymer type, as well as for specific build platform requirements [13]. Typically, polymers with melting and glass transition temperatures (T_m and T_g) at or below 250 °C are best suited for FFF printing. In contrast, high-temperature engineering polymers, such as Polytetrafluoroethylene (PTFE) or Poly-ether-ether-ketone (PEEK), can only be processed using advanced machines that require features like active liquid cooling of the print head, and such systems have only been developed relatively recently. In 2015, Indimatec GmbH, now known as Apium Additive Technologies GmbH, launched the first 3D printer capable of reaching 420 °C, enabling the processing of high-temperature polymers. The rheological properties of the melt are essential for predicting its behaviour within both the liquefier and the extrusion head. Shear-thinning behaviour is desirable because it reduces the torque required by the feeding system while still ensuring precise control during deposition. However, viscosity must be carefully balanced: if it is too low, the molten polymer may flow uncontrollably from the nozzle, compromising print accuracy; if too high, it can hinder proper extrusion. For these reasons, amorphous polymers are generally easier to process, as they are less sensitive to nozzle temperature variations [31]. Among these, acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and polycarbonate (PC) are the most widely used and easiest-to-print materials in FFF. The build platform itself plays a crucial role in ensuring proper adhesion of the printed part, thereby preventing detachment during printing, which would compromise both the integrity and successful fabrication of the component. Carefully controlled temperature ranges contribute to improved surface finish and enhanced mechanical properties, enabling the

application of printed components across a wide range of industrial sectors. Moreover, appropriate thermal management reduces the likelihood of shape defects and void formation, which could otherwise undermine the structural integrity of the final part [14].

Defects in Fused Filament Fabrication arise from the interplay between thermal contraction, material flow behaviour, and machine motion accuracy, and they can be broadly understood in terms of how they affect either the geometry of the printed part or the internal continuity of the material [31]. A major group consists of deformation-related defects, which are primarily driven by thermal gradients and residual stresses during cooling. In this category, shrinkage and warping occur when non-uniform cooling leads to volumetric contraction and uneven stress distribution, causing dimensional distortion and loss of flatness [32]. Delamination results when interlayer adhesion is insufficient to resist internal stresses, leading to separation along layer interfaces and a significant reduction in mechanical performance. Curling typically appears at edges or corners and is associated with localized overheating or imbalanced cooling, which causes upward deformation. Layer shifting differs in origin, as it is linked to mechanical or control-system errors in motion, producing misalignment between successive layers and compromising geometric accuracy. Cracks may develop either during printing or under service loads, often initiating at weak points such as pores or poorly bonded interfaces and propagating as stress increases [33]. Another important category involves material deposition defects, which stem from inconsistencies in extrusion and material feeding. Under-extrusion occurs when insufficient material is delivered, resulting in discontinuities such as weak bonding and internal void formation, while over-extrusion leads to excess deposition that distorts dimensions and degrades surface quality. Stringing arises when molten polymer continues to flow during non-printing movements, forming unwanted filaments between separate features. Blobs are localized accumulations of excess material, often related to poor retraction control or variability in filament diameter. Banding appears as repetitive surface irregularities along the build direction and is commonly associated with fluctuations in extrusion rate or mechanical instability in vertical motion [31]. Finally, internal structural defects such as voids and gaps play a critical role in determining mechanical integrity. Voids are small unfilled regions within the printed structure that weaken the material and act as initiation points for failure, while gaps represent larger discontinuities between deposited roads or layers caused by insufficient fusion. These internal defects are particularly detrimental because they are often not visible externally but significantly reduce strength, fatigue resistance, and overall reliability of printed parts [32]. An explicative picture is presented in Figure 7.

Overall, the severity and impact of these defects depend strongly on their size, location, and how they interact with each other, since small imperfections can evolve into larger failures under thermal cycling or mechanical loading.

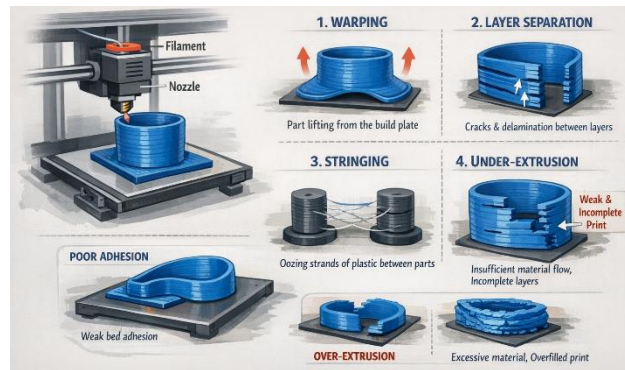


Figure 7: Defects in FFF technology

Raster infill angle (Figure 8) plays a key role in defining the anisotropic response of additively manufactured parts, influencing both their load-bearing capacity and fracture behaviour [35].

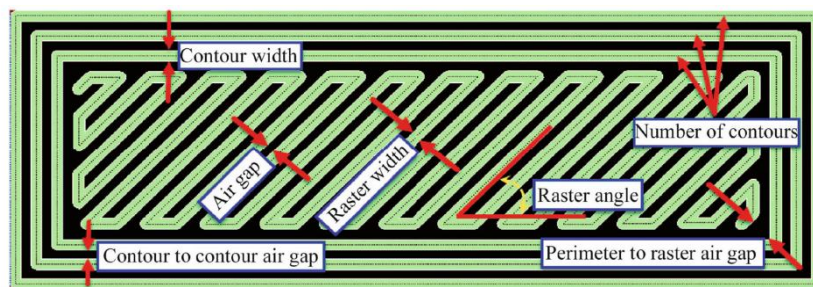


Figure 8: Tool path parameters for FFF printing [34]

Maximum strength is typically achieved with a fully dense (100%) infill where the deposited filaments are oriented parallel to the applied tensile load (0°). However, when loading is applied outside the printing plane (xy-plane), failure often occurs through interlayer delamination. This is mainly attributed to insufficient bonding between layers and the presence of voids at the interfaces. In addition, reducing the infill percentage leads to an evident drop in mechanical performance because the effective load-bearing cross-sectional area is reduced. Several investigations have also highlighted the influence of surface roughness on strength, as well as the weakening effect introduced by thermal contraction during cooling [35], [36], [37]. To improve the consistency and performance of FFF-produced components, extensive research has focused on process optimisation methods, including statistical design approaches [34], [38] and machine learning techniques [39], [40]. In parallel, in-situ monitoring systems have been developed to observe the process during printing and identify deviations from optimal conditions in real time [41], [42]. While optimisation methods are generally applied prior to

fabrication to determine suitable parameter sets, real-time monitoring enables adaptive control during printing, potentially reducing waste and improving efficiency.

Another perspective is to move away from treating additively manufactured parts as homogeneous, isotropic solids, and instead explicitly account for their process-induced anisotropy when modelling their mechanical or thermal response. Numerous studies have employed finite element models with homogenised material properties or lattice-based representations (see Figure 9a) to capture this behaviour [43]. Although such approaches can reproduce experimental trends with reasonable accuracy, their reliability depends strongly on input parameters such as interlayer adhesion strength, which are themselves highly sensitive to processing conditions. To address this limitation, more detailed multi-physics simulations of the deposition process (Figure 9b) have been proposed, focusing on melt flow, cooling and solidification, warpage, bonding mechanisms, and molecular or filler orientation [44]. Despite these advances, significant challenges remain in accurately modelling interfacial behaviour, multiphase materials such as composites, and phenomena that span multiple length scales.

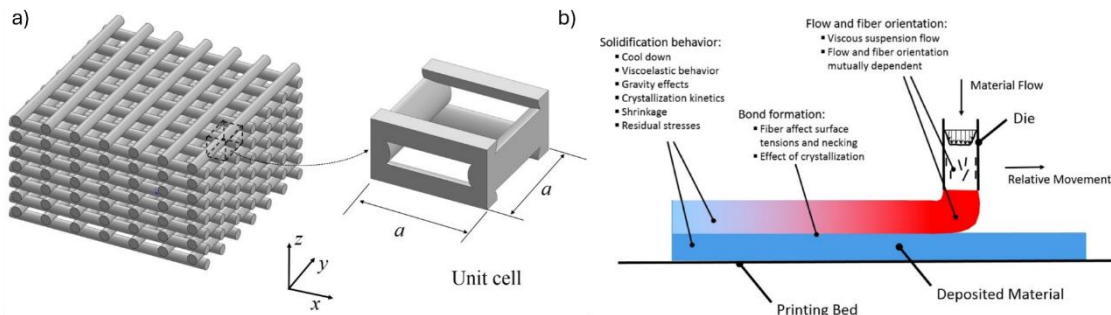


Figure 9 - (a) Example of an FFF raster lattice structure for mechanical simulation of a 3D printed component[43], (b) Schematization of the deposition process [44]

2.2. Innovative Materials

Materials science plays a crucial role in understanding advancements in additive manufacturing technologies. Researchers in this field are particularly interested in developing new materials suited for 3D printing applications [1]. Despite Fused Filament Fabrication (FFF) originally emerged and became widely adopted for conventional thermoplastics such as PLA, ABS, and PC, the range of polymers compatible with this process has significantly expanded over time. Current research increasingly focuses on enabling FFF for high-performance, composite, and emerging polymer systems by addressing two key material-related limitations: elevated processing temperatures and high melt viscosities. High-performance polymers, including

polyaryl-ether-ketones and polysulfones, are of particular interest due to their superior mechanical strength, thermal stability, and chemical resistance. However, these advantages are accompanied by very high glass transition and melting temperatures, as well as pronounced melt viscosities, which introduce substantial processing difficulties. These include stringent requirements for achieving and maintaining elevated thermal conditions, ensuring adequate thermal isolation, and mitigating defects such as warping, residual stresses, and cooling-induced distortion in printed parts [45]. Although the first reports of HPP processing via 3D printing appeared in the literature around 2013 [46], considerably later than those for commodity and engineering polymers, key challenges persist, particularly in improving process reliability and developing robust HPP-based composite systems. A further active area of investigation is the FFF processing of polymer composites aimed at either mechanical enhancement or multifunctional performance [47], [48]. Continuous-fibre-reinforced thermoplastic composites were first demonstrated by Matsuzaki et al. [47], employing the co-deposition of pre-impregnated continuous fibres and thermoplastic matrices through either a single nozzle or dual-printhead systems. Nylon-Kevlar Systems such as PLA-carbon fibre [49], Nylon-carbon fibre [50], and Nylon-Kevlar [51] have since been widely studied. In parallel, extensive research has been conducted on short-fibre and particulate-filled polymer systems, targeting improved mechanical properties as well as functional capabilities such as thermal and electrical conductivity, piezo resistivity, piezoelectric response, and magnetic behaviour [47], [48]. The incorporation of fillers, however, introduces additional processing complexities, including increased melt viscosity, interfacial adhesion issues between matrix and reinforcement, and stringent requirements on filament quality in terms of dimensional consistency and mechanical integrity [47]. Despite these challenges, the combination of multifunctional materials and the geometric freedom offered by additive manufacturing continues to drive significant interest in novel composite filament systems. Finally, an emerging direction in FFF material development involves the processing of new polymer classes beyond traditional thermoplastics. Elastomers, characterized by low stiffness, high elasticity, and large elongation at break, are attractive for applications such as vibration damping systems, soft robotics, and flexible or wearable devices. However, direct 3D printing of elastomeric materials is challenging due to the requirement for post-extrusion crosslinking (vulcanization) of polymer chains. As a result, thermoplastic elastomers (TPEs) are more commonly employed in FFF applications, although they still present processing difficulties related to high viscosity and low modulus, which can lead to filament buckling within the feed system [47]. In addition, shape memory polymers (SMPs) have attracted considerable attention

for use in smart structures, actuators, and biomedical devices, contributing to the development of so-called 4D printing, where printed parts are capable of time-dependent shape transformation [52], [53], [54]. Certain specialized materials that continue to draw significant industrial attention are shown in Figure 10.

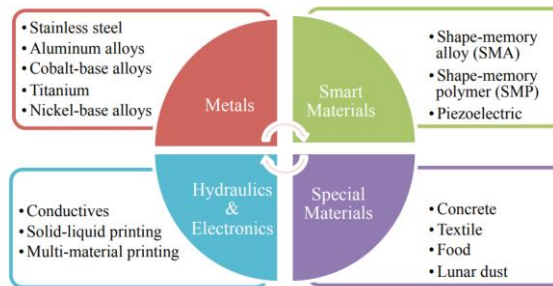


Figure 10: New materials for Additive Manufacturing [1]

2.3. 4D Printing

4D printing can be described as an extension of conventional 3D printing, representing its functional evolution. While it retains the fundamental principles of additive manufacturing, 4D printing introduces a critical advancement: the resulting structures are no longer geometrically and functionally static after fabrication. Instead, 4D-printed components are designed to exhibit time-dependent behaviour, whereby their properties, geometry, or functionality can be actively altered in response to external stimuli (e.g., temperature, humidity, light, pH, or magnetic/electric fields). This capability effectively renders the printed material “dynamic,” enabling controlled transformations in shape, dimensions, or mechanical response after the initial manufacturing stage [55], [56], [57], [58], [59].

Accordingly, 4D printing can be defined as an additive manufacturing (AM) process that integrates programmable or stimuli-responsive (“smart”) materials within a 3D-printed architecture. The overall concept can be summarized by the following expression:

$$\text{“4D printing = 3D printing + time”}$$

Among polymeric systems, shape memory polymers (SMPs) are the most widely investigated class for 4D printing applications. These materials are capable of being deformed into a temporary shape that is stable under specific conditions and subsequently recovering their original configuration upon exposure to an external stimulus, most commonly heat. The underlying mechanism relies on the presence of polymer networks that contain switching segments and fixed phases, allowing reversible transitions. Common SMP systems include

polyurethane-based formulations, polylactic acid blends, polycaprolactone, and epoxy-based networks. These materials are particularly attractive because they are compatible with widely used printing technologies such as fused deposition modelling and stereolithography.

Structures manufactured via this technology are therefore capable of undergoing programmed, time-dependent evolution in accordance with predefined design constraints [60]. Furthermore, the process is largely decoupled from the intrinsic limitations of the printing hardware, as functionality is primarily governed by material behaviour rather than printer configuration. By explicitly accounting for temporal shape transformation, 4D printing enables advanced behaviours such as self-assembly, self-healing, and multifunctionality within a single printed system [61], [62], [63], [64], [65].

As previously discussed, 4D printing facilitates the fabrication of adaptive structures whose geometry, properties, and functional responses can be dynamically tuned [66]. This is achieved through the spatially controlled integration of stimuli-responsive (“smart”) materials within a three-dimensional architecture [67]. The performance of such systems is critically dependent on mathematical modelling approaches that define the spatial distribution and interaction of heterogeneous material phases, ensuring predictable and controllable transformation under external stimuli [68]. The fundamental distinction between 3D and 4D printing is schematically represented in Figure 11 and Figure 12.

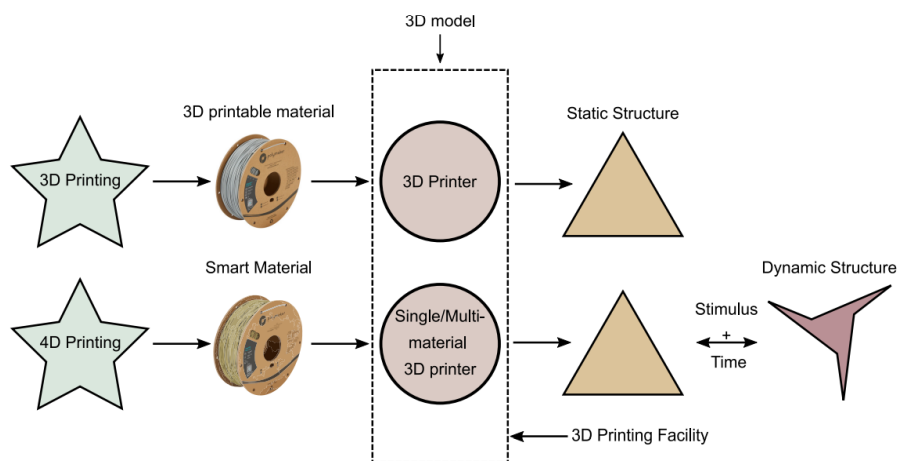


Figure 11: 3D Printing and 4D Printing: differences [69]

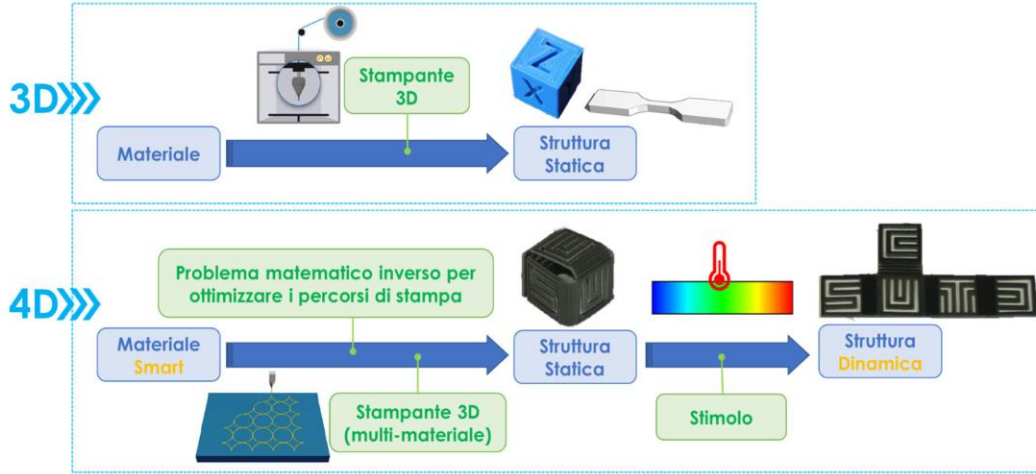


Figure 12: Static structure vs dynamic structure [70]

As illustrated, the 4D printing framework is characterized by the integration of several key components, including the 3D-printed scaffold, external stimulus, stimuli-responsive materials, interaction mechanisms, and an underlying mathematical modelling framework governing the system behaviour [69]. Applications are summarised in Figure 13.

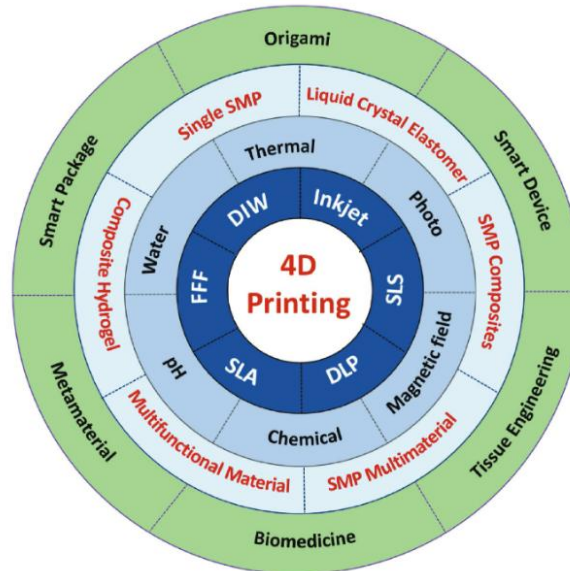


Figure 13: 4D Printing applications

Particular attention should be given to the following key components: stimuli-responsive materials constitute one of the most critical elements in 4D printing systems. These materials can be categorized into several subgroups, as illustrated in Figure 14 [71]. Their functional behaviour is defined by advanced properties such as self-sensing capability, decision-making functionality, environmental responsiveness, shape memory effects, self-adaptability, multifunctionality, and self-healing performance [67].

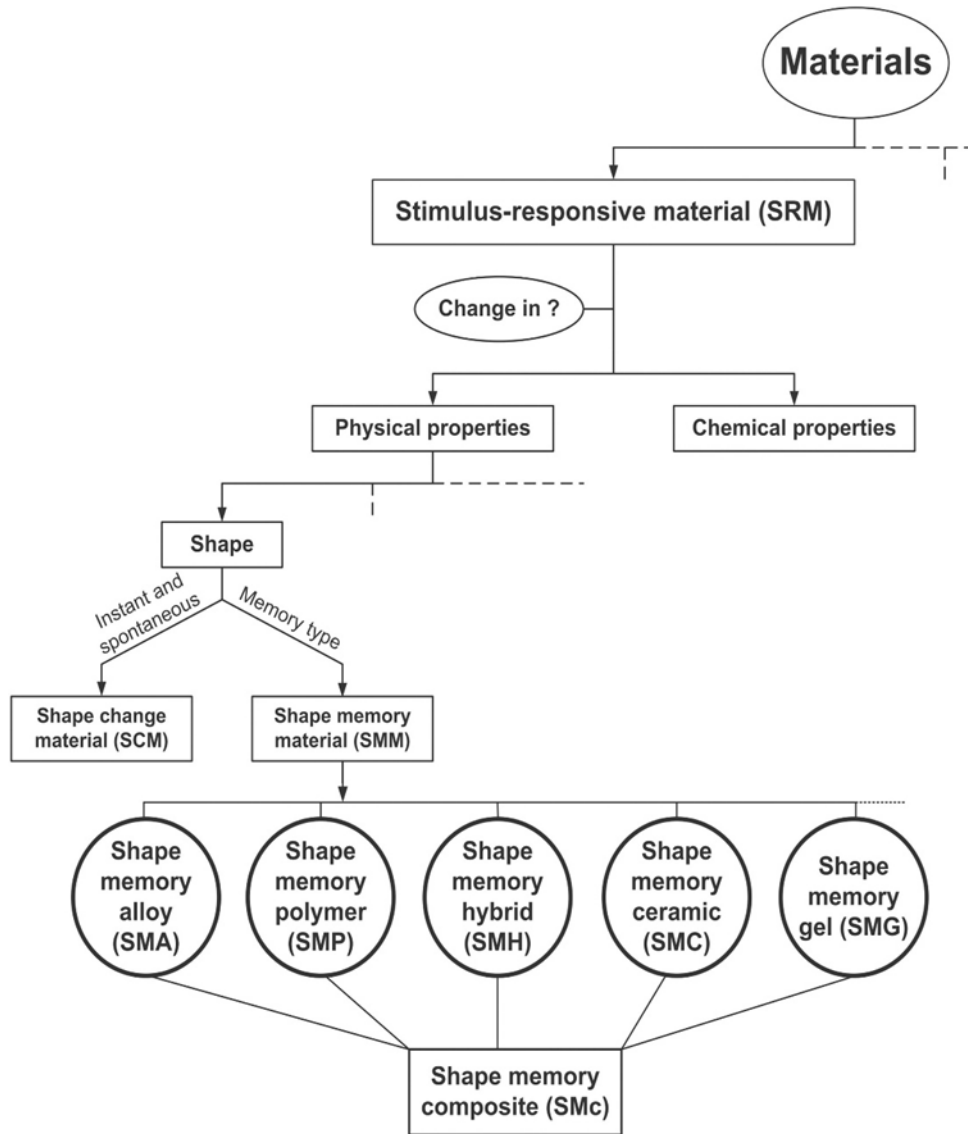


Figure 14: Stimulus-responsive materials [71]

The stimulus represents the driving mechanism responsible for inducing changes in the physical and functional properties of the structure. External stimuli, such as thermal, hydrothermal, or electromagnetic fields, interact with the material system by altering polymer chain conformations and modifying the internal molecular or atomic packing arrangement. This results in macroscopic shape-morphing behaviour. The selection of the appropriate stimulus is application-dependent and directly governs the choice of smart materials incorporated into the 4D-printed architecture, thereby determining the overall functional response of the system [72].

Hydrogels represent another major class of materials in 4D printing, especially relevant for biomedical applications [73]. These hydrophilic polymer networks can absorb significant amounts of water and undergo substantial volumetric changes in response to environmental stimuli such as moisture, temperature, pH, or ionic concentration [74], [75]. Typical hydrogel

systems include poly(N-isopropylacrylamide), alginate-based networks, polyethylene glycol derivatives, and chitosan composites [76], [77], [78]. Their most important advantage lies in their biocompatibility and ability to mimic the mechanical behaviour of soft biological tissues. This makes them highly suitable for applications such as tissue engineering scaffolds and drug delivery systems. Nevertheless, hydrogels generally suffer from low mechanical strength, limited structural stability in dry environments, and relatively slow response times due to diffusion-limited swelling processes.

Liquid crystal elastomers (LCEs) constitute a more recent and highly promising class of active polymers for 4D printing [79], [80]. These materials combine the elastic properties of rubbers with the anisotropic ordering of liquid crystalline phases. When subjected to stimuli such as heat or light, the molecular orientation within the material changes, resulting in significant and reversible macroscopic deformation. LCEs can produce large strains and complex programmable shape changes, making them particularly attractive for soft robotics and adaptive systems [81]. However, their practical application is still limited by the complexity of their synthesis, the requirement for precise molecular alignment, and challenges associated with printing and processing, which often require specialized techniques such as direct ink writing [82].

In addition to these primary classes, composite polymer systems have emerged as a key strategy to enhance performance and introduce multifunctionality [83], [84], [85]. By incorporating nanoparticles such as carbon nanotubes, graphene, magnetic particles, or photothermal agents into polymer matrices, researchers have developed materials capable of responding to multiple stimuli, including light, magnetic fields, and electrical inputs. These composites often exhibit improved mechanical strength, faster actuation, and remote controllability. However, achieving uniform dispersion of fillers and maintaining stable interfacial interactions remain significant technical challenges that can affect reproducibility and performance. High-performance engineering polymers such as polyether ether ketone, polyetherimide, and nylon-based systems are also being adapted for 4D printing, particularly in applications requiring high thermal stability and mechanical robustness [86], [87], [88], [89]. These materials are often modified through blending or chemical functionalization to introduce stimuli-responsive behaviour while maintaining their intrinsic structural advantages. Thermoplastic polyurethane is especially notable in this context due to its inherent elasticity and compatibility with shape memory effects [90]. The most widely utilized class of shape memory polymers (SMPs) is the one-way (unidirectional) SMP, typically activated through thermal excitation. In this context, thermal excitation refers to the process by which the material

is deformed into a temporary shape under specific thermal conditions and subsequently recovers its original (permanent) configuration upon reheating [91]. The term unidirectional denotes that the transition from the temporary shape back to the permanent shape occurs in a single, non-reversible manner; once recovered, the material cannot autonomously revert to the temporary configuration without the reapplication of an external programming process. In contrast, two-way shape memory polymers exhibit reversible shape transformations, enabling them to memorize both a high-temperature and a low-temperature configuration. These materials can repeatedly and autonomously switch between the two states in response to cyclic thermal stimuli, without requiring reprogramming after each cycle [92]. Figure 15 illustrates a general classification of SMPs based on the type of activating stimulus, as well as their corresponding industrial applications.

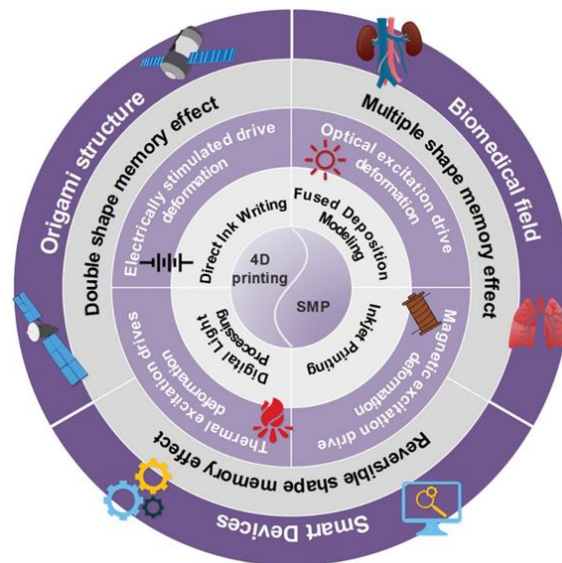


Figure 15: Shape memory polymers [91]

The programming process of shape memory polymers consists of two primary stages: (i) temporary shape fixity and (ii) permanent shape recovery. During the temporary shape programming phase, the polymer is initially heated above a critical transition temperature, or “switch temperature” (e.g., glass transition or melting temperature) [93]. This thermal activation increases molecular mobility by raising configurational entropy and reducing the effective energy barriers associated with chain rearrangement, thereby facilitating deformation. An external mechanical load is then applied to impose the desired temporary geometry. While maintaining the applied stress, the material is subsequently cooled below the transition temperature. This cooling step reduces molecular mobility and effectively “locks” the polymer chains into the deformed configuration, fixing the temporary shape. Once the material has sufficiently cooled, the external load is removed, and the temporary shape remains stable due

to the restricted mobility of the polymer network [94], [95]. Notably, the programmed temporary configuration can be retained over extended periods in the absence of external stimuli. Furthermore, the imposed temporary shape is not unique and can be tailored as a function of the magnitude and mode of the applied deformation during the programming stage. The overall process is schematically illustrated in Figure 16 and Figure 17.

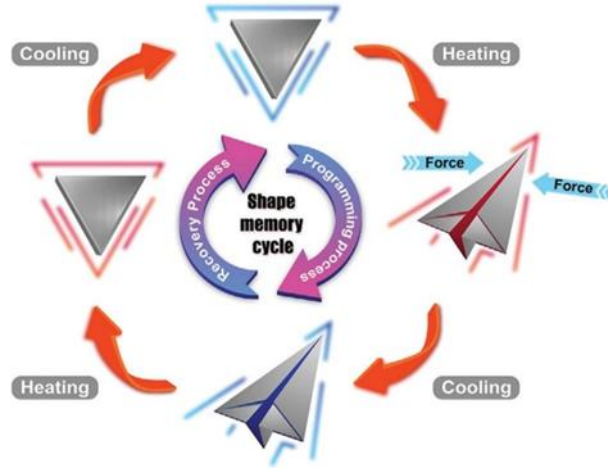


Figure 16: Programming of temporary and permanent shapes [91]

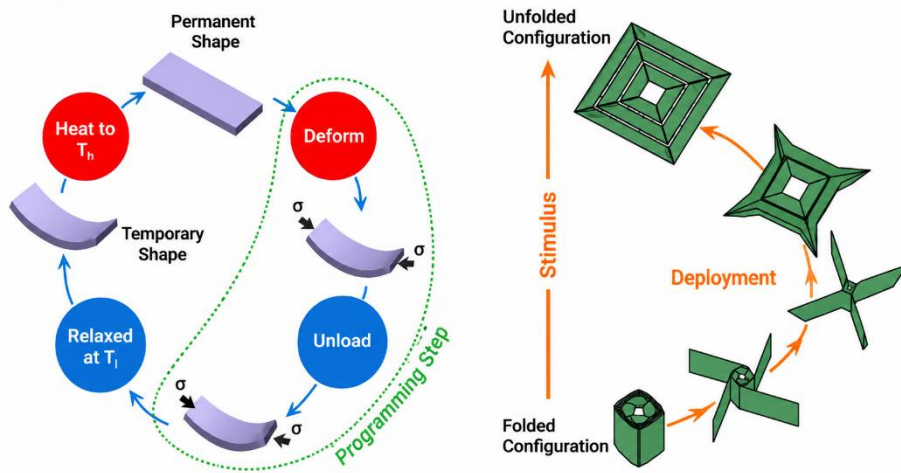


Figure 17: 4D Printing [70]

At the molecular level, the behaviour of polymer chains is strongly temperature-dependent, with significant variations in chain mobility across different thermal regimes. When the polymer is heated above its glass transition temperature (T_g), the molecular chains exhibit high mobility and increased segmental motion. Under the application of external mechanical forces, segments of the polymer chains tend to align along the direction of the applied stress, leading to a modification of the chain conformation and a corresponding reduction in conformational entropy. This process results in the formation of a temporary shape associated with a metastable

state characterized by stored elastic energy [94]. Conversely, when the temperature is reduced below T_g , the polymer chains undergo a transition into a glassy state, in which molecular mobility is significantly restricted. In this condition, the aligned chain configuration is effectively “frozen,” allowing the material to retain the imposed deformation even after the removal of the external load. This mechanism ensures the fixation of the temporary shape over time [96]. Upon reheating above T_g , molecular mobility is restored, enabling the previously oriented chain segments to relax and return to their equilibrium configuration, which corresponds to a state of maximum conformational entropy. This thermally driven relaxation process results in the recovery of the original permanent shape of the polymer. Importantly, this behaviour is repeatable: during successive programming cycles, shape memory polymers can be deformed into different temporary configurations, while consistently recovering the same predefined permanent shape [97], [98], [99]. Examples of 4D printing are reported in Figure 18.

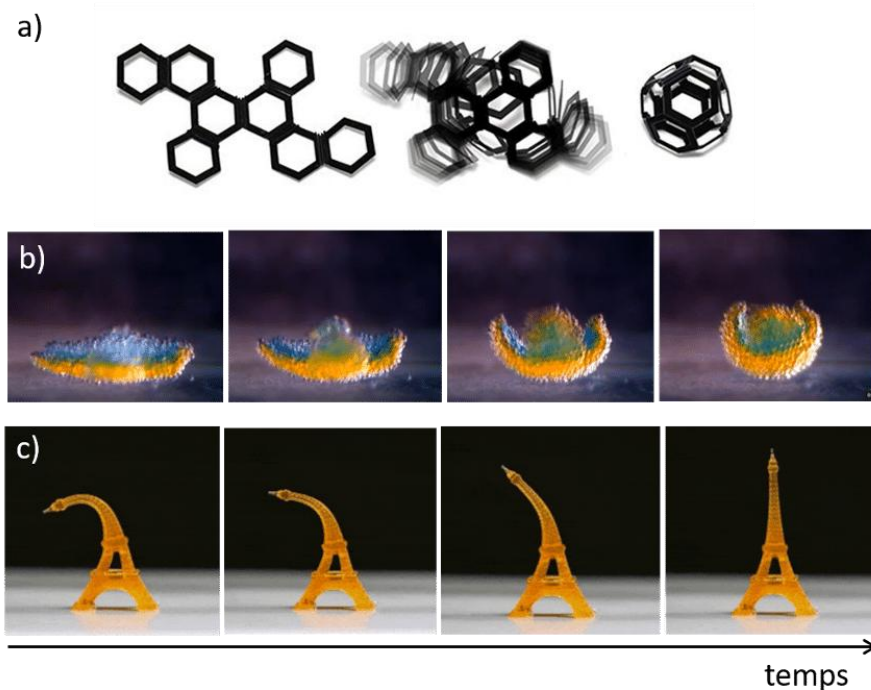


Figure 18: 4D Printing examples [100]

To further elucidate the underlying mechanisms governing shape memory behaviour, theoretical frameworks based on thermo-viscoelasticity and phase transition theory have been developed. These approaches provide complementary descriptions of the phenomenon, capturing both the microscopic molecular dynamics and the macroscopic thermomechanical response of the material system.

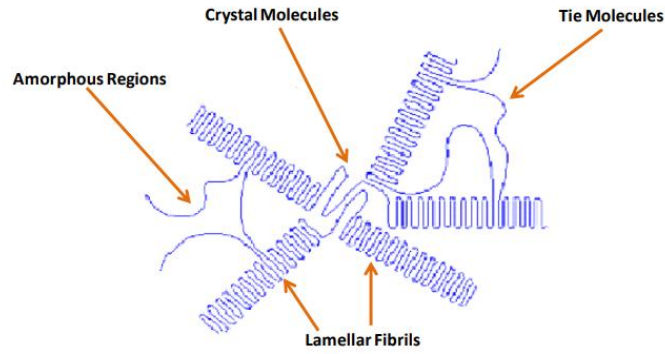


Figure 19: Spherulite [101]

Within the thermo-viscoelastic framework, researchers [55], [58], [102] represent SMP molecular chains as a network of thin, elongated springs that are intertwined, as illustrated in Figure 19 [101].

At ambient temperature, these springs are randomly oriented, corresponding to a state of high entropy in the material. As the temperature rises, molecular motion becomes more active, and the polymer transitions into a thermo-viscoelastic state. When an external load is applied in this state, the springs stretch and progressively align along the direction of the force, resulting in a decrease in entropy. If the load is maintained while the temperature is gradually reduced, the polymer exits the thermo-viscoelastic state and molecular mobility diminishes. Consequently, the springs cannot revert to their initial random arrangement, and the applied stress is retained within them as elastic potential energy [91].

Upon reheating, the springs, and therefore the polymer chains, regain their thermo-viscoelastic behaviour and release the stored elastic potential energy, leading to shape recovery. Polymers, especially thermoplastics, typically consist of both crystalline regions, which are spatially ordered, and amorphous regions, which lack structural order [103].

According to phase transition theory, an SMP is composed of a stationary phase and a reversible phase [104], [105]. The stationary phase determines and preserves the permanent shape, arising from either physical crosslinks, such as chain entanglements or segments, or chemical crosslinks, such as covalent bonds between macromolecular chains. The reversible phase, in contrast, can transition between rigid and softened states in response to temperature changes, enabling the formation and fixation of the polymer's temporary shape during the programming process [91].

Typically, the reversible phase is associated with the crystalline regions of the material, which can switch between crystalline and molten states under thermal activation, with the glass transition temperature serving as a key threshold [106]. In contrast, the stationary phase

corresponds to the amorphous regions of the polymer, which do not undergo chain rearrangement regardless of temperature. The thermo-viscoelastic and phase transition theories are complementary, and their integration allows for the development of a more accurate and comprehensive intrinsic structural model capable of capturing complex SMP deformations [107], [108]. Experimental studies have shown strong agreement between these theoretical predictions and observed behaviour.

2.3.1. Direct activation: Temperature

A representative thermo-mechanical loading-unloading cycle in a shape memory polymer system comprises a sequence of coupled thermal and mechanical processes that govern the programming and subsequent recovery of shape memory behaviour. Initially, the material is heated above its characteristic transition temperature (e.g., the glass transition temperature, T_g), at which point enhanced segmental mobility enables the polymer to transition into a rubbery or thermo-viscoelastic state. Under these conditions, the application of an external mechanical load induces macroscopic deformation, accompanied by the preferential orientation and alignment of polymer chains along the direction of the applied stress [109], [110]. Subsequently, while the applied load is maintained, the material is cooled below the transition temperature. This reduction in temperature suppresses segmental mobility and kinetically constrains the oriented polymer network, effectively fixing the deformed configuration. As a result, the temporary shape is established through the immobilization of the aligned polymer chains [111]. Once the material has been cooled to a temperature well below the transition point, the external load is removed. Owing to the highly constrained segmental dynamics in the glassy state, stress relaxation is significantly inhibited, and the polymer retains the imposed deformation [112], [113]. As a result, the temporary configuration remains mechanically stable in the absence of sustained external loading [114]. During the recovery stage, the material is reheated above the transition temperature, thereby reactivating segmental mobility within the polymer network [115]. This facilitates configurational relaxation toward the thermodynamically favoured equilibrium state, accompanied by the release of stored elastic strain energy, which drives the macroscopic recovery of the original permanent shape. This thermo-mechanical cycle can be carried out repeatedly, allowing SMPs to experience multiple programming and recovery cycles while preserving stable and reliable shape memory behaviour over time [116]. Figure 20 exhibits an example of this model.

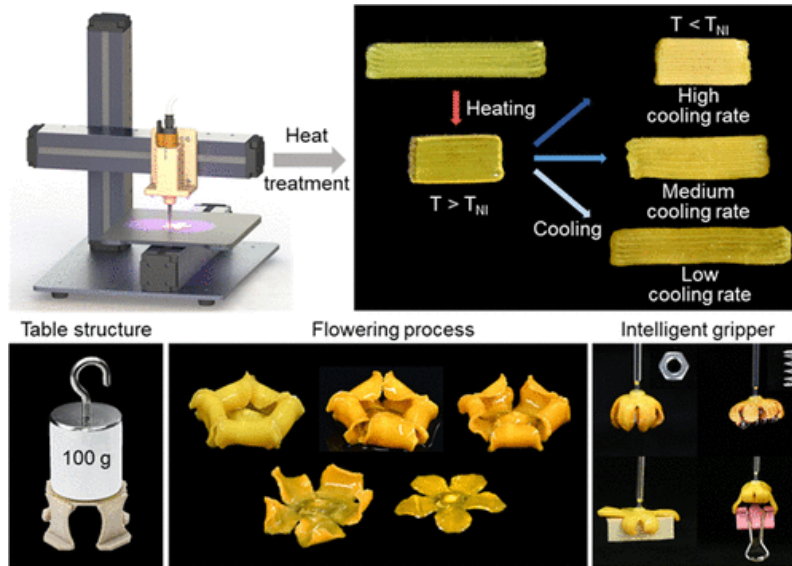


Figure 20: Example of 4D Printing [117]

Thermal responsiveness is a key factor in 4D printing applications because it is compatible with a broad range of materials, including shape memory materials and thermally responsive polymers [118]. Heat is a particularly useful stimulus since it is simple to produce, can be precisely delivered within printed structures, and can trigger controlled shape transformations within specific timeframes [119]. Beyond direct contact heating, thermal energy can also be produced indirectly through the conversion of other energy forms, such as electrical, magnetic, or optical energy [120], [121]. This process is generally based on raising the material temperature above the switching temperature (T_s), which is typically higher than the glass transition temperature (T_g), often by around $T_g + 20\text{ }^{\circ}\text{C}$. At this elevated temperature, the material can be deformed under an applied mechanical load, and the new shape is fixed by cooling it down, leading to a metastable configuration. When the material is reheated to the switching temperature, it returns to its original, pre-programmed shape [122].

The efficiency of thermal stimulation in 4D printing is governed by several important parameters. A primary factor is the material's thermal responsiveness, where the glass transition temperature plays a central role in defining how the material reacts to heat. Materials with sharp, well controlled transition temperatures are generally preferred, as they enable more accurate and repeatable shape transformations [123], [124]. A further important factor is the selected heating strategy. Methods such as direct heating, infrared irradiation, and convective hot-air heating vary in their thermal delivery characteristics, including heating kinetics, spatial temperature uniformity, and penetration depth within the material. Consequently, the specific heating technique employed can have a significant impact on both the rate and reliability of the induced shape transformation [125], [126]. Environmental conditions also contribute to

performance. Variations in ambient temperature and humidity may influence how heat is absorbed and distributed within the material, thereby affecting its thermal response and potentially modifying the overall shape morphing behaviour [127], [128].

Moreover, the heating time must be precisely regulated to ensure that the material attains its glass transition temperature and completes the intended shape transition. Alongside thermal regulation, mechanical boundary conditions are also crucial, as predefined architectures or externally applied loads can either facilitate or hinder deformation of the printed structure. Ultimately, the influence of these mechanical constraints on the transformation response is governed by the component's design and its target functional requirements [122]. Figure 21 illustrates the thermomechanical cycle involved in achieving a metastable shape in a shape memory polymer.

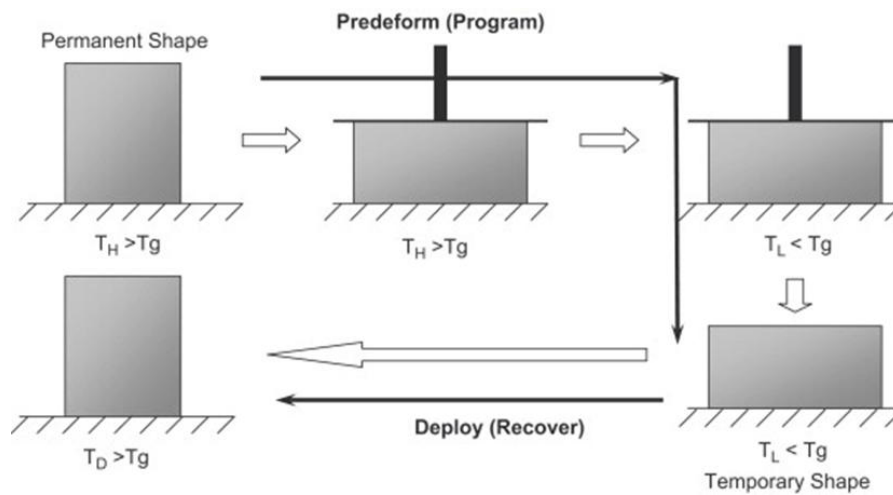


Figure 21: Thermal cycle loading-unloading [58]

For the design of a component based on thermally activated shape memory polymers (SMPs), a thermomechanical loading-unloading cycle is implemented. The SMP is initially subjected to isothermal deformation, transitioning from its original configuration to a prescribed deformed state under an applied mechanical load at an elevated temperature T_H [129]. Upon subsequent cooling to a lower temperature T_L under constraint removal, the material retains the imposed deformation in the absence of external stress. This stress-free configuration at T_L is defined as the temporary (or programmed) shape. The SMP is capable of preserving this metastable configuration over extended durations provided that the thermal conditions remain constant. Recovery of the original geometry is triggered by reheating the material to a recovery temperature T_D exceeding the glass transition temperature T_g , thereby activating the shape memory effect and enabling the restoration of the initial permanent shape [130].

2.3.2. Indirect Activation: Joule Effect

The Joule effect, more commonly referred to as resistive heating, represents the principle by which the energy associated with an electric current is converted, either partially or entirely, into heat [131]. Shape memory polymers exhibit the capability to revert to their predefined original geometry upon thermal activation above a critical transition threshold, typically corresponding to either the glass transition temperature (T_g) or the melting temperature (T_m) [132]. By applying an electrical voltage, these materials can be internally heated as a consequence of the Joule effect, thereby activating their thermally induced shape memory behaviour [133]. Consequently, dedicated heating elements can be integrated into the printing process of the materials to induce the thermal response in a controlled and practical manner, as shown in Figure 22.

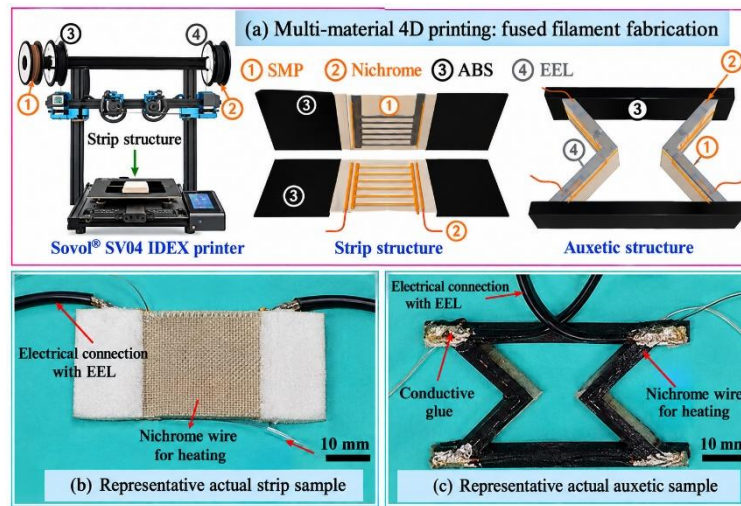


Figure 22: Example of 4D Printing [134]

These are generally favoured over configurations in which the material itself serves as the resistive heating medium, primarily for implementation simplicity and, more critically, to confine Joule heating to specific functional zones. Such a strategy minimizes non-essential energy dissipation and improves thermal efficiency, enabling the attainment of higher localized temperatures where required. Moreover, polymers are typically electrically insulating materials; therefore, the incorporation of conductive fillers alone, especially for high-performance polymers, is often insufficient to simultaneously ensure attainment of the switching temperature while preserving adequate processability and printability [135].

The physical-mathematical analysis underlying this principle explains the implementation of the process by justifying the phenomenon through the generation of power within the heater

itself. In a generic circuit element through which an electric current I [A] flows and across which a potential difference V [V] is applied, the generated power P [W] is given by:

$$P=V \cdot I$$

Under ideal conditions (i.e., neglecting any losses), this power is entirely converted into useful thermal energy [136], [137].

2.3.3. Indirect activation: Microwaves

The use of microwave radiation as an actuator in the field of 4D printing is still a relatively underexplored topic. Nevertheless, the literature reports early studies on the interaction between microwaves and shape memory polymers (SMPs) [138], [139], [140]. Compared to other electromagnetic waves, microwaves have a longer wavelength and therefore exhibit higher penetration depth in dielectric materials. Additionally, due to their low attenuation during propagation, microwaves can activate SMPs from relatively long distances without significant energy losses [141]. These characteristics enable the remote activation of 4D-printed objects in a “wireless” manner. The underlying concept is to exploit microwaves as an indirect stimulus to induce thermal heating and consequently trigger the shape change of the printed component. The actuation mechanism is primarily based on dielectric heating, where electromagnetic energy is converted into thermal energy through dielectric losses, including dipolar polarization and ionic conduction [142].

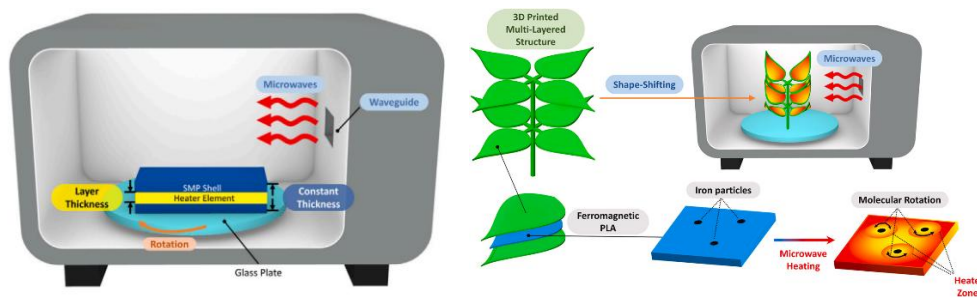


Figure 23: Example of 4D Printing with microwave activation [143]

However, neat SMPs often exhibit limited microwave absorption due to insufficient dielectric loss factors and the absence of strongly polar or conductive domains capable of efficiently coupling with the alternating electromagnetic field [142], [144]. As a result, direct microwave-induced heating of pure SMP systems is generally inefficient, as illustrated in Figure 23.

To overcome this limitation, microwave-absorbing fillers are incorporated into the polymer matrix to enhance electromagnetic-to-thermal energy conversion. In this context, shape

memory polymer composites reinforced with carbon nanotubes (CNTs) have been widely investigated [140]. Under microwave irradiation, CNTs form conductive networks that promote energy dissipation through Joule heating and localized electromagnetic losses, leading to a rapid temperature increase and triggering thermally induced shape recovery in SMP/CNT systems. Similarly, Y. Lim and Y. C. Jun demonstrated the effectiveness of graphite flakes as microwave susceptors [139]. Graphite fillers enhance microwave absorption through interfacial polarization (Maxwell-Wagner-Sillars effects) and conductive loss mechanisms [140].

Upon exposure to microwave fields, the graphite phase rapidly converts electromagnetic energy into heat, enabling fast thermal response of the composite. With appropriate filler loading (approximately 15 wt% in PLA), the material can reach temperatures above the glass transition temperature within tens of seconds, resulting in rapid activation of the shape memory effect. Overall, microwave-assisted actuation offers a promising strategy for non contact and remotely controlled 4D printing systems. However, performance is strongly dependent on filler dispersion, loading fraction, and percolation behaviour, which must be carefully optimized to balance microwave responsiveness with mechanical integrity and processability of the composite system.

2.4. High-Performance Polymers

High-performance polymers (HPPs) are a class of materials distinguished by outstanding mechanical characteristics such as high tensile strength, hardness, toughness, and dimensional stability [145]. A notable feature of these polymers is their ability to maintain such properties even under elevated temperatures (often exceeding 250-300 °C), and aggressive chemical conditions. From a molecular design perspective, these properties are primarily achieved through the incorporation of rigid, highly aromatic backbones and heterocyclic structures, which promote chain stiffness and strong intermolecular interactions. While these features are beneficial for thermal resistance and modulus, they generally result in limited solubility and poor melt processability [146]. Consequently, contemporary research has increasingly focused on mitigating these limitations by introducing structural modifications, such as flexible linkages, bulky substituents, or non-planar moieties, aimed at reducing intermolecular packing efficiency while preserving thermal stability [147], [148]. Among the most advanced material classes are polyimides, polybenzimidazoles, and polybenzoxazoles, which exhibit exceptional resistance to thermal degradation and aggressive chemical environments [149]. Recent progress has emphasized the rational design of polymer architectures to achieve a balanced

combination of properties, including enhanced toughness, reduced moisture uptake, and improved dielectric performance, thereby expanding their applicability in demanding sectors such as aerospace, electronics, and high-temperature composite systems [150].

In parallel, advancements in synthetic methodologies have enabled improved control over molecular weight distribution and structural regularity, contributing to enhanced reproducibility and performance [151]. Particular attention has been devoted to the development of processable high-temperature polymers, including systems amenable to melt processing or derived from soluble precursors, which address longstanding challenges associated with fabrication and scalability [152], [153]. More recently, the field has evolved toward the development of high-performance polymer-based nanocomposites, particularly in the context of advanced manufacturing technologies. The incorporation of nanoscale fillers such as carbon nanotubes, graphene-based materials, and layered silicates, has been shown to significantly enhance mechanical stiffness, thermal stability, and dimensional integrity, while also imparting multifunctional properties including electrical and thermal conductivity. This shift reflects a broader trend toward the design of materials that combine structural performance with functional capabilities [154]. Concurrently, significant advances have been made in adapting additive manufacturing techniques to high-performance polymers and their composites. Processes such as fused deposition modelling and stereolithography enable the fabrication of complex geometries with reduced material waste, offering clear advantages over conventional manufacturing routes. Nevertheless, the implementation of these materials in additive manufacturing remains challenging due to their high processing temperatures, limited flow characteristics, and the tendency to develop anisotropic properties arising from layer-by-layer deposition [154], [155]. From an application perspective, high-performance polymers and their nanocomposites are increasingly considered as potential substitutes for metallic materials in demanding sectors such as aerospace, automotive, and energy, owing to their favourable strength-to-weight ratios and resistance to corrosion. However, widespread adoption in critical load-bearing applications is still constrained by factors including processing costs, scalability, and the need for improved interfacial adhesion and structural homogeneity in manufactured components [156]. Figure 24 provides an overview of the principal high-performance polymers and their corresponding application domains. Overall, the current state of the art reflects a sustained effort to reconcile the intrinsic trade-offs between thermal stability, mechanical performance, environmental resistance, and processability through targeted molecular engineering and innovative processing strategies [157].

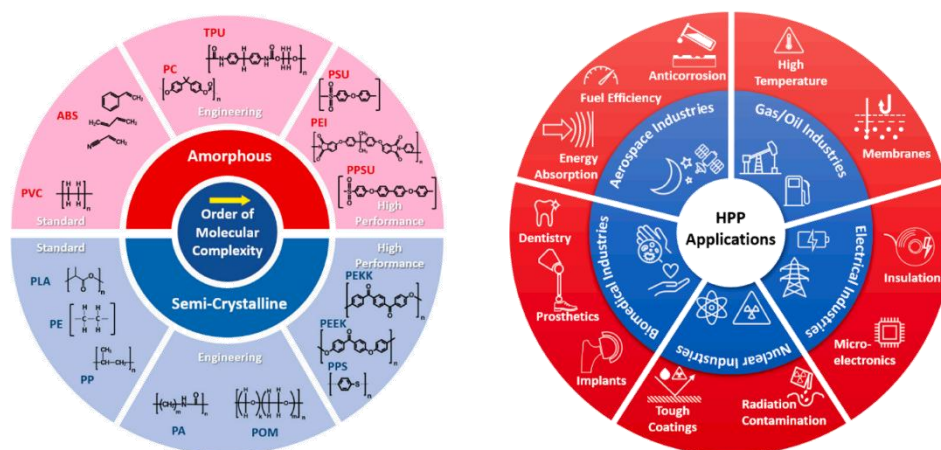


Figure 24: High-Performance Polymers and their applications [145]

2.4.1. Poly-Ether-Ether-Ketone (PEEK)

Polyether ether ketone (PEEK) is a member of the polyaryl ether ketone (PAEK) class, which comprises semicrystalline thermoplastic polymers distinguished by elevated thermal stability and superior mechanical performance [158]. Within this class, PEEK is specifically an aromatic, semicrystalline thermoplastic polymer widely employed as a matrix material in high-performance aerospace components and advanced structural composites [159].

From a chemical synthesis standpoint, PEEK is produced via step-growth polymerization involving difluorobenzophenone (DFBP) and hydroquinone (HQ), typically conducted at elevated temperatures in a high-boiling polar solvent such as diphenyl sulfone. This process yields a polymer backbone consisting of alternating ether and ketone functional groups. The presence of ketone linkages contributes to chain rigidity, while ether linkages impart segmental flexibility, resulting in a well-balanced combination of stiffness and toughness.

Due to this optimized structure-property relationship, PEEK exhibits high durability and mechanical integrity, enabling it to serve as a lightweight alternative to conventional metallic materials such as titanium and aluminium [160]. Its relatively low density, combined with favourable cost-performance characteristics, has facilitated its increasing utilization in aerospace applications, particularly for the production of customized geometries via additive manufacturing technologies [160], [161], [162]. In space-related applications, its use is governed by the ECSS-Q-ST-70-71 standard [162].

In addition, PEEK can be processed into filament form and reinforced with fillers such as carbon fibres, producing additively manufactured components with enhanced stiffness, chemical resistance, and structural density, while maintaining efficient processing times [163].

It should be emphasized that high-performance polymers within the PAEK family exhibit distinct intrinsic properties, largely dictated by their molecular architecture and chemical composition. Variations in polymer structure significantly affect powder and filament characteristics, which in turn influence processability, manufacturing response, and the performance of the final components. [164]. The inherent characteristics of PAEKs are mainly determined by their molecular arrangement and chemical composition [165]. Figure 25 shows the various polymer chain structures found within the PAEK family.

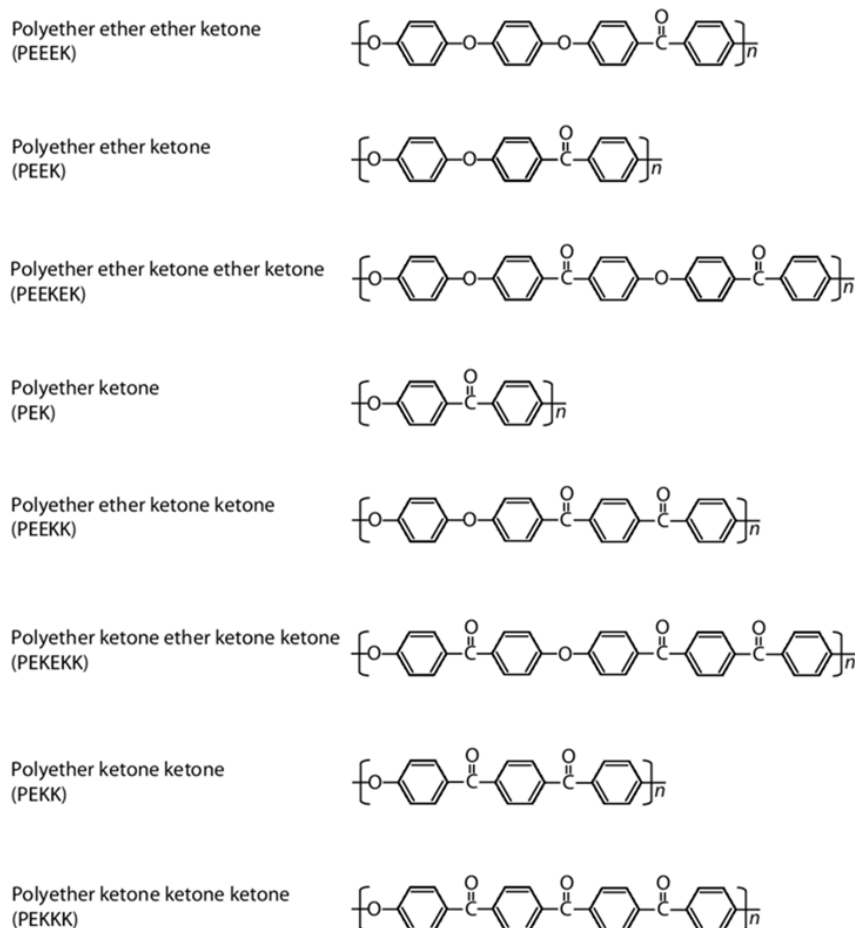


Figure 25: Types of PAEKs [31]

PEEK has high melting and glass transition temperatures ($T_m = 340\text{ }^{\circ}\text{C}$, $T_g = 143\text{ }^{\circ}\text{C}$), along with strong chemical resistance, and it can be processed in its molten state [166]. PEEK exists in an amorphous state in the melt but undergoes crystallization upon solidification, resulting in a semi-crystalline structure [167]. The nature and morphology of the crystalline structure are strongly governed by crystallization kinetics and processing conditions, including cooling rate, melt pressure, and flow history [168]. Even minor variations in molecular weight can markedly influence the rheological, thermal, mechanical, and thermomechanical properties of PEEK. A thorough understanding of how molecular weight affects its crystallization kinetics and rheological behaviour is therefore essential for accurately predicting processing performance

and for the design of components used in critical applications. Accordingly, a systematic investigation of these effects is key to optimizing both primary and secondary processing of PEEK, as well as to advancing the development of high-performance PEEK-based composites. Moreover, insights into the role of molecular weight in PEEK may also be extended to other high-performance polymers characterized by predominantly aromatic backbone structures [168]. As a first approximation, Figure 26 demonstrates that mechanical properties vary markedly as a function of molecular weight.

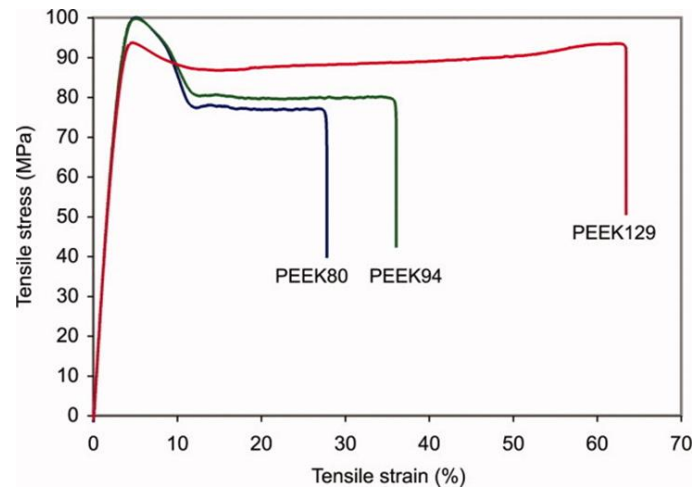


Figure 26: Variation of PEEK mechanical properties at different molecular weights [168]

A comparative analysis of the three PEEK grades can be conducted using tensile strength, yield strength, and tensile strength at break. With increasing molecular weight, the tensile yield strength decreases, while the tensile strength at break increases [168].

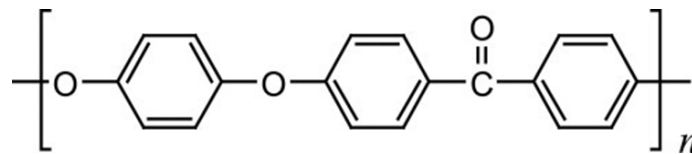


Figure 27: PEEK's molecular structure

The standard molecular structure of PEEK is depicted in Figure 27, in which the two ether groups and the ketone group are arranged sequentially from left to right.

PEEK also shows the characteristic sensitivity to temperature and strain rate under tensile and compressive loading that is typical of semicrystalline polymers. Under tensile loading, its Young's modulus has been reported to be approximately 4.1 GPa [167]. As a member of the PAEK family, PEEK exhibits key characteristics including high thermal stability and excellent chemical resistance [169].

The characteristics described above lead to a key conclusion: PEEK is suitable for demanding applications requiring specific performance attributes, such as high-temperature resistance, without significant degradation of its properties. Supporting this, its semicrystalline

morphology further enhances its physical properties, contributing to excellent chemical resistance and high chemical inertness [170].

Owing to these properties, along with its low outgassing characteristics, PEEK meets the European Space Agency (ESA) ECSS requirements, particularly ECSS-Q-ST-70-71, for use in space applications.

2.4.2. Polyetherimide

Polyetherimide (PEI) is a thermoplastic polymer belonging to the polyimide family [171], [172], [173]. It is a high-performance amorphous thermoplastic exhibiting superior mechanical properties, including high tensile strength and a high flexural modulus of elasticity, as well as excellent retention of mechanical integrity at elevated temperatures. Additionally, PEI demonstrates favourable dielectric properties that remain stable across a broad temperature and frequency spectrum, including microwave frequencies [174]. These properties, comparable to those of PEEK, render PEI suitable for a wide range of high-performance applications, including aerospace engineering and electronic systems [175].

PEI is composed of a regularly repeating backbone featuring ether and imide linkages, as shown in Figure 28. The ether functionalities impart segmental flexibility to the polymer chain, whereas the aromatic imide moieties contribute to the retention of high thermal stability and mechanical strength [176].

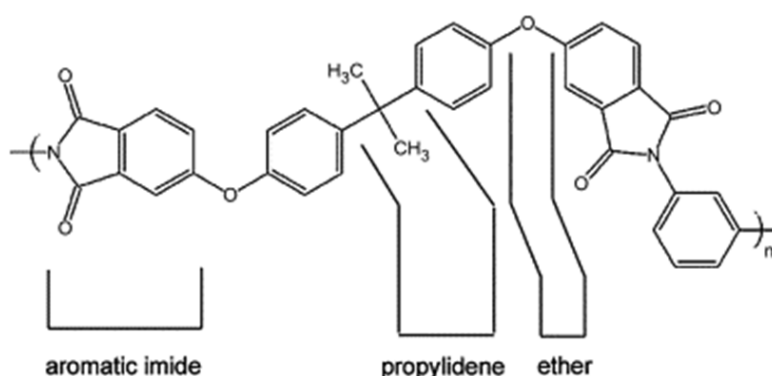


Figure 28: PEI molecular structure

This material exhibits a glass transition temperature (T_g) of approximately 218 °C [40], which enables its processing via conventional thermoplastic manufacturing methods, including injection moulding, extrusion, and blow moulding [177]. The favourable melt flow behaviour of polyetherimide facilitates its processing into geometrically complex, thin-walled components [178]. Furthermore, its performance profile includes high thermal resistance, chemical resistance to lubricants, coolants, and fuels, creep resistance combined with high mechanical strength, excellent dimensional stability under load, and good ductility [179].

From a thermal perspective, one of the key characteristics of PEI is its low coefficient of thermal expansion (CTE), which ensures superior dimensional stability under thermally induced stress conditions [180]. This property renders the material particularly suitable for use in environments that are typically challenging for many alternative materials. From a mechanical standpoint, PEI exhibits a Young's modulus on the order of approximately 3 GPa [181].

Despite its advantageous properties, it is important to note that, owing to its high glass transition temperature, PEI necessitates the use of specialized processing equipment capable of operating at elevated temperatures [182]. Moreover, controlled cooling of the final component is required to mitigate the risk of deformation and/or crack formation in the finished product [183].

PEI is utilized across a broad spectrum of industrial sectors, with particular prominence in aerospace applications. In this domain, it is used for the production of components requiring high resistance to elevated temperatures and open flame, as well as for systems demanding exceptional dimensional stability and resistance to deformation under severe service conditions where structural integrity is critical [184], [185], [186], [187].

Overall, while PEI offers a wide range of advantageous properties, it also presents certain limitations with non-negligible implications. Consequently, its use is generally restricted to applications in which its specific performance characteristics are essential, particularly in light of its relatively high material cost and the need for specialized high-temperature processing equipment, both of which contribute to increased overall manufacturing costs of finished components [182].

Chapter 3. 4D Printing of PEEK-PEI Blends

In this chapter, the development of high-performance PEEK-PEI blends for the Fused Filament Fabrication 4D printing is presented.

The experimental campaign has been conducted in the facilities of the Department of Enterprise Engineering of the University of Rome Tor Vergata.

