Printing temperature effects on the structural and mechanical performances of 3D printed Poly-(phenylene sulfide) material

A El Magri*1, 2, S Vaudreuil1, K El Mabrouk1 and M Ebn Touhami2

1 Euromed research center, Euromed Engineering Faculty, Euro-Mediterranean University of Fes, B.P. 51, Meknes Road, Fes, Morocco.
2 Laboratory of Materials Engineering and Environment: Modeling and Application, Faculty of Sciences, Ibn Tofail University, PO Box 133, 14000 Kenitra, Morocco.

*Email:a.elmagri@ueuromed.org

Abstract. Fused Deposition Modeling (FDM) is the most popular and widely used additive manufacturing techniques for plastic materials. In FDM, the Z-height of the object is achieved by depositing extruded polymer layer upon layer. To reduce the time and cost of printed parts requiring specific properties, many processing parameters can be adjusted to optimize the FDM process. Among those is the nozzle temperature. In this study, Poly-(phenylene sulfide) (PPS) was chosen because of its mechanical performance, making it attractive for high-performance applications. In this work, the impact of printing temperature on the mechanical and structural properties of printed parts was carefully tested. Results show that a 340°C printing temperature yield the parts with the highest tensile properties, with a degree of crystallinity superior to as-received PPS.

1. Introduction
Additive Manufacturing (AM) has shown the possibility of significantly reduce both time and cost of product development. AM, per the ASTM F2792-12a definition, is defined as “a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies”. AM is also called, on a more familiar basis, 3D printing even though it doesn’t reflect the full potential of what AM can achieve. This new integrated technology enable the production of complex geometries hard to impossible to achieve with conventional methods [1]. Thanks to its ease of use and lower investment and operating costs, Fused Deposition Modeling (FDM) [2][3] has become the most used 3D printing process. FDM operates on the basis that a thermoplastic filament is extruded, layer by layer, in its viscous state through a heated nozzle. Literature abound with published works on AM of commodity polymers [4] such as polycarbonate (PC), polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and PC–ABS blends [5]. For high-performance thermoplastics such as PPS in AM, literature is almost nonexistent. While FDM is more user-friendly in its operation, results can be significantly affected by many parameters, including printing temperature and speed, layer thickness and raster orientation. Multiple works have concluded that mechanical properties will depend on those parameters [1], [6]–[10]. Kishore et al [11] have used...
two high performance semi-crystalline polymers (PEEK and PPS) with FDM process to evaluate the relationship between rheological properties and processing conditions. The authors have shown that a rheological analysis is helpful in identifying appropriate FDM processing conditions and key control parameters.

The present study aims to fill some gaps in published literature by investigating the relationship between printing temperature, mechanical and structural properties of PPS parts prepared by FDM process.

2. Materials and methods

The Poly (phenylene sulfide) (PPS) filaments used were purchased from FILOALFA (Italy) and processed using an INTAMSYS (Intelligent Additive Manufacturing Systems) FunMAT HT. This FDM system, having a build volume of 260 x 260 x 260 mm, is equipped with a heated bed and heated build chamber. As the melting temperature of PPS is 280°C, print head temperature above 300°C are required to achieve some flowability. All tensile bars used were printed directly on the heating bed, using a brim to increase adhesion and lower peel off risks. Infill was set to 100 % for all specimens to obtain solid-like samples. The major printing parameters used are listed in Table 1.

| Parameters                      | Values       | Units |
|---------------------------------|--------------|-------|
| Printing temperature            | 320-330-340-350 | °C    |
| Bed temperature                 | 65           | °C    |
| Chamber temperature             | 30           | °C    |
| Infill line directions          | [45/-45]     | °     |
| Layer height                    | 0.15         | mm    |
| Line width                      | 0.4          | mm    |
| Infill density                  | 100          | %     |
| Number of bottom / top layers   | 6 / 6        | layers |
| Number of perimeters            | 2            | wall  |

Thermal and structural properties of PPS were studied by Differential Scanning Calorimetry analysis (DSC Q20 with RCS90 cooling system, TA Instruments). Samples were heated from 25 to 350 °C under a 50 mL/min nitrogen flow before being cooled back to -5°C. A heating / cooling rate of 10°C/min was used for all tests. Glass transition, melting temperatures and enthalpies were calculated from the endothermic and exothermic peaks, using the TA Universal analysis software. The degree of crystallinity (\(X_c\)) was calculated from the first heating as follows:

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X_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^{100\%}} \times 100
\]  

Where \(\Delta H_m\) and \(\Delta H_m^{100\%}\) are respectively the melting enthalpy of PPS and 100% crystalline PPS, \(\Delta H_{cc}\) is the cold crystallization enthalpy. The melting enthalpy of a totally crystalline PPS material is 80 J/g [12].

