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MODELING PEEK CRYSTALLIZATION PROCESS UNDER A 3D PRINTING THERMAL PROFILE WITH FAST SCANNING CALORIMETRY

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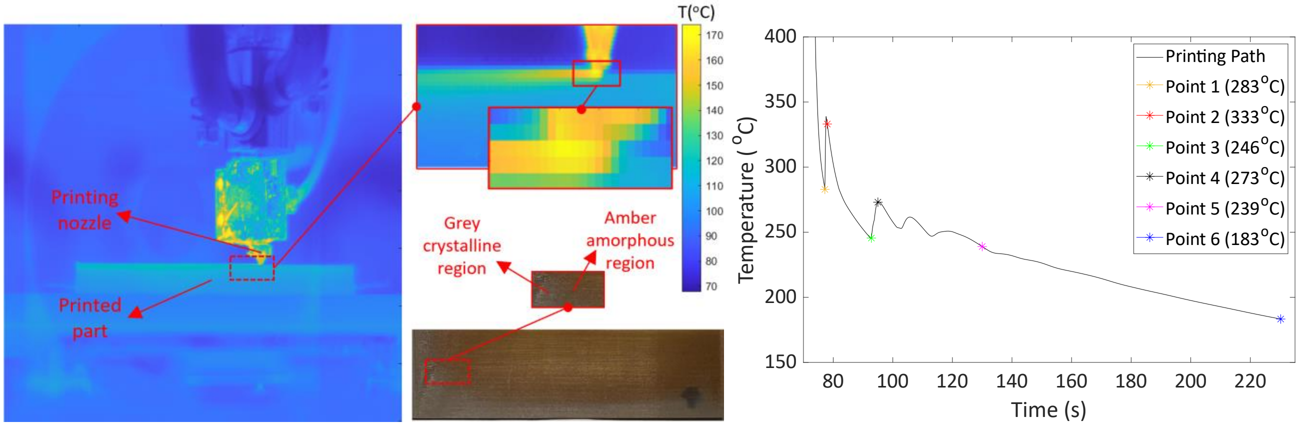
ABSTRACT

During melt extrusion additive manufacturing (MEX) (also known as 3D printing) of polymers, the thermal history profile of deposited material features a complex sequence of isothermal regions, non-linear heating and cooling, and periods of rapid cooling reaching over 16^{o}Cs^{-1}. This complex thermal profile, in part, determines the resultant crystalline morphology and degree of crystallinity for semi-crystalline polymers such as poly-ether-ether-ketone (PEEK). PEEK has been shown to display double peak exotherms with varying ratios of low to high temperature peak enthalpies upon remelting depending on the thermal history. This is due to temperature dependant morphological changes which has been investigated by traditional differential scanning calorimetry (DSC) with simple isothermal tests, though these are not yet well understood. However, due to temperature ramp rate limitations, the DSC is unable to replicate a 3D printing thermal profile. The fast-scanning calorimetry (FSC) features temperature ramp rates exceeding 4000^{o}Cs^{-1}. In this paper, the crystallization kinetics and resulting crystal morphology is characterized for PEEK undergoing an experimentally measured 3D printing thermal profile by utilizing a step wise-interrupted method on the FSC. Under this paradigm, data is collected upon reheating after quenching the melt following a pre-set cooling profile. Simple isothermal tests are also conducted utilizing a wide range of heating and cooling rates not feasible with the DSC. The resulting data is used to produce a crystallization kinetics model for PEEK that can predict the evolution of the crystallization process for a set thermal profile thereby providing insights towards the complex morphology and degree of crystallinity of 3D printed components.

1 INTRODUCTION

The thermal-mechanical properties of semi-crystalline polymers are dependent on the mass fraction crystallinity (also known as degree of crystallinity (DOC)) and morphology of their crystalline phases. Traditionally, mass fraction crystallinity is used to correlate with the properties in engineering applications. The most common method for measuring mass crystallinity is Differential Scanning Calorimetry (DSC). This technique tracks the heat flow associated with the exothermal cooling from the melt or endothermal melting of previously crystallized materials to calculate the mass fraction crystallinity. Wide angle X-ray spectroscopy (WAXS), polarized microscopy (POM), small angle X-ray spectroscopy (SAXS) are some of the characterization methods that have been employed by authors to measure morphological characteristics of the crystalline phase, such as unit cell dimensions, lamellar thickness, and spherulite size [1,2,3]. Several theories have also been proposed to interpret the shapes of DSC endothermic melting curves with respect to morphology [4,5,3].