3.1. Experimental

Commercial Polyether-ether-ketone powder, specifically PEEK 450PF, has been purchased from *Victrex PLC*. PEEK 450PF is a high molecular weight grade specifically developed for extrusion compounding and compression moulding applications and is characterised by a fine particle size distribution. According to the manufacturer's datasheet [188] the material exhibits a combination of high mechanical strength, stiffness, thermal stability, and chemical resistance. The main mechanical, thermal, and physical properties of PEEK 450PF are summarised in Table 1.

Commercial Polyetherimide powder, specifically ULTEM 1000P100 were purchased from *Sabir (Riyadh, Saudi Arabia)*. ULTEM™ 1000P100 is an unfilled PEI grade provided in powder form with an average particle size of approximately 100µm. The material is characterized by high thermal stability, good mechanical performance, dimensional stability, and inherent flame-retardant properties. The principal properties reported by the manufacturer are presented in Table 2 [189].

PEEK/PEI blends containing 20, 30, 40, and 50 wt% PEI were prepared (20.4, 30.5, 40.6, and 50.6 vol% PEI), as listed in Table 3. The polymer powders were compounded and subsequently extruded into continuous filaments suitable for fused filament fabrication (FFF). The resulting filament spools were used for the fabrication of the specimens investigated in this study.

Table 1: Mechanical, thermal and physical properties of Victrex PEEK 450PF [188]

	Conditions	Test	Units	PEEK 450PF
Mechanical Properties				
Tensile Strength	Yield, 23°C	ISO 527	MPa	98
Tensile Elongation	Break, 23°C	ISO 527	%	30
Tensile Modulus	23°C	ISO 527	GPa	4.0
Flexural Strength	23°C	ISO 178	MPa	100
Flexural Modulus	23°C	ISO 178	GPa	3.8
Izod Impact Strength	Notched, 23°C	ISO 180/A	kJ m ⁻²	70
	Unnotched, 23°C	ISO 180/U	kJ m ⁻²	n/b
Thermal Properties				
Melting Point		ISO 11357	°C	343
Glass Transition (T _g)	Onset	ISO 11357	°C	143
	Midpoint	ISO 11357	°C	150
Coefficient of Thermal Expansion	Average, below T _g	ISO 11359	ppm K ⁻¹	55
	Average, above T _g	ISO 11359	ppm K ⁻¹	140
Heat Deflection Temperature		ISO 75-f	°C	152
Physical Properties				
Melt viscosity	400°C	ISO 11443	Pa s	350
Density		ISO 1183	g cm ⁻³	1.30
Average particle size (D ₅₀)		ISO 13320-1	µm	50
Typical Processing Conditions				
Drying temperature – time				150°C/3h or 120°C/5h
Compounding temperatures			°C	380 – 400
Injection moulding temperatures			°C	355 – 375

Table 2: Mechanical, thermal and physical properties of ULTEM 1000P100 [189]

	Conditions	Test	Units	ULTEM 1000P100
Mechanical Properties				
Tensile Strength	Yield, 50 mm/min	ISO 527	MPa	110
Tensile Elongation	Break, 50 mm/min	ISO 527	%	50
Tensile Modulus	23°C, 1 mm/min	ISO 527	GPa	3.2
Flexural Strength	Yield, 2 mm/min	ISO 178	MPa	160
Flexural Modulus	23°C, 2 mm/min	ISO 178	GPa	3.3
Thermal Properties				
Glass Transition (T _g)		ISO 11357	°C	217
Coefficient of Thermal Expansion	Average, below T _g	ISO 11359	ppm K ⁻¹	52
Heat Deflection Temperature		ISO 75-f	°C	209
Thermal conductivity		ISO 8302	W m ⁻¹ K ⁻¹	0.22
Physical Properties				
Density		ISO 1183	g cm ⁻³	1.27

Table 3: PEEK-PEI blends denomination

	PEEK content	PEI content
	(wt%)	(wt%)
PEEK Neat	100	0
PEI Neat	0	100
50PEEK-50PEI	50	50
60PEEK-40PEI	60	40
70PEEK-30PEI	70	30
80PEEK-20PEI	80	20

PEEK/PEI blends were compounded using a custom-built bench-top extruder (*Comet S.r.l.*) equipped with a 20 mm diameter screw, a length-to-diameter (L/D) ratio of 15, and a 1.80 mm die nozzle. The extrusion process was performed at a screw speed of 20 rpm and a processing temperature of 360 °C.

Prior to compounding, PEEK and PEI powders were dried in a ventilated oven at 120 °C for 24 h to remove residual moisture. The dried powders were mechanically premixed according to the compositions reported in Table 3 and subsequently fed into the extruder. The extrudate was continuously collected and wound using a filament spooler (*Filabot, USA*) to produce filaments with a target diameter of 1.75 mm for fused filament fabrication (FFF).

3.1.1. Preliminary Characterisations

Fourier-transform infrared spectroscopy (FTIR; *Cary 630, Agilent, Santa Clara, USA*) was performed on PEEK and PEI powders. Spectra were recorded over the range of 4000-650 cm^{-1} with a resolution of 4 cm^{-1} , and each spectrum represented the average of 32 scans.

Thermogravimetric analysis (TGA; *Pyris 1 TGA Analyzer, PerkinElmer, Waltham, MA, USA*) was conducted to evaluate the thermal stability of carbonyl iron powders. Samples were heated from 25°C to 800°C at a rate of 10°C·min⁻¹ under both air flow (40 mL·min⁻¹) and nitrogen flow (80 mL·min⁻¹). The same analysis was also performed on PEEK and PEI powders, heating from 25°C to 800°C at 10°C·min⁻¹ under a nitrogen flow of 80 mL·min⁻¹.

3.1.2. Compounding and Filaments Characterisations

Blends of the neat materials were premixed using a planetary mixer (*Thinky ARE-250*) to produce batches of approximately 100 g of all the four compositions. The compounds were then extruded using a single-screw extruder (*Comet S.r.l, Italy*, diameter 20 mm, length-to-

diameter ratio of 15) equipped with a 1.8 mm nozzle. Extrusion was carried out at 340°C with a screw speed of 20 rpm, yielding filaments with a diameter of 1.75 ± 0.05 mm. The resulting filaments were pelletized (*Shredder & Granulator 3Devo GP20 Hybrid, Utrecht, Netherlands*) with a 3.5 mm filter screen, in preparation for melt flow index (MFI) testing. MFI measurements were performed on both extruded filaments and neat powders in accordance with ASTM D1238-13 (*MP 1200M Melt Flow Indexer, Tinius Olsens*). The test temperature was set to 400°C, and a constant load of 2.16 kg was applied.

Fourier-Transform Infrared (FTIR) spectroscopy (*Cary 630, Agilent, Santa Clara, USA*) was conducted on the filaments. Spectra were recorded over the range of 4000-600 cm^{-1} with a resolution of 4 cm^{-1} , and each spectrum represents the average of 32 scans.

Thermogravimetric analysis (TGA, *Pyris 1 TGA Analyzer, Perkin-Elmer, Waltham, Massachusetts, USA*) was performed on filaments from the different blends to assess their thermal stability specifically on 7.9 mg of 50PEEK-50PEI, 9.6 mg of 60PEEK-40PEI, 6.91 mg of 70PEEK-30PEI, 5.9 mg of 80PEEK-20PEI. Samples were heated from 25°C to 800°C at a rate of 10°C/min under air flow (40 mL/min) and under nitrogen (120 mL/min).

Differential Scanning Calorimetry (DSC, *DSC 214 Polyma, Netzsch, Selb, Germany*) was carried out under a nitrogen atmosphere on approximately 6.6 mg of 50PEEK-50PEI, 5.7 mg of 60PEEK-40PEI, 4.1 mg of 70PEEK-30PEI, 4.5 mg of 80PEEK-20PEI. Each sample underwent a first heating from 25°C to 400°C, followed by cooling to 25°C at a rate of 10 K/min, and then a second heating up to 400°C at the same rate. The degree of crystallinity χ has been computed using Eq. (1), where ΔH_m is the measured enthalpy of fusion (area under the melting peak), ΔH_f is the enthalpy of fusion of 100% crystalline PEEK (130 J/g [190]), and w is the filler mass fraction.

$$\chi = \frac{\Delta H_m}{\Delta H_f(1 - w)} \quad (1)$$

Dynamic Mechanical Analysis (DMA, *Tritec 2000 DMA, Triton Technology, UK*) was performed on the filaments in tensile mode. The temperature was scanned from 25°C to 250°C at a heating rate of 2°C/min, with an applied displacement of 0.05 mm at 1 Hz frequency. Storage modulus (E') and loss factor ($\tan\delta$, corresponding to the ratio between Loss Modulus E'' and Storage Modulus E') have been measured and reported. The glass transition

temperature (T_g) was identified as the temperature corresponding to the maximum loss factor ($\tan\delta$).

3.1.3. 3D Printing

The produced filaments were used to fabricate 3D-printed specimens via fused filament fabrication (FFF) using an Apium P155 system (*Apium Additive Technologies GmbH, Karlsruhe, Germany*). Rectangular bars (80×10×2 mm) and Type IV tensile specimens (ASTM D638 [191]) were manufactured.

All geometries were designed in SolidWorks (*Dassault Systèmes, Vélizy-Villacoublay, France*) and sliced using Simplify3D (*Simplify3D, Cincinnati, USA*) to generate the G-code, adopting the printing parameters described in Table 4. Printing was performed using a nozzle diameter of 0.8 mm, with nozzle temperatures set from 390 to 410°C, and a build platform temperature of 140°C. A raster angle of +45°/−45°, 100% infill, and a printing speed of 1600 mm/min were applied. The specimens have been printed onto the heated glass printing bed using a polyvinylpyrrolidone-based fixative specific for 3D printing (*Dimafix, Dima 3D*) to increase bed adhesion. A brim has been added to the first and second layers to increase the footprint area, thus adhesion, and to prime the material flow through the nozzle.

Table 4: 3D Printing parameters for PEEK-PEI blends filaments

Parameter	
Nozzle diameter	0.8 mm
Nozzle temperature	390 to 410°C
Bed temperature	140°C
Layer thickness	0.20 mm
Extrusion width	0.96 mm
Extrusion multiplier	93%
Reference printing speed	800 mm/min
Outline	3 perimeters
Outline printing speed	50% reference speed
Infill	100%
Infill angle	+45°, -45°
Infill speed	80% reference speed
Brim	8 outlines (stop at 3 rd layer)

First-layer adhesion is critical when processing PEEK because its high solidification rate and thermal contraction can cause parts to detach from the print bed, particularly at sharp corners, leading to upward bending and deformation.

3.1.4. 3D-Printed Parts Characterisations

Fourier-transform Infrared Spectroscopy (FTIR) has been performed on 3D printed samples using a Cary 630 (*Agilent Technologies*) ZnSe spectrometer, equipped with ATR accessory and diamond prism. The spectra were acquired in the range 4000-650 cm^{-1} , with 4 cm^{-1} resolution averaging 32 scans for each spectrum.

Thermogravimetric analysis (TGA, *Pyris 1 TGA Analyzer, Perkin-Elmer, Waltham, Massachusetts, USA*) was performed on filaments from the different blends to assess their thermal stability specifically on 5.1 mg of 50PEEK-50PEI, 5.7 mg of 60PEEK-40PEI, 2.8 mg of 70PEEK-30PEI, 6.4 mg of 80PEEK-20PEI. Samples were heated from 25°C to 800°C at a rate of 10°C/min under air flow (40 mL/min) and under nitrogen (120 mL/min).

Differential Scanning Calorimetry (DSC, *DSC 214 Polyma, Netzsch, Selb, Germany*) was carried out under a nitrogen atmosphere on approximately 3.7 mg of 50PEEK-50PEI, 3.6 mg of 60PEEK-40PEI, 3.8 mg of 70PEEK-30PEI, 4.2 mg of 80PEEK-20PEI. Each sample underwent a first heating from 25°C to 400°C, followed by cooling to 25°C at a rate of 10 K/min, and then a second heating up to 400°C at the same rate.

Dynamic Mechanical Analysis (DMA, *Tritec 2000 DMA, Triton Technology, UK*) was performed on the filaments in bending mode. The temperature was scanned from 25°C to 250°C at a heating rate of 2°C/min, with an applied displacement of 0.05 mm at 1 Hz frequency. Tensile tests were conducted on five 3D-printed samples for each blend formulation using an *Instron 5869 universal testing machine (Norwood, USA)* equipped with a 50 kN load cell and a contact extensometer. Tests were performed at a crosshead speed of 5 mm/min in accordance with ASTM D-638.

Five 3D printed samples (80x10x4 mm) per formulation were mechanically tested via three-point bending tests using an Instron 5569 universal machine (*Instron, Norwood, MA, USA*), equipped with a 50 kN load cell and a crosshead speed of 2 mm/min, with a length span of 64 mm, according to ISO178.

3.1.5. Shape Memory evaluation

Shape-memory behaviour was assessed via fold-deploy tests for both blend and composite. Samples of rectangular shape were heated at 200°C, and forced to assume a U configuration.

Specimens were then cooled at room temperature (25°C). The blend samples were then reheated inside the furnace, and significant values such as time to recovery were measured. Shape fixity ratio, defined as the ability of the material to hold its temporary shape after deformation and cooling, and the Shape recovery ratio, defined as the ability of the material to recover its permanent shape after the stimulus application, were calculated using Equation 1 and Equation 2.

$$R_f = \frac{\theta_u - \theta_f}{\theta_u} \times 100 \quad (1)$$

$$R_r = \frac{\theta_u - \theta_r(T_s)}{\theta_u - \theta_0} \times 100 \quad (2)$$

Where θ_0 is the initial angle ($\theta_0 = 0^\circ$), θ_u is defined as the maximum deformation angle ($\theta_u = 180^\circ$), θ_f is the fixed angle and θ_r is the residual angle.

3.2. Results and Discussion

3.2.1. Preliminary Characterisations

FT-IR spectroscopy was performed to characterise the chemical structure of pure PEEK (Figure 29a) and pure PEI (Figure 29b). The FT-IR spectrum of PEEK exhibited the characteristic absorption bands typically reported for aromatic poly-ether-ether-ketone. Peaks located at 1590, 1489, and 1411 cm^{-1} were assigned to aromatic ring vibrations [192]. The absorption band at 1306 cm^{-1} was associated with ketone-related vibrations, while bands at 1218, 1156, and 1010 cm^{-1} were attributed to aromatic ether linkages and in-plane aromatic C-H deformation modes. Additional bands observed at 926, 833, and 765 cm^{-1} were assigned to out-of-plane aromatic C-H bending vibrations. A weak absorption band was also detected at approximately 3043 cm^{-1} , which may be attributed to aromatic C-H stretching vibrations, while the band at 1648 cm^{-1} is consistent with vibrations associated with the ketone-containing aromatic structure [193].

The FT-IR spectrum of PEI showed the characteristic absorption bands of polyetherimide. Absorption bands at approximately 3060 cm^{-1} and in the region around 2970 cm^{-1} were assigned to aromatic and aliphatic C-H stretching vibrations, respectively [194], [195]. The characteristic imide carbonyl stretching vibrations were observed at 1777 and 1720 cm^{-1} , confirming the presence of the imide functional group. A band at approximately 1600 cm^{-1} was attributed to aromatic ring vibrations. The peaks located at 1345 and 735 cm^{-1} corresponded to C-N stretching and deformation vibrations of the imide group, respectively. Furthermore, the bands at 1233 and 1070 cm^{-1} were assigned to the aryl-ether-aryl linkage characteristic of PEI

[196], [197], while the absorption band at 834 cm^{-1} was associated with aromatic ring vibrations [198], [199].

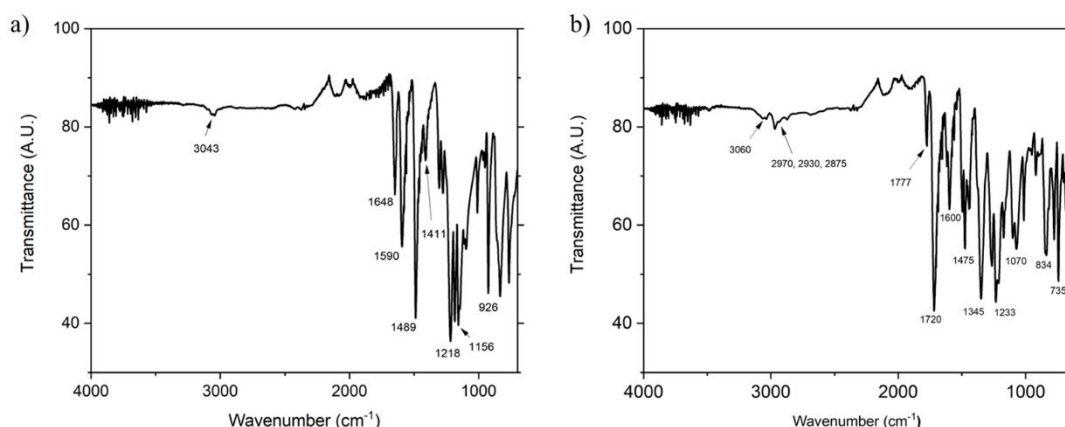


Figure 29: FTIR spectra of a) neat PEEK, b) neat PEI

The thermogravimetric analysis (TGA) curves for pure PEEK and PEI are shown in Figure 30a and Figure 30b, respectively. Both polymers exhibited a two-step degradation behaviour under the adopted testing conditions.

PEEK showed an initial degradation stage at approximately $586\text{ }^{\circ}\text{C}$, which is generally associated with the thermal scission of ether and ketone linkages within the polymer backbone [200]. This process leads to the evolution of volatile degradation products and the formation of a thermally stable carbonaceous residue. A second degradation stage was observed above $600\text{ }^{\circ}\text{C}$ and is attributed to the progressive decomposition and oxidation of the char formed during the primary degradation process. At $800\text{ }^{\circ}\text{C}$, PEEK retained a residual mass of approximately 47%, indicating its high char-forming capability.

Similarly, PEI exhibited a two-step degradation profile, with the onset of the primary degradation stage occurring at approximately $608\text{ }^{\circ}\text{C}$. This stage is commonly associated with chain scission reactions involving imide, ether, and isopropylidene-containing structural units, resulting in the release of volatile decomposition products [203]. The second degradation stage corresponded to the further degradation and oxidation of the remaining carbonaceous residue, leading to a progressive reduction in mass at higher temperatures [204].

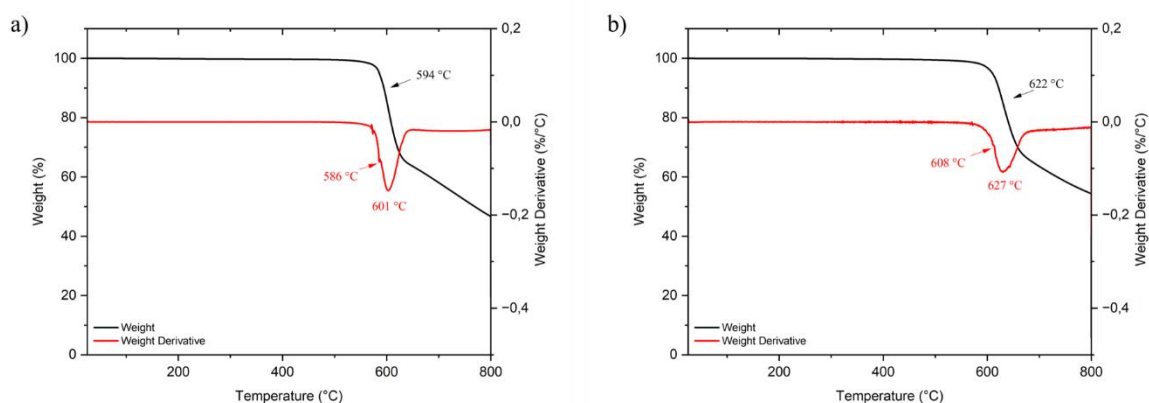


Figure 30: TGA of a) neat PEEK, b) neat PEI

3.2.2. Filaments Characterisations

The Melt Flow Index (MFI) of the neat polymers and PEEK/PEI blends was measured prior to filament production in order to evaluate their processability for extrusion and fused filament fabrication. MFI values were determined as the mass of material extruded over 10 min (g/10 min). To improve the reliability of the measurements, four tests were performed for each formulation, and the average values were calculated.

The corresponding results are presented in Table 5 and are in agreement with values reported in the literature by Shekar et al. [205] and Tolochko et al. [206] and others [207], [208].

Neat PEEK exhibited an MFI of 2.84 g/10 min, reflecting its relatively high melt viscosity and limited chain mobility.

In contrast, neat PEI showed a substantially higher MFI (14.82 g/10 min), indicating greater melt flowability under the selected testing conditions.

The incorporation of PEI into the PEEK matrix resulted in only a moderate increase in MFI. Even at the highest PEI content investigated (50 wt%), the MFI reached approximately 3.55 g/10 min, while intermediate compositions exhibited values within a narrow range of 3.4-3.5 g/10 min. The limited variation in MFI with increasing PEI content suggests that the melt-flow behaviour of the blends remains strongly influenced by the PEEK phase. This behaviour may be associated with the inherently higher viscosity of PEEK and with the morphology developed within the blend system [209], [210].

From a processing perspective, the relatively low MFI values observed for all blend compositions indicate melt viscosities comparable to that of neat PEEK, which may contribute to improved dimensional stability during filament extrusion and subsequent FFF processing.

Overall, the results indicate that the addition of PEI produces only a limited enhancement in melt flowability, and the rheological behaviour of the blends remains closer to that of neat PEEK than to that of neat PEI.

Table 5: Melt Flow Index of neat materials and blends

Material	MFI
PEEK 450 Victrex	2.84 g/10min
PEI ULTEM 1000P100	14.82 g/10min
50PEEK-50PEI	3.55 g/10min
60PEEK-40PEI	3.52 g/10min
70PEEK-30PEI	3.51 g/10min
80PEEK-20PEI	3.43 g/10min

The MFI measurements confirmed that all formulations possess flow properties compatible with material extrusion processes. The observed values suggest sufficient melt flowability for filament production while preserving the dimensional stability necessary for successful fused filament fabrication [211]. Therefore, all investigated compositions can be regarded as suitable candidates for additive manufacturing via fused filament fabrication. Nevertheless, adjustments to processing parameters, including extrusion temperature, feed rate, and printing conditions, may be necessary to accommodate variations in blend composition and ensure optimal processing performance [211], [212].

FT-IR spectroscopy was subsequently conducted on the extruded filaments to evaluate the effect of compounding and extrusion on the chemical structure of the blends. As shown in Figure 31, Figure 32, Figure 33 and Figure 34, the spectra of all formulations exhibited the characteristic absorption bands associated with both PEEK and PEI. No additional absorption peaks or significant spectral changes were observed after processing, indicating the absence of detectable chemical reactions between the constituent polymers. These results suggest that the blending process did not induce significant chemical modifications and that the materials retained their predominantly physical blend character [213].

All spectra exhibited weak absorption bands in the 3049-3066 cm^{-1} region, which were attributed to aromatic C-H stretching vibrations. Additional bands were observed at approximately 2926 and 2851-2853 cm^{-1} , corresponding to aliphatic C-H stretching modes of methylene groups (CH_2) within the polymer backbones [214]. The characteristic carbonyl absorptions of both constituent polymers were also clearly identified. The absorption band

located at approximately 1650-1653 cm^{-1} was assigned to the ketone carbonyl group of PEEK, while the band observed at 1715-1717 cm^{-1} corresponded to the imide carbonyl groups of PEI [214]. As expected, the intensity of the imide-related absorption band increased progressively with increasing PEI content in the blends. This trend is consistent with the higher concentration of PEI present in the formulations and further confirms the successful incorporation of the polymer within the PEEK matrix. The preservation of the characteristic absorption bands of both polymers across all compositions indicates that the fundamental chemical structures of PEEK and PEI were retained during compounding and extrusion.

Additional characteristic absorptions were observed at approximately 1590-1595 cm^{-1} and 1475-1490 cm^{-1} , corresponding to aromatic skeletal vibrations [215]. The absorption band at 1216-1220 cm^{-1} was assigned to the ether linkage of PEEK [216], while bands in the region of 1150 cm^{-1} were associated with PEI [217]. Absorptions between 830 and 838 cm^{-1} were attributed to out-of-plane aromatic C-H bending vibrations [218].

No significant shifts in peak position were observed among the different blend compositions. The spectral differences were mainly limited to variations in the relative intensities of characteristic absorption bands, reflecting the changes in blend composition. The absence of new absorption bands indicates that the chemical structures of both polymers were retained during compounding and extrusion. Furthermore, no evidence of chemical reactions between PEEK and PEI was detected within the sensitivity of the FT-IR technique. Any intermolecular interactions present in the blends were not sufficiently strong to produce measurable changes in the spectra [215], [219]. These observations are consistent with the formation of physical PEEK-PEI blends.

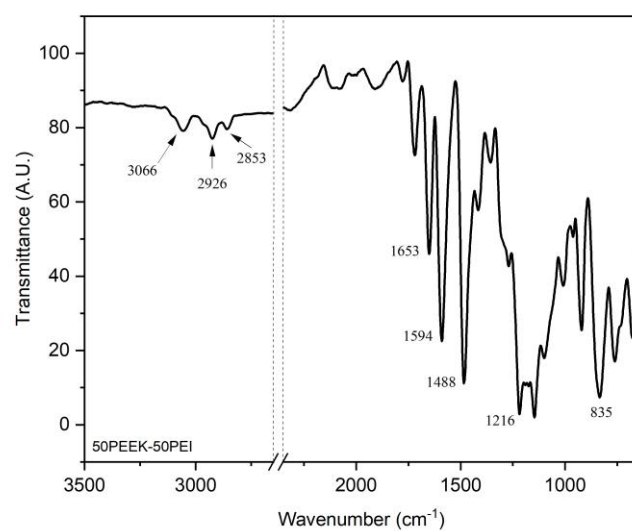


Figure 31: FTIR spectra of 50PEEK-50PEI filaments

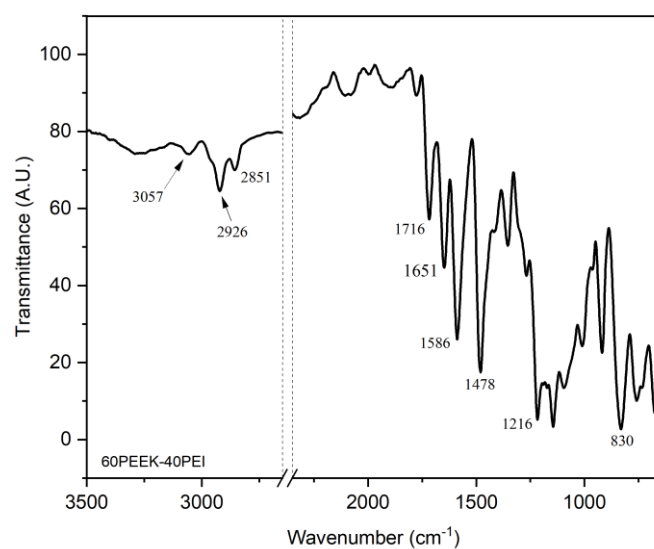


Figure 32: FTIR spectra of 60PEEK-40PEI filaments

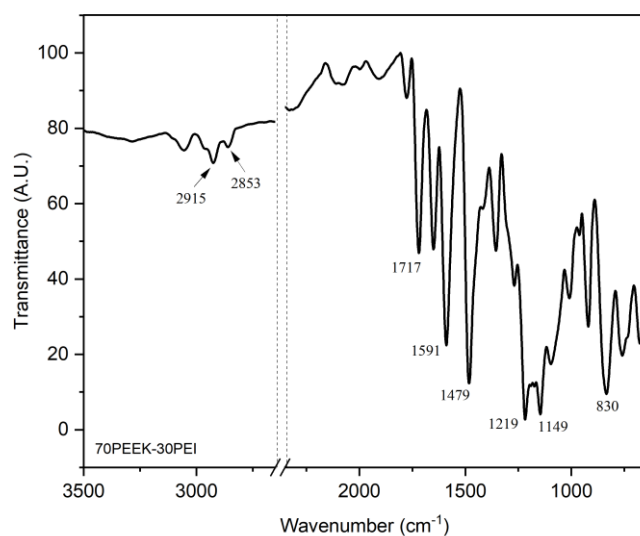


Figure 33: FTIR spectra of 70PEEK-30PEI filaments

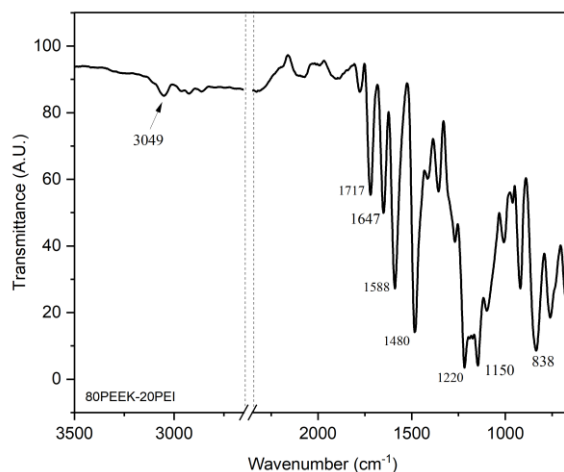


Figure 34: FTIR spectra of 80PEEK-20PEI filaments

The FT-IR spectra of the extruded filaments were consistent with those obtained for the corresponding PEEK and PEI powders, indicating that the compounding and extrusion processes did not produce detectable changes in the chemical structure of either polymer. The characteristic absorption bands of both constituents were retained in all blend compositions, with variations in relative band intensities corresponding to changes in blend composition. A comparison of the spectra presented in Figure 35 shows the gradual change in the relative intensities of the characteristic PEEK and PEI absorption bands across the blend series. In the region around 3050 cm^{-1} , the aromatic C-H stretching bands observed in the neat polymers appeared as a broad absorption band in the blends due to the overlap of vibrational

contributions from both polymer phases. No additional absorption bands or significant peak shifts were observed. These results indicate that blending and processing did not induce detectable chemical modifications and are consistent with the formation of physical PEEK-PEI blends.

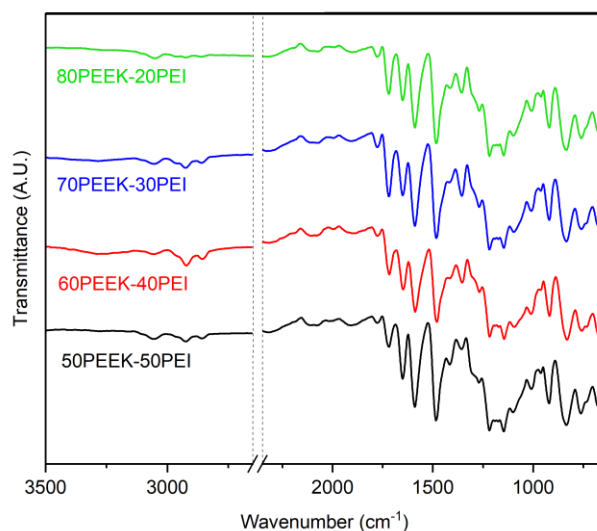


Figure 35: FTIR comparison on all blends filaments

Across the investigated compositions (50PEEK-50PEI, 60PEEK-40PEI, 70PEEK-30PEI, and 80PEEK-20PEI), the FT-IR spectra show the expected changes in relative band intensities as the PEEK-PEI ratio is varied, while the overall spectral features remain consistent across all samples.

The most noticeable differences appear in the carbonyl stretching region. The band at ~ 1716 - 1717 cm^{-1} , associated with the imide $\text{C}=\text{O}$ stretching of PEI, is more pronounced in PEI-rich blends and gradually diminishes as the PEEK content increases. In contrast, the absorption at ~ 1650 - 1653 cm^{-1} , attributed to the ketone carbonyl group of PEEK, is present in all samples but becomes increasingly dominant in blends with higher PEEK fractions. These opposing trends follow the expected variation in composition and confirm the relative contribution of each polymer to the spectra.

Similar behaviour is observed in the fingerprint region. The band at $\sim 1150\text{ cm}^{-1}$, assigned to C-N-C stretching of the PEI imide structure, decreases progressively with lower PEI content. Meanwhile, the ether-related vibration of PEEK at ~ 1216 - 1220 cm^{-1} remains visible across all compositions and increases in relative intensity in PEEK-rich samples. Aromatic skeletal vibrations around ~ 1590 and $\sim 1480\text{ cm}^{-1}$ are present in all blends, consistent with the aromatic

backbones of both polymers, although their intensities do not show a strong dependence on composition.

In the C-H stretching region (approximately 3050 cm^{-1} for aromatic C-H and $2920\text{-}2850\text{ cm}^{-1}$ for aliphatic C-H), no significant changes are observed across the series, apart from minor variations in intensity that can be attributed to differences in polymer ratio.

The FT-IR results indicate that changes in composition are mainly reflected in variations in peak intensities rather than peak positions. No new bands are observed, suggesting that no chemical reaction occurs between PEEK and PEI during processing. The spectra are therefore consistent with a physical blend in which both polymers retain their chemical structures.

Thermogravimetric analysis was conducted on the extruded filaments in order to evaluate their thermal stability in relation to the high-temperature conditions characteristic of the printing process. Figures 36, 37, 38, and 39 present the different analyses performed on filaments composed of varying PEEK-PEI ratios. Each graph is characterized by a black curve, representing the percentage weight as a function of temperature, and a red curve representing its corresponding derivative (Derivative Thermogravimetry, DTG). The onset temperatures (T_{onset}) can be identified on the black curves considering a 5% weight loss criterion.

The thermogravimetric behaviour of the PEEK-PEI blends indicates a two-step degradation process, although the two stages are not always clearly separated in the DTG curves due to partial overlap. The initial stage begins gradually and appears as a broad shoulder or subtle deviation in the TGA trace rather than a well defined peak. This early mass loss can be associated with the decomposition of the less thermally stable components of the system, most likely the imide-related structures in PEI and possibly less ordered or interfacial regions within the blend [220]. Because this process occurs over a relatively slow rate and overlaps with the main degradation event, it is not clearly resolved in the DTG signal. The second degradation step is dominant and clearly visible in all samples as a pronounced DTG minimum between approximately 600 and $680\text{ }^{\circ}\text{C}$. This stage is attributed to the rapid scission of the aromatic backbone, primarily associated with PEEK degradation, leading to the major mass loss event [201]. The exact position and shape of this peak vary slightly with composition, suggesting that the blend ratio influences thermal stability and degradation kinetics. All samples exhibit high thermal stability up to approximately $550\text{-}580\text{ }^{\circ}\text{C}$, with negligible mass loss in this range, which is consistent with the strong thermal resistance of both aromatic polymers.

For the 50PEEK-50PEI blend, the $T_{5\%}$ is estimated at approximately 633°C , indicating the onset of the first degradation stage. This relatively high value reflects the combined thermal

stability of both constituents and suggests some degree of favourable interaction within the blend. The main degradation peak occurs at around 660 °C. The residual char at 800 °C remains relatively high (approximately 55-60%), which is consistent with the formation of a stable carbonaceous residue typical of aromatic polymer systems [215].

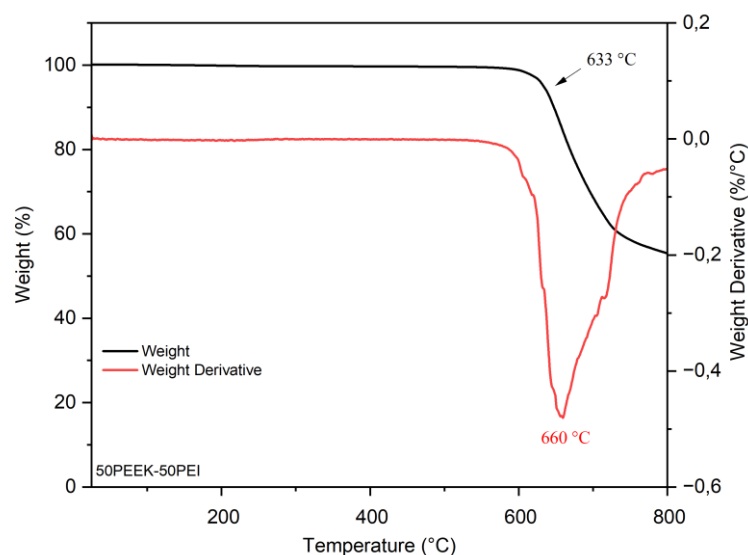


Figure 36: TGA 50PEEK-50PEI filaments

For the 60PEEK-40PEI system, the $T_{5\%}$ is slightly lower, at approximately 622 °C, indicating a marginal reduction in resistance to the initial stages of thermal decomposition. The principal DTG peak, located at around 650 °C, remains well defined, confirming that the main degradation event continues to govern the overall thermal response of the material. Compared with the 50PEEK-50PEI blend, this peak shows only minor shifts, suggesting that the degradation mechanism is largely preserved despite the change in composition.

The residual char yield is comparable, though slightly reduced, remaining in the range of approximately 55-60% at 800 °C. This small decrease may be related to the lower PEI content, which could reduce the fraction of char-forming imide structures, or to subtle differences in the

structure of the thermally degraded residue. The thermal stability of this composition remains high, with behaviour closely resembling that of the equimolar blend.

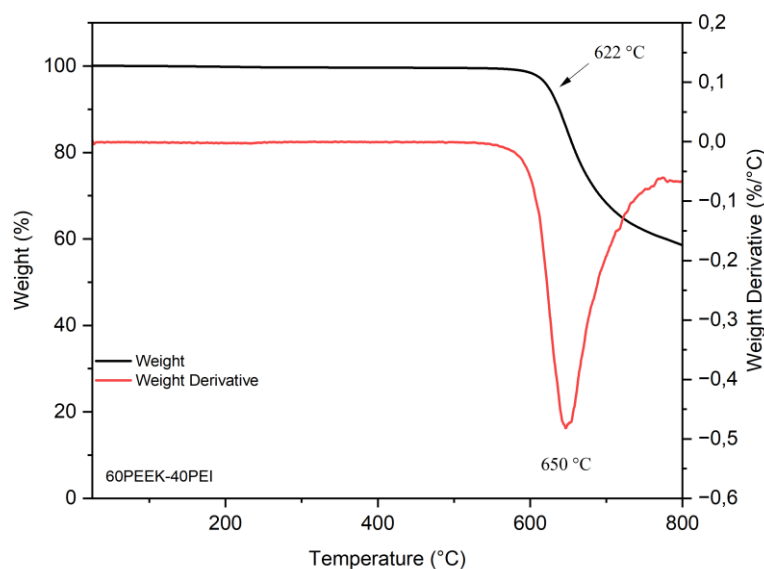


Figure 37: TGA 60PEEK-40PEI filaments

The 70PEEK-30PEI blend exhibits a further decrease in the $T_{5\%}$, reaching approximately 565 °C. This earlier onset suggests that the initial degradation stage becomes more pronounced as the PEI content decreases, indicating a reduction in the overall thermal stability of the blend. This behaviour may be associated with a diminished contribution of the more thermally stable PEI fraction and possible changes in the interactions between the two polymer phases.

The main DTG peak, located at approximately 604 °C, is also shifted to lower temperature compared to the higher PEI-content compositions. In addition, the peak appears sharper, which may indicate a more abrupt degradation process and reduced thermal resistance of the material.

This suggests that the degradation becomes more concentrated within a narrower temperature range as the blend becomes richer in PEEK.

The residual char at 800 °C is slightly lower than in previous compositions, in the range of approximately 50-55%. This trend is consistent with the decreasing PEI content and the associated reduction in char-forming contributions from the imide-based structure.

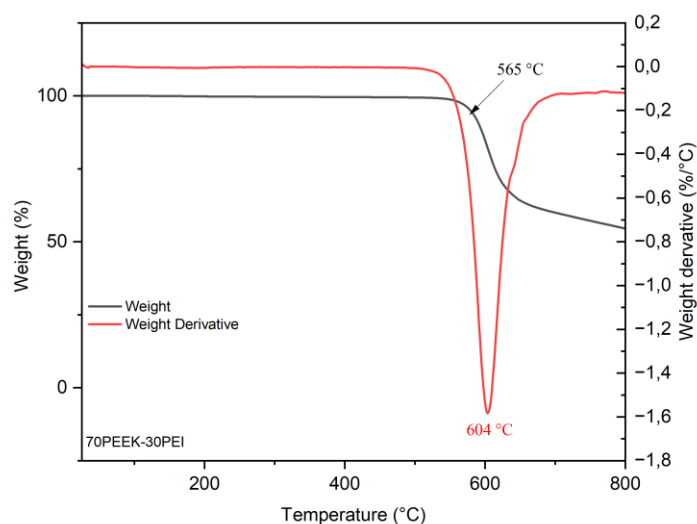


Figure 38: TGA of 70PEEK-30PEI filaments

For the 80PEEK-20PEI blend, the $T_{5\%}$ increases again to approximately 627 °C, representing the highest onset temperature among all the investigated compositions. This suggests that a higher PEEK content enhances the resistance to the initial stage of thermal degradation, likely due to the predominance of its thermally stable aromatic backbone containing ketone linkages. The main degradation event occurs at around 673 °C, which is also the highest peak temperature observed in the series. This shift is consistent with improved thermal stability in

the second degradation stage and indicates that the decomposition of the aromatic backbone is delayed relative to the other compositions.

The residual char yield remains in the range of approximately 50-55% at 800 °C. This value reflects a balance between thermal stability and volatilisation processes, and is broadly consistent with the trends observed across the other blends.

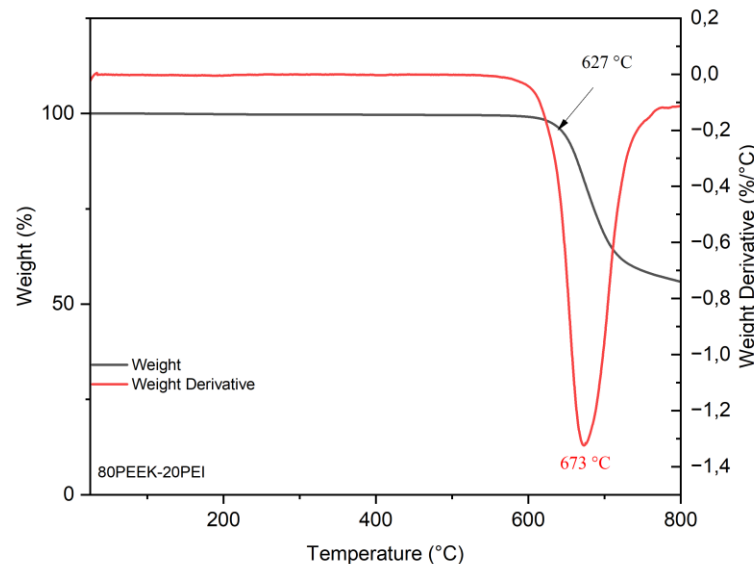


Figure 39:TGA of 80PEEK-20PEI filaments

During pyrolysis, the two polymers follow different degradation pathways. PEEK is known to favour the formation of a stable carbonaceous char, whereas PEI primarily decomposes into volatile products such as carbon monoxide and carbon dioxide [221], [222]. This difference in degradation behaviour contributes significantly to the final residue observed in thermogravimetric analysis.

Although the degradation temperatures of the two polymers are relatively close, PEI generally exhibits higher thermal stability under prolonged thermal exposure, which translates into greater resistance to temperature over extended time scales compared to PEEK [223], [224]. This distinction is particularly relevant when considering long-duration thermal loading conditions.

The onset degradation temperatures ($T_{5\%}$) of all investigated formulations are sufficiently high, indicating that the developed blends are able to withstand the thermal conditions relevant to the intended space environment, where operating temperatures remain well below those associated with the onset of decomposition.

Differential Scanning Calorimetry (DSC) was performed on the blends in order to investigate their thermal behaviour. As previously described, this test consists of three stages:

- First Heating from 25 °C to 400 °C;
- Cooling from 400 °C to 25 °C;
- Second Heating from 25 °C to 400 °C.

From these measurements, the glass transition temperature (T_g), melting temperature (T_m), crystallisation temperature (T_c), and degree of crystallinity were determined. The corresponding thermograms are shown in Figure 40, Figure 41, Figure 42, Figure 43.

The DSC curves of the PEEK-PEI blends exhibit the characteristic thermal transitions of a semicrystalline polymer (PEEK) dispersed within an amorphous matrix (PEI), with clear variations in behaviour depending on composition. In all cases, exothermic events are plotted upwards and endothermic events downwards. Several thermal transitions can be identified within each thermogram, from which the relevant thermal parameters were extracted.

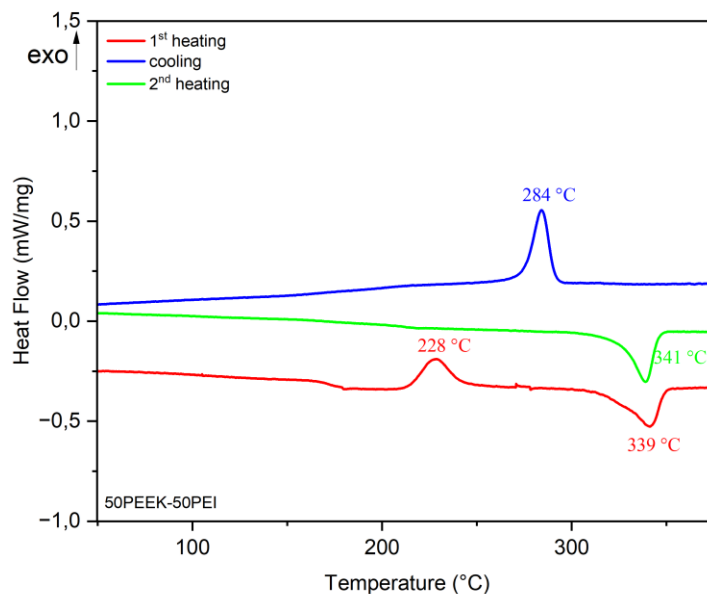


Figure 40: DSC of 50PEEK-50PEI filaments

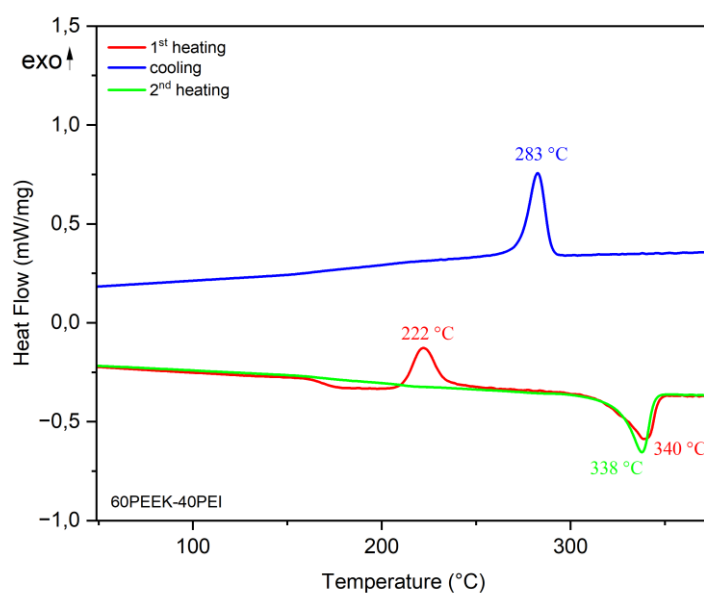


Figure 41: DSC of 60PEEK-40PEI filaments

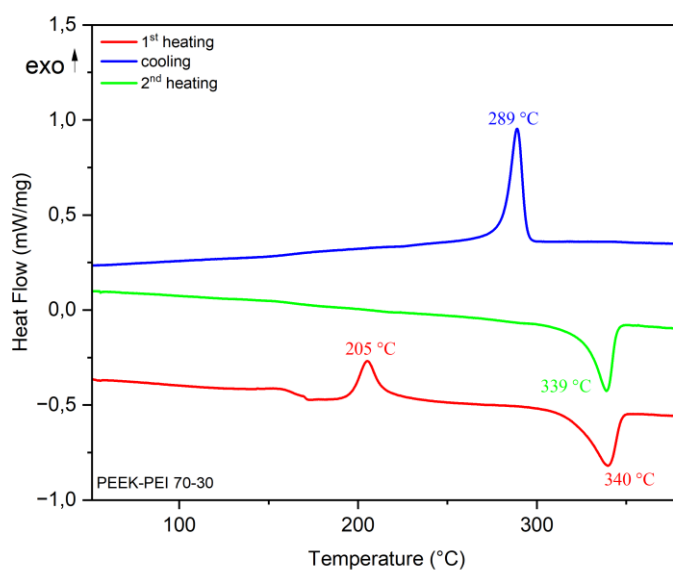


Figure 42: DSC of 70PEEK-30PEI filaments

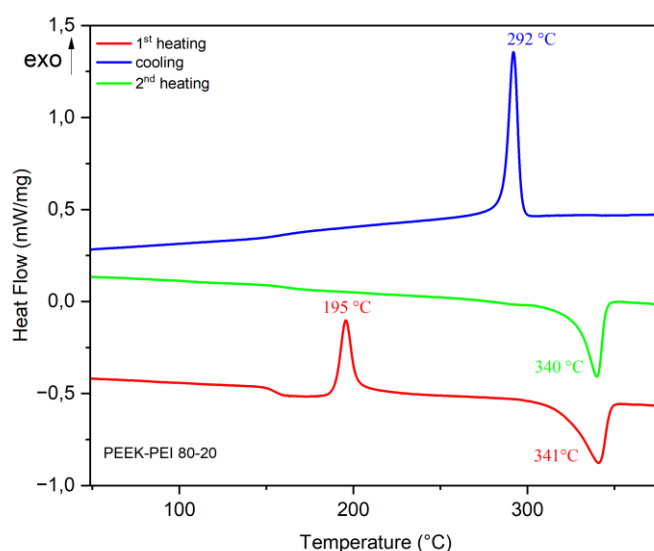


Figure 43: DSC of 80PEEK-20PEI filaments

Across all compositions, the cooling curves exhibit a well defined exothermic peak associated with the crystallisation of PEEK. This peak systematically shifts to higher temperatures with increasing PEEK content, moving from ~ 283 - 284 °C in the 50PEEK-50PEI and 60PEEK-40PEI blends to ~ 289 °C in the 70PEEK-30PEI blend and up to ~ 292 °C in the 80PEEK-20PEI system. This trend indicates progressively faster crystallisation kinetics at higher PEEK fractions, as expected from the increased availability of crystallisable segments and the reduced constraint imposed by the amorphous PEI phase [225]. In contrast, blends with higher PEI content exhibit slightly broader and less intense crystallisation peaks, suggesting reduced chain mobility and delayed nucleation and growth processes [226].

In the first heating cycle, an exothermic event is observed in the approximate range of 150 - 170 °C (depending on composition), which is attributed to cold crystallisation of PEEK segments that did not crystallise during cooling. This behaviour indicates that the as-cooled morphology is partially amorphous, consistent with kinetic suppression of crystallisation in the presence of PEI [227], [228]. Upon heating above the glass transition region, increased chain mobility enables the reorganisation of previously constrained PEEK segments into crystalline structures, giving rise to the observed exothermic peak prior to melting [229]. The position and intensity of this transition are strongly composition dependent. In PEI-rich blends, the peak is more pronounced and shifted to slightly higher temperatures, reflecting stronger restriction of chain mobility and less efficient crystallisation during cooling. As the PEEK content increases, the cold crystallisation peak becomes weaker and shifts to lower temperatures, indicating that

a larger fraction of PEEK crystallises during cooling, leaving less material available for subsequent reorganisation [215], [225].

Within the same heating scan, a weak endothermic transition is observed in the range of approximately ~195-228 °C, which can be associated with the glass transition of PEI and/or enthalpic relaxation phenomena [230], [231]. This transition becomes less evident as the PEEK content increases, consistent with the reduced contribution of the amorphous phase to the overall thermal response. In PEEK-rich blends, this signal is partially masked by overlapping thermal events [215].

A dominant endothermic peak is observed between ~339 °C and 341 °C in all samples corresponds to the melting of PEEK crystals. The near constant position of this peak across all blends suggests that the crystal structure and lamellar thickness of PEEK are not significantly affected by the presence of PEI [232]. However, subtle differences in peak shape and intensity suggest that the degree of crystallinity varies, with sharper and more intense peaks in PEEK-rich systems, consistent with a higher crystalline fraction and improved crystal perfection [233]. The second heating cycle confirms this behaviour, showing reproducible melting transitions and a reduced influence of thermal history. No additional transitions are detected, suggesting that no new crystalline phases are formed and that phase separation remains limited under the processing conditions employed.

From a morphological perspective, semicrystalline PEEK solidifies through the formation of ordered lamellar structures that grow radially from nucleation sites, ultimately assembling into spherulitic superstructures. The final crystalline morphology is strongly governed by the density and effectiveness of nucleation events during cooling [234]. As a result, the crystallinity of PEEK is typically limited, with a theoretical maximum of approximately 40% [235], while commercially processed materials more commonly exhibit values in the range of 30-35% [236], [237]. For additively manufactured PEEK components, the crystalline content is a dominant factor affecting bulk mechanical behaviour. Previous investigations by Yang et al. [237] showed that even moderate differences in crystallinity can alter key performance characteristics, including elastic modulus, tensile strength, and resistance to thermal distortion or dimensional change [238].

To calculate the degree of crystallinity, the enthalpies of fusion were determined by integrating the endothermic peaks over time. The data required for these calculations are reported in Figure 44, Figure 45, Figure 46 and Figure 47. The degree of crystallinity was calculated using the following Equation 3:

$$\chi = \frac{\Delta H}{\Delta H_f * w} \quad (3)$$

where χ is the degree of crystallinity, ΔH is the area under the melting peak, ΔH_f is the theoretical enthalpy of fusion (i.e., that of a fully crystalline PEEK sample), and w is the weight fraction of PEEK in the blend. The value of ΔH_f is equal to 130 J/g [228]. Since PEI is amorphous, its weight fraction is not considered in the crystallinity calculation.

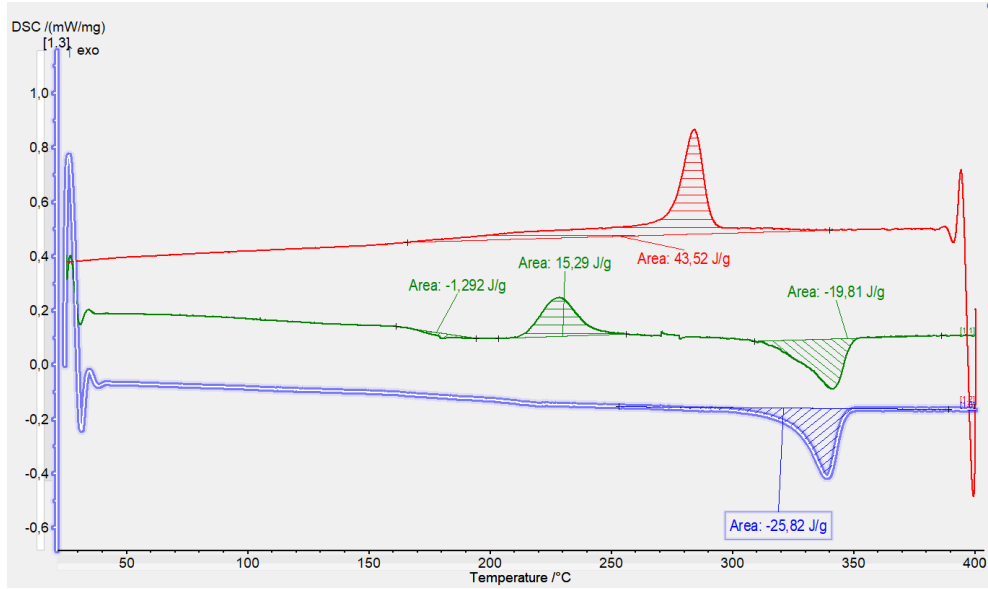


Figure 44: Thermal cycles of 50PEEK-50PEI filaments

For the 50PEEK-50PEI, the following values were obtained (Figure 44):

- $\Delta H_{M1} = 19.81$ J/g (first heating);
- $\Delta H_{M2} = 25.82$ J/g (second heating);
- $\Delta H_C = 43.52$ J/g (cooling);
- $\Delta H_{EFH} = 15.29$ J/g (exothermic peak first heating);
- $\Delta H_{CC} = 1.292$ J/g (cold crystallisation);

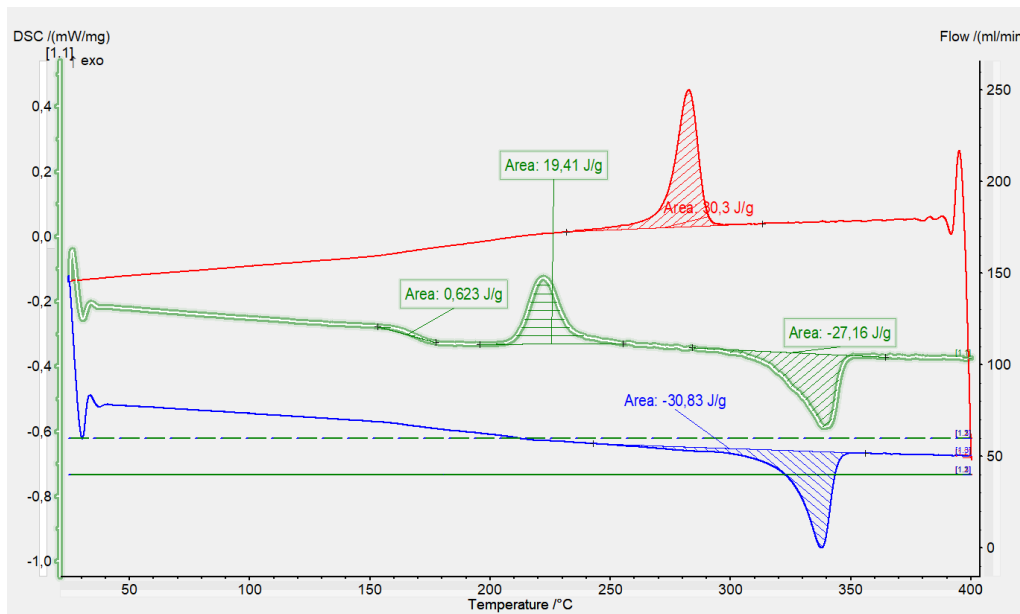


Figure 45: Thermal cycles of 60PEEK-40PEI filaments

For the 60PEEK-40PEI formulation (Figure 45):

- $\Delta H_{M1} = 27.16 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 30.83 \text{ J/g}$ (second heating);
- $\Delta H_C = 30.3 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 19.41 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 0.623 \text{ J/g}$ (cold crystallisation);

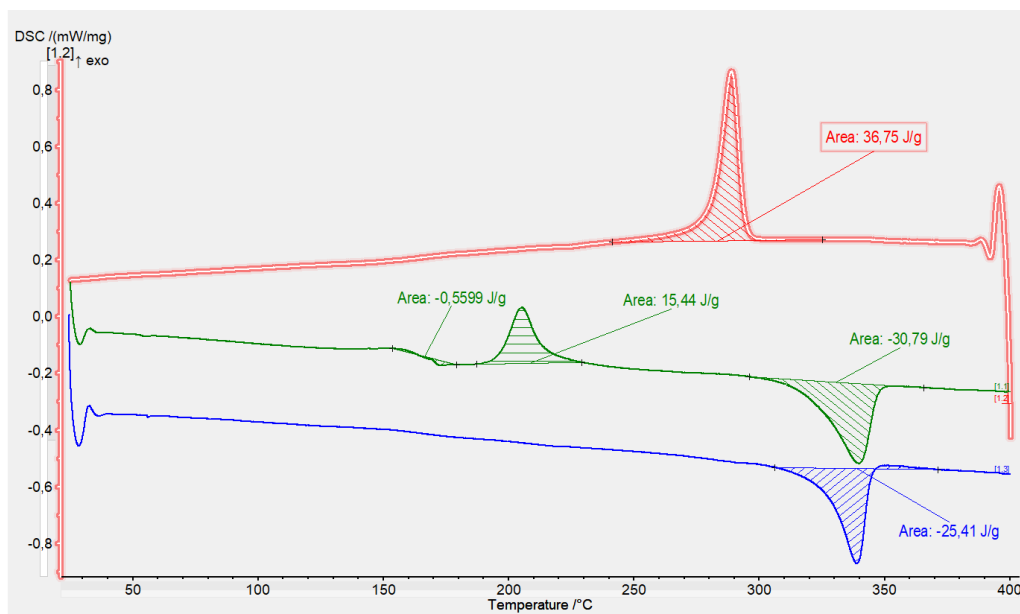


Figure 46: Thermal cycles of 70PEEK-30PEI filaments

For the 70PEEK-30PEI formulation (Figure 46):

- $\Delta H_{M1} = 30.79 \text{ J/g}$ (first heating);

- $\Delta H_{M2} = 25.41 \text{ J/g}$ (second heating);
- $\Delta H_C = 36.75 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 15.44 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 0.5599 \text{ J/g}$ (cold crystallisation);

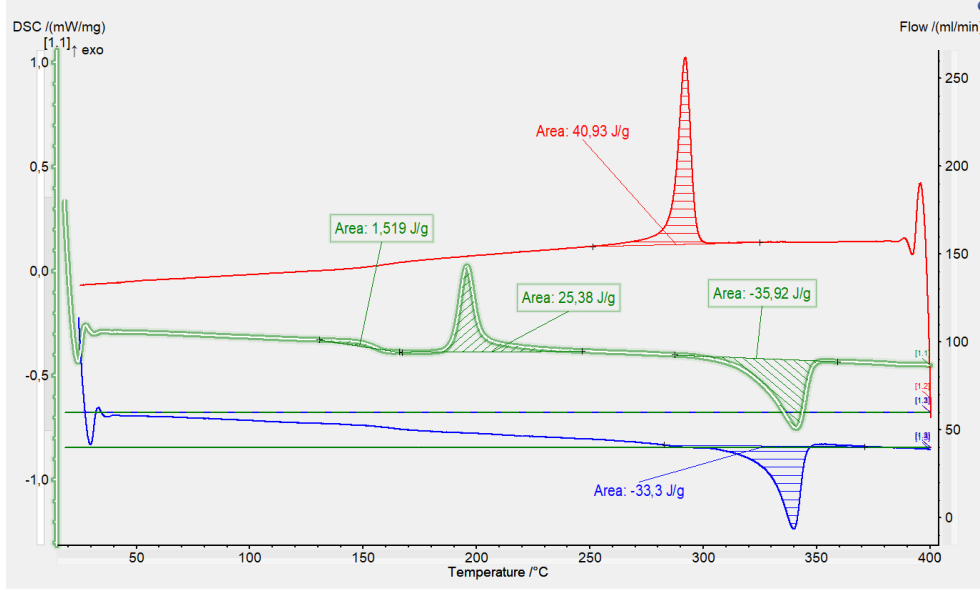


Figure 47: Thermal cycles of 80PEEK-20PEI filaments

For the 80PEEK-20PEI (Figure 47):

- $\Delta H_{M1} = 35.92 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 33.3 \text{ J/g}$ (second heating);
- $\Delta H_C = 40.93 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 25.38 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 1.519 \text{ J/g}$ (cold crystallisation).

Table 6 summarizes the enthalpy values and corresponding degrees of crystallinity for each formulation and heating stage.

Table 6: Enthalpy values and degrees of crystallinity of blend filaments

Formulation	ΔH_{M1}	χ_{M1}	ΔH_{M2}	χ_{M2}	ΔH_C	χ_C	ΔH_{CC}	χ_{CC}	ΔH_{EFH}	χ_{EFH}
50PEEK-50PEI	19.81 J/g	30.48%	25.82 J/g	39.72%	43.52 J/g	66.95%	1.292 J/g	1.99%	15.29 J/g	23.52%
60PEEK-40PEI	27.16 J/g	34.82%	30.83 J/g	39.53%	30.3 J/g	38.85%	0.623 J/g	0.80%	19.41 J/g	24.88%
70PEEK-30PEI	30.79 J/g	33.84%	25.41 J/g	27.93%	36.75 J/g	40.38%	0.5599 J/g	0.62%	15.44 J/g	16.97%
80PEEK-20PEI	35.92 J/g	34.54%	33.3 J/g	32.02%	40.93 J/g	39.36%	1.519 J/g	1.46%	25.38 J/g	24.40%

The reduction in crystallinity observed in 60PEEK-40PEI and 70PEEK-30PEI during cooling (χ_C) as well as in the corresponding cold crystallisation contribution (χ_{CC}), indicates that PEI plays a significant role in limiting the chain mobility and crystallisation kinetics of PEEK [239]. This suppression of crystallisation during cooling, followed by partial recovery upon reheating

(as reflected in ΔH_{M2}), is characteristic of systems in which the amorphous phase increases melt viscosity and restricts nucleation efficiency, leading to kinetically constrained or “trapped” morphologies [240].

Although the enthalpy associated with cold crystallisation is relatively small compared to the melting enthalpy, its presence confirms that a fraction of PEEK remains in an amorphous or poorly ordered state after cooling and is able to reorganise upon heating [241]. This behaviour is particularly evident in the intermediate compositions, suggesting that these blends lie closer to a transitional regime in which confinement effects and partial miscibility between phases become more pronounced [242].

To account for composition differences, the crystallinity values were normalised by the weight fraction of PEEK present in each blend following Equation (4)

$$\Delta H_{c,norm} = \frac{\Delta H_c}{w_{peek}} \quad (4)$$

Table 7: Normalised crystallinity values by the weight fraction of PEEK present in each blend following Equation (4)

Formulation	PEEK fraction	ΔH_c	$\Delta H_{c,norm}$	$X_{c,norm}$
50PEEK-50PEI	0.50	43.52 J/g	87.04 J/g PEEK	66.95%
60PEEK-40PEI	0.60	30.3 J/g	50.50 J/g PEEK	38.85%
70PEEK-30PEI	0.70	36.75 J/g	52.50 J/g PEEK	40.38%
80PEEK-20PEI	0.80	40.93 J/g	51.16 J/g PEEK	39.36%

From Table 7, it can be inferred that the effective crystallisation capacity of PEEK does not scale in a simple linear or additive manner with composition, but instead follows a saturation like behaviour governed by the blend morphology [239]. The relatively constant range of $\Delta H_{c,norm}$ observed for the 60-80 wt% PEEK compositions suggests that, beyond a certain PEI content threshold, crystallisation becomes predominantly controlled by similar kinetic limitations, even with further increases in PEEK fraction [243], [244]. This plateau behaviour is characteristic of systems in which crystallisation is governed more by constraints in segmental mobility than by thermodynamic driving forces [245]. In this regime, the presence of PEI likely contributes to the formation of a highly viscous or partially phase-segregated amorphous matrix during cooling, which hinders chain diffusion and suppresses secondary crystallisation processes. Consequently, even when the PEEK content is increased, the fraction of material that effectively participates in crystallisation during cooling does not increase proportionally, resulting in comparable crystallisation efficiencies per unit mass of PEEK across these compositions [246], [247].

By contrast, the comparatively higher normalized crystallisation enthalpy observed for the 50PEEK-50PEI blend suggests a different morphological behaviour at equimolar composition. At this ratio, the system may exhibit a more finely dispersed or partially co-continuous morphology, with reduced characteristic confinement length scales and a more uniform distribution of phases [248]. This configuration can increase the density of heterogeneous nucleation sites and promote more uniform heat transfer during cooling, thereby enhancing the crystallisation efficiency of the accessible PEEK fraction [249]. Alternatively, the higher value may also be related to reduced crystal impingement effects at lower absolute PEEK content, allowing a greater fraction of available material to crystallise within confined domains [250].

