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Doctoral Dissertation
Doctoral Program in Management, Production and Design (39th cycle)

3D printing of semi-crystalline high-performance polymers for localised production

By

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Politecnico di Torino

2024

Thesis summary

Introduction

Among the AM technologies, Fused Filament Fabrication (FFF) or Fused Deposition Modelling (FDM) is the most commonly used additive manufacturing technique for fabricating thermoplastic polymer parts based on CAD design. In this process, a polymer filament is continuously fed to a liquefier; it is melted and then extruded through a nozzle to construct a layer-by-layer structure on a heated bed. This additive technique offers low manufacturing cost, freedom in design, and supervision-free operation [1]. However, the range of polymeric materials for additive manufacturing remains limited. Additionally, the most popular polymers used in FFF are suitable for prototyping rather than final products. The proposed research activity aims to develop and test new polymeric materials for 3D printing applications, especially high-performance polymers (HPPs). In particular, the semi-crystalline high-performance polymers (SC-HPPs) are considered, such as the Poly-ether-ether-ketone (PEEK) and the Polyvinyl difluoride (PVDF). As a novelty, a multi-disciplinary approach was involved. Firstly, the material characterization analysis was employed to select the proper process parameters, to assess thermal and mechanical properties, and evaluate the final crystallinity. Additionally, statistical tools, such as the Design of Experiments (DOE) and Analysis of variance (ANOVA), were applied for the experimental test design, analyzing data, and estimating the correlation between the process parameters and results. The work is divided into two parts, one dedicated to the PEEK and the other to PVDF.

PEEK has gained interest for outstanding properties in high temperatures and hostile environment [2]. However, the printing of PEEK has some manufacturing limitations, for example, it requires high processing temperatures and, its thermal susceptibility during the cooling step of the process remains the dominant cause of dimensional warping and job failure. Therefore, an investigation was carried out on the FFF of different 3D printed PEEK samples, evaluating the effect of various infill percentages (30%, 50%, 70%, and 100%), temperature parameters (extrusion and chamber temperature) but also of two different heating treatments on the final properties. In this regard, a traditional annealing in oven, post 3D printing, was compared to a direct annealing approach, performed during FFF. The final dimensional accuracy and the mechanical performance of the samples were characterized through tomography and, tensile and compression tests along with the thermal properties and the thermal stability. In addition, for all different cases, energy consumption was measured, to provide an indication of the sustainability of the presented approaches.

PVDF is a thermoplastic semi-crystalline polymer distinguished by its polymorphism, with multiple crystalline phases that significantly impact its properties and applications. The piezoelectric effect of PVDF is closely linked to the β -phase content, morphology, and alignment, all of which are influenced by processing conditions. In this context, a notable opportunity lies in the FFF process for its ability to orient and align polymer chains[3]. Indeed, during the 3D printing process, both the shear flow within the nozzle and the velocity gradients induced by deposition can significantly deform the polymer microstructure. This deformation,

termed flow-induced crystallization (FIC), mitigates kinetic barriers to crystallization and directs the resultant morphology. This phenomenon of enhanced oriented crystallization could be crucial to produce piezoelectric devices of Polyvinylidene fluoride (PVDF). Therefore, an extensive examination was conducted thorough statistical analysis using a DOE approach on the link between the β -phase percentage and processing parameters (extrusion temperature and speed), complemented by analytical techniques to elucidate the potential and limitations of the flow-induced crystallization phenomenon in the manufacturing of piezoelectric devices.

Understanding how process parameters influence the crystallinity of materials, and consequently dictate the final material properties, is a crucial breakthrough for advancing the field of 3D printing. This knowledge forms the backbone of material science innovation, as it directly impacts the mechanical, thermal, and structural characteristics of printed objects. By tuning these parameters, researchers can not only optimize existing materials but also unlock new possibilities for developing novel materials tailored to specific applications. This insight is pivotal for expanding the material portfolio available for 3D printing, enabling the technology to reach new levels of functionality, precision, and adaptability across industries. Therefore, this doctoral thesis aims to bridge a significant gap in understanding these relationships, contributing to the broader goal of transforming 3D printing into a versatile tool for complex and high-performance applications. The first following sections deal with the PEEK work, and the PVDF's one, consequently.

PEEK

The manufacturability of PEEK via FFF meets significant challenges, mostly due to its high melting temperature and its semi-crystalline nature. This last aspect makes PEEK highly subjected to shrinkages during the processing, leading to the formation of defects, geometrical variations or even job failures [4]. Residual stresses can be accumulated during the FFF process, leading to warping and interlayer delamination [5], [6]. All these drawbacks limited the choice of FFF for PEEK in all the applications where quality assurance and reproducibility play a crucial role. In recent years, several researchers examined the effect of process printing parameters on the final performance of 3D printed PEEK, in terms of print orientation, nozzle temperature, speed, chamber, and platform temperatures [7], [8]. In addition, other authors focused their research on investigating crystallization behavior [9]. The degree of crystallinity and crystal orientation are important parameters in microstructure and play an important role in the mechanical properties of PEEK component [10], [11]. For semi-crystalline polymers, the degree of crystallinity and crystal orientation can be controlled by heat treatments. Therefore, since PEEK is a semi-crystalline HPP, it was essential to investigate the possibility of increasing the crystallinity of 3D printed parts through post-printing heat treatment. In this scenario, annealing represents a valid post-printing heat treatment to enhance the physical and mechanical properties, improve the dimensional stability, and remove any residual stress [12], [13]. The present study aims to investigate the effect of different annealing processes on the final mechanical properties of PEEK samples obtained by FFF, while also evaluating the crystallization behavior and its influence on the thermal properties and microstructure. A direct annealing (DA) process, performed simultaneously with the 3D printing, was performed and compared with a traditional post-printing oven annealing (PA). In addition, to assess the overall

sustainability of the two different approaches, the energy consumption of the two annealing processes was also evaluated to determine the different cost-effectiveness of the annealing treatments employed. To the best of the authors' knowledge, studies aimed at improving the crystallization of PEEK components during the FFF process remain extremely limited. This work reports a novel annealing methodology that has the potential to enhance the effectiveness of metal replacement. It is reasonable to think that the innovativeness of this proposed approach could yield positive and substantial impacts across diverse industrial sectors, leading to time and energy savings. Thereby, the sustainability of the HPP manufacturing process via AM can be increased.

The poly(ether-ether-ketone) (PEEK) filament used in this study was sourced from 3DXTech (USA) under the commercial name ThermaX™. The filament had a diameter of 1.75 ± 0.05 mm. To ensure optimal print quality and reduce moisture-induced defects, the filament was dried at 120°C for four hours prior to 3D printing. The samples were fabricated using a CreatBot PEEK-300 3D printer (CreatBot, China), designed specifically for processing high-performance polymers like PEEK. This printer supports temperatures up to 500°C for the dual extruder and 140°C for the heated chamber and build platform, crucial for managing the high processing temperatures required for PEEK. The nozzle used had a diameter of 0.4 mm. The samples were designed using SolidWorks CAD software and sliced with Simplify3D software to generate the G-code for printing. The printing process parameters included a nozzle temperature of 420°C, bed temperature of 140°C, chamber temperature of 140°C, and a printing speed of 25 mm/s. The infill pattern used was rectilinear with angles alternating at $\pm 45^\circ$. Four different infill percentages 30%, 50%, 70%, and 100% were evaluated to study the effect on mechanical properties. Two types of annealing processes were applied to the samples: Direct Annealing (DA) and Post Annealing (PA).

1. Direct Annealing (DA): Conducted simultaneously during the 3D printing process at 320°C using a patented technology in the CreatBot printer. Hot air was directed onto the 3D-printed layers during the printing process to induce crystallization.
2. Post Annealing (PA): Performed after printing by heating the samples to 200°C for 2 hours, followed by a gradual reduction in temperature to 140°C at a rate of 10°C/hour, before cooling to room temperature.

