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ADDITIVE MANUFACTURING OF HIGH PERFORMANCE SEMICRYSTALLINE THERMOPLASTICS AND THEIR COMPOSITES

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Abstract

This work investigates the use of two semi-crystalline high performance thermoplastics, polyphenylene sulfide (PPS) and poly (ether ketone ketone) (PEKK), as feedstock for fused filament fabrication process. Composites of PPS and PEKK are emerging as viable candidates for several components in aerospace and tooling industries and additive manufacturing of these materials can be extremely beneficial to lower manufacturing costs and lead times. However, these materials pose several challenges for extrusion and deposition due to some of their inherent properties as well as thermal and oxidative responses. To better understand the properties of such systems specific to 3D printing and determine the critical parameters that make them "printable", various rheological and thermal properties have been studied for neat as well as short fiber reinforced PPS and PEKK systems. Attempts were also made to print these materials in a customized high temperature fused filament fabrication system.

Introduction

High performance thermoplastics and their fiber reinforced composites are widely used in advanced applications that demand properties such as thermal stability, high continuous use temperature, chemical, wear and flame resistance, and superior mechanical properties. Some of the commonly used high performance or high temperature thermoplastics include amorphous thermoplastics such as polyetherimide (PEI), polyphenyl sulfone (PPSU), and polyether sulfone (PES) and semi-crystalline thermoplastics such as polyphenylene sulfide (PPS), poly(etheretherketone) (PEEK), and poly(etherketoneketone) (PEKK) [1]. Semi-crystalline thermoplastics offer certain advantages over amorphous thermoplastics in terms of higher range of continuous use temperature, the ability to use the material at temperatures even above T_g for short spans without much loss in modulus [2], better resistance to creep deformation [2], and excellent chemical and wear resistance. Many of these properties can be modified by varying the degree of crystallinity.

Specifically, for additive manufacturing (AM) applications, the inherent property of these materials to crystallize offers the potential of additional bonding mechanisms between the printed layers. In amorphous polymers, thermal fusion and polymer interdiffusion is the primary bonding mechanism between printed layers [3]. However, in the case of semi-crystalline polymers, interlayer bonding can be enhanced by mechanisms such as co-crystallization. In some studies done by Gauthier Jarrousse on self-adhesion of semi-crystalline polymers, it was shown that co-crystallization can be an effective method to reinforce interfaces if preceded by some interdiffusion of chains prior to recrystallization [4]. It has also been shown that for semi-crystalline FDM filaments, having a core-shell structure with different peak crystallization temperatures can reduce the level of curling and distortion and also improve interlayer strength [5].

Filaments for fused filament fabrication (FFF) or fused deposition modeling (FDM) processes have been produced using high temperature semi-crystalline materials in recent years. INDMATECH GmbH has developed raw PEEK FDM filaments [6], 3DXTech has developed Firewire™ carbon fiber reinforced PEEK filaments printable at 360°C to 390°C [7] and PPS filaments that can be FDM printed between 325°C and 345°C [8]. Stratasys has developed electrostatic discharge ESD PEKK filaments that have conductive fillers in PEKK base resin [9].

The goal of this study is to explore the use of neat as well as carbon fiber reinforced grades of PPS and PEKK as potential FFF feedstock materials. Thermal analysis of these materials is initially used to identify processing temperature range, followed by rheological analysis to study the effect of parameters such as temperature, shear, and fillers on the viscosity of the selected grades. Upon identifying suitable processing conditions, filaments were made with the PPS and PEKK grades and extrusion was attempted on a customized desktop scale FFF system to determine if the materials would extrude without clogging.

Experimental

Three grades each of PPS and PEKK were procured in the form of pellets. Neat PPS and PPS filled with 40 wt. % and 50 wt. % short carbon fiber were supplied by Techmer Engineered Solutions. Three grades of PEKK from the Kepstan® 8000 series - neat PEKK and PEKK filled with 30 wt.% and 40 wt.% short carbon fiber were supplied by Arkema Inc. Prior to all tests, all PPS pellets were dried at 135°C for 2 hours and all PEKK pellets were dried at 150°C for about 3 hours.