For a better understanding of the thermal-mechanical behaviour, Dynamic Mechanical Analysis (DMA) performed on the filaments in order to evaluate their viscoelastic response. The resulting curves report the evolution of the storage modulus (E') and the damping factor ($\tan\delta$) as a function of temperature, while maintaining a constant oscillation frequency of 1 Hz. In these tests, the samples are subjected to a sinusoidal deformation over a temperature range extending from room temperature (T_{amb}) up to 250 °C [251]. From the measured response, the storage modulus (E') represents the elastic component of the material and is associated with the energy stored during deformation, whereas the loss modulus (E'') describes the viscous contribution and the energy dissipated as heat. The damping factor is defined as:

$$\tan\delta = \frac{E''}{E'}$$

and represents the phase lag between stress and strain, providing a measure of the material's damping behaviour under dynamic loading [251].

Analysis of the DMA curves shown in Figure 48, Figure 49, Figure 50 and Figure 51, reveals clear differences in the viscoelastic response of the various formulations, with particular attention to the $\tan \delta$ peaks, which are commonly used to identify the glass transition temperature (T_g). In all cases, a clear dependence on composition is observed, with systematic variations in both E' and $\tan \delta$ as the PEEK-PEI ratio changes.

For the 50PEEK-50PEI blend in Figure 48, the storage modulus remains relatively high and stable up to ~170 °C, after which marked decrease is observed, corresponding to the onset of increased segmental mobility. This transition is accompanied by a pronounced $\tan \delta$ peak at approximately 187 °C, which is taken as the glass transition temperature of the blend. When determined from the onset of the E' drop, T_g is estimated at around 178 °C. The presence of a secondary shoulder at approximately 217 °C may indicate some degree of phase heterogeneity,

potentially related to distinct relaxation processes in PEEK and PEI-rich domains or partial differences in their mobility within the blend [252].

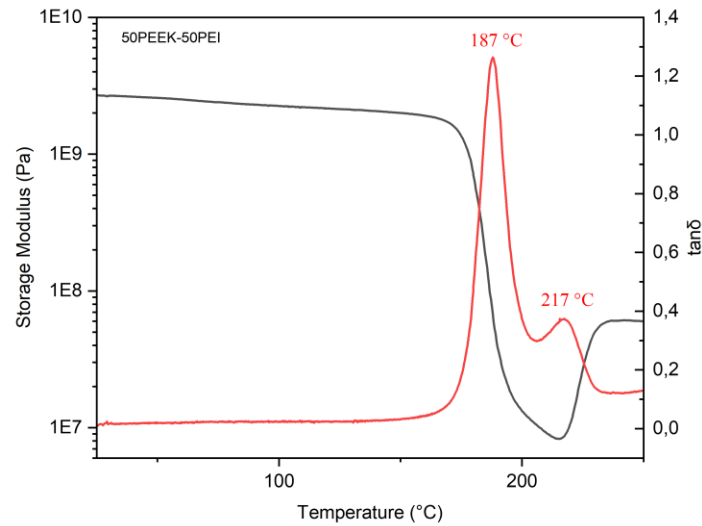


Figure 48: DMA of 50PEEK-50PEI filaments

As the PEEK content increases to 60PEEK-40PEI, as shown in Figure 49 the glass transition temperature shifts to approximately 178 °C, accompanied by a slightly broader tan δ peak. This decrease in T_g suggests a change in the overall segmental dynamics of the system, possibly due to a greater influence of the lower T_g component and/or a reduction in effective intermolecular interactions between PEEK and PEI, which facilitates earlier onset of molecular mobility [253], [254]. When T_g is determined from the onset of the E' drop, a value of approximately 169 °C is obtained. The corresponding decrease in storage modulus remains sharp, indicating a relatively well-defined transition from the glassy to the rubbery state [255]. A minor secondary feature around 204 °C is also observed, which may be associated with

residual phase heterogeneity or the relaxation of more constrained chain segments within the blend structure [232].

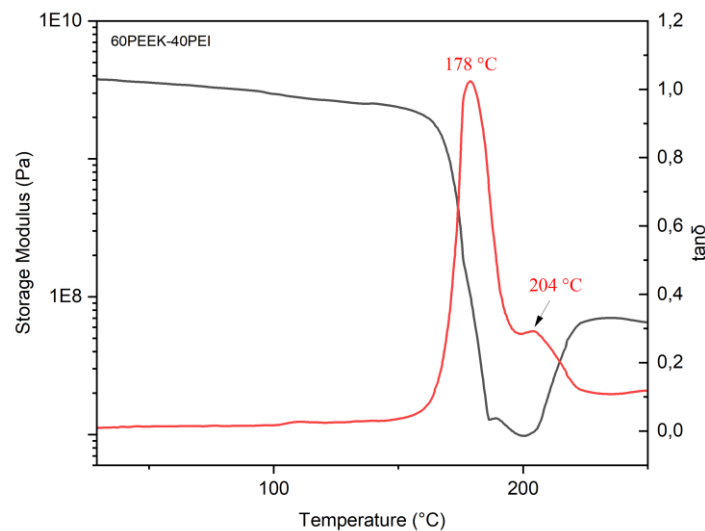


Figure 49: DMA of 60PEEK-40PEI filaments

For the 70PEEK-30PEI composition in Figure 50, the glass transition temperature further decreases to approximately ~ 175 °C. The $\tan\delta$ peak becomes broader and less intense, indicating increased damping behaviour and suggesting a more distributed or heterogeneous relaxation process within the material [256]. When evaluated using the onset of the E' drop, T_g is estimated at around 168 °C. The storage modulus shows a pronounced decrease in the glass transition region, consistent with the transition to a rubbery state; however, a slight recovery at higher temperatures is observed. This behaviour may be associated with thermally activated structural rearrangements in the PEEK-rich phase, such as cold crystallisation or post-mobility-induced ordering. The additional peak observed in the $\tan\delta$ curve at approximately 206 °C further supports the presence of multiple relaxation mechanisms, which may be linked to residual phase heterogeneity and distinct segmental dynamics within the blend [257].

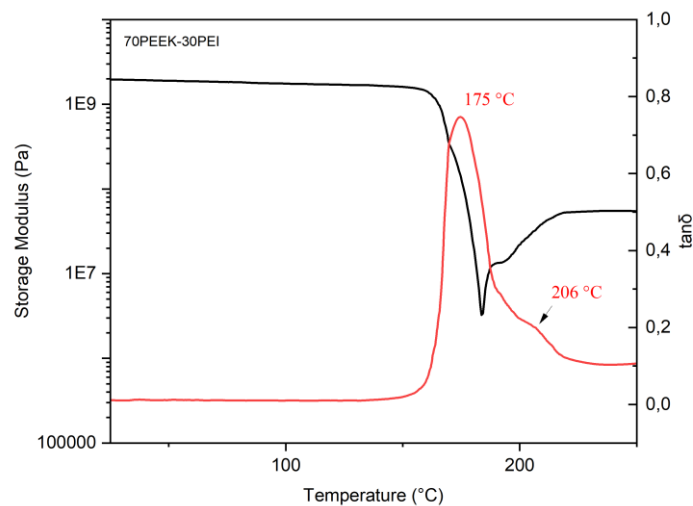


Figure 50: DMA of 70PEEK-30PEI filaments

In the 80PEEK-20PEI in Figure 51, the glass transition temperature decreases further to approximately 165 °C. The corresponding $\tan \delta$ peak remains relatively sharp but exhibits a lower intensity compared to the other blends, indicating that the viscoelastic response is increasingly governed by the PEEK-rich phase, while the influence of PEI on restricting chain mobility becomes less significant [258]. When the onset of the storage modulus reduction is used as the criterion for T_g determination, a value of approximately 157 °C is obtained. As observed for the other PEEK-rich formulations, the storage modulus undergoes a pronounced decrease through the glass transition region, followed by a modest recovery at higher temperatures. This behaviour is consistent with thermally induced structural rearrangements within the PEEK phase, such as cold crystallisation or the development of additional crystalline order during heating. A secondary relaxation feature is still detectable at approximately 185 °C, although it is considerably less pronounced than in the blends containing higher amounts of PEI. The reduced intensity of this feature may indicate a lower degree of phase heterogeneity and a diminished contribution of PEI-rich domains to the overall relaxation behaviour of the material [259]. The DMA response of the 80PEEK-20PEI blend is dominated by the characteristics of the semicrystalline PEEK matrix, while the influence of the amorphous PEI phase becomes progressively less evident.

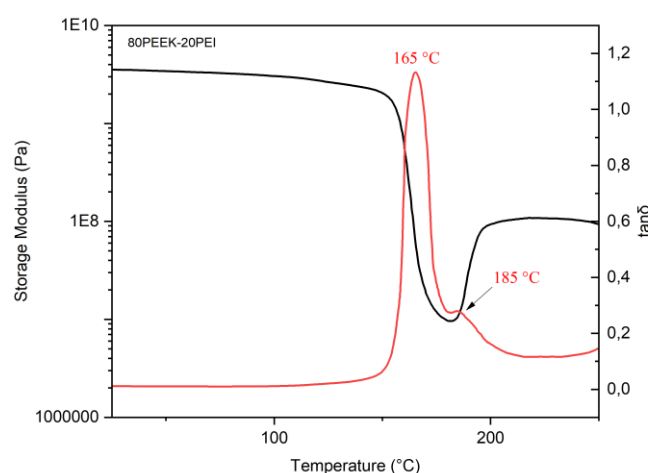


Figure 51: DMA of 80PEEK-20PEI filaments

Increasing the PEEK content results in a progressive reduction in the glass transition temperature and corresponding changes in the damping behaviour of the blends. These trends reflect modifications in segmental mobility, intermolecular interactions, and phase morphology as the relative proportions of the two polymers are varied. The persistence of secondary relaxation features in the $\tan \delta$ curves across all compositions suggests that complete miscibility is not achieved within the investigated composition range. Instead, the blends likely exhibit varying degrees of phase heterogeneity, with the coexistence of PEEK- and PEI-rich regions and/or constrained amorphous domains. A direct comparison of the DMA responses for all compositions is presented in Figure 52. The results indicate that blending PEEK and PEI modifies the thermomechanical behaviour relative to that of the individual polymers, providing a means of tailoring material performance through compositional adjustment. In particular, the combination of the semicrystalline nature of PEEK and the high-temperature amorphous character of PEI produces materials with a balance of stiffness, thermal resistance, and damping behaviour that can be tuned according to application requirements. The DMA results demonstrate that the PEEK-PEI blends retain excellent thermomechanical stability throughout the investigated temperature range while exhibiting clear composition dependent viscoelastic characteristics. Combined with the findings obtained from FTIR, TGA, and DSC analyses, these results confirm that the blends maintain their structural integrity during processing and offer a versatile combination of thermal and mechanical properties. Such characteristics make the investigated materials promising candidates for high-performance applications, including aerospace and space structures, provided that the required qualification and long term durability assessments are successfully completed.

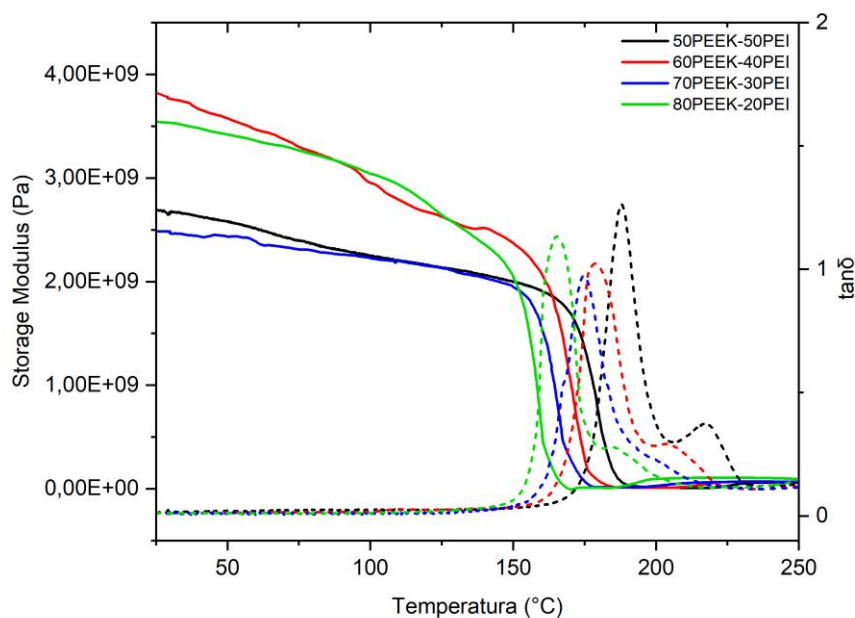


Figure 52: DMA on filaments: comparison

Results of averaged tensile tests on filaments are presented in Figure 53 and in Table 8.

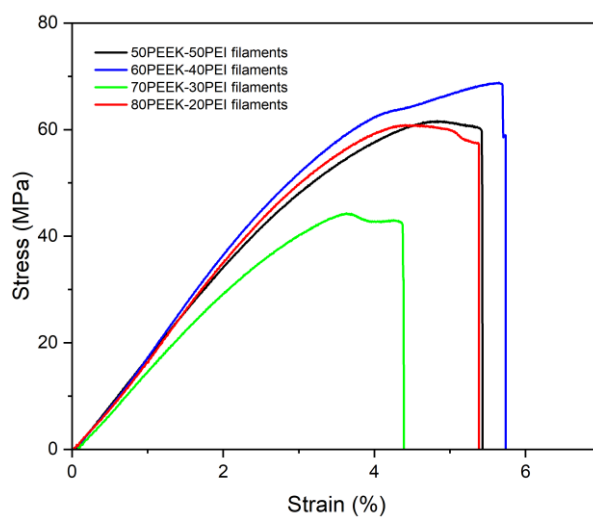


Figure 53: Averaged tensile tests on filaments

Table 8: Tensile test averaged results on filaments

Formulation	Elastic Modulus (E)	SD	Stress (σ)	SD	Strain (ϵ)	SD
50PEEK-50PEI	1.79 GPa	0.92 GPa	61.66 MPa	17.92 MPa	5.41%	1.55%
60PEEK-40PEI	1.71 GPa	0.64 GPa	68.83 MPa	20.66 MPa	5.74%	1.64%
70PEEK-30PEI	1.54 GPa	0.39 GPa	44.32 MPa	13.90 MPa	4.37%	1.24%
80PEEK-20PEI	1.60 GPa	0.71 GPa	60.89 MPa	15.34 MPa	5.39%	1.55%

The tensile stress-strain curves exhibit the characteristic behaviour of thermoplastic materials, consisting of an initial elastic region in which stress increases approximately linearly with strain, followed by plastic deformation and eventual fracture. Differences between the formulations are primarily associated with the relative contributions of the PEEK and PEI phases, the extent of crystallinity developed within the PEEK-rich compositions, and the resulting efficiency of stress transfer throughout the filament structure. Among the investigated formulations, the 60PEEK-40PEI filament exhibits the most favourable tensile performance. It achieves the highest tensile strength, approaching 70 MPa, while also sustaining the greatest strain prior to failure. The stress-strain curve increases smoothly and continues to harden up to fracture, indicating stable plastic deformation and effective load transfer within the material. This behaviour suggests that the 60PEEK-40PEI composition provides an advantageous balance between the semicrystalline reinforcement contributed by PEEK and the amorphous rigidity of PEI. At this composition, sufficient crystallinity appears to be retained to ensure high strength, while the PEI phase may contribute to improved structural continuity and a reduction in defects generated during filament extrusion. Furthermore, the large area under the stress-strain curve indicates enhanced toughness and energy absorption capability compared to the other blends.

The 50PEEK-50PEI filament exhibits slightly lower tensile strength and reduced elongation at break, although its overall mechanical response remains relatively stable and ductile. The higher PEI content may further restrict PEEK crystallisation, thereby limiting the reinforcing contribution of the crystalline phase and reducing the attainable mechanical performance.

In contrast, the 70PEEK-30PEI filament demonstrates the poorest tensile behaviour among all investigated compositions, with both tensile strength and fracture strain decreasing significantly. This reduction in performance may be associated with less efficient stress transfer across the blend morphology, potentially resulting from phase heterogeneity, weak interfacial regions, or the presence of local stress concentration sites. Additionally, the reduced PEI content may decrease intermolecular entanglement and compromise the continuity of the polymer network [225], [239], [256], [257], [260], [261].

The 80PEEK-20PEI filament recovers much of the tensile strength lost in the 70PEEK-30PEI formulation, reaching values comparable to those of the 50PEEK-50PEI blend, although the elongation at break remains lower. This behaviour suggests that, at higher PEEK concentrations, the increased contribution of the crystalline phase restores the material's ability to sustain mechanical loads. However, the reduced PEI content appears to limit ductility and may decrease resistance to crack initiation and propagation.

Comparison of the tensile and DSC results indicates that the 70PEEK-30PEI composition may correspond to a morphological transition region within the blend system. Although this formulation exhibits a degree of crystallinity comparable to those measured for the 60PEEK-40PEI and 80PEEK-20PEI blends, its lower effective fusion enthalpy suggests reduced structural homogeneity and less efficient crystalline organisation. This interpretation is supported by the tensile response, which is characterised by an early stress plateau and premature fracture, indicative of localised deformation and inefficient load transfer. Moreover, the limited contribution of cold crystallisation suggests that crystallisation occurred predominantly during processing, implying that the reduced mechanical performance is not attributable to the amount of crystalline material formed, but rather to its spatial distribution and effectiveness in reinforcing the microstructure. These observations indicate that the tensile behaviour of the blends is governed not only by crystallinity, but also by phase continuity, interfacial quality, and the overall morphological organisation of the system.

3.2.3. 3D-Printed Parts Characterisations

The FTIR spectra of the 3D-printed PEEK-PEI blends exhibit the characteristic absorption bands of both constituent polymers, indicating that the printing process does not significantly alter their chemical structure [262]. Across all compositions, weak bands in the 3060-3050 cm^{-1} region are assigned to aromatic C-H stretching, while the absorptions between 2926-2850 cm^{-1} correspond to aliphatic C-H stretching associated with the polymer backbone. Strong bands observed in the 1650-1715 cm^{-1} region are attributed to the carbonyl (C=O) stretching vibrations originating from the ketone groups of PEEK and the imide functionalities of PEI, confirming the presence of both components within the printed material.

In the fingerprint region, the bands between approximately 1590-1500 cm^{-1} are associated with aromatic ring stretching vibrations, while the peak near 1488 cm^{-1} further support phenyl ring vibrations mode. The intense absorption observed at approximately 1216 cm^{-1} corresponds to C-O-C stretching vibrations of the aromatic ether linkages that are characteristic of PEEK. Additional bands in the of 1140-1100 cm^{-1} region are attributed to aromatic ether and imide-related vibrations, with moderate variations in intensity reflecting differences in blend composition. The low wavenumber absorptions near 830-835 cm^{-1} are assigned to out-of-plane C-H bending vibrations of substituted aromatic rings.

Figure 54 presents the FTIR spectrum on 3D-printed 50PEEK-50PEI specimen. Comparison with the corresponding filament spectrum reveals subtle differences in band shape and

resolution, which may be associated with the different thermal histories experienced during filament extrusion and fused filament fabrication [263], [264].

One notable difference is the increased resolution of the band around 3066 cm^{-1} , associated with aromatic C-H stretching vibrations. The appearance of a more clearly differentiated peak may indicate variations in the local molecular environments of the polymer chains after printing, potentially reflecting changes in chain packing or domain organisation [232].

Similarly, the band near 1216 cm^{-1} appears more clearly resolved in the printed sample than in the filament, where it is partially broadened. This behaviour may result from a reduction in vibrational overlap and could be related to changes in molecular ordering induced during the printing process [215].

Collectively, these observations suggest that fused filament fabrication influences the microstructural organisation of the PEEK-PEI blends while preserving their chemical integrity. Although no new absorption bands are detected and no evidence of chemical degradation is observed, subtle changes in band shape and resolution indicate that the thermal history associated with printing may affect chain organisation and the distribution of the polymer phases, leading to minor differences in the resulting FTIR spectra [265], [266].

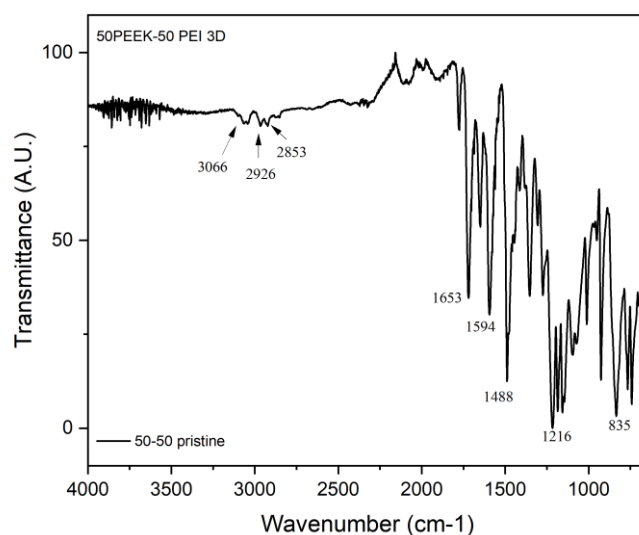


Figure 54: FTIR of 50PEEK-50PEI 3D

The FTIR spectrum of the 3D printed 60PEEK-40PEI sample (Figure 55) exhibits subtle differences compared to that of the corresponding filament, suggesting that the thermal history associated with the FFF process influences the local molecular organisation of the blend [267]. Although the overall spectral profile remains unchanged and no new absorption bands are detected, variations in band intensity, shape, and resolution indicate modifications in the

microstructural arrangement of the polymer phases. Particular differences are observed in the aromatic region, where changes in the relative intensity and definition of the bands near 1586 cm^{-1} and 1488 cm^{-1} can be identified. These bands are associated with aromatic skeletal vibrations and are known to be sensitive to molecular packing, intermolecular interactions, and local chain environment. Rather than indicating the formation of new chemical structures, these variations most likely reflect changes in the relative contributions of PEEK and PEI-rich domains following processing [268]. A similar effect is observed in the region around 1216 cm^{-1} , corresponding primarily to the ether linkages of PEEK. In the printed sample, this feature appears more clearly resolved than in the filament spectrum, where partial band broadening and overlap are evident. The improved definition of this spectral region may be associated with a reduction in vibrational overlap resulting from changes in molecular organisation and local ordering induced during printing [269], [270].

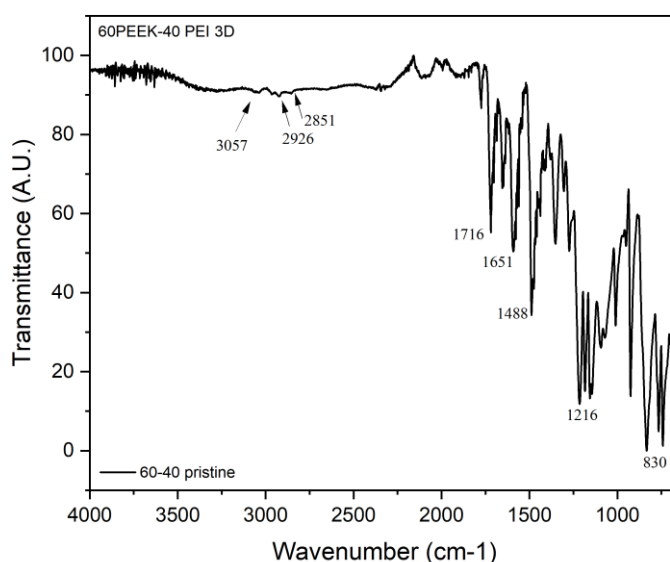


Figure 55: FTIR of 60PEEK-40PEI 3D

For the 70PEEK-30PEI blend in Figure 56, comparison of the filament and 3D-printed FTIR spectra reveals subtle but noticeable differences that suggest modifications in the local molecular environment following processing [271]. Despite these variations, the overall spectral profile remains unchanged, indicating that the chemical structures of both polymers are preserved during the FFF process. Changes are observed in the aromatic region, where the band located at 1479 cm^{-1} in the filament appears at approximately 1488 cm^{-1} in the printed sample. This variation may reflect differences in molecular packing and intermolecular interactions resulting from the distinct thermal histories experienced during printing and

subsequent cooling [272]. Such changes are consistent with modifications in the local environment of the aromatic structures rather than the formation of new chemical species. Additional differences are evident in the ether region of the spectrum. The bands originally at 1219 cm^{-1} and 1149 cm^{-1} in the filament are shifted slightly to lower wavenumbers, appearing near 1212 cm^{-1} and 1144 cm^{-1} , respectively, in the printed material. These modest shifts may indicate variations in the conformational state of the polymer chains and changes in intermolecular interactions induced during solidification. Furthermore, the broad doublet peak observed around 1216 cm^{-1} in the filament spectrum becomes more clearly resolved in the printed specimen, suggesting a reduction in vibrational overlap and a more differentiated contribution from the underlying chemical environments [273].

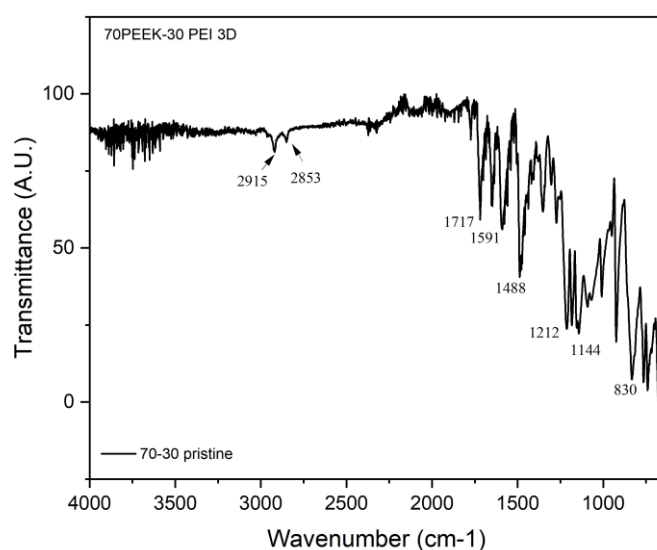


Figure 56: FTIR of 70PEEK-30PEI 3D

For the 80PEEK-20PEI blend in Figure 57, the FTIR spectra of the 3D-printed material compared to the filament reveals several subtle but systematic spectral variations, suggesting that the FFF process influences the local molecular organisation of the material. Despite these differences, the overall spectral profile remains unchanged and no additional absorption bands are observed, confirming that the chemical structures of both polymers are preserved during processing. Several bands associated with the aromatic backbone exhibit small shifts following printing. In particular, the absorption near 1647 cm^{-1} appears at approximately 1653 cm^{-1} in the printed sample, while the peaks located at 1588 cm^{-1} and 1480 cm^{-1} shift to 1595 cm^{-1} and to 1490 cm^{-1} , respectively. These variations suggest modifications in the vibrational environment of the aromatic structures and may be associated with changes in chain packing,

intermolecular interactions, and conformational constraints arising from the thermal cycles experienced during printing [215]. Additional differences are observed in the ether-related region for the duplets around 1220 cm^{-1} . In the filament spectrum, this region appears as a broader and partially overlapped feature, whereas in the printed specimen it becomes more clearly resolved into distinct peaks. This improved spectral definition may indicate a reduction in vibrational overlap and a greater differentiation of local molecular environments following solidification [274]. A slight shift of the band near 838 cm^{-1} to 835 cm^{-1} , associated with out-of-plane aromatic C-H deformations, may reflect subtle variations in chain conformation and local symmetry [275].

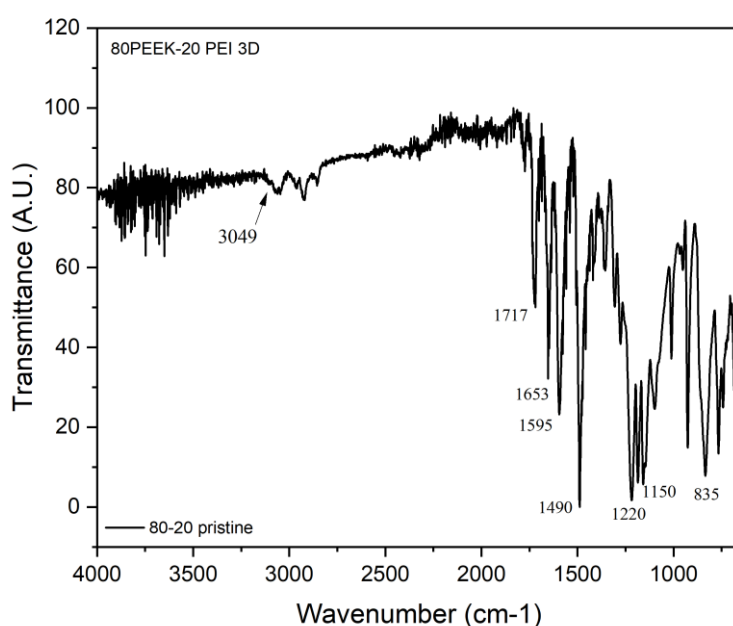


Figure 57: FTIR of 80PEEK-20PEI 3D

Comparison of the FTIR spectra obtained for the different PEEK-PEI compositions reveals no appearance of new absorption bands and no disappearance of characteristic peaks belonging to either polymer. This observation indicates that no new covalent bonds are formed during processing and that the blends are thus physically mixed [232]. However, subtle shifts in peak positions and variations in intensity, particularly in the carbonyl and ether regions, indicate intermolecular interactions such as dipole-dipole interactions or possible partial compatibility between PEEK and PEI phases [260]. As the PEEK content increases, the relative intensity of the characteristic PEEK absorption bands, especially those associated with ether linkages, becomes progressively more pronounced, reflecting the expected compositional dependence of the spectra. The FTIR analysis therefore confirms that the fused filament fabrication process

preserves the chemical integrity of both polymers while inducing subtle modifications in molecular organisation and intermolecular interactions.

Thermogravimetric analysis was subsequently performed on the different formulations of PEEK and PEI in order to evaluate their thermal stability after processing. The resulting thermograms, presented in Figure 58, Figure 59, Figure 60 and Figure 61, show that all blends maintain excellent thermal stability up to approximately 520 °C, confirming their suitability for applications requiring exposure to elevated temperatures.

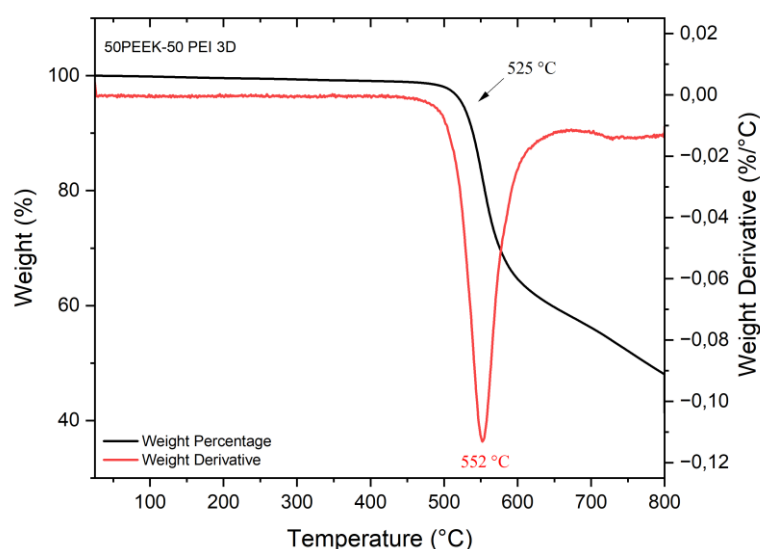


Figure 58: TGA of 50PEEK-50PEI 3D

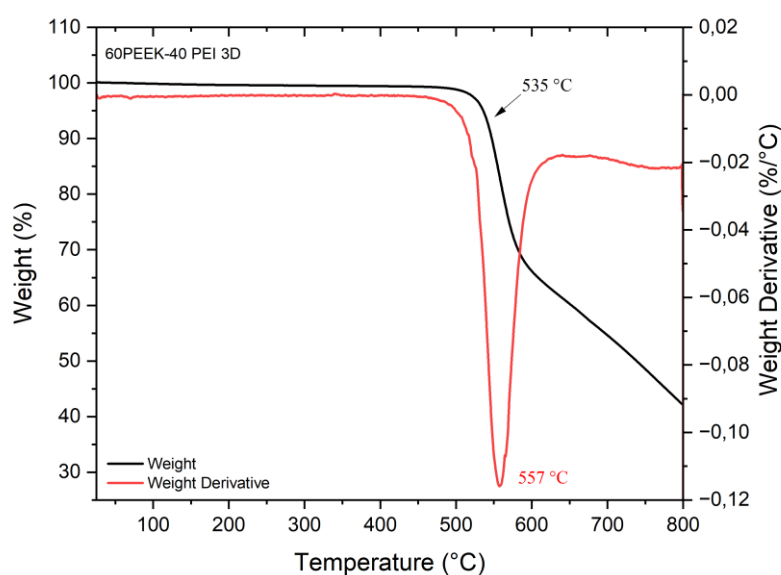


Figure 59: TGA of 60PEEK-40PEI 3D

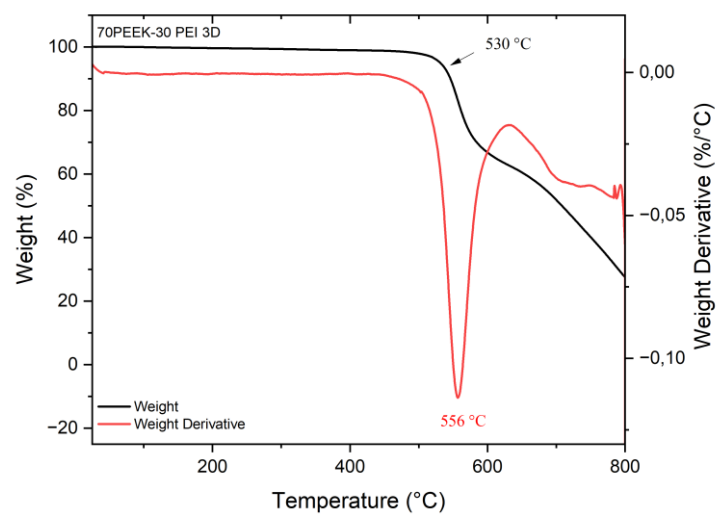


Figure 60: TGA of 70PEEK-30PEI 3D

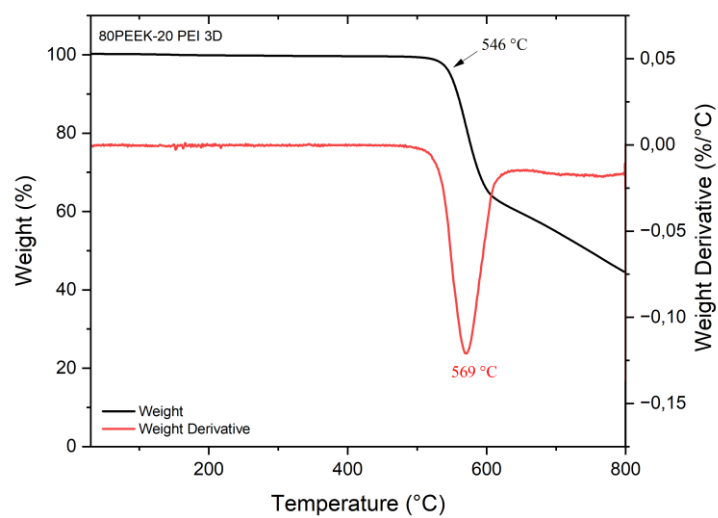


Figure 61: TGA of 80PEEK-20PEI 3D

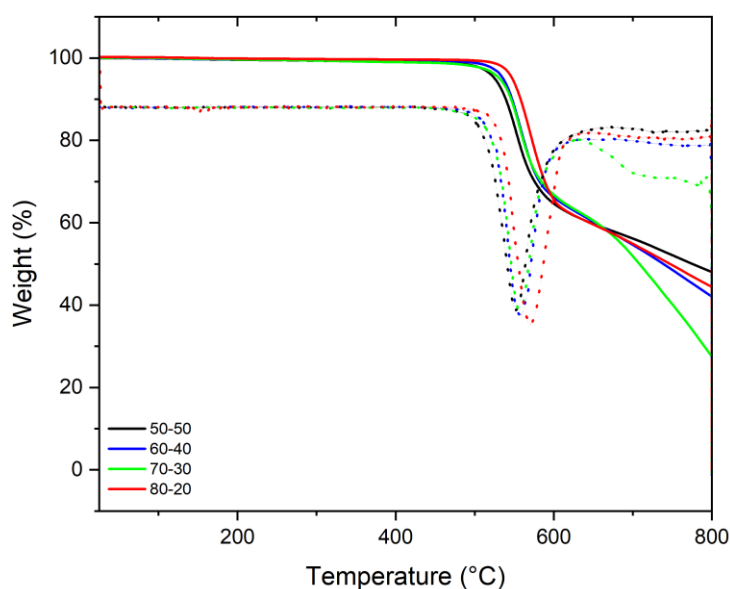


Figure 62: TGA comparison of 3D printed samples

A comparison of all formulation is depicted in Figure 62. For all compositions, the primary mass loss event occurs between 520 °C and 600 °C, and is associated with the degradation of the polymer backbone through chain scission processes [276]. This event is clearly reflected in the DTG curves by a pronounced peak, with the maximum degradation rate occurring between 552 °C and 569 °C, depending on composition. A progressive shift of the degradation onset towards higher temperatures is observed with increasing PEEK content, rising from approximately 525 °C for the 50PEEK-50PEI blend to around 546 °C for the 80PEEK-20PEI composition. This trend indicates an improvement in thermal resistance and is consistent with the high thermal stability of the PEEK-rich phase.

A second, broader mass loss region can be identified at higher temperatures and is associated with the degradation of thermally stable aromatic fragments and carbonaceous residues generated during the initial decomposition stage [258], [277]. The two-step nature of the degradation process becomes more evident when comparing the different compositions. In blends with higher PEI content, such as 50PEEK-50PEI and 60PEEK-40PEI, the secondary degradation stage is more clearly distinguishable, suggesting a greater contribution from thermally stable degradation products that persist to higher temperatures. The imide groups in PEI promote the formation of a thermally stable carbonaceous structure during the first degradation step, which then decomposes more slowly at higher temperatures. In contrast, the 80PEEK-20PEI sample exhibits a more dominant primary degradation step, while the

secondary stage appears less pronounced and is mainly observed as a gradual tailing of the mass loss curve.

Additional evidence for overlapping degradation mechanisms is provided by the slight asymmetry and shoulder formation observed in some DTG traces, particularly for the 70PEEK-30PEI composition, as support of the interpretation of overlapping degradation processes. These features are consistent with the partial superposition of the thermal decomposition processes of PEEK and PEI, which occur over similar but not identical temperature ranges. As a result, the individual degradation events are not fully resolved and appear as overlapping transitions within the overall thermogravimetric response [278], [279].

The degradation behaviour of the blends can therefore be described as a two-step process consisting of an initial rapid decomposition of the polymer chains followed by a slower degradation of the residual aromatic structures and carbonaceous products. Such behaviour is typical of high-performance aromatic polymer systems and indicates that, despite the physical blending of the two polymers, each component largely retains its characteristic thermal degradation pathway [280], [281].

All blends exhibit substantial char formation at elevated temperatures, with residual ashes of approximately 40-45% in all formulations. 50PEEK-50PEI and 60PEEK-40PEI tend to exhibit slightly higher residual masses, than the more PEEK-rich compositions, indicating compositional effects on the stability of the degradation products. While increasing PEEK content enhances resistance to the onset of thermal degradation, the resulting increase in thermal stability is not accompanied by a proportional increase in char yield. This observation suggests that the role of PEEK is primarily to delay decomposition, whereas the final residue is governed by the combined degradation pathways and carbonisation behaviour of both polymer phases [282].

The DSC thermograms of the 3D-printed PEEK-PEI blends exhibit the characteristic thermal transitions associated with both the semicrystalline PEEK phase and the amorphous PEI phase, with clear composition-dependent variations. In all formulations, the cooling curves display pronounced exothermic peaks corresponding to the crystallisation of PEEK, while cold crystallisation is observed during subsequent heating, indicating that crystallisation during cooling remains incomplete regardless of composition.

The 50PEEK-50PEI sample in Figure 63 exhibits a crystallisation peak centred at around 259 °C. Increasing the PEEK content to 60 wt% (Figure 64) and 70 wt% (Figure 65) shifts the crystallisation temperature to approximately 273 °C, while the reach of 80 wt% (Figure 66)

displays a further increase to approximately 282 °C. This trend suggests that higher PEEK concentrations promote more efficient crystallisation kinetics by increasing the availability of crystallisable chain segments and reducing the constraining effect of the amorphous PEI phase [185], [215], [225]. The persistence of cold crystallisation in all compositions indicates that a fraction of the PEEK phase remains amorphous after cooling and subsequently reorganises into crystalline structures during reheating. This behaviour is consistent with the rapid cooling conditions associated with the fused filament fabrication process, which can limit crystal growth and lead to kinetically constrained morphologies. Nevertheless, the gradual shift of the crystallisation peak towards higher temperatures with increasing PEEK content demonstrates that the ability of the material to crystallise during cooling improves as the proportion of the semicrystalline phase increases.

Comparison with the corresponding filament data further suggests that the thermal history imposed by the printing process influences crystallisation behaviour. Although the characteristic thermal transitions are preserved, the differences in crystallisation temperature and cold crystallisation response indicate that the repeated heating and cooling cycles experienced during printing modify the crystalline morphology developed within the PEEK phase.

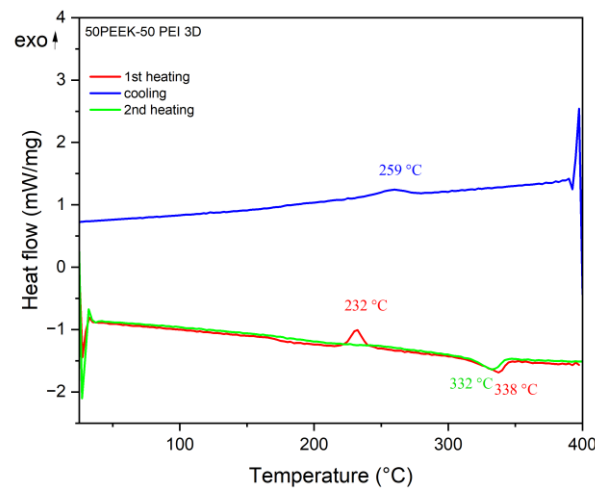


Figure 63: DSC of 50PEEK-50PEI 3D

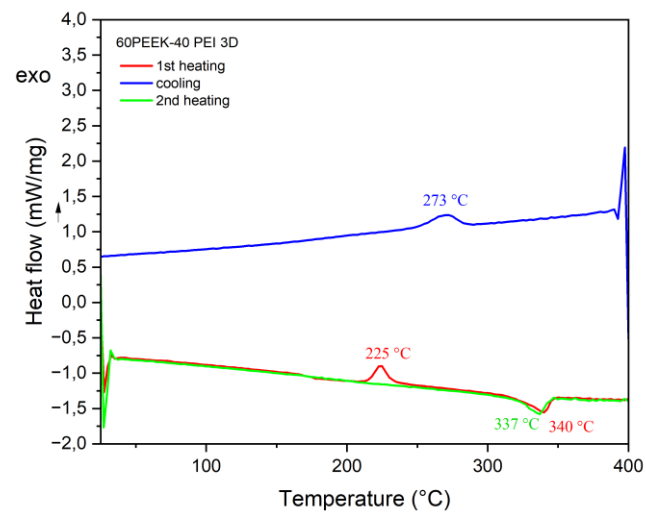


Figure 64: DSC of 60PEEK-40PEI 3D

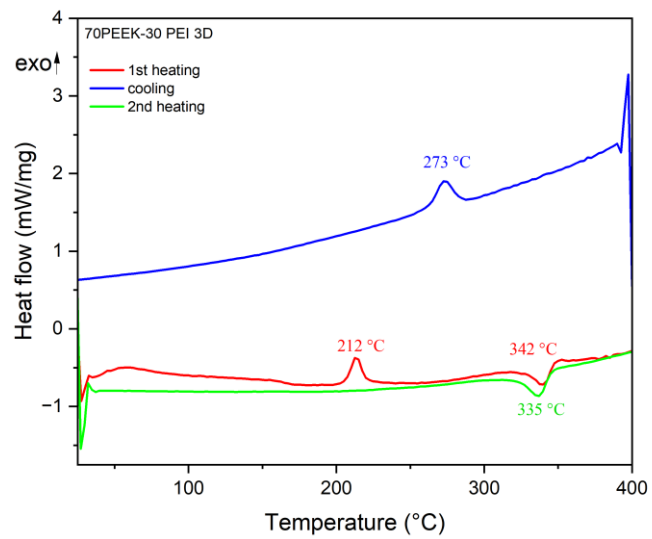


Figure 65: DSC of 70PEEK-30PEI 3D

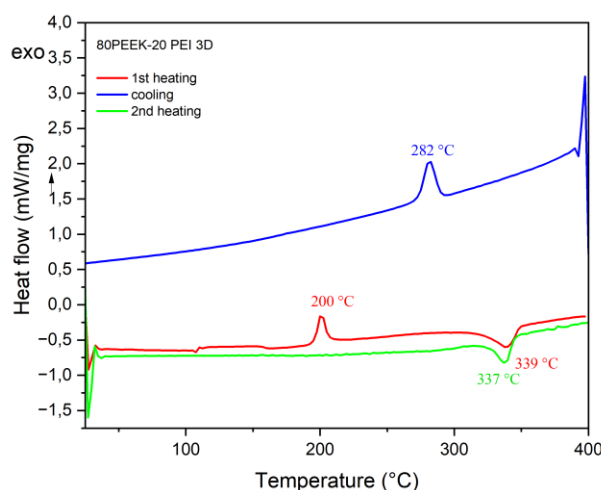


Figure 66: DSC of 80PEEK-20PEI 3D

The dominant endothermic transition observed in all formulations corresponds to the melting of the PEEK crystalline phase, with melting peaks consistently located between approximately 338 °C and 342 °C. The limited variation in melting temperature across the investigated compositions indicates that the crystal structure and lamellar characteristics of PEEK are not significantly affected by the relative PEI content. Although differences in peak intensity and shape are evident, reflecting variations in crystalline content, the melting temperature itself remains largely unchanged.

The second heating scans exhibit more stable and reproducible thermal transitions compared to the first heating cycle, indicating that the thermal history introduced during the fused filament fabrication process is largely removed after the initial DSC cycle. Consequently, the thermal events observed during the second heating are considered more representative of the intrinsic behaviour of the blends, allowing the influence of composition on crystallisation and melting processes to be evaluated independently of prior processing conditions. A comparative overview of the DSC responses for all investigated formulations is presented in Figure 67.

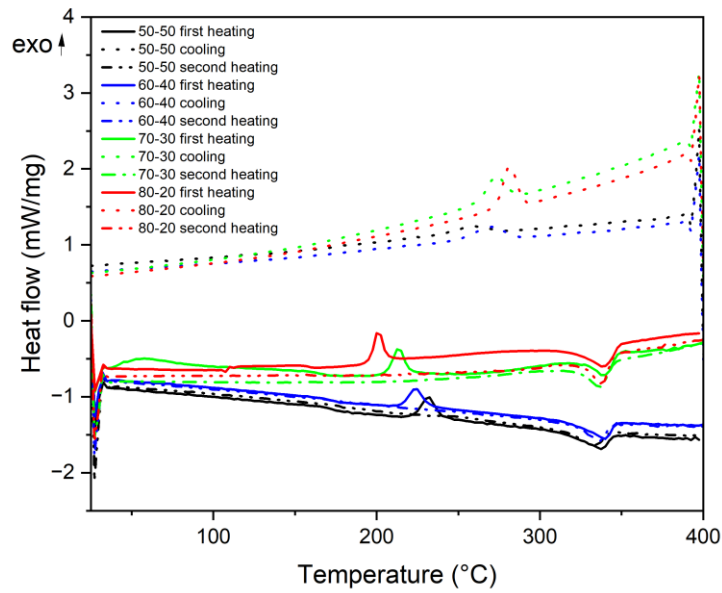


Figure 67: DSC comparison of 3D printed samples

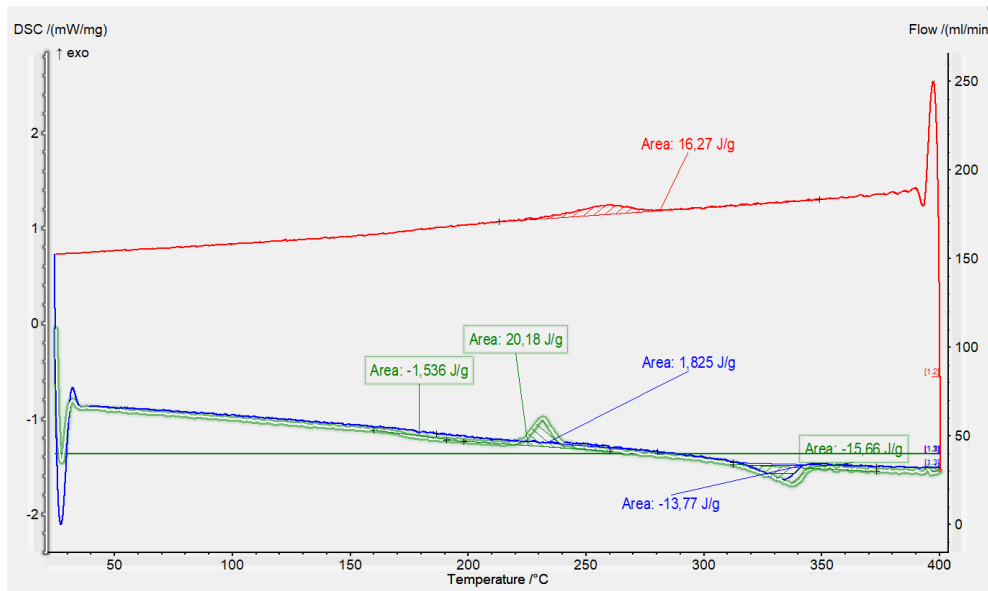


Figure 68: Thermal cycles of 50PEEK-50PEI 3D

For the 50PEEK-50PEI, the following values were obtained (Figure 68):

- $\Delta H_{M1} = 15.66 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 13.77 \text{ J/g}$ (second heating);
- $\Delta H_C = 16.27 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 20.18 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 1.536 \text{ J/g}$ (cold crystallisation);

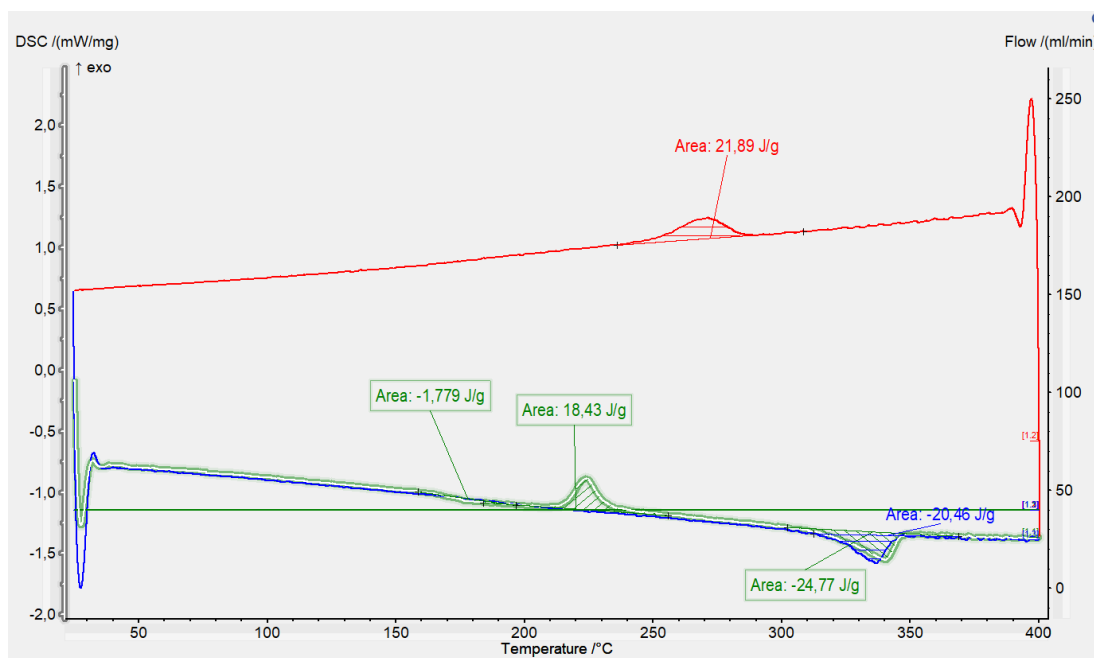


Figure 69: Thermal cycles of 60PEEK-40PEI 3D

For the 60PEEK-40PEI, the following values were obtained (Figure 69):

- $\Delta H_{M1} = 24.77 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 20.46 \text{ J/g}$ (second heating);
- $\Delta H_C = 21.89 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 18.43 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 1.779 \text{ J/g}$ (cold crystallisation);

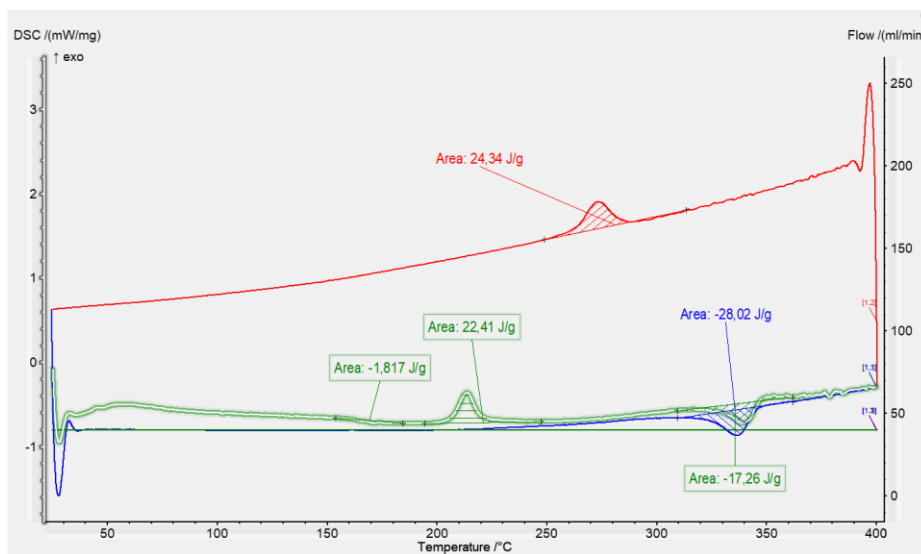


Figure 70: Thermal cycles of 70PEEK-30PEI 3D

For the 70PEEK-30PEI, the following values were obtained (Figure 70):

- $\Delta H_{M1} = 17.26 \text{ J/g}$ (first heating);

- $\Delta H_{M2} = 28.02 \text{ J/g}$ (second heating);
- $\Delta H_C = 24.34 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 22.41 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 1.817 \text{ J/g}$ (cold crystallisation);

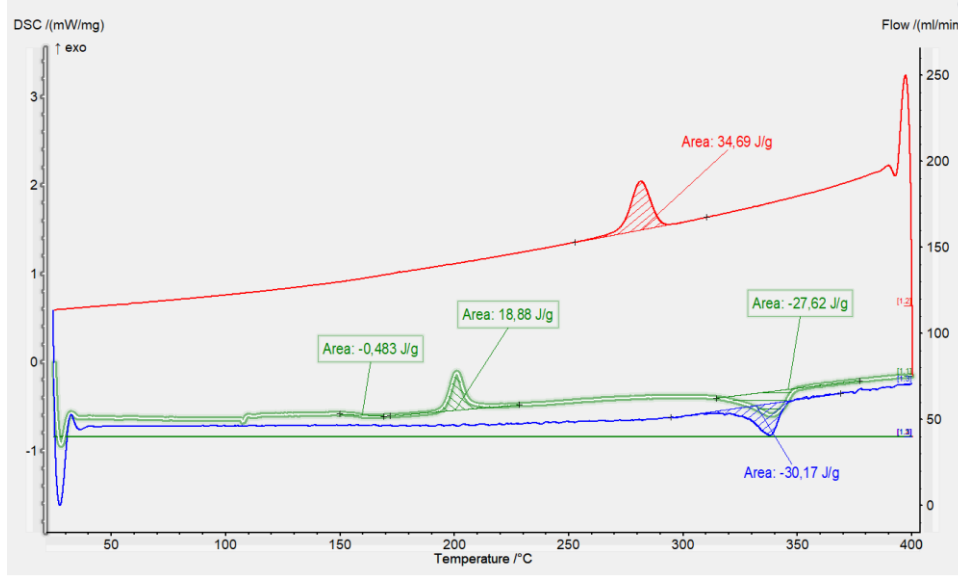


Figure 71: Thermal cycles of 80PEEK-20PEI 3D

For the 80PEEK-20PEI, the following values were obtained (Figure 71):

- $\Delta H_{M1} = 27.62 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 30.17 \text{ J/g}$ (second heating);
- $\Delta H_C = 34.69 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 18.88 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 0.483 \text{ J/g}$ (cold crystallisation);

All the calculated values are summarised in Table 9.

Table 9: DSC values of crystallinity 3D-printed samples

Formulation	ΔH_{M1}	χ_{M1}	ΔH_{M2}	χ_{M2}	ΔH_C	χ_C	ΔH_{CC}	χ_{CC}	ΔH_{EFH}	χ_{EFH}	T _g (°C)
50PEEK-50PEI	15.66 J/g	24.09%	13.77 J/g	21.18%	16.27 J/g	25.03%	1.536 J/g	2.36%	20.18 J/g	31.05%	170
60PEEK-40PEI	24.77 J/g	31.76%	20.46 J/g	26.23%	21.89 J/g	28.06%	1.779 J/g	2.28%	18.43 J/g	23.63%	169.1
70PEEK-30PEI	17.26 J/g	18.97%	28.02 J/g	30.79%	24.34 J/g	26.75%	1.817 J/g	2.00%	22.41 J/g	24.63%	158.4
80PEEK-20PEI	27.62 J/g	26.56%	30.17 J/g	29.01%	34.69 J/g	33.36%	0.483 J/g	0.46%	18.88 J/g	18.15%	153.9

The DSC results reported in Table 9 reveal significant differences in crystallisation behaviour compared to the filament data presented in Table 6, indicating that the fused filament fabrication process strongly substantially influences the thermal history and resulting

semicrystalline morphology of the PEEK phase [283]. The relatively low crystallinity values measured during the first heating cycle across all compositions suggest that the deposited material solidifies under highly non equilibrium conditions, where rapid cooling after extrusion suppresses the development of fully mature crystalline structures [284]. This effect is particularly evident for the 50PEEK-50PEI and 70PEEK-30PEI formulations, which exhibit comparatively low χ_{M1} values despite containing sufficient PEEK fractions to potentially achieve higher crystallinity under slower cooling conditions.

The differences between the first and second heating melting enthalpies further demonstrate that the as-printed morphology undergoes significant reorganisation during reheating [285]. In particular, the 70PEEK-30PEI and 80PEEK-20PEI blends exhibit χ_{M2} values that exceed χ_{M1} , indicating that additional crystallisation and crystal perfection occur during the first DSC cycle [239]. This behaviour is characteristic of semicrystalline polymers processed under rapid cooling conditions, where the crystalline structures initially formed may be imperfect or metastable and subsequently evolve towards more thermodynamically stable configurations during controlled heating [286]. The crystallinity developed during the cooling cycle remains moderate for all formulations and does not increase proportionally with PEEK content. This observation suggests that crystallisation kinetics remain constrained throughout the composition range investigated, even in the PEEK-rich blends. The presence of PEI therefore continues to influence chain mobility and crystal growth behaviour within the printed materials. Furthermore, during fused filament fabrication, each deposited layer is subjected to repeated thermal cycles resulting from the deposition of subsequent layers. These localised reheating events may alter crystallisation pathways by promoting secondary crystallisation in some regions while inhibiting crystal growth in others, leading to a heterogeneous thermal history throughout the printed structure [287].

The relatively low cold crystallization enthalpies measured for all formulations indicate that only a limited fraction of the amorphous phase remains sufficiently mobile to reorganise during reheating. This effect is particularly evident in the 80PEEK-20PEI blend, which exhibits the lowest χ_{cc} value, suggesting that a larger portion of crystallisation occurs during processing and cooling, leaving less residual amorphous material available for subsequent reorganisation [288].

The exothermic peak observed during the first heating cycle remains significant across all compositions, confirming the presence of thermally activated structural rearrangements within the printed material [289]. The relatively high χ_{EFH} values, particularly for the 50PEEK-50PEI and 70PEEK-30PEI formulations, suggest that a substantial portion of the crystalline

morphology formed during printing is imperfect and undergoes further reorganisation upon heating. Such processes may include crystal perfection, lamellar thickening, and secondary crystallisation, all of which contribute to the exothermic response observed prior to melting. To facilitate comparison between formulations with different PEEK contents, the crystallinity values were normalised with respect to the PEEK weight fraction according to Equation 4. The resulting values are reported in Table 10.

Table 10: Normalised crystallinity values with respect to the PEEK weight fraction according to Equation 4

Formulation	PEEK fraction	ΔH_c	$\Delta H_{c,norm}$	$X_{c,norm}$
50PEEK-50PEI	0.50	16.27 J/g	32.54 J/g PEEK	25.03%
60PEEK-40PEI	0.60	21.89 J/g	36.48 J/g PEEK	28.06%
70PEEK-30PEI	0.70	24.34 J/g	34.77 J/g PEEK	26.74%
80PEEK-20PEI	0.80	34.69 J/g	43.36 J/g PEEK	33.36%

After normalisation with respect to the effective PEEK content, the crystallisation behaviour of the 3D-printed samples reveals a significantly lower crystallisation efficiency compared to the corresponding filament materials. The normalised crystallisation enthalpies remain relatively low across all compositions, ranging from approximately 33 to 43 J/g PEEK, corresponding to normalised crystallinity values below $\sim 35\%$. These values are significantly lower than those typically reported for conventionally processed PEEK and indicate that crystals formation during printing is constrained by the processing conditions [237]. In contrast to the filament samples, where the normalised crystallisation enthalpy approached a plateau at intermediate and high PEEK concentrations, the printed materials exhibit a more gradual increase in $\Delta H_{c,norm}$ with increasing PEEK content. This behaviour suggests that, following 3D printing, the concentration of crystallisable PEEK plays a progressively greater role in determining the extent of crystal formation.

The increase observed for the 80PEEK-20PEI composition further suggest that, beyond a certain PEEK concentration, the constraints on crystallisation becomes less severe. This behaviour may be associated with the development of a more interconnected PEEK-rich phase which facilitates chain mobility and promotes crystal growth under the non-equilibrium conditions characteristic of fused filament fabrication. [290]. Nevertheless, the relatively low $\chi_{c,norm}$ values measured across all compositions indicate that crystallisation remains incomplete. Consequently, the printed microstructure is expected to retain a significant fraction of constrained amorphous material together with imperfect or partially developed crystalline domains, implying that the printed structure retains a substantial fraction of constrained amorphous material and imperfect crystalline domains [291].

These results demonstrate that the final crystalline morphology of the printed blends is governed not only by composition but also by the thermal history imposed during processing. While increasing the PEEK content improves crystallisation efficiency, the influence of rapid solidification and repeated thermal cycling remains dominant, limiting the extent to which the material can approach its equilibrium crystalline state.

The DMA result of the 3D-printed PEEK-PEI blends reveal a consistent viscoelastic response characterised by a high initial storage modulus (E') in the glassy region, followed by a pronounced decrease associated with the glass transition temperature (T_g) of the material. For all compositions, the storage modulus remains within the range of approximately 10^9 - 10^{10} Pa at low temperatures, indicating a stiff and consolidated structure typical of semi-crystalline PEEK-dominated systems. As the temperature increases, a gradual reduction in stiffness is observed, followed by a sharp decrease in E' as the polymer chains acquire sufficient mobility to undergo large scale segmental motion.

The $\tan\delta$ curves exhibit distinct peaks corresponding to the glass transition region of the blends. For the 50PEEK-50PEI (Figure 72) and 60PEEK-40PEI (Figure 73) compositions, the maximum of the $\tan\delta$ peak occurs at around ~ 195 - 196 °C. The relatively high transition temperature and the presence of a dominant relaxation peak suggest strong interactions between the PEEK and PEI phases and indicate that the segmental dynamics of the two polymers are substantially coupled within the blend. As the PEI content decreases, as in 70PEEK-30PEI in Figure 74 and 80PEEK-20PEI in Figure 75, the T_g shifts slightly downward to ~ 188 °C and ~ 181 °C, respectively. This trend reflects the increasing influence of the PEEK-rich phase on the overall viscoelastic response, resulting in enhanced chain mobility and an earlier onset of the glass transition. When the onset of the storage modulus reduction is used as the criterion for glass transition determination, T_g values of approximately 184 °C, 182 °C, 175 °C, and 170 °C are obtained for the 50PEEK-50PEI, 60PEEK-40PEI, 70PEEK-30PEI, and 80PEEK-20PEI formulations, respectively. The systematic decrease in both $\tan\delta$ peak temperature and E' onset temperature confirms that the thermos-mechanical response of the printed blends is strongly dependent on composition and reflects the progressive reduction in the constraining effect of the PEI phase as its concentration decreases.

The relatively narrow range of glass transition temperatures observed across the investigated compositions further suggests that the two polymers remain strongly associated after processing, although the gradual shift in T_g with composition indicates that the degree of phase interaction and local molecular organisation continues to evolve as the PEEK-PEI ratio

changes. These observations are consistent with the trends previously identified through DSC and FTIR analyses, which indicated that the fused filament fabrication process influences the microstructural arrangement of the blends while preserving their chemical integrity.

