RHEOLOGICAL CHARACTERISTICS OF FIBER REINFORCED POLY(ETHER KETONE KETONE) (PEKK) FOR MELT EXTRUSION ADDITIVE MANUFACTURING

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ABSTRACT

Several grades of unreinforced and short fiber reinforced poly(ether ketone ketone) (PEKK) copolymers are analyzed for their potential use as feedstock materials in melt extrusion-based additive manufacturing (AM) systems. Rheological characterization has been performed to study the effect of extrusion processing parameters such as time, temperature, environment, and shear rate for the selected materials. The effect of reinforcing filler content on the melt processing conditions of PEKK composites are also reported, and processing conditions for successful extrusion of these materials on AM systems are determined.

1. INTRODUCTION

1.1 High performance thermoplastics for additive manufacturing

The development of high performance polymers and composites that can be processed in extrusion-based additive manufacturing (AM) systems is essential to enable the use of additively manufactured parts in applications that demand high temperature and mechanical performance. Such applications include autoclave tooling, aerospace, automotive, and off-shore oil and gas exploration [1-3]. Some of the high performance polymers and composites that have been used in extrusion AM systems include polyphenylene sulfide (PPS) [4], carbon fiber reinforced PPS [5], polyetherimide (PEI) or Ultem [6,7], polyphenyl sulfone (PPSU) and carbon fiber reinforced PPSU [8] and poly(ether ether ketone) (PEEK) [9]. To further explore and develop new materials for these systems, it is essential to understand material properties that are critical for extrusion and deposition. This is especially crucial for systems such as the Big Area Additive Manufacturing (BAAM) system, which handles large volumes of material and prints at rates as high as 50 kg/h [10-12]. For such production scale systems, the understanding of thermal and rheological properties of the new materials prior to processing helps in determining the most suitable processing conditions, thereby minimizing the risk of system downtime as well as obtaining parts with optimal properties.

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In previous studies [13,14], thermal analysis was performed using differential scanning calorimetry (DSC) and thermogravimetry (TGA) for various grades of PEKK and its carbon fiber reinforced composites to determine the range of temperatures in which these materials can be characterized in the melt. The lower limit of processing temperature was chosen based on the glass transition temperature (T_g) or the melting point (T_m) and the higher limit was set lower than the degradation onset temperature (DOT). Candidate processing temperatures were selected accordingly within these operational bounds. The present work analyzes some of the rheological properties of these grades to determine the impact of temperature, time, processing environment, material grade, reinforcing material content, and shear rate.

1.2 Background on PEKK

Poly(ether ketone ketone) (PEKK) is a high performance thermoplastic in the family of poly (aryl ether ketone)s (PAEK). PEKK homopolymers have a backbone of terephthalic groups. However, different grades of PEKK have been synthesized as co-polymers such that they can exhibit different levels of crystallinity and therefore thermo-physical properties based on the ratio of terephthalic (T) and isophtalic (I) moieties present in their structure, as shown in Figure 1 [15,16]. Increasing amounts of terephthalic moieties increase the melting point of the material. Varying the T/I ratio in a blended co-polymer provides a manner for controlling properties of a material for the intended applications.

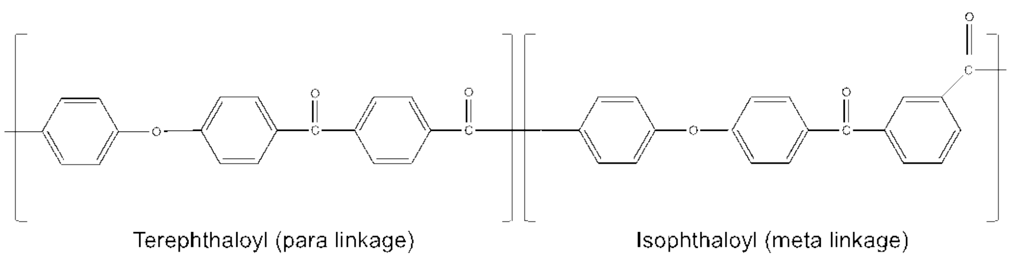

Figure 1. Structure of PEKK copolymer.