Tensile properties were established using a Criterion C45.105 electromechanical universal testing machine (MTS, USA) equipped with a 10 kN load cell, see Figure 1(A). A crosshead displacement speed of 0.1 mm/s was used to apply load through self-tightening jaws. A data acquisition software (MTS TestSuite) was used to collect displacement (mm) and force (N) required for the tensile strain-
stress curves and calculate the Young’s Modulus and maximum tensile strength. For each printing temperature, six specimens were tested to increase accuracy. Figure 1(B) illustrate the tensile bar geometry used. This bar geometry was designed with dimensions divisible by 0.15 mm, which is the layer height used, to avoid creating missing or additional layers during slicing.

Figure 1. (A) MTS machine during tensile test,(B) geometrical illustration of tested specimen.

3. Results and discussion

3.1. Effect of printing temperature on thermal and structural properties
Thermal characteristics of PPS at various printing temperatures were established by differential scanning calorimetry (DSC) analysis. Figure 2 corresponds to the PPS Thermogrammes between 20°C to 330°C, using a 10°C/min heating/cooling rates. Four thermal transitions can be seen for PPS. During the heating phase, the first transition at ~90°C is the glass transition process where PPS change to a high elastic state. The exothermic transition at ~125°C is the cold crystallization, generally caused by an ordering of molecular chains in the crystalline PPS lamellae and associated to increased mobility throughout heating cycle [13]. The endothermic transition at 280°C amount to the melting temperature. During cooling, only an exothermic transition at 224°C is observed which is associated to the crystallization of PPS. This last transition is caused by the rearrangement of molecular chains in the crystalline PPS lamellae due to increased mobility during heating. The first heating cycle in Figure 2 confirm that PPS is a semi-crystalline material.

It should be noted that printed PPS at 340°C exhibit a higher degree of crystallinity (37.32%) than the as-received polymer (Table 2). This higher crystallinity could be attributed to the creation of highly ordered lamella during printing at 340°C. Printing PPS at temperature approaching its degradation temperature will results in polymer chains break. The shorter chains will make more difficult the formation of crystalline lamella formation.
Figure 2. DSC curves of PPS after FDM printing at different printing temperatures.

Table 2. DSC analysis results.

| Material     | $T$  | $T_g$ | $T_{cc}$ | $T_m$ | $\Delta H_m$ | $\Delta H_{cc}$ | $T_c$  | $\chi$  |
|--------------|------|-------|----------|-------|--------------|----------------|-------|---------|
| As received  | -    | 92.3  | 122.9    | 279.6 | 33.3         | 14.8          | 223.9 | 23.0    |
|              | 320  | 91.2  | 122.3    | 279.2 | 31.1         | 9.49          | 224.0 | 27.0    |
|              | 330  | 91.3  | 121.9    | 279.7 | 33.6         | 10.9          | 223.9 | 28.3    |
| After printing | 340 | 91.2  | 122.3    | 280.0 | 35.6         | 5.78          | 224.0 | 37.3    |
|              | 350  | 89.2  | 120.5    | 279.6 | 39.7         | 12.8          | 225.2 | 33.6    |

3.2. Effect of printing temperature on tensile properties

In order to evaluate the effects of printing temperature on the structural properties of printed parts, the behavior of the polymer system must be understood. Previous works reported that printing temperature affect significantly the flowing behavior and solidification process of printed filament [14]–[16] This will in turn influence the resulting properties during cooling phase such as rasters bonding and surface quality.

Figure 3 shows the variation of Young’s Modulus and tensile strength with printing temperature from 320°C to 350°C. The enhancement of Young’s Modulus and tensile strength can be observed with increasing printing temperature until a maximum is reached at 340°C, yielding values of 2030.58 MPa and 47.34 MPa respectively. This increase in mechanical properties with temperature can be explained by the stronger adhesion between rasters which will result automatically in an improvement of tensile properties.

These results illustrate the tendency of tensile behavior to follow the crystallinity degree. When printing temperature is raised from 340°C to 350°C, tensile properties begin to decline, with crystallinity decreasing from 37.3 to 33.6 %. This could be explained by the progressive collapse of the build layers and molecular chains deterioration.
Figure 3. Printing temperature effect on tensile properties.

High printing temperature (350°C) tend to generate parts with more porosity and worst surface quality, things that negatively impact tensile properties (see figure 4).

Figure 4. Effect of printing temperature on printed parts qualities (A) 340°C,(B) 350°C.
4. Conclusion
The objective of this work was to study the effect of the most critical FDM parameter, printing temperature, on final properties of printed parts. In order to investigate the relationship between printing temperatures and final properties of printed parts, temperatures between 320 and 350°C were tested. It was found that crystallinity and tensile properties were strongly affected by printing temperature, with a narrow window yielding the best values.

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