For comparative purposes, unannealed samples, referred to as Not Annealed (NA), were also tested, along with the as-received PEEK filament, referred to as As-Received (AR).

Differential scanning calorimetry (DSC) analyses were carried out using a DSC 214 Polyma Equipment (Netzsch Group, Selb, Germany). Two heating and cooling scans were performed under a nitrogen atmosphere (40 mL/min) from 20 to 400 °C with a heating/cooling rate of 10 °C/min. DSC analysis was performed to determine the glass transition temperature (T_g), the melting temperature (T_m), the crystallization temperature (T_c), the cold crystallization temperature (T_{cc}), their associated enthalpies of fusion (ΔH_m), crystallization (ΔH_c), and cold crystallization (ΔH_{cc}). The degree of crystallization (X_c) for all PEEK samples was estimated using the following Equation:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m is the experimental enthalpy of melting, calculated by the integration of the melting endothermic peak, ΔH_{cc} is the enthalpy of cold crystallization, and ΔH_m^0 is the theoretical melting enthalpy of a purely crystalline PEEK, which was assumed to be equal to 130 J/g [14]. Thermogravimetric (TG) analysis was carried out to investigate the thermal stability of the 3D printed PEEK samples using a Mettler-Toledo TGA 851e instrument (Mettler Toledo, Columbus, Ohio, USA). The samples were heated from 25 to 1000 °C at a heating rate of 10 °C/min under an airflow of 50 mL/min. All the TG curves were normalized to the unit weight of the PEEK samples, and the derivative thermogravimetric (DTG) curves were calculated on their relative thermograms. The uniaxial tensile tests were performed, according to ISO 527 standard, on all 3D printed PEEK specimens. The Aura 5T machine (Easydur, Arcisate, Italy), equipped with a 5 kN load cell, was used with a crosshead speed of 1 mm/min and a pre-load of 150 N. Five specimens were tested for each condition. The uniaxial compression tests were performed, according to ISO 604 standard, on 3D printed PEEK specimens, which were subjected to PA treatment. The Aura 5T machine (Easydur, Arcisate, Italy), equipped with a 5 kN load cell, was used with a crosshead speed of 5 mm/min. Five specimens were tested for each infill percentage. All PEEK samples were weighed with a Gibertini balance (Gibertini, Novate Milanese, Italy), and the effective dimensions were measured with a micrometer. In addition, the power consumption for 3D printing PEEK samples was measured with a Meterk M34EU power meter plug. The following sections describe the results in term of thermal and mechanical properties, and energy consumption.

Thermal properties

Table 1 summarises the DSC analysis results in terms of glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), and their relative enthalpies. Moreover, figure 1 shows the DSC curves of the PEEK samples as received (AR), 3D printed by FFF with annealing (PA and DA), and without annealing (NA), relative to the first and second heating/cooling cycle, as reported in Figure 1a and Figure 1b, respectively.

Table 1. Thermal properties of 3D printed PEEK samples, evaluated by DSC analysis in nitrogen

Sample	1 st heating					Cooling		2 nd heating			
	T_{cc}	ΔH_{cc}	T_m	ΔH_m	X_c	T_c	ΔH_c	T_g	T_m	ΔH_m	X_c
	(°C)	(J/g)	(°C)	(J/g)	(%)	(°C)	(J/g)	(°C)	(°C)	(J/g)	(%)
PEEK AR	/	/	340	37.1	28.5	296	47.4	140	340	47.3	24.7
PEEK NA	176	17.9	340	39.4	16.6	294	50.8	145	339	41.2	25.9
PEEK PA	/	/	338	38.0	29.2	295	53.6	154	340	41.7	32.1
PEEK DA	/	/	338	37.1	28.5	295	48.5	153	340	45.3	34.9

The first heating cycle shows the effect of process parameters on the PEEK's structure in fig.1a; the curves presented a glass transition between 140-160°C, followed by a cold crystallization peak around 176°C for the non-annealed (NA) sample. This peak indicated that the polymer did not have sufficient time to crystallize during FFF due to rapid cooling rates. In contrast, both direct annealed (DA) and post annealed (PA) samples lacked this peak, suggesting that the annealing processes allowed the polymer chains to reorganize into a more stable semi-crystalline structure during the first heating. Additionally, the as-received (AR) and DA samples showed similar crystallinity levels of 28.5%, indicating that direct annealing during the printing process did not significantly affect the crystalline structure compared to the raw material. However, the NA sample had a significantly lower crystallinity (16.6%) due to the cold crystallization observed in the first heating.

The second heating cycle, which erased the thermal history of the samples, showed increased crystallinity for the annealed samples, with X_c values of 32.1% for PA and 34.9% for DA, compared to 24.7% and 25.9% for the NA samples. This increase in crystallinity is attributed to higher molecular mobility during annealing, enabling the polymer chains to reorganize into more ordered structures. During cooling, all samples exhibited a single crystallization peak at approximately 295°C, while the melting behavior remained consistent across the samples, with a broad endothermic peak at 340°C. In the second heating cycle, the T_g values for DA and PA samples were significantly higher (~154°C) compared to the AR (140°C) and NA (145°C) samples. This increase in T_g for annealed samples reflects reduced chain mobility in the amorphous phase, as annealing not only increases crystallinity but also restricts the motion of the amorphous regions, leading to enhanced thermal stability.

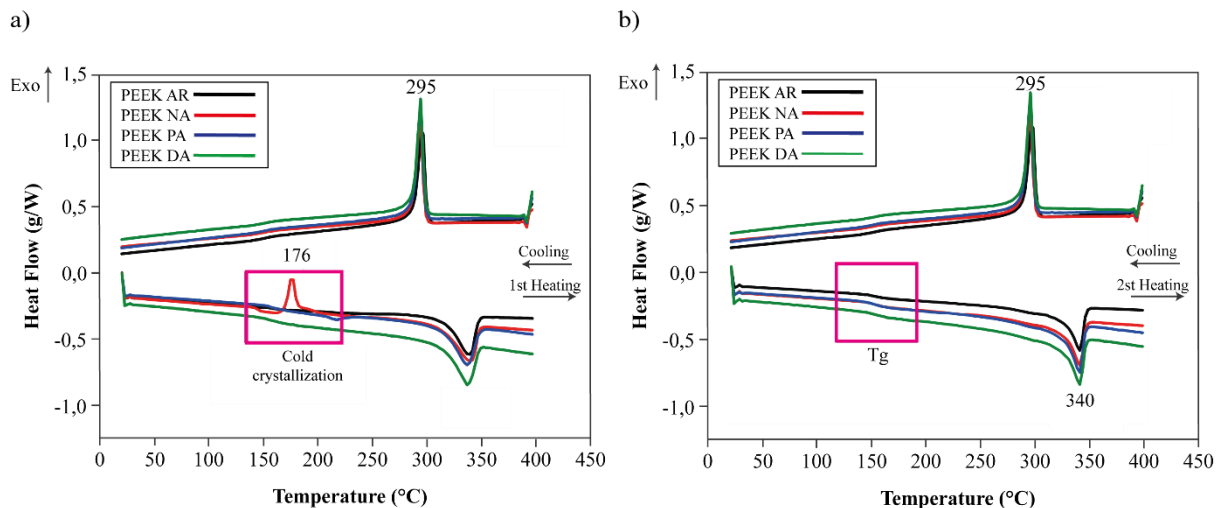


Figure 1 - DSC curves of PEEK samples related to the cooling cycle plus the first (a) and second (b) heating cycle

The thermal stability of the PEEK samples was evaluated through thermogravimetric analysis (TGA) conducted in air. The thermogravimetric and corresponding derivative thermogravimetric (DTG) curves in figure 2 revealed a two-step degradation process.

- Initial Degradation: The first degradation stage, beginning at approximately 585°C, corresponds to the scission of ether and ketone bonds in the PEEK polymer chain. This

stage represents the initial breakdown of the polymer structure, consistent with reported degradation pathways for PEEK.