2. EXPERIMENTATION

2.1 Materials

This work investigates five different grades of Kepstan™ PEKK from Arkema Inc.: 6002, 7002, 8001, 8010C30 and 8010C40. The 6002 PEKK represents a pseudo-amorphous grade with T/I of 60/40 which can undergo crystallization at a very slow rate. The 7002 grade represents a structure with T/I of 70/30, which makes the material semi-crystalline. The 8001 grade represents T/I of 80/20, which is also semi-crystalline but with a higher melting point than 7002 [15]. The grades denoted by 8010C30 and 8010C40 represent an 8001 matrix reinforced with 30 wt. % and 40 wt. % short carbon fibers, respectively. Prior to all tests, the samples were dried in a vacuum oven at 150 ^{o}C for ~3 hr.

2.2 Rheological analysis

Rheological studies were conducted on a stress controlled DHR-2 rheometer (TA Instruments) fitted with 25 mm disposable parallel plates geometry. The system was heated to the desired test temperature and the pellets were directly melted between the plates using melt rings. A gap of 1.4-1.8 mm was maintained for all the tests. Two test temperatures were chosen for each grade of PEKK within the bounds defined by T_g, T_m, and DOT as shown in Table 1, determined in previous studies for the same grades [13,14]. The maximum test temperature was limited to 390 ^oC, as there can be structural modifications due to chain branching and crosslinking around and above this temperature for polymers in the poly(aryl ether ketone) family. [15,17].

Table 1. Selection of test temperatures for rheological analysis

PEKK grade	Glass transition temperature (T_g) (^oC)	Peak melting point (T_m) (^oC)	Degradation onset temperature (^oC)	Test temperatures (T) (^oC)
6002	158	-	> 500	335, 350
7002	161	335		350, 375
8001	158	361		375, 390
8010C30	156	362		375, 390
8010C40	158	361		375, 390

Initially, strain amplitude sweep tests were conducted in the interval 0.001-100 % at a constant frequency (ω) of 10 rad/s to determine the linear viscoelastic region (LVR) for all the grades at each test temperature in the respective test environment. After identifying a suitable strain value in the LVR, time sweep tests were conducted in air for 10 min at 10 rad/s at the selected temperatures for all the five grades to determine the thermal stability of the material in the test environment with time. Frequency sweep tests were then performed at each chosen temperature for all the grades to obtain the variation in complex viscosity (η^*) with frequency. The frequency sweep tests were conducted from 0.1- 628 rad/s as well as 628- 0.1 rad/s (with different samples) and the average values have been reported. This is to minimize the thermal effects of testing time on the flow characteristics of the sample.

3. RESULTS AND DISCUSSION

3.1 Time sweep tests for neat grades

Figure 2 (a-c) represents the variation of complex viscosity (η^*) with time at the candidate test temperatures in air for the unfilled 6002, 7002 and 8001 grades. All the tests were performed using a strain value of 1 % (in LVR). The tests have been performed in air to determine thermal stability as most of the extrusion-based AM processes do not involve the use of a cover gas.

From the variation of complex viscosity with time, it can be observed that the viscosity of all the three grades do not vary significantly with time in 10 min (10-22 % increase), indicating that these grades are stable with time. Though this data represents thermal stability at a particular frequency (10 rad/s), it can be useful to make relative comparisons across various grades.

For the effect of temperature on viscosity, for all the three grades, there has been some decrease in viscosity with increasing temperatures, as expected. By comparing the initial data point (t= 6s) at increasing temperatures, complex viscosity decreases by about 35 %, 47 % and 23 % respectively for 6002, 7002 and 8001. This study indicates that the three neat PEKK grades can be processed in air at the chosen test temperatures for short residence times (< 10 min) without significant thermal degradation (as observed by variations in viscosity).