Thermal Analysis

The first step is to determine the temperature range in which the materials would be processable in an extrusion based system. To identify the upper limit or the decomposition temperature (above which volatiles are released), thermogravimetric (TGA) analysis was conducted using a TA Instruments Q500 instrument. The dried pellets were heated at a rate of 10°C/min in air from 25°C to 800°C.

The lower limit of processing temperature is the melting temperatures, which was determined by Differential Scanning Calorimetry (DSC) using a TA Instruments Q2000 system. The dried pellets were heated at the rate of 10°C/min from 25°C up to 325°C for PPS grades and up to 370°C for PEKK grades to remove thermal history, cooled at the rate of 5°C/min, re-heated at 10°C/min. Peak melting temperatures (T_m) were obtained from the second heating cycle.

Rheological Analysis

Based on the lower and the upper limit of temperatures determined by DSC and TGA analysis, three and four processing temperatures were chosen with 15°C intervals for PEKK and PPS grades respectively for rheology tests. All rheological tests were done on TA Instruments DHR-2 instrument fitted with 25mm parallel plate geometry. The dried pellets were directly melted on the plates using melt rings. Oscillatory amplitude tests were first performed to identify the linear viscoelastic region for each of these materials. A suitable strain value in the linear region (typically 1% or lower) was selected for frequency sweep tests between 0.1 and 628 rad/s. The purge gas used throughout was air.

Filament Making Process and FFF Extrusion

Filaments for the FFF process were extruded using a Filabot EX2 (as shown in Figure 1) fitted with a single screw extruder. Using the temperature range identified for rheological analysis and by varying the screw speed and nozzle diameter, filaments were made from the dried pellets with a target diameter of 1.75mm. The extruded filaments were gently guided and rolled up under ambient conditions with minimum stretching.

Figure 1. Filament making process

For extruding the filaments on a fused filament fabrication system, a Solidoodle 3 was customized with a E3D V6 all metal hot end to reach temperatures as high as 400°C. The nozzle diameter was 0.6 mm for the neat filaments and 1 mm for the carbon fiber reinforced filaments. The print bed temperature was set to 100°C.

<u>Results and Discussion</u>

Thermal Analysis

Figure 2a and 2b show the TGA and DSC (second heating cycle) thermograms for PPS and PEKK grades, respectively. The TGA data indicate that all three grades of PPS are stable at least up to 400°C (less than 2% weight loss) and all PEKK grades are stable at least up to 500°C (less than 2% weight loss). This sets the upper processing temperature limit. For the lower processing temperature limit, peak melting temperatures were obtained in the range of 280°C to 285°C for PPS grades and 359°C to 362°C for PEKK grades.

From these limits, four processing temperatures were selected above the melting point for the PPS grades, specifically: 300°C, 315°C, 330°C and 345°C. Likewise, three candidate processing temperatures above the melting point were identified for the PEKK grades, specifically: 375°C, 390°C and 405°C.