- **Secondary Degradation:** The second degradation phase occurs at temperatures exceeding 660°C and is attributed to the decomposition of the aromatic crosslinked residues formed during the initial stage. The formation of these residues creates a thermally stable char, which acts as a barrier to heat transfer, slowing further degradation of the material. This behavior agrees with similar trends observed in other polymer matrices, where char formation plays a critical role in delaying complete thermal decomposition.

Thermal stability was further quantified by measuring the temperature at which 5% weight loss (T_5) and 50% weight loss (T_{50}) occurred, the results are described in Table 2. The T_5 values were relatively consistent across all samples, with 567°C for the non-annealed (NA) sample and 572°C for the direct annealed (DA) sample. The T_{50} values were also similar for all samples, at approximately 645°C.

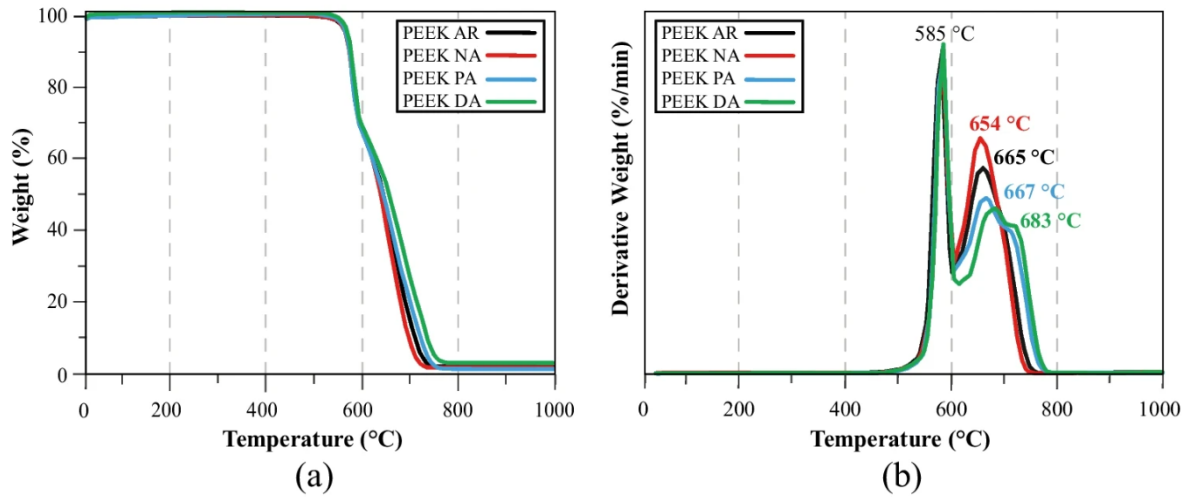


Figure 2 - Thermogravimetric curves of PEEK samples (a) and their DTG curves (b)

Table 2-Thermal properties of 3D printed PEEK samples evaluated by TG analysis performed in air

Sample	T_5 (°C)	T_{50} (°C)	$T_{deg\ peak1}$ (°C)	$T_{deg\ peak2}$ (°C)
PEEK AR	567	645	585	665
PEEK NA	566	645	585	654
PEEK PA	570	645	585	667
PEEK DA	572	645	585	683

Despite these similarities, the annealing treatments significantly affected the peak degradation temperature (T_{deg}). Notably, the second degradation peak for the DA sample occurred at 683°C, which represents a substantial 29°C increase compared to the 654°C observed for the NA sample. In contrast, post-annealed (PA) samples exhibited a minimal improvement in thermal

stability, with the second degradation peak rising only slightly from 665°C to 667°C. This suggests that the direct annealing (DA) process substantially enhances the thermal stability of 3D-printed PEEK, whereas post-annealing (PA) offers only a marginal improvement

Mechanical properties

Tensile and compression tests were conducted to assess the impact of two annealing treatments PA and Da on the mechanical properties of 3D-printed PEEK samples. The tests were performed on specimens with 30% infill, chosen to simulate the worst-case scenario in terms of material usage to minimize the cost of PEEK, which is known for its high material expense. This approach balanced comprehensive mechanical testing with resource efficiency. For comparison, non-annealed (NA) samples were also subjected to tensile tests, focusing on key mechanical properties such as Young's modulus (E) and ultimate tensile strength (UTS), the results are collected in Figure 3.

The results showed that both annealing treatments significantly improved the tensile properties and uniformity of the 3D-printed PEEK samples, resulting in enhanced reproducibility and reduced variability between samples. Notably, the PA-treated samples exhibited the highest stiffness, as evidenced by superior Young's modulus values, which aligns with previous research showing that annealing can substantially increase stiffness. These results are consistent with the higher degree of crystallinity observed in annealed samples. For DA-treated samples, it is hypothesized that in addition to the heat provided by the platform and building chamber, the localized heat flow around the nozzle enhanced polymer chain entanglement, thereby improving adhesion between layers and contributing to superior mechanical properties. The heat flow likely slowed the cooling rate of the extruded filament, further promoting interlayer bonding. Therefore, the polymer underwent to a two-step adhesion process involved initial contact and neck formation, followed by molecular diffusion and chain entanglement at the interface between successive layers. Reducing the temperature gradient between the extruded filament and the preceding layer likely played a key role in enhancing this process. However, the DA treatment may not have fully alleviated internal defects and residual stresses, resulting in lower stiffness in DA samples compared to PA samples.

To further evaluate the impact of infill percentage on mechanical properties, all specimens underwent PA treatment., the tensile test results are reported in Figure 4. The tensile tests showed that Young's modulus (fig.4a) and UTS (fig.4b) increased by approximately 26% and 39%, respectively, as the infill percentage rose from 30% to 100%. The increase in infill percentage directly correlated with improved mechanical performance due to the greater amount of deposited material and changes in the sample's cross-sectional area. However, when normalized for mass (i.e., specific Young's modulus (E) and specific ultimate tensile strength (UTS)), the results indicated an optimal infill percentage of 70%. Above this value, both E and UTS began to decline, suggesting that 70% infill offers the best balance between material efficiency and mechanical strength for tensile load applications. These findings are consistent with prior research, such as the work by Rinaldi et al. [15], which noted that below 50% infill, the mechanical load is largely borne by the outer perimeter of the sample, leading to reduced overall strength. This highlights the importance of infill optimization in balancing material usage and mechanical performance in 3D-printed components.

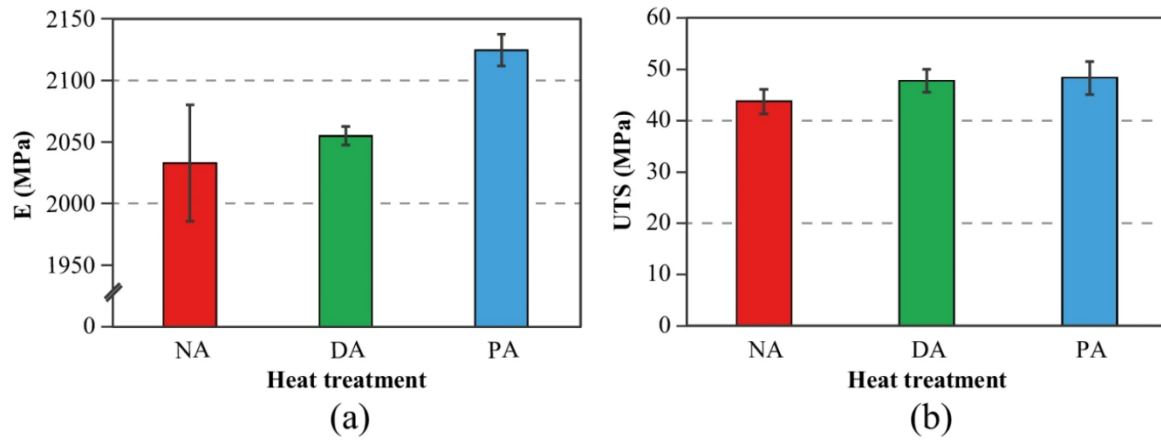


Figure 3 - Comparison of different heating treatments on tensile properties: Young's modulus (a) and ultimate tensile strength (b)