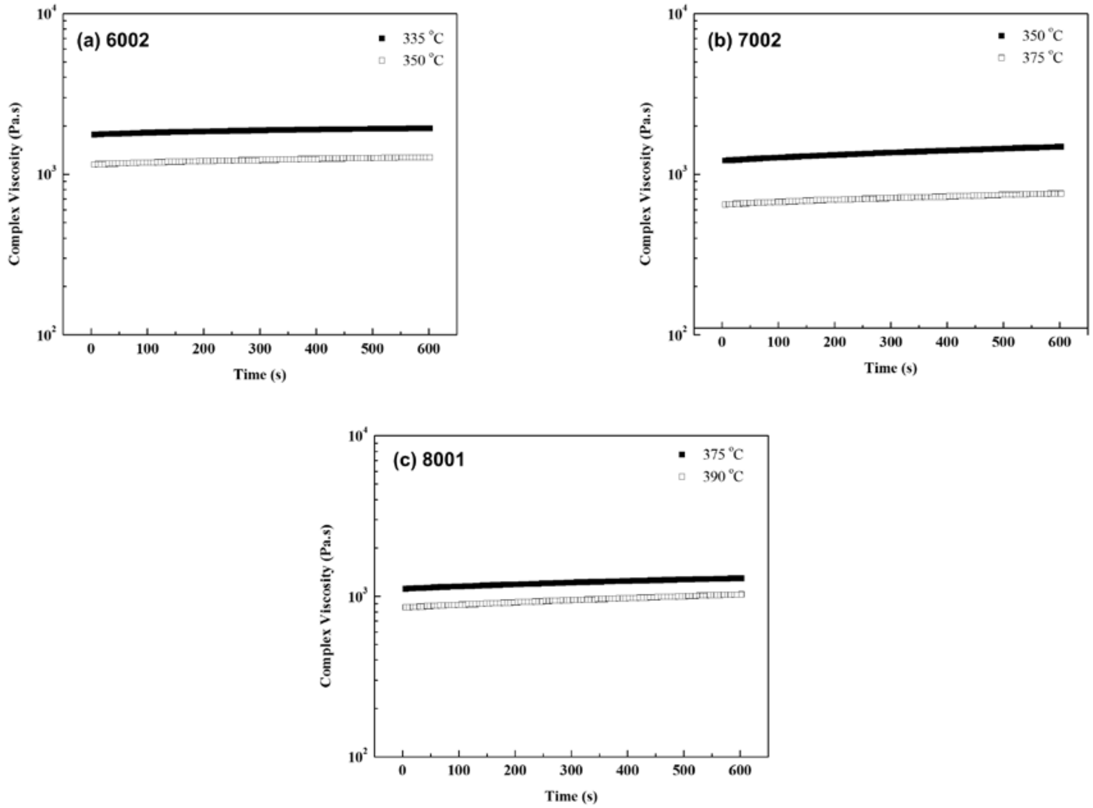

Figure 2. Variation of complex viscosity with time at the candidate test temperatures for (a) 6002, (b) 7002, (c) 8001 grades in air.

3.2 Frequency sweep tests for neat grades

Figure 3 (a-c) indicates the frequency sweep test data for the three neat grades at their candidate processing temperatures, representing the variation of average complex viscosity with frequency. The standard deviations were very low for each case to be represented on the plots. All the three grades exhibit shear thinning, i.e., complex viscosity decreases with increasing frequencies. However, the effect of temperature on viscosity is least pronounced for the 8001 grade when compared to the other two grades (Table 2). For the 6002 and 7002 grades, an increase in temperature reduces viscosity throughout the entire frequency range used in testing. Such tests help in determining the process parameter (shear rate or temperature) that can be used to better control or modify the viscosity during printing.