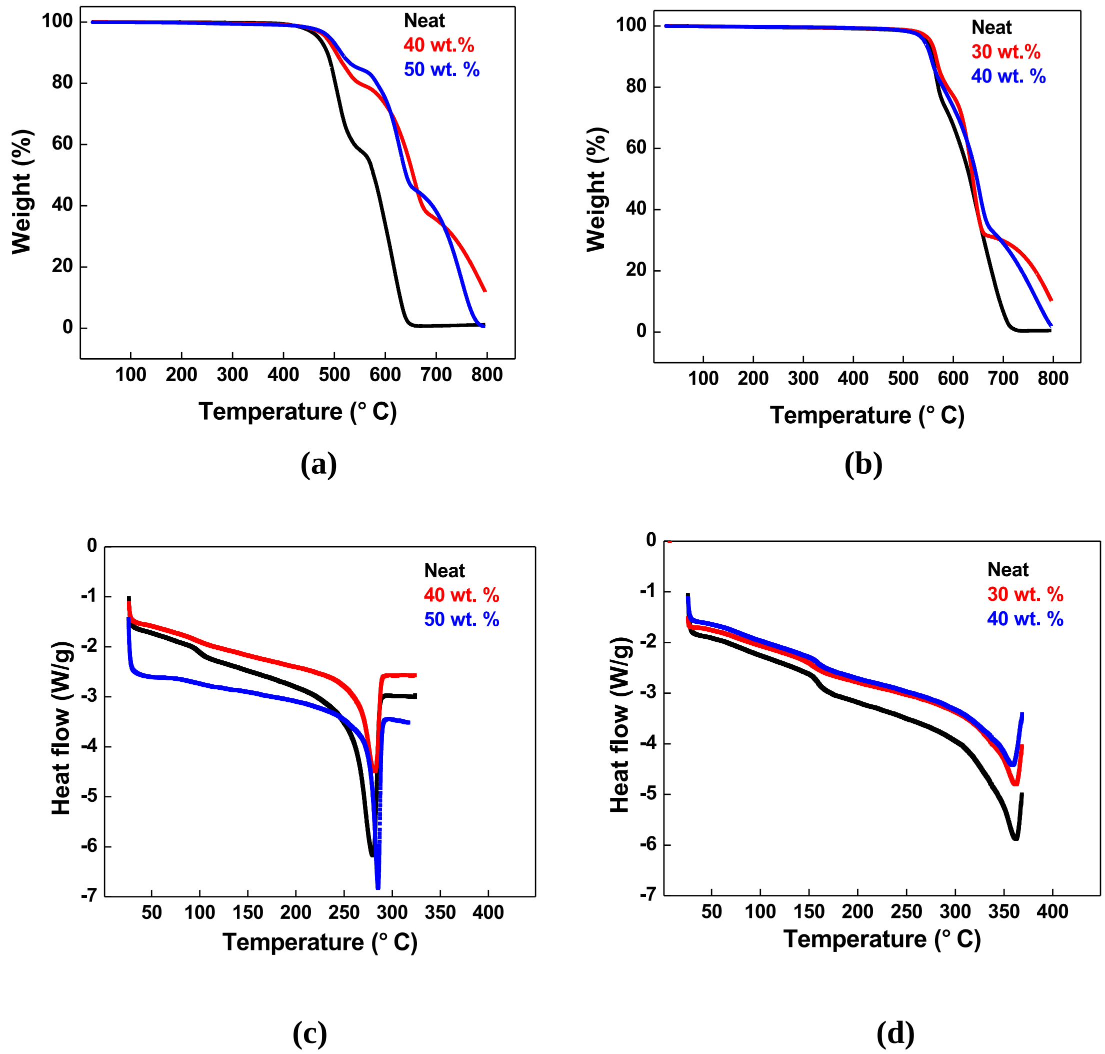
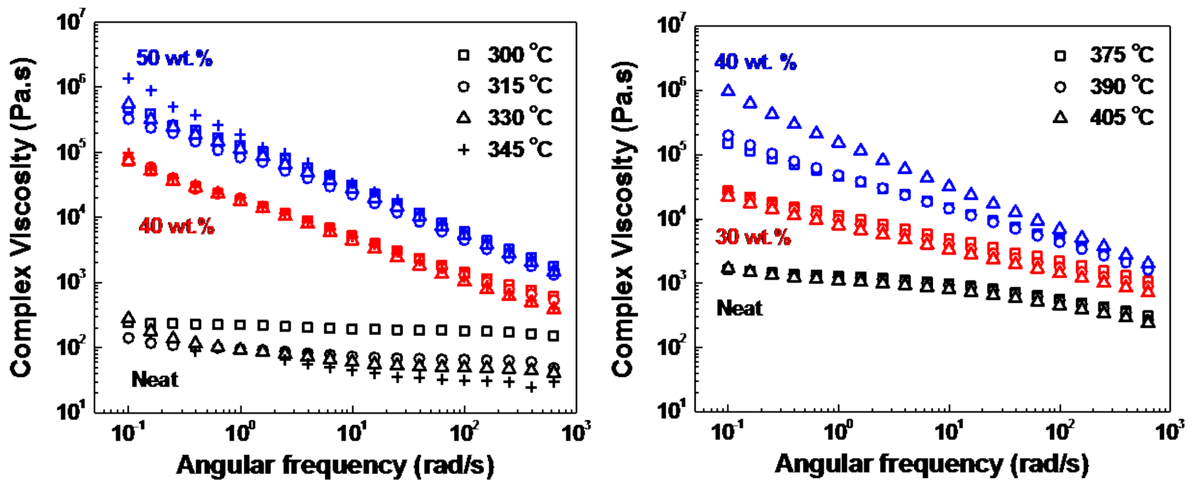