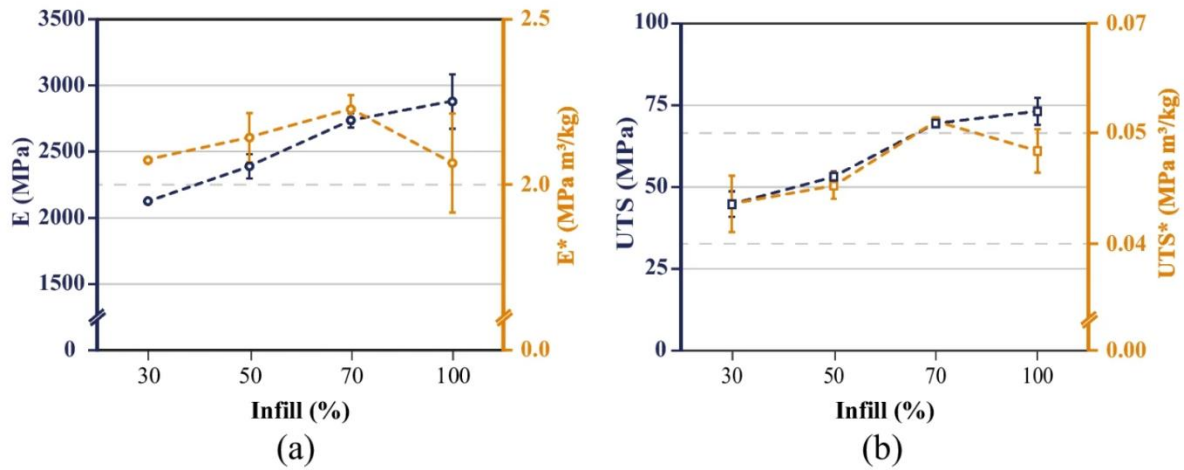


Figure 4 - Comparison of different infill percentages for tensile properties: Young's modulus (a) and ultimate tensile strength (b)

Figure 5 illustrates the compressive stress-strain curves of four different infill percentages: 30%, 50%, 70%, and 100%. In addition, Figure 6 show the comparison of different infill percentages for compression properties, in particular the compressive modulus (a) and compressive strength evaluated at 20% strain (b). The compressive stress-strain curves revealed three characteristic regions: (I) linear elasticity, where the material deformed elastically; (II) plateau, where internal structural deformation occurred without a significant increase in density; and (III) densification, where the material compressed as bulk, leading to a rapid increase in resistance. As the infill percentage increased, the length of the plateau region decreased, reflecting reduced internal rearrangement due to the higher volume of extruded material. Consequently, the compressive strength at 20% strain rose from 46.7 ± 1.6 MPa for 30% infill to 147.2 ± 1.9 MPa for 100% infill. A similar trend was observed in the compressive modulus, which increased from 741.4 ± 12.8 MPa to 2122.0 ± 161.4 MPa as infill increased from 30% to 100%.

When specific compressive properties were evaluated, the highest specific compressive modulus was achieved at 70% infill, suggesting this value is optimal for applications requiring mass optimization and lightweight designs. However, for specific compressive strength at 20% strain, the samples with 100% infill exhibited the highest performance, indicating that fully dense parts may be more suitable for applications demanding maximum strength. These findings are consistent with prior literature, confirming that infill percentage significantly influences compressive performance in 3D-printed parts.

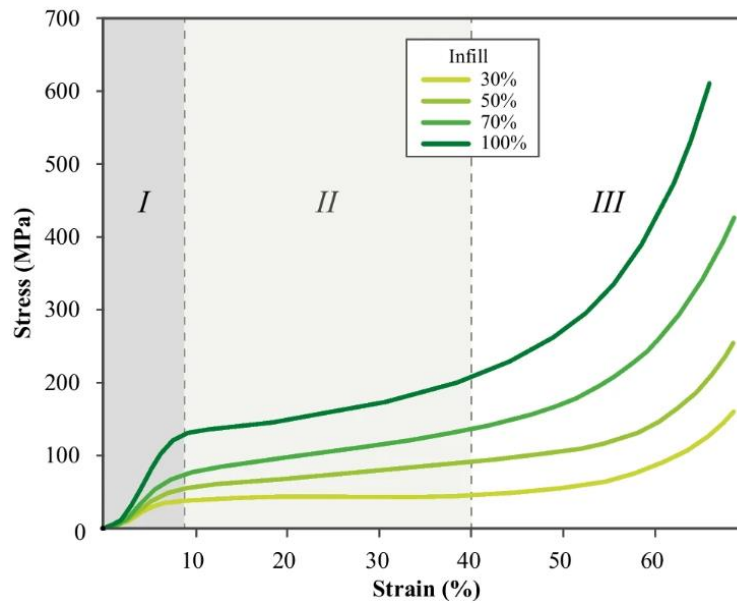


Figure 5. Stress–strain curves for compression testing with four different infill percentages: 30%, 50%, 70%, and 100%. Three stages: (I) linear elasticity, (II) plateau, and (III) densification

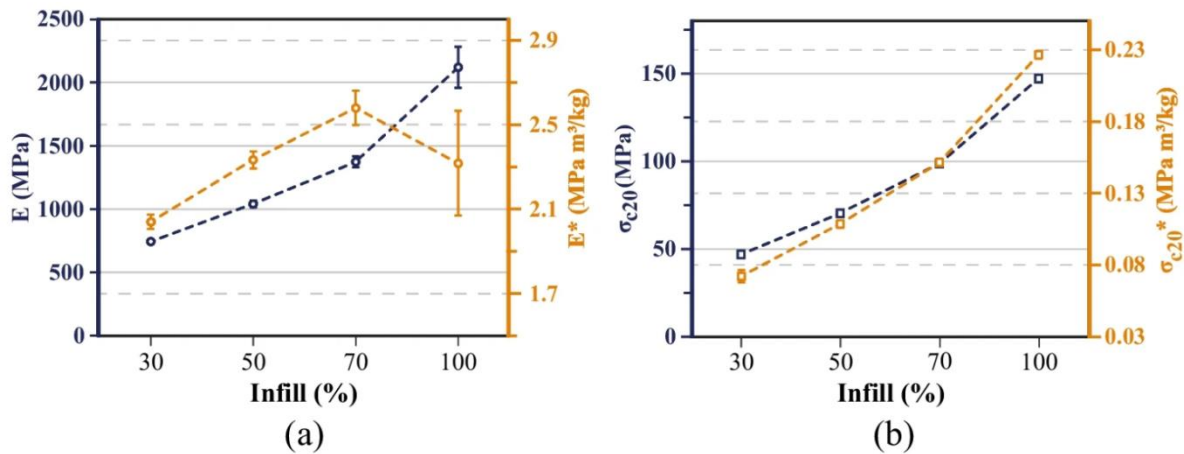


Figure 6. Comparison of different infill percentages for compression properties: compressive modulus (a) and compressive strength evaluated at 20% strain (b)

Energy Consumption

Energy consumption was measured for both the printing process and the annealing treatments, the results are shown in Table 3. The DA approach offered significant time and energy savings compared to PA. While PA required over 8 hours of oven time for proper heat treatment, DA was completed concurrently with the printing process, resulting in minimal additional energy consumption (0.52 kWh for DA compared to 3.18 kWh for PA). This suggests that DA could be a more sustainable approach for high-performance PEEK printing, particularly in industrial applications where time and energy efficiency are critical.