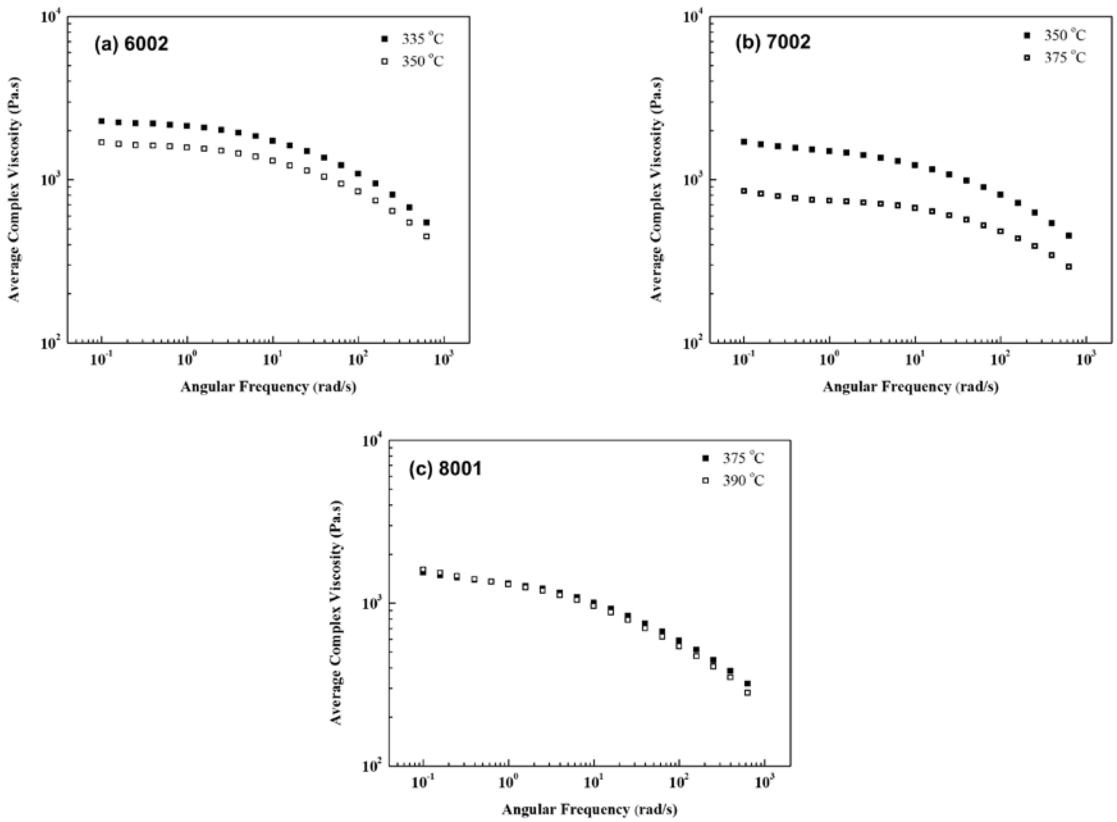

Figure 3. Variation of complex viscosity with frequency at the candidate test temperatures for (a) 6002, (b) 7002, (c) 8001 grades in air.

Table 2. Decrease in η^* with increasing candidate test temperatures at various frequencies (using the lowest temperature as the reference viscosity).

Neat grade	**0.1 rad/s**	**1 rad/s**	**10 rad/s**	**100 rad/s**
6002	26 %	26 %	25 %	22 %
7002	49 %	50 %	45 %	41 %
8001	4 %	1 %	5 %	8 %

3.3 Time sweep tests for the filled grades

Figure 4 (a and b) represents time sweep data for the two filled 8000 series grades at the two test temperatures (375 ^oC and 390 ^oC) in air. The LVR strain amplitude in this case was reduced to 0.04-0.06 % for both the filled grades. Note that these values were chosen from suitable data points with least noise in the LVR. From Figures 4(a) and (b), it can be observed that unlike the neat material 8001 (Figure 2c), the complex viscosity in air for 8010C30 increases by about 47 % and 64 % respectively at 375 ^oC and 390 ^oC over 10 minutes while the complex viscosity of 8010C40 increases by about 67 % and 102 % under similar conditions. Also, an increase in temperature for these materials increases the viscosity, more so for the higher filler loading. This indicates that increasing the filler content and increasing the operating temperature reduces the thermal stability of the material over time. Figure 4 also demonstrates that the initial viscosity is not significantly affected by an increase in operating temperature. However, the increased fiber content can lead to a higher viscosity at elevated temperatures for certain grades (8010C40). Since these grades exhibited an incremental increase in viscosity while heating under air, the following frequency sweep tests for the filled grades were performed in nitrogen environment to minimize viscosity build.

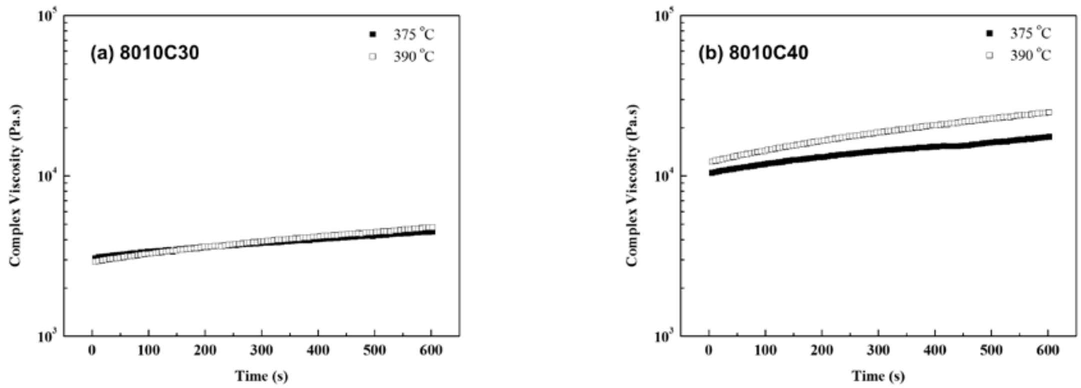

Figure 4. Variation of complex viscosity with time at the candidate test temperatures for (a) 8010C30, (b) 8010C40 grades in air.