Figure 2. TGA analysis of (a) PPS grades and (b) PEKK grades and DSC thermograms showing the second heating cycle for (c) PPS grades and (d) PEKK grades

Rheological Analysis

Figure 3a and 3b show the variation of complex viscosity with frequency, temperature, and filler content for the various PPS and PEKK grades, respectively. For PPS grades (Figure 3a), addition of fillers increase viscosity at all frequencies, with the magnitude of increase being greater for higher filler loadings. For viscosity variation with frequency, at all the chosen temperatures, the viscosity of neat PPS shows only a small dependence on frequency. However, for the filled grades, shear thinning of the material is much stronger. For temperature dependence of viscosity, for neat PPS, viscosity drops with change in temperature from 300°C to 315°C, but beyond that, an increase in the temperature does not change viscosity significantly for the entire frequency range tested. For PPS with 40 wt. carbon fiber (CF), temperature dependence of viscosity is very low for the entire range, and there is no significant difference for 50 wt.% CF at higher frequencies. However at lower frequencies, viscosity increases with an increase in temperature. One of the possible reasons for this could be the occurrence of structural changes in the material due to chain scission and cross-linking reactions [10] at high temperatures. The magnitude of increase depends on the degree of crosslinking and shear rate. Crosslinking reactions increase viscosity. However, the newly formed structure could be sensitive to shear, thereby lowering the viscosity with increasing shear rate.

In the case of PEKK (Figure 3b), the addition of fillers increases viscosity for the entire frequency range studied (similar to PPS grades), with viscosity for 40 wt.% CF PEKK being greater than 30 wt. % CF PEKK. Here, all the three grades exhibit shear thinning behavior and the extent of shear thinning is greater for the filled grades. The temperature dependence of viscosity is very low for neat PEKK and for PEKK with 30 wt.% CF. In the case of PEKK with 40 wt.% CF, viscosities at 375°C and 390°C show a very similar trend. However, for 405°C, at low frequencies, viscosity increases by about an order of magnitude. This could be due to some structural changes induced in the material at temperatures above 400°C.



(a) (b)

Figure 3. Frequency sweep tests for the different grades of (a) PPS and (b) PEKK at the candidate processing temperatures

The frequency sweep data indicate that for filled grades of both PPS and PEKK, shear rate is a much more effective parameter for controlling viscosity than temperature. Such knowledge of the effect of process parameters and fillers on flow properties can be useful while processing such new materials on the FFF system.

Filament Making Process and FFF Extrusion

Filament extrusion was successful for all three chosen grades of PPS and PEKK as shown in Figure 4. Table 1 indicates the extrusion temperature used for the Filabot and the typical diameter of the filaments.

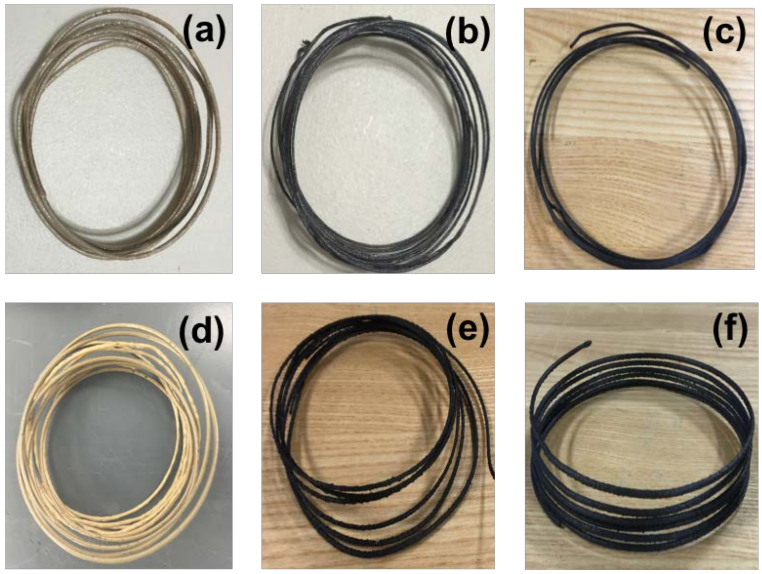
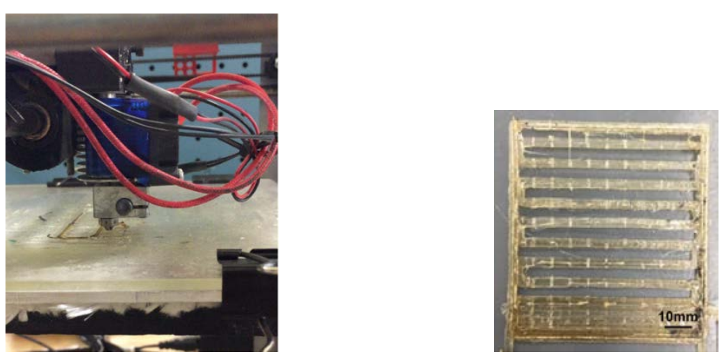