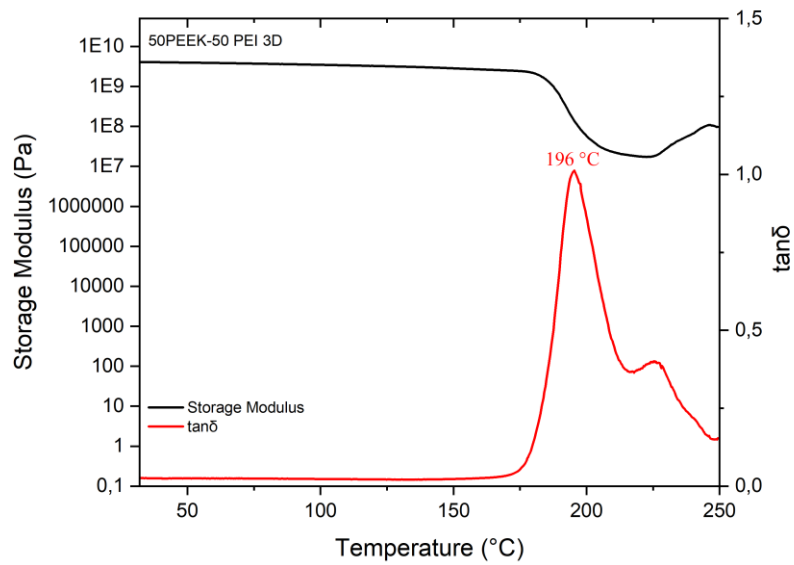


Figure 72: DMA of 50PEEK-50PEI 3D

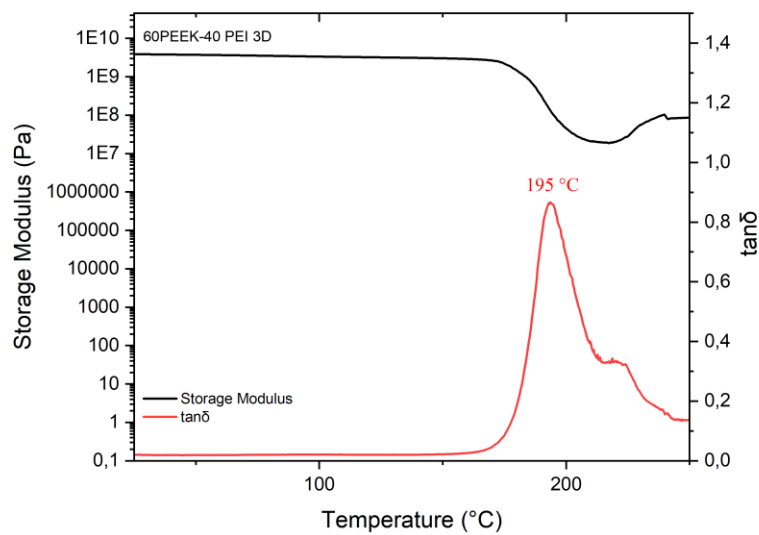


Figure 73: DMA of 60PEEK-40PEI 3D

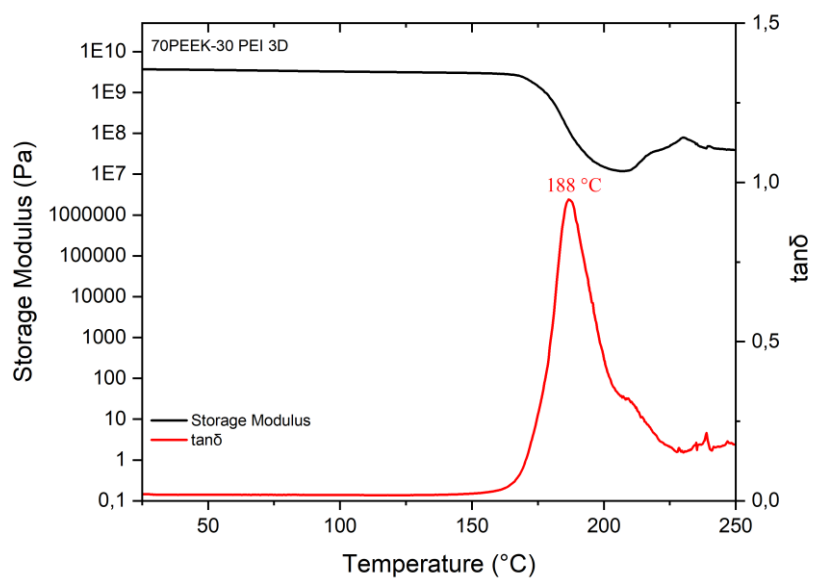


Figure 74: DMA of 70PEEK-30PEI 3D

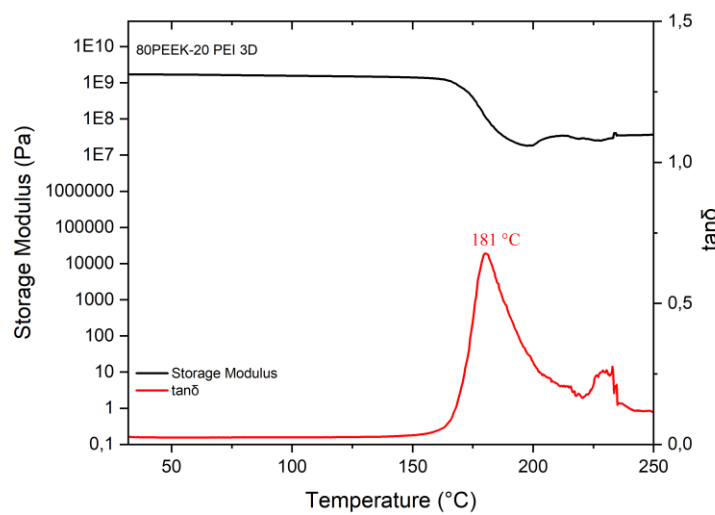


Figure 75: DMA of 80PEEK-20PEI 3D

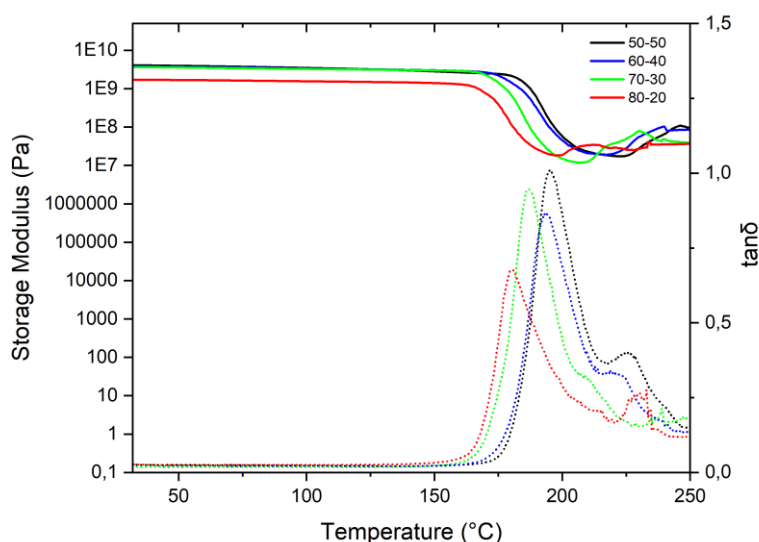


Figure 76: DMA comparison of neat 3D printed samples

A comparison of the DMA for all investigated formulations is presented in Figure 76. Both the magnitude and shape of the $\tan\delta$ peak vary systematically with composition. Blends containing higher PEI content exhibit broader and slightly more intense damping peaks, indicating a greater contribution from the amorphous phase and a wider distribution of relaxation times within the material [292]. This behaviour suggests increased heterogeneity in molecular mobility, which is consistent with the influence of the PEI-rich domains on the viscoelastic response.

Conversely, PEEK-rich samples show narrower $\tan\delta$ peaks with reduced intensity, reflecting the increasing influence of the semicrystalline phase on chain dynamics [167]. The presence of crystalline regions restricts segmental motion and reduces the energy dissipated during cyclic deformation, resulting in lower damping capacity. This interpretation is further supported by the storage modulus behaviour above the glass transition region, where the PEEK-rich formulations retain comparatively higher E' values. The persistence of a higher modulus at elevated temperatures indicates that the crystalline phase continues to provide structural reinforcement even after significant softening of the amorphous regions has occurred [293].

In several formulations, secondary relaxation features or shoulders are observed at temperatures above the principal $\tan\delta$ peak. These features suggest the presence of multiple relaxation processes and may be associated with phase heterogeneity, constrained amorphous regions, or local variations in molecular organisation generated during the fused filament fabrication process [294]. Such behaviour is consistent with the partial phase separation and microstructural complexity inferred from the DSC and FTIR analyses. The gradual reduction

in storage modulus with increasing temperature, together with the retention of measurable stiffness above T_g , indicates that the printed structures preserve a degree of load-bearing capability within the investigated temperature range. This behaviour is particularly relevant for high-temperature engineering applications, where resistance to thermomechanical softening is a critical performance requirement. The DMA results demonstrate that the thermomechanical response of the printed blends can be effectively tailored through adjustment of the PEEK-PEI ratio. Increasing the PEI content promotes higher glass transition temperatures and enhanced damping behaviour, whereas increasing the PEEK content improves stiffness retention and mechanical stability at elevated temperatures through the reinforcing effect of the semicrystalline phase [210].

To evaluate the mechanical properties of the blends, tensile tests were performed in order to determine the elastic modulus (Young's modulus, E), the tensile strength at break (σ), and the strain at break (ϵ). For this purpose, standard Type IV dog-bone specimens were manufactured for each formulation, as shown in Figure 77.



Figure 77: Dog-bone specimen Type IV

Five dog-bone samples per each formulation were tested. The averaged tensile properties are reported in Figure 78 and in Table 11.

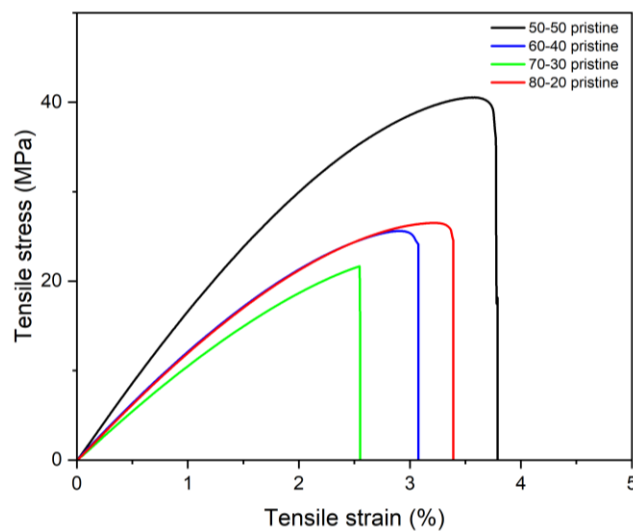


Figure 78: Averaged Tensile Tests 3D Printed Samples Comparison

Table 11: Tensile test averaged results 3D printed samples

Formulation	Elastic Modulus (E)	SD	Stress (σ)	SD	Strain (ϵ)	SD
50PEEK-50PEI	1.79 GPa	0.92 GPa	61.66 MPa	17.92 MPa	5.41%	1.55%
60PEEK-40PEI	1.71 GPa	0.64 GPa	68.83 MPa	20.66 MPa	5.74%	1.64%
70PEEK-30PEI	1.54 GPa	0.39 GPa	44.32 MPa	13.90 MPa	4.37%	1.24%
80PEEK-20PEI	1.60 GPa	0.71 GPa	60.89 MPa	15.34 MPa	5.39%	1.55%

Compared with the corresponding filament materials, the printed specimens exhibit substantially lower tensile strength and elongation at break, indicating that the printing process introduces structural weaknesses that are not present in the continuous extruded filament. Tensile strength decreases from approximately 43-69 MPa in the filament state to 21-41 MPa after printing. Such reductions are commonly reported for FFF manufactured polymers and are primarily attributed to imperfect interlayer adhesion, residual porosity, and incomplete molecular diffusion between adjacent deposited roads [295], [296], [297]. Unlike the filament, which behaves as a continuous structure under load, failure in printed specimens is strongly influenced by the quality of bonding between layers and raster lines.

Among the investigated formulations, 50PEEK-50PEI exhibits the highest tensile strength in the printed condition, suggesting that this composition develops the most effective interlayer bonding during deposition. The higher PEI content may enhance chain mobility and interfacial wetting, thereby promoting molecular diffusion across neighbouring filaments before solidification occurs [298]. This interpretation is consistent with the DSC results, which indicate that the presence of PEI moderates crystallisation during cooling. A slower crystallisation process increases the time available for interfacial healing and may reduce the formation of defects and voids within the printed structure [299]. Consequently, the material behaves more uniformly under tensile loading.

The 60PEEK-40PEI exhibits a markedly different behaviour. Although it provided the best mechanical performance in filament form, this advantage is largely lost after printing. This observation suggests that superior bulk material properties do not necessarily translate into superior performance in additively manufactured components. One possible explanation is that the crystallisation kinetics of this composition are sufficiently rapid to restrict interlayer diffusion during deposition, limiting the development of strong interfacial bonds before solidification occurs [300].

The 70PEEK-30PEI formulation still shows the weakest performance in the printed condition, consistent with its behaviour in the filament state. This consistency indicates that the reduced mechanical performance cannot be attributed solely to interlayer adhesion but is also related to the intrinsic morphology of the blend [252]. DSC analysis previously revealed a lower effective

fusion enthalpy and evidence of less efficient structural organisation. Following printing, these limitations are likely amplified by the introduction of additional processing-related defects, including porosity, thermal gradients, and imperfect interfacial fusion [254], [260].

The 80PEEK-20PEI samples exhibit a partial recovery in tensile strength relative to the 70PEEK-30PEI composition. This result indicates that increasing the PEEK content enhances the intrinsic load-bearing capability of the material through a greater contribution from the semicrystalline phase. However, high PEEK concentrations also promote crystallisation during deposition, which may reduce interlayer healing and prevent a proportional improvement in printed mechanical performance [301], [302].

These observations demonstrate that the mechanical response of the printed specimens is governed by the interaction of several competing factors. First, crystallinity contributes to local stiffness and strength within the PEEK-rich regions [303]. Second, the overall phase morphology determines whether these reinforcing domains form an interconnected network capable of efficiently carrying load [304]. Third, interfacial adhesion controls the transfer of stress both between deposited layers and across PEEK-rich and PEI-rich regions within the blend [305]. Consequently, mechanical performance cannot be interpreted solely on the basis of crystallinity.

The behaviour of the 70PEEK-30PEI composition is particularly informative in this regard. Despite exhibiting crystallinity levels comparable to some of the stronger formulations, its tensile properties remain significantly lower. This discrepancy suggests that the organisation and connectivity of the crystalline domains are more important than their absolute quantity. One possible explanation is that the blend approaches a morphological transition region in which the continuity of the phases changes. Under such conditions, crystalline PEEK domains may become insufficiently connected to provide effective reinforcement, while stress transfer across phase boundaries becomes less efficient [306]. As a result, the relationship between crystallinity and mechanical performance becomes partially decoupled.

This interpretation highlights the distinction between crystallinity and phase connectivity. Crystallinity describes the degree of molecular ordering within the PEEK domains, whereas phase morphology determines whether those ordered regions contribute effectively to the mechanical response of the bulk material. Consequently, the tensile modulus and strength are governed not only by the amount of crystalline material present, but also by the continuity of the reinforcing phase and the efficiency of stress transfer throughout the structure [307], [308]. From a shape-memory perspective, the 70PEEK-30PEI blend may be particularly interesting despite its comparatively poor tensile performance. The DSC results indicate a highly process-

sensitive and thermally responsive morphology, characterised by significant differences between the first and second heating cycles and evidence of extensive structural reorganisation during thermal cycling. Such behaviour suggests the presence of imperfect or constrained crystalline domains formed under non-equilibrium cooling conditions. In shape-memory polymers, these metastable crystalline structures can act as reversible switching domains that facilitate shape recovery through thermally activated reorganisation processes rather than purely elastic recovery mechanisms.

The combination of moderate crystallinity, pronounced thermal reorganisation, and apparent sensitivity to processing conditions suggests that the recovery behaviour of this composition may be highly tuneable through adjustments in cooling rate, annealing treatment, or printing parameters. Although the lower tensile strength and reduced structural stability may limit its use in load-bearing applications, these same characteristics could favour molecular rearrangement during thermal activation, potentially enhancing shape-memory performance.

The averaged three-point bending results are presented in Figure 79 and in Table 12. The data reveal a strong dependence flexural performance on blend composition, indicating that variations in the PEEK-PEI ratio significantly influence the stiffness, strength, and deformation behaviour of the printed structures.

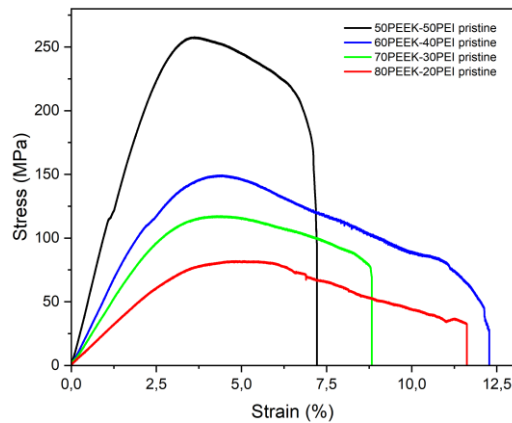


Figure 79: Average Three Point Bending 3D Printed Samples Comparison

Table 12: Three-point bending tests averaged results 3D-printed

Formulation	Elastic Modulus (E)	SD	Stress (σ)	SD	Strain (ϵ)	SD
50PEEK-50PEI	8.76 GPa	0.03 GPa	257.71MPa	75.64 MPa	7.10%	2.05%
60PEEK-40PEI	5.01 GPa	0.03 GPa	149.35MPa	35.96 MPa	12.28%	3.55%
70PEEK-30PEI	3.17 GPa	0.03 GPa	117.34MPa	28.79 MPa	8.80%	2.54%
80PEEK-20PEI	2.81 GPa	0.03 GPa	82.10 MPa	20.32 MPa	11.56%	3.34%

The 50PEEK-50PEI formulation exhibits the highest elastic modulus (8.76 GPa) and flexural strength (257.71 MPa), demonstrating the most efficient load-bearing capability among all investigated compositions. This behaviour suggests that the equal-ratio blend develops a highly effective microstructure during the printing process, characterised by strong interlayer bonding and efficient stress transfer throughout the specimen. The superior flexural properties are consistent with the tensile results, where the same formulation displayed the highest strength in the printed condition. Although the strain at failure remains comparatively low (7.10%), indicating a relatively brittle failure mechanism, the combination of high stiffness and high strength confirms that this composition provides the greatest resistance to bending deformation, exhibiting a lower elastic modulus (5.01 GPa) and flexural strength (149.35 MPa), while showing the highest strain at failure (12.28%). This behaviour indicates a more balanced mechanical response, where a reduction in stiffness is accompanied by increased deformation capability. The higher strain to failure suggests that this formulation dissipates energy more effectively during bending and undergoes more extensive deformation prior to fracture. Such behaviour is consistent with a more ductile response and may reflect a more compliant phase morphology compared with the 50PEEK-50PEI blend.

For the 70PEEK-30PEI formulation, the elastic modulus decreases further to 3.17 GPa, while the flexural strength reaches 117.34 MPa and the strain at failure is 8.80%. These values indicate a reduction in both stiffness and load-bearing efficiency relative to the more PEI-rich formulations. The results are consistent with the tensile analysis, which identified this composition as the mechanically weakest blend. The relatively modest strain at failure suggests that the reduction in strength is not compensated by a significant increase in ductility, indicating that the underlying morphology remains mechanically suboptimal.

The 80PEEK-20PEI composition exhibits the lowest elastic modulus (2.81 GPa) and flexural strength (82.10 MPa), despite maintaining a relatively high strain at failure (11.56%). This behaviour indicates a material that is capable of undergoing substantial deformation but possesses limited resistance to bending loads. Although the higher PEEK content would be expected to enhance the intrinsic stiffness of the polymer phase, the printed structure appears unable to translate these potential benefits into improved macroscopic performance. This observation suggests that factors such as interlayer adhesion, phase morphology, and structural continuity exert a stronger influence on flexural behaviour than composition alone.

When considered together with the tensile results, a clear trend emerges. The 50PEEK-50PEI formulation consistently exhibits the highest mechanical performance after printing, whereas increasing the PEEK content leads to a progressive reduction in stiffness and strength. This

behaviour contrasts with expectations based solely on the intrinsic properties of neat PEEK and indicates that the mechanical response of the printed blends is governed primarily by the microstructure developed during deposition rather than by the properties of the individual constituents. The DSC and DMA analyses suggest that higher PEI contents moderate crystallisation and promote more favourable interfacial interactions, thereby enhancing stress transfer and structural integrity in the printed state.

These results further support the conclusion that the optimal composition for additive manufacturing performance does not necessarily correspond to the composition with the highest intrinsic material strength. Instead, successful mechanical performance arises from the balance between crystallisation behaviour, phase morphology, and interlayer bonding established during the fused filament fabrication process.

3.2.4. Shape Memory Evaluation

To evaluate the shape-memory behaviour of the blends, rectangular specimens measuring 20 mm x 10 mm x 2 mm were fabricated by fused filament fabrication. The experimental procedure is illustrated in Figure 80.

The shape memory behaviour was activated firstly through direct thermal activation inside a Binder furnace at a switch temperature of 200 °C. The switch temperature is generally defined as $T_g + 20\text{ °C}$; once this temperature is reached, the shape memory effect can be activated. The samples were first heated to the switch temperature and then mechanically deformed into a U-bent configuration to fix the temporary shape. Subsequently, the specimens in the temporary configuration were reheated in the oven at 200 °C to recover their original permanent shape. The shape fixity ratio and shape recovery ratio were evaluated, with the blend exhibiting a shape recovery ratio of 97.12% and a recovery time of approximately 11 minutes.

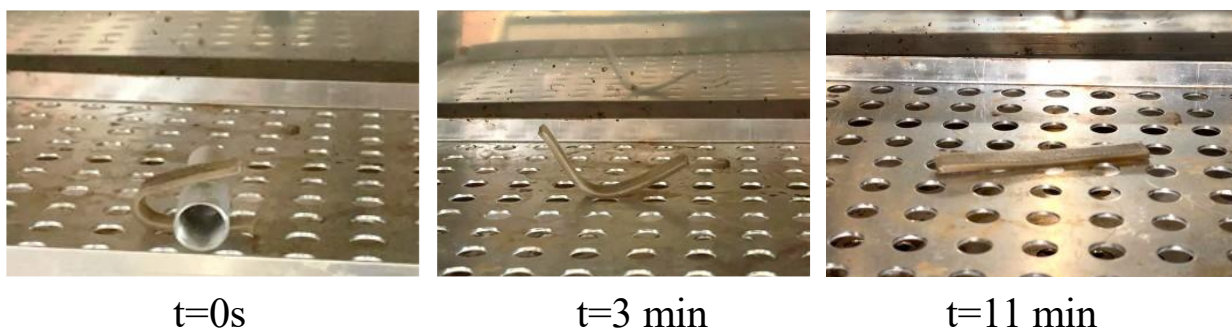


Figure 80: Shape memory on a blend 3D printed sample at 200°C

The experimental campaign was then carried out via direct heating, by placing the samples in an oven (Figure 81, Figure 82) at a temperature 20 °C above their glass transition temperature

(T_g), in order to activate polymer chain mobility, with a vacuum level of 10⁻³ mbar (Figure 83) with the set up in Figure 84. Subsequently, tests were performed using indirect heating, achieved by embedding resistive heaters, previously introduced in this study, during the additive manufacturing process.



Figure 81: Oven Binder VD 115

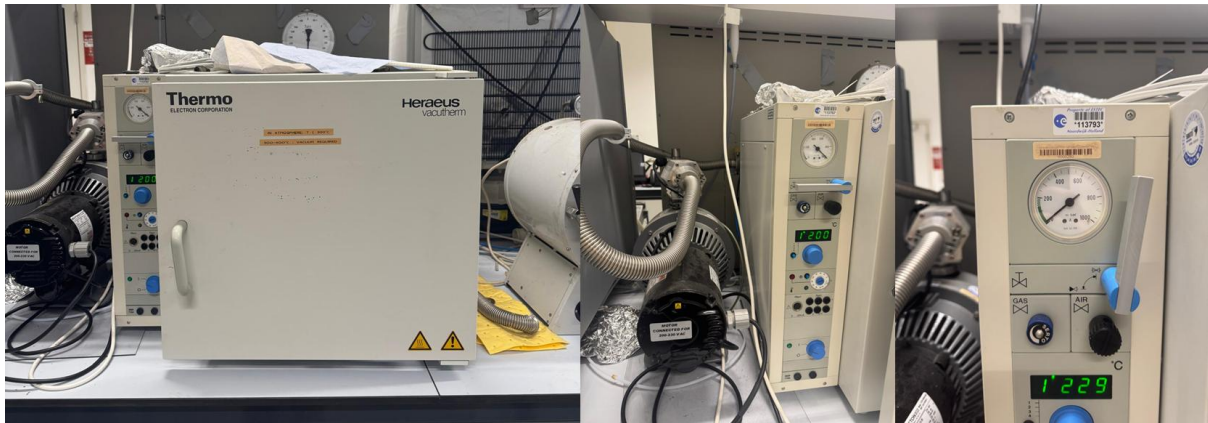


Figure 82: Oven Thermo-Electron Corporation (Thermofisher) Heraeus vacutherm UT6060

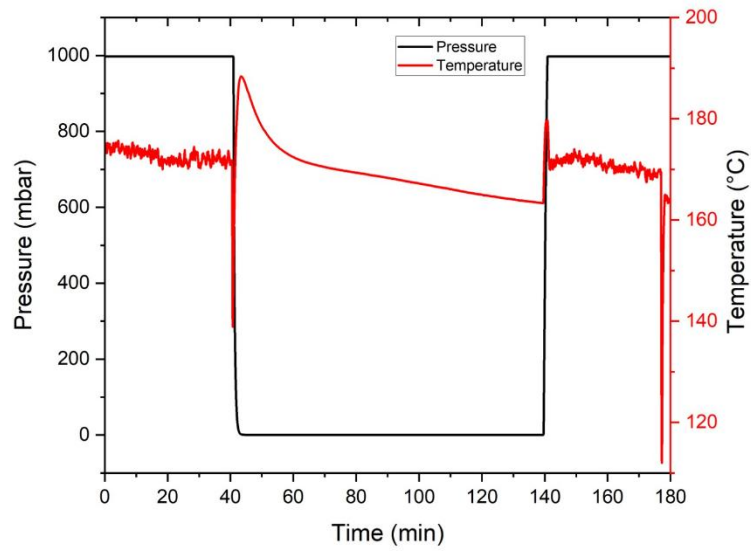


Figure 83: Vacuum level during the test



Figure 84: Shape Memory Test Set-up

Direct heating tests were conducted to preliminarily assess the material's effectiveness, ensuring an adequate response to the applied thermal stimulus while avoiding unnecessary use of high-cost components. This approach yielded satisfactory results, confirming the expected behaviour of the material, with a significant recovery of the original shape. Specifically, the

samples were first placed in the oven , where their initial straight configuration can be observed. Once the target temperature ($T_g + 20\text{ }^{\circ}\text{C}$) was reached, each specimen was removed and deformed into its temporary shape (Figure 85).



Figure 85: Sample forced to assume U-bent configuration

$T= 200^{\circ}\text{C}$

$p= \text{low vacuum } 1\text{E-}3\text{ mbar}$



$t_0=0\text{ s}$



$t_2=7\text{ min}$

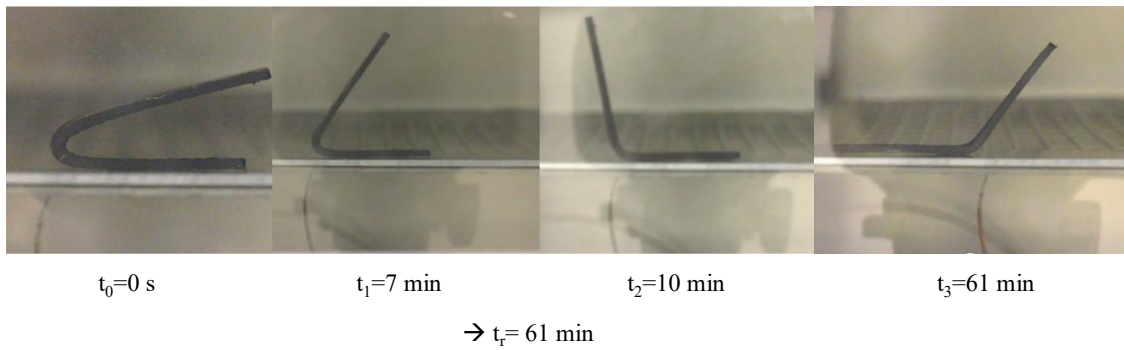


$t_3=13\text{ min}$

$\rightarrow t_r= 13\text{ min}$

Figure 86: Shape-Memory Behaviour of 50PEEK-50PEI

T= 175°C
p= low vacuum 1E-3 mbar



T= 200°C
p= low vacuum 1E-3 mbar

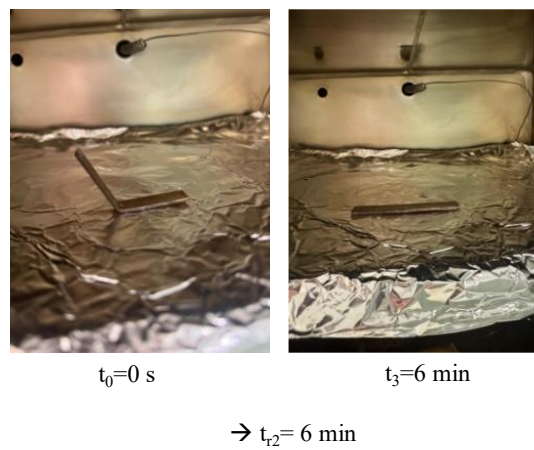


Figure 87: Shape-Memory Behaviour of 60PEEK-40PEI

T= 200°C
p= low vacuum 1E-3 mbar

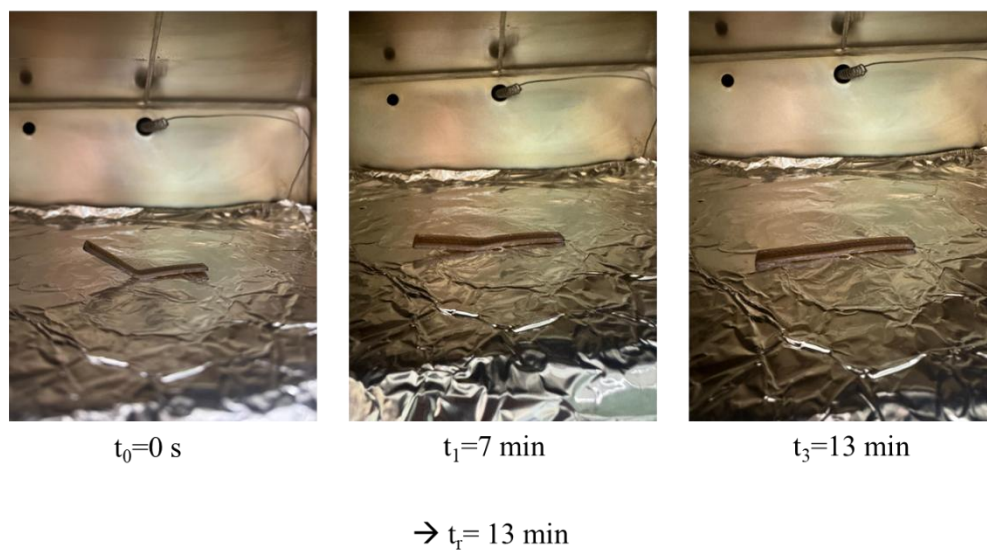


Figure 88: Shape-Memory Behaviour of 70PEEK-30PEI

T= 175°C
p= low vacuum 1E-3 mbar

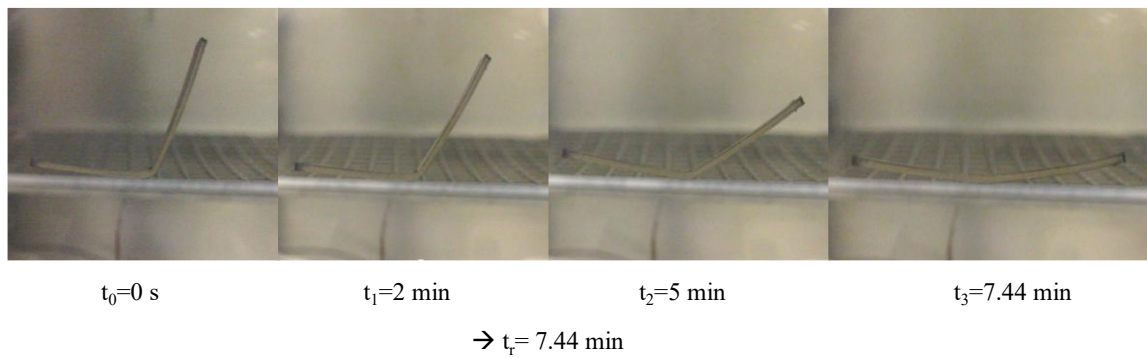


Figure 89: Shape-Memory Behaviour of 80PEEK-20PEI

After cooling and fixation of the temporary configuration, the samples were reheated to evaluate their ability to recover the permanent shape. Figure 86, Figure 87, Figure 88 and Figure 89 illustrate the different recovery stages.

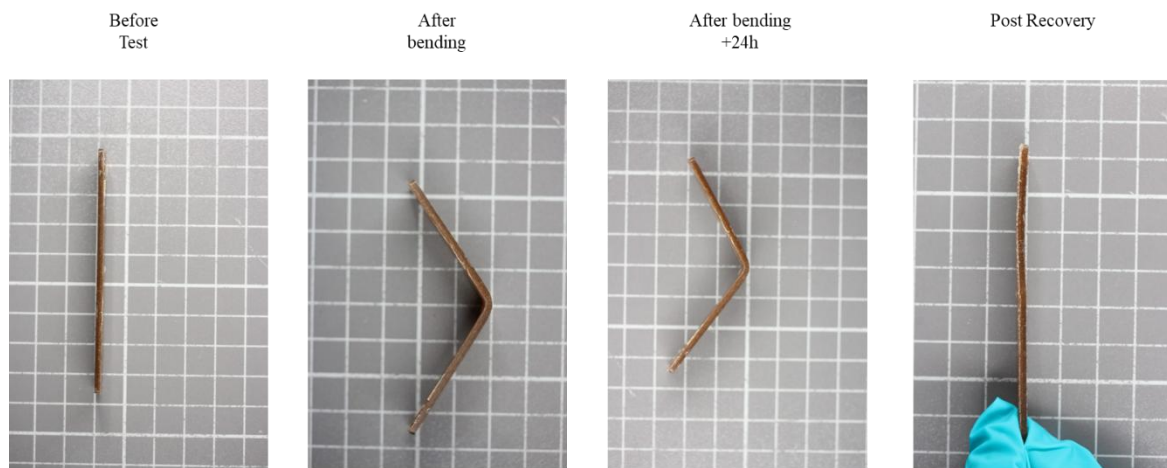


Figure 90: Shape Memory evaluation of 50PEEK-50PEI



Figure 91: Shape Memory evaluation of 60PEEK-40PEI

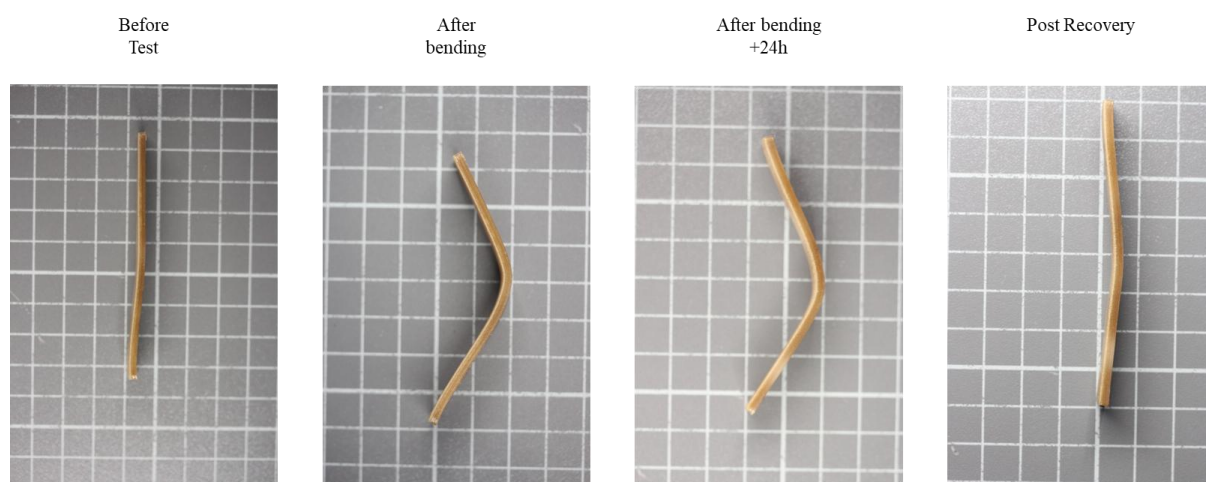


Figure 92: Shape Memory evaluation of 70PEEK-30PEI

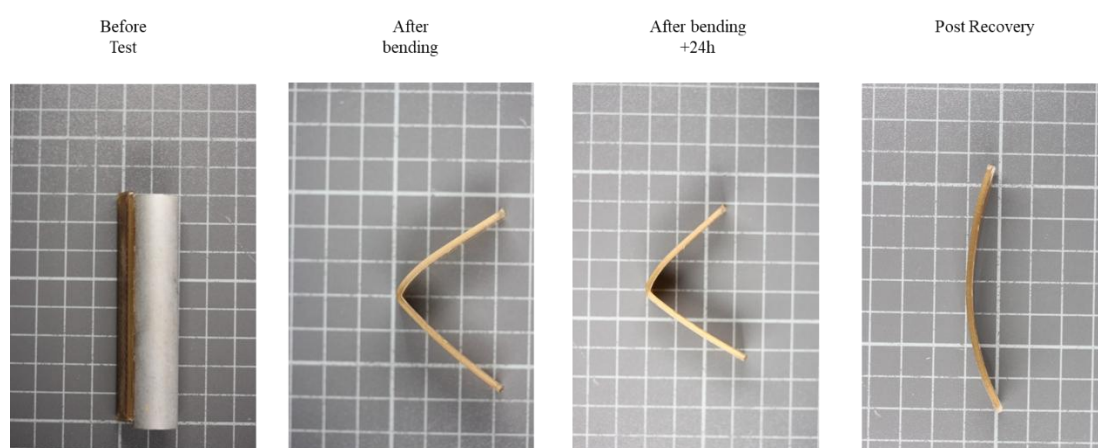


Figure 93: Shape Memory evaluation of 80PEEK-20PEI

To determine the optimal formulation, the Shape Fixity Ratio (R_f) and Shape Recovery Ratio (R_r) were analytically evaluated, along with the corresponding time intervals for each formulation. The results are summarized in Table 13 and Table 14.

Table 13: Summary of Shape-memory parameters on the tested samples

Formulation	θ_0	θ_u	θ_f	θ_r	R_f	R_r
50-50	0.439	113.005	1.058	2.371	99.064	98.924
60-40	1.246	16.707	0.813	8.804	95.134	95.772
70-30	2.325	124.832	1.811	11.076	98.549	95.075
80-20	0.641	73.726	5.336	28.731	92.762	84.339

Table 14: Shape memory parameters on the tested samples

Formulation	Rf	Rr	T Binder	T Heraeus	P (mbar)	t _r Binder	t _r Heraeus
50-50	99.1 %	98.9 %		200°C	1E-3		13 min
60-40	95.1 %	95.8 %	175°C	200°C	1E-3	61 min	6 min
70-30	98.5 %	95.1 %		200°C	1E-3		13 min
80-20	92.8 %	84.3 %	175°C		1E-3	7.44 min	

A strong correlation is observed between the shape-memory performance and the thermal and mechanical behaviour previously identified through DSC and tensile testing. This relationship indicates that the performance of the printed PEEK-PEI blends is governed by the balance between crystalline stabilisation, molecular mobility, and morphological organisation established during processing [309].

The 50PEEK-50PEI composition exhibits the highest shape memory performance, with both shape fixity and shape recovery approaching 99%. These results suggest that this composition provides an optimal balance between structural stability and chain mobility. The crystalline domains are sufficiently developed to stabilise the temporary shape, while the amorphous regions retain enough mobility to enable efficient recovery upon reheating.

The 60PEEK-40PEI formulation exhibits only a slight reduction in shape-memory performance while maintaining excellent fixity and recovery ratios. This behaviour is consistent with the more balanced crystalline-amorphous morphology identified by DSC analysis. The moderate crystallinity provides an effective physical network for shape fixity, whereas the remaining amorphous fraction facilitates the molecular rearrangements required for recovery [310].

Particularly noteworthy is the behaviour of the 70PEEK-30PEI blend. Despite exhibiting the weakest tensile properties among the investigated formulations, its shape-memory performance remains exceptionally high. This apparent discrepancy supports the interpretation that the morphology of this composition is thermally responsive rather than mechanically optimised. The high shape-fixity ratio indicates that the material contains sufficient crystalline or constrained domains to effectively stabilise the programmed configuration. At the same time, the recovery ratio exceeding 95% demonstrates that substantial reversible molecular mobility is preserved. The DSC results previously suggested the presence of imperfect or heterogeneously distributed crystalline structures formed under non-equilibrium cooling conditions. Such metastable domains may be particularly effective as switching segments in shape-memory applications, providing reversible thermal responsiveness while contributing

less effectively to conventional mechanical reinforcement [310]. This provides evidence that increasing crystallinity beyond an optimal level can become detrimental to shape-memory performance. Although this composition exhibits one of the highest levels of post-printing crystallinity, both shape-fixity and recovery performance decrease, with the recovery ratio falling to approximately 84.3%. This behaviour suggests that excessive crystallisation restricts the mobility of the amorphous phase during reheating. While the highly crystalline PEEK-rich structure provides effective fixation of the temporary shape, the reduced molecular mobility limits the ability of the material to fully recover the stored deformation. Furthermore, the lower effective fusion enthalpy observed for this composition may indicate reduced structural continuity within the printed microstructure, potentially hindering cooperative strain release during recovery [297].

The shape-memory results therefore demonstrate that optimal performance is achieved not at maximum crystallinity, but at an intermediate morphological state where crystalline domains provide sufficient physical stabilisation while the amorphous phase retains adequate mobility for thermally activated recovery. This finding is consistent with established shape-memory polymer theory and highlights the importance of balancing structural rigidity and molecular freedom when designing PEEK-PEI systems for functional applications.

To investigate a more practical activation strategy, shape-memory recovery was also evaluated using embedded resistive heaters integrated directly during the additive manufacturing process. Figure 94, shows the fabricated specimen incorporating the heater supplied by Zoppa Industries (*Zoppa Industries, Treviso, Italy*). The heater was powered using a transformer delivering 8.7 V, generating sufficient thermal energy to activate the shape-memory response.

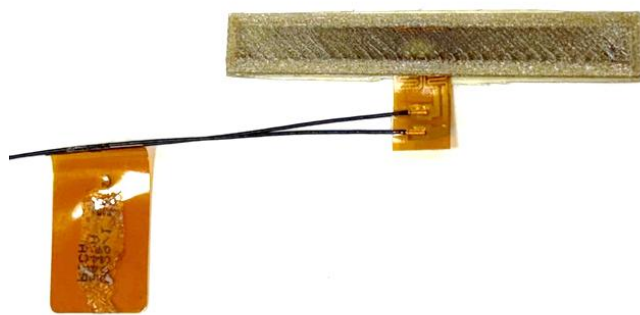


Figure 94: Blend with embedded heater

However, the experimental results demonstrated that the embedded-heating approach was not able to produce complete shape recovery. Although the heater itself reached the target

activation temperature, thermal imaging revealed that the temperature at the external surface of the specimen remained significantly lower than required for effective activation of the shape-memory effect. The low thermal conductivity and insulating nature of the PEEK-PEI blends limited heat transfer from the embedded resistive element to the surrounding material, resulting in a non-uniform temperature distribution throughout the specimen.

Consequently, the polymer matrix did not uniformly exceed the activation temperature necessary to induce sufficient molecular mobility within the switching phase. As a result, only partial recovery was observed, and the shape-memory response was considerably less effective than that obtained through direct thermal activation in the oven.

Thermal images presented in Figure 95 confirm this behaviour, showing that heat remained concentrated in the vicinity of the embedded heater while the outer regions of the specimen remained at substantially lower temperatures.



Figure 95: Thermal camera images of shape-memory recovery

These results indicate that, in its current configuration, the embedded-heater system is insufficient to achieve complete and reliable shape-memory activation. Future developments should focus on improving heat distribution within the structure through optimisation of heater geometry, increased power input, multiple heating elements, or the incorporation of thermally conductive additives capable of enhancing heat transfer throughout the polymer matrix. Despite the unsuccessful recovery performance, the study provides valuable insight into the thermal limitations associated with embedded actuation systems in highly insulating high-performance polymer blends.

3.3. Conclusions

This chapter investigated the development and processing of PEEK-PEI blends for their application 4D printing. Four formulations, namely 50PEEK-50PEI, 60PEEK-40PEI, 70PEEK-30PEI, and 80PEEK-20PEI, were produced and systematically characterised in terms

of chemical structure, thermal stability, rheological behaviour, thermal transitions, viscoelastic properties, mechanical performance, and shape-memory response.

The preliminary characterisation confirmed the preservation of the characteristic chemical structures of both PEEK and PEI. FTIR analysis of the blends and of the processed filaments did not reveal the formation of new chemical bonds or significant changes in the characteristic absorption bands, indicating that the compounding and extrusion processes did not induce detectable chemical reactions between the two polymers.

The rheological characterisation demonstrated that all investigated formulations were compatible with filament extrusion and subsequent FFF processing.

Thermogravimetric analysis confirmed the high thermal stability of all formulations. The blends exhibited multi-stage degradation behaviour associated with the different degradation pathways of the PEEK and PEI phases, while substantial thermal stability was maintained up to temperatures well above those required for the extrusion and printing processes. The results therefore confirmed that the developed materials possess the thermal resistance required for high-temperature processing and for subsequent investigation under demanding environmental conditions.

The DSC analysis highlighted the strong influence of blend composition on the crystallisation behaviour of the PEEK phase. The presence of the amorphous PEI phase restricts PEEK chain mobility and consequently affects nucleation and crystal growth during cooling. Increasing the PEEK content generally promoted crystallisation and shifted the crystallisation temperature towards higher values. At the same time, the presence of cold crystallisation during subsequent heating demonstrated that a significant fraction of the PEEK phase remained amorphous or imperfectly organised after cooling. The melting temperature remained relatively constant across the investigated compositions, indicating that the fundamental crystal structure of PEEK was not substantially altered by the presence of PEI.

A similar influence of composition and processing history was observed after FFF. The printed specimens exhibited lower crystallisation efficiency than the corresponding filament materials, confirming that the rapid cooling and repeated thermal cycles associated with material deposition limit the development of fully developed crystalline structures. The resulting microstructure therefore consists of a combination of crystalline PEEK domains and constrained amorphous regions, with the balance between these phases depending on both composition and processing conditions.

DMA measurements further demonstrated that the blends retain a high degree of stiffness in the glassy state and exhibit a clear transition associated with increased molecular mobility. The glass transition region shifted towards lower temperatures with increasing PEEK content, while the damping behaviour indicated differences in molecular mobility and phase organisation among the formulations. These observations, together with the FTIR and DSC results, indicate that the PEEK-PEI system exhibits composition-dependent morphological and viscoelastic behaviour without evidence of major chemical modification during processing.

The mechanical characterisation of the printed specimens demonstrated that the properties of the final components cannot be predicted solely from the intrinsic properties of the individual polymers. The tensile strength of the printed specimens was substantially lower than that measured for the corresponding continuous filaments, highlighting the influence of FFF-induced features such as interlayer adhesion, porosity, thermal gradients, and incomplete molecular diffusion between adjacent deposited roads. The results therefore demonstrate that the thermal history and phase morphology developed during printing are critical factors governing the final mechanical performance.

Interestingly, the mechanical behaviour did not follow a simple trend with increasing PEEK content. Although a higher PEEK fraction can favour the formation of crystalline domains, excessive or poorly interconnected crystallinity does not necessarily translate into improved mechanical properties in the printed structure. Instead, effective stress transfer depends on the morphology and continuity of the crystalline phase, as well as on the quality of interlayer bonding.

The shape-memory experiments demonstrated that all four formulations were capable of exhibiting a pronounced thermally activated shape-memory response. The 50PEEK-50PEI formulation showed the highest overall performance, with a shape-fixity ratio of approximately 99% and a shape-recovery ratio of approximately 99%. The 60PEEK-40PEI and 70PEEK-30PEI formulations also exhibited high shape-recovery capabilities, with recovery ratios above 95%, while the 80PEEK-20PEI formulation showed a lower recovery performance. These results indicate that shape-memory behaviour is not directly correlated with maximum crystallinity or mechanical strength, but rather depends on the balance between crystalline domains, which provide structural stabilisation, and the amorphous phase, which enables molecular rearrangement during thermal activation.

The experiments using an embedded resistive heater further demonstrated the challenges associated with indirect thermal activation of highly insulating PEEK-PEI structures. Although the embedded heater reached the required activation temperature, heat transfer through the

polymer matrix was insufficient to uniformly heat the external surface above the temperature required for complete shape recovery. As a consequence, only partial recovery was obtained. This result highlights the importance of thermal management and heat distribution when designing integrated actuation systems for 4D-printed high-performance polymer structures. These findings provide the basis for the subsequent investigation of the developed PEEK-PEI materials under simulated space conditions, with particular emphasis on their stability and functional performance following exposure to the environmental conditions relevant to space applications.

Chapter 4. Investigating Simulated Space Conditions

In this chapter, investigation on the survivability of the PEEK-based blends were performed on four different formulations.

The experimental campaign has been conducted during a three months stay at the European Space Research and Technology Centre (ESTEC, Noordwijk, the Netherlands) of the European Space Agency (ESA), in the Materials & Electrical Components Laboratory of the Materials, Environment and Contamination Section (TEC-MSE).

4.1. Experimental

4.1.1. Camera Canon 700D



Figure 96: Canon 700D and macro lens

The samples were photographed before and after the various tests using a Canon 700D camera fitted with an EF-S 60 mm f/2.8 USM macro lens. The laboratory setup involving the Canon 700D is shown in Figure 97.

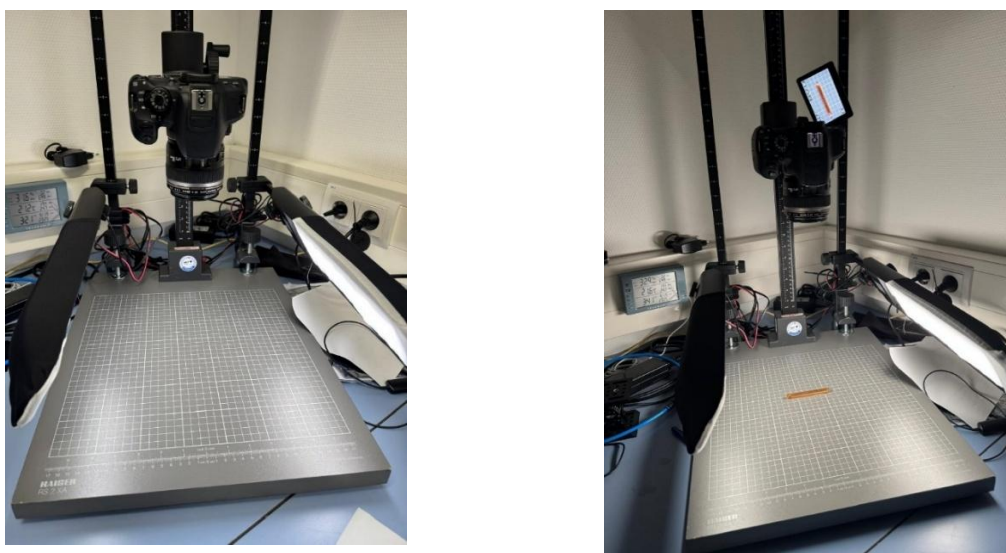


Figure 97: Camera setting

4.1.2. 3D Profilometer (Keyence VR 5000)

A laser measurement is a technique in which a device emits a pulse of laser light toward a target and determines the distance by measuring the time taken for the reflected signal to return. The *Keyence VR-5000* (Figure 98) is a non-contact 3D measurement system capable of rapidly and accurately scanning large areas. It is used to evaluate parameters such as profile, surface roughness, flatness, and wear volume, as well as to compare 3D scan data with digital CAD models to assess whether a component meets specifications.



Figure 98: Keyence VR 5000 [311]

All four developed formulations were analysed using the Keyence 3D profilometer (Figure 99). A comparison between pristine samples and those subjected to ATOX treatment was carried out to assess the effects of atomic oxygen exposure.



Figure 99: Samples being tested in the Keyence VR5000

Surface roughness was evaluated on the samples by considering a set of key parameters that describe different aspects of surface topography. The arithmetical mean height (S_a) represents

the average of the absolute deviations of the surface profile from the mean plane, providing a general indication of surface roughness.

- The maximum height of the surface (S_z) defines the total vertical range between the highest peak and the deepest valley. It is calculated as the sum of the maximum peak height (S_p) and the maximum valley depth (S_v), according to the relation $S_z = S_p + S_v$. This parameter is particularly sensitive to outliers, as the presence of deep scratches or isolated spikes can significantly affect the measured value.
- The texture aspect ratio (Str) characterizes the uniformity of the surface texture by comparing the fastest and slowest decay distances of the autocorrelation function. Its value ranges from 0 to 1, where values close to 0 indicate a highly directional (anisotropic) texture, while values approaching 1 correspond to isotropic surfaces with uniform roughness in all directions. This parameter is especially useful for identifying directional features such as machining marks or anisotropy resulting from additive manufacturing processes.
- The arithmetic mean peak curvature (Spc) provides information on the sharpness of surface peaks by averaging their principal curvatures within the analysed area. Higher Spc values indicate sharper peaks, whereas lower values correspond to broader and more rounded features. This parameter plays an important role in determining surface behaviour in terms of friction, wear, lubrication, and overall functional performance.
- Finally, the developed interfacial area ratio (Sdr) quantifies the increase in the actual surface area relative to a perfectly flat projected area. Values close to zero indicate nearly flat surfaces, while higher values correspond to increasingly complex and rough textures. This parameter is widely used in the study of coatings, adhesion, wetting phenomena, and the characterization of surfaces produced by additive manufacturing.

All the described parameters are illustrated in Figure 100.

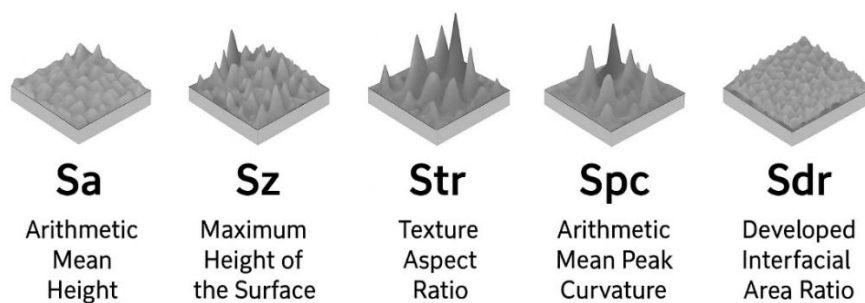


Figure 100: Surface roughness parameters

4.1.3. Balance

The samples were weighed using a Sartorius ME5 analytical balance (Figure 101).

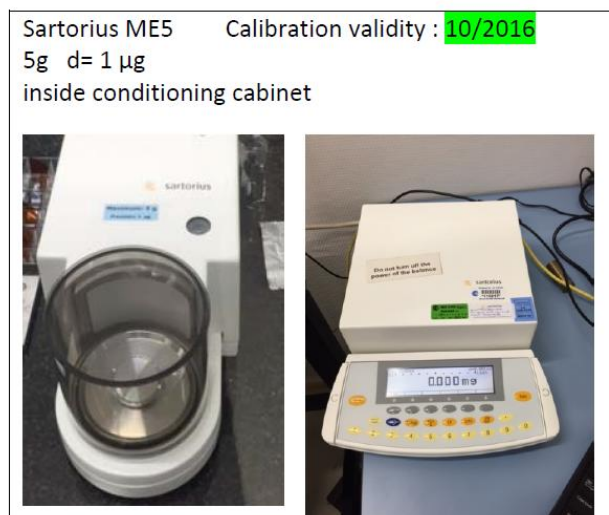


Figure 101: Sartorius balance

4.1.4. Outgassing

The outgassing test was performed using a Micro Volatile Condensable Material (mVCM) apparatus, in accordance with the ECSS-Q-ST-70-02C standard, “Thermal vacuum outgassing test for the screening of space materials” [312].

The mVCM system (Figure 102) consists of a vacuum chamber equipped with two thermally controlled mounting trays. The tray holding the material samples can be heated up to +250 °C, while the tray supporting the collectors is maintained at +25 °C. The collectors, made of aluminium and coated with chromium, are used to capture condensable species released during outgassing. The chamber can also be flushed with dry nitrogen at controlled pressure.

The facility accommodates up to 18 sample cups and 18 collector plates, allowing the simultaneous testing of up to five materials (three replicates per material plus three blanks). In the present case, four different formulations were tested simultaneously, as illustrated in Figure 104 and Figure 105.

The analysis involves weighing both the samples and the collectors before and after the thermal vacuum test to determine the outgassing parameters: Total Mass Loss (TML), Recovered Mass Loss (RML), Water Vapor Regained (WVR), and Collected Volatile Condensable Material (CVCVM). Measurements were carried out using a Sartorius microbalance (Sartorius ME5, *Sartorius AG, Göttingen, Germany*) located inside a humidity-controlled conditioning cabinet. The environmental conditions were maintained at 22 ± 3 °C and $55 \pm 10\%$ relative humidity, monitored by a calibrated sensor. A saturated sodium bromide (NaBr) solution in deionised

water was used to regulate humidity within the cabinet. Access was controlled via a door that remained closed between operations to ensure stable conditions.

Nickel cups were first weighed and placed in a holder inside the cabinet. Three cups were left empty as blanks, while three cups were allocated for each material. Each cup was filled with a sample mass between 100 and 300 mg. Prior to testing, the prepared samples were conditioned inside the cabinet for 24 hours.

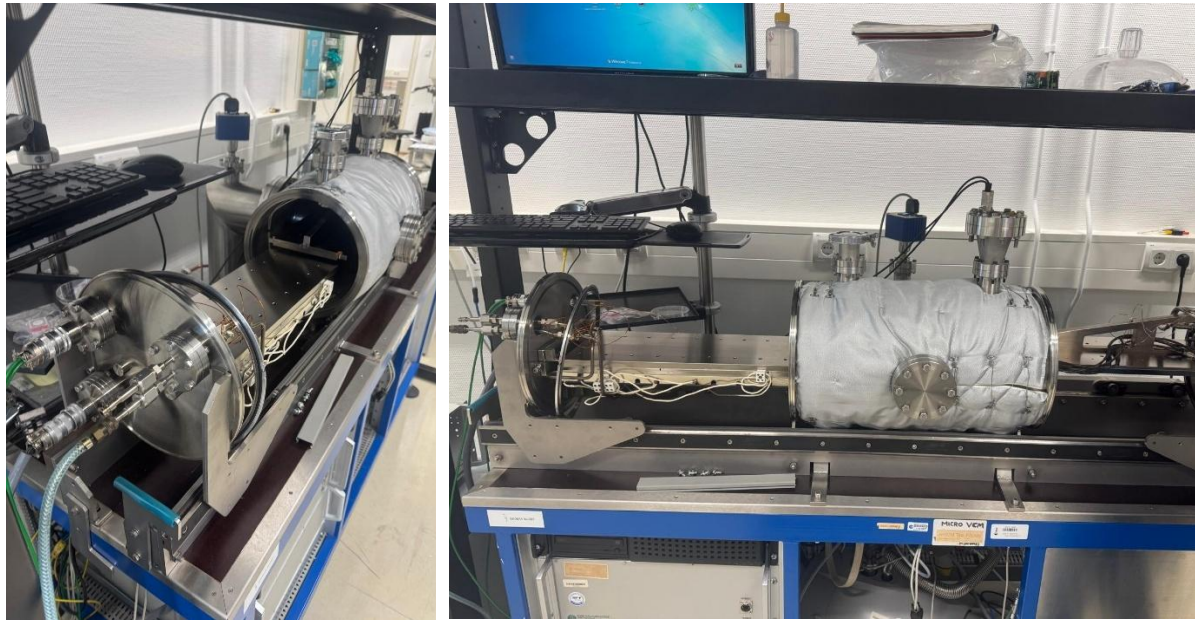


Figure 102: mVCM

After 24 hours, the material samples and collectors are weighed again. The collectors are then placed in a holder (Figure 103) and stored inside a desiccator containing 500 g of silica gel to maintain a dry environment. Subsequently, both the collectors and the sample cup holder are transferred to the mVCM system for testing.

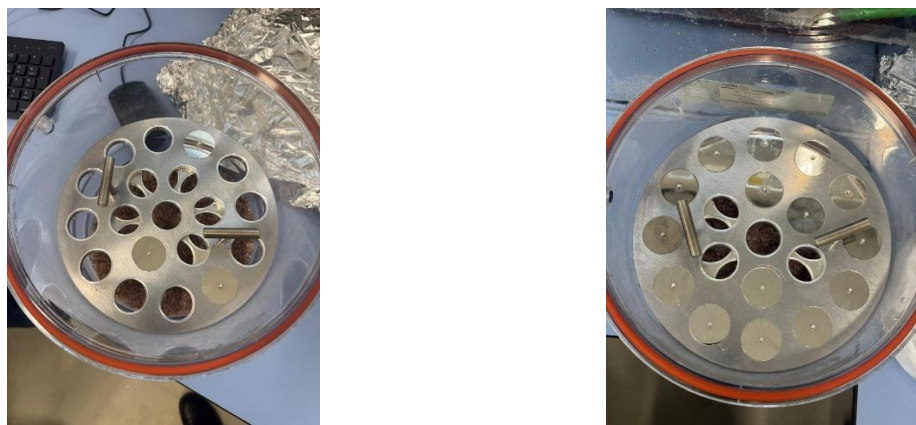


Figure 103: Collectors

The mVCM chamber is then opened and loaded with the samples. The correct arrangement of the samples is illustrated in Figure 104, while the materials tested are shown in Figure 106.

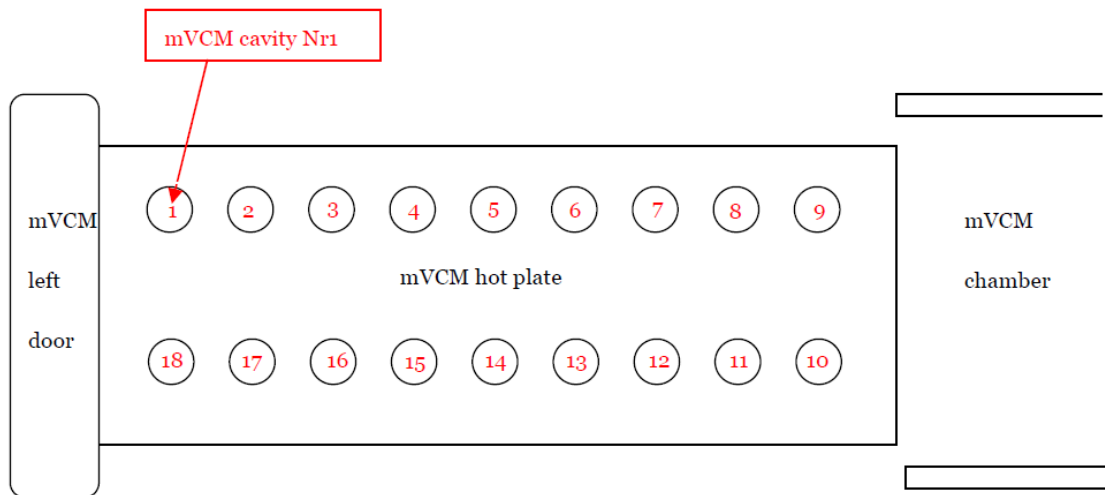


Figure 104: mVCM sample disposition

The collectors are then put inside the chamber, using the correct arrangement shown in Figure 105, and the test set up is depicted in Figure 107.

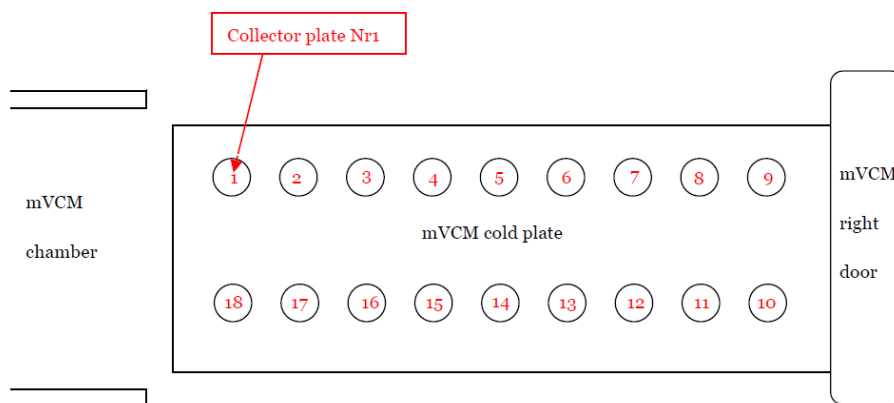


Figure 105: mVCM collector plate disposition

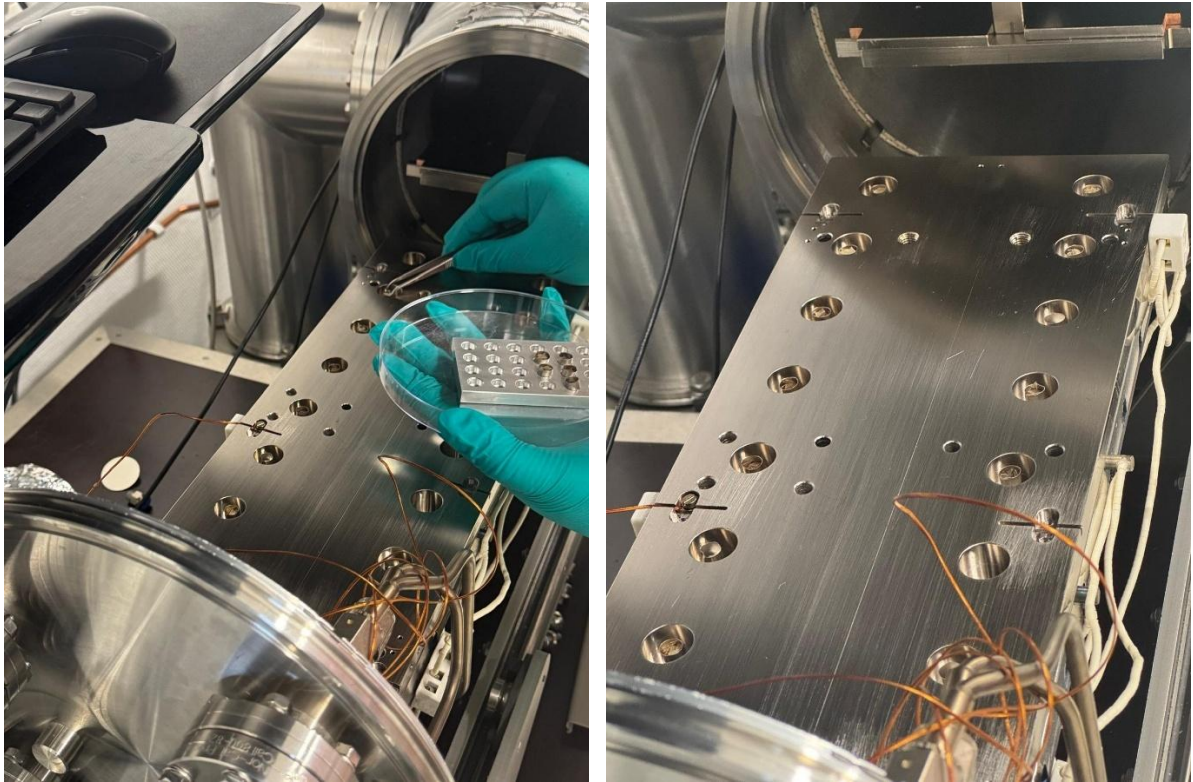


Figure 106: Sample arrangement inside the mVCM

Once the top plates were installed and secured with screws, the chamber was sealed, allowing the test to begin.