Poly-ether-ether-ketone) (PEEK) is a chemically resistant semi-crystalline polymer used in 3D printing of high-performance components used in aerospace, automotive, and medical applications [6]. The complex cooling history during 3D printing influences the crystallization process of PEEK. The thermal profile is dependent on the geometry of the part, printing speed and material deposition temperature among other factors [7]. As new material is added, the previously deposited layers heat up again. Refer to Figure 1(a) to see the varying degrees of crystallinities due to the complex cooling profile. The evolution of DOC can be traced through a standard crystallization kinetics equation from a given time-temperature cooling profile. The dual Nakamura model can be utilized to characterize the crystallization evolution of 3D printed PEEK, provided exothermic data (due to crystallization) from a wide range of cooling rates are collected (refer to [8] for more information regarding the implementation of a dual Nakamura model). This is due to the nature of the 3D printing thermal profile which consists of isothermal and non-linear cooling regions reaching rates beyond 16^{o}Cs^{-1} (refer to Figure 1(b)). However, high cooling rates, which are required for this analysis, are beyond the capability of the standard DSC instrument which is limited to about 1°Cs^{-1}. For PEEK, the DSC melting endotherm can exhibit either one or two peaks, depending on the cooling conditions. There are two conflicting theories that explain the DSC enthalpy profiles. The Dual Lamellar Thickness Model suggests that double melting peaks result from two populations of lamellae with different thicknesses that coexist, where thinner lamellae melt at lower temperatures and thicker ones at higher temperatures [9]. In contrast, the Melting Recrystallization Model attributes the lower temperature peak to the melting of most lamellae, which then recrystallizes into a more thermodynamically stable state that melts at higher temperatures. This model explains the second peak as a measurement artifact resulting from the recrystallization process during the DSC run [4].



(a) (b)

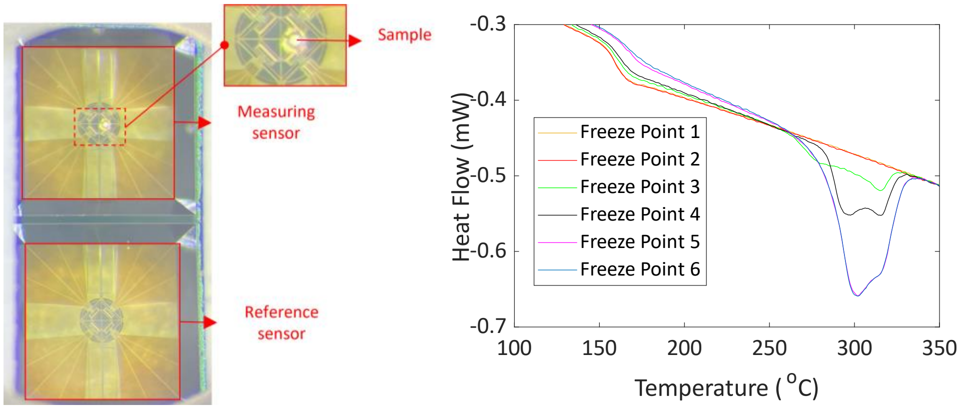
Figure 1. (a) Heat distribution during 3D printing of a part captured by infra-red thermography and, (b) The thermal profile used to replicate 3D printing in the FSC.

This study aims to collect evidence of the evolution of crystalline phase morphology under a typical 3D printing profile and to develop a framework for constructing a crystallization kinetics model using Fast Scanning Calorimetry (FSC). This approach is intended to overcome the limitations of conventional DSC and provide a more accurate description of crystallization behavior under the rapid cooling conditions, typical of 3D printing processes. FSC's capability to achieve high cooling rates of above 4000^{o}Cs^{-1} allows for the interruption of the crystallization process at any point in the 3D printing thermal profile, enabling the measurement of the apparent endothermic enthalpy at those points. Figure 1(b) shows 6 interruption points of the 3D printing thermal profile and Figure 2(b) shows the corresponding endothermic enthalpy. Through the development of such a model, process-structure-property relationships are created by which 3D-printing processes can be optimized to tailor PEEK microstructures for high-performance applications.