Table 3. Effect of different annealing processes on production time and energy consumption for 3D printing of PEEK samples

Parameter	NA	PA	DA
Production time (min)	22	502	22
Energy consumption (kWh)	0.49	3.18*	0.52

*All the energy required for annealing in oven was attributed to a single specimen

PVDF

Polyvinylidene fluoride (PVDF) has gained attention as a promising material due to its unique combination of properties such as chemical resistance, mechanical strength, and ability to generate piezoelectricity. From the molecular point of view, PVDF is a thermoplastic semi-crystalline polymer with well-known polymorphism resulting in multiple crystalline phases that significantly influence its properties and applications [16]. In particular, PVDF crystallizes into several polymorphs: α , β , γ , δ , and ϵ , where α , β , and γ phases are the most commonly seen over the molten crystallization. The α -phase is the most stable and prevalent form, the α -phase with its trans-gauche (TGTG') conformation crystallizes more readily under quiescent conditions [16] due to its lower energy barrier compared to the all-trans (TTTT) conformation of the β -phase [17]. The β -phase, which offers the highest piezoelectric, pyroelectric, and ferroelectric properties, can be obtained through a technological process involving the stretching and poling of extruded thin sheets, leading to permanent polarization and molecular chain alignment [18]. Most of β -phase PVDF-related research has dealt with the fabrication process such as mechanical stretching, application of high pressure, melt-quenching, poling under high electric fields, and electrospinning. Although there have been significant improvements, there are still constraints, such as the cost and the feasibility of utilising these techniques to create energy harvesting or sensing devices with more intricate geometries or scales. The complexity of the mentioned manufacturing processes has motivated numerous researchers to develop filaments with electroactive properties for the printing of functional devices through material extrusion production. Therefore, Saleh et al. [3] focused on the optimization of the electroactive PVDF production (with and without additives) filaments through micro compounder followed by post-treatment (mechanical stretching or electric poling). They attained the highest β -phase fraction (ca. 80%) by fabricating pure (i.e. without

additives) PVDF filament through extrusion at 220°C and mechanical stretching with an average of 4.5 times. Although it has been determined that mechanical stretching has a larger effect on the β -phase content than electric poling one, the latter showed an increment of two orders of magnitude in the output current when compared to the commercially available PVDF filament. Porter et al.[19] investigated the FFF PVDF thick film fabrication under different processing parameters, including in-situ electrical poling. They were not able to produce enough samples to conduct a statistical analysis. However, their results suggested that higher β -phase content was reached at lower extrusion temperatures, faster extrusion rates, and higher hot-end voltages. While all as-printed films exhibited minimal to no measurable piezoelectricity, PVDF films resulted in high β -phase content and, exposed to a post-printing corona poling procedure showed a small but consistent piezoelectric response. In addition, some researchers incorporated fillers to induce the generation of β -phase in the FFF 3D printed PVDF films such as tetraphenylphosphonium chloride (TPPC), nanoparticles ionic liquid [20], trifluoroethylene (TrFE) [21], and more. These additives have led to a significant increase in β -phase content, but they also cause an increase in production times, costs and a necessity for additional safety measures. Despite the growing interest towards the use of innovative printing processes, the literature lacks systematic studies on how the 3d-printing process affects the final PVDF crystalline structure. It is well-established that extrusion processes subject the amorphous melt to high shear forces, causing polymer chains to orient and stretch. This orientation reduces the system's entropy, which in turn elevates the equilibrium melting temperature, providing additional undercooling that triggers crystallization [17]. Consequently, flow can induce the transition of α to the β -phase by promoting the all-trans conformation, thereby accelerating crystallization kinetics and eventually enhancing electroactive properties. Thus, flow-induced crystallisation represents a promising approach for increasing crystallinity and engineering specific crystalline phases. The aim of this work was to address the following research questions:

- Can FIC be harnessed to achieve polarized PVDF samples
- How does the effect of flow during 3D printing alter crystallinity?

To investigate the FIC, the temperature and extrusion speed were tuning to examine how different shear rate influence the β -phase content in PVDF. A statistical approach was employed to ensure the significance of these parameters on crystallinity, involving a Design of Experiments (DOE) to select the appropriate parameter range for printing. Analytical techniques, including DSC, FTIR, POM, and rheology, were utilized to assess crystallinity. The resulting crystalline structures were further analyzed using ANOVA to correlate the β -phase content with FFF processing parameters. In conclusion, the final discussion will elucidate the potential and limitations of the flow-induced crystallization phenomenon in the production of piezoelectric devices through FFF.

In this study, to examine the effect of temperature and extrusion speed on the printing of PVDF, six levels were defined for each of the two parameters as explained in Table 4, and each combination was replicated three times. Consequently, a total of 108 cylindrical samples with a diameter of 20 mm and a height of 3 mm were printed using a commercial filament

(FluorXTM) and a Prusa i3 MK3S printer. The impact of the printing parameters on crystallinity was investigated through DSC and FTIR analyses.

Table 4. Design of Experiment defined as two factor extrusion temperature (T_{ex}) and extrusion speed (S_p) and six levels for each one, for a total of 36 combinations.

T_{ex} (°C)	S_p (mm/s)
215	15
225	25
235	35
245	45
255	55
265	65

The DSC 214 Polyma Equipment was employed to conduct differential scanning calorimetry (DSC) analyses. Under a nitrogen atmosphere (40 mL/min) and a heating/cooling rate of 10 K/min, two heating and cooling studies were conducted from 20 to 400 °C. DSC data allowed measurement of the melting temperatures and enthalpies of the material after process conditions, providing information about the changes in the crystalline fraction. The crystalline fraction was evaluated as:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (2)$$

where ΔH_m is the experimental enthalpy of melting, calculated by the integration of the melting endothermic peak, and ΔH_m^0 is the theoretical melting enthalpy of a purely crystalline PVDF, which was assumed to be equal to 104,7 J/g [22] .

Fourier Transform Infrared Spectroscopy. FTIR analysis was carried out with the Bruker Tensor 27 in combination with the OPUS software. The applied spectral range was 600-1500 cm⁻¹, with a resolution of 2 cm⁻¹ and 64 scans in ATR (attenuated total reflection) mode were collected per sample [22]. The fractions of the different phases have been calculated in accordance with the approach previously employed by Ye et al.[23]. The initial phase involved assessing the α and β , γ -fractions (F_α and $F_{\beta,\gamma}$) as:

$$F_\alpha = \frac{A_{763}}{A_{763} + A_{840,832}} \quad (3)$$

$$F_{\beta,\gamma} = 100 - F_\alpha \quad (4)$$

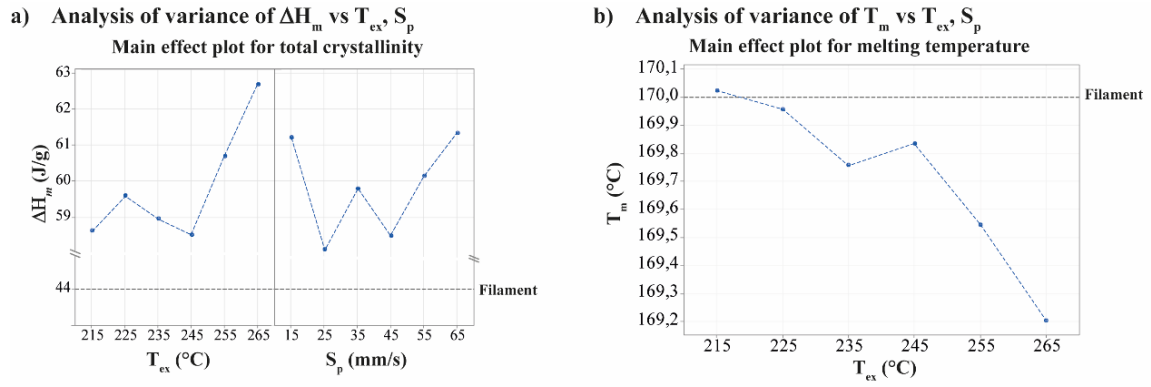
Where, A_{763} and $A_{840,832}$ are the absorbance intensities at 763 cm⁻¹ for α -phase and 840/832 cm⁻¹ for β - and γ -phases, respectively. Following this, the individual fractions of β - and γ -phases (F_β and F_γ) were calculated by

$$F_\beta = F_{\beta,\gamma} \times \frac{A_{1276}}{A_{1276} + A_{1233}} \quad (5)$$

$$F_{\gamma} = F_{\beta,\gamma} \times \frac{A_{1233}}{A_{1276} + A_{1233}} \quad (6)$$