Figure 4. Filaments of (a) Neat PPS, (b) 40 wt.% CF PPS, (c) 50 wt.% CF PPS, (d) Neat PEKK, (e) 30 wt.% CF PEKK, (f) 40 wt.% CF PEKK

Table 1. Filament extrusion temperatures and diameter

Material	**Extrusion temperature (°C)**	**Filament diameter (mm)**
Neat PPS	300	1.5-1.9
PPS 40 wt.% CF	345	1.4-1.65
PPS 50 wt.% CF	345	1.4-1.65
Neat PEKK	370	1.5-1.75
PEKK 30 wt.% CF	375	1.6-1.9
PEKK 40 wt.% CF	375	1.5-1.9

The extruded filaments were deposited on the customized Solidoodle 3 to determine if these materials could be extruded through an FFF nozzle and deposit a few layers as shown in Figures 5a and 5b. This study demonstrated the deposition of neat PPS and PEKK and also the fiber reinforced grades of PEKK. The fiber filled grades of PPS were not successfully deposited due to filament feed issues (rough and rigid filaments), not rheological limitations. Table 2 indicates the processing conditions for FFF extrusion and deposition.



(a) **(b)**

Figure 5. (a) FFF extrusion of neat PPS and (b) Deposited layers of neat PEKK

Table 2. Extrusion temperature on the FFF system

Material	**FFF Extrusion**
Neat PPS	280-290 °C
Neat PEKK	390-400 °C
PPS 40 wt.% CF	Filament feed issues
PPS 50 wt.% CF	Filament feed issues
PEKK 30 wt. % CF	390- 400 °C
PEKK 40. wt% CF	390- 400 °C

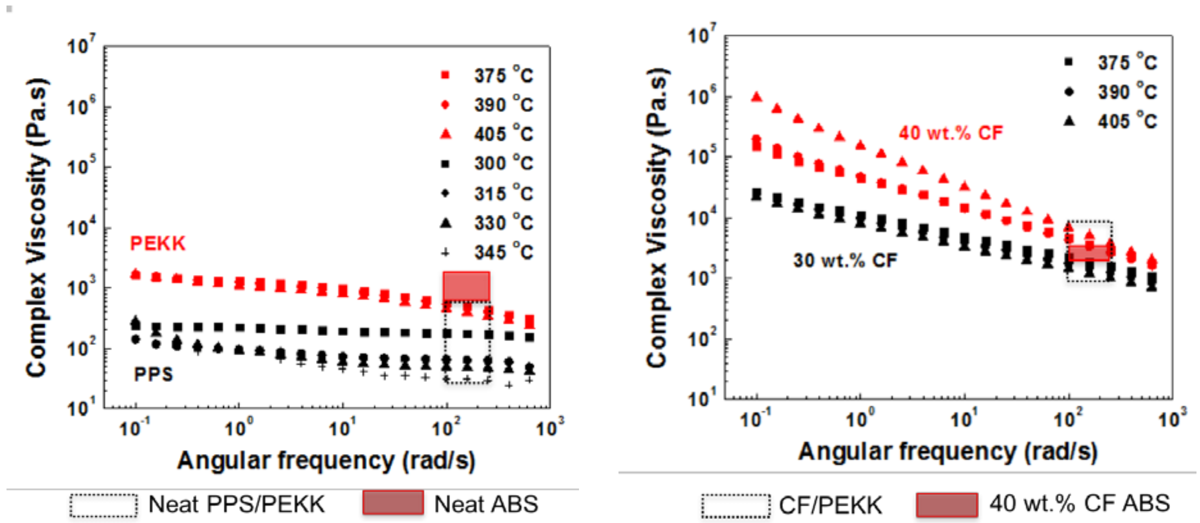
Typically, for most FFF or FDM processes, shear rates in the nozzle range between 100-200 s^{-1} [3,11]. To relate complex viscosities obtained from the frequency sweep tests to viscosities at FFF shear rates, complex viscosities for each of the grades of PPS and PEKK in the frequency range of 100-250 rad/s were identified using the Cox-Merz rule (equation 1)