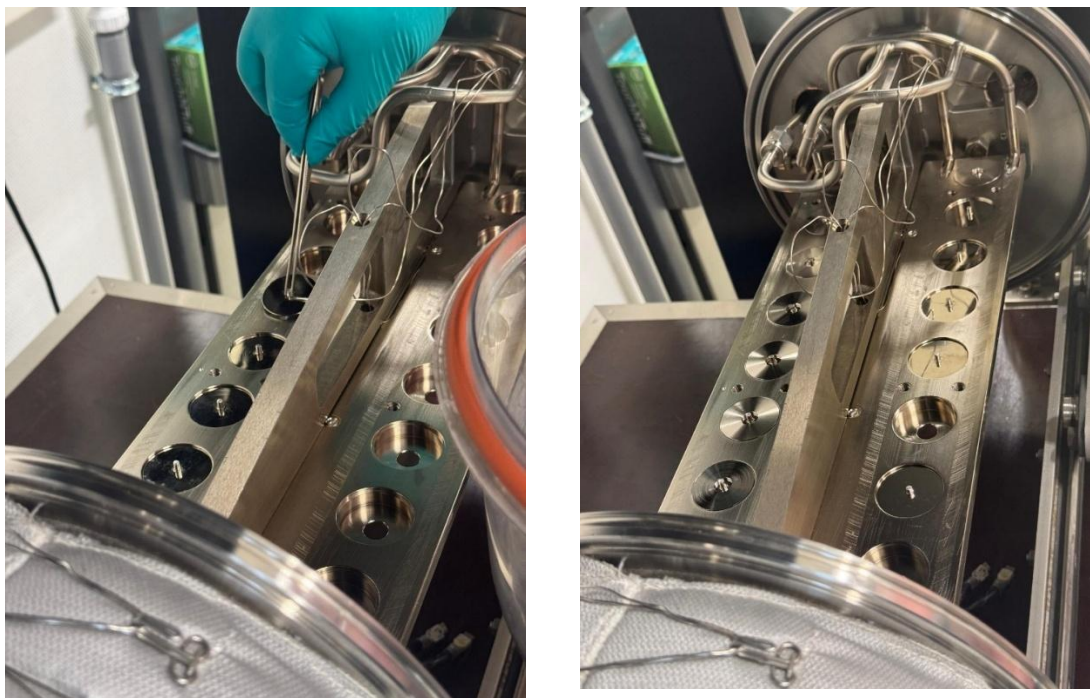


Figure 107: Collectors arrangement

A target temperature of 123.5 °C (equivalent to an actual temperature of 125 °C) was set in the thermal control program, and a pressure of 1×10^{-5} mbar was achieved. The system was maintained for 24 hours, keeping the hot plate at 125 °C and the cold plate at 25 °C.

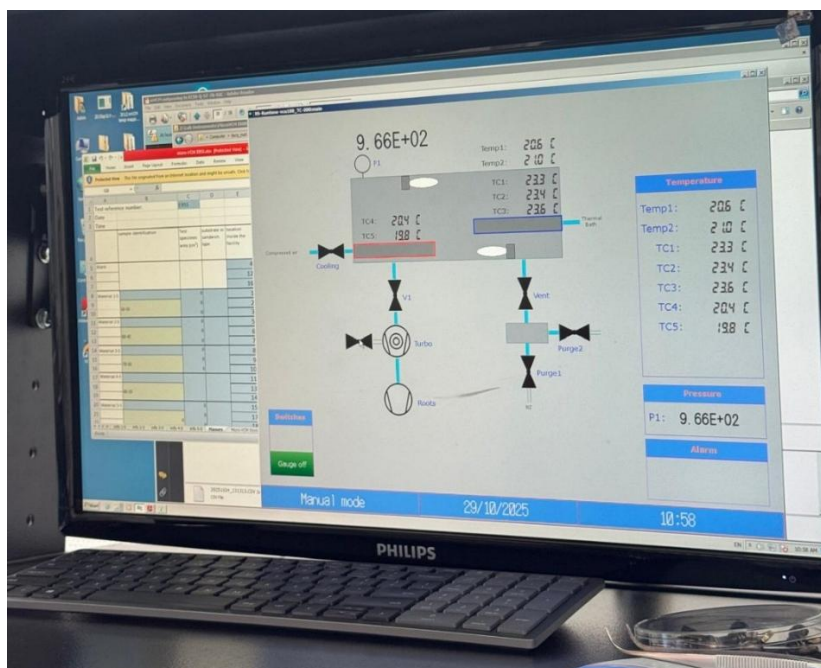


Figure 108: mVCM settings

The sample was tested in accordance with ECSS-Q-ST-70-02C (Figure 109, Figure 110):

- **Pre-test conditioning:** 100–300 mg of the material was conditioned for 24 hours at 22 ± 3 °C and 55 ± 10 % RH.
- **During the 24-hour test:**
 - The sample was exposed to a temperature of 125 °C;
 - Condensable material was collected on collector plates maintained at 25 °C;
 - The test vacuum pressure was maintained below 1×10^{-5} mbar.
- **Post-test conditioning:** The sample was conditioned for 24 hours at 22 ± 3 °C and 55 ± 10 % RH.

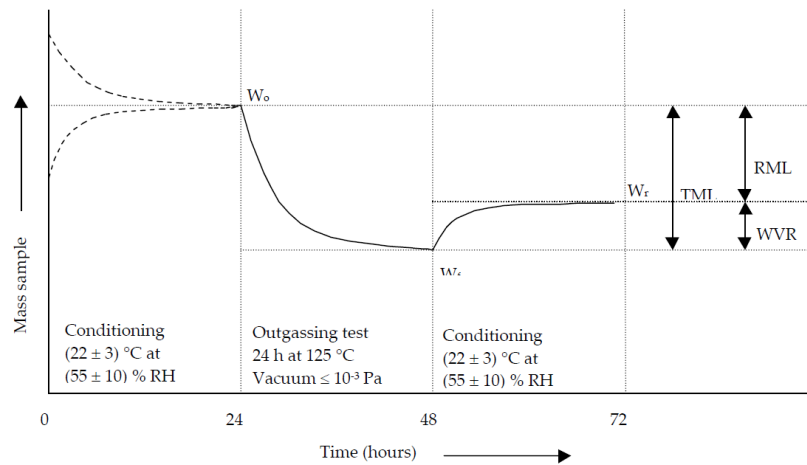


Figure 109- ECSS-Q-ST-70-02C Parameters for sample

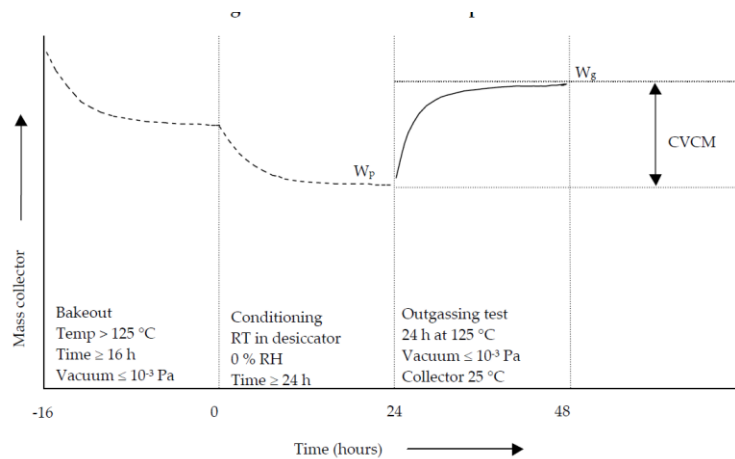


Figure 110- ECSS-Q-ST-70-02C Parameters for collector plate

4.1.5. ATOX

Atomic oxygen resistance was tested at the LEOX facility in the Materials and Electrical Components Laboratory at ESTEC. This ground-based facility is designed to simulate Low Earth Orbit (LEO) conditions and is equipped with a laser detonation source that generates a beam of hypervelocity oxygen atoms. In LEO (200–800 km), atomic oxygen is the dominant residual species. Colliding with spacecraft surfaces at approximately 8 km/s, it can cause significant erosion and material degradation [313]. Polymers are particularly susceptible, though some metals, such as silver, are also affected [314]. The total atomic oxygen dose, or fluence, experienced by a surface during a mission, depends on spacecraft geometry, orbital parameters, and mission duration, and is directly proportional to exposure time. Fluence is generally highest in lower orbits, during periods of intense solar activity, and on surfaces oriented perpendicular to the spacecraft's velocity (ram direction) [315].

Erosion from atomic oxygen is primarily a surface phenomenon, although exceptions exist, such as when self-protecting oxide layers form on the material [316]. In general, degradation is gradual and cumulative, depending on exposure duration, and can manifest as surface erosion, changes in surface roughness, alterations in thermo-optical properties, and variations in surface conductivity. These effects mainly impact thin coatings and foils rather than structural components. Severe erosion, however, can compromise material integrity and generate particulate contamination, for example when a thin foil is fully eroded.

Spacecraft subassemblies most vulnerable to atomic oxygen include solar arrays, optical surfaces, passive thermal control systems, and antennas. Materials requiring evaluation include Kapton-based MLIs, Teflon radiators, polymer-insulated cables, metallic interconnects on solar cells, coated cover glasses, optical coatings on lenses and telescope optics, thermal control paints, and non-structural adhesives.

Ground-based testing of atomic oxygen (AO) presents several challenges due to the high collision velocities experienced in orbit and the tendency of atomic oxygen to rapidly recombine under atmospheric conditions. The most effective method to accurately reproduce in-orbit conditions is the use of an atomic oxygen beam generator. In this approach, the thermal energy of a high-density oxygen plasma is converted into kinetic energy, accelerating oxygen atoms to hypervelocity in a divergent beam. This beam is then directed into a vacuum chamber and onto the test samples.

The ESTEC TEC-QEE Section operates such a source in its Materials and Electrical Components Laboratory, the only facility of its kind in Europe. This atomic beam source is a laser detonation type, employing a high-power CO₂ laser to generate a dense oxygen plasma. The LEOX facility's source operates on the Laser Pulse Induced Breakdown (LPIB) principle. Molecular oxygen is first injected through a nozzle in the form of gas puffs, produced by the rapid piezo-actuation of a pulsed valve. Once the nozzle is partially filled, a pulsed CO₂ laser (wavelengths 10.6 μm and 9.6 μm) is synchronized with the valve and focused on the gas, inducing breakdown and dissociation to form a hot plasma. This plasma emits light, including in the VUV and UV ranges.

The resulting detonation generates a blast wave that travels through the nozzle, converting the plasma's thermal energy into directed kinetic energy. As the plasma expands and cools, charged particles recombine into neutral oxygen atoms. By maintaining a sufficiently high expansion rate and low density, the recombination of these atoms into molecules is prevented. The outcome is a thermally cold, high-velocity AO beam that exits the nozzle and effectively impacts the test samples (Figure 111).

The vacuum system consists of a main chamber, a differential pumping chamber, and a Residual Gas Analyzer (RGA) chamber. The pumping system includes a turbo pump located beneath the main chamber, backed by up to three dry scroll pumps. In the absence of a pulsed beam, the system can achieve a vacuum level of 10^{-7} mbar.

In a standard setup, up to twenty samples (approximately 2×2 cm² each) can be mounted on the sample holder. Custom configurations are also possible, allowing for a maximum exposure area of 140×140 mm². The distance between the atomic oxygen (AO) source and the samples can be adjusted according to the desired flux, and the sample holder can be rotated from 0° to 90°.

Synchronization of the facility is achieved using a digital delay pulse generator. A first pulse triggers the molecular beam valve driver to open and close the valve, injecting O₂ gas into the nozzle with controlled pressure and flow. After a set delay, a second pulse fires the CO₂ laser, which is focused into the nozzle to achieve a minimum intensity of $5 \times 10^9 \frac{W}{cm^2}$. The laser beam is directed into the main chamber via a gilded mirror and focused at the nozzle throat.

A scientific-grade mass spectrometer measures the time of flight of the AO, providing the atomic oxygen velocity. The spectrometer continuously monitors atomic oxygen at $\frac{m}{z} = 16$. AO intensity is recorded as a function of time using a scaler, integrating all signals relative to the 2 Hz trigger pulse. Photons emitted by the hot plasma produce a small initial peak, followed by the main peak corresponding to the pulsed atomic oxygen beam.

The mass spectrometer also monitors the quality and energy distribution of the pulsed beam. During expansion, plasma cooling promotes charge neutralization, forming atomic oxygen. By maintaining a sufficiently high expansion rate and low particle density, recombination into molecular oxygen is effectively suppressed.

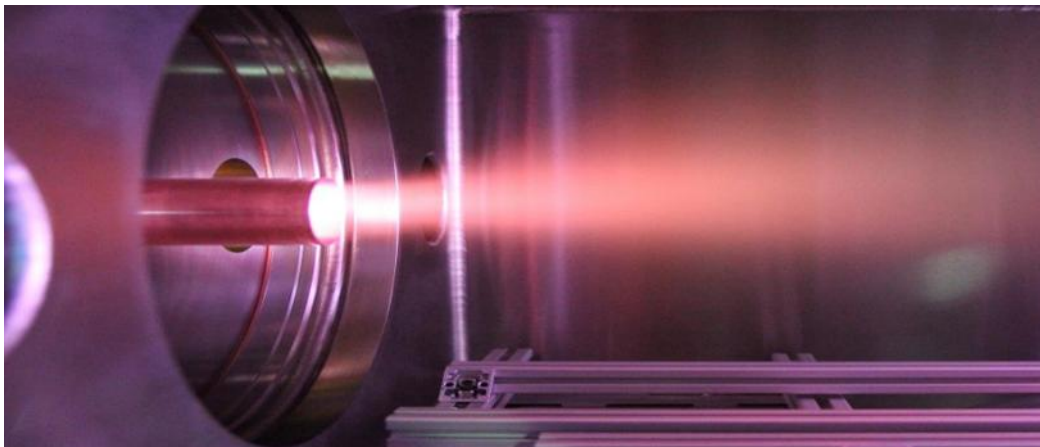


Figure 111: ATOX LEOX (Credits: ESA, Atomic Oxygen Testing in the ESTEC Materials and Electrical Components Laboratory)

Figure 112 illustrates the main components of the vacuum system:

- **Main chamber:** A rectangular vacuum chamber with multiple flanges, where the pulsed atomic oxygen (AO) beam is generated and the samples are mounted on the sample plate
- **Differential pumping chamber:** A smaller vacuum chamber positioned between the main chamber and the RGA chamber, serving to maintain pressure gradients.
- **RGA chamber:** Houses the mass spectrometer and a liquid-nitrogen-cooled (LN₂) shroud for gas analysis.
- **Valve V1:** Located between the main chamber and the differential pumping chamber, and controlled via the vacuum system control panel.
- **Vacuum system control panel:** A touchscreen interface that provides a schematic overview of the vacuum system, allowing the user to operate pumps and valves by selecting their respective icons.

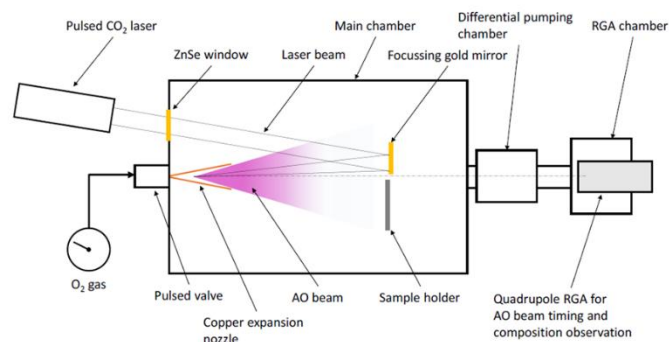


Figure 112: LEOX Facility schematic (Credit: ESA, Atomic Oxygen Testing in the ESTEC Materials and Electrical Components Laboratory)



Figure 113: LEOX facility

Table 15: ATOX LEOX Testing Capabilities

ATOX LEOX Testing capabilities	
Laser Pulse Induced Breakdown (LPIB) principle	
Typical atomic oxygen energy	5.5 eV
AO beam angle with respect to samples	0-90°
Background pressure during exposure	<10 ⁻⁵ mbar with AO beam on
Oxygens atoms neutral and in 3P ground state	
O ⁺ ion concentration	<10 ppm
Source to sample distance	Variable from 45 to 100 cm

Before testing, materials have been kept in the condition cabinet for 24 hours to remove humidity (Figure 114).

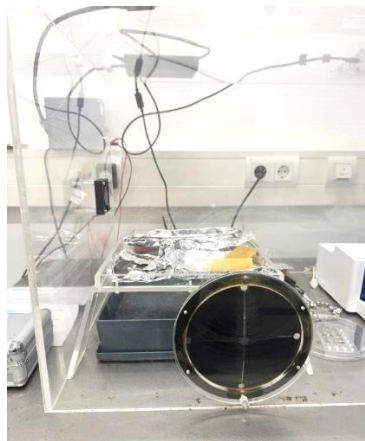


Figure 114: Conditioning cabinet

4.1.5.1. *ATOX flux pre-test*

The purpose of the pre-test was to map the distribution of atomic oxygen (ATOX) flux across the sample plates. To accomplish this, a dedicated test run (Figure 115, left) was conducted to produce an ATOX flux map of the plates. In total, 38 Kapton HN fluence witnesses were mounted on the main and extension plates and exposed to the facility's atomic oxygen environment for approximately 9 hours. The ATOX fluence was calculated from the mass loss of the Kapton samples, and the resulting flux distribution (fluence divided by exposure time) is presented in Figure 115, right, in units of $\times 10^{15}$ atoms/cm²·s, expressed in units of $\times 10^{15}$ atoms/cm²·s.

For subsequent tests, the required ATOX exposure time is determined using the flux measurements obtained from the most recent pre-test. Deviations from the target fluence are common due to the reliance on pre-test data and natural variations in the average flux over the

lifetime of the AO source components. The difference between predicted and actual fluence can be as high as $\pm 30\%$.

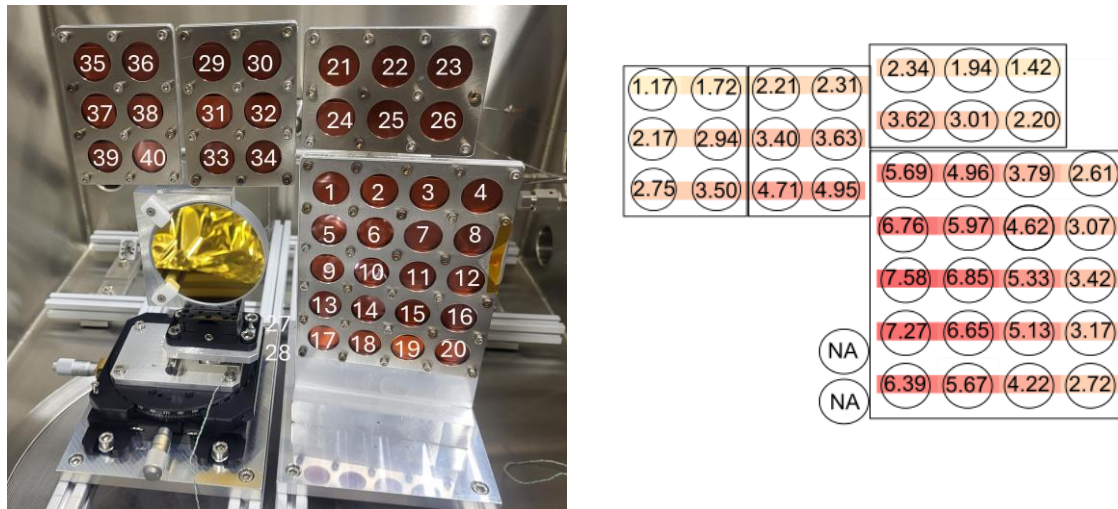


Figure 115: Pre-test to calculate ATOX flux distribution over the sample plates. The image also shows the numbering of the test slots. Right: ATOX flux map [$\times 10^{15}$ atoms/cm²s]

4.1.5.2. Test set-up

The sample arrangements are shown in Figure 116, with the final allocation presented in Figure 117. Figure 117 illustrates the placement of samples within the LEOX facility. The samples were mounted in LEOX positions #35, #36, #37, #38, #39, #40, #29, #30, #31, #32, #33, #34, #21, #22, #23, #24, #25, and #26 (other visible samples belong to different projects). Four Kapton witness samples, used for atomic oxygen fluence measurements, were placed in positions #4, #12, #13, and #20. All samples were tested at ambient temperature, complementing the high-temperature tests conducted previously. Based on prior experience, sample temperatures can rise by approximately 10°C above the laboratory ambient temperature during exposure.



Figure 116: Sample mounting process

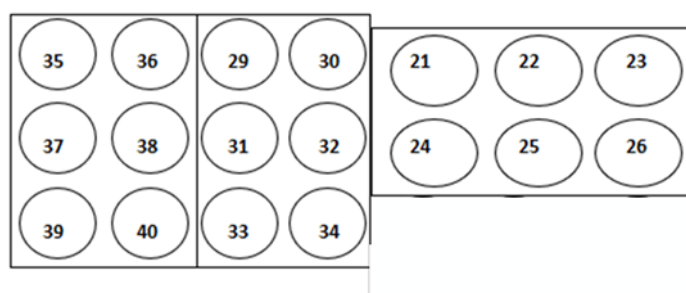


Figure 117: Sample allocation inside the LEOX

Specifically, three samples per formulation were tested, as explained in Figure 118.

Formulation	Sample number
70-30	S1, S2, S3
50-50	S4
50-50	S5
50-50	S6
80-20	S7, S8, S9
60-40	S10, S11, S12

Figure 118: Samples for ATOX

Details are presented in Figure 119.

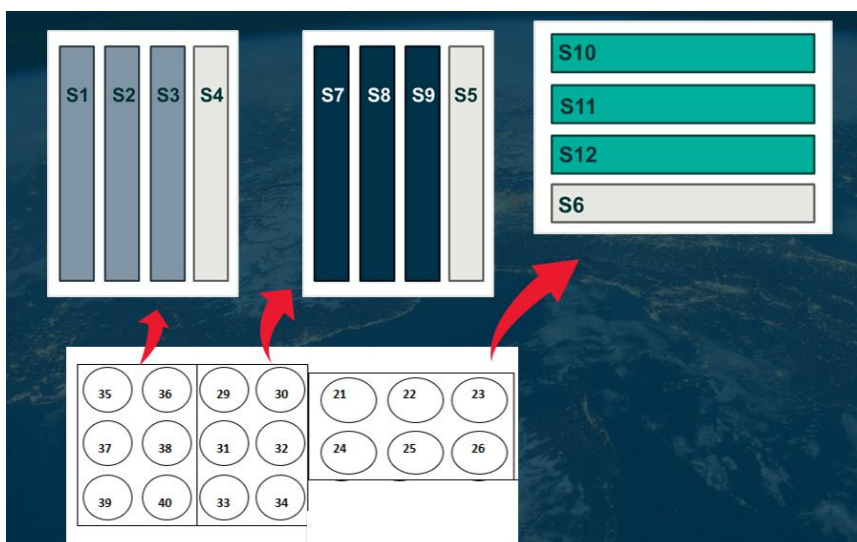


Figure 119: Samples allocation

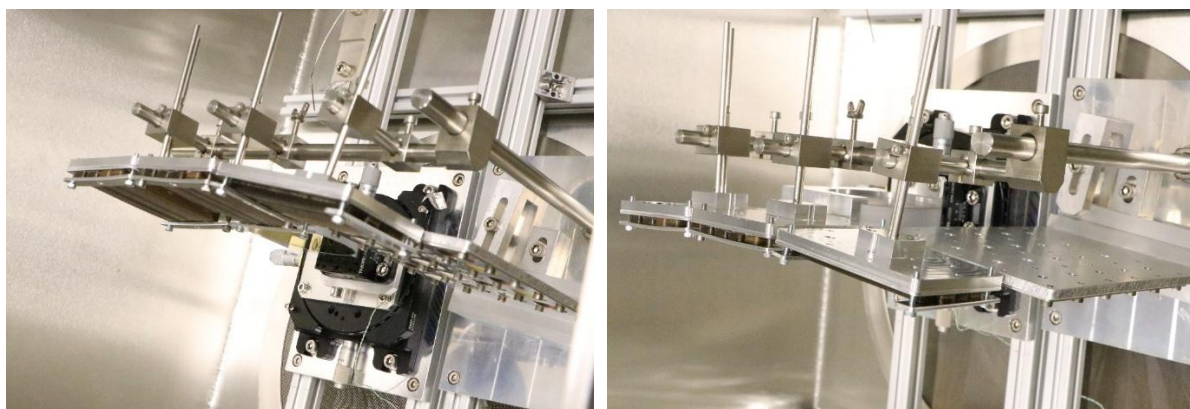


Figure 120: LEOX set up

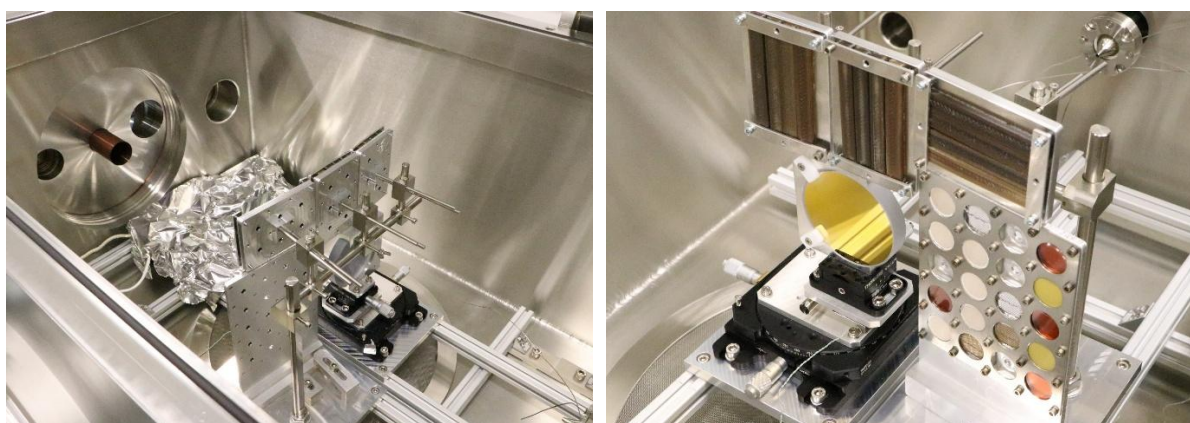


Figure 121: LEOX set up II

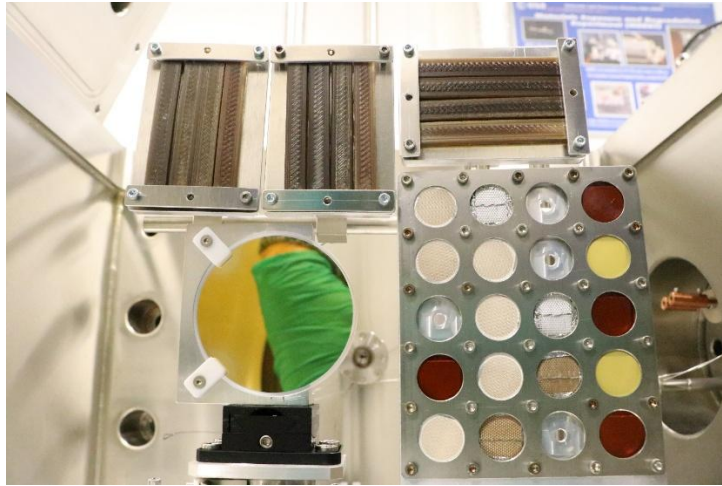


Figure 122: LEOX samples arrangement

4.1.5.3. *Test execution*

The ATOX exposure was carried out during working hours in accordance with the facility's standard internal procedures. The main steps of the ATOX test were:

- Beginning of Test (BoT) analysis: visual inspection followed by mass measurements after conditioning;
- Mounting of samples on the sample plate;
- Photographic documentation of the setup after installation in the ATOX chamber;
- ATOX exposure until the target fluence was reached;
- End of Test (EoT) analysis: removal of samples and repetition of visual inspection and mass measurements, as performed in the BoT.

4.1.5.4. *SEM after ATOX*

A scanning electron microscope (SEM) is a type of electron microscope that employs a focused beam of relatively low-energy electrons as a probe, which is systematically scanned across the surface of a specimen [317]. The electron beam is generated and focused using an electron source combined with electromagnetic lenses [318]. SEM is primarily used to examine the surface features of solid materials. When electrons are accelerated, they acquire significant kinetic energy, which is released in the form of various signals when the electrons interact with and slow down in the sample. These signals include backscattered electrons (BSE), diffracted backscattered electrons (EBSD, used to determine crystal structures and mineral orientations), photons such as X-rays (for elemental analysis via EDX or continuum X-rays), visible light (cathodoluminescence, CL), and heat.

For imaging purposes, secondary electrons are most commonly used because they provide detailed information about morphology and surface topography. Backscattered electrons are employed in multiphase samples to reveal compositional contrasts. X-rays are generated when incident electrons undergo inelastic collisions with electrons in atomic shells, and as these excited electrons return to lower energy states, they emit X-rays with characteristic wavelengths specific to each element. This property allows SEM to perform precise elemental analysis. SEM is a non-destructive technique because X-ray generation does not remove material from the sample, allowing repeated analyses of the same specimen. A schematic representation of the SEM operating principle is shown in Figure 123.

Conductive samples can be analysed using SEM at magnifications ranging from 50× up to 1,000,000×, typically employing a field emission electron gun. Non-conductive samples, such as glass, polymers, paints, and biological materials, are usually coated with conductive layers like carbon, gold, or chromium to prevent charging effects. However, if the SEM is equipped with a variable pressure (low vacuum or environmental) mode, it is possible to examine non-conductive specimens without applying a conductive coating.

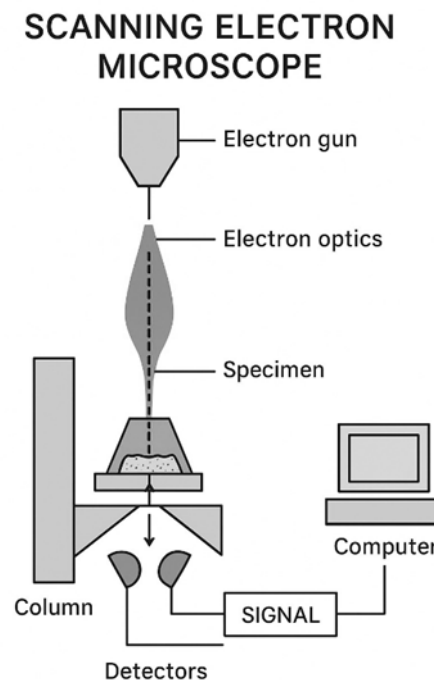


Figure 123: SEM scheme

At the ESTEC Materials and Electrical Components Laboratories, the SEM in use is the TENEO, a Schottky Field Emission microscope. It offers both high- and low-voltage ultra-

high-resolution imaging through a non-immersion lens design and features a low vacuum mode (up to 50 Pa) to compensate for charging on non-conductive materials.

Features and specifications:

- Voltage: 0.2-30 keV Schottky FEG
- Beam current: 1 pA to 400 nA
- SEM resolution: 1 nm at 30 kV; 1.6 nm at 1 kV
- Beam deceleration mode
- Partial vacuum: 10-50 Pa
- Pixel density: 768 x 512, 1536 x 1024, 3072 x 2048, 6144 x 4096

Detection:

- Standard secondary-electron Everhart-Thornley detector (SED)
- Trinity detection system, comprised of a segmented, lower in-lens detector (T1), an upper in-lens detector (T2) and an in-column detector (T3)
- Dedicated Low Vacuum secondary electron detector to provide charge-free topographic contrast imaging of non-conductive samples
- XFlash Silicon drift EDX detector



Figure 124: TENE0 SEM

Additional features include:

- Multiple specimen holder: accommodates up to 18 samples, with three pre-tilted at 45° and an extra clamp for flexibility;
- Stage tilting: allows tilting of the specimen stage up to 90°;

- Decelerating voltage: enhances imaging quality to the extent that conductive coating may become unnecessary;
- Automatic detector insertion : ABS/CBS and STEM3/STEM3+ detectors can be inserted automatically during inspection while the chamber remains under vacuum, eliminating the need to vent and open the chamber;
- NavCAM: integrated internal camera for imaging and navigation within the chamber;
- Liquid nitrogen vessel: for cooling applications;
- Internal illumination: provides illumination inside the chamber for easier sample positioning;
- Automatic aperture system: selects the optimal final lens aperture automatically based on imaging requirements when operating the electron beam.

Hardware configuration of the TENE0 SEM

The TENE0 SEM, manufactured by FEI (formerly PHILIPS), is equipped with the following hardware components:

- System control panel power button
- Software controlled, 5-axes movement stage: X, Y, Z, rotation and tilt
- Automatic Aperture of final lens system 50mm² X-Max, Oxford Instruments
- Energy-dispersive X-ray spectrometer (EDS)
- IR, CCD (Charged Coupled Device) video camera
- NavCAM
- Plasma cleaner
- Secondary electron detector (SED), also known as Everhart-Thornley Detector (ETD)
- Retractable Directional Backscattered Detector (DBS): Angular Backscattered Detector (ABS) and Concentric Backscattered Detector (CBS)
- Retractable Sanning Transmission Electron Microscopy (STEM3/STEM3+) detector
- CryoCleanerEC



EDS



IR CCD camera



Nav CAM



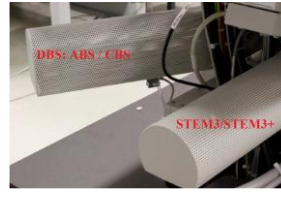
Plasma cleaner



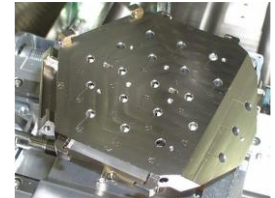
*Everhart-Thornley
Detector (ETD)*



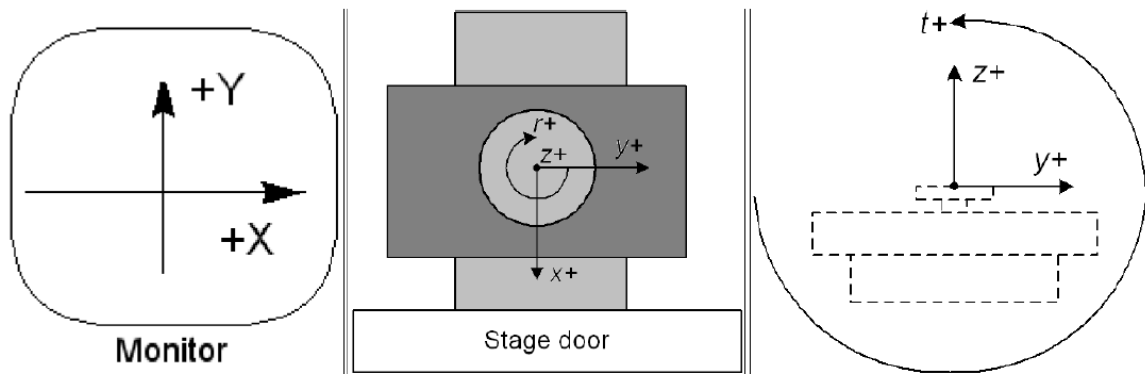
Cryogenic Cleaner



*Retractable
Directional
Backscatter Detector
(DBS)*



Standard Stub Holder



Item	110 × 110 mm	Note
X	-55 to +55 mm	
Y	-55 to +55 mm	
Z	66 mm	
R	360°	continuous
T	-15° to +90°	maximally
Eucentric distance	10 mm	
Maximum sample weight	No restriction: 500 g	including stub holder
	No Tilt: 2 000 g	
	X and Y movements only: 5 000 g	

Figure 125: Details of the base plate

The detector used is the Everhart-Thornley Detector (ETD), a scintillator-photomultiplier type designed to collect secondary electrons (SE) generated when the primary electron beam interacts with the specimen surface. It is permanently mounted inside the chamber, positioned above and to one side of the sample. The ETD operates in two modes: Secondary Electrons (SE) for surface topography imaging, and Backscattered Electrons (BSE) for compositional

contrast. For the analysis, the SEM settings were 2 kV accelerating voltage, with beam current varying between 5 pA and 25 pA.

4.1.6. TVAC

The thermal cycling test was conducted at the ESA/ESTEC/TEC-MSP facility, as shown in Figure 92, in accordance with ECSS-Q-ST-70-04C [319]. The facility can achieve a base vacuum of 5×10^{-6} mbar at room temperature (RT). Both the shroud and the sample plate are temperature-controlled using a gas-mixing system, managed by a dedicated programmer for executing thermal profiles. The temperature control range for both components is from -170°C to +200°C. Measurement and data acquisition were performed using a Data Logger and Yokogawa GP20 temperature sensors (*Yokogawa, Musashino, Tokyo, Japan*) equipped with type K thermocouples. Temperature regulation of the sample plate, based on readings from the type K thermocouples, was achieved using a Proportional-Integral-Derivative (PID) control system.

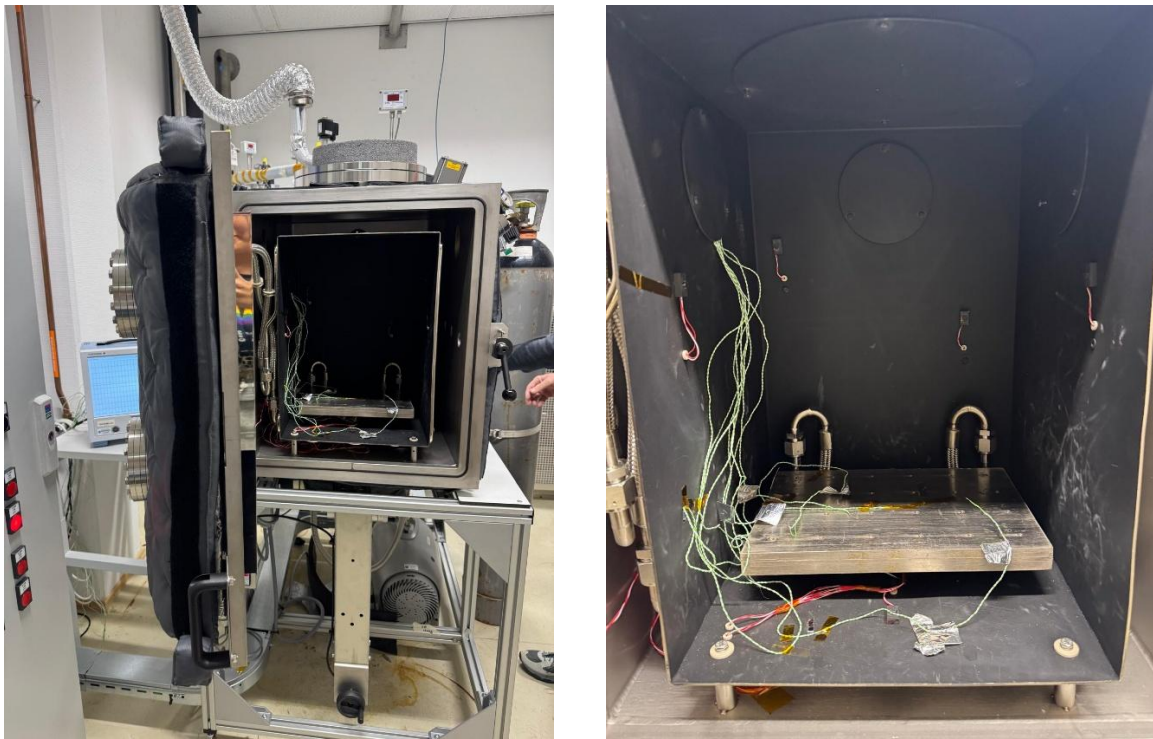


Figure 126: TVAC facility

Samples were arranged following a specific scheme as in Figure 127.

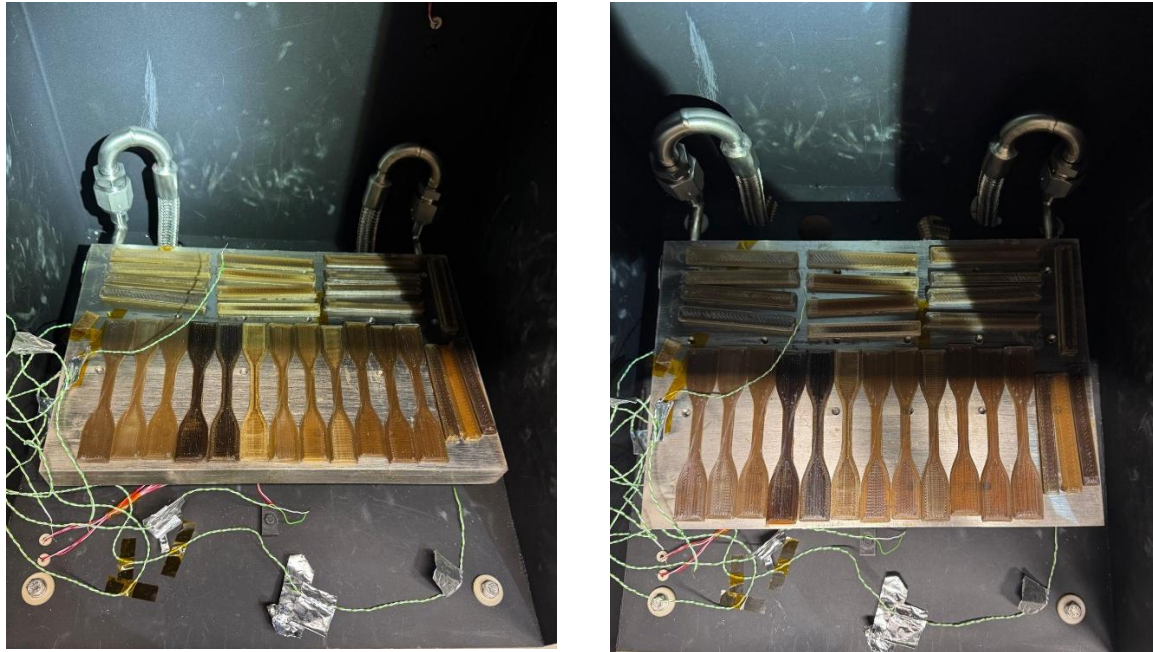


Figure 127: samples arrangement inside the TVAC chamber

Four thermocouples were installed to monitor the sample's temperature, as illustrated in Figure 128 and Figure 129:

- Thermocouple 8 was positioned at the top-left corner of the sample;
- Thermocouple 10 was positioned at the bottom-right corner of the sample;
- Thermocouple 3 was mounted on the base plate;
- Thermocouple 9 was placed on top of the aluminium foil.

The Data Logger and Yokogawa GP20 temperature sensors with type K thermocouples were connected to a laboratory laptop via dedicated software (Figure 130), allowing remote temperature monitoring and control.

Table 16: Summary of the test parameters for the thermal cycling

Test parameter	Conditions
Vacuum inside the facility	$<5 \times 10^{-6}$ mbar
Initial temperature (at least first 12 hours in vacuum)	RT
Maximum temperature during cycling (=extremely high)	$+100^{\circ}\text{C} \pm 1^{\circ}\text{C}$
Minimum temperature during cycling (=extremely low)	$-100^{\circ}\text{C} \pm 6^{\circ}\text{C}$
Temperature rates	$< 10^{\circ}\text{C}/\text{min}$
Dwell time	15 minutes
Number of cycles	25

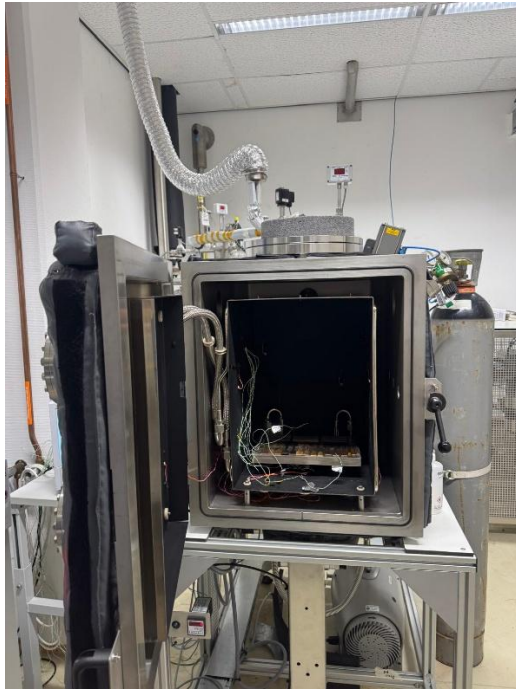


Figure 128: Chamber with thermocouples 8,10 and 3



Figure 129: Thermocouples set up

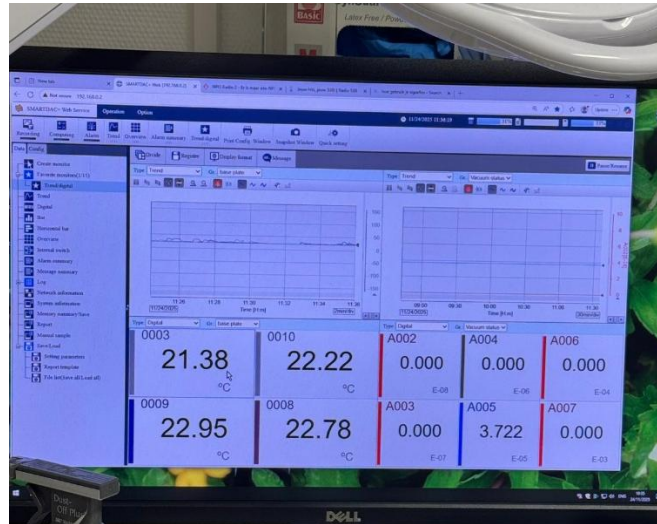


Figure 130: Thermocouples interface

The chamber was then sealed, and the scroll pump was activated to establish low-vacuum conditions (Figure 131). Once the pressure dropped below 3 mbar, the turbo-pump could be engaged to achieve high-vacuum conditions.



Figure 131: TVAC facilities in the ESTEC lab

The vacuum conditions during a single cycle are shown in Figure 132, with a vacuum level of 1×10^{-6} mbar at the highest temperature ($+100^\circ\text{C}$) and 1×10^{-7} mbar at the lowest temperature (-100°C).

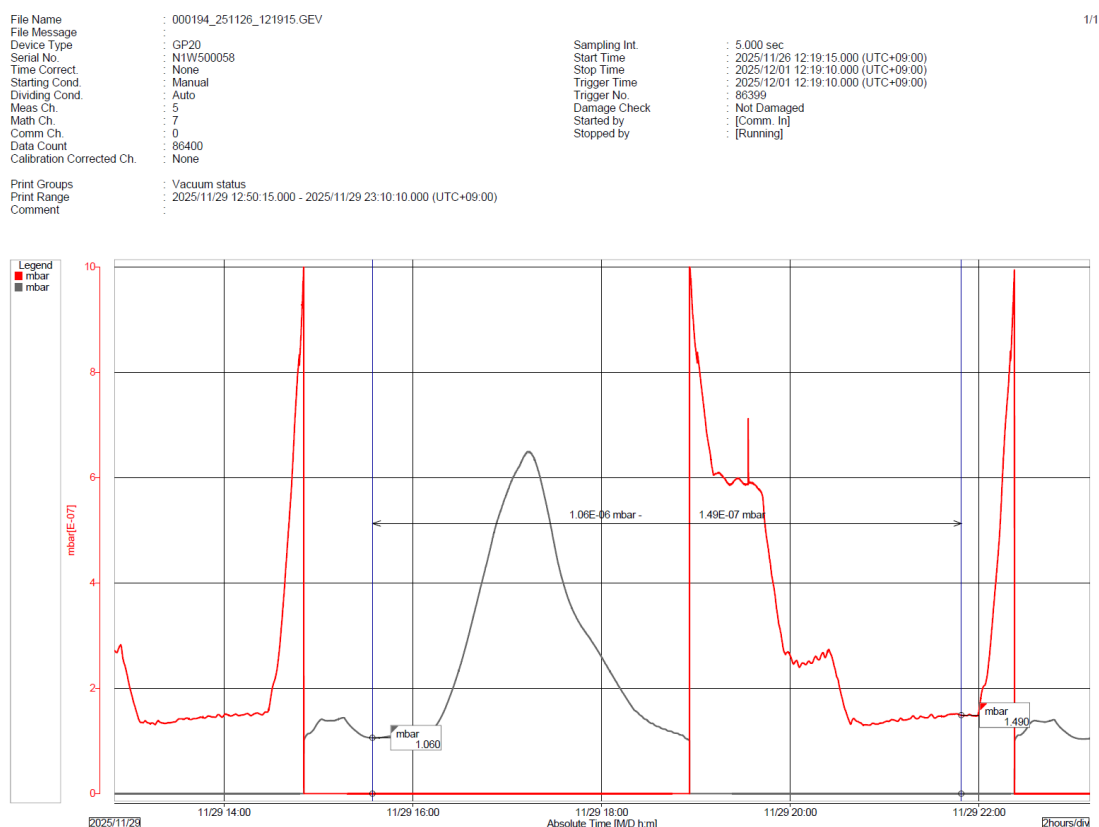


Figure 132: Vacuum status

4.1.7. Shape-shifting Capabilities

The shape-shifting capabilities of both pristine samples and samples subjected to thermal vacuum testing were evaluated using a Binder VD 115 oven and a Heraeus Vacutherm UT6060 oven (Thermo-Electron Corporation, now Thermo Fisher). Key shape memory parameters, including the shape fixity ratio, shape recovery ratio, and recovery time, were measured for each sample. The shape fixity ratio, which quantifies the material's ability to retain its temporary shape, was calculated using the following formula:

$$Rf = \left[\frac{\theta_u - \theta_f}{\theta_u} \right] \%$$

Shape recovery ratio is defined as the ability of a material to recover the permanent shape, and it is calculated via:

$$Rr = \left[\frac{\theta_u - \theta_r}{\theta_u - \theta_0} \right] \%$$

With

θ_0	Original angle
------------	----------------

θ_u	Deformed angle: angle under load at Tswitch
θ_f	Fixed angle: angle after cooling at $T < T_{switch}$, unloading and after 24 hours
θ_r	Recovered angle: angle after shape memory recovery



Figure 133: Binder VD 115 oven

Single Channel Gauge Controller (AGC-100/AGD-100, Agilent Technologies, Santa Clara, California, United States) was used to measure the vacuum status of the dry scroll pump (IDP 15, Agilent Technologies, Santa Clara, California, United States) via a computer with LabVIEW (National Instruments, Austin, Texas, US) (Figure 134).



Figure 134: AGC-100 ad dry scroll pump IDP 15

Trend of the pressure vs time, and temperature vs time recorded with the gauge controller is shown in Figure 135.

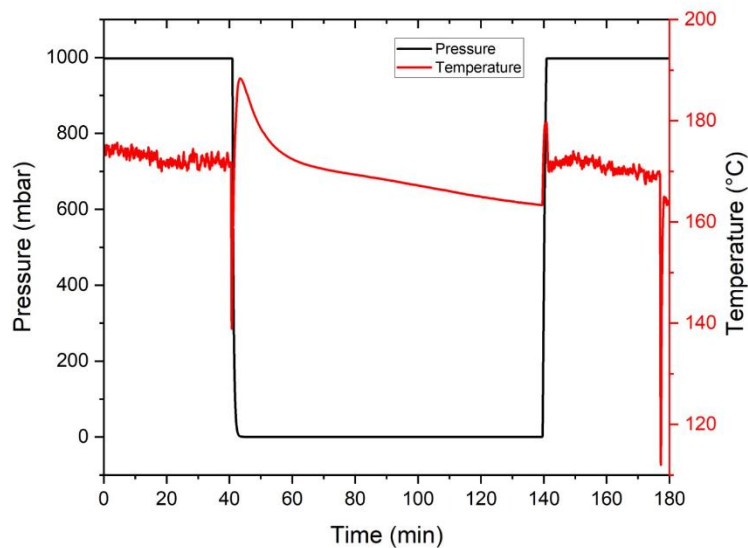


Figure 135: Pressure and Temperature trend

The binder oven (Figure 133) was set at $T=200^{\circ}\text{C}$ and a vacuum level of $1\text{E}-3$ mbar. Actual registered temperature was $T=175^{\circ}\text{C}$.

The temperature reached was not enough for some formulation to reach the switch temperature for the shape memory effect; for this reason, the Heraeus vacutherm UT6060 oven was used (Figure 136).



Figure 136: Heraeus vacutherm UT6060

The oven was connected to a Bluffton Motor Works dry pump 1201006408. Temperature was set at $T=230^{\circ}\text{C}$ with a vacuum level of $1\text{E}-3$ mbar. Actual registered temperature was $T=200^{\circ}\text{C}$.

4.2. Results and Discussion

4.2.1. Camera Canon 700D

Pictures of pristine samples can be seen in Figure 137.

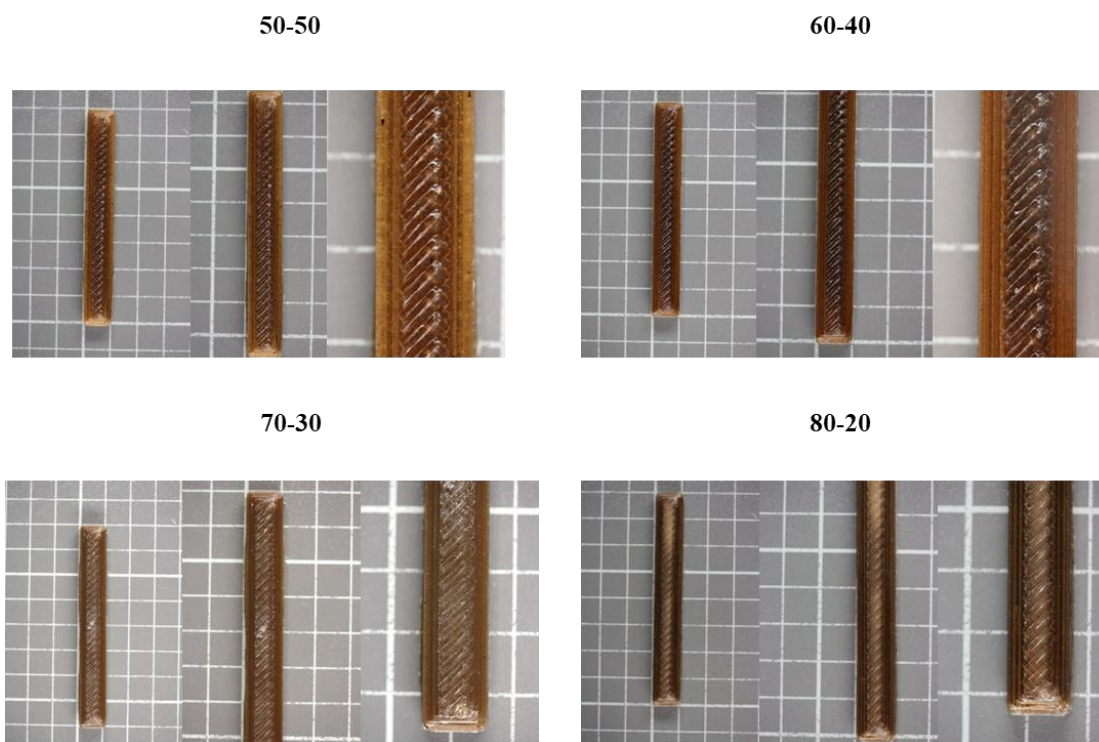


Figure 137: Pictures of pristine samples

4.2.2. 3D Profilometer (Keyence VR 5000)

For each formulation, a visual analysis was conducted, followed by the acquisition of data for the 3D profile. Subsequently, a section of the sample was examined for surface roughness, as illustrated in in Figure 138.

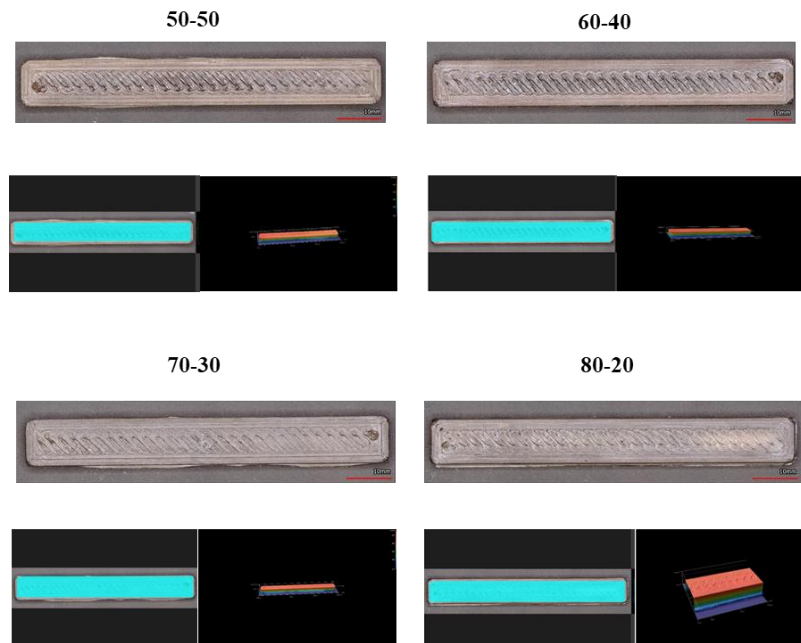


Figure 138: After TVAC Surface roughness

4.2.3. Outgassing

The following parameters were analysed:

- **Wc:** Mass of specimen cup (mg)
- **Wo:** Total specimen mass before test (mg)
- **Wf:** Total specimen mass just after test (mg)
- **Wr:** Total specimen mass after test and after 24h conditioning (mg)
- **Wp:** Initial mass of collector plates before test (mg)
- **Wg:** Final mass of collector plates after test (mg)
- The results of the sample specimen mass measurements, before and after the test, are presented in Table 17
- The final calculations of the outgassing parameters (TML, CVCM, RML, and WVR) are reported in Table 18.

Table 17: Sample mass measurements using external balance

Sample Identification	Location inside the facility	Wc mass of specimen cup (mg)	Wo total specimen mass before test	Wf total specimen mass just after test	Wr total specimen mass after test and after 24 h conditioning	Collector plate and cup number	Wp initial mass collector plate before test (mg)	Wg Final mass of collector plates after test
Blank	4	181489	181486	181488	181491	4	2135983	2135951
	12	180478	180478	180477	180482	12	1930991	1930995
	16	179870	179870	179870	179872	16	1970997	1971008
Materia 11-5	50-50	180868	307940	307171	307833	1	2069415	2069372

		2	181521	322048	321210	321939	2	2125798	2125791
		3	179211	314602	313800	314564	3	2222564	2222553
Materia	60-	5	180184	291300	290711	291216	5	2185019	2185002
I 2-5	40	6	179896	319912	319189	319822	6	2056253	2056201
		7	180382	340076	339256	339967	7	2044997	2044983
Materia	70-	8	179654	296668	296136	296605	8	2080915	2080906
I 3-5	30	9	179965	289513	288933	289397	9	2191129	2191122
		10	179957	284029	283567	283957	10	2159022	2159007
Materia	80-	11	178113	300950	300412	300864	11	2159184	2159185
I 4-5	20	13	178659	314083	313499	313996	13	2184240	2184189
		14	179721	296660	296162	296591	14	2145592	2145567

The final calculations of the outgassing parameters (TML, CVCM, RML, and WVR) are reported in Table 18.

Table 18: Outgassing Values

PEEK-based blends	Formulation	TML (%)		CVCM (%)		RML (%)		WVR (%)	
		Average	SD	Average	SD	Average	SD	Average	SD
	50-50	0.598	0.007	0.011	0.015	0.063	0.031	0.535	0.026
	60-40	0.520	0.009	0.016	0.015	0.069	0.006	0.451	0.005
	70-30	0.476	0.047	0.004	0.004	0.076	0.027	0.400	0.024
	80-20	0.432	0.006	0.018	0.014	0.064	0.006	0.367	0.001

All uncertainties reported are representative of typical conditions and correspond to a coverage factor of $k = 2$, which is equivalent to a 95% confidence level. All measurements performed to obtain the results presented here are fully traceable.

According to ECSS-Q-ST-70-02C, the test is considered passed if $TML < 1\%$, $CVCM < 0.1\%$, and $RML < 1\%$. Based on the results obtained, the tested materials can be deemed acceptable under outgassing conditions, with values of $TML < 0.6\%$, $CVCM < 0.02\%$, $RML < 0.08\%$. Consistent findings reported in the literature indicate that additively manufactured PEEK exhibits comparably low outgassing characteristics, with negligible collected volatile condensable material (CVCM) and minimal moisture uptake, thereby confirming its suitability for applications requiring stringent low-outgassing performance [320], [321], [322], [323], as for neat PEI [324].

4.2.4. ATOX

Atomic Oxygen (ATOX) exposure under simulated Low Earth Orbit (LEO) conditions was conducted to assess the susceptibility of the materials to environmental degradation. The

evaluation focused on three key aspects: potential surface erosion of polymers (such as Kapton, paints, and adhesives), loss of thermal control performance (including degradation of white coatings), and structural weakening that could occur during extended mission durations. These tests provide critical insights into material performance, informing both selection and design strategies for spacecraft intended for long-term operations in LEO.

Atomic Oxygen (ATOX) exposure under simulated Low Earth Orbit (LEO) conditions was conducted to assess the susceptibility of the studied materials to environmental degradation. The study primarily focused on evaluating potential surface erosion of polymers commonly used in spacecraft components. Additionally, it aimed to identify any structural weakening that could occur during prolonged exposure, as such deterioration may compromise mechanical integrity and mission reliability over extended operational lifetimes. The findings provide valuable guidance for material selection and design strategies in long-duration LEO missions. The sample placement and disposal setup during the test are shown in Figure 139 and Figure 140, and reported in Table 19. LEOX flux maps is described in Figure 141.

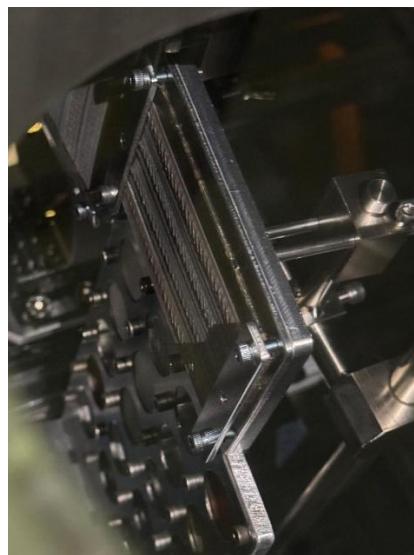


Figure 139: Samples during ATOX testing

Table 19: ATOX Samples' position

Formulation	Sample number	Position
70-30	S1, S2, S3	35 to 40
50-50	S4	35 to 40
50-50	S5	29 to 34
50-50	S6	21 to 26
80-20	S7, S8, S9	29 to 34
60-40	S10, S11, S12	21 to 26



Figure 140: Specimens positioning

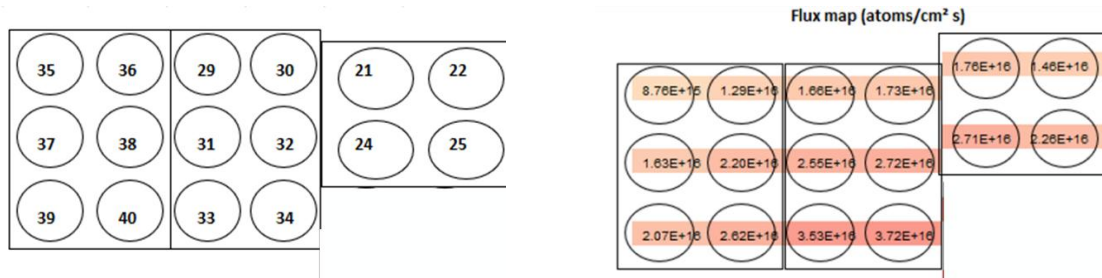


Figure 141: LEOX Flux map

4.2.4.1. *Mass measurements*

Table 20 summarises the mass measurements of the samples before (BoT) and after (EoT) ATOX exposure. All measurements were conducted after conditioning the samples for at least 24 hours in a humidity- and temperature-controlled environment ($T = 22 \pm 3$ °C, $RH = 55 \pm 10\%$) inside a stabilized cabinet, using a Sartorius ME5 microbalance. Although the ATOX fluence target was determined by other samples in the test campaign, all samples received a substantial average fluence of 2.0×10^{21} atoms/cm².

Table 20: Mass measurements

Sample	ATOX(LEOX)				
	Mass (g)		Mass Loss	Mass Loss (%)	Average mass loss (%)
	BoT	EoT			
S1	4.247145	4.209416	0.037729	0.888338	1.04
S2	3.959034	3.920668	0.038366	0.969075	
S3	3.038756	3.000362	0.038394	1.263478	
S4	4.021656	3.972656	0.049000	1.218404	1.37
S5	3.934572	3.874588	0.059984	1.524537	
S6	4.002896	3.94794	0.054956	1.372906	
S7	3.827628	3.775359	0.052269	1.365572	1.34
S8	4.004146	3.952467	0.051679	1.290637	
S9	3.967374	3.913338	0.054036	1.362009	
S10	4.269407	4.230893	0.038514	0.902092	1.06
S11	3.996297	3.95367	0.042627	1.066662	
S12	4.05429	4.005503	0.048787	1.203343	

It can be noted that the average mass loss % for all the formulations is <1.5%. From a mass loss (g) perspective, the measured values are comparable to those reported for analogous high-performance polymers, such as poly(ether sulfone), as documented in the NASA MISSE-7 experiment [325], [326]. This correlation supports the suitability of the developed blend for application in Low Earth Orbit environments.

4.2.4.2. *Visual inspection*

Figure 142 shows the visual appearance of the samples before (BoT) and after (EoT) ATOX exposure, captured with a high-resolution digital camera and macro lens (Canon EOS 700D). The images clearly highlight the contrast between the regions exposed to atomic oxygen and those shielded by the sample holder. Protected surfaces remain smooth and unaffected, whereas exposed areas display noticeable changes, creating a distinct boundary that emphasizes the material's response to ATOX. To further examine these surface modifications, high-resolution imaging was conducted using a Keyence 3D Profilometer and SEM, as detailed in Sections 3.4.3 and 4.2.4.3.

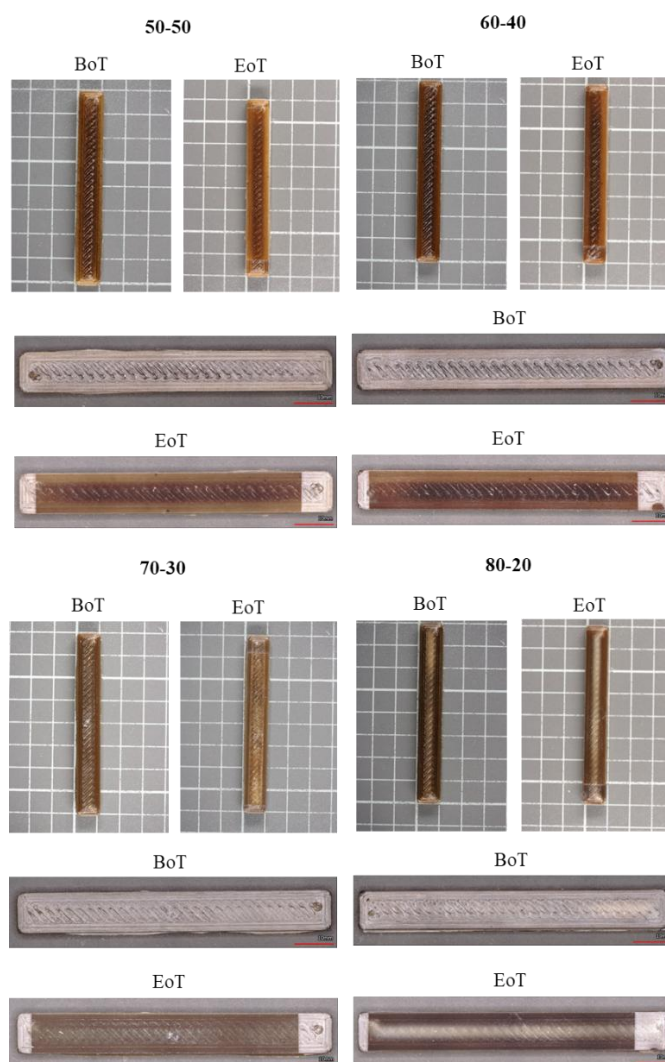


Figure 142: Visual inspection after ATOX

4.2.4.3. *Surface roughness after ATOX*

Surface roughness of all formulations was measured using a Keyence 3D profilometer, on both the exposed and unexposed areas, as shown in Figure 143 and Figure 144.