2 EXPERIMENTAL STUDIES

2.1 Calorimetric Methods for Studying Crystallization Evolution

All calorimetric measurements were carried out using CF10 LS1 3D printing PEEK AM filament provided by Solvay Additive Manufacturing. A nanogram sample of PEEK is prepared by shaving off PEEK filament and incrementally cutting it into a smaller piece using a scalpel before being placed on the center of a UFS 1/ST sensor provided by Mettler-Toledo (refer to Figure 2(a)). There is also a reference sensor which provides the baseline heat flow to track heat evolution from the sample. The samples were then tested using the Mettler-Toledo Flash DSC 2+. The FSC was programmed with the 3D printing thermal profile mentioned in Figure 1(b). The test was interrupted at 6 points of the thermal profile by rapidly quenching the sample at 4000°Cs-1. The sample was then reheated beyond the melting point to 400°C to ensure melting of all crystals and capture the endothermic enthalpy. The test is then restarted from the beginning and interrupted at the second point and so on. The evolution of the melting endotherms for the 6 interruptions is shown in Figure 2(b). Inspection of the endotherms show an increasing enthalpy after each subsequent interruption which translates to a higher DOC. This is expected as the whole thermal profile lies between the glass transition temperature (Tg) and melting temperature (Tm) of PEEK. However, the progression of enthalpy is not linear which signifies that the crystallization kinetics of PEEK are not linear between Tg and Tm. Moreover, the shape of the enthalpic peaks is not consistent. Please refer to section 3 for more information on this phenomenon.

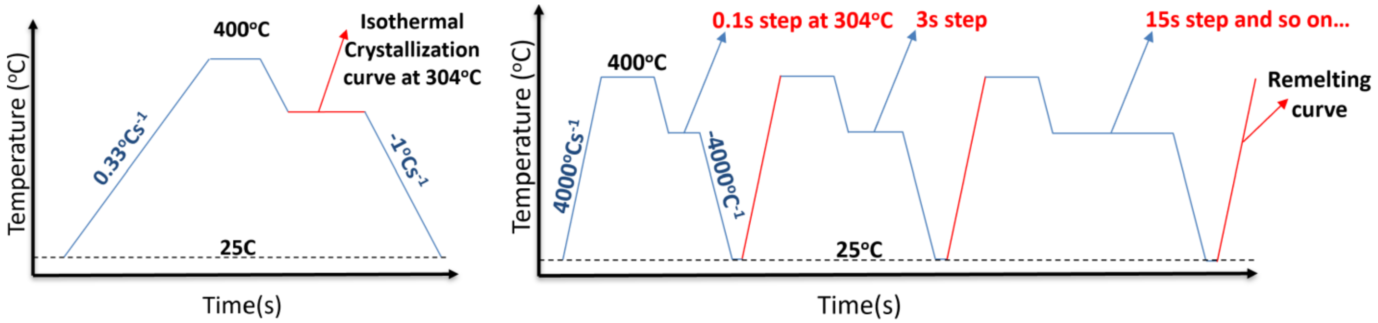


(a) (b)

Figure 2. (a) UFS 1/ST sensor containing the PEEK sample and, (b) Evolution of melting enthalpy over different periods of the thermal profile