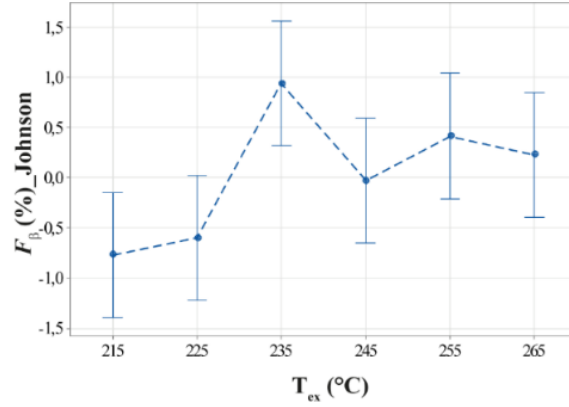
where A_{1276} and A_{1233} are the absorbance intensities at 1276 and 1233 cm^{-1} that are exclusive for the β - and γ -phases, respectively. The FTIR spectra were processed using the EssentialFTIR software. Initially, they were normalized according to the 1070 peak [24], and the intensities of the characteristic peaks (763, 840, 1233, 1276 cm^{-1}) were exported.

Figure 7 shows the results of the ANOVA analysis about the effect of the extrusion temperature and speed on the DSC analysis; the response variables are the melting enthalpy ΔH_m , which is used for the total crystallinity estimation in eq.(2), and the melting temperature T_m . For both response variables the significance level is set at 95%. Figure 7a exhibits the ANOVA analysis results on the total crystallinity reports a p-value lower than 0.5% for both the factors Tex and Sp. Therefore, it is possible to assume with a probability of 95% that both extrusion temperature and speed have significant effects on the response variable. The interaction between temperature and speed (Tex $\times$ Sp) is not statistically significant, with an F-value of 1.34 and a p-value of 0.168, suggesting no significant combined effect. Therefore, the interaction contribute was excluded from the analysis. Moreover, increasing temperature generally leads to higher crystallinity, although not entirely linearly, as seen at 235 and 245 $^{\circ}\text{C}$. The effect of speed requires further clarification, but the correlation between speed and crystallinity appears to be strongly nonlinear. In addition, the ANOVA was also conducted to investigate the effect of printing parameters on the melting temperature, including extrusion temperature, speed, and their interaction, the results are reported in Figure 7b. However, the only factor that affects the melting temperature is the extrusion temperature. The main plot exhibits the relationship between extrusion temperature and melting temperature. Comparing this plot with the one in Figure 7a it can be observed that the two trends are opposite; higher extrusion temperatures favor a higher percentage of crystallinity but a lower melting temperature. Figures 7a and 7b also present the enthalpy and melting temperature values obtained from a DSC analysis of the filament, indicated by a black dashed line, to highlight the effects of the printing process parameters on the material. It can be observed that comparing the filament results and the low extrusion temperatures' ones, there is a slight increase in the total crystallinity, but they show almost the same melting temperature. However, as the extrusion temperature increases, there is a sudden rise in crystallinity and a drastic reduction in the melting temperature. Jalali et al. [25] asserted that the chain orientation induced by high shear rates reduces the system's entropy, leading to an increase in melting temperature. Moreover, the phenomenon of flow-induced orientation is governed by the competition between molecular relaxation and flow strength [26]. Consequently, it is possible to conclude that a high extrusion temperature causes chain relaxation, resulting in a reduction in orientation and, therefore, a decrease in melting temperature.

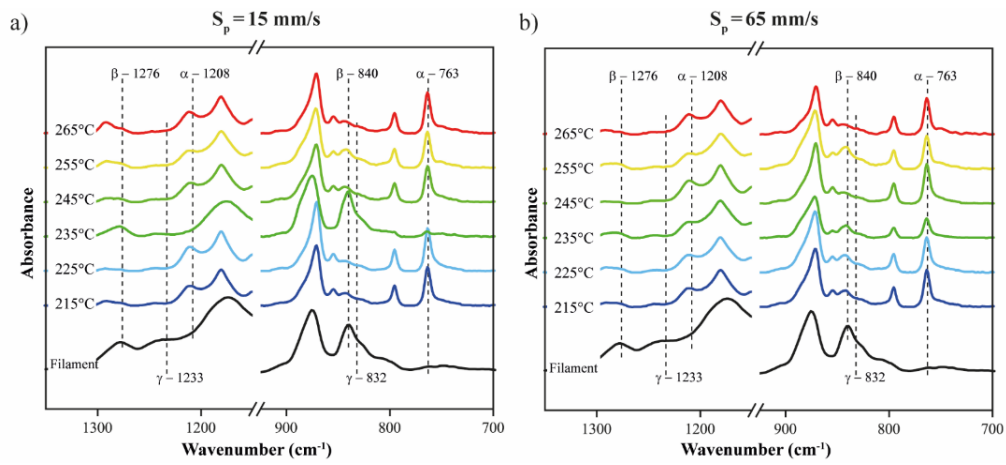


Figures 7. Analysis of variance where the response variable is the melting enthalpy in a) and the melting temperature in b).

ANOVA analysis was also conducted for the β -phase calculated as in eq (5). Before performing the analysis, the normality of the β -phase distribution was verified, but the probability plot recorded a p-value $< 0,005$. Thus, it is impossible to exclude with 95% confidence that the β -phase distribution is normal. Consequently, its distribution was transformed using the Johnson transformation to achieve normality. Subsequently, ANOVA was performed, and the results are presented in Figure 8. Similar to the melting temperature in DSC shown in Fig.7b, the only factor that appears to have an influence is the extrusion temperature. Since the only parameter that appears to influence the percentage of the β -phase is the extrusion temperature, the results for the same extrusion temperature at different speeds have been considered as replicates. The one-way analysis indicates that the p-value for T_{ex} is 0,4%, which suggests a 99,6% probability that the extrusion temperature has a significant effect on the β -phase percentage. Contrary to the assertions made by Porter[19], the observation of the main effect plot reveals that the β -phase percentage increases with rising extrusion temperatures. Figure 9 summarizes the results from the FTIR analysis by comparing the spectra of samples printed at different temperatures at the lowest and highest speeds and the filament's one, respectively in 9a and 9b. Both the 235°C'S spectra at low and high speed confirmed that the extrusion temperature at 235°C reaches the maximum β -fraction value for the two peculiar peaks at 840 and 1276 cm⁻¹. However, by comparing the 3d-printed spectrum with the filament's one, it can be observed that filament presents the highest β -phase fraction that was calculated as described in eq. 4, yielding a value of 82%, consistent with values reported in the literature [3]. The predominance of the β -phase over the α 's one in the filament, compared to the printed samples, could be attributed to the differences in shear rates and cooling speeds between the printing and extrusion processes. The high shear rate during the filament extrusion process, coupled with the significant thermal gradient, promote the formation of the β -phase over the α -phase. In contrast, the printing process, characterized by lower shear rate and slower cooling rates, does not achieve a comparable β -phase fraction.



Figures 8. Analysis of variance where the response variable is b-fraction (transformed by Johnson method)



Figures 9. FTIR spectra comparison of samples printed with different temperatures at a) 15 mm/s and b) 65 mm/s.