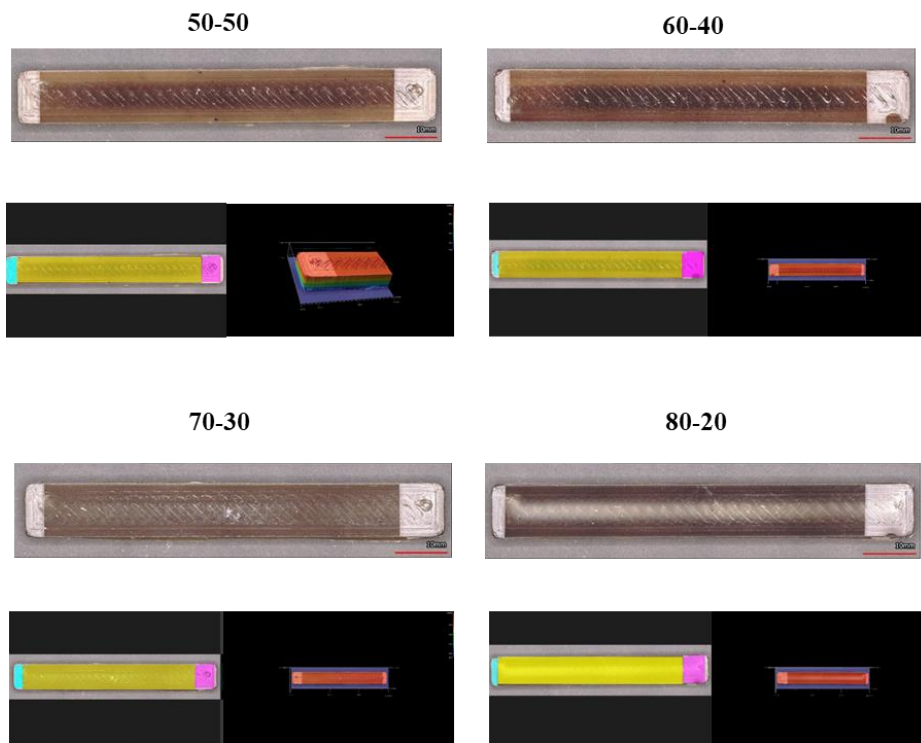


Figure 143: Surface measurement

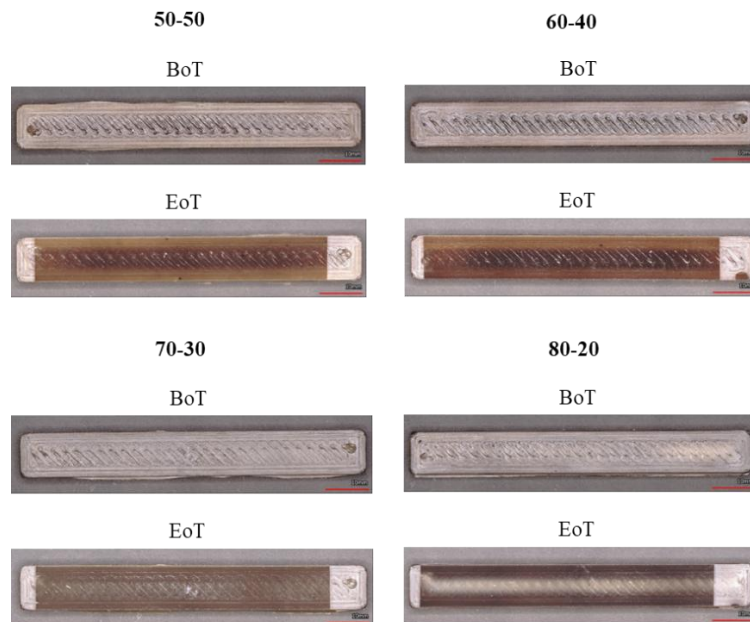


Figure 144: Surface Roughness after ATOX

In conclusion, data of all the formulations before and after ATOX exposure can be summarized in Table 21, Table 22, Table 21 , Table 24.

Table 22: Surface roughness 60-40 summary

60-40	Sa	Sz	Str	Spc	Sdr
	um	um		1/mm	
BoT	111,846	2,918,100	0,041	11,176	0,8765075
EoT ATOX	66,800	972,100	0,047	4,979	0,0398180
EoT non-ATOX sx	33,658	589,800	0,089	7,912	0,0697005
EoT non-ATOX dx	53,002	4,692,800	0,686	4,569	0,7163768

Table 23

Table 21: Surface roughness 50-50 summary

50-50	Sa	Sz	Str	Spc	Sdr
	um	um		1/mm	
BoT	89,173	1,529,100	0,172	6,675	0,1319025
EoT ATOX	97,784	880,300	0,159	5,099	0,0410822
EoT non-ATOX sx	41,326	4,920,900	0,726	4,356	0,8259120
EoT non-ATOX dx	59,645	1,232,000	0,352	5,609	0,1051620

Table 22: Surface roughness 60-40 summary

60-40	Sa	Sz	Str	Spc	Sdr
	um	um		1/mm	
BoT	111,846	2,918,100	0,041	11,176	0,8765075
EoT ATOX	66,800	972,100	0,047	4,979	0,0398180
EoT non-ATOX sx	33,658	589,800	0,089	7,912	0,0697005
EoT non-ATOX dx	53,002	4,692,800	0,686	4,569	0,7163768

Table 23: Surface roughness 70-30 summary

70-30	Sa	Sz	Str	Spc	Sdr
	um	um		1/mm	
BoT	103,990	4,976,500	0,012	8,106	0,6805973
EoT ATOX	92,827	696,700	0,381	4,159	0,0216784
EoT non-ATOX sx	31,681	3,309,600	0,417	3,791	0,1444715
EoT non-ATOX dx	42,826	4,577,000	0,321	6,346	0,2818678

Table 24: Surface roughness 80-20 summary

80-20	Sa	Sz	Str	Spc	Sdr
	um	um		1/mm	
BoT	53,039	2,055,000	0,039	6,339	0,1166289
EoT ATOX	31,643	519,600	0,245	4,341	0,0302605
EoT non-ATOX sx	78,170	4,197,700	0,474	4,331	0,0335490
EoT non-ATOX dx	65,780	4,220,600	0,013	4,631	0,3569965

It can be noted that exposure to ATOX results in a reduction of Sa, Sz, Spc and Sdr, indicating a mild erosive effect on the sample surfaces. This behaviour is attributed to the high reactivity of atomic oxygen species, which induce localized pitting phenomena [323].

4.2.4.4. Visual inspection under SEM

SEM set up is shown in Figure 145, while pictures of the samples are presented in Figure 146, Figure 147 and Figure 148.

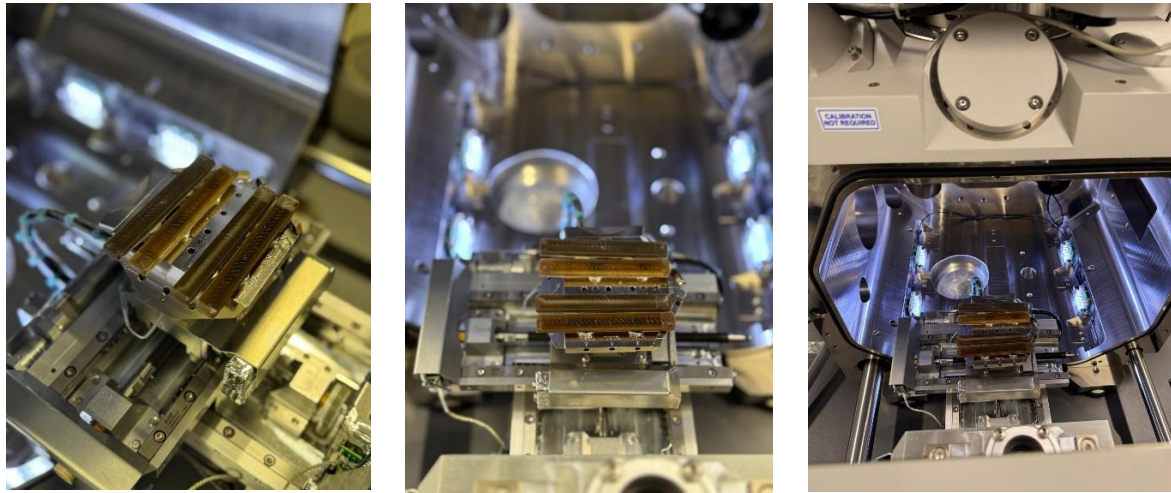


Figure 145: TENE0 (FEI) SEM set up

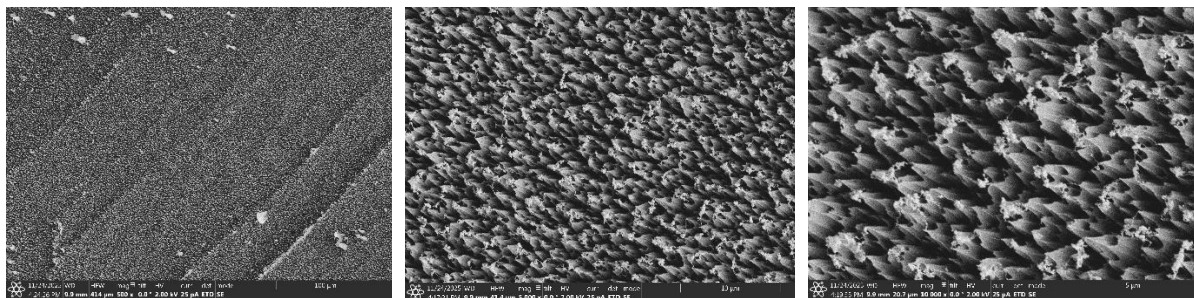


Figure 146: SEM ATOX 60PEEK-40PEI surface with different magnifications: first (500x), second (5000x), third (10000x)

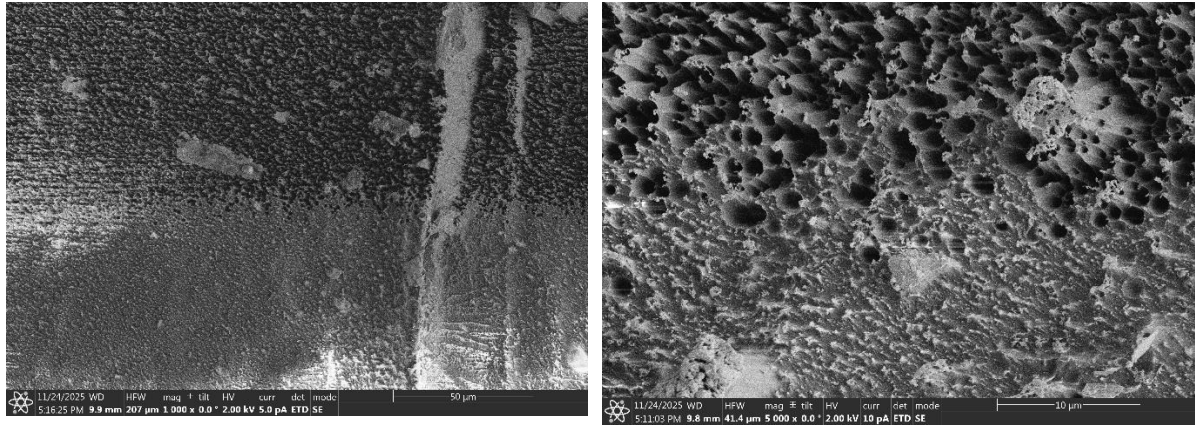


Figure 147: SEM of a 60PEEK-40PEI surface with different magnifications: left (1000x), right (5000x), top area: ATOX, bottom area: non-exposed surface

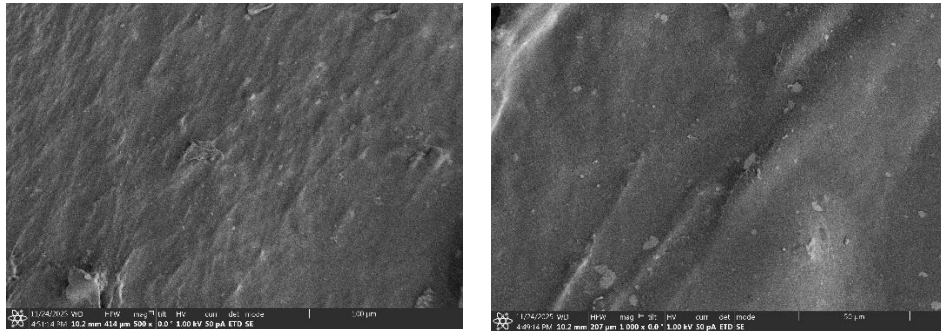


Figure 148: SEM of Non-Exposed 60PEEK-40PEI Surface with different magnifications: left (500x), right (1000x)

Exposure to energetic atomic oxygen results in relatively uniform material erosion, creating a rough surface pattern characterized by cavities, as observed in previous studies [313], [315], [316], [327]. This pattern exhibits a carpet-like morphology typical of ATOX-induced erosion and is likely influenced by the polymer's internal structure, which renders certain regions more susceptible to degradation [328]. This degradation proceeds through an oxidative erosion mechanism, whereby exposed organic surfaces undergo progressive material loss over time. Alongside the gradual reduction in thickness, the process also generates low-mass volatile by-products, which may contribute to the contamination of nearby sensitive surfaces [329].

4.2.5. TVAC

The test was conducted from 24 November to 3 December. Temperatures were continuously monitored throughout the test using thermocouples. A total of 25 thermal cycles were performed, with a maximum temperature of 100 °C (± 1 °C) and a minimum temperature of -100 °C (± 6 °C). Cycles 0 and 1 are shown in Figure 149, which illustrates the temperature trends recorded by the four thermocouples during these cycles. During cycles 0 and 1, the

lowest temperature was reached in approximately 9.5 hours, with the PEEK samples reaching -71 °C.

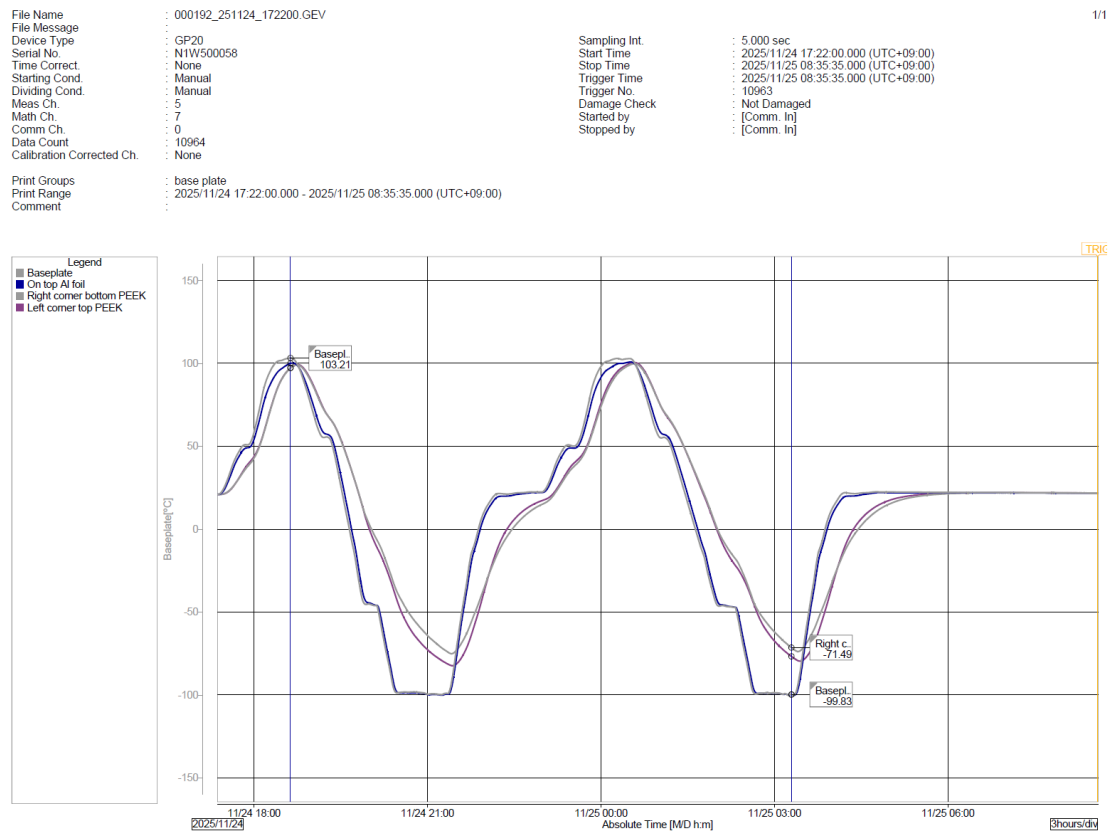


Figure 149: TVAC Cycle 0-1

Adjustments were subsequently made to account for the insulating properties of the polymer samples, increasing the cooling time, as illustrated in Figure 150.

File Name : 000193_251125_084300.GEV
 File Message :
 Device Type : GP20
 Serial No. : N1W500058
 Time Correct : None
 Starting Cond. : Manual
 Dividing Cond. : Manual
 Meas Ch. : 5
 Math Ch. : 7
 Comm Ch. : 0
 Data Count : 19816
 Calibration Corrected Ch. : None

Sampling Int. : 5.000 sec
 Start Time : 2025/11/25 08:43:00.000 (UTC+09:00)
 Stop Time : 2025/11/26 12:14:15.000 (UTC+09:00)
 Trigger Time : 2025/11/26 12:14:15.000 (UTC+09:00)
 Trigger No. : 19815
 Damage Check : Not Damaged
 Started by : [Comm. In]
 Stopped by : [Comm. In]

1/1

Print Groups : base plate
 Print Range : 2025/11/25 08:43:00.000 - 2025/11/25 23:14:15.000 (UTC+09:00)
 Comment :

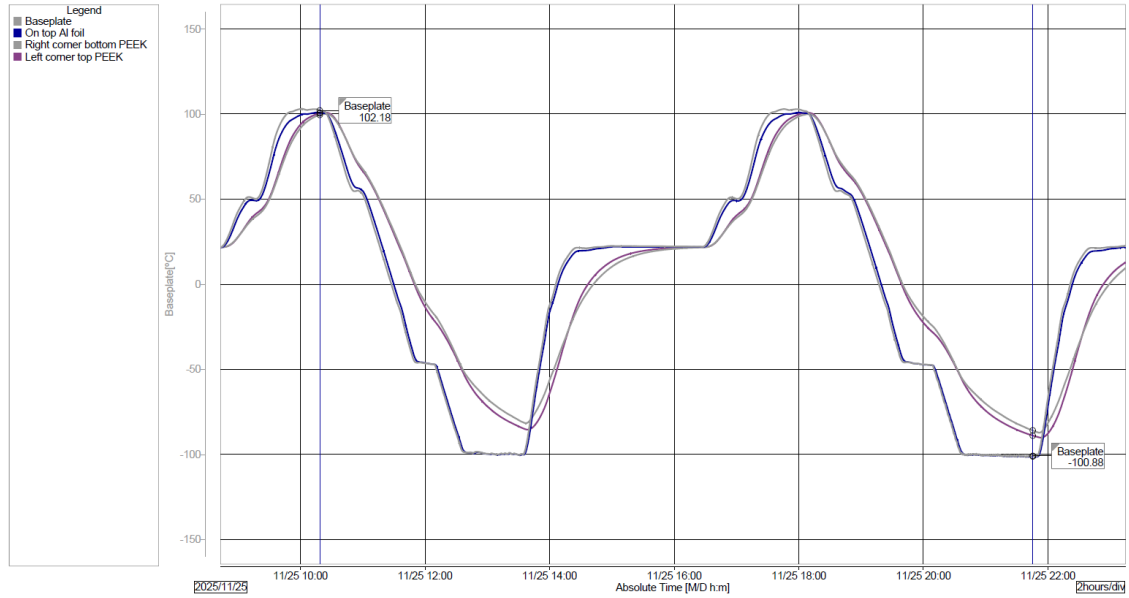


Figure 150: TVAC Cycle 2-3

Cycles 4 through 19 for the baseplate are shown in Figure 151, exhibiting a consistent thermal pattern with a maximum temperature of 101.94 °C and a minimum of -102.20 °C

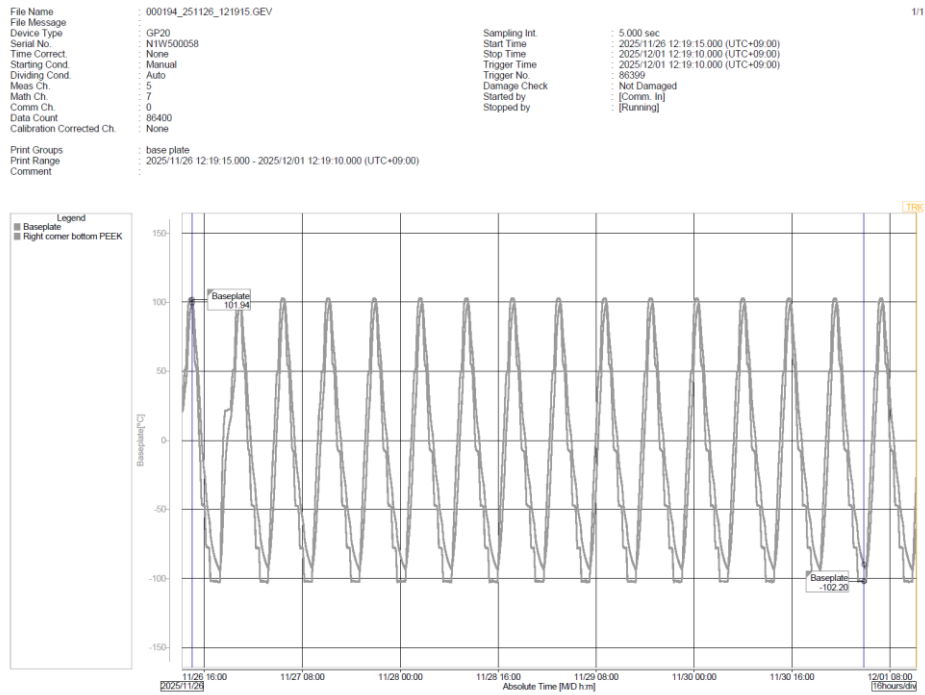


Figure 151: TVAC Cycle 4-19

Figure 152 highlights the baseplate and PEEK during cycles 20 to 25. The thermocouple on the PEEK sample recorded a maximum temperature of 99.88 °C and a minimum of -94.69 °C, likely due to the insulating properties of the polymer.

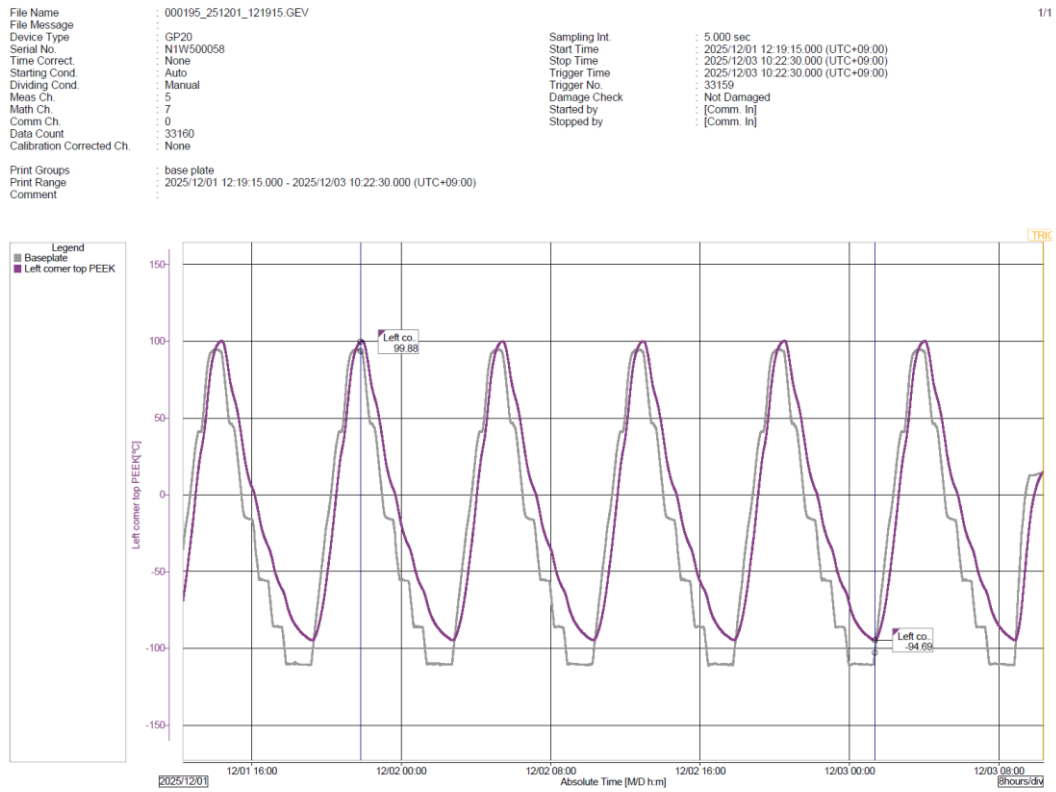


Figure 152: TVAC cycle 20-25

Figure 153 compares the temperatures reached by the baseplate and the PEEK samples. The baseplate attained temperatures of -98.20°C and 101.56°C , whereas the PEEK samples reached slightly lower extremes of -94.74°C and 100.17°C .

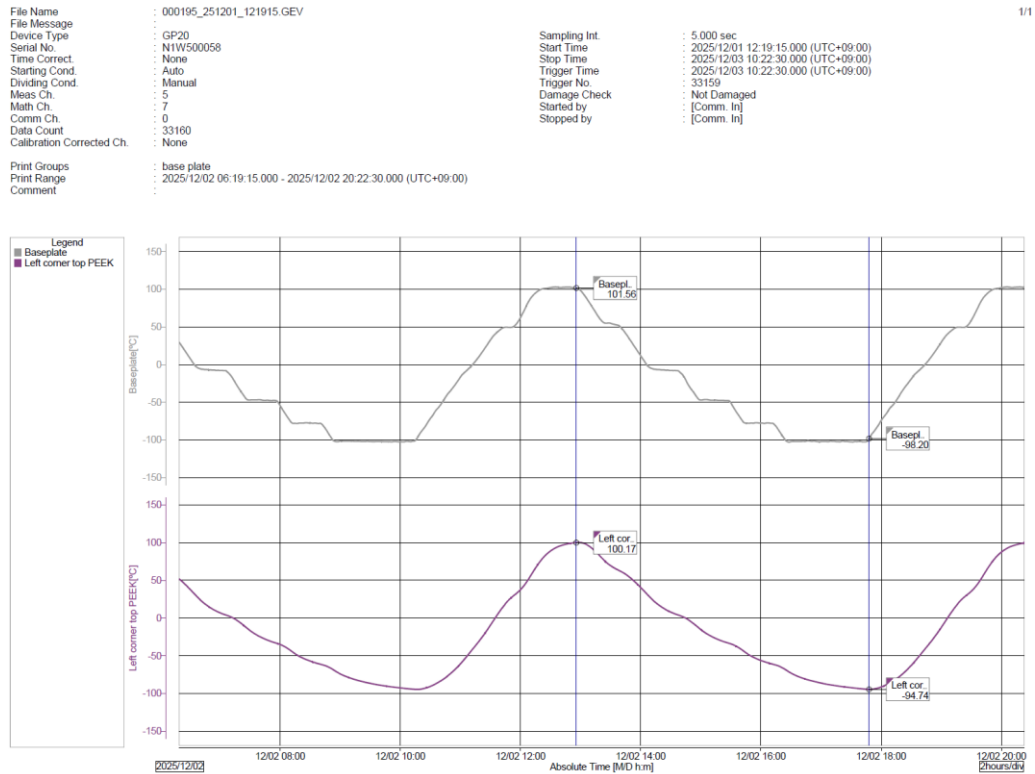


Figure 153: Cycle low-high

It can be concluded that all specimens were subjected to temperatures ranging from -100 °C to +100 °C over 25 cycles, under vacuum levels of approximately 10^{-6} mbar at the maximum temperature and 10^{-7} mbar at the minimum temperature [323].

4.2.5.1. Pictures after TVAC

Post-ATOX and thermal vacuum cycle images were captured using a Canon 700D. Samples are shown in Figure 154.

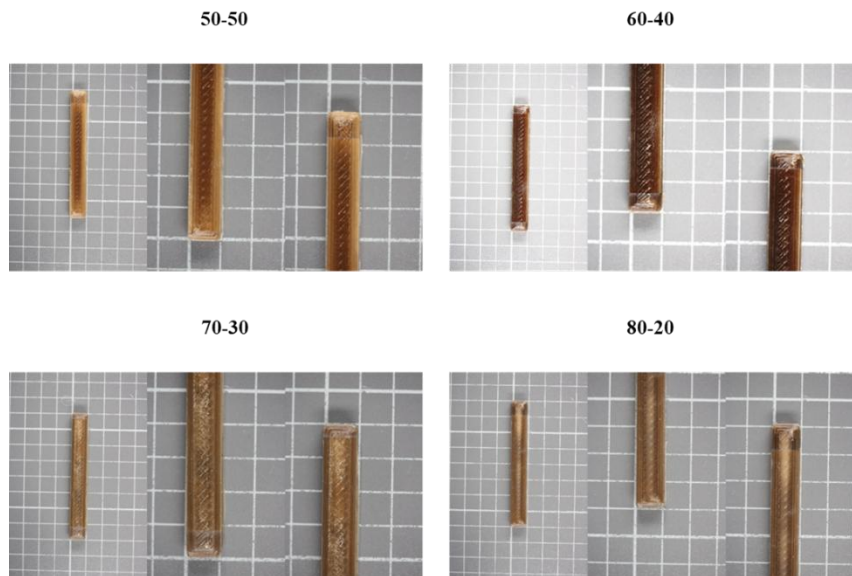


Figure 154: Visual inspection after TVAC

Samples that underwent TVAC exposure (Figure 154) were subsequently subjected to shape memory testing to evaluate whether prolonged exposure to elevated temperatures and vacuum conditions had any impact on their shape memory behaviour.

4.2.6. Shape-memory tests

Sample that underwent TVAC were put in the oven to assess the shape-changing capabilities, in particular the time to recover and the shape recovery ratio. Results can be found in Figure 155, Figure 156, Figure 157 and Figure 158.

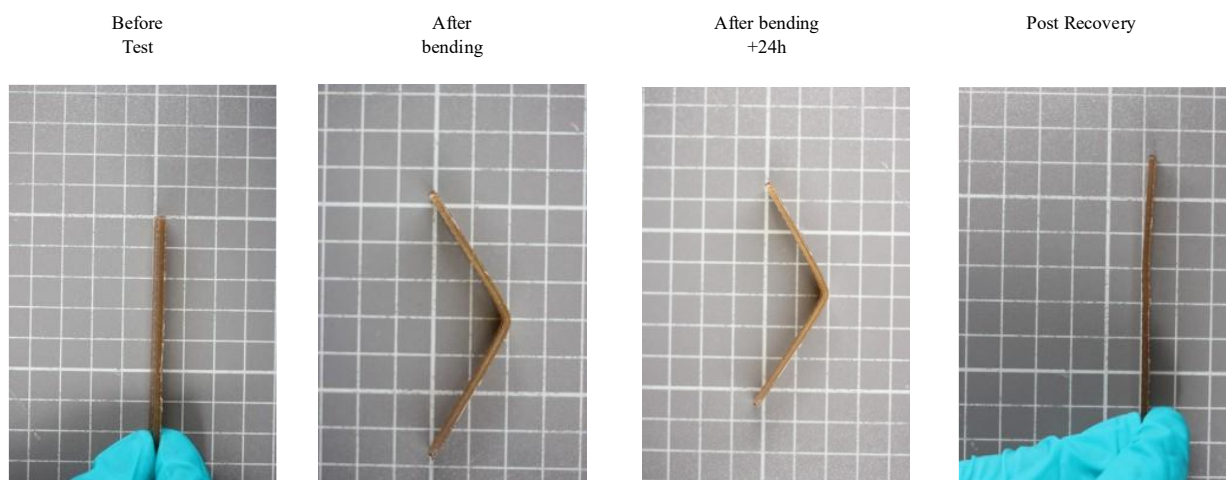


Figure 155: Shape memory evaluation 50PEEK-50PEI after TVAC

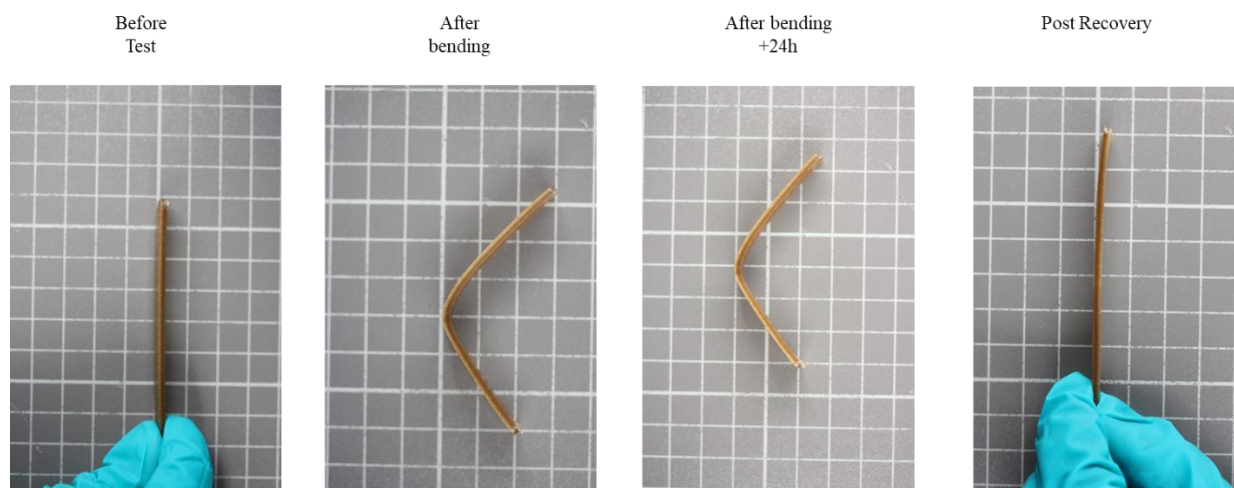


Figure 156: Shape memory evaluation 60PEEK-0PEI after TVAC

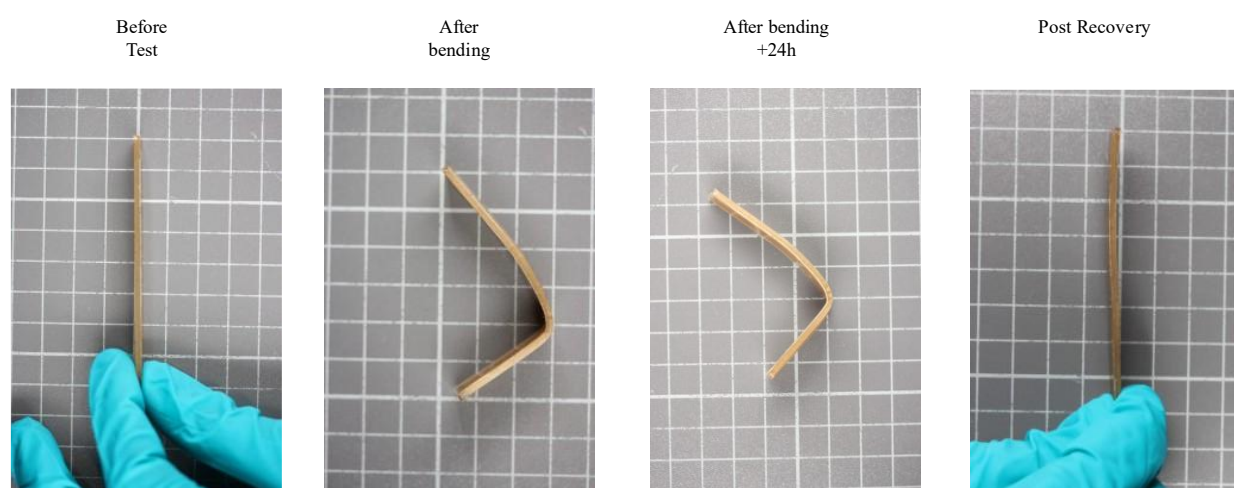


Figure 157: Shape memory evaluation 70PEEK-30PEI after TVAC

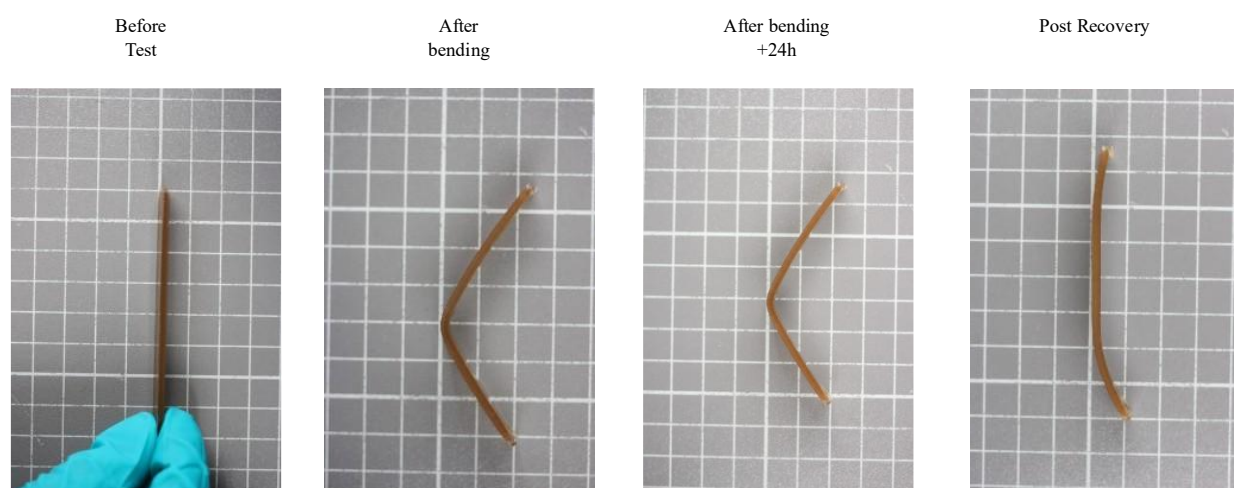


Figure 158: Shape memory evaluation 80PEEK-20PEI after TVAC

Table 25: Summary of Shape-memory parameters after TVAC

Formulation	00	0u	0f	0r	Rf	Rr
50-50	0.993	117.941	0.628	2.916	99.46753	98.92574
60-40	1.104	99.742	3.577	6.732	96.41375	96.85404
70-30	0.995	85.301	0.838	0.408	99.0176	99.77333
80-20	0.898	111.267	2.082	22.306	98.12883	88.04703

Table 26: Shape memory parameters after TVAC

Formulation	Rf	Rr	T Binder	T Heraeus	P (mbar)	t _r Binder	t _r Heraeus
50-50	99.5 %	98.9 %		200°C	1E-3		18 min
60-40	96.4 %	96.9 %		200°C	1E-3		18 min
70-30	99.0 %	99.8 %		200°C	1E-3		18 min
80-20	98.1 %	88.0 %	175°C		1E-3	8.54 min	

The calculated values of shape recovery ratio (Rr) and shape fixity ratio (Rf) ranged between 92% and 99% across all formulations, with the exception of the 80-20 composition, which exhibited slightly lower performance. Post-TVAC exposure, the data indicates a marginal improvement in both Rf and Rr, suggesting that thermal and vacuum conditioning did not adversely affect shape memory behaviour and may have enhanced it slightly. Recovery times for all formulations were observed to fall within the range of 6 to 18 minutes, demonstrating consistent actuation performance under the applied conditions.

The system was designed to operate under vacuum conditions to ensure optimal performance and reliability in space-like environments. Experimental tests were conducted to validate its functionality, and the results yielded the following measured values, confirming compliance with the expected operational parameters. These findings demonstrate the system's capability to maintain stability and efficiency under controlled vacuum conditions, supporting its suitability for the intended application.

4.3. Conclusions and future developments

In this chapter, the simulated space conditions were successfully investigated, and the effects of various composition and printing parameters were evaluated. All formulations meet space compliance requirements regarding outgassing, with TML <1%, CVCM <0.1%, and RML <1%.

Atomic oxygen exposure tests were carried out at the Materials & Electrical Components Laboratory at ESA ESTEC without any non-conformances. The average ATOX fluence across all samples was 2.6×10^{21} atoms/cm², and the average mass loss for all formulations was below 1.5%. Exposure to energetic atomic oxygen caused relatively uniform material erosion, resulting in a rough surface with characteristic cavities.

For thermal vacuum cycling (TVAC), all specimens underwent 25 cycles with temperatures ranging from $-100^{\circ}\text{C} \pm 6^{\circ}\text{C}$ to $+100^{\circ}\text{C} \pm 1^{\circ}\text{C}$. The vacuum levels reached 10^{-6} mbar at the highest temperature and 10^{-7} mbar at the lowest.

Regarding the Shape Memory Effect, shape recovery ratio (Rr) and shape fixity ratio (Rf) values ranged from 92% to 99% for all formulations, except for the 80-20 composition, which showed slightly lower performance. Post-TVAC measurements indicate a minor improvement in both Rf and Rr, suggesting that thermal and vacuum conditioning did not negatively affect, and may even slightly enhance, shape memory behaviour. Recovery times across all formulations were consistent, ranging from 6 to 18 minutes, demonstrating reliable actuation performance under the tested conditions.

Chapter 5. Post Exposure Characterizations after Simulated Space Conditions

In this chapter, post-exposure characterizations on the PEEK-based blends were performed.

The experimental campaign has been conducted in the facilities of the Department of Enterprise Engineering of the University of Rome Tor Vergata, following a three months stay at the European Space Research and Technology Centre (ESTEC, Noordwijk, the Netherlands) of the European Space Agency (ESA), in the Materials & Electrical Components Laboratory of the Materials, Environment and Contamination Section (TEC-MSE).

5.1. Experimental

The materials developed were exposed to simulated space conditions and subsequently underwent comprehensive physic-chemical and mechanical characterization in order to evaluate potential exposure-induced changes in the polymer structure.

FTIR analyses were performed on 3D printed samples exposed to atomic oxygen and thermal vacuum test, using a Cary 630 spectrometer (*Agilent Technologies Inc., Santa Clara, USA*) equipped with a ZnSe ATR accessory and a diamond crystal. Spectra were collected over the wavenumber range of 4000-650 cm^{-1} , with a resolution of 4 cm^{-1} , averaging 32 scans per spectrum.

DSC measurements were conducted on 3D printed samples exposed to atomic oxygen and thermal vacuum test, using a DSC 214 Polyma (*Netzsch group, Selb, Germany*). The analysis was performed under a nitrogen atmosphere in the temperature range of 25-400 $^{\circ}\text{C}$, with both heating and cooling rates set to 10 $^{\circ}\text{C min}^{-1}$. The set cycle was:

- First heating: 25 $^{\circ}\text{C} \rightarrow$ 400 $^{\circ}\text{C}$
- Cooling: 400 $^{\circ}\text{C} \rightarrow$ 25 $^{\circ}\text{C}$
- Second heating: 25 $^{\circ}\text{C} \rightarrow$ 400 $^{\circ}\text{C}$

TGA was conducted using a Pyris 1 TGA Analyzer (*Perkin-Elmer, Waltham, Massachusetts, USA*) to evaluate the thermal stability of the samples after space environment exposure. Samples were heated from room temperature to 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen (80 mL min^{-1}) atmosphere, with a 10 minutes isothermal curve at 800 $^{\circ}\text{C}$ under air atmosphere (40 mL min^{-1}).

Tensile tests have been carried out on five dog-bone exposed 3D-printed samples (85x20x2 mm) per each formulation (Instron 5569 universal testing machine, *Norwood, USA*) with a 50 kN load cell and a crosshead speed of 5 mm/min, according to ASTM D-638.

Exposed 3D printed samples (80x10x4 mm) were mechanically tested via three-point bending tests using an Instron 5569 universal machine (Instron, Norwood, MA, USA), equipped with a 50 kN load cell and a crosshead speed of 2 mm/min, with a length span of 64 mm, according to ISO178.

DMA of the exposed 3D-printed samples was carried out using a Triton 2000 DMA (*Triton Technology, San Juan Capistrano, USA*) operating in tensile mode. Measurements were performed over a temperature range of 25-250 °C at a heating rate of 2 °C min⁻¹, with a frequency of 1 Hz and a displacement amplitude of 50 µm. The storage modulus (E') and loss factor ($\tan \delta$), defined as the ratio between the loss modulus (E'') and the storage modulus (E'), were recorded. The glass transition temperature (T_g) was determined as the temperature corresponding to the maximum of the $\tan \delta$ peak.

5.2. Results

In general, the chemical structure of PEEK exhibits remarkable resistance to gamma and electron beam irradiation, with radical formation levels approximately two orders of magnitude lower than those observed in aliphatic polymers such as polyethylene [330]. This behaviour can be attributed to the molecular architecture of PEEK, in which the aryl rings along the polymer backbone are connected through ketone and ether linkages located at opposite positions of the aromatic units, thereby enabling extensive resonance stabilization throughout the macromolecular chain [331].

Figure 159 represents the FTIR analysis of the pristine 50PEEK-50PEI 3D printed samples, in black, and the 3D printed sample after thermal vacuum test, in red. A zoom is shown in Figure 160. The spectra exhibit a high degree of overlap, with no significant shifts in peak position and no appearance of new absorption bands. This indicates that the thermal-vacuum environment does not induce detectable chemical modifications within the polymer blend and that the characteristic functional groups of both PEEK and PEI remain preserved after testing [332]. The absence of new spectral features associated with oxidation, chain scission, or the formation of degradation products suggests that the material retains its chemical integrity under the investigated conditions. These results are consistent with the inherent stability of high-performance aromatic polymers and confirm that the thermal-vacuum exposure employed in

this study does not produce significant changes in the molecular structure of the 50PEEK-50PEI blend.

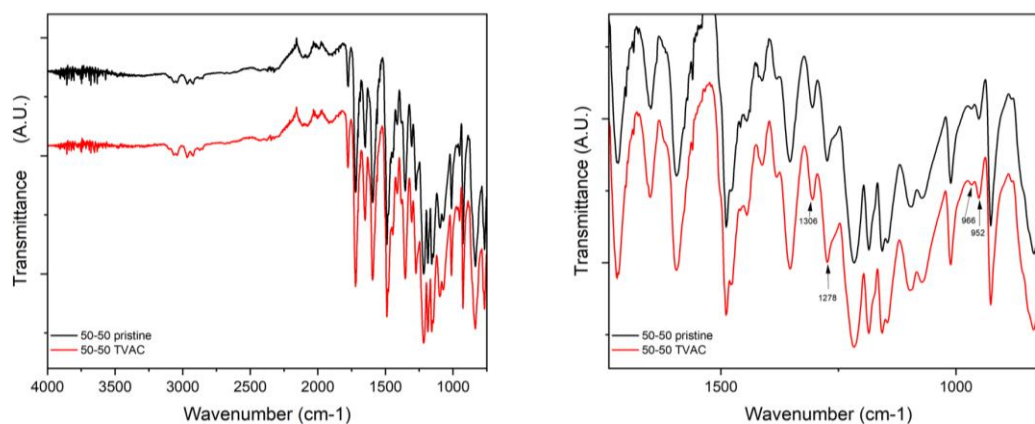


Figure 159: 50PEEK-50PEI pristine vs TVAC

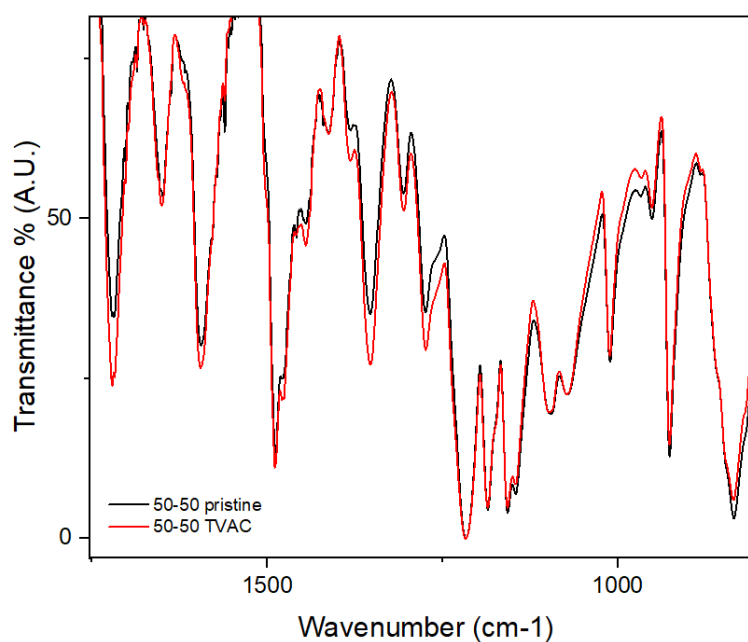


Figure 160: zoom 50PEEK-50PEI pristine vs TVAC

A slight decrease in the I_{1306}/I_{1278} ratio is observed after TVAC exposure, indicating a modification in the relative intensity of the vibrational modes associated with these bands. This variation may reflect subtle changes in chain conformation, local molecular packing, or phase organisation induced by the thermal-vacuum environment. However, the magnitude of the change remains limited, suggesting that any structural reorganisation is minor and does not significantly affect the overall chemical structure of the blend. In contrast, the I_{966}/I_{952} ratio remains essentially unchanged following TVAC treatment, suggesting that the structural features associated with these vibrational modes are largely unaffected by the exposure

conditions. It should also be noted that the use of the 965 cm^{-1} band as a crystallinity indicator has important limitations. Jonas et al. reported that this peak is not suitable for reliably evaluating crystallinity levels above approximately 15%, reducing its usefulness for highly crystalline PEEK-based systems such as those investigated in this work [333]. Consequently, variations in the 1966/1952 ratio should be interpreted with caution and should not be considered a quantitative measure of crystallinity.

Figure 161 depicts the FTIR spectra of the 50PEEK-50PEI blend before and after the combined ATOX+TVAC treatment. The pristine 3D printed sample is shown in black, while the specimen exposed to thermal vacuum conditions followed by atomic oxygen treatment is represented by the orange curve. A zoom is presented in Figure 162.

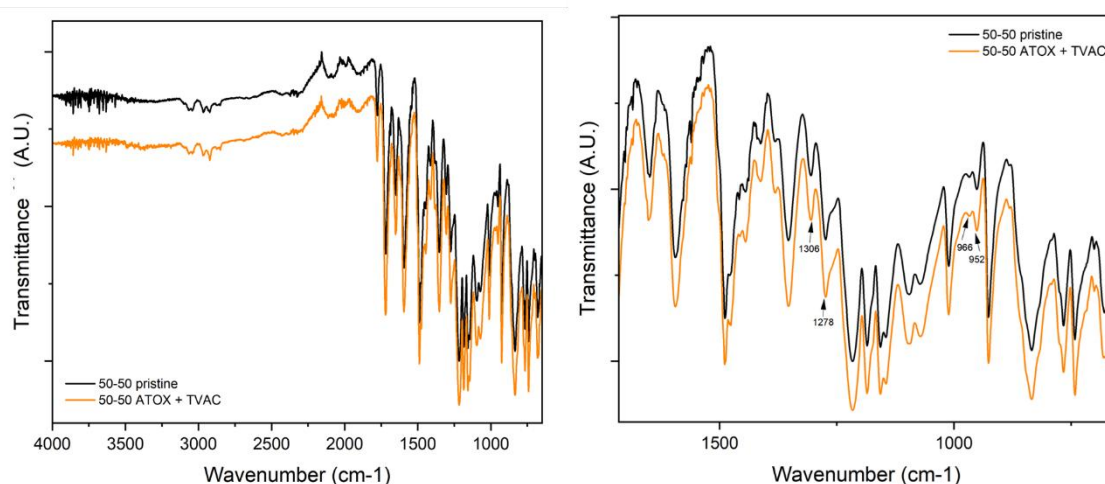


Figure 161: 50PEEK-50PEI pristine vs ATOX + TVAC

A significant change is observed at approximately 2921 cm^{-1} , where the absorption band becomes noticeably more intense, broader, and more extended in the exposed sample. This region is typically associated with aliphatic C-H stretching vibrations. The increase in intensity may indicate modifications in the local molecular environment, potentially arising from surface restructuring and preferential erosion of the outer polymer layers during atomic oxygen exposure [334], [335]. Such changes could increase the relative contribution of hydrocarbon-containing segments to the measured spectrum.

Additional differences are observed in the region extending from approximately 2790 and 1790 cm^{-1} appears shifted toward higher wavenumbers after treatment. where the spectral profile appears slightly shifted towards higher wavenumbers after treatment. Although the displacement is relatively small, it suggests modifications in the local bonding environment and intermolecular interactions. Such behaviour is consistent with changes in polymer packing,

residual stress distribution, or surface oxidation processes induced by the combined effects of thermal-vacuum cycling and atomic oxygen exposure [336].

The absorption band near 1700 cm^{-1} attributed to carbonyl (C=O) stretching vibrations exhibits a reduction in intensity after exposure. This observation may reflect alterations in the carbonyl-containing groups present within the blend, potentially resulting from bond rearrangement, chain scission, or oxidation-induced modification of the polymer surface [337]. Similarly, a decrease in intensity is observed for the band at approximately 1416 cm^{-1} , which is associated with aromatic ring vibrations and C-H bending modes characteristic of the PEEK-PEI backbone. This variation suggests changes in the local organisation of the aromatic structures and may indicate a modification of intermolecular interactions within the blend following environmental exposure [338].

Further differences are evident in the $1425\text{--}1370\text{ cm}^{-1}$ region, where variations in peak shape and relative intensity can be observed. These bands are commonly associated with deformation vibrations of aromatic and alkyl groups. The observed changes may therefore indicate subtle structural reorganisation within the material and possible alterations in the phase morphology or molecular packing of the PEEK-PEI system after ATOX+TVAC treatment [339], [340].

A further modification is observed in the doublet centred around 966 cm^{-1} , which exhibits changes shape in both shape and relative intensity following exposure. This band is generally attributed to aromatic C-H out-of-plane bending and skeletal vibrations of the polymer backbone. Variations in this doublet suggest alterations in the local molecular ordering and possible changes in chain orientation or crystallinity induced by the combined atomic oxygen and thermal vacuum treatment [341].

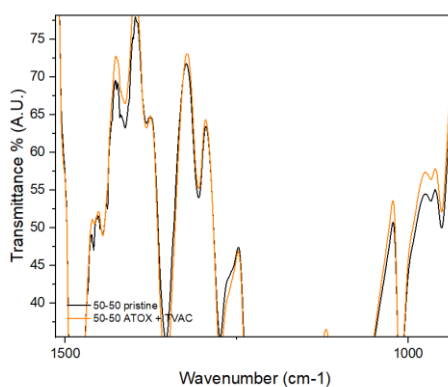


Figure 162: zoom 50PEEK-50PEI pristine vs ATOX + TVAC

A slight decrease in the I_{1306}/I_{1278} ratio is observed after ATOX+TVAC, suggesting a redistribution in the relative contributions of the vibrational modes, potentially reflecting subtle conformational or microstructural changes. Similarly, the I_{966}/I_{952} ratio shows a minor

reduction, indicating that, unlike TVAC alone, the combined treatment has a slightly more pronounced effect on this spectral region. Despite these variations, the observed spectral changes remain relatively limited. No new absorption bands are detected, and the characteristic vibrational features of both PEEK and PEI remain clearly identifiable after exposure. These observations indicate that the fundamental chemical structure of the blend is preserved and that no significant chemical degradation occurs under the investigated conditions.

The modifications observed after ATOX+TVAC exposure are therefore more consistent with localised structural reorganisation, changes in intermolecular interactions, and possible surface oxidation effects than with extensive chemical alteration of the material. Compared with TVAC exposure alone, the slightly larger variations in peak intensity ratios suggest that atomic oxygen contributes to additional surface-level modifications, producing a more pronounced but still moderate effect on the molecular organisation of the blend [342].

Figure 163 presents the FTIR spectra of the pristine 3D-printed samples (depicted in black) and the specimens subjected to the shape-memory cycle and thermal vacuum testing (depicted in green). No detectable shifts in peak positions compared to the pristine material are reported, confirming that the chemical structure remains intact and that no significant degradation or new bond formation occurs during the treatment.

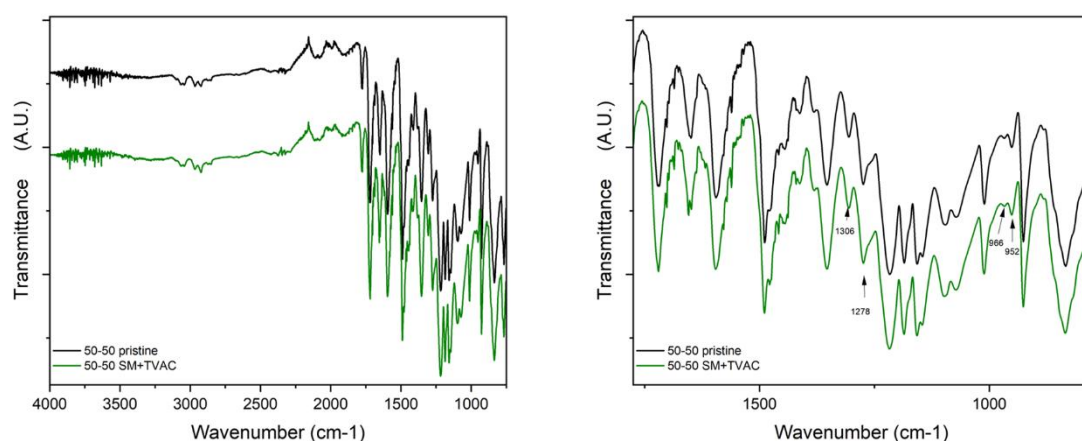


Figure 163: 50PEEK-50PEI pristine vs Shape Memory + TVAC

A modest variation is observed in the doublet around 966 cm^{-1} , which appears slightly shifted towards higher wavenumbers following the shape-memory and thermal-vacuum treatment. This band is associated with aromatic C-H out-of-plane vibrations and backbone skeletal modes. The limited magnitude of the shift suggests subtle modifications in the local molecular environment, potentially related to minor changes in chain orientation, molecular packing, or

local ordering induced by thermal cycling. The absence of significant changes elsewhere in the spectrum indicates that these effects are restricted to structural reorganisation [343].

The I_{1306}/I_{1278} ratio exhibits a slight increase compared to the pristine sample, indicating a change in the relative contribution of the vibrational modes associated with these bands. This variation may reflect a redistribution of local conformational states or a modest reorganisation of the polymer microstructure resulting from the shape-memory activation cycle. Interestingly, this trend differs from the slight decrease observed after the TVAC and ATOX+TVAC treatments, suggesting that thermomechanical cycling promotes a different type of structural rearrangement within the blend.

In contrast, the I_{966}/I_{922} ratio remains essentially unchanged, exhibiting only minor fluctuations within the experimental uncertainty. This observation suggests that the structural motifs associated with these vibrational modes are comparatively insensitive to the shape-memory and thermal-vacuum treatment. These results demonstrate that the thermally activated shape-memory process can be repeatedly triggered without causing detectable alterations to the molecular structure of the material.

Figure 164 represents the FTIR analysis of the pristine 60PEEK-40PEI 3D printed samples, in black, and the 3d printed sample after thermal vacuum test, in red.

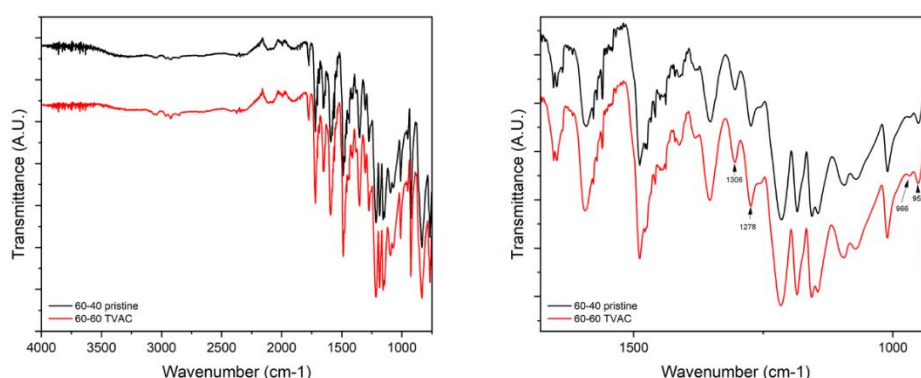


Figure 164: 60-40 pristine vs TVAC

The spectra remain highly similar before and after exposure, indicating that the thermal vacuum treatment does not induce significant chemical degradation or substantial modifications to the molecular structure of the blend. The characteristic absorption bands of both PEEK and PEI are retained, confirming the excellent chemical stability of the material under the tested conditions [258]. Only slight shifts of the absorption bands toward lower wavenumbers are observed after treatment, suggesting minor changes in intermolecular interactions and chain packing. These small displacements may be related to residual stress relaxation, subtle chain

rearrangement, or limited variations in free volume induced by the thermal vacuum environment [344]. The limited magnitude of these changes indicates that any structural reorganisation remains confined to a microstructural level and does not significantly affect the overall integrity of the polymer blend.

Figure 165 represents the FTIR analysis of the pristine 3D printed samples, in black, and the 3D printed sample after thermal vacuum test and exposure to ATOX, in orange. A zoom is depicted in Figure 166.

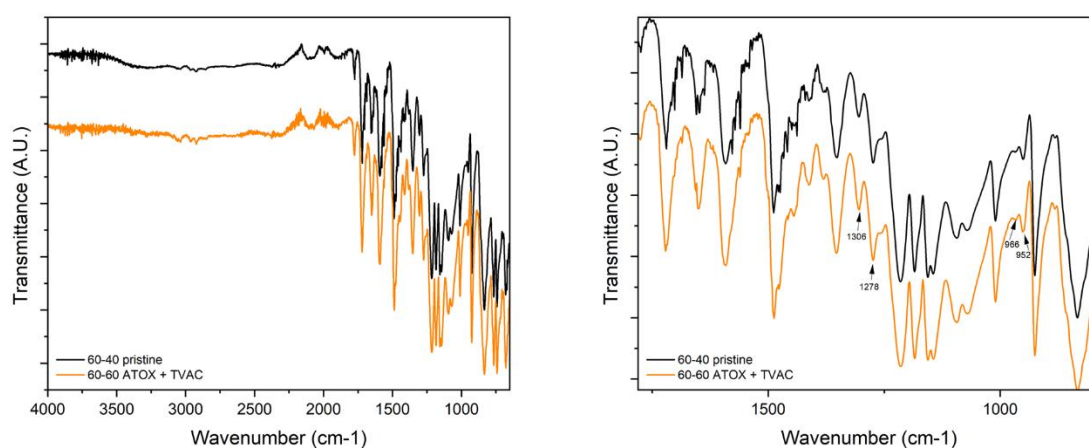


Figure 165: 60-40 pristine vs ATOX + TVAC

Most of the absorption bands exhibit a slight shift toward lower wavenumbers after treatment. This systematic displacement suggests subtle modifications in intermolecular interactions and local molecular organisation within the polymer blend. Such changes are consistent with chain rearrangement, stress relaxation, or surface modifications induced by the combined action of thermal vacuum conditions and atomic oxygen exposure. The observed downshift may also reflect minor alterations in the local bonding environment arising from limited surface oxidation effects or variations in polymer packing density [334]. More pronounced differences are observed in the region between 1420 and 1370 cm^{-1} , where differences in peak shape and relative intensity can be identified between the pristine and treated samples. This spectral region is commonly associated with aromatic ring vibrations (C-H bending) and deformation modes of methyl-related groups within the polymer backbone [340].

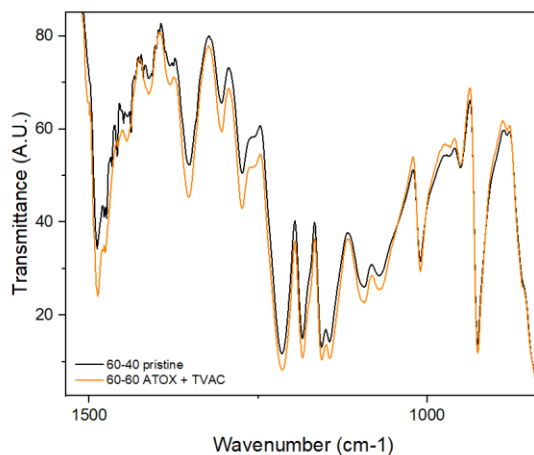


Figure 166: zoom 60-40 pristine vs ATOX + TVAC

Figure 167 represents the FTIR analysis of the pristine 3D printed samples, in black, and the 3d printed sample after Shape-memory effect and thermal vacuum test, in green.

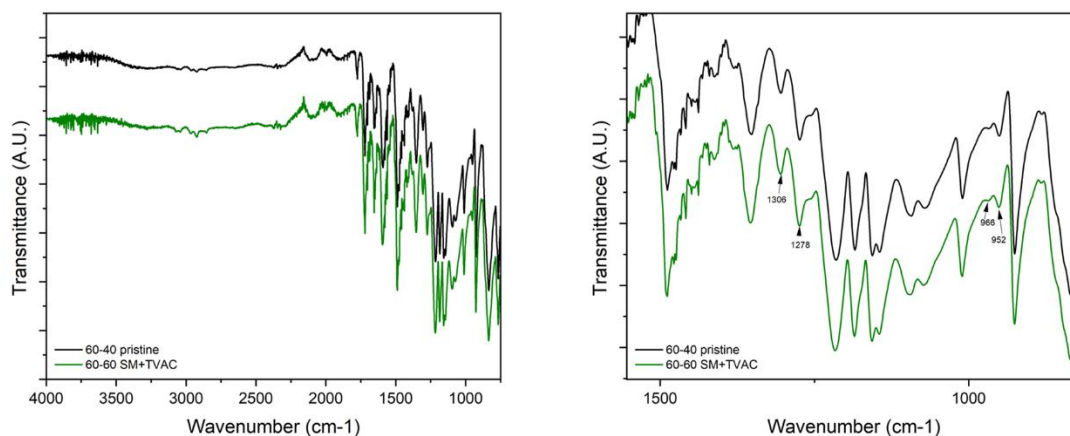


Figure 167: 60-40 pristine vs Shape Memory + TVAC

The spectra exhibit a highly similar overall profile before and after treatment, indicating that the combined shape memory cycle and thermal vacuum exposure does not induce significant chemical degradation or major structural modifications within the polymer blend. The characteristic absorption bands associated with both PEEK and PEI remain clearly identifiable following exposure, confirming the excellent chemical stability of the material under these conditions.

Figure 168 represents the FTIR analysis of the pristine 70PEEK-30PEI 3D printed samples, in black, and the 3D printed sample after thermal vacuum test, in red. The strong overlap between the spectra indicates that the material retains its fundamental chemical structure, with only limited spectral variations resulting from thermal and vacuum-induced ageing effects. Minor

changes are observed in the region around 3100-2800 cm^{-1} , corresponding to aromatic and aliphatic C-H stretching vibrations. These variations may be associated with restricted chain mobility, physical aging, or minor thermally induced rearrangements within the polymer matrix [345]. The characteristic absorption bands attributed to the aromatic ketone groups of PEEK and the imide functionalities of PEI remain unchanged after exposure, providing no evidence of significant chemical decomposition, backbone scission, or formation of new functional groups during testing [346]. Slight variations in peak sharpness can also be observed throughout the fingerprint region (1800-700 cm^{-1}), suggesting minor changes in molecular organisation without alteration of the underlying chemical structure.

Moderate intensity variations are particularly evident in the 1300-1000 cm^{-1} region, which may be attributed to slight modifications in ether linkages and intermolecular interactions caused by thermal relaxation effects under vacuum conditions [347]. The absence of substantial band broadening or pronounced oxidation related features suggests that TVAC exposure alone did not induce extensive oxidative degradation. Importantly, no significant band broadening, disappearance of characteristic peaks, or emergence of oxidation-related absorption features is observed. This indicates that thermal-vacuum exposure alone does not promote extensive chemical degradation of the material.