$$\eta(\dot{\gamma}) = \eta^{*}(\omega) \text{ for } \dot{\gamma} = \omega \quad (1)$$

where η is steady shear viscosity, η^{*} is complex viscosity, $\dot{\gamma}$ represents shear rate, and ω represents frequency [12]. Using this relation, the complex viscosities and frequencies can be related to steady shear viscosities at FDM shear rates.

To correlate the FFF extrusion conditions of PPS and PEKK with the viscosity data from rheological studies, the viscosities of these materials were compared with that of acrylonitrile butadiene styrene (ABS), a successfully printed FDM material, in the frequency range of 100-250 rad/s. For ABS, frequency sweep tests were performed using the filaments (neat and 40 wt.% CF) used previously to deposit these materials on a Solidoodle 3 at 205°C in a study by Tekinalp et.al. [13].

Figures 6a and 6b represent frequency sweep data for neat materials (PPS and PEKK) and carbon fiber reinforced grades of PEKK respectively at different temperatures, indicating the viscosity range for these materials at the typical FFF shear rates (here, frequency) along with the complex viscosity range for neat ABS and ABS with 40 wt.% CF in the same frequency range (measured at 205°C – the FFF deposition temperature).



(a) (b)

Figure 6. Frequency sweep comparison for (a) neat PPS and PEKK with neat ABS and (b) CF filled PEKK with CF filled ABS

In comparison with neat ABS, between 100-250 s^{-1}, the viscosity of neat PPS and neat PEKK is lower. This indicates that neat PPS and PEKK can flow through a similar FFF system as that of ABS without clogging at the mentioned temperatures. For fiber reinforced PEKK systems, the viscosity of 30 wt.% CF PEKK is lower than ABS 40 wt. % CF. For 40 wt.% CF PEKK, at the extrusion temperature, the viscosity is in the upper limit of that of filled ABS, indicating that these materials with similar viscosities can extrude through the FFF nozzle.

It should also be noted that the comparisons made here involve some approximations and the following parameters are to be considered as well:

1. The applicability of Cox-Merz rule to the fiber filled systems used here is an approximation. Previous studies [14] on LLDPE filled with glass fiber have shown that the dynamic viscosity data for fiber reinforced systems is higher than steady shear viscosity obtained by capillary rheometry. This was attributed to the reduction in steady shear viscosity due to fiber orientation along the flow direction in a capillary rheometer, which does not happen in the case of oscillatory frequency tests done at low strains.

2. The viscosities compared are at the typical steady state FDM shear rates. It is assumed the material would be able to flow with viscosities in this range, provided the torque of the extrusion system is high enough to get the material flowing initially (overcome zero shear viscosity which can be much higher than the viscosities shown in the frequency sweep tests).

Conclusions and Future Work

This study was the very first attempt at understanding rheological properties of the chosen grades of PPS and PEKK and correlating it to FFF processing conditions. This work has demonstrated that rheological analysis can be helpful in identifying appropriate FFF processing conditions and understanding the key control parameters. The effect of factors such as temperature, shear rate, and fillers on viscosity have been studied for both neat and carbon fiber reinforced PPS and PEKK grades. Filaments for all the chosen materials were successfully extruded from pellets, and four grades were deposited on a customized desktop sized FFF system. Also, the rheological properties of these candidate materials were compared with that of a common FDM material (ABS).

Future work will involve comparisons of this data with steady shear tests using a capillary rheometer, understanding the effect of filler size on flow, improvements to the filament making process, and correlating experimental data with theoretical models.

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