2.2 Setup for Measuring Crystallization Kinetics

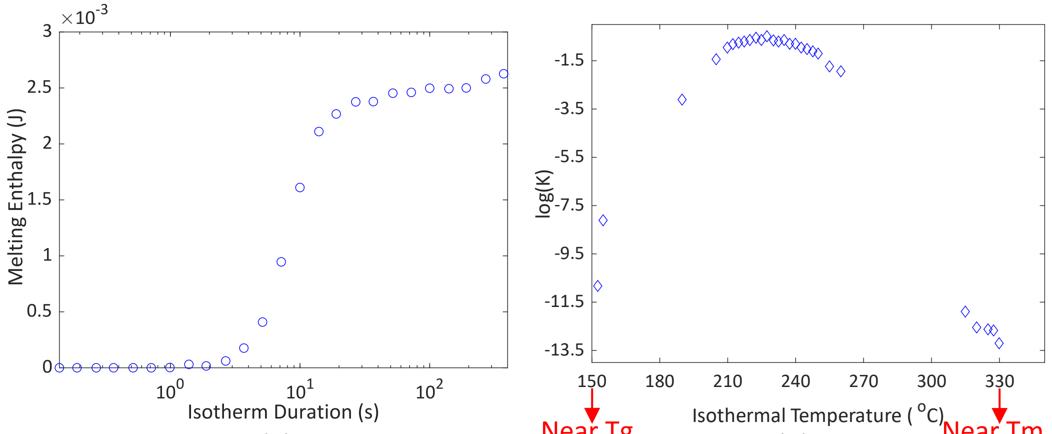
Authors such as Brenken [7] and Perez-Martin et al. [8] have used the DSC to conduct isothermal tests directly from melt to characterize the crystallization kinetics of semi-crystalline polymers (refer to Figure 3(a)). However, as the FSC uses a nanogram scale sample, the heat generated with the direct method is too small to be measured accurately [4]. Therefore, the interrupted method was used to conduct isothermal tests. The interrupted method uses melting endotherms of a sample isothermally held at the temperature of interest in increments (steps). After each step, the sample is quenched and remelted to capture the melting endotherm, which provides information about the transformation that occurred in the preceding isotherm. Refer to Figure 3(b) for the interrupted-stepwise thermal profile. The enthalpies from each melting endotherm are then plotted against the corresponding isothermal step time to track the progression of crystallization by using an Avrami curve (refer to Figure 4(a)). The temperature ramp rates upon cooling are required to be high enough to suppress any further crystallization. Therefore, the highest rate capable by the Flash DSC 2+ (4000°Cs^{-1}) was used although a rate as low as 45°Cs^{-1} has been shown to be equally effective for PEEK [6]. The high heating rate also produces a very sharp endothermic peak which enables the FSC sensor to minimize the heat flow noise.



(a) (b)

Figure 3. Isothermal test thermal profile of (a) Direct method used in DSC and, (b) Stepwise method used in FSC.

Semi-crystalline polymers show a parabolic behavior of crystallization rate constants (K) when plotted against the isothermal test temperatures. The crystallization rate constant is a temperature dependent parameter which is found by fitting an Avrami equation to the enthalpy evolution. Refer to [8] for further information on fitting the enthalpy data. The kinetics slow down near Tg due to decreasing chain mobility which increases the activation barrier for polymer diffusion. The kinetics peak in the middle of the range before slowing down again near Tm due to the high free energy barrier reducing the nucleation rate (refer to Figure 4(b)) [1]. This theory helps explain the varying speeds of melting endotherm evolution seen in Figure 2(b) due to the complex 3D printing thermal profile.



(a) (b)

Figure 4. (a) Avrami curve of a 200°C stepwise isothermal test and, (b) temperature vs crystallization rate constant (K) (data obtained from [6]).

3 ANALYSIS OF DOUBLE PEAK PHENOMENON

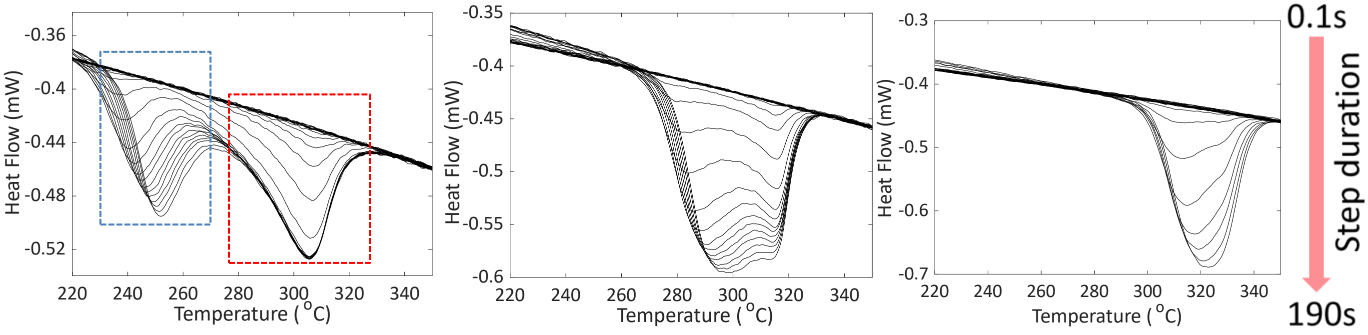
Analysis of the stepwise isothermal remelting curves displayed in Figure 5 show higher degrees of crystallization with increasing step duration. The initial remelting of the steps exhibits no significant deviation from the baseline heat flow around Tm suggesting no crystal formation. This time delay before crystallization is observed is also known as the induction time [1]. The kinetics depend on the temperature as expected from Figure 3, with 280°C (Figure