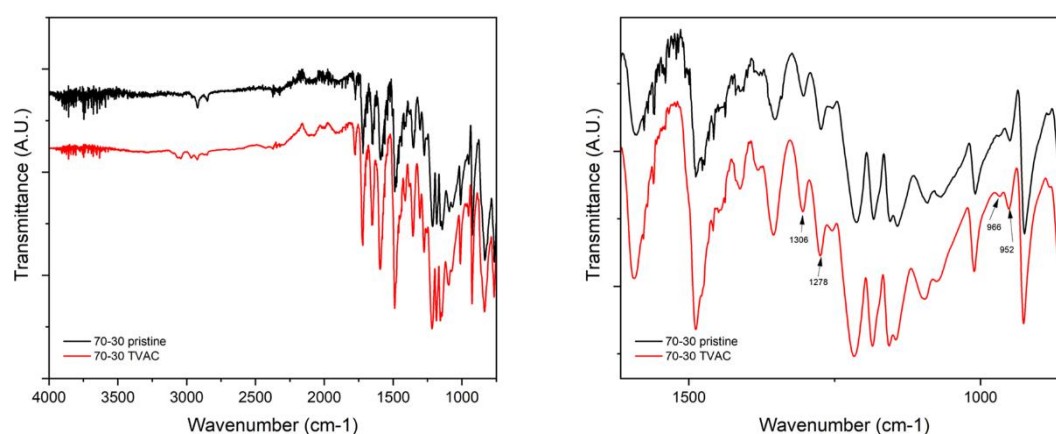


Figure 168: 70PEEK-30PEI pristine vs TVAC

Figure 169 represents the FTIR analysis of the pristine 3D printed samples, in black, and the 3d printed sample after thermal vacuum test and exposure to ATOX, in orange. A zoom is shown in Figure 170.

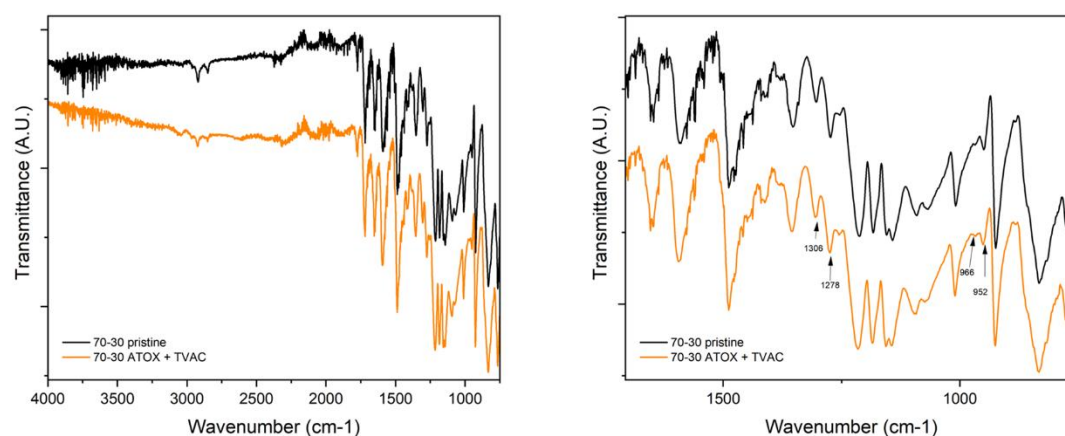


Figure 169: 70PEEK-30PEI pristine vs ATOX + TVAC

The treated samples exhibit noticeable modifications in peak position, intensity and shape, indicating that the environmental exposure produces measurable changes in the surface chemistry of the material relative to the pristine condition. Despite these alterations, the characteristic spectral features of both PEEK and PEI remain clearly identifiable, demonstrating that the treatment affects primarily the surface layers of the material while preserving the fundamental aromatic polymer framework. The most evident changes are observed in the $3400\text{--}3200\text{ cm}^{-1}$ region, where variations in the absorption profile are consistent with the formation of hydroxyl-containing species generated through oxidative reactions between atomic oxygen and the polymer surface [348]. Minor changes in the $2950\text{--}2850\text{ cm}^{-1}$ region further suggest modification of C-H bonding environments which may be associated with limited chain scission, surface oxidation, and rearrangement of near-surface molecular segments induced by the combined environmental exposure [349]. A reduction in transmittance intensity together with localized band broadening throughout portions of the fingerprint region ($1800\text{--}700\text{ cm}^{-1}$) further supports the occurrence of oxidation-driven surface modification. The characteristic absorption bands associated with the aromatic ketone groups of PEEK and the imide functionalities of PEI remain clearly distinguishable after exposure, indicating that the primary polymer backbone is not significantly degraded. However, noticeable intensity variations in the $1300\text{--}1000\text{ cm}^{-1}$ region suggest the formation of additional oxygen-containing functionalities, potentially arising from oxidation of ether linkages and carbonyl-containing structures generated during atomic oxygen exposure [334], [350]. Further alterations observed in the lower wavenumber fingerprint region are consistent with surface erosion and molecular restructuring effects associated with energetic atomic oxygen bombardment [334]. These spectral changes indicate that the ATOX treatment predominantly affects the outermost layers

of the material through oxidative surface reactions, while the bulk chemical structure of the PEEK-PEI blend remains largely preserved.

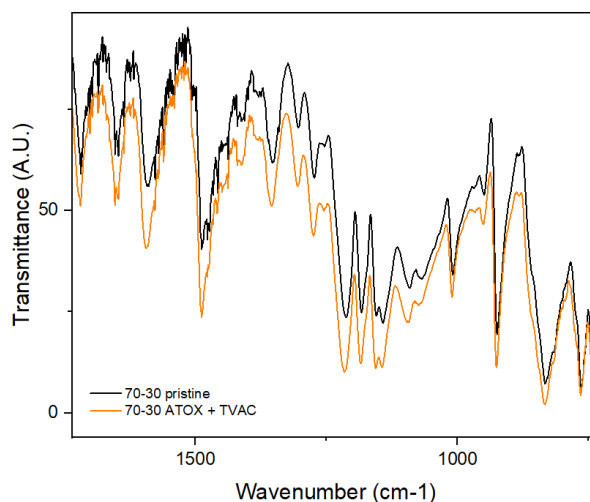


Figure 170: zoom 70PEEK-30PEI pristine vs ATOX + TVAC

Figure 171 represents the FTIR analysis of the pristine 3D printed samples, in black, and the 3d printed sample after Shape-memory effect and thermal vacuum test, in green.

The spectral profiles exhibit negligible variation following treatment, suggesting that the combined shape-memory activation and thermal vacuum exposure do not induce measurable alterations in the polymer blend's chemical structure. The persistence of the characteristic absorption bands attributable to both PEEK and PEI confirms the system's high chemical stability and structural integrity under the applied conditions [225].

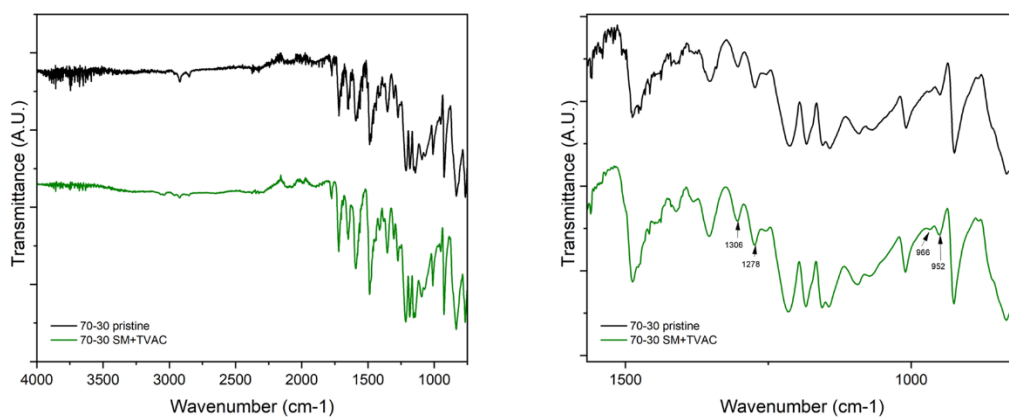


Figure 171: 70PEEK-30PEI pristine vs Shape Memory + TVAC

Minor spectral changes in the $3100\text{--}2800\text{ cm}^{-1}$ region are associated with alterations in aromatic and aliphatic C-H vibrational environments, likely resulting from thermally induced segmental

relaxation and conformational reorganization during shape recovery processes. Pronounced intensity fluctuations within the 1600-1000 cm^{-1} range may be associated with changes in ether linkages, aromatic skeletal vibrations, and dipolar interactions arising from molecular orientation effects induced during shape memory deformation and recovery [351]. Furthermore, no new absorption features associated with degradation products are detected. These observations indicate that the combined treatment does not promote substantial chain scission, oxidation, or chemical decomposition of the blend. Instead, the limited spectral modifications are more consistent with physical restructuring phenomena and localised molecular reorganisation within the existing polymer framework.

The FTIR results therefore suggest that the 70PEEK-30PEI blend possesses excellent chemical stability during shape memory operation under thermal vacuum conditions. The retention of the principal characteristic absorption bands demonstrates that the material can withstand combined thermomechanical activation and simulated space environmental exposure without significant deterioration of its molecular framework, supporting its potential applicability in deployable aerospace and space-adaptive structures.

The FTIR spectra in Figure 172 comparing the pristine 80PEEK-20PEI sample (black curve) with the sample subjected only to TVAC exposure (red curve) indicate minimal chemical alteration, suggesting that thermal vacuum cycling alone does not significantly modify the material's molecular structure.

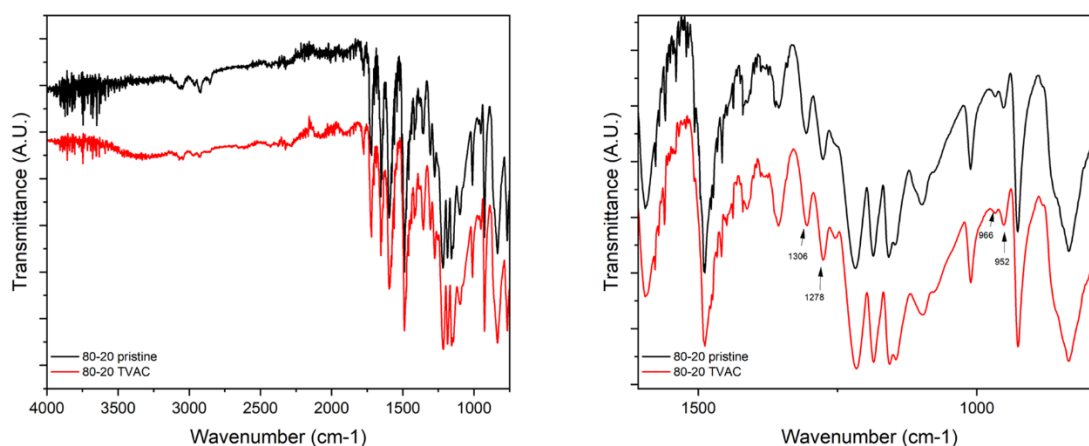


Figure 172: 80PEEK-20PEI pristine vs TVAC

In the high wavenumber region (4000-3000 cm^{-1}), both spectra exhibit similar broad features associated with O-H or N-H stretching, although the TVAC-treated sample shows slightly

reduced noise and a smoother profile, which may be attributed to desorption of physically adsorbed moisture or surface contaminants under vacuum [352]. The C-H stretching region around $3000\text{--}2800\text{ cm}^{-1}$ remains largely unchanged, indicating stability of the aliphatic backbone [332]. Across the mid-wavenumber range ($\approx 2500\text{--}1800\text{ cm}^{-1}$), both spectra follow nearly identical trends with only minor intensity variations. More noticeable differences appear in the fingerprint region ($1800\text{--}800\text{ cm}^{-1}$), where the TVAC spectrum exhibits subtle changes in band intensity and slight shifts in peak positions compared to the pristine sample, particularly near $\sim 1700\text{--}1500\text{ cm}^{-1}$ and below 1200 cm^{-1} ; however, no new peaks emerge. These variations are consistent with small conformational rearrangements or changes in intermolecular interactions rather than chemical degradation [353]. The data support the assumption that TVAC exposure primarily induces physical effects such as outgassing and structural relaxation, with negligible impact on the fundamental chemical functionality of the material.

The FTIR spectra of the 80PEEK-20PEI sample in Figure 173 before (black curve) and after ATOX + TVAC exposure (orange curve) show broadly similar profiles, indicating that the overall chemical structure remains largely intact after environmental treatment, with no evidence of major degradation pathways such as chain scission or formation of entirely new functional groups.

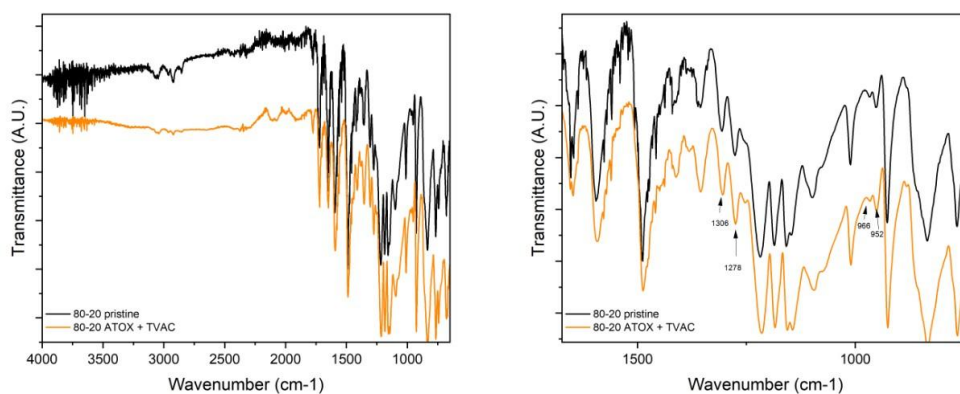


Figure 173: 80PEEK-20PEI pristine vs ATOX + TVAC

In the high wavenumber region ($4000\text{--}3000\text{ cm}^{-1}$), both spectra exhibit relatively weak and broad features, suggesting limited changes in O-H or N-H stretching, although the treated sample shows slightly smoother behaviour, possibly due to reduced surface contamination or moisture. In the mid-region around $3000\text{--}2800\text{ cm}^{-1}$, small differences in the C-H stretching bands are observed, which may reflect minor alterations in aliphatic content or molecular packing. The most pronounced variations occur in the fingerprint region ($1800\text{--}800\text{ cm}^{-1}$),

where both spectra display multiple strong absorption bands; here, the treated sample exhibits slight shifts in peak positions and variations in intensity compared to the pristine sample, particularly near $\sim 1700\text{-}1500\text{ cm}^{-1}$ and below 1200 cm^{-1} . These changes suggest subtle modifications in functional group environments, such as carbonyl or C-O related vibrations, potentially due to oxidation or rearrangement induced by atomic oxygen exposure and thermal cycling under vacuum. Moreover, a reduction in the intensity of the 1215 cm^{-1} peak is associated with the aromatic ether functionality; therefore, its attenuation indicates a decrease in ether bond concentration, which can be attributed to photo-induced degradation processes [354].

The FTIR spectra in Figure 174 of the pristine 80PEEK-20PEI sample (black curve) and the sample subjected to shape memory processing followed by TVAC exposure (green curve) remain broadly similar, indicating that the fundamental chemical structure is largely preserved through the shape memory cycle.

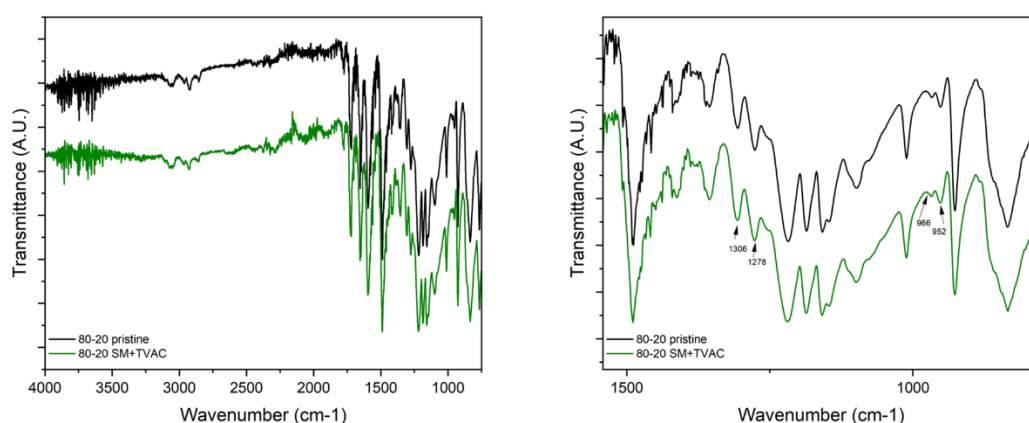


Figure 174: 80PEEK-20PEI pristine vs Shape Memory + TVAC

In the high wavenumber region ($4000\text{-}3000\text{ cm}^{-1}$), both spectra show comparable broad features, with the treated sample exhibiting slightly reduced intensity and smoother behaviour, which may reflect partial removal of absorbed moisture or subtle changes in hydrogen bonding. In the C-H stretching region ($3000\text{-}2800\text{ cm}^{-1}$), only minor differences are observed, suggesting that the aliphatic backbone remains stable. In the mid-wavenumber region ($\approx 2500\text{-}1800\text{ cm}^{-1}$), the spectra remain highly similar, although the treated specimen exhibits a slight reduction in transmittance intensity. This behaviour may be associated with subtle changes in chain packing, local density, or molecular organisation resulting from the thermomechanical cycle and subsequent thermal-vacuum exposure. Such variations are consistent with physical ageing and structural relaxation processes rather than chemical modification of the polymer network.

More evident differences are observed within the fingerprint region ($1800\text{-}800\text{ cm}^{-1}$), where modest variations in band intensity and slight shifts in peak position can be identified, particularly in the $\sim 1700\text{-}1500\text{ cm}^{-1}$ and $1200\text{-}900\text{ cm}^{-1}$ ranges. These spectral changes involve vibrational modes associated with aromatic skeletal structures, carbonyl-containing groups, ether linkages, and intermolecular interactions within the blend. The observed variations are therefore consistent with conformational rearrangements, changes in local molecular packing, and modifications in phase morphology induced by the shape-memory activation process and thermal-vacuum exposure, rather than the formation of new chemical functionalities. The absence of new absorption bands, together with the preservation of the characteristic spectral features of both PEEK and PEI, indicates that the combined treatment does not produce significant chemical degradation. Instead, the FTIR results suggest that shape-memory activation under thermal-vacuum conditions primarily promotes microstructural and morphological reorganisation within the material while preserving the chemical integrity of the polymer blend.

The doublets observed at $1306/1278\text{ cm}^{-1}$ and $966/952\text{ cm}^{-1}$ have been reported in the literature as being sensitive to structural organisation and crystallinity in PEEK [355], [356]. Accordingly, the intensity ratios I_{1306}/I_{1278} and I_{966}/I_{952} were evaluated as qualitative indicators of changes in the microstructural state of the blends. The corresponding values are summarised in Table 27.

Compared to neat PEEK ($I_{1306}/I_{1278} \approx 1.017$), all blends exhibit lower values, indicating that the presence of PEI significantly influences the vibrational environment associated with these bands. Among the 3D-printed samples the ratio increases progressively from approximately 0.71 (50PEEK-50PEI) to 0.86 (80PEEK-20PEI). This trend suggests that increasing PEEK content shifts the spectral response towards that of neat PEEK, consistent with the greater contribution of the semicrystalline PEEK phase to the overall blend behaviour [357].

The effect of environmental and thermomechanical treatments on the I_{1306}/I_{1278} ratio remains relatively modest. For 50PEEK-50PEI blends, the ratio remains within a narrow range ($\approx 0.67\text{-}0.74$), indicating limited sensitivity to the applied conditions. For 60PEEK-40PEI and 70PEEK-30PEI blends, there is a slight increase after ATOX+TVAC (up to $\sim 0.76\text{-}0.81$), which may indicate subtle structural or chemical changes induced by these treatments. For 80PEEK-20PEI, SM+TVAC gives the highest value (0.88), even closer to neat PEEK, hinting at a possible reorganization or enrichment of PEEK-like features. This may suggest a reorganisation of the structure toward more PEEK-like characteristics, potentially associated

with increased ordering or crystallinity induced by the shape memory cycle [358]. However, given the complex relationship between FTIR band intensities and crystallinity in polymer blends, these variations should be interpreted as qualitative indicators of microstructural evolution.

The second ratio (I_{966}/I_{952}) exhibit a substantially smaller variation, with values generally ranging between approximately 0.90 and 0.98. This limited variation suggests that the vibrational modes associated with this doublet are less sensitive to both blend composition and environmental treatment. The highest values are observed for the 70PEEK-30PEI composition and several treated specimens, approaching unity and indicating a more balanced contribution of the two bands. Lower values, typically between 0.90 and 0.92, are mainly observed in 50PEEK-50PEI and 80PEEK-20PEI under specific treatment conditions.

The comparison of the two parameters indicates that I_{1306}/I_{1278} ratio is the more sensitive indicator of compositional and treatment-related effects, displaying a clear dependence on PEEK content together with a moderate response to environmental exposure and thermomechanical cycling. In contrast, I_{966}/I_{952} remains comparatively stable across the investigated conditions, suggesting that it is less effective for distinguishing subtle structural variations within the blend system [359].

Table 27: Intensity ratios

Formulation		I_{1306}	I_{1278}	I_{1306}/I_{1278}	I_{966}	I_{952}	I_{966}/I_{952}
PEEK neat				1.017			
50 PEEK-50 PEI	3D	45.85	65.00	0.71	46.45	49.87	0.93
	ATOX+TVAC	44.51	66.40	0.67	43.56	47.59	0.92
	TVAC	48.51	65.68	0.74	43.65	48.06	0.91
	SM+TVAC	44.51	61.87	0.72	43.8	47.50	0.92
60 PEEK-40 PEI	3D	33.76	45.07	0.75	45.78	47.83	0.96
	ATOX+TVAC	39.67	52.39	0.76	44.00	46.50	0.95
	TVAC	39.70	54.05	0.72	45.80	47.40	0.97
	SM+TVAC	39.50	52.90	0.75	48.32	50.40	0.96
70 PEEK-30 PEI	3D	28.13	36.88	0.76	44.00	44.94	0.98
	ATOX+TVAC	43.60	53.80	0.81	50.46	53.08	0.95
	TVAC	45.70	59.30	0.77	40.80	44.85	0.91
	SM+TVAC	40.48	51.61	0.78	46.38	49.25	0.94
80 PEEK-20 PEI	3D	49.83	58.16	0.86	36.55	40.65	0.90
	ATOX+TVAC	40.41	49.55	0.82	43.67	47.08	0.93
	TVAC	48.3	60.1	0.80	47.18	48.24	0.98
	SM+TVAC	56.27	64.25	0.88	45.92	48.83	0.94

The DSC thermograms for the PEEK-PEI blends after combined atomic oxygen and thermal vacuum exposure continue to exhibit the characteristic thermal transitions of both the semicrystalline PEEK phase and the amorphous PEI phase, indicating that the fundamental

thermal behaviour of the blends is largely retained after environmental ageing. Nevertheless, subtle modifications in the thermal response suggest that the combined exposure induces measurable microstructural changes, primarily affecting the amorphous regions and interfacial domains of the material.

Across all compositions, the endothermic peak observed in the ~335-342 °C range during the first heating correspond to the melting of the PEEK crystalline domains. The limited variation in melting temperature (T_m) following ATOX+TVAC exposure indicates that the crystalline lamellae remain largely stable and that the bulk crystalline structure of PEEK is not significantly disrupted by the environmental treatment [339], [360]. However, slight peak broadening and, in some cases, a modest reduction in peak sharpness, particularly in blends containing higher PEI fractions, may indicate a decrease in crystal perfection or the presence of localised structural defects generated by oxidation-induced modifications within the surrounding amorphous regions [209].

During cooling, the exothermic crystallisation peak associated with PEEK is observed in the temperature range of approximately ~270-282 °C. As expected, the crystallisation temperature (T_c) increases with increasing PEEK content, reflecting the greater concentration of crystallisable segments and the reduced constraining effect of the amorphous PEI phase on crystal nucleation and growth [361]. Following ATOX+TVAC exposure, the crystallisation peaks of the PEI-rich blends become slightly broader and less intense. This behaviour suggests that oxidative modifications and possible structural rearrangements within the amorphous phase may reduce chain mobility and partially hinder crystallisation kinetics during cooling [262]. Additional evidence of microstructural alteration is provided by the reduced heat-flow intensity and smoother thermal transitions observed during the second heating cycle. These changes are consistent with limited oxidation-induced ageing effects, which are expected to be concentrated near the exposed surfaces because of the inherently surface-dominated nature of atomic oxygen degradation [345]. The persistence of all major thermal transitions nevertheless indicates that the bulk thermal properties of the blends remain largely unaffected.

DSC analysis of 50PEEK-50PEI 3D printed samples after ATOX exposure and thermal vacuum test is represented in Figure 175. Compared to Figure 40, representing the 3D printed neat sample, it can be noted that the first heating cycle retains both the glass transition and melting events at similar temperatures, although the associated transitions appear less pronounced after environmental exposure. The cooling curve exhibits a slightly sharper crystallisation peak shifted towards higher temperatures, suggesting modest changes in nucleation behaviour and crystallisation kinetics. During the second heating cycle, the thermal

transitions remain detectable but appear smoother and less steep than those of the pristine material, indicating a more relaxed microstructure and a degree of reorganisation induced by the environmental ageing process [334], [362].

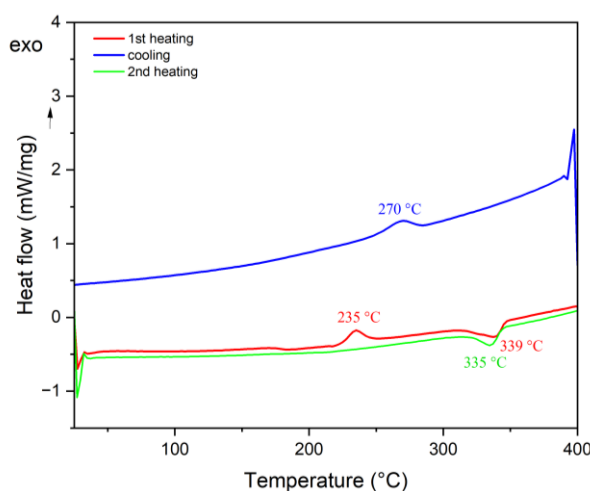


Figure 175: 50PEEK-50PEI DSC after ATOX + TVAC

DSC analysis of 60PEEK-40PEI 3D printed samples after ATOX exposure and thermal vacuum test is represented in Figure 176. Compared with the untreated material shown in Figure 41, the first heating cycle retains both the glass transition temperature (T_g) and the melting temperature (T_m) at essentially unchanged values, indicating that the fundamental thermal transitions of the blend are preserved after environmental ageing. Nevertheless, the associated thermal events appear less pronounced, with smoother and less steep transitions than those observed in the pristine specimen. During cooling, the crystallisation peak remains centred at approximately the same temperature as that of the untreated sample, indicating that the onset of crystallisation and the overall nucleation temperature are not significantly affected by the ATOX+TVAC treatment. This suggests that the balance between nucleation and crystal-growth mechanisms remains largely unchanged despite environmental exposure [363]. crystallisation peak exhibits a lower intensity, indicating a reduction in the overall crystallisation enthalpy and suggesting a less efficient crystallisation process during cooling [364]. This behaviour may be attributed to subtle modifications within the amorphous regions of the blend, where atomic oxygen exposure and thermal-vacuum ageing can alter intermolecular interactions and reduce chain mobility. Such changes may restrict the ability of PEEK chains to reorganise into crystalline structures during cooling, thereby reducing crystallisation efficiency without significantly affecting the crystallisation temperature itself [365]. The second heating cycle exhibits similarly smoother transitions and reduced peak

sharpness compared with the pristine material, further indicating a degree of structural relaxation and microstructural reorganisation induced by the environmental treatment.

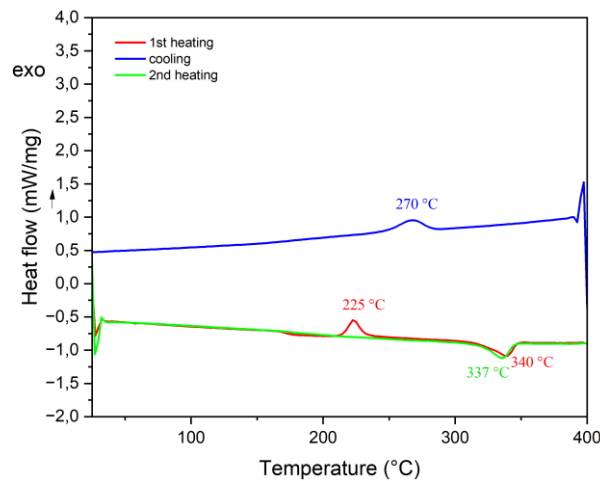


Figure 176: 60PEEK-40PEI DSC after ATOX + TVAC

DSC analysis of 70PEEK-30PEI 3D printed samples after ATOX exposure and thermal vacuum test is represented in Figure 177. Compared to Figure 42, representing the 3D printed neat sample, it can be noted that the first heating again preserves transition temperatures but becomes less steep after AO. More evident differences are observed during the cooling stage. The pristine specimen exhibits a sharper crystallisation peak, whereas the exposed sample shows a broader crystallisation event accompanied by a shift in crystallisation temperature of approximately 3 °C. This behaviour indicates that the environmental treatment influences the crystallisation process, modifying the balance between nucleation and crystal growth during cooling. The shift in T_c suggests that the thermal history imposed by the ATOX+TVAC exposure alters the crystallisation kinetics of the PEEK phase, although the magnitude of the change remains relatively limited.

In contrast to the first heating cycle, the second heating curve of the exposed specimen appears steeper and more defined than that of the untreated material. This behaviour may indicate that the environmental exposure promotes a degree of structural reorganisation within the blend, resulting in a more ordered semicrystalline morphology after the first thermal cycle. Such a response is consistent with enhanced crystal perfection, recrystallisation phenomena, or rearrangement of previously constrained polymer chains during thermal treatment. The preservation of the principal transition temperatures, together with the relatively modest changes in crystallisation behaviour, indicates that the bulk thermal characteristics of the 70PEEK-30PEI blend remain largely unaffected by the combined ATOX and TVAC exposure.

Nevertheless, the observed variations in peak shape and crystallisation behaviour suggest that the treatment induces measurable microstructural evolution, particularly within the semicrystalline PEEK phase, leading to a more organised morphology upon subsequent thermal cycling.

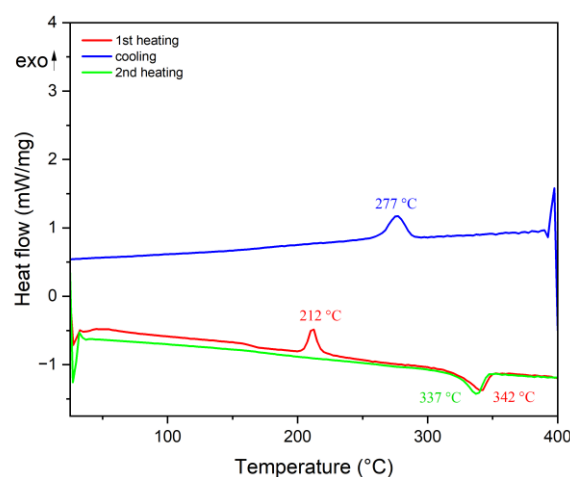


Figure 177: 70PEEK-30PEI DSC after ATOX + TVAC

Figure 178 presents the DSC thermogram of the 80PEEK–20PEI 3D-printed specimen following combined atomic oxygen (ATOX) and thermal-vacuum (TVAC) exposure. Compared with the untreated material shown in Figure 43, the first heating cycle retains both the glass transition temperature (T_g) and the melting temperature (T_m), indicating that the principal thermal transitions of the blend remain unchanged after environmental ageing. However, the thermal events appear more pronounced following exposure, suggesting a more defined thermal response and possible changes in the organisation of the semicrystalline phase. During cooling, the crystallisation peak becomes steeper and exhibits a slight shift towards higher temperatures. This behaviour indicates an enhancement in crystallisation efficiency and suggests that the environmental treatment may promote a more favourable nucleation process or facilitate the formation of a more ordered crystalline structure during cooling. The increase in crystallisation temperature (T_c) further supports the hypothesis that the exposed material requires less undercooling to initiate crystallisation, which is commonly associated with improved crystal nucleation and growth kinetics.

In contrast, the second heating cycle exhibits a smoother and less steep thermal response while maintaining essentially unchanged transition temperatures. The preservation of the melting peak position indicates that the crystal structure remains stable after exposure, whereas the reduced sharpness of the thermal transitions may reflect minor modifications within the

amorphous phase, including local chain rearrangement, stress relaxation, or subtle changes in intermolecular interactions.

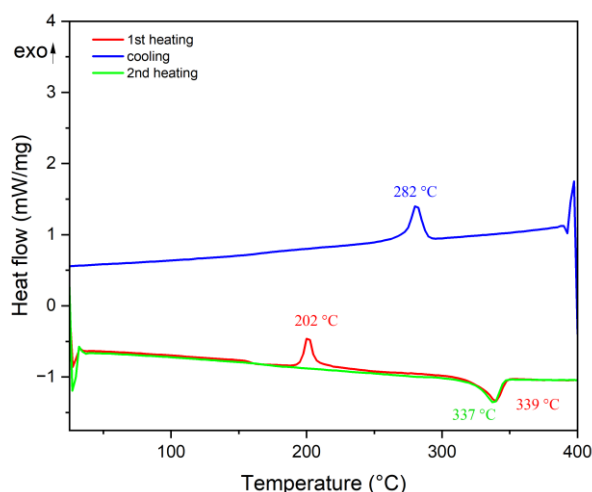


Figure 178: 80PEEK-20PEI DSC after ATOX + TVAC

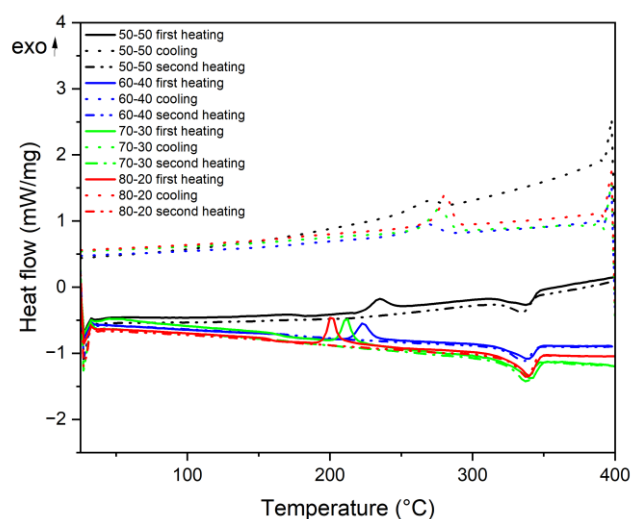


Figure 179: DSC comparison after ATOX + TVAC

Figure 179 shows the comparison of all formulations. Across all compositions, the DSC thermograms show a consistent evolution from filament to 3D-printed state and then after atomic oxygen plus thermal vacuum exposure, with the main transitions being the PEI glass transition (~ 200 - 235 °C depending on composition) and the PEEK melting peak (~ 270 - 295 °C). In the filament condition, the blends exhibit relatively well-defined PEI Tg and sharp PEEK melting peaks, with crystallization during cooling visible as exothermic features around ~ 330 - 340 °C, indicating a baseline semi-crystalline morphology governed by the blend ratio.

After 3D printing, the T_g of the PEI phase generally shifts slightly (often to lower temperatures for higher PEI contents and slightly higher or broader for higher PEEK contents), while the PEEK melting peak becomes broader and in some cases shifts marginally, reflecting reduced crystallinity and increased thermal history effects due to layer-by-layer deposition and rapid cooling; this is also supported by weaker or shifted crystallization exotherms during cooling, indicating constrained crystal growth. Following AO + TVAC exposure, the thermograms largely retain the same transition temperatures but show subtle sharpening or slight increases in melting peak intensity in some compositions (notably higher PEEK fractions), suggesting post-processing annealing or recrystallization under thermal cycling, whereas in PEI-rich blends the T_g becomes slightly more pronounced or shifts marginally upward, consistent with physical aging or oxidative crosslinking effects induced by atomic oxygen.

To calculate the degree of crystallinity, the enthalpies of fusion were determined by integrating the endothermic peaks over time. The data required for these calculations are reported in Figure 44, Figure 45, Figure 46 and Figure 47. The degree of crystallinity was calculated using the following Equation 4:

$$\chi = \frac{\Delta H}{\Delta H_f * w}$$

where χ is the degree of crystallinity, ΔH is the area under the melting peak, ΔH_f is the theoretical enthalpy of fusion (i.e., that of a fully crystalline PEEK sample), and w is the weight fraction of PEEK in the blend. The value of ΔH_f is equal to 130 J/g [228]. Since PEI is amorphous, its weight fraction is not considered in the crystallinity calculation.

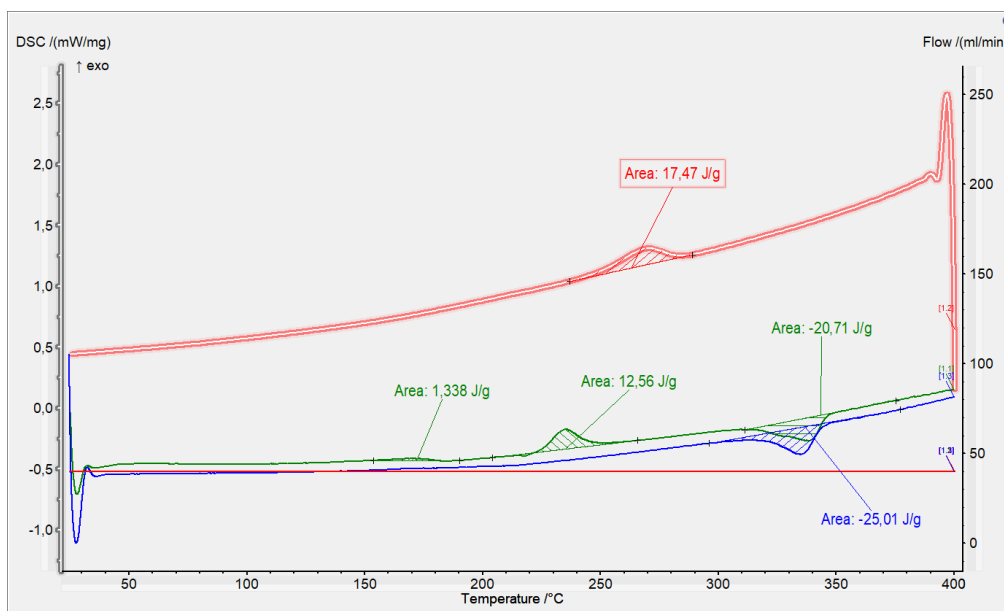


Figure 180: DSC Area 50PEEK-50PEI DSC after ATOX + TVAC

For the 50PEEK-50PEI after ATOX+TVAC, the following values were obtained (Figure 180):

- $\Delta H_{M1} = 20.71 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 25.01 \text{ J/g}$ (second heating);
- $\Delta H_C = 17.47 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 12.56 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 1.338 \text{ J/g}$ (cold crystallisation);

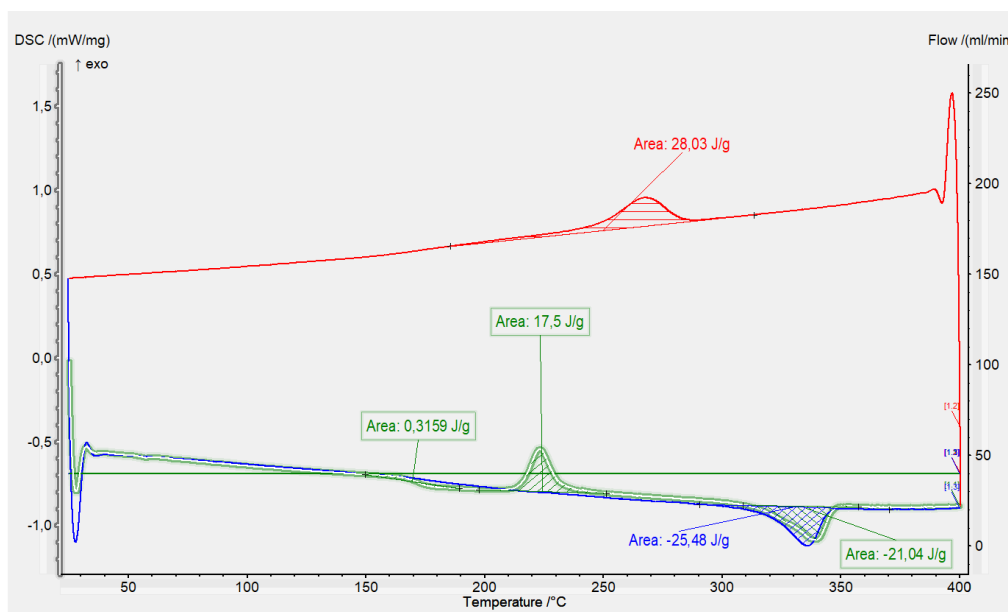


Figure 181: DSC Area 60PEEK-40PEI DSC after ATOX + TVAC

For the 60PEEK-40PEI after ATOX+TVAC, the following values were obtained (Figure 181):

- $\Delta H_{M1} = 21.04 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 25.48 \text{ J/g}$ (second heating);

- $\Delta H_C = 28.03 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 17.5 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 0.3159 \text{ J/g}$ (cold crystallisation);

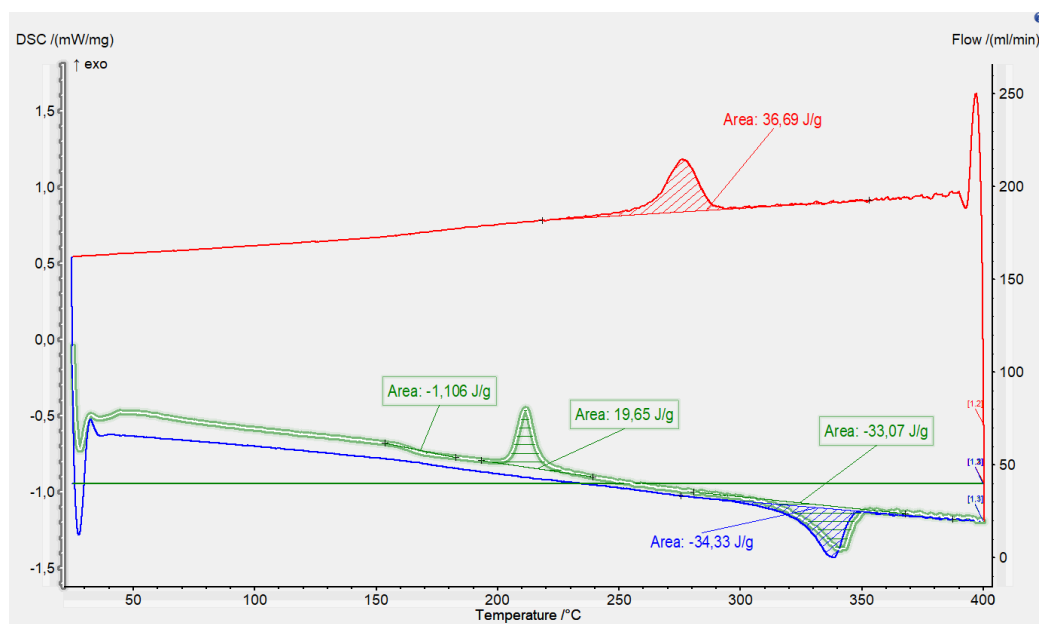


Figure 182: DSC Area 70PEEK-30PEI DSC after ATOX + TVAC

For the 70PEEK-30PEI after ATOX+TVAC, the following values were obtained (Figure 182):

- $\Delta H_{M1} = 33.07 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 34.33 \text{ J/g}$ (second heating);
- $\Delta H_C = 36.69 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 19.65 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 1.106 \text{ J/g}$ (cold crystallisation);

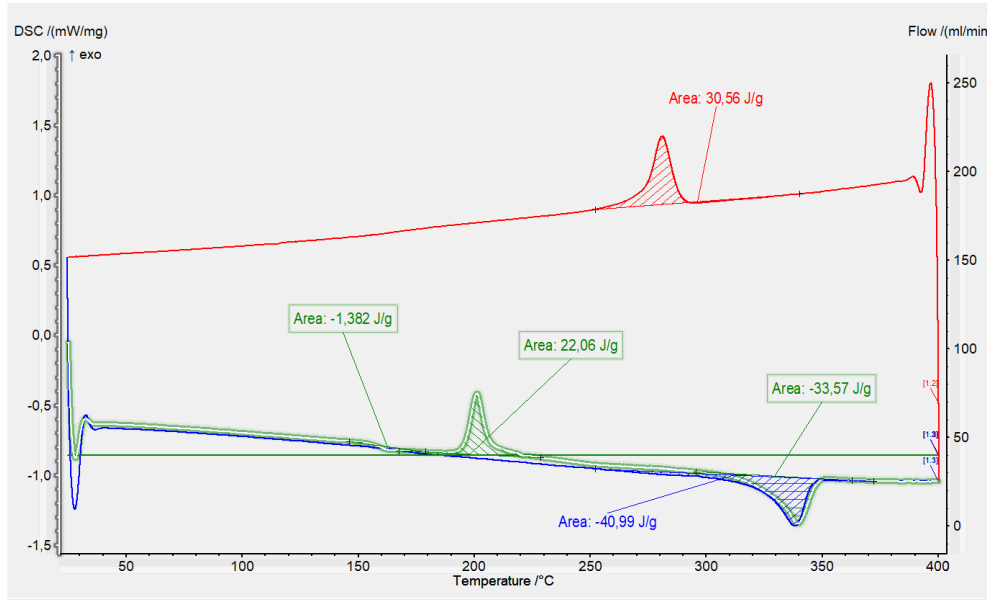


Figure 183: DSC Area 80PEEK-20PEI DSC after ATOX + TVAC

For the 80PEEK-20PEI after ATOX+TVAC, the following values were obtained (Figure 183):

- $\Delta H_{M1} = 33.57 \text{ J/g}$ (first heating);
- $\Delta H_{M2} = 40.99 \text{ J/g}$ (second heating);
- $\Delta H_C = 30.56 \text{ J/g}$ (cooling);
- $\Delta H_{EFH} = 22.06 \text{ J/g}$ (exothermic peak first heating);
- $\Delta H_{CC} = 1.382 \text{ J/g}$ (cold crystallisation);

The summarised values obtained are reported in Table 28.

Table 28: DSC crystallinity after ATOX and TVAC

Formulation	ΔH_{M1}	χ_{M1}	ΔH_{M2}	χ_{M2}	ΔH_C	χ_C	ΔH_{CC}	χ_{CC}	ΔH_{EFH}	χ_{EFH}	Tg (°C)
50PEEK-50PEI	20.71 J/g	31.86%	25.01 J/g	38.48%	17.47 J/g	26.88%	1.338 J/g	2.06%	12.56 J/g	19.32%	167.6
60PEEK-40PEI	21.04 J/g	26.97%	25.48 J/g	32.67%	28.03 J/g	35.94%	0.3159 J/g	0.41%	17.5 J/g	22.44%	166.5
70PEEK-30PEI	33.07 J/g	36.34%	34.33 J/g	37.73%	36.69 J/g	40.32%	1.106 J/g	1.22%	19.65 J/g	21.59%	160.8
80PEEK-20PEI	33.57 J/g	32.28%	40.99 J/g	39.41%	30.56 J/g	29.38%	1.382 J/g	1.33%	22.06 J/g	21.21%	155.6

The results obtained in Table 28 indicate that the environmental treatments induce clear modifications in the semicrystalline morphology and thermal relaxation state of the PEEK-PEI blends. The combined exposure to atomic oxygen, thermal vacuum conditions, and repeated thermal cycling promotes a progressive structural reorganisation of the PEEK phase, leading to changes in crystallisation behaviour and crystal stability compared to the as-printed state [285], [366].

The increase in first-heating melting enthalpy observed particularly in the 70PEEK-30PEI and 80PEEK-20PEI compositions suggests that the environmental exposure facilitates the formation and/or stabilisation of crystalline domains. The corresponding χ_{M1} values indicate

that the thermal vacuum environment acts as a mild annealing stage, allowing partial relaxation of the highly non-equilibrium microstructure generated during fused filament fabrication. Within this environment, residual mobility in the amorphous regions enables imperfect lamellae to reorganise into thicker and more thermodynamically stable crystalline structures [367].

The comparatively smaller difference between χ_{M1} and χ_{M2} in the PEEK-rich compositions further supports this interpretation. In the as-printed samples, substantial recrystallisation occurred during DSC reheating, reflecting the presence of metastable crystalline populations formed during rapid deposition cooling. After environmental exposure, however, the reduced discrepancy between first and second heating crystallinity indicates that a significant portion of this reorganisation had already occurred during the thermal vacuum treatment itself. This suggests that the exposure conditions acted as an effective low level annealing process, partially relaxing the constrained morphology imposed by fused filament fabrication.

The cooling crystallisation behaviour also reveals important structural changes induced by exposure. The 70PEEK-30PEI composition exhibits the highest χ_c value, indicating that this formulation achieved the most favourable balance between chain mobility and nucleation efficiency after exposure to simulated space environment. In contrast, the lower χ_c observed for the 50PEEK-50PEI and 80PEEK-20PEI systems suggests that both excessive amorphous confinement and excessive crystalline continuity can limit efficient crystallisation under post-exposure conditions, albeit through different mechanisms.

The persistence of low cold crystallisation enthalpies across all formulations demonstrates that the exposed materials retained only a limited amount of mobile amorphous PEEK capable of reorganising during reheating. This behaviour indicates that the thermal vacuum exposure substantially reduced the fraction of kinetically trapped amorphous material originally generated during printing.

The treatments reduce the strongly nonequilibrium morphology characteristic of fused filament fabrication, promotes crystal stabilisation and lamellar perfection, and decreases the fraction of constrained amorphous material. Moreover, the persistence of significant exothermic reorganization features confirms that the blends remain structurally heterogeneous and retain a partially metastable morphology even after environmental conditioning.

To account for composition differences, the crystallinity values were normalised by the weight fraction of PEEK present in each blend following the Equation 4 and reported in Table 29:

Table 29: Normalised crystallinity values with respect to the PEEK weight fraction according to Equation 4

Formulation	PEEK fraction	ΔH_c	$\Delta H_{c,norm}$	$X_{c,norm}$
50PEEK-50PEI	0.50	17.47 J/g	34.94 J/g PEEK	26.88%
60PEEK-40PEI	0.60	28.03 J/g	46.72 J/g PEEK	35.94%
70PEEK-30PEI	0.70	36.69 J/g	52.41 J/g PEEK	40.32%
80PEEK-20PEI	0.80	30.56 J/g	38.20 J/g PEEK	29.38%

The normalised crystallization data reveal that the environmental conditioning substantially altered the crystallisation efficiency of the 3D-printed PEEK-PEI blends, but in a composition-dependent manner. Unlike the as-printed materials, the exposed samples display a pronounced maximum in the intermediate composition range, particularly for the 70PEEK-30PEI formulation. This behaviour indicates that the exposure conditions did not simply increase crystallinity globally, but instead promoted selective structural relaxation and recrystallization depending on the balance between semicrystalline and amorphous phases [368], [369].

The progressive increase in $\Delta H_{c,norm}$ from 50PEEK-50PEI to 70PEEK-30PEI suggests that thermal vacuum exposure enhanced the ability of PEEK chains to reorganise during cooling by partially relieving the kinetic constraints initially imposed by the printing process.. The 70PEEK-30PEI composition appears to represent an optimal morphological balance in which chain diffusion, nucleation density, and interfacial mobility collectively maximize crystallization efficiency.

The subsequent decrease observed for the 80PEEK-20PEI system is particularly significant because it demonstrates that increasing PEEK concentration beyond this optimum does not necessarily enhance effective crystallisation after environmental exposure. This reduction in normalised crystallisation efficiency may reflect the development of a more rigid semicrystalline network in the highly PEEK-rich material, where chain mobility becomes increasingly constrained by pre-existing crystalline regions and reduced amorphous free volume.

Thermogravimetric analysis of the different PEEK-PEI blends before and after combined atomic oxygen and thermal vacuum exposure reveals only subtle variations in degradation behaviour, suggesting that the observed effects are mainly associated with surface-driven oxidative modifications rather than bulk polymer deterioration.

Thermal gravimetric results of 50PEEK-50PEI are reported in Figure 184, comparing the 3D printed samples pristine (black curve) and the 3D printed samples after ATOX exposure and TVAC (red curve). Thermal stability is maintained up until 500°C, for both conditions,

confirming the high intrinsic resistance of the blend to thermal decomposition. The residual char yield remains essentially unchanged, with values of ~50% for the pristine material and ~48% after exposure, indicating only a marginal reduction in carbonaceous residue formation. The onset temperature of degradation shows a slight increase after environmental exposure, shifting from 539 °C in the pristine condition to 549 °C in the treated sample. This small shift suggests a minor improvement in apparent thermal stability, which can be associated with limited post-processing annealing effects induced by the thermal vacuum cycling.

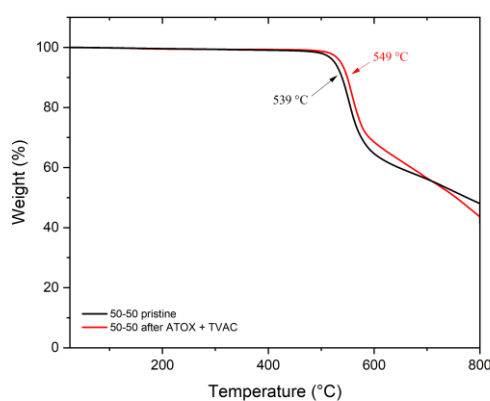


Figure 184: 50PEEK-50PEI TGA comparison 3D pristine vs ATOX + TVAC

Thermal gravimetric results of 60PEEK-40PEI are reported in Figure 185. Figure 184, comparing the 3D printed samples pristine (black curve) and the 3D printed samples after ATOX exposure and TVAC (red curve). Thermal stability is maintained up to approximately 500 °C in both conditions, confirming the high inherent resistance of the material to thermal degradation.

A noticeable difference is observed in the residual char yield, which decreases from ~55% in the pristine sample to ~43% after exposure. This reduction may indicate a slightly lower tendency for carbonaceous residue formation following atomic oxygen exposure, potentially linked to minor surface-level oxidative effects that influence the degradation pathway of the outermost polymer layers, without affecting the bulk material.

Despite this variation in char formation, the onset temperature of degradation increases slightly after exposure, shifting from 547 °C in the pristine condition to 554 °C in the treated sample. This marginal increase suggests a small apparent enhancement in thermal stability, which is more consistent with thermally induced physical rearrangements or post-processing annealing effects during the TVAC cycles than with any intrinsic chemical strengthening of the polymer backbone.

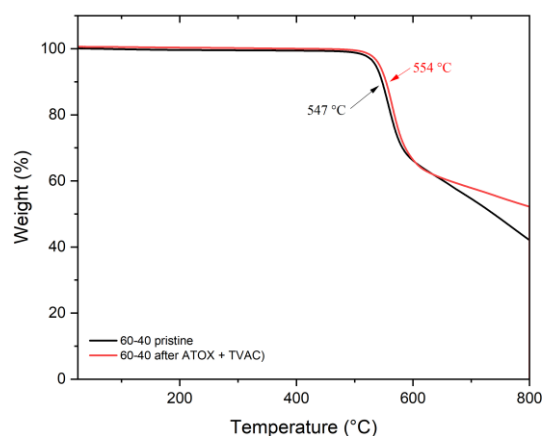


Figure 185: 60PEEK-40PEI TGA comparison 3D pristine vs ATOX + TVAC

Thermal gravimetric results of 70PEEK-30PEI are reported in Figure 184, comparing the 3D printed samples pristine (black curve) and the 3D printed samples after ATOX exposure and TVAC (red curve). Thermal stability is maintained up to approximately 500 °C in both conditions, confirming the high thermal resistance of the material even under the most PEEK-rich intermediate composition.

The residual char yield remains unchanged at ~25% for both pristine and exposed samples, indicating that the exposure does not significantly affect the final carbonaceous residue formation pathway. This consistency suggests that the bulk decomposition mechanism is preserved despite the environmental conditioning, with no meaningful alteration in the overall thermal degradation behaviour.

A slight increase in the onset temperature is observed after exposure, shifting from 534 °C in the pristine state to 538 °C in the treated sample. This marginal shift is indicative of a very limited change in thermal stability, which is more plausibly associated with minor physical reorganisation or stress relaxation effects induced by the combined thermal vacuum cycling rather than any chemical modification of the polymer backbone.

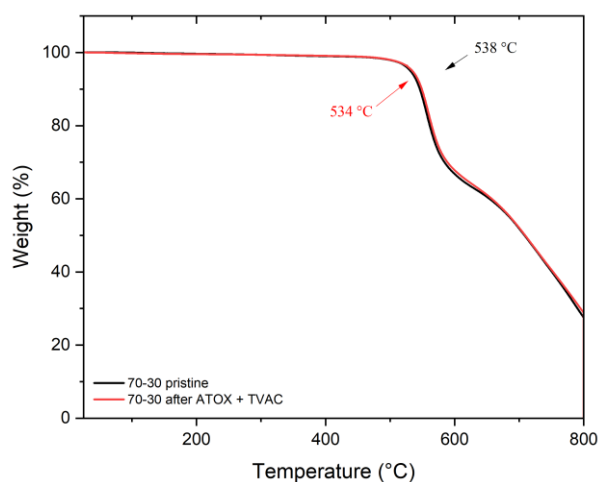


Figure 186: 70PEEK-30PEI TGA comparison 3D pristine vs ATOX + TVAC

Thermal gravimetric results of 80PEEK-20PEI are reported in Figure 184, comparing the 3D printed samples pristine (black curve) and the 3D printed samples after ATOX exposure and TVAC (red curve). Thermal stability is kept up until 500°C. The residual char yield shows a slight decrease after exposure, from ~55% in the pristine sample to ~50% in the treated sample. This modest reduction may be associated with minor surface-level oxidative effects induced by atomic oxygen, which can slightly alter the degradation pathway of the outer polymer layers without significantly affecting the bulk composition or thermal response.

The onset temperature remains essentially unchanged, increasing only marginally from 541 °C in the pristine condition to 543 °C after exposure. This negligible shift indicates that the thermal stability of the material is effectively preserved, with no meaningful alteration of the degradation mechanism.

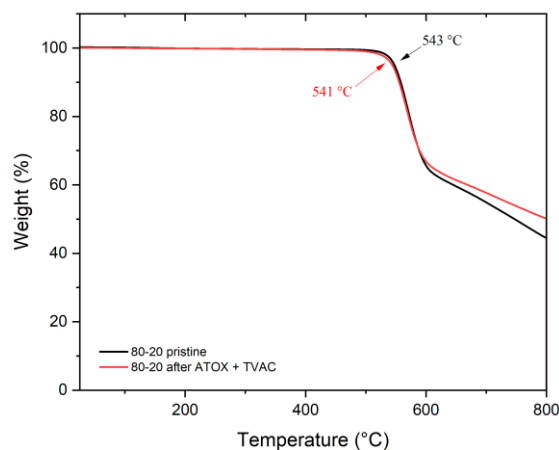


Figure 187: 80PEEK-20PEI TGA comparison 3D pristine vs ATOX + TVAC

The balance between oxidative crosslinking and chain scission is strongly influenced by blend composition. Intermediate formulations (50PEEK-50PEI and 60PEEK-40PEI) display slight enhancements in degradation onset stability, while PEEK-rich blends (70PEEK-30PEI and 80PEEK-20PEI) experience modest reductions in stability after exposure. These observations indicate that the post-ATOX and TVAC thermogravimetric behaviour is controlled by the combined effects of PEEK's intrinsic thermal robustness and the higher oxidative sensitivity of PEI.

Results of averaged tensile tests on 3D printed samples exposed to TVAC are reported in Figure 188 and in Table 30, representing 50PEEK-50PEI in black, 60PEEK-40PEI in blue, 70PEEK-30PEI in green and 80PEEK-20PEI in red. Compared to the pristine 3D printed samples, shown in Figure 78, it can be noted that the tensile response shows only subtle modifications, indicating that the overall mechanical integrity of the blends is largely preserved after exposure to the thermal vacuum environment.

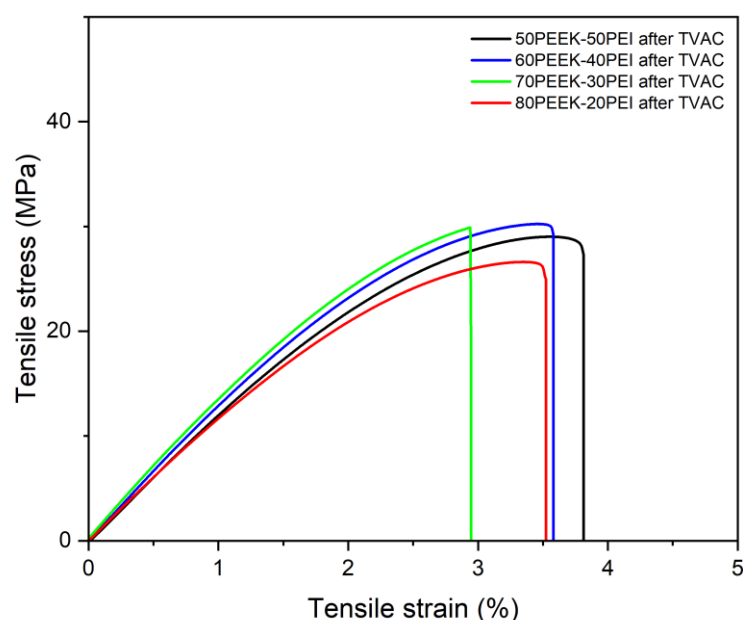


Figure 188: Averaged tensile tests after TVAC

Table 30: Tensile test averaged results of 3D printed samples after TVAC

Formulation	Elastic Modulus (E)	SD	Stress (σ)	SD	Strain (ϵ)	SD
50PEEK-50PEI	1.24 GPa	0.63 GPa	29.02 MPa	8.45 MPa	3.80%	1.09%
60PEEK-40PEI	1.34 GPa	0.67 GPa	30.23 MPa	5.69 MPa	3.57%	1.03%
70PEEK-30PEI	1.40 GPa	0.70 GPa	29.89 MPa	7.92 MPa	2.92%	0.84%
80PEEK-20PEI	1.24 GPa	0.62 GPa	26.61 MPa	4.89 MPa	3.52%	1.01%

The tensile strengths of the printed samples become closer to each other, varying from 1.24 and 1.40 GPa, suggesting that TVAC affects the blends differently depending on composition [370]. The 50PEEK-50PEI sample experiences a reduction in tensile strength (29.02 MPa) after TVAC, suggesting that the thermal vacuum environment may have weakened the polymer network or reduced the effectiveness of interfacial bonding. In contrast, the 60PEEK-40PEI and 70PEEK-30PEI samples show improved or more stable tensile performance after TVAC exposure (30.23 MPa and 29.89 MPa respectively). This may be associated with thermally induced relaxation and enhanced molecular rearrangement during the TVAC cycle, which can improve stress transfer across printed layers [371].

The strain at break after TVAC remains relatively low for all printed samples, ranging from 2.90% to 3.80%, compared to the neat filaments, indicating that the printed structure still governs the failure behaviour. The 60PEEK-40PEI and 70PEEK-30PEI compositions demonstrate comparatively better tensile stability after TVAC exposure, whereas the 50PEEK-50PEI blend shows greater sensitivity to the thermal-vacuum environment.

Results of three-point bending averaged tests are reported in Figure 189 (50PEEK-50PEI), Figure 190 (60PEEK-40PEI), Figure 191 (70PEEK-30PEI) and Figure 192 (80PEEK-20PEI).

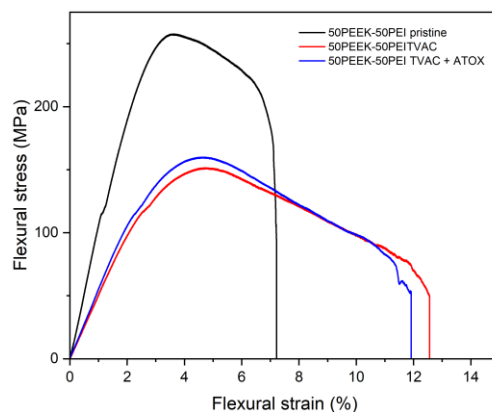


Figure 189: Average Three-Point Bending 50-50

Figure 189 highlights the reduction of 50PEEK-50PEI after both TVAC alone and combined ATOX+TVAC.

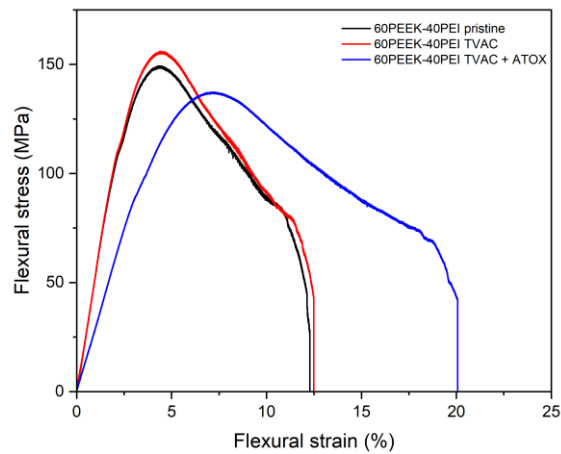


Figure 190: Average Three-Point Bending 60-40

Figure 190 shows that the 60PEEK-40PEI specimens exhibit an almost overlapping behaviour after TVAC exposure, whereas a noticeable change is observed after ATOX+TVAC exposure. In particular, the strain increases from approximately 12-13% to around 20%, accompanied by a reduction in tensile strength.

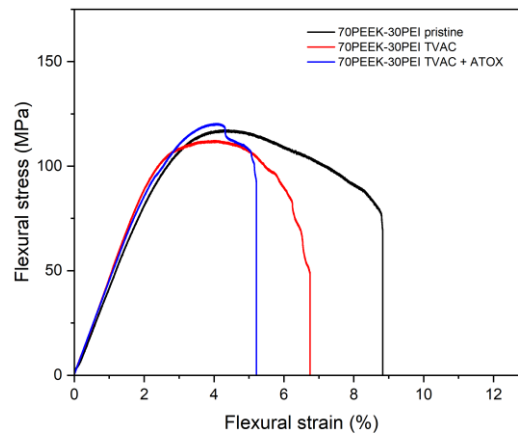


Figure 191: Average Three-Point Bending 70-30

Figure 191 underlines a clear reduction in strain for both the TVAC and ATOX+TVAC conditions, accompanied by a slight reduction in tensile strength.

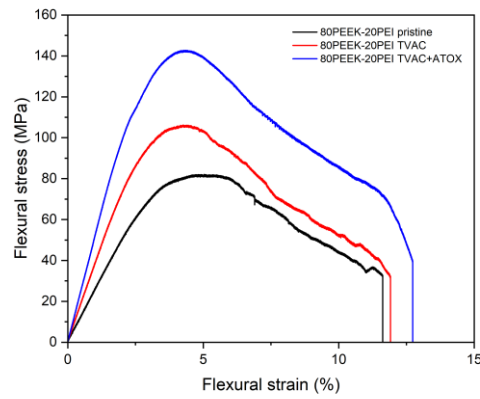


Figure 192: Average Three-Point Bending 80-20

Figure 192 shows an increase in tensile strength under both TVAC and ATOX+TVAC conditions, with a more pronounced effect observed after ATOX+TVAC exposure. In the case of TVAC, a slight increase in tensile strain is observed, whereas for ATOX+TVAC the strain increases by approximately 3%.