In order to investigate the effect of printing parameters on the PVDF flow-induced-crystallisation, a polarized optical microscope analysis was employed. Since the previous sections point out that the main parameter that influences the crystals is the extrusion temperature, it was decided to analyse samples printed at different temperatures but with the same printing speed of 35 mm/s. The literature frequently states that the melting temperature is mainly related to the thickness of the crystals. Therefore, in this analysis, the radius of the spherulitic crystals was calculated, as shown in the images in Figure 10. Various optical microscope images were taken at the same magnification (1000x) for each specimen, and the radius of more than twenty crystals was measured. The mean and distribution of the crystal size obtained from these measurements are reported in the graph in Figure 8. Considering the average radii with respect to the extrusion temperature, a trend like that observed for the melting temperatures is noted, specifically, lower extrusion temperatures lead to a higher melting temperature and a larger crystal radius. Previous studies [27] have demonstrated that applying flow at higher temperatures leads to an increase in the density of crystallization nuclei and the formation of spherulites with smaller diameters due to the enhanced crystallization rate at higher temperature. However, this trend is not strictly decreasing, and it should be noted that the distribution of radii at higher extrusion temperatures is broader compared to those recorded at lower temperature.

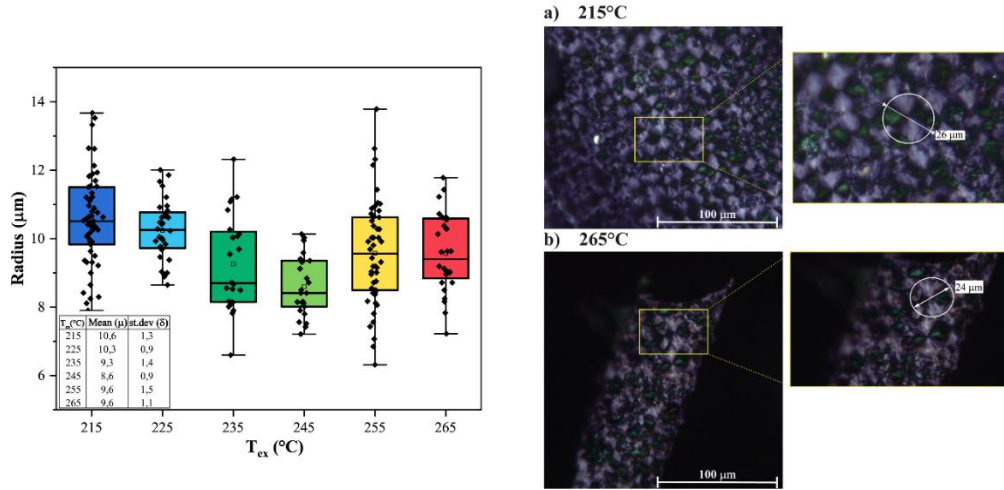


Figure 10. On the left side: mean and distribution of the crystal radius at different extrusion temperatures; on the right side: POM analysis of the 215°C and 265°C-printed samples.

The effect of the different printing temperatures was investigated by analysing its rheological properties with an Anton Paar rheometer (MCR 702) equipped with an oven CTD600. The geometry used was a plate-plate geometry with 25mm diameter. Rheological data were collected to study the effect of the flow, 3d-printed discs (25mm diameter and 1mm thickness) at different extrusion temperatures. Figure 11 illustrates the viscosity (η) versus shear rate ($\dot{\gamma}$) behavior of a 3D-printed polymer samples printed at various temperatures and measured at a constant temperature of 180°C. The three different plot lines correspond to PVDF sample printed at the lowest, medium and highest extrusion temperature. At very low shear rates (near zero), the polymer chains are in an equilibrium state where they are not significantly oriented or stretched by the flow. The viscosity in this regime is dominated by the polymer's molecular weight and degree of entanglement. In this regime, the viscosity is more reflective of the inherent properties of the polymer, such as molecular weight distribution and chain entanglement density. This value is identified in the literature as zero-shear viscosity (η_0). The value of zero-shear viscosity decreases as the T_{ex} increases. Even if the difference is small that one could consider it negligible, this still allow allows speculation of molecular weight changes during processes at different T_{ex} . In fact, as afroed explained, the decrease of zero shear rate viscosity could be an indication of a decrease of molecular weight. Another interesting behaviour to point out is the changing of the curve shape between the material processed at 215 °C and the other two. For the samples extruded at 215 °C, the shear thinning happens more abruptly then for the others. The reason could be due to the widening of the molecular weight distribution of the polymer [24]. This is linked to a type of degradation process happening by chain scission, which increases the number of smaller oligomers.

In Fig 11 the data were fitted using the Carreau Model in this formulation:

$$\eta = \eta_{inf} + (\eta_0 - \eta_{inf}) [1 + (t\dot{\gamma})^a]^{\frac{n-1}{a}}$$

Where η_{inf} is the viscosity for an infinite value of shear rate (corresponding to the value at the second Newtonian plateau), η_0 is the viscosity for a low value of shear rate (corresponding to the value at the first Newtonian plateau, a is the transition control factor and n is the power

index. The slope of the curve corresponds to $n-1$ and it is an indication on the magnitude of the shear thinning effect. In fact, we notice that the n increases for lower T_{ex} .

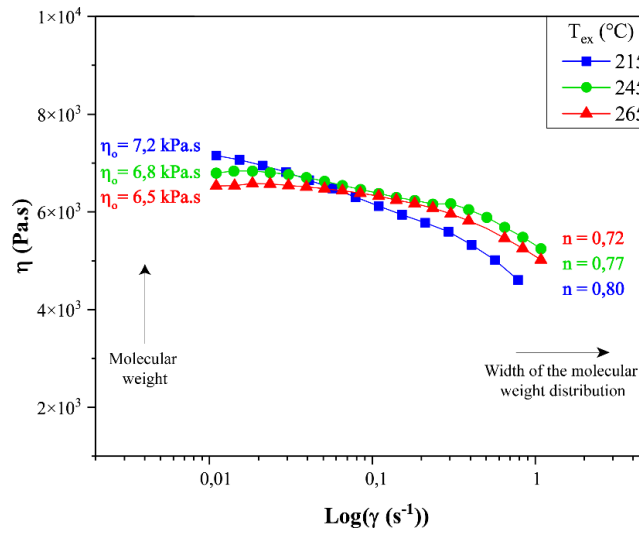


Figure 11. Effect of process parameters on viscosity.

PVDF thermal degradation consist in of two different mechanisms. One of them includes the scission of the C-H bond followed by the H-X bond. The other consist in backbone scission with consequent formation of halogenated compounds. Silva et al. [28] found out that in the presence of any other solvent the main mechanism is represented by the first one. However, the material can become more sensitive to thermal degradation process if treated in an alkaline solvent. This will lead to more severe chain scission process [29].

Conclusion

PEEK

This work aims to investigate the effects of different annealing and varying infill densities on the thermal and mechanical properties of 3D-printed PEEK components. Additionally, the investigation aimed to assess the impact of these factors on energy consumption during the Fused Filament Fabrication (FFF) process. Figure 12 illustrates a summary of the work.

As a novel aspect of this study, the potential of employing a new annealing strategy, specifically direct annealing (DA), was explored. This approach leverages the use of a heat collector positioned at the nozzle to optimize the thermal conditions during the printing process. This method could improve the crystallinity of PEEK components while saving time and reducing costs. The analysis focused initially on the evaluation of different annealing effects under the most challenging infill condition, specifically at 30% infill density. This condition was chosen as it represents the worst-case scenario for material behavior and property optimization, allowing for a robust comparison of the annealing treatments. The next phase of the research involved assessing the mechanical properties, particularly tensile and compressive strength, at varying infill percentages (30%, 50%, 70%, and 100%). This step was crucial to identify how different levels of material infill influence the structural performance of the printed PEEK samples. Lastly, the study examined the effects of annealing treatments and infill densities on

the energy consumption required during the printing process, aiming to find an optimal balance between mechanical performance and eco-efficiency.