5(c)), progressing the slowest. The dense accumulation of heating curves suggests an end to which the sample can crystallize at that temperature. However, upon further analysis of the remelting curves, it can be noticed that the melting endotherms display varying shapes which depend on the isothermal test temperature. A double peak is apparent for the test conducted at 200^{o}C. The double peak can be classified as the low temperature endotherm peak and the high temperature endotherm peak (marked blue and red respectively in Figure 5(a)). Both the peaks shift to a higher temperature when the samples are isothermally crystallized at a higher temperature. The low temperature endotherm eventually becomes convoluted with the high temperature endotherm at 250^{o}C and completely disappears beyond isothermal crystallization temperatures of 280^{o}C (see Figure 5(b) and 5(c)).

It is widely acknowledged that PEEK displays double peak endotherms, however, authors have reported several different hypotheses to describe this phenomenon. The dual lamellar thickness model was proposed by Cebe and Hong and by Bassett et al. [9]. This model suggests that there simultaneously exist two populations of crystal lamellae with different thicknesses [9]. The melting of the thinner lamellae produces the low temperature endotherm while the melting of the thicker lamellae produces the high temperature endotherm. Figure 5 shows that Isothermal tests conducted at higher temperatures (280^{o}C) produce melting endotherms at a higher temperature compared to low temperature isothermal tests (200^{o}C). This is in accordance with the double lamellar thickness model which suggests that annealing the samples at a higher isothermal temperature for longer periods of time achieves thicker lamellae making them more stable at higher temperatures.

Tardif et al. suggested a melting-recrystallization model for the double peak behavior for PEEK for isothermal tests conducted below 260^{o}C [4]. This model states that the remelting heating rate determines the formation of two peaks. As the sample is reheated to melt temperature, the lamellae reorganize into a more thermodynamically stable state which eventually melts to form the high temperature endotherm. Tardif et al. proved this theory by conducting remelting experiments with crystallized PEEK samples in an FSC with varying rates. It was shown that the high temperature melting peak shifted to lower temperatures while the low temperature melting peak shifted to higher temperatures with higher heating rates [4]. At a heating rate of more than 10000^{o}Cs^{-1}, only one melting peak remained which suggested the melting of only one crystal population [4].

Wei et al. suggested a combination of the two theories. He utilized the temperature modulated DSC (TMDSC) to track the behaviour of PEEK for different isothermal test conditions [5]. The TMDSC analysis showed that the recrystallization mechanism stops for isothermal tests above 320^{o}C meaning, two different crystal populations create the double peak with a remelting rate of 2^{o}Cmin^{-1}. However, the melting-recrystallisation mechanism convoluted with melting enthalpy of two different crystal populations produced the total melting endotherms for isothermal tests conducted below 320^{o}C [5].



(a) (b) (c)

Figure 5. Remelting curves of stepwise isothermal test conducted at (a) 200^{o}C, (b) 250^{o}C and, (c) 280^{o}C.

4 CONCLUSION

The FSC is an effective tool to characterize the crystallization kinetics of PEEK undergoing a complex 3D printing cooling profile. Isothermal tests can be conducted either directly with the DSC or with the stepwise method in the FSC to produce the DOC evolution. This data can then be used to generate a model which can predict the degree of crystallinity of a 3D printed part. The ability to freeze the thermal profile using the FSC is helpful to track the evolution of the degree of crystallinity at any point of a 3D printing process. This technique can both assist in verification of the crystallization kinetics model and potentially help distinguish the morphological changes that occur. Although the stepwise isothermal test results presented in this study established a clear trend in the double melting endotherms converging and then disappearing beyond 280^{o}C; more characterization methods are needed to understand this behavior. Additional characterization methods should be employed along with the FSC, DSC and, TMDSC to explore the models of PEEK polymorphism. Jin et al. utilized the polarized optical microscope (POM), small angle X-ray scattering (SAXS) and atomic force microscopy (AFM) to characterize PEEK polymorphism at different scales [3]. SAXS data for PEEK showed increased lamellar thickness for samples prepared with isothermal temperatures closer to Tm compared to samples crystallized at lower temperatures [2]. Examination of Jin et al.'s POM experiments revealed a crystal structure containing smaller spherulites for a sample that underwent constant cooling and larger spherulites for a sample held isothermally at 315^{o}C for 3 hours [3]. Understanding PEEK's double peak behavior at a fundamental level will provide future opportunities to build models that can better predict the mechanical properties of 3D printed PEEK.

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