A comparison of the results after TVAC exposure for all formulations is presented in Figure 193, while the corresponding results after ATOX+TVAC exposure are shown in Figure 194, with all data summarised in Table 31 and Table 32.

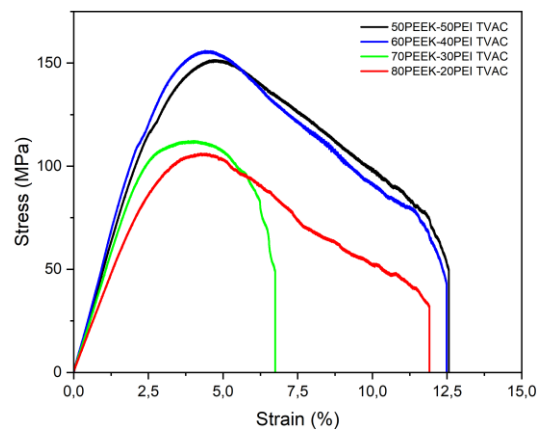


Figure 193: Average Three-Point Bending after TVAC Comparison

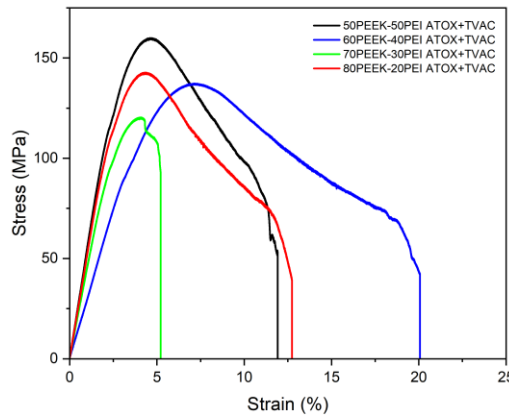


Figure 194: Average Three-Point Bending after ATOX+TVAC Comparison

Table 31: Three-point bending tests averaged results after TVAC

Formulation	Elastic Modulus (E)	SD	Stress (σ)	SD	Strain (ϵ)	SD
50PEEK-50PEI	4.37 GPa	0.03 GPa	151.53MPa	37.86 MPa	12.61%	3.63%
60PEEK-40PEI	5.61 GPa	0.03 GPa	156.09MPa	39.29MPa	12.51%	3.60%
70PEEK-30PEI	4.56 GPa	0.03 GPa	130.75MPa	29.11 MPa	6.75%	1.95%
80PEEK-20PEI	3.99 GPa	0.03 GPa	106.22MPa	25.95 MPa	11.80%	3.41%

Table 32: Three-point bending tests averaged results after ATOX+TVAC

Formulation	Elastic Modulus (E)	SD	Stress (σ)	SD	Strain (ϵ)	SD
50PEEK-50PEI	5.39 GPa	2.58 GPa	160.03MPa	45.20 MPa	11.92%	3.44%
60PEEK-40PEI	2.96 GPa	2.30 GPa	137.31MPa	36.75MPa	20.06%	5.79%
70PEEK-30PEI	4.64 GPa	2.40 GPa	120.41MPa	35.84 MPa	5.21%	1.50%
80PEEK-20PEI	5.13 GPa	2.44 GPa	142.74MPa	38.09 MPa	12.73%	3.67%

The three point bending results show a clear dependence of mechanical response on blend composition, with distinct differences between the TVAC and ATOX+TVAC exposure conditions. Under TVAC (Table 30), the elastic modulus varies between approximately 4.0 and 5.6 GPa, with the 60PEE-40PEI formulation exhibiting the highest stiffness (5.61 GPa), indicating an optimal balance of phase interaction and load transfer efficiency at this composition. In contrast, 80PEEK-20PEI shows the lowest modulus, suggesting reduced structural reinforcement from the PEI phase at higher PEEK content.

The flexural strength follows a similar trend, with 60PEEK-40PEI and 50PEEK-50PEI exhibiting the highest values (156 MPa and 151 MPa respectively), while 80PEEK-20PEI presents a marked reduction (106 MPa). This indicates that intermediate compositions promote more effective stress transfer mechanisms, whereas PEEK-rich systems do not translate into proportional strength gains under TVAC conditions. The strain at failure remains relatively high for 50PEEK-50PEI and 60PEEK-40PEI formulations (approximately 12-13%), whereas a pronounced reduction is observed for 70PEEK-30PEI (6.75%), suggesting a composition-

dependent transition toward reduced plastic deformation capacity, likely associated with changes in phase continuity or constrained molecular mobility [372].

Following ATOX+TVAC exposure the mechanical response becomes significantly more scattered, particularly in terms of elastic modulus, where standard deviations increase substantially. This indicates that the material system becomes more sensitive to environmental degradation mechanisms or exhibits increased heterogeneity in mechanical response. The 60PEEK-40PEI formulation is notably affected, with the modulus decreasing to 2.96 GPa and strain increasing to approximately 20%. Such behaviour may be attributed to environmentally induced modifications in interphase adhesion or partial chain scission leading to increased segmental mobility [368], [369].

The flexural strength remains comparatively less sensitive to environmental exposure, remaining within a narrower band of approximately 120 to 160 MPa across all compositions. The 50PEEK-50PEI formulation maintains the highest strength under ATOX+TVAC conditions (160 MPa), suggesting superior resistance to environmentally induced damage accumulation and more stable load-bearing capability.

Although the 70PEEK-30PEI formulation appears mechanically inferior in the bending data, this behaviour is actually consistent with a material that is mechanically constrained in the permanent configuration, which is a desirable prerequisite for shape memory functionality [373], [374]. In shape memory systems, high flexural ductility is not necessarily advantageous; instead, what matters is the ability to sustain deformation in a controlled, recoverable manner and to store elastic energy rather than dissipate it irreversibly through plastic flow.

The reduced strain to failure observed for the 70PEEK-30PEI composition suggests a higher effective network rigidity and more restricted segmental mobility. This type of response is often associated with more stable switching segments and a better defined phase contrast between hard and soft domains, which are critical for shape memory activation.

Furthermore, the relatively consistent low strain behaviour of 70PEEK-30PEI across both TVAC and ATOX+TVAC conditions indicates that its deformation mechanism is less sensitive to environmental perturbation. This stability is important for shape memory applications in aerospace or space like environments, where reproducibility of the programmed shape and resistance to environmental aging are often more critical than maximizing ultimate elongation or flexural compliance [375], [376].

DMA analysis show consistent viscoelastic trends across the PEEK-PEI blends. For all compositions, the storage modulus in the region below 150 °C remains largely unchanged after

exposure, indicating that neither AO nor TVAC induces significant bulk chain scission or crosslinking that would affect the elastic response at low temperatures [377]. This suggests that degradation is predominantly surface limited, typical for atomic oxygen interactions with aromatic polymers [334].

Comparison of DMA analysis on a 50PEEK-50PEI 3D printed pristine sample and a 3D printed samples exposed to ATOX and TVAC is reported in Figure 195. The glass transition temperature increased from 196 °C for the neat 3D-printed sample to 201 °C for the exposed sample, while the corresponding transition peak became less intense after exposure. This behaviour may indicate a slight restriction of polymer chain mobility induced by the environmental treatment [232], [378]. When the onset of E' is used as the evaluation criterion, the resulting value is 189 °C. Furthermore, the storage modulus of the exposed sample remains comparable to that of the pristine material, suggesting that the thermo-mechanical stiffness of the blend was substantially preserved after ATOX and TVAC exposure [379].

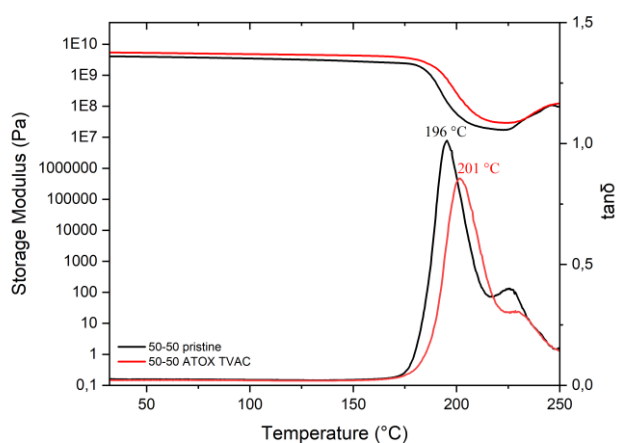


Figure 195: 50PEEK-50PEI DMA comparison

An evaluation of DMA analysis on a 60PEEK-40PEI 3D printed pristine sample and 3D printed samples exposed to ATOX and TVAC is reported in Figure 196. The exposed sample exhibits a lower T_g , decreasing from 195 °C for the pristine material to 188 °C after environmental exposure, together with a less pronounced transition peak. When evaluated as the onset of the E' , the value becomes 174 °C. In addition, the lower E' values observed for the exposed sample indicate a reduction in stiffness, suggesting that ATOX and TVAC conditions may have induced slight degradation or increased molecular mobility within the material [380].

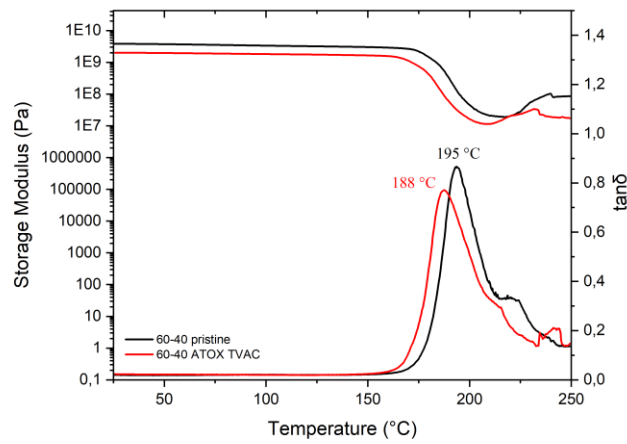


Figure 196: 60PEEK-40PEI DMA comparison

Figure 197 represents the comparison of DMA analysis on a 70PEEK-30PEI 3D printed pristine sample and a 3D printed samples exposed to ATOX and TVAC. The glass transition temperature remains substantially unchanged after exposure, varying only from 187 °C for the neat material to 186 °C for the exposed sample. Using the onset of E' for evaluation yields a value of 175 °C. Moreover, the storage modulus curves are nearly superimposable over the investigated temperature range, indicating that the thermo-mechanical behaviour of the material was not significantly affected by the simulated space environment exposure [345].

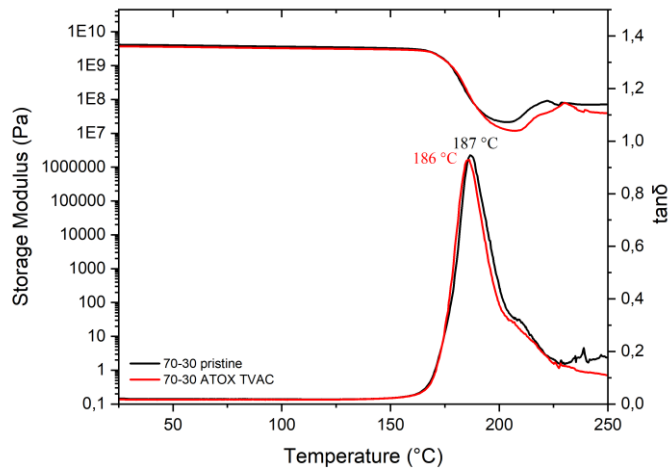


Figure 197: 70PEEK-30PEI DMA comparison

Figure 198 shows the DMA responses of pristine 80PEEK-20PEI 3D-printed sample and specimens exposed to ATOX and TVAC conditions. A progressive reduction in the storage modulus is observed with increasing temperature for both conditions. The Tg shows only a negligible variation, decreasing slightly from 182.5 °C for the neat material to 182 °C after

exposure. The T_g value is determined to be 168 °C when the onset of E' is considered. In addition, the overlap of the E' curves suggests that the environmental treatment did not significantly alter the viscoelastic response or the overall thermo-mechanical stability of the blend.

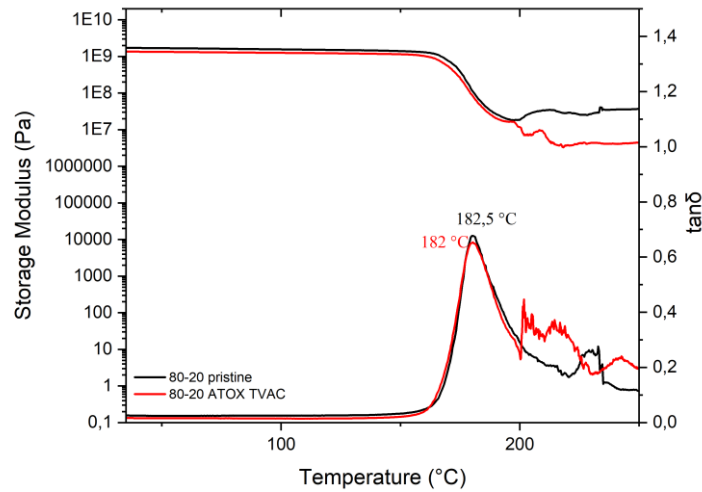


Figure 198: 80PEEK-20PEI DMA comparison

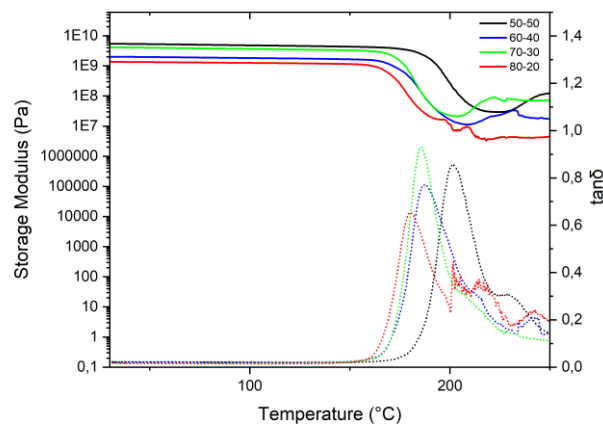


Figure 199: DMA after TVAC + ATOX comparison

A summary of all DMAs is presented in Figure 199.

5.3. Conclusions

The post-exposure characterisations of the 3D-printed PEEK-PEI blends demonstrated that the simulated space environment conditions, including thermal vacuum cycling and atomic oxygen exposure, did not induce severe chemical degradation of the polymeric systems. FTIR analyses confirmed the preservation of the characteristic absorption bands associated with both PEEK

and PEI phases across all investigated compositions, indicating that the fundamental aromatic backbone architecture remained substantially intact after exposure. The spectral modifications observed after ATOX+TVAC treatments were primarily associated with subtle surface oxidation phenomena, conformational rearrangements, and localised variations in intermolecular interactions. The detected variations in the 1700-1500 cm^{-1} and 1300-1000 cm^{-1} regions with the evolution of the I_{1306}/I_{1278} and I_{966}/I_{952} intensity ratios, suggest that the environmental conditioning promoted moderate structural reorganisation and partial relaxation of the non-equilibrium morphology generated during fused filament fabrication.

The thermal analyses further confirmed the high stability of the investigated blends under simulated space conditions. DSC measurements showed that the principal thermal transitions, including the PEI glass transition and the PEEK melting peak, remained substantially preserved after environmental exposure. Nevertheless, modifications in melting enthalpy, crystallisation behaviour, and peak sharpness demonstrated that the combined action of thermal cycling and atomic oxygen induced measurable changes in semicrystalline morphology and crystallisation kinetics. In particular, the environmental exposure acted as a low level annealing process capable of promoting partial lamellar thickening, crystal stabilisation, and relaxation of kinetically constrained amorphous regions generated during printing. The 70PEEK-30PEI formulation exhibited the highest normalised crystallization efficiency after exposure, indicating the existence of an optimal balance between chain mobility, nucleation density, and interfacial constraints within the blend system. Conversely, excessively high PEI or PEEK fractions limited crystallization efficiency through either excessive amorphous confinement or restricted segmental mobility within highly crystalline networks.

TGA analyses demonstrated that all formulations retained excellent thermal stability after ATOX and TVAC exposure, with degradation onset temperatures consistently remaining above 530 °C and only limited variations in residual char content. These results confirm that the environmental treatments did not significantly compromise the bulk thermal resistance of the materials.

Tensile testing after TVAC showed relatively limited variations in tensile modulus and strength, suggesting that the structural integrity of the printed architectures was substantially maintained. The intermediate compositions, particularly 60PEEK-40PEI and 70PEEK-30PEI, displayed the most stable tensile behaviour, likely due to improved stress transfer and thermally induced molecular rearrangement occurring during the exposure cycle. Flexural testing highlighted a more pronounced sensitivity to environmental conditioning, especially after combined ATOX+TVAC exposure, where increased scatter in elastic modulus and strain at

failure indicated enhanced heterogeneity in the deformation mechanisms. Despite this, the 50PEEK-50PEI formulation maintained the highest flexural strength after exposure, while the 70PEEK-30PEI system exhibited the lowest strain at failure and the most mechanically constrained behaviour. This reduced ductility is particularly relevant for shape memory applications, as it indicates a more stable network architecture capable of storing elastic deformation energy while limiting irreversible plastic dissipation.

DMA investigations confirmed that the viscoelastic response of the blends remained largely preserved after environmental exposure. The storage modulus profiles showed negligible variations below the glass transition region, indicating the absence of extensive bulk degradation phenomena. Only limited shifts in T_g were observed, depending on composition, reflecting minor modifications in chain mobility and intermolecular interactions induced by the exposure conditions. Among the investigated systems, the 70PEEK-30PEI and 80PEEK-20PEI blends demonstrated the highest thermo-mechanical stability, with nearly superimposable DMA curves before and after exposure, confirming the strong resistance of these formulations to combined atomic oxygen and thermal vacuum environments.

The experimental results demonstrate that the developed PEEK-PEI blends possess excellent resistance to simulated space environmental conditions, maintaining their chemical integrity, thermal stability, and functional mechanical behaviour after exposure. The combined characterisation results indicate that the dominant effects induced by the environmental treatments are associated with physical restructuring, stress relaxation, and localised surface oxidation. Among the investigated formulations, the 70PEEK-30PEI composition emerges as the most promising candidate for aerospace and deployable space applications due to its optimal balance between crystallisation behaviour, environmental stability, thermo-mechanical integrity, and mechanically constrained response favourable for shape memory functionality.

Chapter 6. 4D printing of high-performance PEEK-based Composites (Microwave Actuation)

This chapter focuses on the development and analysis of a 4D printed composite materials made from Polyether Ether Ketone (PEEK), Polyetherimide (PEI), and carbonyl iron particles. The composite was fabricated using extruded filaments for 3D printing through Fused Filament Fabrication (FFF). A successful formulation consisting of 50 wt% carbonyl iron, 35 wt% PEEK, and 15 wt% PEI was achieved and extensively characterised.

6.1. Experimental

6.1.1. Materials and Preliminary characterizations

Polyether ether ketone (PEEK 450PF, *Victrix PLC, UK*) and polyetherimide (PEI, ULTEM™ 1000P100, *Sabir, Riyadh, Saudi Arabia*) powders were employed as the polymeric matrix materials for the composites. Carbonyl iron powder (CIP SP-I, 99.5Fe, 0.05C, d50 value 6–10 μ , *BASF, Ludwigshafen, Germany*) served as the reinforcing filler. Prior to processing, all powder constituents were conditioned by oven drying at 60 °C for 24 h to eliminate residual moisture.

Phase identification of the carbonyl iron powders was carried out using X-ray diffraction (XRD, *Philips X'Pert PRO*) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Diffraction patterns were collected over a $2\theta = 10\text{--}90^\circ$, employing a step increment of 0.020° , an acquisition time of 2 s per step, and a scanning rate $0.01^\circ/\text{s}$.

Thermal stability of the carbonyl iron powders was characterised via thermogravimetric analysis (Pyris 1 TGA Analyzer, *Perkin-Elmer, Waltham, Massachusetts, USA*). Measurements were conducted by heating the samples from 25 °C to 800 °C at a heating rate of $10^\circ\text{C min}^{-1}$, under both oxidative and inert atmospheres, using airflow and nitrogen flow rates of 40 ml min^{-1} and 80 ml min^{-1} , respectively.

6.1.2. Compounding, filament manufacturing and 3D printing

Composite materials were fabricated and subsequently characterised. PEEK-PEI blends containing 70 wt% PEEK and 30 wt% PEI, together with corresponding composites incorporating iron carbonyl particles, were first homogenised using a planetary mixer (Thinky ARE-250). Approximately 100 g of material was prepared for each formulation. The compositions, listed in Table 33, were subsequently processed using a single-screw extruder (*Comet S.r.l., Italy*; screw diameter: 20 mm; L/D ratio: 15) equipped with a 1.8 mm die. Extrusion was carried out at 340°C for the PEEK-PEI blend and 370°C for the iron carbonyl-

filled composite, with a screw rotation speed of 20 rpm. Continuous filaments with a target diameter of 1.75 ± 0.05 mm were produced as shown in Figure 200.

Table 33. Composition of blend and composites

Formulation	PEEK (wt%)	PEI (wt%)	Carbonyl Iron (wt%)
PEEK-PEI	70	30	–
PEEK-PEI - 40Fe	42	18	40
PEEK-PEI - 50Fe	35	15	50
PEEK-PEI - 60Fe	28	12	60

Subsequently, the extruded filaments were pelletised (*Shredder & Granulator 3Devo GP20 Hybrid, Utrecht, Netherlands*) with a 3.5 mm screen filter to prepare the material for melt flow index (MFI) testing. Melt flow index measurements were conducted in accordance with ASTM D1238-13 (MP 1200M *Melt Flow Indexer, Tinius Olsens*). The analysis was carried out at a test temperature of 400 °C under an applied load of 2.16 kg.



Figure 200: Produced filaments of blend (left) and composite (right)

The fabricated filaments have been used for the manufacturing of test specimens via Fused Filament Fabrication additive manufacturing process using an Apium P155 (*Apium Additive Technologies GmbH, Karlsruhe, Germany*). Rectangular specimens with dimensions of 80 x 10 x 2 mm and Tensile Tests type IV (ASTM D638 [381]) were produced. All specimen geometries were designed using Solidworks (*Dassault Systèmes, Vélizy-Villacoublay, France*) and processed with Simplify3D (*Simplify 3D, Cincinnati, USA*) to generate a g-code. Samples have been 3D printed with nozzle with the diameter of 0.8 mm, a nozzle temperature set at 410°C for the composite. The building platform temperature was maintained at 140°C throughout the printing process. A raster orientation of +45°/-45°, a 100% infill and a speed of 1600 mm/min were adopted for all fabricated samples.

6.1.3. Chemical, mechanical, thermal, and morphological characterization of composites

Phase identification of the composite filaments was conducted by X-ray diffraction analysis (XRD, *Philips X'Pert PRO*) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Diffraction data were acquired over a 2θ range of $10\text{-}90^\circ$, employing a step increment of 0.020° , a counting time of 2 s per step, and a scanning rate of $0.01^\circ/\text{s}$.

Fourier-transform infrared spectroscopy (FTIR, Cary 630, *Agilent, Santa Clara, USA*) was conducted on the composite filaments. Spectra were collected within the wavenumber range of $4000\text{-}600 \text{ cm}^{-1}$, employing a spectral resolution of 4 cm^{-1} , with each spectrum averaged over 32 scans.

Thermogravimetric analysis was performed on the composite filaments using a Pyris 1 TGA Analyzer (*Perkin-Elmer, Waltham, Massachusetts, USA*) to evaluate thermal stability. Samples were heated from 25°C to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ under air flow (40 ml min^{-1}) and nitrogen flow (120 ml min^{-1}).

Differential scanning calorimetry measurements were carried out under a nitrogen atmosphere using a DSC 214 Polyma system (*Netzsch, Selb, Germany*). Approximately 10 mg of the composite material were analysed. The thermal cycle consisted of a first heating stage from 25°C to 400°C , followed by cooling to 25°C , and a subsequent second heating cycle up to 400°C . Both heating and cooling rates were maintained at 10 K/min .

Dynamic mechanical analysis was conducted on the filaments using a Tritec 2000 DMA instrument (*Triton Technology, UK*). Measurements were performed in tensile mode over a temperature range of $25\text{-}250^\circ\text{C}$ employing a heating rate of 2°C/min , an oscillation frequency of 1 Hz, and a displacement amplitude of 0.05 mm.

Mechanical characterisation was performed through tensile testing on composite filaments using an Instron 5869 universal testing machine (*Norwood, USA*). Tests were conducted using a 50 kN load cell and a contact extensometer at a crosshead speed of 5 mm/min , in accordance with ASTM D-638.

Morphological characterisation and evaluation of carbonyl iron powder dispersion within the composites were performed using field-emission gun scanning electron microscopy (FEG-SEM, *Leo Supra-35, Zeiss, Oberkochen, Germany*) operated at an accelerating voltage of 5 kV. Prior to imaging, cross-sections of the PEEK-PEI-50Fe specimens were sputter-coated with an approximately 10 nm thick gold layer using an EMITECH K550X sputter coater (*Quorum*

Technologies Ltd, Laughton, East Sussex, UK) to minimise electrostatic charge accumulation during SEM observation.

6.1.4. Shape memory evaluation

Shape-memory performance was evaluated through fold-deploy experiments conducted on the composite specimens. Rectangular samples were heated to 200 °C and mechanically deformed into a U-shaped configuration. The deformed specimens were subsequently cooled to room temperature (25 °C) in order to stabilise the temporary shape.

Indirect activation of the shape-memory effect in the composite specimens was achieved using microwave irradiation at a power level of 750 W and an operating frequency of 2.45 GHz. Electromagnetic leakage within the microwave cavity was considered negligible, in accordance with FDA safety regulations. In the present investigation, only the 2.45 GHz operating mode was considered. Due to the rectangular geometry and dimensions of the microwave cavity, the resonance spectrum is characterised by very narrow bandwidths (<0.5 MHz); therefore, the electromagnetic field distribution can reasonably be approximated by considering only the dominant resonant mode at 2.45 GHz [382].

The shape-fixity ratio (R_f), representing the capability of the material to maintain its temporary configuration after deformation and cooling, and the shape-recovery ratio (R_r), corresponding to the ability of the material to recover its original geometry following external stimulation, were determined according to Equations (5) and (6), respectively

$$R_f = \frac{\theta_u - \theta_f}{\theta_u} \times 100 \quad (5)$$

$$R_r = \frac{\theta_u - \theta_r(T_s)}{\theta_u - \theta_0} \times 100 \quad (6)$$

Where θ_0 represents the initial angle ($\theta_0 = 0^\circ$), θ_u corresponds to the maximum deformation angle ($\theta_u = 180^\circ$), θ_f is the fixed angle after cooling and θ_r is the residual angle following shape recovery. Time to recover was also investigated.

6.2. Results and discussion

6.2.1. Phase analysis, chemical composition and morphology of raw materials

The X-ray diffraction pattern of Carbonyl Iron powder, presented in Figure 201a, exhibits three main diffraction peaks at 2θ values of 44.69° , 65.31° , and 82.37° . These reflections correspond

to hkl planes (110), (200) and (211) planes [383]. The identified diffraction planes are characteristic of the Body Centred Cubic (BCC) α -Fe crystal system, in agreement with previously reported studies [384], [385].

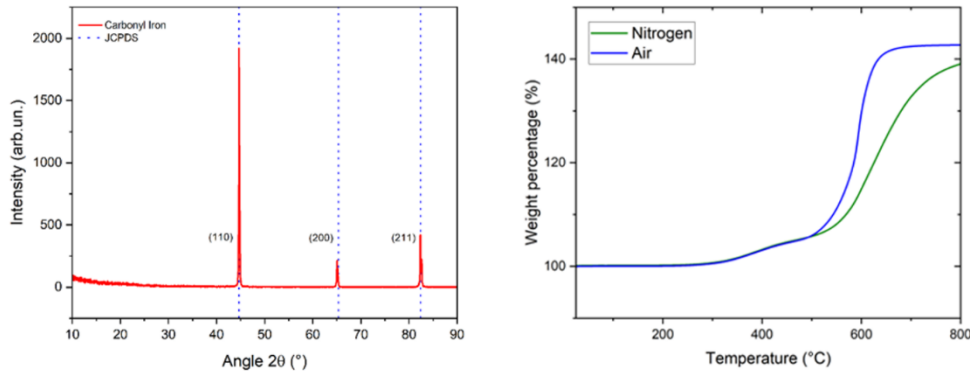
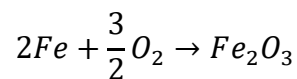


Figure 201: a) XRD Carbonyl Iron, b) TGA Carbonyl Iron in air and in nitrogen

TGA curves of Carbonyl Iron powders under airflow (blue curve) and under nitrogen atmosphere (green curve) are presented in Figure 201b. The thermograms indicate that the powders remain thermally stable up to approximately 400 °C under oxidative conditions. Beyond this temperature, a slight increase in mass is observed, indicating the onset of oxidation phenomena [386], [387]. Furthermore, the derivative thermogravimetric curve reveals a small peak around 450 °C, confirming the initiation of measurable mass gain associated with iron oxidation [388].

A significant mass increase is observed at approximately 600°C, corresponding to the accelerated oxidation of iron and the formation of oxide phases such as magnetite (Fe_3O_4) and hematite (Fe_2O_3) [389], [390], [391]. Beyond 700°C, the thermogravimetric curve reaches a plateau, with a total mass increase of approximately 42.5%. This value is consistent with the theoretical mass gain associated with the complete oxidation of metallic iron into hematite according to the following reaction:



The theoretical mass increase derived from this reaction, calculated as

$$\frac{M_{Fe_2O_3} - 2M_{Fe}}{2M_{Fe}} \sim 43\%$$

is in close agreement with the experimental value, thereby confirming the oxidation mechanism [392].

Under nitrogen atmosphere, the TGA curve (green line) exhibits an almost stable trend up to approximately 500 °C, followed by a gradual increase in mass, reaching nearly 135% of the

initial weight at 800 °C, corresponding to an overall mass gain of approximately 35%. Although the analysis was performed in inert conditions, previous investigations have demonstrated that partial oxidation of iron powders may still occur, leading to the formation of oxide phases such as magnetite and wüstite [390], [393]. Considering that the carbonyl iron powders contain trace amounts of nitrogen and carbon, the mass increase observed near 600 °C may also be associated with gas release phenomena and/or the formation of heavier solid compounds, including iron nitrides [391].

6.2.2. Chemical, mechanical, thermal, and morphological characterization of composites

The Melt Flow Index of the pelletised composite materials was evaluated prior to additive manufacturing in order to identify the most appropriate processing conditions for extrusion and fused filament fabrication. The obtained results, summarised in Table 34, are consistent with values reported in previous studies by Shekar et al [205], Tolochko et al [206], and related investigations [207], [208]. The measured MFI values indicate that all investigated formulations are compatible with material extrusion technologies. In particular, the comparatively low MFI value obtained for the 70PEEK-30PEI blend suggests an elevated melt viscosity, which is generally beneficial for filament dimensional stability during extrusion and layer deposition processes [209]. For the composites, the MFI progressively decreases as the iron carbonyl content increases, confirming the influence of filler loading on melt flow behaviour. The PEEK-PEI-60Fe formulation exhibits the lowest MFI, indicating excessive melt viscosity that prevents reliable extrusion, making this composition unsuitable for printing. In contrast, the PEEK-PEI-30Fe and PEEK-PEI-50Fe composites display MFI values within the range typically considered appropriate for extrusion-based additive manufacturing, suggesting that an adequate compromise between melt flowability and shape retention can be achieved [211].

Consequently, both formulations are expected to be processable by material extrusion, although optimization of processing conditions, such as extrusion temperature and printing speed, may be necessary depending on the filler concentration [211], [212]. Among the printable composites, PEEK-PEI-50Fe presents the lowest MFI (1.51 g/10 min), corresponding to the highest melt viscosity. As a result, this formulation is likely to require higher processing temperatures and/or lower printing speeds to ensure stable material flow during printing. Despite these adjustments, its rheological characteristics remain compatible with extrusion-based additive manufacturing, confirming its suitability for the fabrication of printed

components [394]. The decision to proceed with testing only the PEEK-PEI-50Fe formulation was based on the results of the shape-memory evaluation, as it was the only formulation that maintained satisfactory performance and was able to recover its original shape upon microwave activation, as will be further explained in Chapter 3.1.5: Shape Memory evaluation. From this point onward, all references to the composite refer to the PEEK-PEI-50Fe formulation (35 wt% PEEK, 15 wt% PEI, and 50 wt% Fe).

Table 34: MFI results

Material	Melt Flow Index (g/10 min) @400°C
PEI ULTEM 1000P100	14.82
PEEK 450PF	2.84
PEEK-PEI	3.51
PEEK-PEI 40Fe	2.65
PEEK-PEI 50Fe	1.50
PEEK-PEI-60Fe	0.61

Figure 202 reports the X-ray diffraction pattern of the composite material. The diffractogram shows the same characteristic reflections observed for pristine carbonyl iron powder, with peaks located at 2θ values of 44.69° , 65.31° , 82.37° , corresponding to (100), (210) and (211) planes (BCC of α -Fe crystal system [384], [385]).

The presence of an identical set of diffraction peaks in both the pure carbonyl iron and the composite indicates that the incorporation of the filler into the polymer matrix does not alter its crystalline structure, confirming the retention of the metallic BCC phase after processing. This observation further supports that the carbonyl iron powder predominantly consists of elemental iron, in agreement with the reference diffraction standard JCPDS 06-0696 [395]. In both diffractograms, the (110) reflection of α -Fe is the most intense and well defined peak, consistent with its preferential orientation and dominant contribution to the diffraction pattern [396].

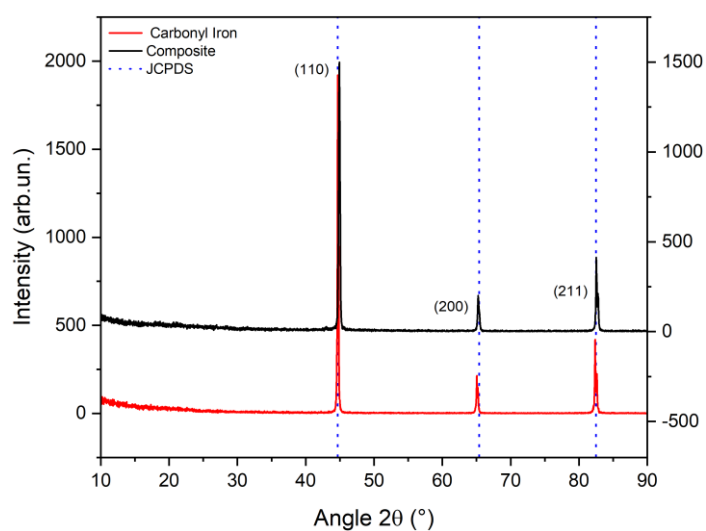


Figure 202: XRD on PEEK-PEI-50Fe and comparison

Figure 203 presents the FTIR spectra of the composite material together with a comparative analysis against the neat PEEK and PEI components. The composite spectrum exhibits characteristic absorption bands associated with both constituent polymers. Specifically, the peaks located at 3066, 2921 and 2851 cm^{-1} correspond to C-H stretching vibrations, consistent with features typically observed in PEI. The absorption band at 1720 cm^{-1} is attributed to the stretching of the imide carbonyl group, also characteristic of PEI [397]. The peak at 1646 cm^{-1} is assigned to C-O stretching vibrations, as observed in PEEK, while the bands at 1592 and 1487 cm^{-1} are associated with aromatic benzene ring vibrations of the PEEK structure. The absorption at 1275 cm^{-1} corresponds to C-N stretching vibrations originating from PEI. In addition, the bands at 1216 cm^{-1} and 926 cm^{-1} are attributed to in-plane deformation and out-of-plane bending of aromatic C-H groups in PEEK, respectively, whereas the peak at 833 cm^{-1} is linked to aromatic ring vibrations of PEI.

The absence of significant peak shifts or notable band broadening suggests limited molecular level interactions between the PEEK and PEI phases. This behaviour indicates that the system does not exhibit full miscibility but rather partial compatibility, which is consistent with previous interpretations [398], [399]. Miscibility refers to the ability of two polymers to form a single homogeneous phase through strong intermolecular interactions, typically resulting in a single glass transition temperature (T_g) and noticeable spectral shifts or band broadening in techniques such as FTIR, DSC, or XRD [400]. In contrast, immiscible systems display phase separation with two distinct T_g s corresponding to each polymer [401]. For the PEEK-PEI system, the lack of significant spectral changes indicates weak interchain interactions and

incomplete molecular mixing. Consequently, the blend can be classified as partially miscible, meaning that limited interdiffusion occurs between phases without achieving full homogeneity. This condition implies the coexistence of distinct polymer-rich domains with only partial interfacial adhesion and restricted chain interpenetration [402], [403]. This interpretation is further supported by dynamic mechanical analysis, which reveals two separate glass transition temperatures. The presence of two T_gs confirms a biphasic morphology consisting of PEEK-rich and PEI-rich domains, each retaining its intrinsic thermal behaviour. The results demonstrate that the PEEK-PEI system forms a partially compatible blend with restricted but non-negligible interphase interactions [260], [404].

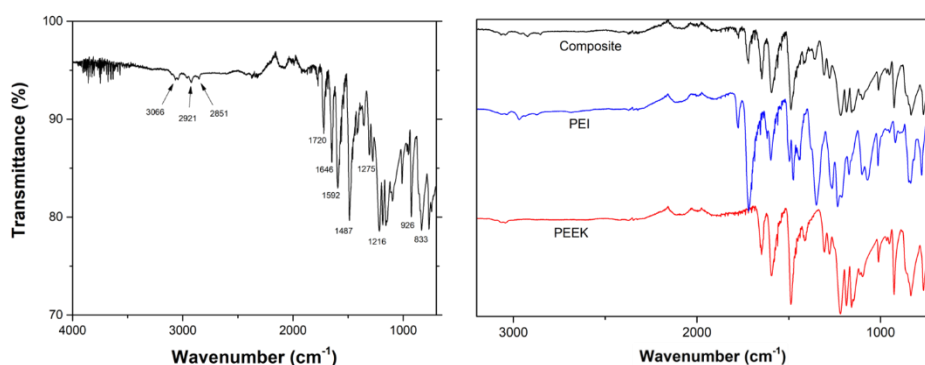


Figure 203: FTIR on PEEK-PEI-50Fe composite and comparison with PEEK and PEI

Figure 204a reports the comparison of the TGA of the 70PEEK-30PEI blend under nitrogen atmosphere, together with the PEEK-PEI-50Fe composite evaluated under both air and nitrogen environments. In all cases, the mass loss curves remain nearly constant up to approximately 500 °C, indicating high thermal stability of both systems within this temperature range.

The onset of degradation is identified at 561 °C for the blend, 523 °C for the composite in air, and 518 °C for the composite in nitrogen, defined by an initial 2% weight loss. The thermal decomposition proceeds through a two steps mechanism. The first degradation stage occurs at approximately 603 °C for the blend, 575 °C for the composite in air, and 542 °C for the composite in nitrogen. The second stage is observed at around 640 °C for the blend, and at higher temperatures for the composite, namely 718 °C in nitrogen and 728 °C in air.

The initial decomposition step can be attributed to the inherent thermal degradation behaviour of the polymer constituents, considering that PEEK typically degrades in the 570-600 °C range and PEI in the 500-550 °C range, indicating overlapping matrix decomposition processes. The second degradation stage is associated with further breakdown of residual polymeric structures and/or structural rearrangement and oxidation of the charred residue. At 800 °C, the residual

mass is approximately 55% for the PEEK-PEI blend, 72% for the composite under nitrogen, and 77% under air atmosphere. The residual weight of the composites is mainly associated with the presence of carbonyl iron particles, which constitute 50 wt% of the formulation and remain thermally stable over the investigated temperature range. An additional contribution arises from the carbonaceous residue generated by the PEEK-PEI matrix during thermal degradation. Considering that the neat blend retains approximately 55% of its initial mass at 800 °C and represents 50 wt% of the composite, its contribution to the overall residue can be estimated at about 27.5%. Therefore, the combined contributions of the inorganic filler ($\approx 50\%$) and the polymer-derived char ($\approx 27.5\%$) yield a theoretical residual mass of approximately 77.5%, in good agreement with the experimental value measured in air. The slightly lower residue observed under nitrogen (72%) suggests differences in the degradation pathway and char evolution, whereas the higher residual mass in air is consistent with the formation of stable iron oxide species during oxidation.

Figure 204b and Table 35 present the DSC results for the 70PEEK-30PEI blend and the PEEK-PEI-50Fe composite (black and red curves, respectively). During the first heating cycle of the blend, a pronounced exothermic event is observed in the 180-200 °C range, which is attributed to cold crystallisation. This indicates that the material initially contains a significant amorphous fraction that reorganises into ordered crystalline regions upon heating [405], [406], [407]. This crystallisation process is followed by a strong endothermic peak at approximately 320-340 °C, corresponding to the melting of the crystalline phase. The relatively high melting enthalpy suggests that a considerable degree of crystallisation develops during the thermal scan itself. Moreover, the composite exhibits a markedly reduced exothermic signal in the same temperature range during the first heating, indicating suppressed cold crystallisation. This behaviour is attributed to the restriction of polymer chain mobility induced by the presence of carbonyl iron particles, which limits chain rearrangement and crystal growth [408]. Consistently, the melting peak of the composite is less intense than that of the blend, suggesting reduced crystallinity or hindered crystalline development within the filled system [409]. During the second heating cycle, both materials show a strong reduction or complete disappearance of the exothermic crystallisation peak, indicating that the thermal history has been erased and a more thermally stable structure has been established [410]. The persistence of the melting transition, with minor variations in peak position and shape, suggests the formation of more stable and possibly more uniformly distributed crystalline domains after controlled thermal cycling [411].

Table 35: DSC Results

DSC	Melting (I)		Crystallization	Melting(II)	
	T _{m1} [°C]	X _{m1} [%]		T _{m2} [°C]	X _{m2} [%]
70PEEK-30PEI	340	33,64	289	339	35,36
PEEK-PEI-50Fe	345	37,25	275	338	33,54

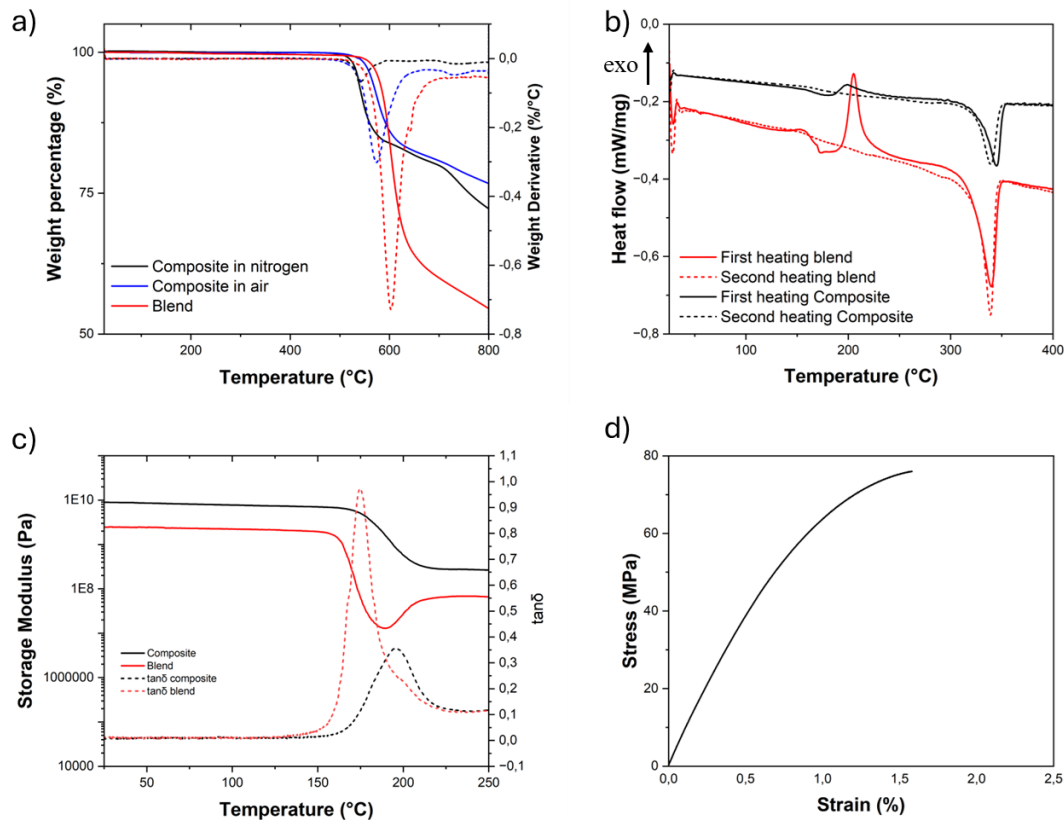


Figure 204: PEEK-PEI-50Fe and 70PEEK-30PEI a) TGAs, b) DSCs, c) DMAs, d) Tensile Tests

Figure 204c presents the DMA results for both the 70PEEK-30PEI blend and the 50Fe-35PEEK-15PEI composite, highlighting a clear reinforcement effect induced by the incorporation of magnetic filler. The peak of the loss factor ($\tan \delta$) is commonly used to identify the glass transition temperature (T_g). As the material approaches T_g , increased molecular mobility and reduced chain entanglement lead to a marked decrease in the storage modulus (E'), while the loss modulus (E'') and $\tan \delta$ reach a maximum, reflecting the increased dissipation of mechanical energy as heat.

The DMA results reveal two distinct glass transition temperatures, particularly evident for the PEEK-PEI blend. The blend exhibits a first transition (T_{g1}) at approximately 175 °C and a second transition (T_{g2}) near 200 °C, whereas the composite shows T_{g1} and T_{g2} at

approximately 196 °C and 220 °C, respectively. The occurrence of two glass transition temperatures indicates that the PEEK and PEI phases preserve a certain degree of phase individuality. At the same time, the shift of both transitions relative to the neat constituents suggests significant intermolecular interactions, confirming the partially miscible nature of the blend. The T_g values measured for the blend are consistent with those reported in the literature for PEEK-PEI systems [225], [385], [412], [413].

The incorporation of carbonyl iron particles produces a noticeable increase in the glass transition temperature, with T_{g1} shifting by approximately 20 °C. This behaviour can be attributed to restricted polymer chain mobility at the filler-matrix interface, resulting from strong interfacial adhesion and a reduction in the local free volume (confinement effect) [414], [415]. The rigid nature of the filler also substantially enhances the storage modulus, with the composite exhibiting E' values approximately one order of magnitude higher than those of the unfilled blend over the entire temperature range, confirming the reinforcing effect of the carbonyl iron particles.

Furthermore, the dynamic mechanical response of the composite differs significantly from that of the blend. Across the entire temperature range, the storage modulus of the composite remains approximately one order of magnitude higher than that of the unfilled blend, confirming the strong stiffening effect of the reinforcement. While the unfilled material displays a pronounced decrease in E' accompanied by a sharp and intense tan δ peak at T_g, the composite shows a more gradual reduction in stiffness and a broader, less intense tan δ maximum. The attenuation and broadening of the relaxation peak further demonstrate the restricted mobility of the polymer chains and the strong interfacial interactions established between the polymer matrix and the carbonyl iron particles.

Figure 204d exhibit the tensile stress and strain behaviour of the 50Fe-35PEEK-15PEI composite. The results are consistent with the DMA analysis, showing a significant increase in stiffness after the incorporation of carbonyl iron particles. The composite exhibits an elastic modulus of 9.06 ± 0.70 GPa, which is substantially higher than the value measured for the blend (1.31 ± 0.65 GPa) [416], [417]. This substantial increase highlights the reinforcing capability of the carbonyl iron filler and its ability to improve the load-bearing response of the polymer matrix. The composite also achieves a higher maximum tensile stress, with a value of approximately 76.83 ± 4.17 MPa, whereas the PEEK/PEI blend reaches 46.33 ± 1.12 MPa. However, this improvement in strength is accompanied by a significant reduction in deformability, as the composite fails at a strain of only $1.78 \pm 0.31\%$, compared with $7.66 \pm 0.45\%$ for the unfilled blend. These results demonstrate that the addition of 50 wt% carbonyl

iron particles effectively enhances stiffness and tensile strength but compromises ductility and toughness, which is consistent with the embrittlement effect typically observed in highly filled polymer composites [418], [419]. The reduced strain to failure can be attributed to the presence of a large fraction of rigid filler particles within the polymer matrix. Under tensile loading, carbonyl iron particles can act as stress concentration sites, promoting localised stress accumulation and limiting polymer chain mobility. At high filler contents, the probability of particle-particle interactions and interfacial defects increases, which can facilitate crack initiation and propagation. In particular, insufficient interfacial adhesion or the formation of micro voids at the filler-matrix interface may contribute to premature failure [420]. Therefore, the mechanical response of the composite represents a compromise between enhanced stiffness and strength provided by the carbonyl iron reinforcement and the reduced ability of the polymer matrix to accommodate plastic deformation. The final performance is strongly governed by filler concentration, particle dispersion, and the quality of the interfacial bonding between the carbonyl iron particles and the PEEK-PEI matrix.

SEM micrographs of the sample cross-sections are presented in Figure 205. Figure 205 a-b) corresponds to the PEEK-PEI-50Fe filaments, while Figure 205 c-d) shows the 3D printed sample. The filament morphology reveals a compact structure with only limited porosity. Carbonyl iron particles, appearing as light-grey spherical inclusions, are uniformly distributed within the darker polymer matrix, with an average particle diameter of approximately 3.8 μm . The spherical morphology is consistent with that typically reported for carbonyl iron particles [421]. The relatively good adhesion between the particles and the surrounding polymer phase suggests effective filler incorporation during the compounding process and indicates efficient wetting of the metallic particles by the PEEK-PEI matrix [422]. Despite the high filler concentration, only limited regions of particle-particle contact and localised heterogeneities are observed. The absence of extensive agglomeration indicates that the adopted mixing procedure provided adequate dispersion of the magnetic filler. This microstructural arrangement promotes effective stress transfer from the polymer matrix to the rigid particles, contributing to the enhanced mechanical response observed for the composite [424]. The small amount of isolated voids and local variations in particle distribution can be attributed to the high CI loading, which may influence powder packing, melt viscosity, and material flow during processing [423]. The composite maintains a continuous matrix structure capable of accommodating a significant fraction of metallic filler, confirming the effectiveness of the extrusion-based compounding approach.

The SEM images of the 3D-printed specimens provide additional information regarding the effects of the fused filament fabrication process on the composite microstructure. Compared with the filament cross-section, the printed samples exhibit morphological characteristics associated with the layer-by-layer deposition process, including interlayer interfaces, porosity, and variations in local filler distribution [425]. The printed structure remains relatively compact; however, localised pores are visible (Figure 205 c-d). Both interlayer and intralayer voids can be identified. Interlayer porosity is associated with incomplete bonding between adjacent deposited roads, typically resulting from insufficient thermal fusion or limited polymer chain diffusion between layers. Intralayer defects may originate from air entrapment, unstable material flow, or rapid solidification during deposition [426].

A horizontal interface visible near the upper region of the specimen corresponds to an interlayer boundary, a typical feature of fused filament fabrication. The irregular morphology of this interface and the presence of discontinuities suggest that complete interlayer adhesion was not achieved. This behaviour is particularly relevant for highly filled composites, where the presence of a large amount of rigid particles reduces polymer chain mobility and limits diffusion across adjacent layers during printing [427], [428]. The observed voids, attributed to incomplete fusion, trapped air, or shrinkage during cooling, may act as stress concentration sites and contribute to the reduction of mechanical performance, especially along the build direction [429], [430].

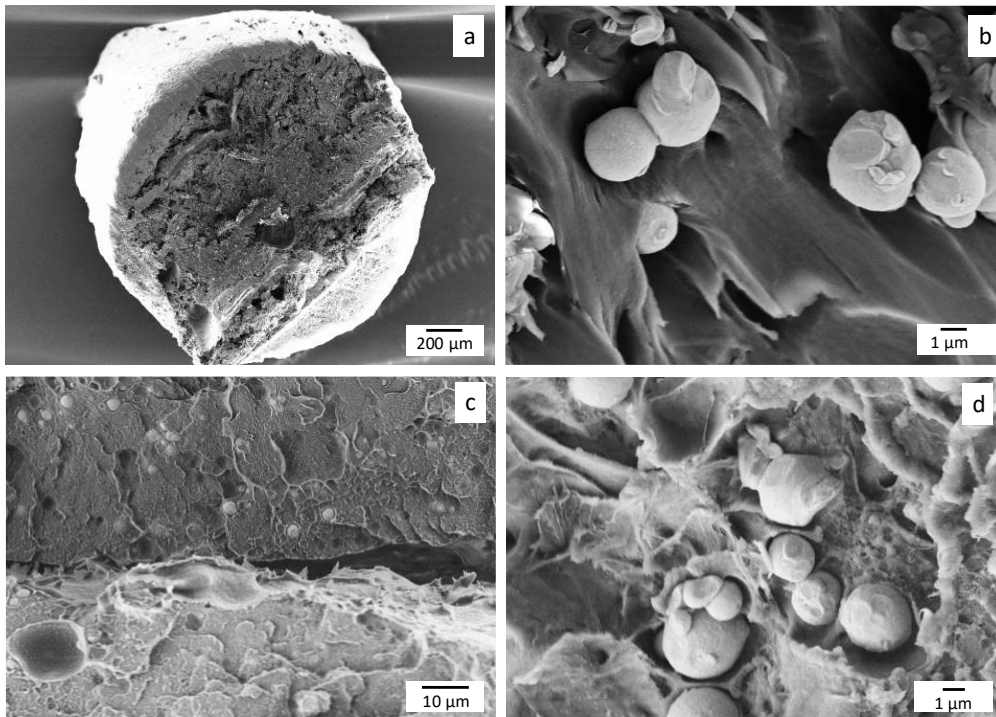


Figure 205: SEM of PEEK-PEI-50Fe a-b) filament, c-d) 3D-printed sample

At higher magnification, the printed composite maintains the spherical morphology of the CI particles observed in the filaments, indicating that the printing process does not significantly modify the filler structure [421]. The particles remain embedded within the polymer matrix, although some localised particle clusters and polymer-rich regions are visible, reflecting the challenges associated with processing highly filled systems [431]. Furthermore, the rough and irregular fracture morphology is consistent with the brittle behaviour observed during tensile testing, characterised by limited plastic deformation before failure [426], [432]. The SEM observations demonstrate the combined influence of high filler content and additive manufacturing-induced defects on the final microstructure, while confirming the successful incorporation of carbonyl iron particles within the PEEK-PEI matrix.

6.2.3. Shape-memory evaluation

Shape memory performance was evaluated on the 3D-printed specimens. To assess shape recovery, samples of the neat PEEK-PEI blend were first fixed in their temporary configuration and subsequently heated in an oven at 200°C. Upon heating, the specimens recovered their original permanent shape, as illustrated in Figure 206. The measured shape recovery ratio ranged from 96% to 97%, with complete recovery occurring within approximately 10 min. The corresponding results are summarized in Table 36.

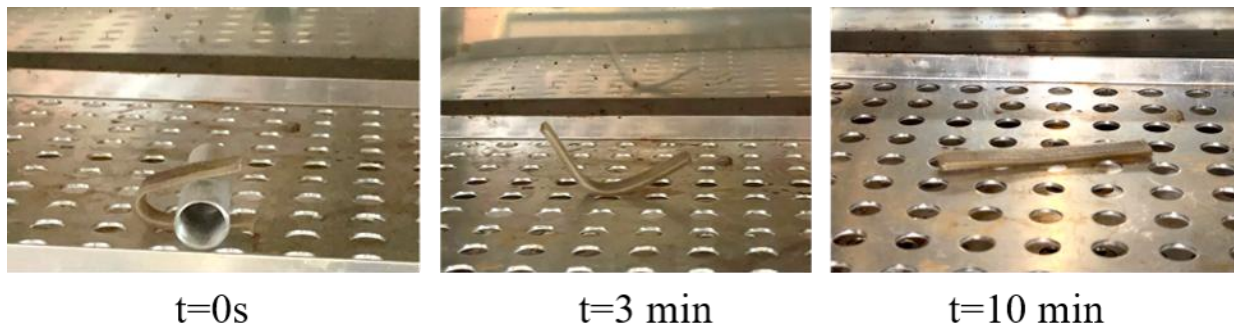


Figure 206: Shape memory of 70PEEK-30PEI on a blend 3D printed sample at 200°C

Table 36: Values of Shape Fixity Ratio and Shape Recovery Ratio

Material	Rf (%)	Rr (%) Thermal	Rr (%) MW
PEEK-PEI	91.44	97.12	0
PEEK-PEI-40Fe MW	89.32	96.95	21.12
PEEK-PEI-50Fe MW	88.58	96.84	87.77

Shape memory behaviour was further investigated on both the 3D-printed specimens and the corresponding filaments containing carbonyl iron particles (Figure 207). In this case, samples previously deformed into their temporary shape were recovered by microwave irradiation. Since the heating mechanism relies on the presence of magnetic particles, which convert electromagnetic energy into heat and subsequently activate the polymer matrix, this approach can be regarded as an indirect microwave activation process.

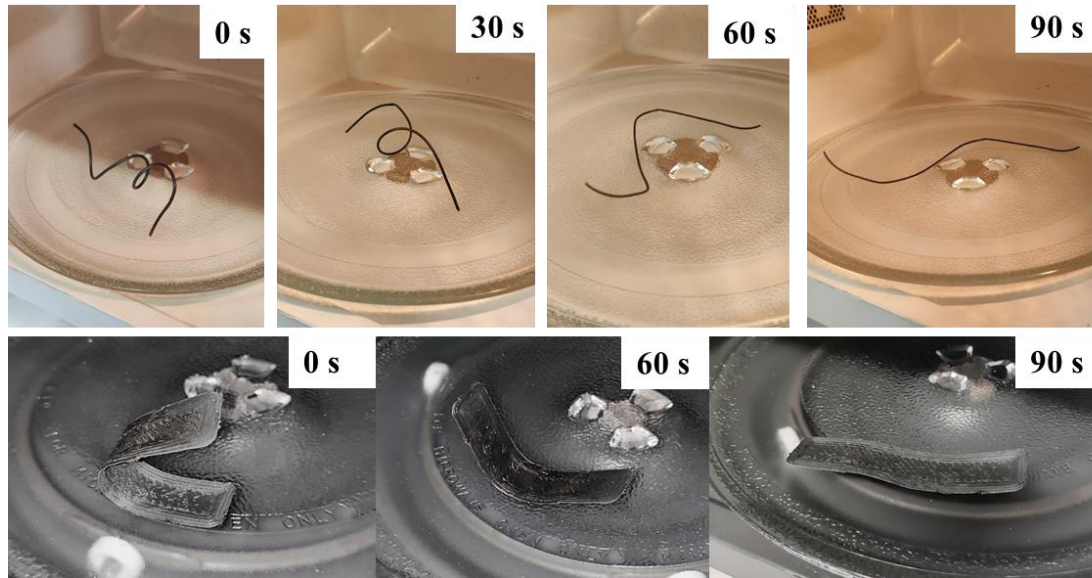


Figure 207: Shape-memory activation in a microwave with a power of 750W for the PEEK-PEI-50Fe filament (first row) and composite (second row)

Among the investigated formulations, only the PEEK-PEI-50Fe composite achieved effective recovery of its original geometry, reaching a shape recovery ratio of 87.77% after 90 s of microwave exposure. In contrast, the PEEK-PEI-40Fe formulation exhibited only limited recovery ($R_r = 21\%$), indicating that the filler content was insufficient to generate the temperature required to exceed the switching temperature of the shape-memory polymer.

The observed temperature increase is associated with dielectric heating promoted by the carbonyl iron particles. Under microwave irradiation, the particles generate localized heat through magnetic hysteresis losses, which soften the surrounding polymer matrix [434], [435]. Simultaneously, the alternating high-frequency electromagnetic field induces continuous oscillation and reorientation of polar molecules, converting electromagnetic energy into thermal energy through intermolecular friction [382], [433]. Once the switching temperature is reached, polymer chain mobility increases, allowing the elastic strain stored during programming to be released and driving the recovery of the permanent shape.

The incorporation of 50 wt% carbonyl iron particles represents an effective compromise between printability and shape-memory performance. At this filler concentration, the composite retains adequate processability for material extrusion while providing sufficient magnetic response for rapid thermal activation under microwave irradiation. As a result, the PEEK-PEI-50Fe formulation recovers its permanent shape within 90 s, demonstrating the synergistic contribution of the magnetic filler to efficient and reliable shape-memory actuation.

6.3. Conclusions

A high-performance 4D-printable PEEK-PEI composite reinforced with carbonyl iron (CI) particles was successfully fabricated through melt extrusion and fused filament fabrication. Among the investigated formulations, PEEK-PEI-50Fe provided the most suitable combination of printability and functional properties, despite the increased melt viscosity associated with the high filler loading. Thermal characterisation demonstrated excellent thermal stability, with degradation temperatures exceeding 500°C and a glass transition temperature of approximately 196°C, confirming the material's suitability for applications in demanding thermal environments. The addition of CI particles significantly enhanced the elastic modulus, reaching approximately 9 GPa, while reducing ductility as a consequence of the increased rigidity of the composite. Microscopic observations indicated a reasonably homogeneous distribution of the magnetic filler within the polymer matrix, which contributed to both mechanical reinforcement and efficient microwave responsiveness.

Shape-memory characterisation confirmed that the composite retained excellent functional performance. In particular, the PEEK-PEI-50Fe formulation exhibited high shape fixity and recovery capabilities and could be remotely activated by microwave irradiation. The magnetic filler enabled rapid internal heat generation, allowing the programmed geometry to recover considerably faster than with conventional oven heating. These findings demonstrate that PEEK/PEI-CI composites represent a promising class of materials for high-performance 4D printing, combining the thermal and mechanical advantages of high-performance polymers with remote, non-contact actuation. Further research should address improvements in filler dispersion and processing to mitigate the effects of high viscosity, while also optimising the balance between stiffness and toughness. Such developments could further expand the potential of these materials for advanced applications, particularly in aerospace, space, and other high-performance engineering sectors.

Chapter 7. Conclusions

In this work, high-performance shape-memory systems based on PEEK-PEI blends and PEEK-based composites were successfully developed, processed through fused filament fabrication (FFF), and evaluated for aerospace 4D-printing applications under both standard and simulated space environmental conditions. The investigation demonstrated that the combination of high-performance thermoplastics, additive manufacturing, and stimuli-responsive behaviour constitutes a promising strategy for the realisation of lightweight deployable and adaptive space structures.

Four blend formulations were produced containing 20, 30, 40, and 50 wt% PEI within the PEEK matrix. The materials were successfully compounded using a single-screw extrusion system operating at temperatures between 340°C and 360°C and processed into 1.75 ± 0.05 mm filaments suitable for FFF manufacturing. The extrusion process demonstrated adequate melt processability despite the high melt viscosity of PEEK, reported at approximately 350 Pa·s at 400°C. Stable filament production confirmed that the selected processing window was sufficient to ensure polymer flow while minimising thermal degradation.

The fabricated filaments were subsequently processed through FFF using nozzle temperatures ranging from 390°C to 410°C and a heated build platform maintained at 140°C. The selected printing strategy, including 100% infill density and $\pm 45^\circ$ raster orientation, enabled the fabrication of defect-minimised specimens characterized by acceptable dimensional stability and interlayer adhesion. The use of a 0.8 mm nozzle and controlled extrusion multiplier allowed the reduction of typical high-temperature FFF defects such as warpage, delamination, and excessive thermal shrinkage.

Thermal characterisations through DSC and DMA analyses revealed that the incorporation of PEI strongly influenced the thermal transitions and crystallisation behaviour of the PEEK matrix. Increasing PEI concentration progressively reduced PEEK crystallinity due to the restriction of molecular chain mobility and interference with crystalline phase formation. DMA investigations demonstrated that the viscoelastic response and storage modulus were strongly dependent on blend composition, confirming the coexistence of rigid amorphous phases associated with PEI and semicrystalline domains associated with PEEK.

The thermogravimetric analyses confirmed the excellent thermal stability of all investigated systems up to temperatures exceeding 500°C under nitrogen atmosphere, demonstrating the suitability of the blends for extreme aerospace thermal environments. FTIR analyses performed on powders, filaments, and printed parts confirmed the preservation of the characteristic

functional groups of both PEEK and PEI after processing, indicating the absence of significant chemical degradation phenomena during extrusion and printing.

Mechanical characterisations demonstrated that the blends maintained high structural performance after additive manufacturing. The neat PEEK material exhibited a flexural modulus of approximately 3.8 GPa and elongation at break of approximately 30%, while PEI showed flexural strength values reaching 160 MPa. The resulting blends exhibited intermediate behaviour depending on composition, enabling the tailoring of stiffness, ductility, and thermomechanical response through compositional control. The obtained results confirmed that the additive manufacturing process preserved acceptable load-bearing capability despite the anisotropic nature typically associated with layer-by-layer deposition technologies.

Shape-memory characterization through fold-deploy testing demonstrated successful temporary shape fixity and thermally induced recovery for all investigated formulations. The programming cycle was conducted at around 200°C, enabling deformation into U-shaped temporary configurations followed by cooling at room temperature. Upon reheating above the transition temperature, the specimens recovered their original geometry, confirming the activation of entropy driven molecular relaxation mechanisms typical of shape-memory polymers. The observed behaviour demonstrated that the combined amorphous and semicrystalline morphology of the PEEK-PEI systems effectively enabled elastic energy storage and subsequent thermally activated release.

A major contribution of the present work concerns the environmental qualification of the developed materials under simulated space conditions. Outgassing analyses demonstrated that the investigated PEEK-based systems exhibited low volatile release compatible with aerospace material requirements and ECSS standards for space applications. Thermal vacuum cycling and atomic oxygen exposure tests further demonstrated the environmental robustness of the developed materials.

Atomic oxygen exposure produced localised surface erosion phenomena and measurable modifications in surface roughness, as confirmed through profilometry and SEM analyses. Nevertheless, the materials maintained structural continuity and functional integrity after exposure. Thermal vacuum testing additionally confirmed the dimensional stability and thermal resistance of the blends under cyclic temperature fluctuations representative of orbital environments. Post-exposure analyses indicated that the intrinsic chemical resistance of PEEK effectively limited severe degradation phenomena.

The final phase of the work demonstrated the successful development of microwave-responsive PEEK-based composites for indirect and remote actuation. Conductive microwave-absorbing fillers enabled electromagnetic-to-thermal energy conversion through dielectric and conductive loss mechanisms, promoting rapid heating and activation of the shape-memory effect under microwave irradiation. The incorporation of these fillers allowed wireless actuation capability while maintaining acceptable processability and mechanical integrity, thus expanding the multifunctional potential of 4D-printed aerospace structures.

In conclusion, the present research demonstrated that PEEK-PEI blends and PEEK-based composites represent highly promising materials for advanced aerospace 4D-printing applications. The combination of high thermal stability, mechanical robustness, low outgassing behaviour, environmental resistance, and programmable shape-memory capability enables the development of lightweight deployable structures suitable for harsh operational environments. Furthermore, the integration of remote microwave actuation introduces additional multifunctionality relevant for next-generation adaptive aerospace systems and smart space mechanisms.

Future work should focus on optimising filler dispersion, improving interfacial compatibility between phases, and implementing advanced multi-material printing strategies capable of locally tailoring mechanical and actuation behaviour. Additional investigations involving long-term thermal cycling, radiation exposure, and real orbital validation will be essential for the complete qualification of these systems in aerospace applications.

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