The results highlighted:

- In terms of thermal properties, both DA and PA increased the glass transition temperature (T_g), shifting it to higher temperatures, though DA did not appear to affect the overall percentage of crystallinity. Importantly, DA significantly increased the degradation temperature, enhancing the thermal stability of the PEEK samples.
- Regarding mechanical properties, DA improved the performance by reducing the temperature gradient during printing, which positively affected the interlayer adhesion. However, the Young's modulus of DA samples was lower than that of PA-treated samples, indicating a reduction in stiffness. Consequently, PA was selected as the annealing method for samples with varying infill percentages. Moreover, the infill percentage plays a critical role in determining the mechanical performance of the printed parts. Specifically, an infill density of 70% yielded the best balance between material optimization and mechanical strength, providing the highest specific tensile and compressive properties. Above 70% infill, further material use did not lead to significant improvements in performance.
- Lastly, the study highlighted the energetic efficiency of the direct annealing process. As the infill percentage increased, the specific energy consumption decreased. Moreover, DA significantly reduced both the production cycle time and overall energy requirements, making it a more efficient process than traditional post-annealing methods.

In conclusion, direct annealing demonstrated clear advantages in terms of energy consumption, production efficiency, and thermal stability. However, the mechanical properties achieved with DA were still inferior to those obtained through post-annealing. Further research into optimizing the DA process, such as real-time heat flow control, is recommended to enhance its mechanical performance, potentially aligning it with that of traditional PA methods. The results of this study are promising and lay the groundwork for advancing the use of high-performance polymers in additive manufacturing, particularly for metal replacement in industrial applications.

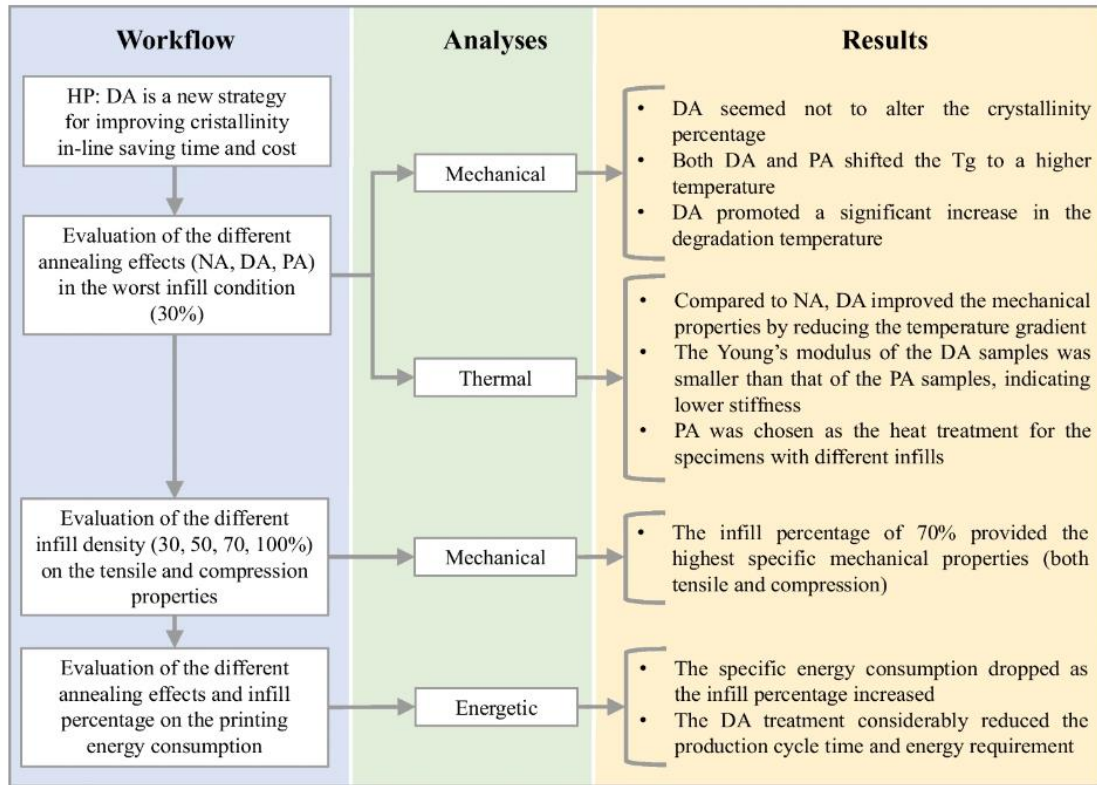


Figure 12. Scheme of the logical workflow of research, highlighting the main analyses and related results

PVDF

To summarise the PVDF work, this conclusion section answers the initial research questions.

Q1: Can Flow-Induced Crystallization (FIC) Be Harnessed to Achieve Polarized PVDF Samples?

Flow-induced crystallization (FIC) plays a crucial role in achieving polarization in polyvinylidene fluoride (PVDF) during the fused filament fabrication (FFF) process. During FFF, the polymer melt undergoes shear and extensional flows as it passes through the nozzle. This mechanical deformation orients and stretches the polymer chains, which accelerates the nucleation and growth of specific crystalline phases. In PVDF, FIC significantly promotes the formation of the β -phase, the electroactive phase essential for piezoelectric applications. Under static (quiescent) conditions, PVDF predominantly crystallizes into the non-polar α -phase, which lacks piezoelectric properties. However, in this study, the FFF process generated a notable β -phase fraction in all samples, confirming that FIC successfully induces polarization in PVDF. The experimental results, validated by both Differential Scanning Calorimetry (DSC) and Fourier-Transform Infrared Spectroscopy (FTIR) analyses, demonstrate that the content of the β -phase varies depending on the extrusion temperature.

Q2: How Does the Effect of Flow During 3D Printing Alter Crystallinity?

The flow conditions during 3D printing, particularly as influenced by extrusion temperature and speed, significantly alter the overall crystallinity of PVDF. The shear and extensional forces generated within the nozzle play a pivotal role in breaking down the kinetic barriers to crystallization, thereby increasing the crystallization rate and facilitating the formation of specific crystalline phases. The experimental data revealed that extrusion temperature is the most dominant factor affecting crystallinity. Higher extrusion temperatures generally led to increased crystallinity, as confirmed by DSC analysis, which showed elevated melting enthalpies at these higher temperatures. However, this relationship was not strictly linear. For example, at 235°C, a significant enhancement in crystallinity was observed, with the β -phase fraction also increasing, indicating that this temperature is optimal for both maximizing overall crystallinity and encouraging the formation of the desired polymorphic phase. Conversely, extrusion speed had a more complex and less predictable effect on crystallinity. While higher speeds did not significantly alter the crystallinity or β -phase content, they did not negatively impact these properties either. This suggests that faster extrusion speeds may be employed without compromising the crystallinity or electroactive properties of the printed samples. This finding has potential implications for increasing production speed without sacrificing material performance, which is particularly advantageous for industrial applications. Interestingly, the study also observed a decrease in the melting temperature with increasing extrusion temperatures. This reduction could be attributed to several factors, including polymer degradation, the stability of the crystalline phases, and relaxation of the polymer chains. Specifically, at higher temperatures, the polymer chains undergo relaxation, reducing the molecular orientation induced by flow and thus lowering the melting temperature. Despite the reduction in melting temperature, the overall crystallinity and β -phase content remained high at these elevated temperatures, suggesting a complex interplay between chain relaxation and flow-induced crystallization.

As a limitation of this study, it is important to declare that the effect of shear rate was investigated in a narrow range. Indeed, the design of experiment did not consider the nozzle diameter as factor, therefore a nozzle of 0,4 mm was kept constant. Future work will focus on exploring a wider range of shear rates by reducing nozzle size, as shear rate is more affected by nozzle diameter than by extrusion speed. Additionally, we plan to compare the effects of process parameters on different feedstock materials. Previous works demonstrated that feedstock with high initial β -crystallinity could undergo to β to α -phase conversion during post-processing. By addressing these areas, future research can further optimize the 3D printing of PVDF, enabling the production of advanced functional devices with enhanced electroactive properties.

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