3.4 Frequency sweep tests for filled grades

Figure 5 (a and b) represent freqency sweep test data in nitrogen for 8010C30 and 8010C40 respectively. Both the grades exhibit shear thinning, which is much more pronounced than the neat grades (Figure 3). Also, viscosity increases with higher filler loadings throughout the entire frequency range as expected. However, for both the filled grades, temperature does not have a significant effect on complex vicosity across all frequencies when tested in nitrogen.

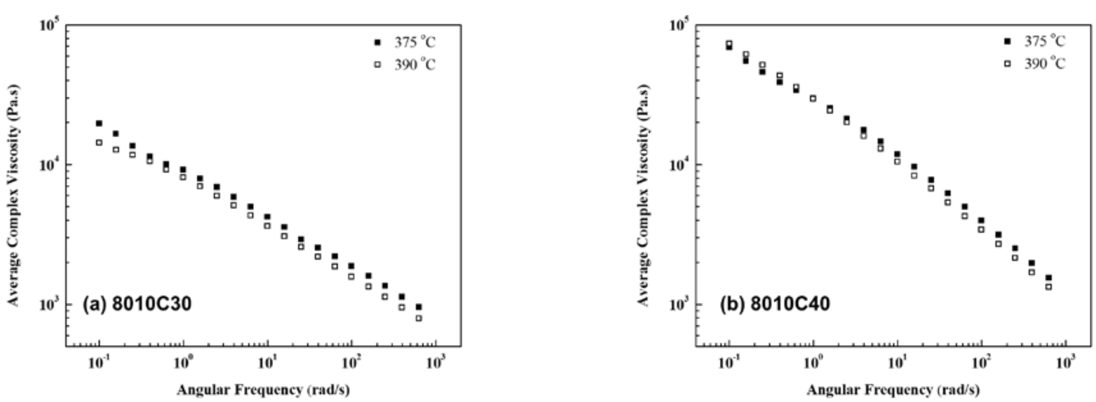

Figure 5. Variation of complex viscosity with frequency at the candidate test temperatures for (a) 8010C30, (b) 8010C40 grades in nitrogen.

Close analysis of these rheological characteristics can reveal the impact that various process parameters can affect have on the flow behavior (and printing success) of various grades of PEKK. Depending upon the processing environment, it is possible to determine the material's thermal stability at processing temperatures and the variation of viscosity with time. In addition, rheological characteristics of the material can reveal any structural changes happening in the system during processing. Such knowledge is very important prior to processing new materials, especially on the large scale system.

4. CONCLUSIONS

This work investigates the rheological properties of five different grades of poly(ether ketone ketone) (PEKK) for use as a feedstock in extrusion-based additive manufacturing process. From the rheological studies, it has been observed that the unreinforced materials exhibit superior viscosity stability in air at elevated temperatures versus the carbon fiber reinforced grades. As a result, using a cover gas would be more suitable while processing carbon fiber reinforced grades on large scale systems, where the total material residence time can be longer. The effect of temperature on rheological properties, mainly viscosity, is more evident for the 6002 and 7002 grades than the three 8000 grades. All five grades exhibit a degree of shear thinning, but the effect is much more pronounced for the fiber reinforced grades of PEKK. As expected, the addition of fillers also increases the viscosity of the material. Table 3 (a and b) summarizes the effect of time, temperature, environment and frequency on the complex viscosity of all the five grades.

Table 3. (a) Thermal stability in air and (b) Change in complex viscosity ($\Delta\eta^*$) of various grades with an increase in processing parameters (T, ω) (All values in %).

PEKK Grade	$\Delta\eta^*$ after 10 min (%)
6002	10
7002	20
8001	18
8010C30	55*
8010C40	85**

(a)

PEKK Grade	Environment	ΔT = 15 ºC	ω (10-100 rad/s)
6002	Air	- 25	-36
7002	Air	-45	-31
8001	Air	-6	-43
8010C30	Nitrogen	-26†	-55
8010C40	Nitrogen	-4†	-68

(b)

*Varies ± 10% with temperature
**Varies ± 17% with temperature

† Varies ± 10% with frequency

5. ACKNOWLEDGEMENT

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